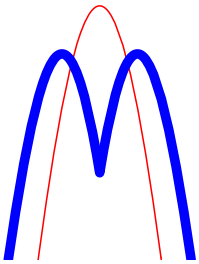
MOLPRO



User's Manual
Version 2006.1

H.-J. Werner

Institut für Theoretische Chemie
Universität Stuttgart
Pfaffenwaldring 55
D-70569 Stuttgart
Federal Republic of Germany

P. J. Knowles

School of Chemistry
Cardiff University
Main Building, Park Place, Cardiff CF10 3AT
United Kingdom

May 2006

Introduction to MOLPRO

MOLPRO is a complete system of *ab initio* programs for molecular electronic structure calculations, designed and maintained by H.-J. Werner and P. J. Knowles, and containing contributions from a number of other authors. As distinct from other commonly used quantum chemistry packages, the emphasis is on highly accurate computations, with extensive treatment of the electron correlation problem through the multiconfiguration-reference CI, coupled cluster and associated methods. Using recently developed integral-direct local electron correlation methods, which significantly reduce the increase of the computational cost with molecular size, accurate *ab initio* calculations can be performed for much larger molecules than with most other programs.

The heart of the program consists of the multiconfiguration SCF, multireference CI, and coupled-cluster routines, and these are accompanied by a full set of supporting features. The package comprises

- Integral generation for generally contracted symmetry adapted gaussian basis functions (*spdfghi*). There are two programs with identical functionality: the preferred code is SEWARD (R. Lindh) which is the best on most machines; ARGOS (R. M. Pitzer) is available as an alternative, and in some cases is optimum for small memory scalar machines. Also two different gradient integral codes, namely CADPAC (R. Amos) and ALASKA (R. Lindh) are available. Only the latter allows the use of generally contracted symmetry adapted gaussian basis functions.
- Effective Core Potentials (contributions from H. Stoll).
- Many one-electron properties.
- Some two-electron properties, e.g. L_x^2, L_y^2, L_z^2, L_xL_y etc..
- Closed-shell and open-shell (spin restricted and unrestricted) self consistent field.
- Density-functional theory in the Kohn-Sham framework with various gradient corrected exchange and correlation potentials.
- Multiconfiguration self consistent field. This is the quadratically convergent MCSCF procedure described in J. Chem. Phys. 82 (1985) 5053. The program can optimize a weighted energy average of several states, and is capable of treating both completely general configuration expansions and also long CASSCF expansions as described in Chem. Phys. Letters 115 (1985) 259.
- Multireference CI. As well as the usual single reference function approaches (MP2, SDCI, CEPA), this module implements the internally contracted multireference CI method as described in J. Chem. Phys. 89 (1988) 5803 and Chem. Phys. Lett. 145 (1988) 514. Non variational variants (e.g. MR-ACPF), as described in Theor. Chim. Acta 78 (1990) 175, are also available. Electronically excited states can be computed as described in Theor. Chim. Acta, **84** 95 (1992).
- Multireference second-order and third-order perturbation theory (MR-PT2, MR-PT3) as described in Mol. Phys. **89**, 645 (1996) and J. Chem. Phys. **112**, 5546 (2000).
- Møller-Plesset perturbation theory (MPPT), Coupled-Cluster (CCSD), Quadratic configuration interaction (QCISD), and Brueckner Coupled-Cluster (BCCD) for closed shell systems, as described in Chem. Phys. Lett. 190 (1992) 1. Perturbative corrections for triple excitations can also be calculated (Chem. Phys. Letters **227** (1994) 321).

- Open-shell coupled cluster theories as described in J. Chem. Phys. 99 (1993) 5219, Chem. Phys. Letters **227** (1994) 321.
- Full Configuration Interaction. This is the determinant based benchmarking program described in Comp. Phys. Commun. 54 (1989) 75.
- Analytical energy gradients for SCF, DFT, state-averaged MCSCF/CASSCF, MRPT2/CASPT2, MP2 and QCISD(T) methods.
- Analytical non-adiabatic coupling matrix elements for MCSCF.
- Valence-Bond analysis of CASSCF wavefunction, and energy-optimized valence bond wavefunctions as described in Int. J. Quant. Chem. **65**, 439 (1997).
- One-electron transition properties for MCSCF, MRCI, and EOM-CCSD wavefunctions, CASSCF and MRCI transition properties also between wavefunctions with different orbitals.
- Spin-orbit coupling, as described in Mol. Phys., **98**, 1823 (2000).
- Some two-electron transition properties for MCSCF wavefunctions (e.g., L_x^2 etc.).
- Population analysis.
- Orbital localization.
- Distributed Multipole Analysis (A. J. Stone).
- Automatic geometry optimization as described in J. Comp. Chem. **18**, (1997), 1473.
- Automatic calculation of vibrational frequencies, intensities, and thermodynamic properties.
- Reaction path following, as described in Theor. Chem. Acc. **100**, (1998), 21.
- Various utilities allowing other more general optimizations, looping and branching (e.g., for automatic generation of complete potential energy surfaces), general housekeeping operations.
- Geometry output in XYZ, MOLDEN and Gaussian formats; molecular orbital and frequency output in MOLDEN format.
- Integral-direct implementation of all Hartree-Fock, DFT and pair-correlated methods (MP, CCSD, MRCI etc.), as described in Mol. Phys., **96**, (1999), 719. At present, perturbative triple excitation methods are not implemented.
- Local second-order Møller-Plesset perturbation theory (LMP2) and local coupled cluster methods, as described in in J. Chem. Phys. **104**, 6286 (1996), Chem. Phys. Lett. **290**, 143 (1998), J. Chem. Phys. **111**, 5691 (1999), J. Chem. Phys. **113**, 9443 (2000), J. Chem. Phys. **113**, 9986 (2000), Chem. Phys. Letters **318**, 370 (2000), J. Chem. Phys. **114**, 661 (2001), Phys. Chem. Chem. Phys. **4**, 3941 (2002).
- Local density fitting methods, as described in J. Chem. Phys. **118**, 8149 (2003), Phys. Chem. Chem. Phys. **5**, 3349 (2003), Mol. Phys. **102**, 2311 (2004).
- Analytical energy gradients for LMP2 and DF-LMP2, as described in J. Chem. Phys. **108**, 5185, (1998), J. Chem. Phys. **121**, 737 (2004).

- Explicit correlation methods, as described in J. Chem. Phys. **119**, 4607 (2003), J. Chem. Phys. **121**, 4479 (2004), J. Chem. Phys. **124**, 054114 (2006), J. Chem. Phys. **124**, 094103 (2006).
- Parallel execution on distributed memory machines, as described in J. Comp. Chem. **19**, (1998), 1215. At present, SCF, DFT, MRCI, MP2, LMP2, CCSD(T) energies and SCF, DFT gradients are parallelized when running with conventional integral evaluation; integral-direct and density fitted SCF, DFT, LMP2, and LCCSD(T) are also parallel.

The program is written mostly in standard Fortran–90. Those parts which are machine dependent are maintained through the use of a supplied preprocessor, which allows easy interconversion between versions for different machines. Each release of the program is ported and tested on a number of IBM RS/6000, Hewlett-Packard, Silicon Graphics, Compaq, and Linux systems. A fuller description of the hardware and operating systems of these machines can be found at `http://www.molpro.net/supported`. The program additionally runs on Cray, Sun, Convex, Fujitsu and NEC SX4 platforms, as well as older architectures and/or operating systems from the primary list; however, testing is not carried out regularly on these systems, and hand-tuning of code may be necessary on porting. A large library of commonly used orbital basis sets is available, which can be extended as required. There is a comprehensive users' manual, which includes installation instructions. The manual is available in PostScript, PDF and also in HTML for mounting on a Worldwide Web server.

New methods and enhancements in Version 2006.1 include:

1. More consistent input language and input pre-checking.
2. More flexible basis input, allowing to handle multiple basis sets.
3. New more efficient density functional implementation, additional density functionals.
4. Low-order scaling local coupled cluster methods with perturbative treatment of triples excitations (LCCSD(T) and variants like LQCISD(T))
5. Efficient density fitting (DF) programs for Hartree-Fock (DF-HF), Density functional Kohn-Sham theory (DF-KS), Second-order Møller-Plesset perturbation theory (DF-MP2), as well as for all local methods (DF-LMP2, DF-LMP4, DF-LQCISD(T), DF-LCCSD(T))
6. Analytical QCISD(T) gradients
7. Analytical MRPT2 (CASPT2) and multi-state CASPT2 gradients, using state averaged MCSCF reference functions
8. Analytical DF-HF, DF-KS, DF-LMP2, and DF-SCS-LMP2 gradients
9. Explicitly correlated methods with density fitting: DF-MP2-R12/2A', DF-MP2-F12/2A' as well as the local variants DF-LMP2-R12/2*A(loc) and DF-LMP2-F12/2*A(loc).
10. Multi-state MRPT2, MS-CASPT2
11. Coupling of multi-reference perturbation theory and configuration interaction (CIPT2)
12. DFT-SAPT
13. Transition moments and transition Hamiltonian between CASSCF and MRCI wavefunctions with different orbitals.
14. Douglas-Kroll-Hess Hamiltonian up to arbitrary order.

15. A new spin-orbit integral program for generally contracted basis sets.
16. Improved procedures for geometry optimization and numerical Hessian calculations, including constrained optimization.
17. Improved facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients.
18. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.
19. Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (`mppx Version`).
20. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).

Future enhancements presently under development include

- Automatic calculation of anharmonic vibrational spectra using vibrational CI.
- Coupling of DFT and coupled cluster methods.
- Open-shell local coupled cluster methods.
- Explicitly correlated local coupled cluster methods.
- Local response methods (CC2, EOM-CCSD) for computing excitation energies and transition properties in large molecules.
- Analytical energy gradients for CCSD(T)
- Analytic second derivatives for DFT

These features will be included in the base version at later stages. The above list is for information only, and no representation is made that any of the above will be available within any particular time.

MOLPRO on the WWW

The latest information on MOLPRO, including program updates, can be found on the worldwide web at location `http://www.molpro.net/`.

References

All publications resulting from use of this program must acknowledge the following.

MOLPRO, version 2006.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel and G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer and M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni and T. Thorsteinsson , see http://www.molpro.net .

Some journals insist on a shorter list of authors; in such a case, the following should be used instead.

MOLPRO, version 2006.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, and others , see http://www.molpro.net .

Depending on which programs are used, the following references should be cited.

Integral evaluation (`SEWARD`**)**
R. Lindh, U. Ryu, and B. Liu, J. Chem. Phys. **95**, 5889 (1991).

Integral-direct Implementation
M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. **96**, 719 (1999).

`MCSCF/CASSCF`**:**
H.-J. Werner and P. J. Knowles, J. Chem. Phys. **82**, 5053 (1985);
P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **115**, 259 (1985).

See also:

H.-J. Werner and W. Meyer, J. Chem. Phys. **73**, 2342 (1980);
H.-J. Werner and W. Meyer, J. Chem. Phys. **74**, 5794 (1981);
H.-J. Werner, Adv. Chem. Phys. **LXIX**, 1 (1987).

Internally contracted MRCI:
H.-J. Werner and P.J. Knowles, J. Chem. Phys. **89**, 5803 (1988);
P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988).

See also:

H.-J. Werner and E.A. Reinsch, J. Chem. Phys. **76**, 3144 (1982);
H.-J. Werner, Adv. Chem. Phys. **LXIX**, 1 (1987).

Excited states with internally contracted MRCI:
P. J. Knowles and H.-J. Werner, Theor. Chim. Acta **84**, 95 (1992).

Internally contracted MR-ACPF, QDVPT, etc:
H.-J. Werner and P. J. Knowles, Theor. Chim Acta **78**, 175 (1990).

The original reference to uncontracted MR-ACPF, QDVPT, MR-ACQQ are:
R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988);
R. J. Cave and E. R. Davidson, J. Chem. Phys. **89**, 6798 (1988);
P. G. Szalay and R. J. Bartlett, Chem. Phys. Lett. **214**, 481 (1993).

Multireference perturbation theory (CASPT2/CASPT3):
H.-J. Werner, Mol. Phys. **89**, 645 (1996);
P. Celani and H.-J. Werner, J. Chem. Phys. **112**, 5546 (2000).

Coupling of multi-reference configuration interaction and multi-reference perturbation theory, P. Celani, H. Stoll, and H.-J. Werner, Mol. Phys. **102**, 2369 (2004).

Analytical energy gradients and geometry optimization
Gradient integral evaluation (ALASKA): R. Lindh, Theor. Chim. Acta **85**, 423 (1993);
MCSCF gradients: T. Busch, A. Degli Esposti, and H.-J. Werner, J. Chem. Phys. **94**, 6708 (1991);
MP2 and LMP2 gradients: A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **108**, 5185 (1998);
DF-LMP2 gradients: M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, J. Chem. Phys. **121**, 737 (2004).
QCISD and LQCISD gradients: G. Rauhut and H.-J. Werner, Phys. Chem. Chem. Phys. **3**, 4853 (2001);
CASPT2 gradients: P. Celani and H.-J. Werner, J. Chem. Phys. **119**, 5044 (2003).
Geometry optimization: F. Eckert, P. Pulay and H.-J. Werner, J. Comp. Chemistry **18**, 1473 (1997);
Reaction path following: F. Eckert and H.-J. Werner, Theor. Chem. Acc. **100**, 21, 1998.

Harmonic frequencies
G. Rauhut, A. El Azhary, F. Eckert, U. Schumann, and H.-J. Werner, Spectrochimica Acta **55**, 651 (1999).

Møller-Plesset Perturbation theory (MP2, MP3, MP4):
Closed-shell Møller-Plesset Perturbation theory up to fourth order [MP4(SDTQ)] is part of the coupled cluster code, see CCSD.

Open-shell Møller-Plesset Perturbation theory (RMP2):
R. D. Amos, J. S. Andrews, N. C. Handy, and P. J. Knowles, Chem. Phys. Lett. **185**, 256 (1991).

Coupled-Cluster treatments (QCI, CCSD, BCCD):
C. Hampel, K. Peterson, and H.-J. Werner, Chem. Phys. Lett. **190**, 1 (1992) and references therein. The program to compute the perturbative triples corrections has been developed by M. J. O. Deegan and P. J. Knowles, Chem. Phys. Lett. **227**, 321 (1994).

Equation-of-Motion Coupled Cluster Singles and Doubles (EOM-CCSD):
T. Korona and H.-J. Werner, J. Chem. Phys. **118**, 3006 (2003).

Open-shell coupled-cluster (RCCSD, UCCSD):
P. J. Knowles, C. Hampel and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993); Erratum: J. Chem. Phys. **112**, 3106 (2000).

Local MP2 (LMP2):
G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. **290**, 143 (1998)
M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999)
G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, J. Chem. Phys. **113**, 9443 (2000)
See also references on energy gradients and density fitting.

Local Coupled Cluster methods (LCCSD, LQCISD, LMP4):
C. Hampel and H.-J. Werner, J. Chem. Phys. **104** 6286 (1996)
M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001)
M. Schütz, Phys.Chem.Chem.Phys. 4, 3941 (2002)
See also references on energy gradients and density fitting.

Local triple excitations:
M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000);
M. Schütz, J. Chem. Phys. **113**, 9986 (2000).
M. Schütz, J. Chem. Phys. 116, 8772 (2002).

Density fitting methods:

DFT, Poisson fitting:	F. R. Manby, P. J. Knowles, and A. W. Lloyd, J. Chem. Phys. **115**, 9144 (2001).
DF-MP2, DF-LMP2:	H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003).
DF-LCCSD:	M. Schütz and F. R. Manby, Phys. Chem. Chem. Phys. **5**, 3349 (2003)
DF-HF:	R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004).
DF-LMP2 gradients:	M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, J. Chem. Phys. **121**, 737 (2004).
DF-LCCSD(T):	H.-J. Werner and M. Schütz, in prepation.

Explicitly correlated methods with density fitting:

DF-MP2-R12:	F. R. Manby, J. Chem. Phys. **119**, 4807 (2003).
DF-MP2-F12:	A. J. May and F. R. Manby, J. Chem. Phys. **132**, 4479 (2004).
DF-LMP2-R12(loc):	H.-J. and F. R. Manby, J. Chem. Phys., **124**, 054114 (2006).
DF-LMP2-F12(loc):	F. R. Manby H.-J. Werner, T. B. Adler, and A. J. May, J. Chem. Phys. **124**, 094103 (2006).

Full CI (FCI):
P. J. Knowles and N. C. Handy, Chem. Phys. Letters **111**, 315 (1984);
P. J. Knowles and N. C. Handy, Comp. Phys. Commun. **54**, 75 (1989).

Distributed Multipole Analysis (DMA):
A. J. Stone, Chem. Phys. Letters **83**, 233 (1981).

Valence bond:
D. L. Cooper, T. Thorsteinsson, and J. Gerratt, Int. J. Quant. Chem. **65**, 439 (1997);
D. L. Cooper, T. Thorsteinsson, and J. Gerratt, Adv. Quant. Chem. **32**, 51-67 (1998).
See also "An overview of the CASVB approach to modern valence bond calculations",
T. Thorsteinsson and D. L. Cooper, in *Quantum Systems in Chemistry and Physics. Volume 1: Basic problems and models systems*, eds. A. Hernndez-Laguna, J. Maruani, R. McWeeny, and S. Wilson (Kluwer, Dordrecht, 2000); pp 303-26.

Spin-orbit coupling:
A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles, and P. Palmieri, Mol. Phys., **98**, 1823 (2000).

Diabatization procedures:
H.-J. Werner and W. Meyer, J. Chem. Phys. **74**, 5802 (1981);
H.-J. Werner, B. Follmeg, and M. H. Alexander, J. Chem. Phys. **89**, 3139 (1988);
D. Simah, B. Hartke, and H.-J. Werner, J. Chem. Phys. **111**, 4523 (1999).

Contents

1 HOW TO READ THIS MANUAL

This manual is organized as follows: The next chapter gives an overview of the general structure of MOLPRO. It is essential for the new user to read this chapter, in order to understand the conventions used to define the symmetry, records and files, orbital spaces and so on. The later chapters, which describe the input of the individual program modules in detail, assume that you are familiar with these concepts. The appendices describe details of running the program, and the installation procedure.

Throughout this manual, words in `Typewriter Font` denote keywords recognized by MOLPRO. In the input, these have to be typed as shown, but may be in upper or lower case. Numbers or options which must be supplied by the user are in *italic*. In some cases, various different forms of an input record are possible. This is indicated as [*options*], and the possible options are described individually in subsequent subsections.

2 RUNNING MOLPRO

On Unix systems, MOLPRO is accessed using the *molpro* unix command. The syntax is

`molpro` [*options*] [*datafile*]

MOLPRO's execution is controlled by user-prepared data; if *datafile* is not given on the command line, the data is read from standard input, and program results go to standard output. Otherwise, data is taken from *datafile,* and the output is written to a file whose name is generated from *datafile* by removing any trailing suffix, and appending `.out`. If the output file already exists, then the old file is appended to the same name with suffix `.out_1`, and then deleted. This provides a mechanism for saving old output files from overwriting. Note that the above behaviour can be modified with the `-o` or `-s` options.

Unless disabled by options, the user data file is prepended by one or more default procedure files, if these files exist. These are, in order of execution, the file `molproi.rc` in the system directory containing the molpro command itself, `$HOME/.molproirc` and `./molproi.rc`.

2.0.1 Options

Most options are not required, since sensible system defaults are usually set. Options as detailed below may be given, in order of decreasing priority, on the command line, in the environment variable MOLPRO, or in the files `./molpro.rc`, `$HOME/.molprorc`, and `molpro.rc` in the system directory.

`-o` | `--output` *outfile* specifies a different output file.

`-x` | `--executable` *executable* specifies an alternative MOLPRO executable file.

`-d` | `--directory` *directory1*`:`*directory2*... specifies a list of directories in which the program will place scratch files. For detailed discussion of optimal specification, see the installation guide.

`-s` | `--nobackup` disables the mechanism whereby an existing output file is saved. `--backup` switches it on again.

`-v` | `--verbose` causes the procedure to echo debugging information; `--noverbose` selects quiet operation (default).

`-e|--echo-procedures` causes the contents of the default procedure files to be echoed at run time. `--noecho-procedures` selects quiet operation (default).

`-f|--procedures` enables the automatic inclusion of default procedure files (the default); `--noprocedures` disables such inclusion.

`-g|--use-logfile` causes some long parts of the program output, for example during geometry optimizations and finite-difference frequency calculations, to be diverted to an auxiliary output file whose name is derived from the output file by replacing its suffix (usually `.out`) by `.log`. `--nouse-logfile` disables this facility, causing all output to appear in the normal output file.

`-m|--memory` *memory* specifies the working memory to be assigned to the program, in 8-byte words. The memory may also be given in units of 1000 words by appending the letter `k` to the value, or in units of 1000000 with the key `m`, or 10^9 with `g`. `K, B, G` stand for 2^{10}, 2^{20} and 2^{30}.

`-I|--main-file-repository` *directory* specifies the directory where the permanent copy of any integral file (file 1) resides. This may be a pathname which is absolute or relative to the current directory (e.g., '`.`' would specify the current directory). Normally, the `-I` directory should be equal to the `-d` working directory to avoid copying of large integral files.

`-W |--wavefunction-file-repository` is similar to `--wavefunction-file-repository` except that it refers to the directory for the wavefunction files (2,3 and 4).

`-X |--xml-output` specifies that the output file will be a well-formed XML file suitable for automatic post-processing. Important data such as input, geometries, and results are tagged, and the bulk of the normal descriptive output is wrapped as XML comments. `--no-xml-output` switches off this behaviour and forces a plain-text output file to be produced.

`-L|--library` *directory* specifies the directory where the basis set library files (`LIBMOL*`) are found.

`-1|--file-1-directory` *directory:directory:...* specifies the directory where the runtime file 1 will be placed, overriding `--directory` for this file only. `-2`, `-3`, `-4`, `-5`, `-6`, `-7`, `-8` and `-9` may be used similarly. Normally these options should not be given, since the program tries to use what is given in `-d` to optimally distribute the I/O.

There are a number of other options for tuning and system parameters, but these do not usually concern the general user.

It is not usually necessary to specify any of these options; the defaults are installation dependent and can be found in the system configuration file `molpro.rc` in the same directory as the `molpro` command itself.

2.0.2 Running MOLPRO on parallel computers

MOLPRO will run on distributed-memory multiprocessor systems, including workstation clusters, under the control of the Global Arrays parallel toolkit. There are also some parts of the

code that can take advantage of shared memory parallelism through the OpenMP protocol, although these are somewhat limited, and this facility is not at present recommended. It should be noted that there remain some parts of the code that are not, or only partly, parallelized, and therefore run with replicated work. Additionally, some of those parts which have been parallelized rely on fast inter-node communications, and can be very inefficient across ordinary networks. Therefore some caution and experimentation is needed to avoid waste of resources in a multiuser environment.

Molpro can be compiled in three different ways:

1. Serial execution only. In this case, no parallelism is possible at run time.
2. 'MPP': a number of copies of the program execute simultaneously a single task. For example, a single CCSD(T) calculation can run in parallel, with the work divided between the processors in order to achieve a reduced elapsed time.
3. 'MPPX': a number of copies of the program run in serial executing identical independent tasks. An example of this is the calculation of gradients and frequencies by finite difference: for the initial wavefunction calculation, the calculation is replicated on all processes, but thereafter each process works in serial on a different displaced geometry. At present, this is implemented only for numerical gradients and Hessians.

Which of these three modes is available is fixed at compilation time, and is reported in the job output. The options, described below, for selecting the number and location of processors are identical for MPP and MPPX.

Specifying parallel execution The following additional options for the `molpro` command may be used to specify and control parallel execution.

`-n` | `--tasks` *tasks/tasks_per_node:smp_threads* *tasks* specifies the number of Global Array processes to be set up, and defaults to 1. *tasks_per_node* sets the number of GA processes to run on each node, where appropriate. The default is installation dependent. In some environments (e.g., IBM running under Loadleveler; PBS batch job), the value given by `-n` is capped to the maximum allowed by the environment; in such circumstances it can be useful to give a very large number as the value for `-n` so that the control of the number of processes is by the batch job specification. *smp_threads* relates to the use of OpenMP shared-memory parallelism, and specifies the maximum number of OpenMP threads that will be opened, and defaults to 1. Any of these three components may be omitted, and appropriate combinations will allow GA-only, OpenMP-only, or mixed parallelism.

`-N` | `--task-specification` *user1:node1:tasks1,user2:node2:tasks2...* *node1, node2* etc. specify the host names of the nodes on which to run. On most parallel systems, node1 defaults to the local host name, and there is no default for node2 and higher. On Cray T3E and IBM SP systems, and on systems running under the PBS batch system, if -N is not specified, nodes are obtained from the system in the standard way. *tasks1, tasks2* etc. may be used to control the number of tasks on each node as a more flexible alternative to `-n` / *tasks_per_node*. If omitted, they are each set equal to `-n` / *tasks_per_node*. *user1,*

user2 etc. give the username under which processes are to be created. Most of these parameters may be omitted in favour of the usually sensible default values.

`-G|--global-memory` *memory* Some parts of the program make use of Global Arrays for holding and communicating temporary data structures. This option sets the amount of memory to allocate in total across all processors for such activities.

3 DEFINITION OF MOLPRO INPUT LANGUAGE

3.1 Input format

MOLPRO's execution is controlled by an input file. In general, each input record begins with a keyword, which may be followed by data or other keywords. Molpro input contains commands, directives, options and data. The commands and directives are sequentially executed in the order they are encountered. Furthermore, procedures can be defined anywhere in the input, which can include any number of commands and directives. They are only executed when called (which may be before or after the definition in the input file).

The input file can be written in free format. The following conversions take place:

, (comma)	move to next tab stop, i.e. this delimits input fields
; (semicolon)	end of record, i.e. a new record is started
! (exclamation mark)	ignore rest of input line (useful for comments)
--- (three dashes)	end of file (rest of input is ignored)

Input may be given upper or lower case. The input processor converts all characters to upper case. All integers are appended with "." (only floating point numbers are read by the program).

Several logical input records can actually be typed on one line and separated by semicolons, i.e., a given input line may contain many actual commands (separated by semicolons), or just one, as you prefer. These basic command units (records) delimited by semicolons are also frequently referred to as *cards* throughout this manual.

Exception to these general rules are:

`***`	first data line always
`INCLUDE`	include other input file
`FILE`	definition of named files
`TEXT`	prints text
`TITLE`	defines a title for the run or a table
`CON`	specifies orbital configurations
`---`	last line of input

These commands always occupy a whole line. Using `INCLUDE` it is possible to open secondary input files. If an `INCLUDE` command is encountered, the new input file is opened and read until its end. Input is then continued after the include card in the first file. `INCLUDE`'s may be nested.

A MOLPRO input record (card) contains a number of input *fields*. Input fields may be up to 256 characters wide and contain either expressions or strings. The fields can be separated by commas or blanks. We recommend the general use of commas in order to avoid unexpected results.

Each line may start with a label. A label is separated from the body of the line by a colon (:). The colon is part of the label. The length of the label must not exceed 6 characters (including the colon) and the labels must be unique. Labels may be useful with `GOTO` commands. Example:

```
GOTO,START:
...
START: CCSD(T)
```

Here `START:` is a label, and `CCSD(T)` is a command.

Strings containing blanks can be entered using quotes. For instance, `'This is a string'` is interpreted as one string, but `This is a string` is a sequence of four strings in four subsequent fields. Strings in quotes are not converted to upper case.

Input lines may be concatenated using \ at the end of the line(s) to be continued. Any number of lines may be concatenated up to a total length of 1024 characters (only 500 characters are possible on older IBM systems).

Filenames may be up to 31 characters long, provided that long filenames are supported by the Unix system used. An exception are older CRAY systems, which allow only 8 characters for the names of binary MOLPRO files.

3.2 Commands

A command invokes a particular program. It may be followed by local input for this program, enclosed in curley brackets[1]

The general format is either

`COMMAND`, *options*

or

{ `COMMAND`,*options*
directives
data
}

Examples for commands are `HF, MP2, CCSD(T), MCSCF, MRCI`. Examples for directives are `OCC, CLOSED, WF, PRINT`. Directives can be in any order, unless otherwise noted. Data can follow certain directives. For the format of options, directives and data see subsections 3.3, 3.5, and 3.6, respectively.

In the following, such a sequence of input will be denoted a *command block*. Special command blocks are the geometry and basis blocks.

The options given on the command line may include any options relevant to the current program. For instance, in DF-LMP2-R12 this could be options for density fitting, local, explicit, and/or thresholds. Alternatively, options can be specified on individual directives like

`DFIT`,*options*
`LOCAL`,*options*
`EXPLICIT`,*options*
`THRESH`,*options*

In these cases, only the options belong to the corresponding directive are valid; thus, if an option for `EXPLICIT` would be specified, e.g., on the `DFIT` directive, an error would result. This error would be detected already in the input prechecking stage.

[1] Depending on the parameter `STRICTCHECK` in file `lib/variable.registry` the program may tolerate directives given after commands without curley brackets. The program checks for ambiguities in the input. A directive is considered ambiguous if a command or procedure with the same name is known, and the directive is not in a command block (i.e., no curley brackets are used). `STRICTCHECK=0`: The input checker tolerates ambiguous directives if they a are followed by a non ambiguous directive which is valid for the current command. `STRICTCHECK=1`: The input checker does not tolerate any ambiguous directives. `STRICTCHECK=2`: The input checker does not tolerate any directives outside curley brackets. The default is `STRICTCHECK=0`, which gives the maximum possible compatibility to previous Molpro versions.

As already mentioned, the use of curly brackets is normally compulsary if more than one input line is needed. In the case of one-line commands, curley brackets are needed as well if the next command or procedure has the same name as a directive valid for the current command.

Note: DIRECT and associated options cannot be specified on command lines any more.

3.3 Directives

Directives serve to specify input data and special options for programs. They start with a keyword, followed by data and/or options. The general format is

DIRECTIVE,*data*,*options*

The format of data and options is specified in the subsequent sections. Data must always be given before any options.

Examples for directives are

OCC,CORE, CLOSED, WF, LOCAL, DFIT, ...

3.4 Global directives

Certain directives can be given anywhere in the input, i.e. either inside or outside command blocks. If they are given inside of command blocks, the specified options are valid only locally for the current program. However, if they are given outside a command block, they act globally, and are used for all programs executed after the input has been encountered. Local options have preference over global options.

The following directives can be either local or global:

Wavefunction definition: OCC,CORE, CLOSED, FROZEN, WF
Thresholds and options: LOCAL, DFIT, DIRECT, EXPLICIT, THRESH, PRINT, GRID

If such options are given outside a command block, a context can be specifiied

DIRECTIVE,*data*,CONTEXT=*context*,

e.g.,

OCC,3,1,1,CONTEXT=HF
OCC,4,1,2,CONTEXT=MCSCF

CONTEXT can be any valid command name (or any valid alias for this), but internally these are converted to one of the following: HF (Hartree-Fock and DFT), MC (MCSCF and CASSCF), CC (single reference correlation methods, as implemented in the CCSD program), CI (multireference correlation methods, as implemented in the MRCI program). The directive will then be applied to one of the four cases. Several contexts can be specified separated by colon, e.g.,

CONTEXT=HF:CCSD

If only a single context is given (no colon), shortcuts for the specifying the CONTEXT option are obtained by postfixing *context* to the command name, e.g.,

OCC_HF,3,1,1
OCC_MCSCF,4,1,2

If no context is given, the default is HF. The default occupations for single reference methods (e.g., MP2, CCSD) are the ones used in HF, the defaults for multireference methods (e.g. RS2, MRCI) correspond to those used in MCSCF.

3.5 Options

Options have the general form NAME[=*value*]

where value can be a number, and expression, or a string. Several options are separated by comma or blank. NAME must begin with a character [A-Z]. If options are given on a COMMAND line or on directives within a command block, they are valid only for the corresponding program (see Sec. 3.3). If options are given in a procedure, they are valid only in the procedure and procedures called from the current procedure; whenever a procedure is terminated, the options of the previous level are restored.

Options can also be single keywords, like SYM or NOSYM. In this case, the option is switched on or off, depending whether or not the key begins with NO. Alternatively, such logical options can also be set or unset using NAME=ON or NAME=OFF. For instance, SYM=OFF is equivalent to NOSYM. Furthermore, YES and NO are aliases for ON and OFF, respectively.

3.6 Data

Data are defined as a sequence of numbers, expressions, or strings, separated by commas or blanks. Generally, the order of data is essential. Empty fields are interpreted as zeros. Strings and variables must begin with a character [A-Z]. If + or − follows blank and directly precedes a number or variable it is interpreted as sign and not a binary operator. If there are no blanks before and after such operators, or blanks follow them, they are interpreted as binary operators. Examples:

```
3 - 4 4     yields [-1,4]
3-4 4       yields [-1,4]
3 -4 4      yields [3,-4,4]
3,-4 4      yields [3,-4,4]
3, -4, 4    yields [3,-4,4]
```

Expressions (including numbers) may contain variables.

Examples for the use of data: geometry and basis input, LATTICE, OCC, CLOSED, CORE, WF directives.

In some cases several lines of data are needed for a certain command or directive; in such cases the data must follow directly the corresponding command|directive, and must be enclosed in square brackets:

```
COMMAND,options
[data]
```

Normally, the input format of data is MOLPRO style, i.e., numbers are separated by commas, and variables as well as expressions can be used.

If data are included using external files, the input format of *data* is free format: no commas are needed, but no variables and expressions can be used.

3.7 Expressions

In any input field, data can be entered in the form of expressions. Numbers and variables are special cases of expressions. An expression is typed in Fortran style and may contain any number of nested parenthesis. The standard intrinsic functions are also available (see next section).

MOLPRO understands both arithmetic and logical expressions. The result of an arithmetic expression is a *real* (double precision) number. Internally, all integers are also converted to *real* numbers. The result of a logical expression is either `.TRUE.` or `.FALSE.`. Internally, `.TRUE.` is stored as a one (1.0), and `.FALSE.` as zero (0.0). Expressions may contain any number of variables.

The following standard operations can be performed :

expr + *expr*	Addition
expr − *expr*	Subtraction
expr * *expr*	Multiplication
expr / *expr*	Division
expr .OR. *expr*	Logical OR
expr .AND. *expr*	Logical AND
expr .XOR. *expr*	Exclusive OR
.NOT.*expr*	Logical NOT
expr .GT. *expr*	Greater Than
expr .EQ. *expr*	Equal
expr .LT. *expr*	Less Than
expr .GE. *expr*	Greater Equal
expr .LE. *expr*	Less Equal
expr .NE. *expr*	Not Equal
expr **expr*	Exponentiation
expr ^ *expr*	Exponentiation
(*expr*)	Parenthesis (no effect)
−*expr*	Change sign
+*expr*	Keep sign (no effect)

3.8 Intrinsic functions

Expressions may contain the following intrinsic functions:

ABS(*expr*)	Absolute value
MAX(*expr*,*expr*, ...)	Largest value of arbitrary number of numbers or expressions
MIN(*expr*,*expr*, ...)	Smallest value of arbitrary number of numbers of expressions
EXP(*expr*)	Exponential
LOG(*expr*)	Natural Logarithm
LOG10(*expr*)	Common Logarithm
SQRT(*expr*)	Square Root
NINT(*expr*)	Next nearest integer
INT(*expr*)	Truncate to integer
SIN(*expr*)	Sine

COS(*expr*)	Cosine
TAN(*expr*)	Tangent
ASIN(*expr*)	Arcsine
ACOS(*expr*)	Arccosine
ATAN(*expr*)	Arctangent
COSH(*expr*)	Hyperbolic cosine
SINH(*expr*)	Hyperbolic sine
TANH(*expr*)	Hyperbolic tangent
MOD(*expr1* , *expr2*)	Remainder: expr1-INT(expr1/expr2)*expr2

Note: all trigonometric functions use or produce angles in degrees.

3.9 Variables

3.9.1 Setting variables

Data and results can be stored in MOLPRO variables. Variables can be of type string, floating, or logical and may be used anywhere in the input.

The syntax for setting variables is

VARNAME1=*expression* [unit],VARNAME2=*expression* [unit]

where unit is optional. If a variable is undefined, zero is assumed.

Variables are useful for running the same input with different actual parameters (e.g. geometries or basis function exponents), and to store and manipulate the results. *Arrays* are variables with an index in parenthesis, e.g., var(1). The number of elements in an array var is #var. The array length can be reset to zero by the CLEAR directive or simply by modifying #var. Variables and variable arrays may be displayed at any place in the output by the SHOW command, and whole tables of variables can be generated using the TABLE command. For more details about variables see section 8.

3.9.2 String variables

Special care is necessary when using strings. In order to avoid unexpected results, either a $ has to be prefixed whenever a string variable is set, or the string has to be given in quotes. Possible forms are

$name=string
name='string'
name=*string variable*
$name=*string variable*

Examples:

```
string1='This is a string'  !define a string variable. Text in quotes is not
                            ! converted to upper case.
string2=string1             !assign string variable string1 to a new variable.
$string3=string1            !equivalent to previous case.
$string4=mystring           !define a string variable. Since ''mystring'' is not
                            !given in quotes, !it will be converted to upper case.
string5=mystring            !string5 will not be a string variable since $ is missing.
```

yields

```
 SETTING STRING1        =    This is a string
 SETTING STRING2        =    This is a string
 SETTING STRING3        =    This is a string
 SETTING STRING4        =    MYSTRING
 VARIABLE MYSTRING UNDEFINED, ASSUMING 0
 SETTING STRING5        =         0.00000000
```

For more information concerning strings and string variables, see section 8.3

3.10 Procedures

3.10.1 Procedure definition

Procedures are sequences of commands and/or options. They can be defined anywhere in the input as

[PROC]*procname*={
command blocks
directives
}

or

PROC *procname*
command blocks
directives
ENDPROC

In order to avoid unexpected results, *procname* must differ from all known command names. Procedures must not contain geometry blocks.

Note that procedures are not executed when encountered in the input, but only when called. Procedure definitions must not be nested. Procedures can contain procedure calls up to a nesting level of 10.

3.10.2 Procedure calls

Procedures can be called anywhere in the input. The syntax is the same as for commands (cf. section 3.2), except that the procedure name replaces the command name.

PROCEDURE

No options are allowed on procedure calls. However, specific options may be set using directives within the procedure, and these are then valid for all programs within the procedure which follow the directive. When execution of the procedure is finished, the previous global options are restored. The hierarchy in which options are processed is as follows:

Global options
Options in procedures
Command line options
Options given on directives within a command block

The last option set is then actually used. Thus, options specified on command lines or within command blocks have preference over procedure options, and procedure options have preference over global options.

4 GENERAL PROGRAM STRUCTURE

This chapter gives an overview of the most important features of MOLPRO. For the new user, it is essential to understand the strategies and conventions described in this section, in particular the meaning of *files* and *records*, and the use of *symmetry*. This chapter will focus on general aspects; detailed information about each command will be given in later chapters. Information about commands and parameters can also be obtained using the MOLPRO help facility (see section 4.13).

4.1 Input structure

A typical MOLPRO input has the following structure:

```
***,title                    !title (optional)
memory,4,m                   !memory specification (optional)
file,1,name.int              !permanent named integral file (optional)
file,2,name.wfu              !permanent named wavefunction file (optional)

gprint,options               !global print options (optional)
gthresh,options              !global thresholds (optional)
gdirect[,options]            !global direct (optional)
gexpec,opnames               !global definition of one-electron operators (optional)

basis=basisname              !basis specification. If not present, cc-pVDZ is used
geometry={...}               !geometry specification

var1=value,var2=value,...    !setting variables for geometry and/or wavefunction definitions

{command,options             !program or procedure name
 directive,data,option       !directives for command (optional)
...
}                            !end of command block
---                          !end of input (optional)
```

If the memory card is given, it should be the first card (after the optional title card). If any file cards are given, they should follow immediately. The order of `basis`, `geometry`, `gprint`, `gdirect`, `gthresh`, `gexpec`, and variable definitions is arbitrary. It is possible to call several programs one after each other. It is also possible to redefine basis set and/or geometry between the call to programs; the program will recognize automatically if the integrals have to be recomputed.

4.2 Files

MOLPRO uses three sequential text files, namely the *input file*, the *output file*, and the *punch file*. The punch file is a short form of the output which contains the most important data and results, such as geometries, energies, dipole moments, etc. The punch file can be processed by the separate program *READPUN*, which selects specific results by keywords and is able to produce ordered tables in user supplied format. Furthermore, there are up to 9 binary MOLPRO

files available, each one known to the program simply by its number (1 to 9). By default, they are temporary files, usually allocated dynamically by the program, but they can be connected to permanent files with the FILE command. Each file is direct access, and word addressable (word=64 bit usually), but is organised in *records* of any length. The name, address and length of each record is held in a directory at the start of the file.

File 1 is the *main file*, holding basis set, geometry, and the one and two electron integrals. By default, file 2 is the *dump file* and used to store the wavefunction information, i.e. orbitals, CI coefficients, and density matrices. File 3 is an auxiliary file which can be used in addition to file 2 for restart purposes. Often files 1 and 2 (and 3) are declared as permanent files (see FILE) to enable restarts. Storing the wavefunction information on file 2 is useful, since the integral file is overwritten at each new geometry, while the orbitals and CI coefficients of one calculation can be used as a starting guess for the next calculation at a neighbouring geometry. Files 4 to 8 are used as scratch space, e.g., for sorting the integrals, storage of transformed integrals and of the CI vectors. These files should normally not be made permanent.

4.3 Records

Record names are positive integers, and are usually referred to in the format *record.file*, e.g., 2100.2 means the record called 2100 on file 2. Note that these names are quite arbitrary, and their numerical values have nothing to do with the order of the records in the file. Record names ≤ 2000 are reserved for standard quantities (e.g. integrals, properties etc.) and you should never use these in an input, unless you know exactly what you are doing. Some important default records to remember are

2100	RHF dump record (closed and open-shell)
2200	UHF dump record
2140	MCSCF dump record
4100	CPHF restart information
5000	MCSCF gradient information
5100	CP-MCSCF gradient information
5200	MP2 gradient information
5300	Hessian restart information
5400	Frequencies restart information
6300	Domain restart information

If an input contains several wavefunction calculations of the same type, e.g., several MCSCF calculations with different active spaces, the record number will be increased by 1 for each calculation of the same type. Thus, the results of the first SCF calculation in an input are stored in dump record 2100.2, the second SCF in record 2101.2, the first MCSCF in 2140.2, the second MCSCF in 2141.2 and so on. Note that these numbers refer to the occurrence in the input and not on the order in which the calculations are performed in the actual run. If an input or part of it is repeated using DO loops, this ensures that each calculation will start with the orbitals from the corresponding orbitals from the previous cycle, as long as the order of the commands in the input remains unchanged. If for instance the first SCF would be skipped in the second cycle using some IF / ENDIF structure, the second SCF would still use record 2101.2. Thus, under most circumstances the program defaults are appropriate, and the user does not have to specify the records.

After a restart this logic will still work correctly if the number and sequence of SCF and MCSCF commands is kept unchanged. Thus, if you want to skip certain parts of the input after a restart, it is recommended to use IF / ENDIF structures or the GOTO command rather than to delete or comment certain commands. If for some reason this is not possible, the START and ORBITAL directives can be used to specify explicitely the records to be used.

In general we recommend the use of program defaults whenever possible, since this minimizes the probability of input errors and frustration!

After completion of each program step, MOLPRO prints a summary of the records on each file.

4.4 Restart

Information from the permanent files is automatically recovered in subsequent calculations. This can be controlled using the RESTART directive.

4.5 Data set manipulation

It is possible to truncate files and rename or copy records using the DATA command. Several standard matrix operations can be performed with MATROP, e.g., printing records, linearly combining or multiplying matrices, or forming the trace of a product of two matrices.

4.6 Memory allocation

MOLPRO allocates memory dynamically as required by the user on the MEMORY card. Thus it is not necessary to maintain different versions of the program with different memory sizes. If the MEMORY command is omitted, the program will use a default memory size, which depends on the hardware used and how the program was installed. Note that, on Unix machines, the default memory can be set on the molpro command line using the flag -m.

4.7 Multiple passes through the input

It is possible to perform loops over parts of the input using DO loops, very much as in FORTRAN programs. DO loops may be nested to any reasonable depth. This can be conveniently used, for instance, to compute automatically whole potential energy surfaces.

4.8 Symmetry

MOLPRO can use Abelian point group symmetry only. For molecules with degenerate symmetry, an Abelian subgroup must be used — e.g., C_{2v} or D_{2h} for linear molecules. The symmetry group which is used is defined in the integral input by combinations of the symmetry elements x, y, and z, which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose z to be the unique axis where appropriate (essential for C_2 and C_{2h}). The possibilities in this case are shown in Table 1.

Normally, MOLPRO determines the symmetry automatically, and rotates and translates the molecule accordingly. However, explicit symmetry specification is sometimes useful to fix the orientation of the molecule or to use lower symmetries.

The irreducible representations of each group are numbered 1 to 8. Their ordering is important and given in Tables 2 – 4. Also shown in the tables are the transformation properties of products

Table 1: The symmetry generators for the point groups

Generators	Point group
(null card)	C_1 (i.e. no point group symmetry)
`X` (or `Y` or `Z`)	C_s
`XY`	C_2
`XYZ`	C_i
`X,Y`	C_{2v}
`XY,Z`	C_{2h}
`XZ,YZ`	D_2
`X,Y,Z`	D_{2h}

Table 2: Numbering of the irreducible representations in D_{2h}

	D_{2h}	
No.	Name	Function
1	A_g	s
2	B_{3u}	x
3	B_{2u}	y
4	B_{1g}	xy
5	B_{1u}	z
6	B_{2g}	xz
7	B_{3g}	yz
8	A_u	xyz

of x, y, and z. s stands for an isotropic function, e.g., s orbital, and for these groups, this gives also the transformation properties of x^2, y^2, and z^2. Orbitals or basis functions are generally referred to in the format *number.irrep*, i.e. 3.2 means the third orbital in the second irreducible representation of the point group used.

4.9 Defining the wavefunction

In all program modules where such information is required, the total symmetry of the N-electron wavefunction is defined on `WF` (wavefunction) cards in the following way:

`WF`,*nelec,irrep,spin*

or, alternatively

`WF`,[`NELEC`=*nelec*],[`SYM[METRY]`=*irrep*],[`spin`=*spin*],[`CHARGE`=*charge*]

where *nelec* is the total number of electrons, *irrep* is the number of the irreducible representation,

Table 3: Numbering of the irreducible representations in the four-dimensional groups

	C_{2v}		C_{2h}		D_2	
No.	Name	Function	Name	Function	Name	Function
1	A_1	s,z	A_g	s,xy	A	s
2	B_1	x,xz	A_u	z	B_3	x,yz
3	B_2	y,yz	B_u	x,y	B_2	y,xz
4	A_2	xy	B_g	xz,yz	B_1	xy

Table 4: Numbering of the irreducible representations in the two-dimensional groups

	C_s		C_2		C_i	
No.	Name	Function	Name	Function	Name	Function
1	A'	s,x,y,xy	A	s,z,xy	A_g	s,xy,xz,yz
2	A''	z,xz,yz	B	x,y,xz,yz	A_u	x,y,z

and *spin* equals $2 \times S$, where S is the total spin quantum number. Instead of *nelec* also *charge* can be given, which specifies the total charge of the molecule. For instance, for a calculation in C_{2v} symmetry with 10 electrons, `WF,10,3,0` denotes a $^1B_2$ state, and `WF,10,1,2` a $^3A_1$ state. The charge can also be defined by setting the variable `CHARGE`:

`SET,CHARGE=`*charge*

This charge will be used in all energy calculations following this input. Not that `SET` is required, since `CHARGE` is a system variable (cf. section 8.4).

Although in principle each program unit requires a `WF` command, in practice it is seldom necessary to give it. The program remembers the information on the `WF` card, and so one might typically specify the information in an SCF calculation, but then not in subsequent MCSCF or CI calculations; this also applies across restarts. Furthermore, *nelec* defaults to the sum of the nuclear charges, *irrep* to 1 and *spin* to 0 or 1; thus in many cases, it is not necessary to specify a `WF` card at all.

4.10 Defining orbital subspaces

In the SCF, MCSCF, and CI programs it may be necessary to specify how many orbitals in each symmetry are *occupied* (or *internal* in CI), and which of these are *core* or *closed shell* (doubly occupied in all CSFs). This information is provided on the `OCC`, `CORE`, and `CLOSED` cards in the following way:

`OCC,`$m_1,m_2,\ldots,m_8$; `CORE,`$co_1,co_2,\ldots,co_8$; `CLOSED,`$cl_1,cl_2,\ldots,cl_8$; `FROZEN,`$fr_1,fr_2,\ldots,fr_8$;

where m_i is the number of occupied orbitals (including core/frozen and closed), co_i the number of core orbitals, and cl_i is the number of closed-shell orbitals (including the core orbitals) in the irreducible representation i. In general, $m_i \geq cl_i$, and $cl_i \geq co_i$. It is assumed that these numbers refer to the first orbitals in each irrep. `FROZEN` only exists in the MCSCF program and denotes

frozen core orbitals that are not optimized (note that in older MOLPRO versions frozen core orbitals were denoted CORE).

Note that the OCC and CLOSED cards have slightly different meanings in the SCF, MCSCF and CI or CCSD programs. In SCF and MCSCF, *occupied* orbitals are those which occur in any of the CSFs. In electron correlation methods (CI, MPn, CCSD etc), however, OCC denotes the orbitals which are occupied in any of the *reference* CSFs. In the MCSCF, FROZEN orbitals are doubly occupied in all CSFs and *frozen* (not optimized), while *closed* denotes all doubly occupied orbitals (frozen plus optimized). In the CI and CCSD programs, *core* orbitals are those which are not correlated and *closed* orbitals are those which are doubly occupied in all reference CSFs.

OCC, CORE and CLOSED commands are generally required in each program module where they are relevant; however, the program remembers the most recently used values, and so the commands may be omitted if the orbital spaces are not to be changed from their previous values. Note that this information is also preserved across restarts. Note also, as with the WF information, sensible defaults are assumed for these orbital spaces. For full details, see the appropriate program description.

4.11 Selecting orbitals and density matrices (ORBITAL, DENSITY)

As outlined in section 4.3, the information for each SCF or MCSCF calculation is stored in a *dump record*. Dump records contain orbitals, density matrices, orbital energies, occupation numbers, fock matrices and other information as wavefunction symmetries etc. Subsequent calculation can access the orbitals and density matrices from a particular record using the ORBITAL and DENSITY directives, respectively. These input cards have the same structure in all programs. The general format of the ORBITAL and DENSITY directives is as follows.

ORBITAL[,[RECORD=]*record*] [,[TYPE=]*orbtype*] [,STATE=*state*] [,SYM[METRY]=*symmetry*]
[,SPIN=*spin*] [,MS2=*ms2*] [,[N]ELEC=*nelec*] [,SET=*iset*] [,OVL] [,NOCHECK] [,IGNORE[_ERROR]]

DENSITY[,[RECORD=]*record*] [,[TYPE=]*dentype*] [,STATE=*state*] [,SYM[METRY]=*symmetry*]
[,SPIN=*spin*] [,MS2=*ms2*] [,[N]ELEC=*nelec*] [,SET=*iset*]

where the (optional) specifications can be used to select specific orbitals, if several different orbital sets are stored in the same record. The meaning of the individual specifications are as follows:

orbtype — Orbital type. This can be one of
CANONICAL: canonical or pseudo-canonical orbitals;
NATURAL: natural orbitals;
LOCAL: localized orbitals;
LOCAL(PM) : localized Pipek-Mezey orbitals;
LOCAL(BOYS) : localized Boys orbitals;
PROJECTED: projected virtual orbitals used in local calculations.
Without further specification, the most recently computed orbitals of the specified type are used. If the orbital type is not specified, the program will try to find the most suitable orbitals automatically. For instance, in MRCI calculations NATURAL orbitals will be used preferentially if available; MRPT (CASPT2) calculations will first search for CANONICAL orbitals, and local calculations will first look for LOCAL orbitals. Therefore, in most cases the orbital type needs not to be specified.

state	Specifies a particular state in the form *istate.isym*. For instance, 2.1 refers to the second state in symmetry 1. This can be used if density matrices or natural orbitals have been computed for different states in a state-averaged CASSCF calculation. If not given, the state-averaged orbitals are used. The specification of *isym* is optional; it can also be defined using the SYMMETRY key.
dentype	Density type. This can be one of CHARGE: charge density; SPIN: UHF spin density; TRANSITION: transition density matrix; The default is CHARGE.
symmetry	Specifies a particular state symmetry. Alternatively, the state symmetry can be specified using STATE (see above).
spin	Spin quantum number, i.e. 0 for singlet, 1/2 for doublet, 1 for triplet, etc. Alternatively MS2 can be used.
ms2	$2M_S$, i.e. 0 for singlet, 1 for doublet, 2 for triplet etc. Alternatively, SPIN can be used.
nelec	Number of electrons.
iset	Set number of orbitals. The orbital sets are numbered in the order they are stored.

If OVL is specified, the starting orbitals are obtained by maximizing the overlap with previous orbitals. By default, this is used if the basis dimension of the previous orbitals is different then the current one. If OVL is specified this procedure is used even if the basis dimensions are the same, which is occasionally useful if the contraction scheme changed.

If NOCHECK is specified, some consistency checks for finding correct orbitals are skipped, and error messages like "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" are ignored.

If IGNORE_ERROR is specified, MPn or triples calculations can be forced with other than canonical orbitals. Note that this can lead to meaningless results!

If any of the above options are given, they must be obeyed strictly, i.e., the program aborts if the request cannot be fulfilled.

Examples:

```
ORBITAL,2100.2                    !Use SCF orbitals
ORBITAL,2140.2                    !Use (state-averaged) MCSCF orbitals
ORBITAL,2140.2,CANONICAL          !use canonical MCSCF orbitals
ORBITAL,2140.2,NATURAL,STATE=2.1  !use natural MCSCF orbitals for second state in sym. 1
```

4.12 Summary of keywords known to the controlling program

This is a summary of all keywords presently implemented in the controlling program. Each module knows further keywords, which are described in the chapters about the individual programs. For detailed information about the use of the commands listed below, consult the following chapters.

Program control:

`***`	indicates start of a new calculation
`MEMORY`	allocates dynamic memory
`PUNCH`	opens a punch file
`FILE`	connects units to permanent files
`RESTART`	recovers file information
`INCLUDE`	includes other input files
`BASIS`	can be used to define default basis sets
`GEOMETRY`	can be used to specify the geometry
`ZMAT`	can be used to define the Z-matrix
`PARALLEL`	can be used to control parallelization
`STATUS`	checks status of program steps
`PRINT`,`GPRINT`	controls global print levels
`THRESH`,`GTHRESH`	controls global thresholds
`DIRECT`,`GDIRECT`	flags direct computation of integrals and for setting direct options
`EXPEC`,`GEXPEC`	controls computation of expectation values
`TEXT`	prints text
`EXIT`	stops execution
`DO`	controls do loops
`ENDDO`	end of do loops
`IF`	controls conditional actions
`ELSEIF`	controls conditional actions
`ENDIF`	end of `IF block`
`GOTO`	used to skip part of input and for loops over input
`LABEL`	no action
`DATA`	data set management
`DELETE`, `ERASE`	data set deletion
`MATROP`	performs matrix operations
`GRID`	Define grid
`CUBE`	Dump data to grid
`CARTESIAN`	Use cartesian basis functions
`SPHERICAL`	Use spherical harmonic basis functions
`USER`	calls user-supplied subroutine
`---`	last line of input

Variables:

`SET`	sets variables (obsolete)
`SETI`	sets variables or numbers to their inverse (obsolete)
`SETA`	sets variable arrays (obsolete)
`CLEAR`	clears variables

CLEARALL	clears all variables
GETVAR	recovers variables from file
SHOW	displays the values of variables
TABLE	prints tables

Wave function optimization:

INT	calls the machine default integral program. This is optional and needs not to be given.
LSINT	calls the spin-orbit integral program
SORT	calls two-electron sorting program. This is called automatically and needs not to be given
CPP	compute core polarization potential integrals
HF, RHF, HF-SCF, or RHF-SCF	calls spin-restricted Hartree-Fock program (open or closed shell)
UHF or UHF-SCF	calls spin-unrestricted Hartree-Fock program
DFT	calls the density functional program
KS, RKS	call the Kohn-Sham spin restricted density functional program
UKS	call the Kohn-Sham spin-unrestricted density functional program
MULTI, MCSCF, or CASSCF	calls MCSCF/CASSCF program
CASVB	calls the CASVB valence bond program
CI, MRCI, or CI-PRO	calls internally contracted MRCI program
CIPT2	calls internally contracted CIPT2 program
ACPF, AQCC	calls internally contracted MR-ACPF program
CEPA	calls single-reference CEPA program (closed- or open-shell)
RS2, RS3	calls internally contracted multireference perturbation theory
RS2C	faster program for internally contracted multireference perturbation theory
MP2	calls closed-shell MP2 program
MP3	calls closed-shell MP3 program
MP4	calls closed-shell MP4 program
CISD	calls closed-shell CISD program
CCSD	calls closed-shell coupled cluster program
BCCD	calls closed-shell Brueckner CCD program
QCI,QCSID	calls closed-shell quadratic configuration interaction program
UCCSD	calls spin-unrestricted open-shell coupled cluster program
RCCSD	calls spin-restricted open-shell coupled cluster program
FCI or FULLCI	calls determinant based full CI program

Local correlation methods:

LMP2	calls closed-shell local MP2 program
LMP3	calls closed-shell local MP3 program
LMP4	calls closed-shell local MP4 program

LCISD	calls closed-shell local CISD program
LCCSD	calls closed-shell local coupled cluster program
Explicitly correlated methods:	
DF-MP2-R12	MP2-R12 program with density fitting
DF-MP2-F12	MP2-F12 program with density fitting
DF-LMP2-R12	Local MP2-R12 program with density fitting
DF-LMP2-F12	Local MP2-F12 program with density fitting
Orbital manipulation:	
LOCALI	calls orbital localization program
MERGE	calls orbital manipulation program
Properties and wavefunction analysis:	
POP	calls population analysis program
DMA	calls distributed multipole analysis program
PROPERTY	calls properties program
DIP	adds dipole field to *h*
QUAD	adds quadrupole field to *h*
LATTICE	read or disable lattice of point charges
Gradients and geometry optimization:	
FORCES	calls gradient program
OPTG	performs automatic geometry optimization
MIN	performs energy minimization with respect to some parameters
PUT	print or write geometry to a file
HESSIAN	calculate Hessian
FREQUENCY	calculate vibrational frequencies
MASS	define atomic masses
DDR	evaluates approximate non-adiabatic coupling matrix elements

The command names for single reference coupled cluster methods QCISD, CCSD, LQCISD, LCCSD can be appended by (T) and then a perturbative correction for triple excitations will be computed (e.g., CCSD(T)).

HF, KS, MP2 and all local correlation methods can be prepended by DF- to invoke density fitting.

4.13 MOLPRO help

The help command can be used to obtain a short description of commands, input parameters, and variables. The syntax is:

HELP,*set*,*name*,[*keys*]

where *set* is either COMMAND, VARIABLE, or the name of the input set (e.g., THRESH, PRINT, LOCAL, EOM, CFIT), and *name* is the name of the parameter. If *name* is blank, all parameters of the set are shown. Optionally, *keys* can be specified to request specific information (e.g.,

short_description, long_description, default_value, type, program). If *keys* are not given, short_description is assumed.

Currently, help is only available for a limited number of parameters and commands. However, the database will be extended in the near future.

5 INTRODUCTORY EXAMPLES

This section explains some very simple calculations in order to help the new user to understand how easy things can be.

5.1 Using the molpro command

1. Perform a simple SCF calculation for molecular hydrogen. The input is typed in directly and the output is sent to the terminal:

```
molpro <<!
basis=vdz;
geometry={angstrom;h1;h2,h1,.74}
hf
!
```

2. The same calculation, with the data taken from the file h2.com. The output is sent to h2.out. On completion, the file h2.pun is returned to the current directory and the file h2.wf to the directory $HOME/wfu (this is the default):

```
molpro h2.com
```

h2.com contains:

```
***,H2
file,2,h2.wf;
punch,h2.pun;
basis=vdz;
geometry={angstrom;h1;h2,h1,.74}
hf
```

examples/
h2.com

3. As before, but the file h2.wf is sent to the directory /tmp/wfu:

```
molpro -W /tmp/wfu h2.com
```

5.2 Simple SCF calculations

The first example does an SCF calculation for H_2O, using all possible defaults.

```
***,h2o                    !A title
r=1.85,theta=104           !set geometry parameters
geometry={O;               !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
hf                         !closed-shell scf
```

examples/
h2o˙scf.com

In the above example, the default basis set (VDZ) is used. We can modify the default basis using a BASIS directive.

```
***,h2o cc-pVTZ basis     !A title
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;                                          examples/
          H2,O,r,H1,theta}                                 h2o˙scf˙vtz.com
basis=VTZ                 !use VTZ basis
hf                        !closed-shell scf
```

5.3 Geometry optimizations

Now we can also do a geometry optimization, simply by adding the card `OPTG`.

```
!examples/h2o_scfopt_631g.com $Revision: 2002.10 $
***,h2o                   !A title
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;                                          examples/
          H2,O,r,H1,theta}                                 h2o˙scfopt˙631g.com
basis=6-31g**             !use Pole basis set
hf                        !closed-shell scf
optg                      !do scf geometry optimization
```

5.4 CCSD(T)

The following job does a CCSD(T) calculation using a larger (`VTZ`) basis (this includes an f function on oxygen and a d function on the hydrogens).

```
***,h2o                   !A title
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}                                 examples/
basis=VTZ                 !use VTZ basis                   h2o˙ccsdt˙vtz.com
hf                        !closed-shell scf
ccsd(t)                   !do ccsd(t) calculation
```

5.5 CASSCF and MRCI

Perhaps you want to do a CASSCF and subsequent MRCI for comparison. The following uses the full valence active space in the CASSCF and MRCI reference function.

```
***,h2o                   !A title
r=1.85,theta=104          !set geometry parameters
geometry={o;              !z-matrix geometry input
          h1,O,r;
          h2,O,r,H1,theta}
basis=vtz                 !use VTZ basis                   examples/
hf                        !closed-shell scf                h2o˙mrci˙vtz.com
ccsd(t)                   !do ccsd(t) calculation
casscf                    !do casscf calculation
mrci                      !do mrci calculation
```

5.6 Tables

You may now want to print a summary of all results in a table. To do so, you must store the computed energies in variables:

```
***,h2o                    !A title
r=1.85,theta=104           !set geometry parameters
geometry={o;               !z-matrix geometry input
          h1,O,r;
          h2,O,r,H1,theta}
basis=vtz                  !use VTZ basis
hf                         !closed-shell scf
e(1)=energy                !save scf energy in variable e(1)
method(1)=program          !save the string 'HF' in variable method(1)

ccsd(t)                    !do ccsd(t) calculation
e(2)=energy                !save ccsd(t) energy in variable e(2)
method(2)=program          !save the string 'CCSD(T)' in variable method(2)

casscf                     !do casscf calculation
e(3)=energy                !save scf energy in variable e(3)
method(3)=program          !save the string 'CASSCF' in variable method(3)
mrci                       !do mrci calculation
e(4)=energy                !save scf energy in variable e(4)
method(4)=program          !save the string 'MRCI' in variable method(4)

table,method,e             !print a table with results
title,Results for H2O, basis=$basis  !title for the table
```

examples/h2o˙table.com

This job produces the following table:

```
 Results for H2O, basis=VTZ

 METHOD        E
 HF        -76.05480122
 CCSD(T)   -76.33149220
 CASSCF    -76.11006259
 MRCI      -76.31960943
```

5.7 Procedures

You could simplify this job by defining a procedure SAVE_E as follows:

```
! $Revision: 2006.0 $
***,h2o                    !A title

proc save_e                !define procedure save_e
if(#i.eq.0) i=0            !initialize variable i if it does not exist
i=i+1                      !increment i
e(i)=energy                !save scf energy in variable e(i)
method(i)=program          !save the present method in variable method(i)
endproc                    !end of procedure


r=1.85,theta=104           !set geometry parameters
geometry={o;               !z-matrix geometry input
          h1,O,r;
          h2,O,r,H1,theta}
basis=vtz                  !use VTZ basis
hf                         !closed-shell scf
save_e                     !call procedure, save results

ccsd(t)                    !do ccsd(t) calculation
save_e                     !call procedure, save results

casscf                     !do casscf calculation
save_e                     !call procedure, save results

mrci                       !do mrci calculation
save_e                     !call procedure, save results

table,method,e             !print a table with results
title,Results for H2O, basis=$basis  !title for the table
```

examples/
h2o˙proce.com

The job produces the same table as before. If you put the procedure SAVE_E in a file molproi.rc or $HOME/.molproirc, it would be automatically included in all your jobs (./molproi.rc is searched first; if this file does not exist, molpro looks for $HOME/.molproirc. If this also does not exist, molpro uses the default file in the system directory).

5.8 Do loops

Now you have the idea that one geometry is not enough. Why not compute the whole surface? DO loops make it easy. Here is an example, which computes a whole potential energy surface for H_2O.

```
! $Revision: 2006.0 $
***,H2O potential
geometry={x;                              !use cs symmetry
         o;                               !z-matrix
         h1,o,r1(i);
         h2,o,r2(i),h1,theta(i) }
basis=vdz                                  !define basis set
angles=[100,104,110]                       !list of angles
distances=[1.6,1.7,1.8,1.9,2.0]            !list of distances
i=0                                        !initialize a counter
do ith=1,#angles                           !loop over all angles H1-O-H2
do ir1=1,#distances                        !loop over distances for O-H1
do ir2=1,ir1                               !loop over O-H2 distances(r1.ge.r2)
i=i+1                                      !increment counter
r1(i)=distances(ir1)                       !save r1 for this geometry
r2(i)=distances(ir2)                       !save r2 for this geometry
theta(i)=angles(ith)                       !save theta for this geometry
hf;                                        !do SCF calculation
escf(i)=energy                             !save scf energy for this geometry
ccsd(t);                                   !do CCSD(T) calculation
eccsd(i)=energc                            !save CCSD energy
eccsdt(i)=energy                           !save CCSD(T) energy
enddo                                      !end of do loop ith
enddo                                      !end of do loop ir1
enddo                                      !end of do loop ir2
{table,r1,r2,theta,escf,eccsd,eccsdt       !produce a table with results
head, r1,r2,theta,scf,ccsd,ccsd(t)         !modify column headers for table
save,h2o.tab                               !save the table in file h2o.tab
title,Results for H2O, basis $basis        !title for table
sort,3,1,2}                                !sort table
```

examples/
h2o˙pes˙ccsdt.com

This produces the following table.

```
 Results for H2O, basis VDZ

    R1    R2   THETA       SCF           CCSD          CCSD(T)
   1.6   1.6   100.0   -75.99757338   -76.20140563   -76.20403920
   1.7   1.6   100.0   -76.00908379   -76.21474489   -76.21747582
   1.7   1.7   100.0   -76.02060127   -76.22812261   -76.23095473
   ...
   2.0   1.9   110.0   -76.01128923   -76.22745359   -76.23081968
   2.0   2.0   110.0   -76.00369171   -76.22185092   -76.22537212
```

You can use also use `DO` loops to repeat your input for different methods.

```
! $Revision: 2006.0 $
***,h2o benchmark
$method=[hf,fci,ci,cepa(0),cepa(1),cepa(2),cepa(3),mp2,mp3,mp4,\
      qci,ccsd,bccd,qci(t),ccsd(t),bccd(t),casscf,mrci,acpf]
basis=dz                                   !Double zeta basis set
geometry={o;h1,o,r;h2,o,r,h1,theta}        !Z-matrix for geometry
r=1 ang, theta=104                         !Geometry parameters
do i=1,#method                             !Loop over all requested methods
$method(i);                                !call program
e(i)=energy                                !save energy for this method
enddo
escf=e(1)                                  !scf energy
efci=e(2)                                  !fci energy
table,method,e,e-escf,e-efci               !print a table with results
!Title for table:
title,Results for H2O, basis $basis, R=$r Ang, Theta=$theta degree
```

examples/
h2o˙manymethods.co

This calculation produces the following table.

```
Results for H2O, basis DZ, R=1 Ang, Theta=104 degree

METHOD        E             E-ESCF       E-EFCI
HF        -75.99897339     .00000000    .13712077
FCI       -76.13609416    -.13712077    .00000000
CI        -76.12844693    -.12947355    .00764722
CEPA(0)   -76.13490643    -.13593304    .00118773
CEPA(1)   -76.13304720    -.13407381    .00304696
CEPA(2)   -76.13431548    -.13534209    .00177868
CEPA(3)   -76.13179688    -.13282349    .00429728
MP2       -76.12767140    -.12869801    .00842276
MP3       -76.12839400    -.12942062    .00770015
MP4       -76.13487266    -.13589927    .00122149
QCI       -76.13461684    -.13564345    .00147732
CCSD      -76.13431854    -.13534515    .00177561
BCCD      -76.13410586    -.13513247    .00198830
QCI(T)    -76.13555640    -.13658301    .00053776
CCSD(T)   -76.13546225    -.13648886    .00063191
BCCD(T)   -76.13546100    -.13648762    .00063315
CASSCF    -76.05876129    -.05978790    .07733286
MRCI      -76.13311835    -.13414496    .00297580
ACPF      -76.13463018    -.13565679    .00146398
```

One can do even more fancy things, like, for instance, using macros, stored as string variables. See example `oh_macros.com` for a demonstration.

6 PROGRAM CONTROL

6.1 Starting a job (***)

The first card of each input should be:

***,*text*

where *text* is arbitrary. If file 1 is restarted, *text* must always be the same. The effect of this card is to reset all program counters, etc. If the *** card is omitted, *text* assumes its default value, which is all blank.

6.2 Ending a job (---)

The end of the input is signaled by either an end of file, or a

---

card. All input following the --- card is ignored.

Alternatively, a job can be stopped at at some place by inserting an EXIT card. This could also be in the middle of a DO loop or an IF block. If in such a case the --- card would be used, an error would result, since the ENDDO or ENDIF cards would not be found.

6.3 Restarting a job (RESTART)

In contrast to MOLPRO92 and older versions, the current version of MOLPRO attempts to recover all information from all permanent files by default. If a restart is unwanted, the NEW option can be used on the FILE directive. The RESTART directive as described below can still be used as in MOLPRO92, but is usually not needed.

RESTART,$r_1, r_2, r_3, r_4, \ldots$;

The r_i specify which files are restarted. These files must have been allocated before using FILE cards. There are two possible formats for the r_i:

a) $0 < r_i < 10$:	Restart file r_i and restore all information.
b) $r_i =$ *name.nr*:	Restart file *nr* but truncate before record *name*.

If all $r_i = 0$, then all permanent files are restarted. However, if at least one r_i is not equal to zero, only the specified files are restarted.

Examples:

`RESTART;`	will restart all permanent files allocated with FILE cards (default)
`RESTART,1;`	will restart file 1 only
`RESTART,2;`	will restart file 2 only
`RESTART,1,2,3;`	will restart files 1-3
`RESTART,2000.1;`	will restart file 1 and truncate before record 2000.

6.4 Including secondary input files (INCLUDE)

INCLUDE,*file,echo*;

Insert the contents of the specified *file* in the input stream. In most implementations the file name given is used directly in a Fortran open statement. If the parameter *echo* is nonzero, the included file is echoed to the output in the normal way, but by default its contents are not printed. The included file may itself contain INCLUDE commands up to a maximum nesting depth of 10.

6.5 Allocating dynamic memory (MEMORY)

MEMORY,*n,scale*;

Sets the limit on dynamic memory to *n* floating point words. If *scale* is given as K, *n* is multiplied by 1000; if *scale* is M, *n* is multiplied by 1 000 000.

Note: The MEMORY card must precede all FILE cards!

Examples:

MEMORY,90000	allocates 90 000 words of memory
MEMORY,500,K	allocates 500 000 words of memory
MEMORY,2,M	allocates 2 000 000 words of memory

6.6 DO loops (DO/ENDDO)

DO loops can be constructed using the DO and ENDDO commands. The general format of the DO command is similar to Fortran:

DO *variable=start, end* [[,]*increment*] [[,]*unit*]

where *start, end, increment* may be expressions or variables. The default for *increment* is 1. In contrast to Fortran, these variables can be modified within the loop (to be used with care!). For instance:

```
DR=0.2
DO R=1.0,6.0,DR,ANG
IF (R.EQ.2) DR=0.5
IF (R.EQ.3) DR=1.0
....
ENDDO
```

performs the loop for the following values of R: 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0 Ångstrøm. The same could be achieved as follows:

```
RVEC=[1.0,1.2,1.4,1.6,1.8,2.0,2.5,3.0,4.0,5.0,6.0] ANG
DO I=1,#RVEC
R=RVEC(I)
....
ENDDO
```

Up to 20 DO loops may be nested. Each DO must end with its own ENDDO.

Jumps into DO loops are possible if the DO variables are known. This can be useful in restarts, since it allows to continue an interrupted calculation without changing the input (all variables are recovered in a restart).

6.6.1 Examples for do loops

The first example shows how to compute a potential energy surface for water.

```
! $Revision: 2006.0 $
***,H2O potential
geometry={x;                          !use cs symmetry
         o;                           !z-matrix
         h1,o,r1(i);
         h2,o,r2(i),h1,theta(i) }
basis=vdz                              !define basis set
angles=[100,104,110]                   !list of angles
distances=[1.6,1.7,1.8,1.9,2.0]        !list of distances
i=0                                    !initialize a counter
do ith=1,#angles                       !loop over all angles H1-O-H2
do ir1=1,#distances                    !loop over distances for O-H1
do ir2=1,ir1                           !loop over O-H2 distances(r1.ge.r2)
i=i+1                                  !increment counter
r1(i)=distances(ir1)                   !save r1 for this geometry
r2(i)=distances(ir2)                   !save r2 for this geometry
theta(i)=angles(ith)                   !save theta for this geometry
hf;                                    !do SCF calculation
escf(i)=energy                         !save scf energy for this geometry
ccsd(t);                               !do CCSD(T) calculation
eccsd(i)=energc                        !save CCSD energy
eccsdt(i)=energy                       !save CCSD(T) energy
enddo                                  !end of do loop ith
enddo                                  !end of do loop ir1
enddo                                  !end of do loop ir2
{table,r1,r2,theta,escf,eccsd,eccsdt    !produce a table with results
head, r1,r2,theta,scf,ccsd,ccsd(t)     !modify column headers for table
save,h2o.tab                           !save the table in file h2o.tab
title,Results for H2O, basis $basis    !title for table
sort,3,1,2}                            !sort table
```

examples/
h2o˙pes˙ccsdt.com

The next example shows how to loop over many methods.

```
! $Revision: 2006.0 $
***,h2o benchmark
$method=[hf,fci,ci,cepa(0),cepa(1),cepa(2),cepa(3),mp2,mp3,mp4,\
      qci,ccsd,bccd,qci(t),ccsd(t),bccd(t),casscf,mrci,acpf]
basis=dz                                !Double zeta basis set
geometry={o;h1,o,r;h2,o,r,h1,theta}     !Z-matrix for geometry
r=1 ang, theta=104                      !Geometry parameters
do i=1,#method                          !Loop over all requested methods
$method(i);                             !call program
e(i)=energy                             !save energy for this method
enddo
escf=e(1)                               !scf energy
efci=e(2)                               !fci energy
table,method,e,e-escf,e-efci            !print a table with results
!Title for table:
title,Results for H2O, basis $basis, R=$r Ang, Theta=$theta degree
```

examples/
h2o˙manymethods.co

6.7 Branching (IF/ELSEIF/ENDIF)

IF blocks and IF/ELSEIF blocks can be constructed as in FORTRAN.

6.7.1 IF statements

IF blocks have the same form as in Fortran:

IF (*logical expression*) THEN
statements
ENDIF

If only one statement is needed, the one-line form

IF (*logical expression*) *statement*

can be used, except if *statement* is a procedure name.

ELSE and ELSE IF can be used exactly as in Fortran. IF statements may be arbitrarily nested. Jumps into IF or ELSE IF blocks are allowed. In this case no testing is performed; when an ELSE is reached, control continues after ENDIF.

The logical expression may involve logical comparisons of algebraic expressions or of strings. Examples:

```
IF(STATUS.LT.0) THEN
TEXT,An error occurred, calculation stopped
STOP
ENDIF
```

```
IF($method.eq.'HF') then
...
ENDIF
```

In the previous example the dollar and the quotes are optional:

```
IF(METHOD.EQ.HF) then
...
ENDIF
```

6.7.2 GOTO commands

GOTO commands can be used to skip over parts of the input. The general form is

GOTO,*command*,[*n*],[*nrep*]

Program control skips to the $|n|$'th occurrence of *command* (Default: $n = 1$). *command* must be a keyword in the first field of an input line. If *n* is positive, the search is forward starting from the current position. If *n* is negative, search starts from the top of the input. The GOTO command is executed at most *nrep* times. The default for *nrep* is 1 if $n < 0$ and infinity otherwise. We recommend that GOTO commands are never used to construct loops.

Alternatively, one can jump to labels using

GOTO,*label*

Since labels must be unique, the search starts always from the top of the input. It is required that the *label* ends with a colon.

6.7.3 Labels (LABEL)

LABEL

This is a dummy command, sometimes useful in conjunction with GOTO.

6.8 Procedures (PROC/ENDPROC)

Procedures can be defined at the top of the input, in the default file `molproi.rc`, or in `INCLUDE` files as follows:

`PROC` *name*
statements
`ENDPROC`

Alternatively, one can use the form

`PROC` *name*`[=]`{*statements*}

In the latter case, it is required that the left curly bracket ({) appears on the same line as `PROC`, but *statements* can consist of several lines. If in the subsequent input *name* is found as a command *in the first field* of a line, it is substituted by the *statements*. Example:

```
PROC SCF
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN
  HF
ELSE
  RHF
ENDIF
ENDPROC
```

Alternatively, this could be written as

```
PROC SCF={
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN; HF; ELSE; RHF; ENDIF}
```

Procedures may be nested up to a depth of 10. In the following example `SCF` is a procedure:

```
PROC CC
SCF
IF (SPIN.EQ.0) THEN
  CCSD
ELSE
  RCCSD
ENDPROC
```

Note: Procedure names are substituted only if found in the first field of an input line. Therefore, they must not be used on one-line `IF` statements; please use `IF / ENDIF` structures instead.

If as first statement of a procedure `ECHO` is specified, the substituted commands of the present and lower level procedures will be printed. If `ECHO` is specified in the main input file, all subsequent procedures are printed.

Certain important input data can be passed to the program using variables. For instance, occupancy patterns, symmetries, number of electrons, and multiplicity can be defined in this way (see section 8.8 for more details). This allows the quite general use of procedures. For example, assume the following procedure has been defined in `molproi.rc`:

```
PROC MRCI
IF (INTDONE.EQ.0) INT
IF (SCFDONE.EQ.0) THEN
SCF
```

```
ENDIF
MULTI
CI
ENDPROC
```

This procedure can be used for a calculation of a vertical ionization potential of H_2O as follows:

```
R=1 ANG           !Set bond distance
THETA=104 DEGREE  !Set bond angle

BASIS=VTZ         !Define basis set

GEOMETRY          !Geometry input block
O                 !Z-matrix
H1,O,R
H2,O,R,H1,THETA
ENDG              !End of geometry input
HF
MRCI              !Compute mrci energy of water using defaults
EH2O=ENERGY       !save mrci energy in variable EH2O

SET,NELEC=9       !Set number of electrons to 9
SET,SYMMETRY=2    !Set wavefunction symmetry to 2
HF
MRCI              !Compute mrci energy of H2O+ (2B2 state)

IPCI=(ENERGY-EH2O)*TOEV  !Compute MRCI ionization potential in eV
```

Note: At present, all variables are *global*, i.e., variables are commonly known to all procedures and all variables defined in procedures will be subsequently known outside the procedures as well. The reason is that procedures are included into the internal input deck at the beginning of the job and not at execution time; for the same reason, variable substitution of procedure names is not possible, e.g. one cannot use constructs like

```
method=scf
$method       !this does not work!
```

6.9 Text cards (TEXT)

TEXT,*xxxxxx*

will just print *xxxxxx* in the output. If the text contains variables which are preceded by a dollar ($), these are replaced by their actual values, e.g.

```
r=2.1
text,Results for R=\$r
```

will print

```
Results for R=2.1
```

6.10 Checking the program status (STATUS)

STATUS,[ALL|LAST|*commands*],[IGNORE|STOP|CRASH],[CLEAR]

This command checks and prints the status of the specified program steps. *commands* may be a list of commands for wavefunction calculations previously executed in the current job. If no *command* or LAST is specified, the status of the last step is checked. If ALL is given, all program steps are checked.

If CRASH or STOP is given, the program will crash or stop, respectively, if the status was not o.k. (STOP is default). If IGNORE is given, any bad status is ignored. If CLEAR is specified, all status information for the checked program steps is erased, so there will be no crash at subsequent status checks.

Examples:

STATUS,HF,CRASH; will check the status of the last HF-SCF step and crash if it was not o.k. (i.e. no convergence). CRASH is useful to avoid that the next program in a chain is executed.

STATUS,MULTI,CI,STOP; will check the status of the most previous MULTI and CI steps and stop if something did not converge.

STATUS,RHF,CLEAR; will clear the status flag for last RHF. No action even if RHF did not converge.

Note that the status variables are not recovered in a restart.

By default, the program automatically does the following checks:

1.) If an orbital optimization did not converge, and the resulting orbitals are used in a subsequent correlation calculation, an error will result. This the error exit can be avoided using the IGNORE_ERROR option on the ORBITAL directive.

2.) If a CCSD|QCI|BCC|LMPn calculation did not converge, further program steps which depend on the solution (e.g, Triples, CPHF, EOM) will not be done and an error will result. This can be avoided using the NOCHECK option on the command line.

3.) In geometry optimizations or frequency calculations no convergence will lead to immediate error exits.

6.11 Global Thresholds (GTHRESH)

A number of global thresholds can be set using the GTHRESH command outside the individual programs (the first letter G is optional, but should be used to avoid confusion with program specific THRESH cards). The syntax is

GTHRESH,*key1=value1*,*key2=value2*,...

key can be one of the following.

ZERO	Numerical zero (default 1.d-12)
ONEINT	Threshold for one-electron integrals (default 1.d-12, but not used at present)
TWOINT	Threshold for the neglect of two-electron integrals (default 1.d-12)
PREFAC	Threshold for test of prefactor in TWOINT (default 1.d-14)
LOCALI	Threshold for orbital localization (default 1.d-8)
EORDER	Threshold for reordering of orbital after localization (default 1.d-4)

ENERGY	Convergence threshold for energy (default 1.d-6)
GRADIENT	Convergence threshold for orbital gradient in MCSCF (default 1.d-2)
STEP	Convergence threshold for step length in MCSCF orbital optimization (default 1.d-3)
ORBITAL	Convergence threshold for orbital optimization in the SCF program (default 1.d-5).
CIVEC	Convergence threshold for CI coefficients in MCSCF and reference vector in CI (default 1.-d.5)
COEFF	Convergence threshold for coefficients in CI and CCSD (default 1.d-4)
PRINTCI	Threshold for printing CI coefficients (default 0.05)
PUNCHCI	Threshold for punching CI coefficients (default 99 - no punch)
SYMTOL	Threshold for finding symmetry equivalent atoms (default 1.d-6)
GRADTOL	Threshold for symmetry in gradient (default 1.d-6).
THROVL	Threshold for smallest allowed eigenvalue of the overlap matrix (default 1.d-8)
THRORTH	Threshold for orthonormality check (default 1.d-8)

6.12 Global Print Options (GPRINT/NOGPRINT)

Global print options can be set using the GPRINT command outside the individual programs (the first letter G is optional, but should be used to avoid confusion with program specific PRINT cards). The syntax is

GPRINT,*key1*[=*value1*],*key2*[=*value2*],...
NOGPRINT,*key1*,*key2*,...

Normally, *value* can be omitted, but values > 0 may be used for debugging purposes, giving more information in some cases. The default is no print for all options, except for DISTANCE, ANGLES (default=0), and VARIABLE. NOGPRINT,*key* is equivalent to PRINT,*key*=−1. *key* can be one of the following:

BASIS	Print basis information
DISTANCE	Print bond distances (default)
ANGLES	Print bond angle information (default). If > 0, dihedral angles are also printed.
ORBITAL	Print orbitals in SCF and MCSCF
CIVECTOR	Print CI vector in MCSCF
PAIRS	Print pair list in CI, CCSD
CS	Print information for singles in CI, CCSD
CP	Print information for pairs in CI, CCSD
REF	Print reference CSFs and their coefficients in CI
PSPACE	Print p-space configurations
MICRO	Print micro-iterations in MCSCF and CI
CPU	Print detailed CPU information

IO	Print detailed I/O information
VARIABLE	Print variables each time they are set or changed (default).

6.13 One-electron operators and expectation values (GEXPEC)

The operators for which expectation values are requested, are specified by keywords on the global GEXPEC directive. The first letter G is optional, but should be used to avoid confusion with program specific EXPEC cards, which have the same form as GEXPEC. For all operators specified on the GEXPEC card, expectation values are computed in all subsequent programs (if applicable).

For a number of operators it is possible to use *generic* operator names, e.g., DM for dipole moments, which means that all three components DMX, DMY, and DMZ are computed. Alternatively, individual components may be requested.

The general format is as follows:

[G]EXPEC,*opname*[,][*icen*,[*x,y,z*]],...

where

opname	operator name (string), either generic or component.
icen	z-matrix row number or z-matrix symbol used to determine the origin (x,y,z must not be specified). If *icen*= 0 or blank, the origin must be specified in *x,y,z*

Several GEXPEC cards may follow each other, or several operators may be specified on one card.

Examples:

GEXPEC,QM computes quadrupole moments with origin at (0,0,0),

GEXPEC,QM1 computes quadrupole moments with origin at centre 1.

GEXPEC,QM,O1 computes quadrupole moments with origin at atom O1.

GEXPEC,QM,,1,2,3 computes quadrupole moments with origin at (1,2,3).

The following table summarizes all available operators:

Expectation values are only nonzero for symmetric operators (parity=1). Other operators can be used to compute transition quantities (spin-orbit operators need a special treatment). By default, the dipole moments are computed.

6.13.1 Example for computing expectation values

The following job computes dipole and quadrupole moments for H_2O.

```
! $Revision: 2006.0 $
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
gexpec,dm,sm,qm                       !compute dipole and quarupole moments
$methods=[hf,multi,ci]                !do hf, casscf, mrci
do i=1,#methods                       !loop over methods
$methods(i)                           !run energy calculation
e(i)=energy
dip(i)=dmz                            !save dipole moment in variable dip
quadxx(i)=qmxx                        !save quadrupole momemts
quadyy(i)=qmyy
quadzz(i)=qmzz
smxx(i)=xx                            !save second momemts
smyy(i)=yy
smzz(i)=zz
enddo
table,methods,dip,smxx,smyy,smzz        !print table of first and second moments
table,methods,e,quadxx,quadyy,quadzz    !print table of quadrupole moments
```

examples/h2o˙gexpec2.com

This Job produces the following tables

```
METHODS     DIP           SMXX          SMYY          SMZZ
HF        0.82747571   -5.30079792   -3.01408114   -4.20611391
MULTI     0.76285513   -5.29145148   -3.11711397   -4.25941000
CI        0.76868508   -5.32191822   -3.15540500   -4.28542917

METHODS       E             QUADXX        QUADYY        QUADZZ
HF        -76.02145798   -1.69070039   1.73937477   -0.04867438
MULTI     -76.07843443   -1.60318949   1.65831677   -0.05512728
CI        -76.23369821   -1.60150114   1.64826869   -0.04676756
```

6.13.2 Example for computing relativistic corrections

```
***,ar2
geometry={ar1;ar2,ar1,r}   !geometry definition
r=2.5 ang                  !bond distance
{hf;                       !non-relativisitic scf calculation
expec,rel,darwin,massv}    !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy              !save non-relativistic energy in variable enrel
show,massv,darwin,erel     !show individual contribution and their sum
dkroll=1                   !use douglas-kroll one-electron integrals
hf;                        !relativistic scf calculation
e_dk=energy                !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel     !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel           !show relativistic correction using Douglas-Kroll
```

examples/ar2˙rel.com

This jobs shows at the end the following variables:

```
MASSV / AU              =       -14.84964285
DARWIN / AU             =        11.25455679
EREL / AU               =        -3.59508606
```

Table 5: One-electron operators and their components

Generic name	Parity	Components	Description
OV	1		Overlap
EKIN	1		Kinetic energy
POT	1		potential energy
DELT	1		delta function
DEL4	1		Δ^4
DARW	1		one-electron Darwin term, i.e., DELT with appropriate factors summed over atoms.
MASSV	1		mass-velocity term, i.e., DEL4 with appropriate factor.
REL	1		total Cowan-Griffin Relativistic correction, i.e., DARW+MASSV.
DM	1	DMX, DMY, DMZ	dipole moments
SM	1	XX, YY, ZZ, XY, XZ, YZ	second moments
TM	1	XXX, XXY, XXZ, XYY, XYZ, XZZ, YYY, YYZ, YZZ, ZZZ	third moments
MLTP*n*	1	all unique Cartesian products of order *n*	multipole moments
QM	1	QMXX, QMYY, QMZZ, QMXY, QMXZ, QMYZ, QMRR=XX + YY + ZZ, QMXX=(3 XX - RR)/2, QMXY=3 *XY* / 2 etc.	quadrupole moments and R^2
EF	1	EFX, EFY, EFZ	electric field
FG	1	FGXX, FGYY, FGZZ, FGXY, FGXZ, FGYZ	electric field gradients
DMS	1	DMSXX, DMSYX, DMSZX, DMSXY, DMSYY, DMSZY, DMSXZ, DMSYZ, DMSZZ	diamagnetic shielding tensor
LOP	-1	LX, LY, LZ	Angular momentum operators $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$
LOP2	1	LXLX, LYLY, LZLZ, LXLY, LXLZ, LYLZ. The symmetric combinations	one electron parts of products of angular momentum operators. $\frac{1}{2}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$ etc. are computed
VELO	-1	D/DX, D/DY, D/DZ	velocity
LS	-1	LSX, LSY, LSZ	spin-orbit operators
ECPLS	-1	ECPLSX, ECPLSY, ECPLSZ	ECP spin-orbit operators

7 FILE HANDLING

7.1 FILE

The FILE directive is used to open permanent files, which can be used for later restarts. The syntax in MOLPRO94 and later versions is

FILE,*file*,*name*,[*status*]

file is the logical MOLPRO file number (1-9). *name* is the file name (will be converted to lower case). *status* can be one of the following:

UNKNOWN	A permanent file is opened. If it exists, it is automatically restarted. This is the default.
OLD	Same effect as UNKNOWN. No error occurs if the file does not exist.
NEW	A permanent file is opened. If it already exists, it is erased and not restarted.
ERASE	Same effect as NEW.
SCRATCH	A temporary file is opened. If it already exists, it is erased and not restarted. After the job has finished, the file is no longer existent.
DELETE	Same effect as SCRATCH.

Note that RESTART is now the default for all permanent files. All temporary files are usually allocated automatically where needed. I/O buffers are allocated at the top of the dynamic memory, and the available memory decreases by the size of the buffers. The MEMORY card must therefore be presented before the first FILE card!

Examples:

FILE,1,H2O.INT	allocates permanent file 1 with name H2O.INT. Previous information on the file is recovered.
FILE,2,H2O.WFU,NEW	allocates permanent file 2 with name H2O.WFU. All previous information on the file is erased.

Note that filenames are converted to lower case on unix machines.

7.2 DELETE

DELETE,*file1, file2, ...*

Deletes the specified files. *file* refers to the logical MOLPRO file numbers as specified on the FILE card.

7.3 ERASE

ERASE,*file1, file2, ...*

Erases the specified files. *file* refers to the logical MOLPRO file numbers as specified on the FILE card.

7.4 DATA

The DATA command can be used to modify the MOLPRO binary files.

UNIT	Alias for NPL (should never be used)
RENAME,*rec1*,*rec2*	used to rename *rec1* to *rec2*. *rec1* and *rec2* must be given in the form *name.ifil*, where *ifil* is the number of a MOLPRO binary file (alias for NAME).
TRUNCATE,*nen*	used to truncate files after *nen-1* records (alias for NEN).
TRUNCATE,*rec*	used to truncate before record *rec*. *rec* must be given in the form *name.ifil*, where *ifil* is the number of a MOLPRO binary file.
COUNT	Alias for NRE (presently not used)
COPY,*rec1*,*rec2*	Copies record *rec1* to *rec2*. *rec1* and *rec2* must be given in the form *nam1.ifil1*, *nam2.ifil2*. If *nam2=0*, *nam2=nam1*. If *nam1=0*, all records are copied from file *ifil1* to file *ifil2*.

7.5 Assigning punch files (PUNCH)

PUNCH,*filename*,[REWIND]

Opens punch file named *filename*. If this file already exists, it is appended, unless the REWIND or NEW option is specified; in that case, any previous information on the punch file is overwritten. See FILE for machine dependent interpretation of filename. The punch file contains all important results (geometries, energies, dipole, transition moments etc). It can be read by a separate program *READPUN*, which can produce tables in user supplied format.

Example:

PUNCH,H2O.PUN allocates punch file H2O.PUN

Note that the file name is converted to lower case on unix machines.

7.6 MOLPRO system parameters (GPARAM)

The GPARAM card allows to change MOLPRO system parameters. This should only be used by experts!

GPARAM,*option=value*,...

The following options can be given in any order.

NOBUFF	if present, disable system buffering
LSEG	disk sector length
INTREL	number of integer words per real word (should never be modified!)
IBANK	number of memory banks. Default is 2, which should always be o.k.
IVECT	0=scalar, 1=vector machine
MINVEC	minimum vector length for call to mxmb
LTRACK	page size in buffer routines (must be multiple of *lseg*)

LENBUF	length of integral buffer (file 1)
NTR	length of integral records (must be multiple of 3·*ltrack*)
LTR	disk sector length assumed in CI (default 1 is reasonable)
NCACHE	machine cache size in bytes
IASYN	if nonzero, use asynchronous I/O on CONVEX
MXMBLK	column/row block size for mxma
MXMBLN	link block size for mxma
NCPUS	maximum number of cpus to be used in multitasking
MINBR1	min number of floating point ops per processor
MXDMP	highest file number to be treated as dump file with full functionality ($1 \leq$. MXDMP$\leq .3$).

The MXDMP option is for experts only! This prevents basis and geometry information from being written to dump files with higher file number than the given *value*, and can sometimes be useful for counterpoise corrected geometry optimizations. Note that some functionality is lost by giving this option, and errors will result unless all input is correct!

8 VARIABLES

Data may be stored in *variables*. A variable can be of type *string*, *real* or *logical*, depending on the type of the expression in its definition. Any sequence of characters which is not recognized as expression or variable is treated as string. In this section, we will discuss only *real* and *logical* variables. *String* variables will be discussed in more detail in section 8.3. Variables can be used anywhere in the input, but they can be set only outside the input blocks for specific programs. For example, if a variable is used within the input block for HF, it must have been set before the HF{...} input block.

MOLPRO automatically stores various results and data in system variables (see section 8.8.1), which can be used for further processing. A new feature of MOLPRO2002 is that most system variables are write protected and cannot be overwritten by the user. The input is automatically checked before the job starts, and should a system variable be set in the input the job will stop immediately with an error message. Only in some exceptions (see section 8.4), system variables can be modified using the SET command (but not with the simple NAME=*value* syntax). Note that due to the changed usage and syntax of the SET command, compatibility with MOLPRO92 input syntax is no longer maintained.

8.1 Setting variables

A variable can be defined using

variable1=*value1*, *variable2*=*value2*, ...

A variable definition is recognized by the equals sign in the *first* field of the input card. For example,

```
THRESH,ENERGY=1.d-8,GRADIENT=1.d-5
```

does *not* define variables; here ENERGY and GRADIENT are options for the THRESH directive.

Variables can have different types:

Numbers: The value is a number or an expression. The general form of *value* is *expression* [,] [*unit*]
unit is an optional string which can be used to associate a unit to the value. ANG[STROM], DEGREE, HARTREE are examples. Undefined variables in expressions are assumed to be zero (and defined to be zero at the same time).

Logicals: The value can be .TRUE. or .FALSE. (.T. and .F. also work), or a logical expression. Internally, .TRUE. is stored as 1 and .FALSE. as zero.

Strings: The value can either be a string enclosed in quotes or a string variable. See section 8.3 for more details.

8.2 Indexed variables

Variables can be indexed, but only one-dimensional indexing is available. Indexed variables can be defined either individually, e.g.

```
R(1)=1.0 ANG
R(2)=1.2 ANG
R(3)=1.3 ANG
```

or as a vector of values enclosed by square brackets:

```
R=[1.0,1.1,1.2] ANG
```

Subranges can also be defined, e.g.

```
R(1)=1.0 ANG
R(2:3)=[1.1,1.2] ANG
```

leads to the same result as the above two forms.

The type of each element depends on the type of the assigned value, and it is possible to mix types in one variable. Example:

```
geometry={he}
hf
result=[program,energy,status.gt.0]
```

yields:

```
RESULT(1)       =    HF-SCF
RESULT(2)       =        -2.85516048  AU
RESULT(3)       =    TRUE
```

In this example the variables PROGRAM, ENERGY, and STATUS are system variables, which are set by the program (see section 8.4).

8.3 String variables

As explained already in section 8.1, string variables can be set as other variables in the form

variable = '*string*'
variable = *string_variable*

Strings must be enclosed by quotes. Otherwise the string is assumed to be a variable, and if this is undefined it is assumed to be zero.

Alternatively, if the name of the variable is preceded by a dollar ($), all values is assumed to be a string. This can a string variable, a quoted string, or an unquoted string. Note that unquoted strings are converted to upper case. Also note that quotes are compulsory if the string contains blanks.

Example:

```
$str=[a,b+4,'This is an example for strings']
```

yields

```
STR(1)          =    A
STR(2)          =    B+4
STR(3)          =    This is an example for strings
```

As a general rule, string variables are replaced by their value only if they are preceded by a dollar ($) (exceptions: in variable definitions, on SHOW cards, and in logical expressions on IF cards, the dollar is optional). This is a precaution to avoid commands which have the same name as a variable being interpreted as variables. Variables may also appear on TEXT or TITLE cards or in strings, but must be preceded by $ in these cases. Example:

```
$METHOD=MCSCF
R=1.5
TEXT,$method results for R=$R Bohr
```

prints

```
MCSCF results for R=1.5 Bohr
```

String variables can be concatenated with strings or other string variables in the following way. Assume that variable PROGRAM has the value MRCI. Setting

```
METHOD='$PROGRAM+Q'
```

sets METHOD to MRCI+Q. Alternatively, if we would also have a variable VERSION with value Q, we could write

```
METHOD='$PROGRAM+$VERSION'
```

Again, the value of METHOD would be MRCI+Q. Note that the quotes are necessary in these cases.

Substring operations are not implemented.

8.4 System variables

As mentioned above, most system variables cannot be written by the user. In some exceptions, it is possible to redefine them using the SET command:

SET,*variable* = *expression* [,] [*unit*]

This holds for the following variables:

CHARGE	Total charge of the molecule
NELEC	Number of electrons
SPIN	Spin quantum number, given as $2 \cdot M\_S$ (integer)
SCFSPIN	Same as SPIN, but only for HF
MCSPIN	Same as SPIN, but only for MCSCF
CISPIN	Same as SPIN, but only for MRCI
STATE	State to be optimized
MCSTATE	Same as STATE but only for MCSCF
CISTATE	Same as STATE but only for MRCI
SYMMETRY	State symmetry
SCFSYM[METRY]	Same as SYMMETRY but only for HF
MCSYM[METRY]	Same as SYMMETRY but only for MCSCF
CISYM[METRY]	Same as SYMMETRY but only for MRCI
ZSYMEL	Symmetry elements
LQUANT	Lambda quantum number for linear molecules
OPTCONV	Geometry optimization convergence criterion
PROGRAM	Last program name
CPUSTEP	CPU-time of last program step
SYSSTEP	System-time of last program step
WALLSTEP	Elapsed-time of last program step
FOCKDONE	Indicates if closed-shell fock operator is available.

8.5 Macro definitions using string variables

String variables for which the stored string has the form of an algebraic expression are evaluated to a number if they are preceded by two dollars ($$). Example:

```
string='a+b'
a=3
b=4
text,This is string $string which evaluates to $$string
```

prints

```
** This is string a+b which evaluates to 7
```

This can be used to define simple macros, which can be used at various places in the subsequent input. For instance,

```
ECORR='ENERGY-ESCF' !define a macro
HF                  !do SCF calculation
ESCF=ENERGY         !store SCF energy in variable ESCF
MULTI               !do CASSCF
DEMC=$$ECORR        !store CASSCF correlation energy in variable DEMC
MRCI                !do MRCI
DECI=$$ECORR        !store MRCI correlation energy in variable DECI
```

Here is an example of advanced use of macros and string variables:

examples/oh˙macros.com

```
! $Revision: 2006.0 $
***,test for parser
text,This fancy input demonstrates how string variables and macros can be used
text
basis=vdz               !define basis set
geometry={O;H,O,r}      !define geometry (z-matrix)

text,methods
$method=[rhf,2[casscf,2[mrci]]]
text,active spaces
spaces=['[3,1,1]',3['[4,2,2]'],3['[5,2,2]']]
text,symmetries
symset=['1',2['[1,2,3]','1','2']]
text,weight factors for state averaged casscf
weights=['1','[1,1,1]',2[' '],'[1,0.5,0.5]',2[' ']]
text,scf occupation
set,scfocc=[3,2[1]]
text,bond distance
r=1.85

hf
do i=1,#method         !loop over methods
occ=$$spaces(i)        !set active space for this run
set,symmetry=$$symset(i)   !set symmetries for this run
set,weight=$$weights(i)    !set weights for this run
$method(i)             !now run method
e(i)='$energy'         !save energies in strings
dipol(i)='$dmz'        !save dipole moments in strings
enddo
table,method,spaces,symset,weights,e,dipol
title,Results for OH, r=$r, basis=$basis
head,method,spaces,symmetries,weights,energies,'dipole moments'
exit
```

8.6 Indexed Variables (Vectors)

Variables may be indexed, but only one-dimensional arrays (vectors) are supported. The index may itself be a variable. For instance

```
METHOD(I)=PROGRAM
E(I)=ENERGY
```

are valid variable definitions, provided `I`, `PROGRAM`, and `ENERGY` are also defined variables. Indices may be nested to any depth.

Different elements of an array can be of different type (either *real* or *logical*). However, only one *unit* can be assigned to an array. String variables have no associated value and cannot be mixed with the other variable types. Therefore, a given variable name can only be used either for a *string* variable or a *real* (*logical*) variable.

Vectors (arrays) can be conveniently defined using square brackets:

```
R=[1.0,1.2,1.3] ANG
```

This defines an array with three elements, which can be accessed using indices; for instance, `R(2)` has the value `1.2 ANG`. A repeat specifier can be given in front of the left bracket: `5[0]` is equivalent to `[0,0,0,0,0]`. Brackets can even be nested: for instance, `2[1,2,2[2.1,3.1]]` is equivalent to `[1,2,2.1,3.1,2.1,3.1,1,2,2.1,3.1,2.1,3.1]`.

Arrays can be appended from a given position just by entering additional elements; for instance,

```
R(4)=[1.4,1.5] ANG
```

or

```
R(4:)=[1.4,1.5] ANG
```

extends the above array to length 5. Previously defined values can be overwritten. For instance

```
R(2)=[1.25,1.35,1.45]
```

modifies the above vector to (1.0, 1.25, 1.35, 1.45, 1.5).

If no index is given on the left hand side of the equal sign, an existing variable of the same name is replaced by the new values, and all old values are lost. For instance

`THETA=[100,110,120,130]` set four values

...

`THETA(1)=104` replace `THETA(1)` by a new value; `THETA(2:4)` are unchanged

...

`THETA=[140,150]` old variable `THETA` is replaced; `THETA(3:4)` are deleted

Square brackets can also be used to define an array of strings, e.g.,

```
METHOD=[INT,HF,CASSCF,MRCI]
```

These could be used as follows:

```
DO I=1,4
$METHOD(I)
ENDDO
```

The above input would be equivalent to

```
INT
HF
CASSCF
MRCI
```

The current length of an array can be accessed by preceding # to the variable name. For instance, in the above examples `#R` and `#METHOD` have the values 5 and 4, respectively. If a variable is not defined, zero is returned but no error occurs. This can be used to test for the existence of a variable, for example:

```
IF(#SPIN.EQ.0.AND.#NELEC.EQ.1) SET,SPIN=MOD(NELEC,2)
```

This defines variable `SPIN` if it is unknown and if `NELEC` is a scalar (one dimensional) variable.

8.7 Vector operations

The following simple vector operations are possible:

- Copying or appending a vector to another vector. For instance `S=R` copies a vector `R` to a vector `S`. `S(3)=R` copies `R` to `S(3), S(4), ....` `S(#S+1)=R` appends vector `R` to vector `S`. It is also possible to access a range of subsequent elements in a vector: `S=R(2:4)` copies elements 2 to 4 of `R` to `S(1), S(2), S(3)`. Note that `R(2:)` denotes elements `R(2)` to `R(#R)`, but `R(2)` denotes a single element of `R`.
- Vector-scalar operations: `R=R*2` multiplies each element of `R` by 2. Instead of the number 2, also scalar (one dimensional) variables or expressions can be used, e.g., `R=R*ANG` converts all elements of `R` from Ångstrøm to bohr, or `Z=R*COS(THETA)` creates a vector `Z` with elements `Z(i) = R(i)*COS(THETA)`. All other algebraic operators can be used instead of "*".
- Vector-vector operations: If `A` and `B` are vectors of the same length, then `A` $\times$ `B` is also a vector of this length. Here $\times$ stands for any algebraic operator, and the operation is done for each pair of corresponding elements. For instance, `A + B` adds the vectors `A` and `B`, and `A * B` multiplies their elements. Note that the latter case is not a scalar product. If an attempt is made to connect two vectors of different lengths by an algebraic operator, an error occurs.
- Intrinsic functions: Assume `THETA=[100,110,120,-130]` to be a vector of angles (in degrees). In this case `X=2*COS(THETA)` is also a vector containing the cosines of each element of `THETA` multiplied by two, i.e., `X(i) = 2*COS(THETA(i))`. `MAX(THETA)` or `MIN(THETA)` return the maximum and minimum values, respectively, in array `THETA`. Vector operations can also be nested, e.g., `MAX(ABS(THETA))` returns the maximum value in array `ABS(THETA)`.

At present, vector operations are not supported with `string` variables.

8.8 Special variables

8.8.1 Variables set by the program

A number of variables are predefined by the program. The following variables can be used to convert between atomic units and other units:

```
EV=1.d0/27.2113961d0 HARTREE
KELVIN=1.d0/3.157733d5 HARTREE
KJOULE=1.d0/2625.500d0 HARTREE
KCAL=1.d0/627.5096d0 HARTREE
CM=1.d0/219474.63067d0 HARTREE
CM-1=1.d0/219474.63067d0 HARTREE
HZ=1.d0/6.5796838999d15 HARTREE
HERTZ=1.d0/6.5796838999d15 HARTREE
ANG=1.d0/0.529177249d0 BOHR
ANGSTROM=1.d0/0.529177249d0 BOHR

TOEV=27.2113961d0 EV
TOK=3.157733d5 K
TOKELVIN=3.157733d5 K
TOCM=219474.63067d0 CM-1
```

```
TOHERTZ=6.5796838999d15 HZ
TOHZ=6.5796838999d15 HZ
TOKJ=2625.500d0 KJ/MOL
TOKJOULE=2625.500d0 KJ/MOL
TOKCAL=627.5096d0 KCAL/MOL
TOA=0.529177249d0 ANGSTROM
TOANG=0.529177249d0 ANGSTROM
TODEBYE=2.54158d0 DEBYE
```

Further variables which are set during execution of the program:

INTYP	defines integral program to be used. Either INTS (Seward) or INTP (Argos).
INTDONE	has the value .true. if the integrals are done for the current geometry.
CARTESIAN	Set to one if Cartesian basis functions are used.
SCFDONE	has the value .true. if an SCF calculation has been done for the current geometry.
NUMVAR	number of variables presently defined
STATUS	status of last step (1=no error, -1=error or no convergence)
CHARGE	Total charge of the molecule
NELEC	number of electrons in last wavefunction
SPIN	spin multiplicity minus one of last wavefunction
ORBITAL	record of last optimized orbitals (set but never used in the program)
LASTORB	Type of last optimized orbitals (RHF, UHF, UHFNAT, or MCSCF.
LASTSYM	Symmetry of wavefunction for last optimized orbitals.
LASTSPIN	$2 * M_S$ for wavefunctions for last optimized orbitals.
LASTNELEC	Number of electrons in wavefunction for last optimized orbitals.
ENERGR(istate)	Reference energy for state *istate* in MRCI and CCSD.
ENERGY(istate)	last computed total energy for state *istate* for the method specified in the input (e.g., HF, MULTI, CCSD(T), or CCSD[T].
ENERGD(istate)	Total energy for state *istate* including Davidson correction (set only in CI).
ENERGP(istate)	Total energy for state *istate* including Pople correction (set only in CI).
ENERGT(1)	Total energy including perturbative triples (T) correction (set only in CCSD(T), QCI(T)).
ENERGT(2)	Total energy including perturbative triples [T] correction (set only in CCSD(T), QCI(T)).
ENERGT(3)	Total energy including perturbative triples -t correction (set only in CCSD(T), QCI(T)).
EMP2	holds MP2 energy in MPn, CCSD, BCCD, or QCISD calculations, and RS2 energy in MRPT2 (CASPT2) calculations.
EMP3	holds MP3 energy in MP3 and MP4 calculations, and RS3 energy in MRPR3 (CASPT3) calculations.

EMP4	holds MP4(SDQ) energy in MP4 calculations. The MP4(SDTQ) energy is stored in variable ENERGY.
METHODC	String variable holding name of the methods used for ENERGC, e.g., CCSD, BCCD, QCI.
METHODT(1)	String variable holding name of the methods used for ENERGT(1), e.g., CCSD(T), BCCD(T), QCI(T).
METHODT(2)	String variable holding name of the methods used for ENERGT(2), e.g., CCSD[T], BCCD[T], QCI[T].
METHODT(3)	String variable holding name of the methods used for ENERGT(3), e.g., CCSD-T, BCCD-T, QCI-T.
ENERGC	Total energy excluding perturbative triples correction (set only in QCI or CCSD with triples correction enabled).
DFTFUN	total value of density functional in DFT or KS.
DFTFUNS(ifun)	value of ifun'th component of density functional in DFT or KS.
DFTNAME(ifun)	name of ifun'th component of density functional in DFT or KS.
DFTFAC(ifun)	factor multiplying ifun'th component of density functional in DFT or KS.
DFTEXFAC	factor multiplying exact exchange in KS.
PROP(istate)	computed property for state *istate*. See below for the names PROP of various properties.
PROGRAM	last program called, as specified in the input (e.g., HF, CCSD(T), etc.)
ITERATIONS	Number of iterations used. Set negative if no convergence or max number of iterations reached.
CPUSTEP	User-CPU time in seconds for last program called.
SYSSTEP	System-CPU time in seconds for last program called.
WALLSTEP	Elapsed time in seconds for last program called.

The variable names for properties are the same as used on the EXPEC input cards.

OV	Overlap
EKIN	Kinetic energy
POT	Potential
DELT	Delta function
DEL4	∇^4
DARWIN	Darwin term of relativistic correction
MASSV	Mass-velocity term of relativistic correction
EREL	Total relativistic correction
DMX, DMY, DMZ	Dipole moments
XX, YY, ZZ, XY, XZ, XY	Second moments
XXX, XXY, XXZ, XYY, XYZ, XZZ, YYY, YYZ, YZZ, ZZZ	Third moments
QMXX, QMYY, QMZZ, QMXY, QMXZ, QMXY	Quadrupole moments

EFX, EFY, EFZ	Electric field
FGXX, FGYY, FGZZ, FGXY, FGXZ, FGXY	Electric field gradients
D/DX, D/DY, D/DZ	Velocity
LSX, LSY, LSZ	One-electron spin-orbit
LL	Total angular momentum squared L^2
LX, LY, LZ	Electronic angular momentum
LXLX, LYLY, LZLZ, LXLY, LXLZ, LYLZ	Two-electron angular momentum

By default, only the dipole moments are computed and defined. The values of other properties are only stored in variables if they are requested by EXPEC cards. If more than one state is computed (e.g., in state-averaged MCSCF, corresponding arrays PROP(istate) are returned. If properties are computed for more than one center, the center number is appended to the name, e.g. EFX1, EFX2 etc.

If transition properties are computed, their values are stored in corresponding variables with prefix TR, e.g., TRDMX, TRDMY, TRDMZ for transition dipole moments. If more than two states are computed, the index is $(i-1)*(i-2)/2+j$, where $i > j \geq 1$ are state numbers. In a state-averaged calculation, states are counted sequentially for all state symmetries.

For instance, in the following state-averaged MCSCF

```
MULTI;WF,14,1,0;STATE,3;WF,14,2,0;STATE,2;WF,3,0
```

the states are counted as

i	1	2	3	4	5	6
Symmetry	1	1	1	2	2	3
Root in Sym.	1	2	3	1	2	1

8.8.2 Variables recognized by the program

All variables described below are checked by the program, but not set (except NELEC and SPIN). If these are not defined by the user, the program uses its internal defaults. The variables have no effect if the corresponding input cards are present.

Variables recognized by the SCF program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
SPIN	spin multiplicity minus one
SCFSYM[METRY]	wavefunction symmetry
SYMMETRY	as SCFSYMM; only used if SCFSYMM is not present.
SCFOC[C]	number of occupied orbitals in each symmetry for SCF
SCFCL[OSED]	number of closed-shell orbitals in each symmetry for SCF
SCFORB	record of saved orbitals in SCF
SCFSTART	record of starting orbitals used in SCF

Variables recognized by the MCSCF program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
MCSYM[METRY]	wavefunction symmetry. This can be an array for state-averaged calculations.
SYMMETRY	as MCSYMM; only used if MCSYMM is not present.
MCSPIN	spin multiplicity minus one. This can be an array for state-averaged calculations, but different spin multiplicities can only be used in determinant CASSCF. If only one value is specified, this is used for all states
SPIN	as MCSPIN; only used if MCSPIN is not present.
MCSTATE	number of states for each symmetry in MCSCF
STATE	as MCSTATE; only used if MCSTATE is not present.
WEIGHT	weight factors for all states defined by SYMMETRY and STATE
LQUANT	Eigenvalues of L_z^2 for linear molecules for each state defined by SYMMETRY and STATE.
MCSELECT	records from which configurations can be selected and selection threshold
SELECT	as MCSELECT; only used if MCSELECT is not present.
MCRESTRICT	can be used to define occupancy restrictions
RESTRICT	as MCRESTRCT; only used if MCRESTRICT is not present:
CONFIG	if set to .true. or to one triggers use of CSFs
MCOC[C]	number of occupied orbitals in each symmetry
OCC	as MCOCC; only used if MCOCC is not present.
MCCL[OSED]	number of optimized closed-shell orbitals in each symmetry
CLOSED	as MCCLOSED; only used if MCCLOSED is not present.
MCFROZEN	number of frozen core orbitals in each symmetry
FROZEN	as MCFROZEN; only used if MCFROZEN is not present.
MCSTART	record of starting orbitals
COREORB	record of frozen core orbitals
MCORB	record for saving optimized orbitals
MCSAVE	records for saving CI wavefunction (like SAVE card in MCSCF)

Variables recognized by the CI/CCSD program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
SPIN	spin multiplicity minus one
CISYM[METRY]	wavefunction symmetry. If this is an array, only SYMMETRY(1) is used.
SYMMETRY	as CISYMM; only used if CISYMM is not present.
CISTATE	number of states in CI
STATE	as CISTATE, only used if CISTATE is not present.

CISELECT	records from which configurations can be selected
SELECT	as CISELECT; only used if CISELCT is not present.
CIRESTRICT	defines occupancy restrictions
RESTRICT	as RESTRICT; only used if CIRESTRICT is not present.
CIOC[C]	number of occupied orbitals in each symmetry
OCC	as CIOCC; only used if CIOCC is not present.
CICL[OSED]	number of closed-shell orbitals in each symmetry
CLOSED	as CICLOSED; only used if CICLOSED is not present.
CICO[RE]	number of core orbitals in each symmetry
CORE	as CICORE; only used if CICORE is not present.
CIORB	record of orbitals used in CI
CISAVE	records for saving CI wavefunction (like SAVE card in CI)
CISTART	records for restarting with previous CI wavefunction (like START card in CI)

Variables recognized by the DFT/KS program:

DF(ifun) or DFTNAME(ifun)	name of ifun'th component of density functional.
DFTFAC(ifun)	factor multiplying ifun'th component of density functional.
DFTEXFAC	factor multiplying exact exchange in KS.

Example for the use of these variables for a state-averaged MCSCF (note that system variables can only be modified using the SET command, see section 8.4):

SET,NELEC=9	defines number of electrons
SET,SPIN=1	defines wavefunction to be a doublet
SET,SYMMETRY=[1,2,3]	defines wavefunction symmetries for state averaged calculation
SET,STATE=[2,1,1]	defines number of states to be averaged in each symmetry
WEIGHT=[2,2,1,1]	defines weights for the above four states
OCC=[5,2,2]	number of occupied orbitals in each symmetry
CLOSED=2	number of closed-shell orbitals in symmetry 1
MCORB=3100.2	record for optimized orbitals
MULTI	do mcscf with above parameters

8.9 Displaying variables

Variables or the results of expressions can be displayed in the output using SHOW and TABLE.

8.9.1 The SHOW command

The general form of the SHOW command is as follows:

SHOW[*ncol*,*format*],*expression*

where *expression* can be an expression or variable, *ncol* is the number of values printed per line (default 6), and *format* is a format (default 6F15.8). This can be used to print vectors in matrix form. The specification of *ncol* and *format* is optional. Assume that E is a vector:

SHOW,E	prints E using defaults.
SHOW[n],E	prints E with n elements per line; (if n>6, more than one line is needed, but in any case a new line is started after n elements).
SHOW[n,10f10.4],E	prints E in the format given, with newline forced after n elements.

Note that the total length of the format should not exceed 100 characters (a left margin of 30 characters is always needed).

A *wild card* format can be used to show several variables more easily:

SHOW,qm*,dm*

shows all variables whose names begin with QM and DM. Note that no letters must appear after the *, i.e., the wild card format is less general than in UNIX commands.

See the TABLE command for another possibility to tabulate results.

8.10 Clearing variables

Variables can be deleted using

CLEAR,*name1, name2, ...*

Wild cards can be used as in SHOW, e.g.,

CLEAR,ENERG*

clears all variables whose names begin with ENERG. All variables can be cleared using

CLEARALL

The length of vectors can be truncated simply by redefining the length specifier: #R=2 truncates the array R to length 2. Higher elements are no longer available (but could be redefined). Setting #R=0 is equivalent to the command CLEAR,R.

8.11 Reading variables from an external file

Variables can be read from an external file using

READVAR, *filename*

Such files can be save, for instance by the geometry optimization program, and reused later to recover a certain optimized geometry. The format of the input in *filename* is the same as for ordinary input.

9 TABLES AND PLOTTING

9.1 Tables

Variables can be printed in Table form using the command

TABLE,*var1*,*var2*,...

The values of each variable are printed in one column, so all variables used must be defined for the same range, and corresponding elements should belong together. For example, if in a calculation one has stored R(i), THETA(i), ECI(i) for each geometry *i*, one can print these data simply using

```
TABLE, R, THETA, ECI
```

By default, the number of rows equals the number of elements of the first variable. This can be changed, however, using the RANGE subcommand.

The first ten columns of a table may contain string variables. For instance,

```
hf;etot(1)=energy;method(1)=program;cpu(1)=cpustep
ccsd;etot(2)=energy;method(2)=program;cpu(2)=cpustep
qci;etot(3)=energy;method(3)=program;cpu(3)=cpustep
table,method,etot,cpu
```

prints a table with the SCF, CCSD, and QCI results in the first, second, and third row, respectively. For other use of string variables and tables see, e.g. the examples h2o_tab.com and oh_macros.com

The apparence of the table may be modified using the following commands, which may be given (in any order) directly after the the TABLE card:

HEADING,*head1, head2,...*	Specify a heading for each column. By default, the names of the variables are used as headings.
FORMAT,*format*	Specify a format for each row in fortran style. *format* must be enclosed by quotes. Normally, the program determines automatically an appropriate format, which depends on the type and size of the printed data.
FTYP,*typ1, typ2, typ3, ...*	Simplified form to modify the format. This gives the type (A, F, or D) for each column (sensible defaults are normally used).
DIGITS,*dig1, dig2, dig3, ...*	Give the number of digits after the decimal points to be printed for each column (sensible defaults are normally used).
TYPE	Specify a data format for the table. The default is TEXT which gives a plain text file. Other possibilities are CSV (comma-separated fields suitable for a spreadsheet), LATEX (a LaTeX table environment), MATHEMATICA (Mathematica code that assigns the table to an array), MATLAB (Matlab code that assigns the table to an array), MAPLE (Maple code that assigns the table to an array), HTML (an HTML TABLE construction), and XML (an XML document containing a tree representing the table. The actual format is XHTML).

SAVE,*file,status*	Specify a file on which the table will be written. If status is NEW, the file is rewound, otherwise it is appended. If *file* has a suffix that is one of txt, csv, tex, m, mpl, html, xml, and a TYPE command is not specified, then the type will be set to that which is conventionally appropriate for the suffix.
TITLE,*title*	Specify one line of a title (several TITLE cards may follow each other). Note that titles are only displayed in the SAVE file, if the SAVE command is given before the TITLE card.
SORT,*col1,col2,...*	Sort rows according to increasing values of the given columns. The columns are sorted in the order they are specified.
PRINT,*key1,key2,...*	Specify print options (TABLE, HEADING, TITLE, WARNING, FORMAT, SORT). The default is print for the first three, and noprint for the last three.
NOPRINT,*key1,key2,...*	Disable print for given keys.
NOPUNCH	Don't write data to the punch file (data are written by default).
RANGE,*start,end*	Specify start and end indices of the variables to be printed.
STATISTICS	Print also linear regression and quadratic fits of the data columns.

9.2 Plotting

[PLOT,[[CMD=]*unix_plot_command*],[FILE=*plotfile*],[NOPLOT]

Execute a plotting program using the table as data. PLOT is a subcommand of TABLE and must follow TABLE or any of its valid subcommands given in the previous section. *unix_plot_command* consists of the unix command needed to start the plotting program, followed by any required options. The whole thing should normally be enclosed in quotation marks to preserve lowercase letters. The default is 'xmgrace'. At present, only the *xmgrace, grace, gracebat* and *xmgr* programs with all numerical data are supported, although use of *xmgr* is deprecated, and may not be possible in future versions.

By default the input file for the plotting program is saved in molpro_plot.dat. The name of the plotfile can be modified using the FILE (or PLOTFILE) option. FILE implies that the plot is not shown on the screen but all plot data are saved in the given file. The plot on the screen can also be suppressed with the NOPLOT option.

The following additional directives can be given *before* the PLOT directive:

NOSPLINE	Prevents spline interpolation of data points
NSPLINE,*number*	Number of interpolation points (default 20)
COLOR,*icolor1, icolor2,...*	Colour map to be used for columns 1,2,...; zero means to use default values (colors black, blue, red, green cycle)
SYMBOL,*isymb1, isymb2,...*	Symbol types to be used for columns 1,2,...; -1 means no symbols; zero means to use default values.

10 INTEGRAL-DIRECT CALCULATIONS (GDIRECT)

References:

Direct methods, general: M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999).
Linear scaling LMP2: M. Schütz, G. Hetzer, and H.-J. Werner J. Chem. Phys. **111**, 5691 (1999).

All methods implemented in MOLPRO apart from full CI (FCI) and perturbative triple excitations (T) can be performed integral-direct, i.e., the methods are integral driven with the two-electron integrals in the AO basis being recomputed whenever needed, avoiding the bottleneck of storing these quantities on disk. For small molecules, this requires significantly more CPU time, but reduces the disk space requirements when using large basis sets. However, due to efficient prescreening techniques, the scaling of the computational cost with molecular size is lower in integral-direct mode than in conventional mode, and therefore integral-direct calculations for extended molecules may even be less expensive than conventional ones. The break-even point depends strongly on the size of the molecule, the hardware, and the basis set. Depending on the available disk space, calculations with more than 150–200 basis functions in one symmetry should normally be done in integral-direct mode.

Integral-direct calculations are requested by the DIRECT or GDIRECT directives. If one of these cards is given outside the input of specific programs it acts globally, i.e. all subsequent calculations are performed in integral-direct mode. On the other hand, if the DIRECT card is part of the input of specific programs (e.g. HF, CCSD), it affects only this program. The GDIRECT directive is not recognized by individual programs and always acts globally. Normally, all calculations in one job will be done integral-direct, and then a DIRECT or GDIRECT card is required before the first energy calculation. However, further DIRECT or GDIRECT directives can be given in order to modify specific options or thresholds for particular programs.

The integral-direct implementation in MOLPRO involves three different procedures: (i) Fock matrix evaluation (DFOCK), (ii) integral transformation (DTRAF), and (iii) external exchange operators (DKEXT). Specific options and thresholds exist for all three programs, but it is also possible to specify the most important thresholds by general parameters, which are used as defaults for all programs.

Normally, appropriate default values are automatically used by the program, and in most cases no parameters need to be specified on the DIRECT directive. However, in order to guarantee sufficient accuracy, the default thresholds are quite strict, and in calculations for extended systems larger values might be useful to reduce the CPU time.

The format of the DIRECT directive is

DIRECT, key1=*value1*, key2=*value2*...

The following table summarizes the possible keys and their meaning. The default values are given in the subsequent table. In various cases there is a hierarchy of default values. For instance, if THREST_D2EXT is not given, one of the following is used: [THR_D2EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*]. The list in brackets is checked from left to right, and the first one found in the input is used. *default* is a default value which depends on the energy threshold and the basis set (the threshold is reduced if the overlap matrix contains very small eigenvalues).

General Options (apply to all programs):

THREST	Integral prescreening threshold. The calculation of an integral shell block is skipped if the product of the largest estimated integral value (based on the Cauchy-Schwarz inequality) and the largest density matrix element contributing to the shell block is

smaller than this value. In DTRAF and DKEXT effective density matrices are constructed from the MO coefficients and amplitudes, respectively.

THRINT — Integral prescreening threshold. This applies to the product of the exact (i.e. computed) integral value and a density matrix. This threshold is only used in DTRAF and DKEXT. A shell block of integrals is skipped if the product of the largest integral and the largest element of the effective density matrix contributing to the shell block is smaller than this threshold. If it set negative, no computed integrals will be neglected.

THRPROD — Prescreening threshold for products of integrals and MO-coefficients (DTRAF) or amplitudes (DKEXT). Shell blocks of MO coefficients or amplitudes are neglected if the product of the largest integral in the shell block and the largest coefficient is smaller than this value. If this is set negative, no product screening is performed.

THRMAX — Initial value of the prescreening threshold THREST for DFOCK and DKEXT in iterative methods (SCF, CI, CCSD). If nonzero, it will also be used for DKEXT in MP3 and MP4(SDQ) calculations. The threshold will be reduced to THREST once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. In CI and CCSD calculations, also the initial thresholds THRINT_DKEXT and THRPROD_DKEXT are influenced by this value. For a description, see THRMAX_DKEXT. If THRMAX=0, the final thresholds will be used from the beginning in all methods.

SCREEN — Enables or disables prescreening.
SCREEN≥ 0: full screening enabled.
SCREEN< 0: THRPROD is unused. No density screening in direct SCF.
SCREEN< -1: THRINT is unused.
SCREEN< -2: THREST is unused.

MAXRED — Maximum number of iterations after which thresholds are reduced to their final values in CI and CCSD calculations. If MAXRED=0, the final thresholds will be used in CI and CCSD from the beginning (same as THRMAX=0, but MAXRED has no effect on DSCF. In the latter case a fixed value of 10 is used.

VARRED — Thresholds are reduced to their final values if the sum of squared amplitude changes is smaller than this value.

SWAP — Enables or disables label swapping in SEWARD. Test purpose only.

Specific options for direct SCF (DFOCK):

THREST_DSCF — Final prescreening threshold in direct SCF. If given, it replaces the value of THREST.

THRMAX_DSCF — Initial prescreening threshold in direct SCF. This is used for the first 7-10 iterations. Once a certain accuracy is reached, the threshold is reduced to THREST_DSCF

SWAP_DFOCK	Enables or disables label swapping in fock matrix calculation (test purpose only).

General options for direct integral transformation (DTRAF):

PAGE_DTRAF	Selects the transformation method. PAGE_DTRAF=0: use minimum memory algorithm, requiring four integral evaluations. PAGE_DTRAF=1: use paging algorithm,leading to the minimum CPU time (one integral evaluation for DMP2/LMP2 and two otherwise).
SCREEN_DTRAF	If given, replaces value of SCREEN for DTRAF.
MAXSHLQ1_DTRAF	Maximum size of merged shells in the first quarter transformation step (0: not used).
MINSHLQ1_DTRAF	Shells are only merged if their size is smaller than this value (0: not used).
MAXSHLQ2_DTRAF	Maximum size of merged shells in the second quarter transformation step (0: not used).
MINSHLQ2_DTRAF	Shells are only merged if their size is smaller than this value (0: not used).
MAXCEN_DTRAF	Maximum number of centres in merged shells (0: no limit).
PRINT_DTRAF	Print parameter for DTRAF.

General thresholds for all direct integral transformations:

THR_DTRAF	General threshold for DTRAF. If given, this is taken as default value for all thresholds described below.
THREST_DTRAF	AO prescreening threshold for DTRAF. Defaults: [THR_DTRAF, THREST, *default*].
THRINT_DTRAF	Integral threshold for DTRAF. Defaults: [THR_DTRAF, THRINT, *default*].
THRPROD_DTRAF	Product threshold for DTRAF. Defaults: [THR_DTRAF, THRPROD, *default*].

Thresholds specific to direct integral transformations:

THR_D2EXT	General threshold for generation of 2-external integrals. If given, this is used as a default for all D2EXT thresholds described below.
THREST_D2EXT	Prescreening threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D2EXT	Integral threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D2EXT	Product threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].

THR_D3EXT	General threshold for generation of 3-external integrals. If given, this is used as a default for all D3EXT thresholds described below.
THREST_D3EXT	Prescreening threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D3EXT	Integral threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D3EXT	Product threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THR_D4EXT	General threshold for generation of 4-external integrals. If given, this is used as a default for all D4EXT thresholds described below.
THREST_D4EXT	Prescreening threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D4EXT	Integral threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D4EXT	Product threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THR_DCCSD	General threshold for generalized transformation needed in each CCSD iteration. If given, this is used as a default for THREST_DCCSD, THRINT_DCCSD, and THRPROD_DCCSD described below.
THREST_DCCSD	Prescreening threshold for DCCSD transformation. Defaults: [THR_DCCSD, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_DCCSD	Integral threshold for DCCSD transformation. Defaults: [THR_DCCSD, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_DCCSD	Product threshold for DCCSD transformation. Defaults: [THR_DCCSD, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THRMAX_DCCSD	Initial value for THREST_DCCSD in CCSD calculations. The threshold will be reduced to THREST_DCCSD once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT_DCCSD and THRPROD_DCCSD are obtained by multiplying their input (or default) values by THRMAX_DCCSD/THREST_DCCSD, with the restriction that the initial values cannot be smaller than the final ones.

Specific options for direct MP2 (DMP2**):**

DMP2 — Selects the transformation method for direct MP2:
DMP2=−1: automatic selection, depending on the available memory.
DMP2=0: use fully direct method for DMP2 (min. two integral evaluations, possibly multipassing, no disk space).
DMP2=1: use semi-direct method for DMP2 (one to four integral evaluations, depending on PAGE_DTRAF).
DMP2=2: use DKEXT to compute exchange operators in DMP2 (one integral evaluation). This is only useful in local DMP2 calculations with many distant pairs.

THR_DMP2 — General threshold for generation of 2-external integrals in DMP2. If given, this is used as a default for all DMP2 thresholds described below.

THREST_DMP2 — Prescreening threshold for generation of 2-external integrals. Defaults: [THR_DMP2, THREST_DTRAF, THR_DTRAF, THREST, *default*].

THRINT_DMP2 — Integral threshold for generation of 2-external integrals. Defaults: [THR_DMP2, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].

THRPROD_DMP2 — Product threshold for generation of 2-external integrals Defaults: [THR_DMP2, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].

Specific options for direct local MP2 (LMP2**):**

DTRAF — Selects the transformation method for direct LMP2:
DTRAF ≥ 0: generates the 2-external integrals (exchange operators) first in AO basis and transforms these thereafter in a second step to the projected, local basis. The disk storage requirements hence scale cubically with molecular size.
DTRAF $= -1$: generates the 2-external integrals (exchange operators) directly in projected basis. The disk storage requirements hence scale linearly with molecular size. This (together with PAGE_DTRAF = 0) is the recommended algorithm for very large molecules (cf. linear scaling LMP2, chapter 28).
DTRAF $= -2$: alternative algorithm to generate the exchange operators directly in projected basis. Usually, this algorithm turns out to be computationally more expensive than the one selected with DTRAF $= -1$. Note, that neither DTRAF $= -1$ nor DTRAF $= -2$ work in the context of LMP2 gradients.

THR_LMP2 — General threshold for generation of 2-external integrals in linear scaling LMP2. If given, this is used as a default for all LMP2 thresholds described below.

THREST_LMP2 — Prescreening threshold for generation of 2-external integrals. Defaults: [THR_LMP2, THREST_DTRAF, THR_DTRAF, THREST, *default*].

THRQ1_LMP2 — Threshold used in the first quarter transformation. Defaults: [THR_LMP2, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].

THRQ2_LMP2	Threshold used in the second and subsequent quarter transformations. Defaults: [THR_LMP2, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRAO_ATTEN	Special threshold for prescreening of attenuated integrals $(\mu\mu\|\nu\nu)$ Default: THREST_LMP2

Options for integral-direct computation of external exchange operators (DKEXT):

DKEXT	Selects driver for DKEXT. DKEXT=−1: use paging algorithm (minimum memory). This is automatically used if in-core algorithm would need more than one integral pass. DKEXT=0: use in-core algorithm, no integral triples. DKEXT=1: use in-core algorithm and integral triples. DKEXT=2: use in-core algorithm and integral triples if at least two integrals of a triple differ. DKEXT=3: use in-core algorithm and integral triples if all integrals of a triple differ.
SCREEN_DKEXT	if given, replaces value of SCREEN for DKEXT.
MAXSIZE_DKEXT	Largest size of merged shells in DKEXT (0: not used).
MINSIZE_DKEXT	Shells are only merged if their size is smaller than this value. (0: not used).
MAXCEN_DKEXT	Maximum number of centres in merged shells (0: no limit).
SCREEN_DKEXT	Enables of disables screening in DKEXT.
PRINT_DKEXT	Print parameter for DKEXT.
SWAP_DKEXT	Enables of disables label swapping in DKEXT (test purpose only)
MXMBLK_DKEXT	Largest matrix block size in DKEXT (only used with DKEXT≥ 1).

Thresholds for integral-direct computation of external exchange operators (DKEXT):

THR_DKEXT	General threshold for DKEXT. If given, this is used as a default for all DKEXT thresholds described below.
THREST_DKEXT	Prescreening threshold for DKEXT. Defaults: [THR_DKEXT, THREST, *default*].
THRINT_DKEXT	Integral threshold for DKEXT. Defaults: [THR_DKEXT, THRINT, *default*].
THRPROD_DKEXT	Product threshold for DKEXT. Defaults: [THR_DKEXT, THRPROD, *default*].
THRMAX_DKEXT	Initial value for THREST_DKEXT in CI, and CCSD calculations. If nonzero. it will also be used for DKEXT in MP3 and MP4 (SDQ) calculations. The threshold will be reduced to THREST_DKEXT once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT_DKEXT and THRPROD_DKEXT are obtained by multiplying their input (or default) values by THRMAX_DKEXT/THREST_DKEXT,

with the restriction that the initial values cannot be smaller than the final ones.

For historical reasons, many options have alias names. The following tables summarize the default values for all options and thresholds and also gives possible alias names.

Table 6: Default values and alias names for `direct` options.

Parameter	Alias	Default value
SCREEN		1
MAXRED		7
VARRED		1.d-7
SWAP		1
SWAP_DFOCK		SWAP
DMP2	DTRAF	−1
PAGE_DTRAF	PAGE	1
SCREEN_DTRAF		SCREEN
MAXSHLQ1_DTRAF	NSHLQ1	32
MINSHLQ1_DTRAF		0
MAXSHLQ2_DTRAF	NSHLQ2	16
MINSHLQ2_DTRAF		0
MAXCEN_DTRAF		0
PRINT_DTRAF		−1
SWAP_DTRAF		SWAP
DKEXT	DRVKEXT	3
SCREEN_DKEXT		SCREEN
MAXSIZE_DKEXT		0
MINSIZE_DKEXT		5
MAXCEN_DKEXT		1
PRINT_DKEXT		−1
SWAP_DKEXT		SWAP
MXMBLK_DKEXT		depends on hardware (-B parameter on `molpro` command)

Table 7: Default thresholds and alias names for direct calculations

Parameter	Alias	Default value
THREST	THRAO	$\min(\Delta E \cdot 1.d-2, 1.d-9)^{a,b}$
THRINT	THRSO	$\min(\Delta E \cdot 1.d-2, 1.d-9)^{a,b}$
THRPROD	THRP	$\min(\Delta E \cdot 1.d-3, 1.d-10)^{a,b}$
THRMAX		1.d-8^{b}
THREST_DSCF	THRDSCF	$\leq$ 1.d-10 (depending on accuracy and basis set)
THRMAX_DSCF	THRDSCF_MAX	THRMAX
THR_DTRAF	THRDTRAF	
THREST_DTRAF	THRAO_DTRAF	[THR_DTRAF, THREST]
THRINT_DTRAF	THRAO_DTRAF	[THR_DTRAF, THRINT]
THRPROD_DTRAF	THRP_DTRAF	[THR_DTRAF, THRPROD]
THR_D2EXT	THR2EXT	THR_DTRAF
THREST_D2EXT	THRAO_D2EXT	[THR_D2EXT, THREST_DTRAF]
THRINT_D2EXT	THRSO_D2EXT	[THR_D2EXT, THRINT_DTRAF]
THRPROD_D2EXT	THRP_D2EXT	[THR_D2EXT, THRPROD_DTRAF]
THR_D3EXT	THR3EXT	THR_DTRAF
THREST_D3EXT	THRAO_D3EXT	[THR_D3EXT, THREST_DTRAF]
THRINT_D3EXT	THRSO_D3EXT	[THR_D3EXT, THRINT_DTRAF]
THRPROD_D3EXT	THRP_D3EXT	[THR_D3EXT, THRPROD_DTRAF]
THR_D4EXT	THR4EXT	THR_DTRAF
THREST_D4EXT	THRAO_D4EXT	[THR_D4EXT, THREST_DTRAF]
THRINT_D4EXT	THRSO_D4EXT	[THR_D4EXT, THRINT_DTRAF]
THRPROD_D4EXT	THRP_D4EXT	[THR_D4EXT, THRPROD_DTRAF]
THR_DCCSD	THRCCSD	THR_DTRAF
THREST_DCCSD	THRAO_DCCSD	[THR_DCCSD, THREST_DTRAF]
THRINT_DCCSD	THRSO_DCCSD	[THR_DCCSD, THRINT_DTRAF]
THRPROD_DCCSD	THRP_DCCSD	[THR_DCCSD, THRPROD_DTRAF]
THRMAX_DCCSD	THRMAX_DTRAF	THRMAX
THR_DMP2	THRDMP2	THR_DTRAF
THREST_DMP2	THRAO_DMP2	[THR_DMP2, THREST_DTRAF, *default*^{c}]
THRINT_DMP2	THRSO_DMP2	[THR_DMP2, THRINT_DTRAF, *default*^{c}]
THRPROD_DMP2	THRP_DMP2	[THR_DMP2, THRPROD_DTRAF, *default*^{c}]
THR_LMP2	THRLMP2	THR_DTRAF
THREST_LMP2	THRAO_LMP2	[THR_LMP2, THREST_DTRAF, *default*^{c}]
THRQ1_LMP2	THRQ1	[THR_LMP2, THRPROD_DTRAF, *default*^{c}]
THRQ2_LMP2	THRQ2	[THR_LMP2, THRINT_DTRAF, *default*^{c}]
THRAO_ATTEN]	THRATTEN	THREST_LMP2
THR_DKEXT	THRKEXT	
THREST_DKEXT	THRAO_DKEXT	[THR_DKEXT, THREST]
THRINT_DKEXT	THRSO_DKEXT	[THR_DKEXT, THRINT]
THRPROD_DKEXT	THRP_DKEXT	[THR_DKEXT, THRPROD]
THRMAX_DKEXT		THRMAX

a) ΔE is the requested accuracy in the energy (default 1.d-6).

b) The thresholds are reduced if the overlap matrix has small eigenvalues.

c) The default thresholds for DMP2 and LMP2 are $0.1 \cdot \Delta E$.

10.1 Example for integral-direct calculations

examples/h2o_direct.com

```
! $Revision: 2006.0 $
memory,2,m
$method=[hf,mp2,ccsd,qci,bccd,multi,mrci,acpf,rs3]          !some methods
basis=vdz                                                   !basis
geometry={o;h1,o,r;h2,o,r,h1,theta}                         !geometry
gdirect                                                     !direct option
r=1 ang,theta=104                                           !bond length and angle
do i=1,#method                                              !loop over methods
$method(i)                                                  !run method(i)
e(i)=energy                                                 !save results in variables
dip(i)=dmz
enddo
table,method,e,dip                                          !print table of results
```

This jobs produces the following table:

```
METHOD       E            DIP
HF       -76.02145798   0.82747348
MP2      -76.22620591   0.00000000
CCSD     -76.23580191   0.00000000
QCI      -76.23596211   0.00000000
BCCD     -76.23565813   0.00000000
MULTI    -76.07843443   0.76283026
MRCI     -76.23369819   0.76875001
ACPF     -76.23820180   0.76872802
RS3      -76.23549448   0.75869972
```

11 DENSITY FITTING

Density fitting can be used to approximate the integrals in spin restricted Hartree-Fock (HF), density functional theory (KS), second-order Møller-Plesset perturbation theory (MP2) and all levels of closed-shell local correlation methods (LMP2-LMP4, LQCISD(T), LCCSD(T)). Density fitting is invoked by adding the prefix DF- to the command name, e.g. DF-HF, DF-KS, DF-MP2 and so on. Gradients are available for DF-HF, DF-KS, and DF-LMP2. By default, a fitting basis set will be chosen automatically that corresponds to the current orbital basis set and is appropriate for the method. For instance, if the orbital basis set is VTZ, the default fitting basis is VTZ/JKFIT for DF-HF or DF-KS, and VTZ/MP2FIT for DF-MP2. Other fitting basis sets from the library can be chosen using the DF_BASIS option, e.g.

```
BASIS=VTZ               !use VTZ orbital basis
DF-HF,DF_BASIS=VQZ     !use VQZ/JKFIT fitting basis
DF-MP2,DF_BASIS=VQZ    !use VQZ/MP2FIT fitting basis
```

The program then chooses automatically the set which is appropriate for the method. Alternatively, fitting basis sets can be defined in a preceding basis block (see 13), and then be refered to with their set names, e.g.,

```
DF-HF, DF_BASIS=MYJKBASIS
DF-MP2, DF_BASIS=MYMP2BASIS
```

where MYJKBASIS and MYMP2BASIS are sets defined in a basis block. In this case it is the responsibility of the user to ensure that the basis set is appropriate for the method.

Further options, as fully described in section 11.1, can be added on the command line. In this case they are valid only for the current command. Alternatively, the options can be specifed on a separate DFIT directive. If this is given within a command block, the options are used only for the current program; this is entirely equivalent to the case that the options are specified on the command line. However, if a DFIT (or GDFIT) directive is given outside of a command block, the specified options are used globally in all subsequent density fitting calculations in the same run.

The options specified on a global DFIT directive are also passed down to procedures. However, if a DFIT is given within a procedure, the corresponding options are used only in the same procedure and procedures called from it. When the procedure terminates, the options from the previous level are recovered.

11.1 Options for density fitting

The options described in this section have sensible default values and usually do not have to be given. Many options described below have alias names. These can be obtained using

```
HELP,CFIT,ALIASES.
```

11.1.1 Options to select the fitting basis sets

BASIS	Basis set for fitting (Default: set corresponding to the orbital basis)
BASIS_COUL	Basis set for Coulomb fitting (default BASIS)
BASIS_EXCH	Basis set for exchange fitting (default BASIS)

BASIS_MP2	Fitting basis set for DF-MP2 (default BASIS)
BASIS_CCSD	Fitting basis set for DF-LCCSD (default BASIS)

11.1.2 Screening thresholds

THRAO	Threshold for neglecting contracted 3-index integrals in the AO basis (default 1.d-8).
THRMO	Threshold for neglecting half-transformed 3-index integrals (default 1.d-8).
THRSW	Threshold for Schwarz screening (default 1.d-5).
THROV	Threshold for neglecting 2-index integrals in the AO (default 1.d-10.
THRPROD	Product screening threshold for first half transformation (default 1.d-8).

Analogous thresholds for specfic programs can be set by appending the above keywords by the following specifications

_SCF	Coulomb and exchange fitting in DF-HF/DF-KS
_COUL	Coulomb fitting in DF-HF/DF-KS
_EXCH	Exchange fitting in DF-HF/DF-KS
_CPHF	Coulomb and exchange fitting in CPHF
_SCFGRD	Coulomb and exchange fitting in DF-HF/DF-KS gradients

The default values are the same as for the general thresholds.

Further thresholds:

THR2HLF	Threshold for second-half transformation in exchange fitting (default THRAO_SCF)
THRASM_SCF	Threshold for local assembly of exchange matrix (default THRAO_SCF)
THRAO_FOCK	Threshold for Coulomb fitting in DF-KS (default MIN(THRAO_SCF*1.d-2,1.d-12))

11.1.3 Parameters to enable local fitting

Local fitting as described in H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003), Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004), and M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, J. Chem. Phys. **121**, 737 (2004). can be activated by setting LOCFIT=1. By default, local fitting is disabled, because under certain circumstances it can lead to unacceptable errors. For instance, local fitting must not be used in counter-poise calculations, since the lack of fitting functions at the dummy atoms can lead to wrong results.

Local fitting can be restricted to certain programs, using the following options:

LOCFIT	If positive, use local fitting in all programs in which it is available (default 0).

LOCFIT_SCF	If positive, use local fitting in SCF (default LOCFIT)
LOCFIT_MP2	If positive, use local fitting in DF-LMP2; 1: use orbital domains; 2: use pair domains (default LOCFIT)
LOCFIT_F12	If positive, use local fitting in DF-LMP2-F12 (default LOCFIT)
LOCFIT_CCSD	If positive, use local fitting in DF-LCCSD (default LOCFIT)
LOCFIT_2EXT	If positive, use local fitting in LCCSD 2ext transformation (default LOCFIT_CCSD)
LOCFIT_3EXT	If positive, use local fitting in LCCSD 3ext transformation (default LOCFIT_CCSD)
LOCFIT_4EXT	If positive, use local fitting in LCCSD 4ext transformation (default LOCFIT_CCSD)
LOCFIT_CPHF	If positive, use local fitting in CPHF (default LOCFIT)
LOCFIT_SCFGRD	If positive, use local fitting in gradient calculations (default LOCFIT)
LOCORB	If positive, use localized orbitals in DF-HF (default 1)
LOCTRA	If positive, use local screening in first half transformation (default LOCFIT).
DSCREEN	If positive, enable density screening in LMP2 (default 0)
KSCREEN	If positive, enable fit-basis Schwarz screening in LMP2 (default depends on LOCTRA).

11.1.4 Parameters for fitting domains

The following options can be used to modify the domains used in local fitting. These parameters only have an effect if LOCFIT=1. The local fitting domains are determined in two steps: first *primary* orbital domains are deterimined. In the LMP2 and LCCSD programs, the primary orbital domains are the same as used for excitation domains and determined by the Boughton-Pulay procedure, as described in Sect. 28. Depending on the value of FITDOM_MP2 or FITDOM_CCSD for LMP2 and LCCSD, respectively, either the orbital domains are used directly or united pair domains are generated. In DF-HF the primary orbital domains include all basis functions at atoms which have Löwdin charges greater or equal to THRCHG_SCF. In the second step the primary fitting domains are extended using either distance criteria (RDOMAUX, in bohr) or bond connectivity criteria (IDOMAUX). IDOMAUX=1 means to include all functions at atoms wich are at most one bond distant from the primary domains. By default, distance criteria are used. However, if IDOMAUX.ge.0, the distance criteria are ignored and connectivity is used.

THRCHG_SCF	Parameter to select the primary orbital domains in local exchange fitting (default 0.1). All atoms are include which have L"owdin charges greater than this value. The primary domains are extended according to RDOMAUX_SCF or IDOMAUX_SCF.
FITDOM_MP2	Parameter to select primary fitting domains in LMP2 transformation (default 3). 1: use orbital domains; 2: use united orbital domains of strong pairs; 3: use united orbital domains of strong and weak pairs (default 3). The primary domains are extended according to RDOMAUX_MP2 or IDOMAUX_MP2

FITDOM_CCSD	Similar to FITDOM_MP2 but used for LCCSD 2-ext transformation.
RDOMAUX_SCF	Distance criterion for fitting domain extension in SCF (default 5.0)
IDOMAUX_SCF	Connectivity criterion for fitting domain extension in SCF (default 0)
RDOMAUX_CORE	Distance criterion for core orbital fitting domain extension in SCF (default RDOMAUX_SCF).
IDOMAUX_CORE	Connectivity criterion for core orbital fitting domain extension in SCF (default IDOMAUX_SCF).
RDOMSCF_START	Distance criterion for fitting domain extension in the initial SCF iterations (default 3.0).
IDOMSCF_START	Connectivity criterion for fitting domain extension in the initial SCF iterations (default 1).
RDOMSCF_FINAL	Distance criterion for fitting domain extension in the final SCF iterations (default RDOMAUX_SCF).
IDOMSCF_FINAL	Connectivity criterion for fitting domain extension in the final SCF iterations (default IDOMAUX_SCF).
RDOMAUX_MP2	Distance criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2
IDOMAUX_MP2	Connectivity criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2
RDOMAUX_CCSD	Distance criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD).
IDOMAUX_CCSD	Connectivity criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD.
RDOMAUX_CPHF	Distance criterion for fitting domain extension in CPHF (default 3.0).
RDOMAUX_SCFGRD	Distance criterion for fitting domain extension in gradients (default 5.0).
SCSGRD	Switches the DF-LMP2 analytic gradient to Grimmes SCS scaled MP2 energy functional (default 0).

11.1.5 Miscellaneous control options

There is a rather large number of parameters. Many of these should normally not be changed, and therefore only a subset is described here. A full list can be obtained using

```
HELP,CFIT
```

12 GEOMETRY SPECIFICATION AND INTEGRATION

Before starting any energy calculations, MOLPRO checks if the one-and two-electron integrals are available for the current basis set and geometry and automatically computes them if necessary. It is therefore not necessary any more to call the integral program explicitly, as was done in older MOLPRO versions using the `INT` command. The program also recognizes automatically if only the nuclear charges have been changed, as is the case in counterpoise calculations. In this case, the two-electron integrals are not recomputed.

Before any energy calculation, the geometry and basis set must be defined in `GEOMETRY` and `BASIS` blocks, respectively.

12.1 Sorted integrals

By default, two electron integrals are evaluated once and stored on disk. This behaviour may be overridden by using the input command `gdirect` (see section 10) to force evaluation of integrals on the fly. If the integrals are stored on disk, immediately after evaluation they are sorted into complete symmetry-packed matrices, so that later program modules that use them can do so as efficiently as possible. The options for the integral sort can be specified using the `AOINT` parameter set, using the input form

`AOINT`, *key1=value1*, *key2=value2*, ...

The following summarizes the possible keys, together with their meaning, and default values.

c_final	Integer specifying the compression algorithm to be used for the final sorted integrals. Possible values are 0 (no compression), 1 (compression using 1, 2, 4 or 8-byte values), 2 (2, 4 or 8 bytes), 4 (4, 8 bytes) and 8. Default: 0
c_sort1	Integer specifying the compression algorithm for the intermediate file during the sort. Default: 0
c_seward	Integer specifying the format of label tagging and compression written by the integral program and read by the sort program. Default: 0
compress	Overall compression; c_final, c_seward and c_sort1 are forced internally to be not less than this parameter. Default: 1
thresh	Real giving the truncation threshold for compression. Default: 0.0, which means use the integral evaluation threshold (`GTHRESH,TWOINT`)
io	String specifying how the sorted integrals are written. Possible values are `molpro` (standard MOLPRO record on file 1) and `eaf` (Exclusive-access file). `eaf` is permissible only if the program has been configured for MPP usage, and at present `molpro` is implemented only for serial execution. `molpro` is required if the integrals are to be used in a restart job. For maximum efficiency on a parallel machine, `eaf` should be used, since in that case the integrals are distributed on separate processor-local files.

For backward-compatibility purposes, two convenience commands are also defined: `COMPRESS` is equivalent to `AOINT,COMPRESS=1`, and `UNCOMPRESS` is equivalent to `AOINT,COMPRESS=0`.

12.2 Symmetry specification

If standard Z-matrix input is used, MOLPRO determines the symmetry automatically by default. However, sometimes it is necessary to use a lower symmetry or a different orientation than obtained by the default, and this can be achieved by explicit specification of the symmetry elements to be used, as described below.

On the first card of the integral input (directly after the `INT` card or as first card in a geometry block), generating symmetry elements can be given, which uniquely specify the point group. The dimension of the point group is 2**(number of fields given). Each field consists of one or more of `X`, `Y`, or `Z` (with no intervening spaces) which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose z to be the unique axis where appropriate (essential for C_2 and C_{2h}). In that case, the possibilities are:

(null card)	C_1 (i.e., no point group symmetry)
`Z`	C_s
`XY`	C_2
`XYZ`	C_i
`X,Y`	C_{2v}
`XY,Z`	C_{2h}
`XZ,YZ`	D_2
`X,Y,Z`	D_{2h}

Note that Abelian point group symmetry only is available, so for molecules with degenerate symmetry, an Abelian subgroup must be used — e.g, C_{2v} or D_{2h} for linear molecules.

See section 4.8 for more details of symmetry groups and ordering of the irreducible representations. Also see section 12.3.1 for more information about automatic generation of symmetry planes.

12.3 Geometry specifications

The geometry may be given in standard Z-matrix form, XYZ form, or cartesian and polar coordinate MOLPRO92 format. The geometry specifications are given in the form

```
geometry={,
options
atom specifications
}
```

The following are permitted as options:

	Any valid combination of symmetry generators, as described in the previous section.
`NOSYM`	Disable use of symmetry.
`ANGSTROM`	Bond lengths specified by numbers, or variables without associated units, are assumed to be in Å.
`CHARGE`	Orient molecule such that origin is centre of charge, and axes are eigenvectors of quadrupole moment.

MASS	Orient molecule such that origin is centre of mass, and axes are eigenvectors of inertia tensor (default).
NOORIENT	Disable re-orientation of molecule.
ZSIGNX+	Force first non-zero x-coordinate to be positive. Similarly, ZSIGNY+, ZSIGNZ+ can be set for the y- and z-coordinates, respectively. If − is used instead of + as last character, the corresponding coordinate is forced to be negative. This can be useful to fix the orientation of the molecule across different calculations and geometries. Alternatively, the system variables ZSIGNX, ZSIGNZ, ZSIGNZ can be set to positive or negative values to achieve the same effect.
PLANEXZ	For the C_{2v} and D_{2h} point groups, force the primary plane to be *xz* instead of the default *yz*. The geometry builder attempts by swapping coordinate axes to place as many atoms as possible in the primary plane, so for the particular case of a planar molecule, this means that all the atoms will lie in the primary plane. The default implements recommendation 5*a* and the first part of recommendation 5*b* specified in J. Chem. Phys. 55, 1997 (1955). PLANEYZ and PLANEXY may also be specified, but note that the latter presently generates an error for C_{2v}.

12.3.1 Z-matrix input

The general form of an atom specification line is

[*group*[,]]*atom*, p_1, *r*, p_2, α, p_3, β, *J*

or, alternatively,

[*group*[,]]*atom*, p_1, *x*, *y*, *z*

where

group	atomic group number (optional). Can be used if different basis sets are used for different atoms of the same kind. The basis set is then referred to by this group number and not by the atomic symbol.
atom	chemical symbol of the new atom placed at position p_0. This may optionally be appended (without blank) by an integer, which can act as sequence number, e.g., C1, H2, etc. Dummy centres with no charge and basis functions are denoted either Q or X, optionally appended by a number, e.g, Q1; note that the first atom in the z-matrix must not be called X, since this may be confused with a symmetry specification (use Q instead).
p_1	atom to which the present atom is connected. This may be either a number *n*, where *n* refers to the *n*'th line of the Z-matrix, or an alphanumeric string as specified in the *atom* field of a previous card, e.g., C1, H2 etc. The latter form works only if the atoms are numbered in a unique way.
r	Distance of new atom from p_1. This value is given in bohr, unless ANG has been specified directly before or after the symmetry specification.

p_2	A second atom needed to define the angle $\alpha(p_0,p_1,p_2)$. The same rules hold for the specification as for p_1.
α	Internuclear angle $\alpha(p_0,p_1,p_2)$. This angle is given in degrees and must be in the range $0 < \alpha < 180^0$.
p_3	A third atom needed to define the dihedral angle $\beta(p_0,p_1,p_2,p_3)$. Only applies if $J = 0$, see below.
β	Dihedral angle $\beta(p_0,p_1,p_2,p_3)$ in degree. This angle is defined as the angle between the planes defined by (p_0,p_1,p_2) and (p_1,p_2,p_3) $(-180^0 \leq \beta \leq 180^o)$. Only applies if $J = 0$, see below.
J	If this is specified and nonzero, the new position is specified by two bond angles rather than a bond angle and a dihedral angle. If $J = \pm 1$, β is the angle $\beta(p_0,p_1,p_3)$. If $J = 1$, the triple vector product $(\mathbf{p}_1 - \mathbf{p}_0) \cdot [(\mathbf{p}_1 - \mathbf{p}_2) \times (\mathbf{p}_1 - \mathbf{p}_3)]$ is positive, while this quantity is negative if $J = -1$.
x,y,z	Cartesian coordinates of the new atom. This form is assumed if $p_1 \leq 0$; if $p_1 < 0$, the coordinates are frozen in geometry optimizations.

All atoms, including those related by symmetry transformations, should be specified in the Z-matrix. Note that for the first atom, no coordinates need be given, for the second atom only p_1, r are needed, whilst for the third atom p_3, β, J may be omitted. The 6 missing coordinates are obtained automatically by the program, which translates and re-orients the molecule such that the origin is at the centre of mass, and the axes correspond to the eigenvectors of the inertia tensor (see also `CHARGE` option above).

Once the reorientation has been done, the program then looks for symmetry (D_{2h} and subgroups), unless the `NOSYM` option has been given. It is possible to request that reduced symmetry be used by using appropriate combinations of the options `X,Y,Z,XY,XZ,YZ,XYZ`. These specify symmetry operations, the symbol defining which coordinate axes change sign under the operation. The point group is constructed by taking all combinations of specified elements. If symmetry is explicitly specified in this way, the program checks to see that the group requested can be used, swapping the coordinate axes if necessary. This provides a mechanism for ensuring that the same point group is used, for example, at all points in the complete generation of a potential energy surface, allowing the safe re-utilization of neighbouring geometry molecular orbitals as starting guesses, etc..

12.3.2 *XYZ* input

Simple cartesian coordinates in Ångstrom units can be read as an alternative to a Z matrix. This facility is triggered by setting the MOLPRO variable `GEOMTYP` to the value `XYZ` before the geometry specification is given. The geometry block should then contain the cartesian coordinates in Minnesota Computer Centre, Inc. XYZ format. Variable names may be used as well as fixed numerical values.

The XYZ file format consists of two header lines, the first of which contains the number of atoms, and the second of which is a title. The remaining lines each specify the coordinates of one atom, with the chemical symbol in the first field, and the x, y, z coordinates following. A sequence number may be appended to the chemical symbol; it is then interpreted as the atomic group number, which can be used when different basis sets are wanted for different atoms of the same kind. The basis set is then specified for this group number rather than the atomic symbol.

```
geomtyp=xyz
geometry={
3           ! number of atoms
This is an example of geometry input for water with an XYZ file
O ,0.0000000000,0.0000000000,-0.1302052882
H ,1.4891244004,0.0000000000, 1.0332262019
H,-1.4891244004,0.0000000000, 1.0332262019
}
hf
```

examples/
h2o˙xyzinput.com

The XYZ format is specified within the documentation distributed with MSCI's XMol package. Note that MOLPRO has the facility to write XYZ files with the PUT command (see section 12.4).

12.3.3 MOLPRO92 input

A subset of the MOLPRO92 atom specification commands are retained for compatibility. These may be interspersed with Z-matrix lines, and are of the form

A[*group*],*atom*,x,y,z

A[*group*],*atom*,POL,r,θ,ϕ

giving, respectively, cartesian or polar coordinates of the atom to be added. Note that the internal coordinate specifications NPCC, CCPA, TCT, LC, RCP, RCF are no longer available, and Z-matrix input should be used instead.

If any MOLPRO92-style atom specifications appear in the input, the NOORIENT option is enforced, and the handling of symmetry is slightly different. No automatic search for symmetry takes place, and all symmetry required should be specified. Furthermore, only symmetry-unique atoms need be given, the others being generated automatically.

12.4 Writing Gaussian, XMol or MOLDEN input (PUT)

The PUT command may be used at any point in the input to print, or write to a file, the current geometry. The syntax is

PUT,*style,file,status,info*

If *style* is GAUSSIAN, a complete Gaussian input file will be written; in that case, info will be used for the first (route) data line, and defaults to '# SP'.

If *style* is XYZ, an XYZ file will be written (see also section 12.3.2). If *style* is CRD, the coordinates will be written in CHARMm CRD format.

If *style* is MOLDEN, an interface file for the MOLDEN visualization program is created; further details and examples are given below.

If *style* is omitted, the Z-matrix, current geometry, and, where applicable, gradient are written.

file specifies a file name to which the data is written; if blank, the the data is written to the output stream. If *status* is omitted or set to NEW, any old contents of the file are destroyed; otherwise the file is appended.

12.4.1 Visualization of results using Molden

Geometry, molecular orbital, and normal mode information, when available, is dumped by PUT,MOLDEN in the format that is usable by MOLDEN .

The interface to the gOpenMol program offers an alternative visualization possibility, and is described in section 32.7.

The example below generates all the information required to plot the molecular orbitals of water, and to visualize the normal modes of vibration:

examples/
h2o˙put˙molden.com

```
! $Revision: 2006.0 $
***,H2O
geometry={angstrom;o;h,o,roh;h,o,roh,h,theta};
roh=1.0
theta=104.0
rhf;
optg;
{frequencies;
print,low,img;}
put,molden,h2o.molden;
```

The example below does a difference density by presenting its natural orbitals to MOLDEN. Note that it although MOLDEN has internal features for difference density plots, the approach show here is more general in that it bypasses the restriction to STO-3G, 3-21G, 4-31G and 6-31G basis sets.

examples/
h2o˙diffden˙molden.c

```
! $Revision: 2006.0 $
gprint,orbitals
geometry={y;planexz;O;H1,O,r;h2,O,r,h1,alpha}
r=1.8
alpha=104
int;
{hf;wf,10,1;orbital,2100.2}
{multi;wf,10,1;orbital,2140.2}

{matrop
load,dscf,density,2100.2       !load scf density
load,dmcscf,density,2140.2     !load mcscf density
add,ddiff,dmcscf,-1,dscf       !compute dmcscf-dscf
natorb,neworb1,dscf
natorb,neworb2,dmcscf
natorb,neworbs,ddiff
save,neworbs,2110.2
save,ddiff,2110.2}

put,molden,h2o_ddens.molden;orb,2110.2
```

12.5 Geometry Files

Using the format

GEOMETRY=*file*

the geometry definitions are read from *file*, instead of inline. This file must contain all information of the symmetry block, i.e. symmetry specifications (optional), z-matrix, or xyz-input.

12.6 Lattice of point charges

LATTICE,[INFILE=*input_file*,][OUTFILE=*output_file*,] [VARGRAD,][NUCONLY,][REMOVE]

A lattice of point charges is included in the calculation through the use of this card. An external file (*input_file*) should be given as input, with the following format:

Comment line
number of point charges N
$x1, y1, z1, q1$,*flag*1
⋮
xN, yN, zN, qN,*flagN*

The x, y and z fields stand for the point charge coordinates (in Å), q for its charge and *flag=1* indicates that gradients should be computed for this lattice point (0 means no gradient).

outfile specifies a file name to which the lattice gradient is written; if blank, it will be written to the output stream.

VARGRAD	(logical) Stores the lattice gradient in variable VARGRAD.
NUCONLY	(logical) Disables gradient evaluation with respect to the lattice, independent of *flag* in the lattice file.
REMOVE	(logical) Removes the lattice.

Symmetry is not supported for lattice gradients.

12.7 Redefining and printing atomic masses

The current masses of all atoms can be printed using

MASS, PRINT

The atomic masses can be redefined using

MASS, [*type*,] [*symbol=mass*, ...]

The optional keyword *type* can take either the value AVER[AGE] for using average isotope masses, or ISO[TOPE] for using the masses of the most abundant isotopes. This affects only the rotational constants and vibrational frequencies. As in most quantum chemistry packages, the default for *type* is AVERAGE. If INIT is given, all previous mass definitions are deleted and the defaults are reset.

Individual masses can be changed by the following entries, where *symbol* is the chemical symbol of the atom and *mass* is the associated mass. Several entries can be given on one MASS card, and/or several MASS cards can follow each other. The last given mass is used.

Note that specifying different isotope masses for symmetry related atoms lowers the symmetry of the system if the molecular centre of mass is taken as the origin. This effect can be avoided by using the charge centre as origin, i.e., specifying CHARGE as first entry in the GEOMETRY input:

```
GEOMETRY={CHARGE; ...}
```

12.8 Dummy centres

DUMMY,*atom1,atom2,...*

Sets nuclear charges on atoms 1,2 etc. to zero, for doing counterpoise calculations, for example. *atom1, atom2,...* can be Z-matrix row numbers or tag names. Note that the current setting of dummies is remembered by the program across restarts via the MOLPRO variable

DUMMYATOMS. Dummies can be reset to their original charges using a DUMMY card with no entries. Dummy centres are also reset to their original charges if (i) and INT command is encountered, or (ii) a new geometry input is encountered.

The program does not recognize automatically if the symmetry is reduced by defining dummy atoms. Therefore, for a given dummy atom, either all symmetry equivalent atoms must also be dummies, or the symmetry must be reduced manually as required. An error will result if the symmetry is not consistent with the dummy centre definitions.

12.8.1 Counterpoise calculations

Counterpoise corrections are easily performed using dummy cards. One first computes the energy of the total system, and then for the subsystems using dummy cards.

12.8.2 Example: interaction energy of OH-Ar

examples/ohar˙bsse.com

```
! $Revision: 2006.0 $
***,OH(2Sig+)-Ar linear
memory,2,m
geometry={q1;                  !dummy center in center of mass
o,q1,ro;h,q1,rh,o,180;         !geometry of OH
ar,q1,rar,o,theta,h,0}         !geometry of Ar
roh=1.8                        !OH bond-length
rar=7.5                        !distance of Ar from center of mass
theta=0                        !angle OH-Ar
ro=roh*16/17                   !distance of O from center of mass
rh=roh*1/17                    !distance of H from center of mass
basis=avdz                     !basis set

text,calculation for complex
{rhf;occ,8,3,3;wf,27,1,1}      !RHF for total system
rccsd(t)                       !CCSD(T) for total system
e_ohar=energy                  !save energy in variable e_ohar

text,cp calculation for OH
dummy,ar                       !make Ar a dummy center
{rhf;occ,3,1,1;wf,9,1,1}       !RHF for OH
rccsd(t)                       !CCSD(T) for OH
e_oh=energy                    !save energy in variable e_oh

text,cp calculation for Ar
dummy,o,h                      !make OH dummy
hf                             !scf for Ar
ccsd(t)                        !CCSD(T) for Ar
e_ar=energy                    !save energy in variable e_ar

text,separate calculation for OH
geometry={O;H,O,roh}           !geometry for OH alone
{rhf;occ,3,1,1;wf,9,1,1}       !RHF for OH
rccsd(t)                       !CCSD(T) for OH
e_oh_inf=energy                !save energy in variable e_oh_inf

text,separate calculation for Ar
geometry={AR}                  !geometry for OH alone
hf                             !scf for Ar
ccsd(t)                        !CCSD(T) for Ar
e_ar_inf=energy                !save energy in variable e_ar_inf

de=(e_ohar-e_oh_inf-e_ar_inf)*tocm    !compute uncorrected interaction energy
de_cp=(e_ohar-e_oh-e_ar)*tocm         !compute counter-poise corrected interaction energy
bsse_oh=(e_oh-e_oh_inf)*tocm          !BSSE for OH
bsse_ar=(e_ar-e_ar_inf)*tocm          !BSSE for Ar
bsse_tot=bsse_oh+bsse_ar              !total BSSE
```

For performing counterpoise corrected geometry optimizations see section 39.4.7.

13 BASIS INPUT

13.1 Overview: sets and the basis library

Basis functions are used in Molpro not just for representing orbitals, but also for providing auxiliary sets for density fitting (see 11) and for simplifying integrals through approximate identity resolution in explicitly-correlated methods (see 29). In order to accommodate this, the program maintains internally a number of different *sets*. The first of these always has the name ORBITAL and is the primary basis set for representing orbitals, and others can be defined as necessary as described below, or else are constructed automatically by the program when required. In the

latter case, the density-fitting and other modules attempt to guess a reasonable libary fitting basis that should be appropriate for the orbital basis set; it is advisable to check the choice when using anything other than a standard orbital basis set.

The basis sets may either be taken from the program library, or may be specified explicitly, or any combination. Optionally, the basis function type can be chosen using the CARTESIAN or SPHERICAL commands.

13.2 Cartesian and spherical harmonic basis functions

MOLPRO uses spherical harmonics ($5d$, $7f$, etc) by default, even for Pople basis sets like 6-31G**. This behaviour may be different to that of other programs; However, cartesian functions can be requested using the CARTESIAN command.

CARTESIAN

If this command is encountered, the logical MOLPRO variable CARTESIAN is set to true (1.0), and all subsequent calculations use cartesian basis functions. This is remembered across restarts. One can switch back to spherical harmonics using the command

SPHERICAL

13.3 The basis set library

The basis set library consists of a set of plain text files, together with an associated index, that constitute a database of commonly-used basis sets (primitive gaussians and associated contractions) and effective core potentials. These files can be found in the source tree as lib/*.libmol and lib/libmol.index, but it is usually more convenient to query the database using one of the provided tools.

Many of the basis sets are taken directly from the Pacific Northwest National Laboratory basis set database , but there are others, notably the Stuttgart effective core potentials and bases .

A simple command-line interface to the database is provided through the libmol program. It requires the environment variable LIBMOL to point to the lib/ directory, but this will default to the location of the source tree at compile time, so it is often not necessary to specify it. The command-line syntax is

libmol [-p *print*] [-e *element*] [-k *key*] [-t *type*] [-f *format*]

where the parameters are

print:	Output level; 0 means list matching keys, 1 means print also the entry.
element:	Specify chemical element. If omitted, all elements are searched.
key:	Specify record key. If omitted, all keys are searched.
type:	Specify entry type, i.e. $s, p, \ldots$. If omitted, all types are searched.
format:	One of text (default), molpro (MOLPRO input format), table (tabular) or html (html table) to govern the output format.

A more convenient way of browsing the basis library is through a web-based interface. The CGI script molpro_basis presents a graphical and forms based interface for performing searches. It may be installed locally, but is also normally available at

http://www.molpro.net/current/molpro_basis .

13.4 Default basis sets

If a basis is not specified at all for any unique atom group, then the program assumes a global default. Presently, this default is VDZ, but may be overridden using

BASIS,*basis*

or

BASIS=*basis*

basis is looked up in the file lib/defbas, which generates an appropriate request for a complete contracted set, together in some cases with an ECP, from the library . This mapping includes the following commonly-used basis sets.

- All of the Dunning correlation-consistent sets, through the use of either the standard name of the basis set (e.g., aug-cc-pVDZ) or an abbreviation (e.g., AVDZ).
- The older segmented Dunning/Hay double-zeta sets for the first row (DZ and DZP).
- The Roos ANO basis sets (ROOS).
- The Stuttgart ECPs and associated basis sets (e.g., ECP10MWB).
- The Hay ECPs and corresponding basis sets (ECP1 and ECP2).
- Some of the Karslruhe basis sets (SV, TZV, and, for some elements, SVP, TZVP, TZVPP, TZVPPP).
- The Binning/Curtiss sets for Ga–Kr (BINNING-SV, BINNING-SVP, BINNING-VTZ and BINNING-VTZP)
- Most of the Pople basis sets, using their standard names (e.g., 6-31G*, 6-311++G(D,P), etc.). Note that specially in this case, the mechanism described below using parenthesized modifiers to restrict the basis set is disabled to allow the full range of standard basis sets to be specified.

Example:

BASIS=VTZ

generates valence triple zeta basis set for all atoms. Thus, the input

```
***,h2o cc-pVTZ basis     !A title
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;                                                    examples/
          H2,O,r,H1,theta}                                          h2o˙scf˙vtz.com
basis=VTZ                 !use VTZ basis
hf                        !closed-shell scf
```

is entirely equivalent to

```
***,h2o cc-pVTZ basis     !A title
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}                                           examples/
basis={                                                             h2o˙scf˙vtz˙explicit.c
spdf,o,vtz;c;
spd,h,vtz;c}
hf;
```

Default basis sets can be defined anywhere in the input before the energy calculation to which it should apply using a single BASIS cards. The default basis set applies to all types of atoms but can be superceded by different basis sets for specific atoms as explained later. Some restrictions concerning the maximum angular momentum functions to be used, or the number of contracted functions are possible as follows:

The maximum angular momentum in the basis set can be reduced using syntax such as

```
BASIS,VQZ(D)
```

which would omit the *f* and *g* functions that would normally be present in the VQZ basis set.

```
BASIS,VQZ(D/P)
```

would specify additionally a maximum angular momentum of 1 on hydrogen, i.e. would omit *d* orbitals on hydrogen.

For generally contracted basis sets, an extended syntax can be used to explicitly give the number of contracted functions of each angular momentum. For example,

```
BASIS,ROOS(3s2p1d/2s)
```

generates a 6-31G*-sized basis set from the Roos ANO compilation.

13.5 Default basis sets for individual atoms

More specific basis set definitions for individual atoms can be given BASIS input blocks, which have the following general form:

```
BASIS
SET=type                ! type can be ORBITAL, DENSITY or any other name,
                        ! as used in basis specifications for density
                        ! fitting; optional; default=ORBITAL
DEFAULT=name            ! sets the default basis to name ;
atom1=name1             ! Use basis name1 for atom1
atom2=name2             ! Use basis name1 for atom2
primitive basis set specifications   !additional basis functions
SET=type                ! specify basis of another type in following lines
...
END
```

Any number of basis sets can be be given in a basis block.

The default and atom specifications can also be merged to one line, separated by commas:

DEFAULT=*name*,*atom1*=*name1*,*atom2*=*name2*

Here the basis sets *name1*, *name2* overwrite the default basis set *name* for specific atoms *atom1*, *atom2*, respectively. For instance,

```
DEFAULT=VTZ,O=AVTZ,H=VDZ
```

uses VTZ as the default basis sets, but sets the basis for oxygen to AVTZ and for hydrogen to VDZ

This name conventions for the atom specific basis sets work exactly as described above for default basis sets. The keyword DEFAULT can be abbreviated by DEF. Any DEFAULT basis set defined in a basis set block supercedes a previous one given outside the basis block.

The specifications SET, DEFAULT, atom=name are all optional. If DEFAULT is not given, the previous default, as specified on the last previous BASIS card, is used.

If no further primitive basis set specifications follow, one can also use the one-line form

```
BASIS,DEFAULT=VTZ,O=AVTZ,H=VDZ
```

or

```
BASIS=VTZ,O=AVTZ,H=VDZ
```

Both of these are equivalent to

```
BASIS
DEFAULT=VTZ
O=AVTZ
H=VDZ
END
```

Note that any new BASIS card supercedes all previous basis input, except for the default basis (unless this is given).

The optional additional primitive basis set specifications (see next section) are appended to the given atom-specific basis sets, i.e., the union of atom-specific and primitive basis set definitions is used for the atom.

Examples:

```
BASIS
DEFAULT=VTZ             ! use cc-pVTZ basis as default
H=VDZ                   ! use cc-pVDZ for H-atoms
END
```

This could also be written as

```
BASIS={DEF=VTZ,H=VDZ}
```

```
BASIS
DEFAULT=VTZ             ! use cc-pVTZ basis as default
H=VDZ                   ! use cc-pVDZ for H-atoms
D,H,VTZ                 ! add the VTZ d-function to the VDZ basis for H
END

BASIS
SPD,O,VTZ               !use uncontracted s,p,d functions of basis VTZ for oxygen
S,H,H07                 !use Huzinaga 7s for Hydrogen
C,1.4                   !contract first four s-functions
P,H,1.0,0.3             !add two p-functions for hydrogen
END
```

Several BASIS cards and/or blocks can immediately follow each other. Always the last specification for a given atom and type is used. Defaults given using BASIS commands can be overwritten by specifications in the integral input. If an individual basis function type is specified for an atom, it is required that all other types are also defined. For example, in the above example, no f-functions are included for O, even if the global default would include f-functions. Also, defining the s functions for hydrogen switches off the default basis set for hydrogen, and so the p functions must be defined. Instead of the atomic symbol, the atom group number can also be used.

The same input forms are also possible as direct input to the integral program. In contrast to MOLPRO92, now the atomic symbol can be used in field 2 of a basis specification instead of the atom group number:

```
SPD,O,VTZ          !use VTZ basis for all oxygen atoms
SPD,1,VTZ          !use VTZ basis for atom group 1
```

Instead of the BASIS...END block one can also use the structure BASIS[=]{...}

If a basis is not specified at all for any unique atom group, then the program assumes a default. For further details, including respecifying the default to be used, see the specification of the BASIS subcommand below.

13.6 Primitive set definition

A group of basis functions is defined by a data card specifying a set of primitive gaussians, optionally followed by one or more cards specifying particular contractions of primitives to be included in the final basis (see section 13.7 for specification of contractions). When all contraction definitions have been read (delimited by the next data card other than a contraction definition), the remaining primitives in the set which have not been included in any contraction set are added uncontracted to the basis set.

There are four different input forms, as explained below under a) to d). In case that options (e.g. SCALE, NPRIM) are specified, they can be given in any order, but no value without option key must be given after an option.

In all cases *type* defines the angular symmetry (S, P, D, F, G, H, or I). *type* can include several types, e.g., SPD or DF. This usually makes sense only with or default library contractions or no contractions.

The basis is loaded for all atoms with tag name *atom* in the geometry input. If *atom* is an integer, it refers to a z-matrix row.

a) Library basis sets:

type,atom,key,scale2,nprim;

or

type,atom,key,[SCALE=*scale*|SCALE2=*scale2*],[NPRIM=*nprim*|DELETE=*ndel*];

Load basis named *key* from the library

If *scale* or *scale2* is present, all exponents are scaled by *scale* or *scale**2*, respectively. If *nprim* is specified, the first *nprim* exponents only are taken from the library . If *nprim* is negative or *ndel* is given, the last |*nprim*| (*ndel*) basis functions from the library set are deleted. Associated with the library basis may be a set of default contraction coefficients which may be accessed in subsequent contraction cards. *type* can include several types, e.g., SPD or DF. This usually makes sense only with default contractions, i.e., such cards should be followed only by "C" without any other specifications for contractions.

b) Explicit basis input:

type,atom,exp1,exp2,...expn;expn+1,...;

General specification of exponents; continuation onto subsequent cards (separated by semicolon) is permitted as shown (the first card can hold up to 19 exponents, each following card 20 exponents.

The exponents (and other numerical parameters described below such as numbers of functions, and contraction coefficients) can be given as general input expressions, possibly involving variables. It is important to note, however, that these expressions are evaluated typically just once,

at the same time as the complete basis set is parsed. This generally happens the first time that the basis set is required, perhaps before the first SCF calculation can be done. If the variables on which the basis depends are altered, this will not be noticed by the program, and the new basis set will not be used for subsequent stages of the computation. If, however, a new basis block is presented in the input, then the program marks as outdated any quantities such as integrals that have been calculated with the old basis set; subsequent job steps will then use the new basis.

c) Even tempered basis sets:

type,atom,EVEN,*nprim,ratio,centre,dratio*

or

type,atom,EVEN,NPRIM=*nprim*,[RATIO=*ratio*],[CENTRE=*centre*],[DRATIO=*dratio*]

Generates a generalized even tempered set of functions. The number of functions n is specified by *nprim*, their geometric mean c by *centre*, the mean ratio of successive exponents r by *ratio*, and the variation of this ratio, d, by *dratio*. If *centre* is not given, the previous basis of the same type is extended by diffuse functions. If in this case *ratio* is not given, r is determined from the exponents of the last two function of the previous basis. If this is not possible, the default $r = 2.5$ is adopted. $d = 1$ (the default) specifies a true even-tempered set, but otherwise the ratio between successive exponents changes linearly; the exponents are given explicitly by

$$\log e_i = \log c + ((n+1)/2 - i)\log r + \frac{1}{2}((n+1)/2 - i)^2 \log d \quad i = 1,2,\ldots,n$$

Example 1

```
SP,1,VTZ;C;SP,1,EVEN,1;
```

generates the generally contracted s and p triple-zeta basis sets for atom 1 and extends these by one diffuse function.

Example 2

```
SPD,1,VTZ,DELETE=1;C;
SP,1,EVEN,NPRIM=2,RATIO=2.5;
```

generates the generally contracted s, p triple-zeta basis sets for atom 1. Two energy optimized d-functions of Dunning are included. The last s and p functions are deleted and replaced by two even tempered functions with ratio 2.5.

d) 3-term tempered basis sets:

type,atom,EVEN3,*nprim*,α, β, γ

Generates a 3-parameter set of *nprim* functions with exponents given by

$$e_i = \alpha; \qquad e_i = e_{i-1}\beta\left(1 + \frac{\gamma i^2}{(nprim+1)^2}\right)$$

e) Regular even tempered basis sets:

type,atom,EVENR,*nprim,aa,ap,bb,bp*

Generates an even tempered set of *nprim* functions according to the "regular" prescription described in M W Schmidt and K Ruedenberg, J. Chem. Phys. 71 (1970) 3951. If any of the parameters *aa, ap, bb, bp* is zero or omitted, the values are taken from table III of the above.

13.7 Contracted set definitions

a) C,*first.last,c1,c2,...cn;cn+1,...*;

General specification of a contracted function. *first.last* defines the range of primitives to be contracted. The order corresponds to the primitives as specified on the previous input card. *c1, c2...* are the $last - first + 1$ contraction coefficients. Continuation onto a subsequent card is permitted as shown.

b) C;

Use default contractions from the library . This applies to both the number of contracted primitives and also to the number of different contraction sets.

c) *n*C,*first.last*;

n contracted functions taken from library . *first.last* defines the range of primitives to be contracted. If *n* is omitted and *first.last* is specified, $n = 1$. If *first.last* is omitted, the library default values are used. If both *n* and *first.last* are omitted, default values for both are used.

d) *n*C,*first.last,record.file,orb.sym*;

n contracted functions taken from orbitals *orb*, $orb+1$,..,$orb+n-1$ of symmetry *sym* on molpro file *record.file*. The first nonzero coefficient in the specified orbital corresponds to the first associated basis function. *first.last* specifies the range of primitives to be contracted. If *first.last* is omitted, all coefficients from the specified orbitals are used.

Example `2C,1.12,2100.2,1.1`
generates two contractions, using the first 12 coefficients from orbitals 1.1 and 2.1. The orbitals are read from record 2100.2.

13.8 Examples

This shows the use of default basis sets for H_2O:

```
***,H2O
basis=VQZ(f/p)
R=0.95 ANG,THETA=104 DEGREE                                    examples/
geometry={O;H1,O,R;H2,O,R,H1,THETA}                          h2o˙vqz˙fp.com
hf              !do closed-shell SCF
```

This is equivalent to the explicit input form

```
***,H2O
R=0.95 ANG,THETA=104 DEGREE
geometry={O;H1,O,R;H2,O,R,H1,THETA}                            examples/
basis={spdf,o,vqz;c;sp,h,vqz,c;}                             h2o˙vqz˙fp˙explicit.co
hf              !do closed-shell SCF
```

14 EFFECTIVE CORE POTENTIALS

Pseudopotentials (effective core potentials, ECPs) may be defined at the beginning of BASIS blocks.

The general form of the input cards is

ECP,*atom*,[*ECP specification*]

which defines a pseudopotential for an atom specified either by a chemical symbol or a group number. The *ECP specification* may consist either of a single keyword, which references a pseudopotential stored in the library , or else of an explicit definition (extending over several input cards), cf. below.

14.1 Input from ECP library

The basis set library presently contains the pseudopotentials and associated valence basis sets by a) the Los Alamos group (P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985) and following two papers), and b) the Stuttgart/Köln group (e.g., A. Nicklass, M. Dolg, H. Stoll and H. Preuß, J. Chem. Phys. **102**, 8942 (1995); for more details and proper references, see the web page `http://www.theochem.uni-stuttgart.de/pseudopotentials/`). Pseudopotentials a) are adjusted to orbital energies and densities of a suitable atomic reference state, while pseudopotentials b) are generated using total valence energies of a multitude of atomic states.

Library keywords in case a) are `ECP1` and `ECP2`; `ECP2` is used when more than one pseudopotential is available for a given atom and then denotes the ECP with the smaller core definition. (For Cu, e.g., `ECP1` refers to an Ar-like $18e^-$-core, while `ECP2` simulates a Ne-like $10e^-$ one with the $3s$ and $3p$ electrons promoted to the valence shell). For accurate calculations including electron correlation, promotion of all core orbitals with main quantum number equal to any of the valence orbitals is recommended.

Library keywords in case b) are of the form `ECP`nXY; n is the number of core electrons which are replaced by the pseudopotential, X denotes the reference system used for generating the pseudopotential ($X = S$: single-valence-electron ion; $X = M$: neutral atom), and Y stands for the theoretical level of the reference data ($Y = HF$: Hartree-Fock, $Y = WB$: quasi-relativistic; $Y = DF$: relativistic). For one- or two-valence electron atoms $X = S$, $Y = DF$ is a good choice, while otherwise $X = M$, $Y = WB$ (or $Y = DF$) is recommended. (For light atoms, or for the discussion of relativistic effects, the corresponding $Y = HF$ pseudopotentials may be useful.) Additionally, spin-orbit (SO) potentials and core-polarization potentials (CPP) are available, to be used in connection with case b) ECPs, but these are not currently contained in the library, so explicit input is necessary here (cf. below).

In both cases, a) and b), the same keywords refer to the pseudopotential and the corresponding basis set, with a prefix `MBS-`... in case a).

14.2 Explicit input for ECPs

For each of the pseudopotentials the following information has to be provided:

- a card of the form
  `ECP`,*atom*,$n_{core}, l_{max}, l'_{max}$;
  where n_{core} is the number of core electrons replaced by the pseudopotential V_{ps}, l_{max} is the number of semi-local terms in the scalar-relativistic part of V_{ps}, while l'_{max} is the corresponding number of terms in the SO part:

$$V_{ps} = -\frac{Z - n_{core}}{r} + V_{l_{max}} + \sum_{l=0}^{l_{max}-1} (V_l - V_{l_{max}})\mathcal{P}_l + \sum_{l=1}^{l'max} \Delta V_l \mathcal{P}_l \vec{l} \cdot \vec{s} \mathcal{P}_l;$$

  the semi-local terms (with angular-momentum projectors $\mathcal{P}_l$) are supplemented by a local term for $l = l_{max}$.

- a number of cards specifying $V_{l_{max}}$, the first giving the expansion length $n_{l_{max}}$ in

$$V_{l_{max}} = \sum_{j=1}^{n_{l_{max}}} c_j r^{m_j-2} e^{-\gamma_j r^2}$$

and the following $n_{l_{max}}$ ones giving the parameters in the form

$$m_1, \gamma_1, c_1; m_2, \gamma_2, c_2; \ldots$$

- a number of cards specifying the scalar-relativistic semi-local terms in the order $l = 0, 1, \ldots, l_{max} - 1$. For each of these terms a card with the expansion length n_l in

$$V_l - V_{l_{max}} = \sum_{j=1}^{n_l} c_j^l r^{m_j^l-2} e^{-\gamma_j^l r^2}$$

has to be given, and immediately following n_l cards with the corresponding parameters in the form $m_1^l, \gamma_1^l, c_1^l; m_2^l, \gamma_2^l, c_2^l; \ldots$

- analogously, a number of cards specifying the coefficients of the radial potentials ΔV_l of the SO part of V_{ps}.

14.3 Example for explicit ECP input

examples/
cu_ecp_explicit.com

```
***,CU
! SCF d10s1 -> d9s2 excitation energy of the Cu atom
!  using the relativistic Ne-core pseudopotential
! and basis of the Stuttgart/Koeln group.
gprint,basis,orbitals
geometry={cu}
basis
ECP,1,10,3;   ! ECP input
 1; ! NO LOCAL POTENTIAL
 2,1.,0.;
 2; ! S POTENTIAL
 2,30.22,355.770158;2,13.19,70.865357;
 2; ! P POTENTIAL
 2,33.13,233.891976;2,13.22,53.947299;
 2; ! D POTENTIAL
 2,38.42,-31.272165;2,13.26,-2.741104;
! (8s7p6d)/[6s5p3d] BASIS SET
s,1,27.69632,13.50535,8.815355,2.380805,.952616,.112662,.040486,.01;
c,1.3,.231132,-.656811,-.545875;
p,1,93.504327,16.285464,5.994236,2.536875,.897934,.131729,.030878;
c,1.2,.022829,-1.009513;C,3.4,.24645,.792024;
d,1,41.225006,12.34325,4.20192,1.379825,.383453,.1;
c,1.4,.044694,.212106,.453423,.533465;
end
rhf;
e1=energy
{rhf;occ,4,1,1,1,1,1,1;closed,4,1,1,1,1,1;wf,19,7,1;}
e2=energy
de=(e2-e1)*toev  ! Delta E = -0.075 eV
```

14.4 Example for ECP input from library

examples/
auh˙ecp˙lib.com

```
***,AuH
! CCSD(T) binding energy of the AuH molecule at r(exp)
! using the scalar-relativistic 19-valence-electron
! pseudopotential of the Stuttgart/Koeln group
gprint,basis,orbitals;
geometry={au}
basis={
ecp,au,ECP60MWB;              ! ECP input
spd,au,ECP60MWB;c,1.2;        ! basis set
f,au,1.41,0.47,0.15;
g,au,1.2,0.4;
spd,h,avtz;c;
}
rhf;
{rccsd(t);core,1,1,1,,1;}
e1=energy
geometry={h}
rhf
e2=energy;
rAuH=1.524 ang                ! molecular calculation
geometry={au;h,au,rAuH}
hf;
{ccsd(t);core,2,1,1;}
e3=energy
de=(e3-e2-e1)*toev            ! binding energy = 3.11 eV
```

15 CORE POLARIZATION POTENTIALS

15.1 Input options

The calculation of core-polarization matrix elements is invoked by the CPP card, which can be called at an arbitrary position in the MOLPRO input, provided the integrals have been calculated before. The CPP card can have the following three formats:

- CPP,INIT,*ncentres*;
- CPP,ADD[,*factor*];
- CPP,SET[,*fcpp*];

CPP,INIT,$<ncentres>$;

abs($<ncentres>$) further cards will be read in the following format:

$<atomtype>,<ntype>,<\alpha_d>,<\alpha_q>,<\beta_d>,<cutoff>$;

$<atomtype>$ corresponds to the recognition of the atomic centres in the integral part of the program,
$<ntype>$ fixes the form of the cutoff-function (choose 1 for Stoll/Fuentealba and 2 for Mueller/Meyer);
$<\alpha_d>$ is the static dipole polarizability,
$<\alpha_q>$ is the static quadrupole polarizability,
$<\beta_d>$ is the first non-adiabatic correction to the dipole-polarizability and
$<cutoff>$ is the exponential parameter of the cutoff-function.

When $<ncentres>$ is lower than zero, only the integrals are calculated and saved in the record 1490.1. Otherwise, the h_0 matrix (records 1200.1 and 1210.1) and the two-electron-integrals (record 1300.1) will be modified.

CPP,ADD,$< factor >$;

With this variant, previously calculated matrix elements of the polarization matrix can be added with the variable factor $< factor >$ (default: $< factor >$ = 1) to the h_0-matrix as well as to the two-electron-integrals. In particular, CPP,ADD,-1.; can be used to retrieve the integrals without the polarization contribution.

CPP,SET,$< fcpp >$;

normally not necessary but may be used to tell MOLPRO after a restart, with what factor the polarization integrals are effective at the moment.

15.2 Example for ECP/CPP

examples/
na2˙ecp˙cpp.com

```
! $Revision: 2006.0 $
***,Na2
! Potential curve of the Na2 molecule
! using 1-ve ECP + CPP
gprint,basis,orbitals;
rvec=[2.9,3.0,3.1,3.2,3.3] ang
do i=1,#rvec
rNa2=rvec(i)
geometry={na;na,na,rNa2}
basis={
ecp,na,ecp10sdf;         ! ecp input
s,na,even,8,3,.5;        ! basis input
p,na,even,6,3,.2;
d,na,.12,.03;
}
cpp,init,1;              ! CPP input
na,1,.9947,,,.62;
hf;
ehf(i)=energy
{cisd;core;}
eci(i)=energy
enddo
table,rvec,ehf,eci
---
```

16 RELATIVISTIC CORRECTIONS

There are three ways in MOLPROto take into account scalar relativistic effects:

1. Use the Douglas-Kroll relativistic one-electron integrals.
2. Compute a perturbational correction using the Cowan-Griffin operator (see section 6.13).
3. Use relativistic effective core potentials (see section 14).

16.1 Using the Douglas–Kroll–Hess Hamiltonian

For all-electron calculations, the prefered way is to use the Douglas–Kroll–Hess (DKH) Hamiltonian, which is available up to arbitrary order in MOLPRO. It is activated by setting

```
DKROLL=1
```

somewhere in the input before the first energy calculation. If no further input is specified, the standard second-order Douglas–Kroll–Hess Hamiltonian (DKH2) is used.

Starting with this release (2006.1), MOLPRO does, however, also provide the DKH Hamiltonian up to any arbitrary order of decoupling (DKHn). The desired DKH order (DKHO) and the chosen parametrization for the unitary transformations have to be specified by

DKHO=n, $(n = 2,\ldots,14)$,
DKHP=m, $(m = 1,\ldots,5)$

below the DKROLL=1 statement in the input file. The possible parametrizations supported by MOLPRO are:

DKHP=1:	Optimum parametrization (OPT)
DKHP=2:	Exponential parametrization (EXP)
DKHP=3:	Square-root parametrization (SQR)
DKHP=4:	McWeeny parametrization (MCW)
DKHP=5:	Cayley parametrization (CAY)

Example:

```
DKROLL=1   !  activate Douglas–Kroll–Hess one-electron integrals
DKHO=8     !  DKH order = 8
DKHP=4     !  choose McWeeny parametrization for unitary transformations
```

(Note: For DKHO $\geq$ 11 the values of some parameters in the file src/common/parameters.h have to be suitably increased. Only recommended for experts who do exactly know what they are doing!! For most cases DKHO=10 is sufficient.)

Up to fourth order (DKHO=4) the DKH Hamiltonian is independent of the chosen paramterization. Higher-order DKH Hamiltonians depend slightly on the chosen paramterization of the unitary transformations applied in order to decouple the Dirac Hamiltonian.

For details on the infinite-order DKH Hamiltonians see

M. Reiher, A. Wolf, JCP **121**, 2037–2047 (2004),
M. Reiher, A. Wolf, JCP **121**, 10945–10956 (2004).

For details on the different parametrizations of the unitary transformations see
A. Wolf, M. Reiher, B. A. Hess, JCP **117**, 9215–9226 (2002).

16.2 Example for computing relativistic corrections

examples/ar2_rel.com

```
***,ar2
geometry={ar1;ar2,ar1,r}   !geometry definition
r=2.5 ang                  !bond distance
{hf;                       !non-relativisitic scf calculation
expec,rel,darwin,massv}    !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy              !save non-relativistic energy in variable enrel
show,massv,darwin,erel     !show individual contribution and their sum

dkroll=1                   !use douglas-kroll one-electron integrals
hf;                        !relativistic scf calculation
e_dk=energy                !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel     !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel           !show relativistic correction using Douglas-Kroll
```

17 THE SCF PROGRAM

The Hartree-Fock self-consistent field program is invoked by one of the following commands:

HF or RHF	calls the spin-restricted Hartree-Fock program
UHF or UHF-SCF,*options*	calls the spin-unrestricted Hartree-Fock program

In contrast to older versions of MOLPRO, the HF and RHF directives have identical functionality and can both be used for closed-shell or open-shell calculations. Other aliases are HF-SCF or RHF-SCF.

Often, no further input is necessary. By default, the number of electrons is equal to the nuclear charge, the wavefunction is assumed to be totally symmetric (symmetry 1), and the spin multiplicity is 1 (singlet) for an even number of electrons and 2 (doublet) otherwise. The Aufbau principle is used to determine the occupation numbers in each symmetry. Normally, this works well in closed-shell cases, but sometimes wrong occupations are obtained or the wavefunction alternates between different orbital spaces. In such cases, the OCC directive must be used to force convergence to the desired state. The default behaviour can be modified either by options on the command line, or by directives.

In open-shell cases, we recommend to use the WF, OCC, CLOSED, or OPEN cards to define the wavefunction uniquely. Other commands frequently used are START and ORBITAL (or SAVE) to modify the default records for starting and optimized orbitals, respectively. The SHIFT option or directive allows to modify the level shift in the RHF program, and EXPEC to calculate expectation values of one-electron operators (see section 6.13).

17.1 Options

In this section the options for HF|RHF|UHF are described. For further options affecting Kohn-Sham caluculations see section 18. For compatibility with previous *MOLPRO* versions, options can also be given on subsequent directives, as described in later sections.

17.1.1 Options to control HF convergence

ACCU[RACY]=*accu*	Convergence threshold for the density matrix (square sum of the density matrix element changes). Tf *accu*>1, a threshold of 10^{-}*accu*) is used. The default depends on the global ENERGY threshold.
ENERGY=*thrden*	The convergence threshold for the energy. The default depends on the global ENERGY threshold.
START=*record*	Record holding start orbitals.
SAVE|ORBITAL=*record*	Dump record for orbitals.
MAXIT=*maxit*	Maximum number of iterations (default 60)
SHIFTA|SHIFTC=*shifta*	Level shift for closed-shell orbitals in RHF (default -0.3) and α-spin orbitals in UHF (default 0).
SHIFTB|SHIFTO=*shiftb*	Level shift for open-shell orbitals in RHF and β-spin orbitals in UHF (default 0)

NITORD=*nitord*	In open-shell calculations, the orbitals are reordered after each iteration to obtain maximum overlap with the orbitals from the previous iteration. This takes only effect after *nitord* iterations. The default is *nitord*=*maxit*/4 if no start card is present and *nitord*= 1 if a START card is found.
NITOCC=*nitocc*	Starting with iteration *nitocc* the occupation pattern is kept fixed. The default depends on the quality of the starting guess.
NITCL=*nitcl*	If the iteration count is smaller than *nitcl*, only the closed-shell part of the Fock matrix is used (default *nitcl*= 0).
NITORT=*nitort*	The orbitals are reorthonormalized after every *nitort* iterations. The default is *nitort*= 10.
POTFAC=*potfac*	Scale factor for potential energy in first iteration (default 1.0).

17.1.2 Options for the diagonalization method

In calculations with very large basis sets, the diagonalization time becomes a significant fraction of the total CPU time. This can be reduced using the orbital rotation method as described in R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004))

MINROT=*minrot*	If *minrot*$\geq$ 0, the orbital rotation method is employed. Explicit diagonalization of the full Fock matrix is performed in the first *minrot* iterations and in the last iteration. If *minrot*=0, a default is used which depends on the starting guess.
NEXPR=*nexpr*	Number of terms used in the exponential expansion of the unitary orbital transformation matrix (default 4).
DEROT=*nexpr*	Energy gap used in the orbital rotation method. For orbitals within $\pm$*derot* hartree of the HOMO orbital energy the Fock matrix is constructed and diagonalized (default 1.0)
JACOBI=*jacobi*	If nonzero, use Jacobi diagonalization.

17.1.3 Options for convergence acceleration methods (DIIS)

For more details, see IPOL directive.

IPTYP=*iptyp*	Interpolation type (default DIIS, see IPOL directive).
IPNIT|DIIS_START=*ipnit*	First iteration for DIIS interpolation.
IPSTEP|DIIS_STEP=*ipstep*	Iteration increment for DIIS interpolation.
MAXDIS|MAXDIIS=*maxdis*	Max number of Fock matrices used in DIIS interpolation (default 10).

17.1.4 Options for integral direct calculations

DIRECT	(logical). If given, do integral-direct HF.
THRMIN|THRDSCF_MIN=*value*	Final integral screening threshold for DSCF.
THRMAX|THRDSCF_MAX=*value*	Initial integral screening threshold for DSCF.
THRINT|THRDSCF=*value*	Same as THRDSCF_MIN.

PRESCREEN=*value*	If nonzero, use density screening (default).
DISKSIZE]=*value*	Max disk size in Byte for semi-direct calculations (currently disabled).
BUFSIZE=*value*	Max memory buffer size for semi-direct calculations (currently disabled).
THRDISK=*value*	Threshold for writing integrals to disk (currently disabled).
PRINT_DFOCK=*value*	Print option for direct Fock matrix calculation.

17.1.5 Special options for UHF calculations

NATORB=*record*	Save natural charge orbitals in given record.
UNOMIN=*unomin*	Minimum occpation number for UNO-CAS (default 0.02)
UNOMAX=*unomax*	Maximum occupation number for UNO-CAS (default 1.98)

17.1.6 Options for local density-fitting calculations

Please refer section 11 for more options regarding density fitting. The following options affect local density fitting, as described in H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003), and R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004)). Note that local fitting affects the accuracy.

LOCFIT=*locfit*	If nonzero, use local fitting for exchange. If > 1, also use local fitting for Coulomb (not recommended).
RDOM=*locfit*	Radius for fitting domain selection in local fitting (default 5 bohr).
RDOMC=*locfit*	Radius for fitting domain selection for core orbitas in local fitting (default RDOM).
DOMSEL=*domesel*	Criterion for selecting orbital domains in local fitting (default 0.1).

17.1.7 Options for CPP and polarizabilities

CPP=*cpp*	to be described.
MAXCPP=*maxcpp*	to be described.
PRINT_CPP=*maxcpp*	to be described.
PROJECT_CPP=*maxcpp*	to be described.
POLARI=*value*	If nonzero, compute analytical dipole polarizabilities.

17.1.8 Printing options

PRINT|ORBPRINT=*value*	Number of virtual orbitals to be printed. If *value*=0, the occupied orbitals are printed.
DEBUG=*value*	Option for debug print.

17.2 Defining the wavefunction

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF,*elec,sym,spin*

where

elec	is the number of electrons
sym	is the number of the irreducible representation
spin	defines the spin symmetry, $spin = 2 * S$ (singlet=0, doublet=1, triplet=2 etc.)

Note that these values take sensible defaults if any or all are not specified (see section 4.8).

17.2.1 Defining the number of occupied orbitals in each symmetry

OCC,$n_1, n_2, \ldots, n_8$

To avoid convergence problems in cases with high symmetry, this card should be included whenever the occupation pattern is known in advance. n_i is the number of occupied orbitals in the irreducible representation i. The total number of orbitals must be equal to (*elec*+*spin*)/2 (see WF card).

17.2.2 Specifying closed-shell orbitals

CLOSED,$n_1, n_2, \ldots, n_8$

This optional card can be used in open-shell calculations to specify the number of closed-shell orbitals in each symmetry. This makes possible to force specific states in the absence of an OPEN card.

17.2.3 Specifying open-shell orbitals

OPEN,$orb_1.sym_1, orb_2.sym_2, \ldots, orb_n.sym_n$

This optional card can be used to specify the singly occupied orbitals. The number of singly occupied orbitals must be equal to *spin*, and their symmetry product must be equal to *sym* (see WF card). If the OPEN card is not present, the open shell orbitals are selected automatically. The algorithm tries to find the ground state, but it might happen that a wrong state is obtained if there are several possibilities for distributing the open shell electrons among the available orbitals. This can also be avoided using the CLOSED card. If $orb_i.sym$ is negative, this orbital will be occupied with negative spin (only allowed in UHF).

17.3 Saving the final orbitals

ORBITAL,*record.file*
SAVE,*record.file*

The optimized orbitals, and the corresponding density matrix, fock matrix, and orbital energies are saved on *record.file*. SAVE is an alias for ORBITAL. If this card is not present, the defaults for *record* are:

RHF	2100	
UHF	2200	(holds both α and β-spin orbitals and related quantities)

These numbers are incremented by one for each subsequent calculation of the same type in the same input. Note that this holds for the sequence number in the input, independently in which order they are executed (see section 4.3).

The default for *file* is 2.

17.4 Starting orbitals

The START directive can be used to specify the initial orbitals used in the SCF iteration. It is either possible to generate an initial orbital guess, or to start with previously optimized orbitals. Alternatively, one can also use a previous density matrix to construct the first fock operator.

If the START card is absent, the program tries to find suitable starting orbitals as follows:

First:	Try to read orbitals from *record* specified on the ORBITAL or SAVE card or the corresponding default (see ORBITAL). All files are searched.
Second:	Try to find orbitals from a previous SCF or MCSCF calculation. All files are searched.
Third:	If no orbitals are found, the starting orbitals are generated using approximate atomic densities or eigenvectors of *h* (see below).

Since these defaults are usually appropriate, the START card is not required in most cases.

17.4.1 Initial orbital guess

An initial orbital guess can be requested as follows:

START,[TYPE=]*option*

The *option* keyword can be:

H0	Use eigenvectors of *h* as starting guess.
ATDEN	Use natural orbitals of a diagonal density matrix constructed using atomic occupation numbers.

The atomic density guess works very well with minimal or generally contracted basis sets for which the first contracted basis functions correspond to the atomic $1s$, $2s$, $2p$ ... orbitals, e.g., Dunning's cc-pVnZ sets, the STO-3G, or the 6-31G bases. For such basis sets ATDEN is used by default. If a segmented basis set with several contractions for each shell is used, ATDEN should not be specified and H0 is used by default. Since eigenvectors of *h* are often a very poor starting guess, it is recommended to generate the starting orbitals using a small basis like STO-3G (see section 17.4.2 below).

Example:

```
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
basis=STO-3G              !first basis set
hf                        !scf using STO-3G basis
basis=6-311G              !second basis set
hf                        !scf using 6-311G basis set
```

examples/
h2o˙sto3gstart1.com

The second calculation uses the optimized orbitals of the STO-3G calculation as starting guess. This is done by default and no START card is necessary. The explicit use of START and SAVE cards is demonstrated in the example in the next section.

The following input is entirely equivalent to the one in the previous section:

```
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
basis=STO-3G              !first basis set
hf                        !scf using STO-3G basis
start,atdens              !use atomic density guess
save,2100.2               !save orbitals to record 2100.2
basis=6-311G              !second basis set
hf                        !scf using 6-311G basis set
start,2100.2              !start with orbitals from the previous STO-3G calculation.
save,2101.2               !save optimized orbitals to record 2101.2
```

examples/
h2o˙sto3gstart2.com

17.4.2 Starting with previous orbitals

START,[RECORD=]*record.file*,[*specifications*]

reads previously optimized orbitals from record *record* on file *file*. Optionally, a specific orbital set can be specified as described in section 4.11.

The specified dump record may correspond to a different geometry, basis set, and/or symmetry than used in the present calculation. Using starting orbitals from a different basis set can be useful if no previous orbitals are available and the ATDENS option cannot be used (see above).

The following example shows how to change the symmetry between scf calculations. Of course, this example is quite useless, but sometimes it might be easier first to obtain a solution in higher symmetry and then convert this to lower symmetry for further calculations.

```
r1=1.85,r2=1.85,theta=104          !set geometry parameters
geometry={O;                       !z-matrix geometry input
          H1,O,r1;
          H2,O,r2,H1,theta}
basis=vdz
hf                                 !scf using c2v symmetry
orbital,2100.2                     !save on record 2100.2

set,zsymel=x

hf
start,2100.2                       !start with previous orbitals from c2v symmetry
orbital,2101.2                     !save new orbitals

set,zsymel=[x,y]
hf
start,2101.2                       !start with orbitals from cs symmetry
orbital,2102.2                     save new orbitals
```

examples/
h2o˙c2v˙cs˙start.com

Note, however, that this only works well if the orientation of the molecule does not change. Sometimes it might be helpful to use the `noorient` option.

Note also that a single dump record cannot hold orbitals for different basis dimensions. Using `save=2100.2` in the second calculation would therefore produce an error.

If orbitals from a corresponding SCF calculation at a neighbouring geometry are available, these should be used as starting guess.

17.4.3 Starting with a previous density matrix

START,DENSITY=*record.file*,[*specifications*]

A density matrix is read from the given dump record and used for constructing the first fock matrix. A specific density matrix can be specified as described in section 4.11. It is normally not recommended to use the `DENSITY` option.

17.5 Rotating pairs of orbitals

ROTATE,$orb_1.sym, orb_2.sym, angle$

Performs a 2×2 rotation of the initial orbitals orb_1 and orb_2 in symmetry *sym* by *angle* degrees. With *angle*$= 0$ the orbitals are exchanged. See `MERGE` for other possibilities to manipulate orbitals. In `UHF`, only the β-spin orbitals are rotated.

17.6 Using additional point-group symmetry

Since *MOLPRO* can handle only Abelian point-groups, there may be more symmetry than explicitly used. For instance, if linear molecules are treated in C_{2v} instead of $C_{\infty v}$, the $\delta_{(x^2-y^2)}$-orbitals appear in symmetry 1 (A_1). In other cases, a linear geometry may occur as a special case of calculations in C_S symmetry, and then one component of the π-orbitals occurs in symmetry 1 (A'). The program is able to detect such hidden "extra" symmetries by blockings in the one-electron hamiltonian h and the overlap matrix S. Within each irreducible representation, an "extra" symmetry number is then assigned to each basis function. These numbers are printed at the end of the integral output. Usually, the extra symmetries are ordered with increasing l-quantum number of the basis functions. This information can be used to determine and fix the extra symmetries of the molecular orbitals by means of the `SYM` command.

SYM,$irrep, sym(1), sym(2), , , sym(n)$

$sym(i)$ are the extra symmetries for the first n orbitals in the irreducible representation *irrep*. For instance, if you want that in a linear molecule the orbitals 1.1 to 3.1 are σ and 4.1, 5.1 δ, the `SYM` card would read (calculation done with X,Y as symmetry generators):

```
SYM,1,1,1,1,2,2
```

If necessary, the program will reorder the orbitals in each iteration to force this occupation. The symmetries of occupied and virtual orbitals may be specified. By default, symmetry contaminations are not removed. If *irrep* is set negative, however, symmetry contaminations are removed. Note that this may prevent convergence if degenerate orbitals are present.

17.7 Expectation values

EXPEC,$oper_1, oper_2, \ldots, oper_n$

Calculates expectation values for one-electron operators $oper_1$, $oper_2$, ..., $oper_n$. See section 6.13 for the available operators. By default, the dipole moments are computed. Normally, it is recommended to use the GEXPEC directive if expectation values for other operators are of interest. See section 6.13 for details.

17.8 Polarizabilities

POLARIZABILITY[,$oper_1, oper_2, \ldots, oper_n$]

Calculates polarizabilities for the given operators $oper_1$, $oper_2$, ..., $oper_n$.. See section 6.13 for the available operators. If no operators are specified, the dipole polarizabilities are computed.

Presently, this is working only for closed-shell without direct option.

17.9 Miscellaneous directives

All commands described in this section are optional. Appropriate default values are normally used.

17.9.1 Level shifts

SHIFT,*shifta,shiftb,nitord,nitcl,nitocc*

A level shift of *shifta* and *shiftb* hartree for α- and β-spin orbitals, respectively, is applied. This can improve convergence, but has no effect on the solution. *shifta*= −0.2 to −0.3 are typical values. The defaults are *shifta*= 0 and *shifta*= −0.3 in closed and open-shell calculations, respectively, and *shiftb*= 0.

In open-shell calculations, the orbitals are reordered after each iteration to obtain maximum overlap with the orbitals from the previous iteration. This takes only effect after *nitord* iterations. The default is *nitord*=*maxit*/4 if no start card is present and *nitord*= 1 if a START card is found.

Starting with iteration *nitocc* the occupation pattern is kept fixed. The default depends on the quality of the starting guess.

If the iteration count is smaller than *nitcl*, only the closed-shell part of the Fock matrix is used (default *nitcl*= 0).

17.9.2 Maximum number of iterations

MAXIT,*maxit*

sets the maximum number of iterations to *maxit*. The default is *maxit*= 30.

17.9.3 Convergence threshold

ACCU,*accu*

The convergence threshold is set to 10**(-*accu*). This applies to the square sum of the density matrix element changes. The default is *accu*= 10.

17.9.4 Print options

ORBPRINT,*print*,*test*

This determines the number of virtual orbitals printed at the end of the calculation. By default, *print*= 0, i.e., only the occupied orbitals are printed. *print*= −1 suppresses printing of orbitals entirely. *test*= 1 has the additional effect of printing the orbitals after each iteration.

17.9.5 Interpolation

IPOL,*iptyp,ipnit,ipstep,maxdis*

This command controls DIIS interpolation. *iptyp* can be:

DIIS	direct inversion of the iterative subspace. This is the default and yields mostly fastest convergence.
DM	obsolete. No effect in MOLPRO98
HFM	obsolete. No effect in MOLPRO98
NONE	No interpolation.

ipnit is the number of the iteration in which the interpolation starts. *ipstep* is the iteration increment between interpolations. *maxdis* is the maximum dimension of the DIIS matrix (default 10).

17.9.6 Reorthonormalization of the orbitals

ORTH,*nitort*

The orbitals are reorthonormalized after every *nitort* iterations. The default is *nitort*= 10.

17.9.7 Direct SCF

DIRECT,*options*

If this card is present, the calculation is done in direct mode. See section 10 for options. Normally, it is recommended to use the global GDIRECT command to request the direct mode. See section 10 for details.

18 THE DENSITY FUNCTIONAL PROGRAM

Density-functional theory calculations may be performed using one of the following commands:

DFT	calculate functional of a previously computed density.
RKS or RKS-SCF	calls the spin-restricted Kohn-Sham program. KS and KS-SCF are aliases for RKS.
UKS or UKS-SCF	calls the spin-unrestricted Kohn-Sham program

Each of these commands may be qualified with the key-names of the functional(s) which are to be used, and further options:

command, key1, key2, key3, ..., options

If no functional keyname is given, the default is LDA (see below). Following this command may appear directives specifying options for the density-functional modules (see section 18.2) or the Hartree-Fock program (see section 17.1).

On completion of the functional evaluation, or self-consistent Kohn-Sham calculation, the values of the individual functionals are stored in the MOLPRO vector variable DFTFUNS; the total is in DFTFUN, and the corresponding individual functional names in DFTNAME.

Energy gradients are available for self-consistent Kohn-Sham calculations.

Normally, sensible defaults are used to define the integration grid. The accuracy can be controlled using options as described in section 18.1 or directives as described in section 18.2). More control is provided by the GRID command, as described in section 18.3.

18.1 Options

The following options may be specified on the KS or UKS command lines:

GRID=*target*	Specifies the grid target accuracy (per atom). The default is 1.d-6 unless this has been modeified using a global THRESH, GRID option.
GRIDMAX=*gridmax*	In the initial iterations, the grid accuracy is min(*gridmax, target*coarsefac*).
COARSEFAC=*coarsefac*	Factor for initial grid accuracy (see above). The default is 1000.
DFTFAC=[*fac1,fac2,..*]	Factors for each functional. The number of given values must agree with the number of functionals.
EXFAC=*factor*	Fraction of exact exchange added to the functional. The default depends on the functional.
TOLORB=*value*	Threshold for orbital screening (current default 1.d-15).
MATRIX=*matrix*	Option to select integrator. *matrix=0*: use old (slow) integrator; *matrix=1*: Use new matrix-driven integrator (default).

In addition, all options valid for HF (see section 17.1) can be given.

18.2 Directives

The following options may be used to control the operation of the DFT modules. In the Kohn-Sham case, these may come in any order before or after directives for the SCF program as described in Section 17.

18.2.1 Density source (DENSITY, ODENSITY)

DENSITY,*orbc.filec*,... ODENSITY,*orbo.fileo*,...

For non-self-consistent DFT calculations, specifies the source of the density matrix. The total density is read from *orbc.filec*, with further options specifying density sets in the standard way as described in Section 4.11. ODENSITY can be used to specify the spin density. The defaults are the densities last written by an SCF or MCSCF program.

18.2.2 Thresholds (DFTTHRESH)

DFTTHRESH,*key1=value1,key2=value2*...

Sets various truncation thresholds. *key* can be one of the following.

TOTAL	Overall target accuracy (per atom) of density functional. Defaults to the value of the global threshold GRID or the value specified by option GRID. For proper use of this threshold, other thresholds should be left at their default value of zero.
ORBITAL	Orbital truncation threshold.
DENSITY	Density truncation threshold.
FOCK	Fock matrix truncation threshold.

18.2.3 Exact exchange computation (EXCHANGE)

EXCHANGE,*factor*

For Kohn-Sham calculations, compute exchange energy according to Hartree-Fock formalism and add the contribution scaled by *factor* to the fock matrix and the energy functional. Otherwise, the default is *factor=0*, i.e., the exchange is assumed to be contained in the functional, and only the Coulomb interaction is calculated explicitly.

DFTFACTOR,*fac1, fac2, ...*

Provide a factor for each functional specified. The functionals will be combined accordingly. By default, all factors are one.

18.2.4 Exchange-correlation potential (POTENTIAL)

POTENTIAL,*rec.fil*

For stand-alone DFT calculations, compute exchange-correlation potential pseudo-matrix elements, defined formally as the differential of the sum of all specified functionals with respect to elements of the atomic orbital density matrix. The matrix is written to record *rec* on file *fil*.

18.2.5 Grid blocking factor (DFTBLOCK)

DFTBLOCK,*nblock*

Respecify the number of spatial integration points treated together as a block in the DFT integration routines (default 128). Increasing *nblock* may enhance efficiency on, e.g., vector architectures, but leads to increased memory usage.

18.2.6 Dump integrand values(DFTDUMP)

DFTDUMP,*file,status*

Write out values of the integrand at grid points to the file *file*. The first line of *file* contains the number of functional components; there then follows a line for each functional giving the input key of the functional. Subsequent lines give the functional number, cartesian coordinates, integrand value and integration weight with Fortran format (I2,3F15.10,F23.15).

18.3 Numerical integration grid control (GRID)

Density functionals are evaluated through numerical quadrature on a grid in three-dimensional space. Although the sensible defaults will usually suffice, the parameters that define the grid can be specified by using the GRID top-level command, which should be presented *before* the the DFT or KS commands that will use the grid. Alternatively, GRID and its subcommands can be presented as directives within the KS program.

GRID,*orb.file*,*status*

The integration grid is stored on record *orb.file* (default 1800.2). The information on disk consists of two parts: the parameters necessary to define the grid, and a cache of the evaluated grid points and weights. The latter is flagged as 'dirty' whenever any parameters are changed, and whenever the geometry changes; if the cache is dirty, then when an attempt is made to use the grid, it will be recalculated, otherwise the cached values are used.

If *status* is OLD, an attempt to restore the grid from a previous calculation is performed; effectively, the old grid provides a template of parameters which can be adjusted using the parameter commands described below. If *status* is NEW, the grid is always created with default parameters. If *status* is UNKNOWN (the default), a new grid is created either if record *orb.file* does not exist; otherwise the old grid is used.

The GRID command may be followed by a number of parameter-modifying subcommands. The currently implemented default parameters are equivalent to the following input commands.

```
GRIDTHRESH,1e-5,0,0
RADIAL,LOG,3,1.0,20,25,25,30
ANGULAR,LEBEDEV,0.0,0.0
LMIN,3,5,5,7
LMAX,53,53,53,53
VORONOI,10
GRIDSAVE
GRIDSYM
```

18.3.1 Target quadrature accuracy (GRIDTHRESH)

GRIDTHRESH,*acc*,*accr*,*acca*

Specify the target accuracy of integration. Radial and angular grids are generated adaptively, with the aim of integrating the Slater-Dirac functional to the specified accuracy. *acc* is an overall target accuracy, and is the one that should normally be used; radial and angular grid target accuracies are generated algorithmically from it. However, they can be adjusted individually by specifying *accr* and *acca* respectively.

18.3.2 Radial integration grid (RADIAL)

RADIAL,*method*,m_r,*scale*,n_0,n_1,n_2,n_3

Specify the details of the radial quadrature scheme. Four different radial schemes are available, specified by *method* = EM, BECKE, AHLRICHS or LOG, with the latter being the default.

EM is the Euler-Maclaurin scheme defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997. m_r, for which the default value is 2, is defined in equation (6) of the above as

$$r = \alpha \frac{x^{m_r}}{(1-x)^{m_r}} \tag{1}$$

whilst *scale* (default value 1) multiplied by the Bragg-Slater radius of the atom gives the scaling parameter α.

LOG is the scheme described by M. E. Mura and P. J. Knowles, J. Chem. Phys. 104 (1996) 9848. It is based on the transformation

$$r = -\alpha \log_e(1-x^{m_r}) \,, \tag{2}$$

with $0 \leq x \leq 1$ and simple Gauss quadrature in x-space. The recommended value of m_r is 3 for molecular systems, giving rise to the Log3 grid; m_r=4 is more efficient for atoms. α is taken to be *scale* times the recommended value for α given by Mura and Knowles, and *scale* defaults to 1.

BECKE is as defined by A. D. Becke, J. Chem. Phys. 88 (1988) 2547. It is based on the transformation

$$r = \alpha \frac{(1+x)}{(1-x)} \,, \tag{3}$$

using points in $-1 \leq x \leq +1$ and standard Gauss-Chebyshev quadrature of the second kind for the x-space quadrature. Becke chose his scaling parameters to be half the Bragg-Slater radius except for hydrogen, for which the whole Bragg-Slater radius was used, and setting *scale* to a value other than 1 allows a different α to be used. m_r is not necessary for this radial scheme.

AHLRICHS is the radial scheme defined by O. Treutler and R. Ahlrichs, J. Chem. Phys. 102 (1995) 346. It is based on the transformation their M4 mapping

$$r = \frac{\alpha}{\log_e 2}(1+x)^{0.6} \log_e \left(\frac{2}{1-x} \right) \,, \tag{4}$$

with using standard Gauss-Chebyshev quadrature of the second kind for the x-space integration. m_r is not necessary for this radial scheme.

n_0, n_1, n_2, n_3 are the degrees of quadrature n_r (see equation (3) of Murray et al.), for hydrogen/helium, first row, second row, and other elements respectively.

accr as given by the THR command specifies a target accuracy; the number of radial points is chosen according to a model, instead of using an explicit n_i. The stricter of n_i, accr is used, unless either is zero, in which case it is ignored.

18.3.3 Angular integration grid (ANGULAR)

ANGULAR,*method,acca,crowd*
LMIN,$l_0^{\min}, l_1^{\min}, l_2^{\min}, l_3^{\min}$
LMAX,$l_0^{\max}, l_1^{\max}, l_2^{\max}, l_3^{\max}$

Specify the details of the angular quadrature scheme. The default choice for *method* is LEBEDEV (ie. as in A. D. Becke, J. Chem. Phys. 88 (1988) 2547) which provides angular grids of octahedral symmetry. The alternative choice for *method* is LEGENDRE which gives Gauss-Legendre quadrature in θ and simple quadrature in ϕ, as defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997.

Each type of grid specifies a family of which the various members are characterized by a single quantum number l; spherical harmonics up to degree l are integrated exactly. $l\min_i$ and $l\max_i, i = 0,1,2,3$ specify allowed ranges of l for hydrogen/helium, first row, second row, and other elements respectively. For the Lebedev grids, if the value of l is not one of the set implemented in MOLPRO (3, 5, 7, 9, 11, 13, 15, 17, 19, 23, 29, 41, 47, 53), then l is increased to give the next largest angular grid available. In general, different radial points will have different l, and in the absence of any moderation described below, will be taken from $l_i^{\max}$.

crowd is a parameter to control the reduction of the degree of quadrature close to the nucleus, where points would otherwise be unnecessarily close together; larger values of crowd mean less reduction thus larger grids. A very large value of this parameter, or, conventionally, setting it c;to zero, will switch off this feature.

acca is a target energy accuracy. It is used to reduce l for a given radial point as far as possible below $l_i^{\max}$ but not lower than $l_i^{\max}$. The implementation uses the error in the angular integral of the kernel of the Slater-Dirac exchange functional using a sum of approximate atomic densities. If *acca* is zero, the global threshold is used instead, or else it is ignored.

18.3.4 Atom partitioning of integration grid (VORONOI)

VORONOI,m_μ

Controls Becke-Voronoi partitioning of space. The algorithm of C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997 is used, with m_μ defined by equation (24). The default value is 10.

18.3.5 Grid caching (GRIDSAVE, NOGRIDSAVE)

NOGRIDSAVE

disables the disk caching of the grid, i.e, forces the recalculation of the grid each time it is needed.

GRIDSAVE

forces the use of a grid cache where possible.

18.3.6 Grid symmetry (GRIDSYM, NOGRIDSYM)

NOGRIDSYM

switches off the use of symmetry in generating the integration grid, whereas

GRIDSYM

forces the use of any point-group symmetry.

18.3.7 Grid printing (GRIDPRINT)

GRIDPRINT,*key*=*value*,...

controls printing of the grid, which by default is not done. At present, the only possible value for *key* is GRID, and *value* should be specified as an integer. GRID=0 causes the total number of integration points to be evaluated and reported; GRID=1 additionally shows the number of points on each atom; GRID=2 causes the complete set of grid points and weights to be printed.

18.4 Density Functionals

In the following, ρ_α and ρ_β are the α and β spin densities; the total spin density is ρ;

The gradients of the density enter through

$$\sigma_{\alpha\alpha} = \nabla\rho_\alpha \cdot \nabla\rho_\alpha \, , \sigma_{\beta\beta} = \nabla\rho_\beta \cdot \nabla\rho_\beta \, , \sigma_{\alpha\beta} = \sigma_{\beta\alpha} = \nabla\rho_\alpha \cdot \nabla\rho_\beta \, , \sigma = \sigma_{\alpha\alpha} + \sigma_{\beta\beta} + 2\sigma_{\alpha\beta} \quad (5)$$

$$\chi_\alpha = \frac{\sqrt{\sigma_{\alpha\alpha}}}{\rho_\alpha^{4/3}} \, , \chi_\beta = \frac{\sqrt{\sigma_{\beta\beta}}}{\rho_\beta^{4/3}} \, . \quad (6)$$

$$\upsilon_\alpha = \nabla^2\rho_\alpha \, , \upsilon_\beta = \nabla^2\rho_\beta \, , \upsilon = \upsilon_\alpha + \upsilon_\beta \, . \quad (7)$$

Additionally, the kinetic energy density for a set of (Kohn-Sham) orbitals generating the density can be introduced through

$$\tau_\alpha = \sum_i^\alpha |\nabla\phi_i|^2 \, , \tau_\beta = \sum_i^\beta |\nabla\phi_i|^2 \, , \tau = \tau_\alpha + \tau_\beta \, . \quad (8)$$

All of the available functionals are of the general form

$$F\left[\rho_s, \rho_{\bar{s}}, \sigma_{ss}, \sigma_{\bar{s}\bar{s}}, \sigma_{s\bar{s}}, \tau_s, \tau_{\bar{s}}, \upsilon_s, \upsilon_{\bar{s}}\right] = \int d^3\mathbf{r} K\left(\rho_s, \rho_{\bar{s}}, \sigma_{ss}, \sigma_{\bar{s}\bar{s}}, \sigma_{s\bar{s}}, \tau_s, \tau_{\bar{s}}, \upsilon_s, \upsilon_{\bar{s}}\right) \quad (9)$$

where $\bar{s}$ is the conjugate spin to s.

Below is a list of keywords for the functionals supported by MOLPRO. Additionally there are a list of alias keywords deatailed in the next section for various combinations of the primary functionals listed below.

B86MGC: Xαβγ with Modified Gradient Correction
B86R: Xαβγ Re-optimised
B86: Xαβγ
B88C: Becke88 Correlation Functional
B88: Becke88 Exchange Functional
B95: Becke95 Correlation Functional
B97R: Density functional part of B97 Re-parameterized by Hamprecht et al
B97: Density functional part of B97
BR: Becke-Roussel Exchange Functional
BRUEG: Becke-Roussel Exchange Functional — Uniform Electron Gas Limit
BW: Becke-Wigner Exchange-Correlation Functional
CS1: Colle-Salvetti correlation functional
CS2: Colle-Salvetti correlation functional

DIRAC: Slater-Dirac Exchange Energy
G96: Gill's 1996 Gradient Corrected Exchange Functional
HCTH120: Handy least squares fitted functional
HCTH147: Handy least squares fitted functional
HCTH93: Handy least squares fitted functional
LTA: Local τ Approximation
LYP: Lee, Yang and Parr Correlation Functional
MK00B: Exchange Functional for Accurate Virtual Orbital Energies
MK00: Exchange Functional for Accurate Virtual Orbital Energies
P86:
PBEC: PBE Correlation Functional
PBEXREV: Revised PBE Exchange Functional
PBEX: PBE Exchange Functional
PW86:
PW91C: Perdew-Wang 1991 GGA Correlation Functional
PW91X: Perdew-Wang 1991 GGA Exchange Functional
PW92C: Perdew-Wang 1992 GGA Correlation Functional
STEST: Test for number of electrons
TH1: Tozer and Handy 1998
TH2:
TH3:
TH4:
THGFCFO:
THGFCO:
THGFC:
THGFL:
VSXC:
VWN3: Vosko-Wilk-Nusair (1980) III local correlation energy
VWN5: Vosko-Wilk-Nusair (1980) V local correlation energy

18.4.1 Alias density functionals

Additional functional keywords are also defined as convenient aliases. The following table gives the translations.

alias	functionals	Ref
B	B88	[1]
B-LYP	B88 + LYP	
B-P	B88 + P86	
B-VWN	B88 + VWN5	
B3LYP	0.2d0 EXACT + 0.72d0 B88 + 0.08d0 DIRAC + 0.81d0 LYP + 0.19d0 VWN5	
B3LYP3	0.2d0 EXACT + 0.72d0 B88 + 0.08d0 DIRAC + 0.81d0 LYP + 0.19d0 VWN3	
B3LYP5	0.2d0 EXACT + 0.72d0 B88 + 0.08d0 DIRAC + 0.81d0 LYP + 0.19d0 VWN5	
B88X	B88	[1]
B97	0.1943d0 EXACT + B97DF	
B97R	0.21d0 EXACT + B97RDF	
BECKE	B88	[1]
BH-LYP	0.5d0 EXACT + 0.5d0 B88 + LYP	
CS	CS1	
D	DIRAC	
HFB	B88	[1]
HFS	DIRAC	
LDA	DIRAC + VWN5	
LSDAC	PW92C	[2]
LSDC	PW92C	[2]
LYP88	LYP	
PBE	PBEX + PBEC	[3]
PBE0	0.25d0 EXACT + 0.75d0 PBEX + PW91C	[4]
PBEREV	PBEXREV + PBEC	
PW91	PW91X + PW91C	[5]
S	DIRAC	
S-VWN	DIRAC + VWN5	
SLATER	DIRAC	
VS99	VSXC	
VWN	VWN5	
VWN80	VWN5	

18.4.2 ACG documentation

The automatic code generation (ACG) program [6] is used to implement new density functionals into Molpro. In order to work the program requires the maple mathematics program and the xsltproc xml parser. The program requires a file with extension `.df` containing all of the information about the new functional. All density functional files are placed in the directory `lib/df` and are automatically activated on the next instance of the `make` command in the MOLPRO base directory.

The file format consists of expressions which must be separated by a blank line. Expressions consist of a quantity and value and the syntax is given by

```
quantity:=value:
```

The syntax of `value` is a maple expression, and `quantity` may take any name the user chooses with the exception of the special quantity names listed in table 8.

18.5 Examples

The following shows the use of both non-self-consistent and self-consistent DFT.

blurb	Text to document the functional
ref	Alias for reference contained in `doc/references.xml`
title	Text to appear as a heading for the functional documentation

Table 8: ACG special quantity names and definitions of their values

```
geometry={c;n,c,r}
r=1.1 angstrom
df=[b,lyp]
rhf;method(1)=program
dft;edf(1)=dftfun
uhf;method(2)=program
dft;edf(2)=dftfun
uks;method(3)=program,edf(3)=dftfun
dft;method(4)=program,edf(4)=dftfun
table,dftname,dftfuns
table,method,edf
```

examples/
cndft.com

19 ORBITAL LOCALIZATION

Localized orbitals are calculated according to the Boys or Pipek-Mezey criteria. Localization takes place within each symmetry species separately. If complete localization is desired, no symmetry should be used. All subcommands can be abbreviated by three characters.

The localization program is invoked by the LOCALI command

LOCALI [,*method*]

The keyword *method* can be either BOYS or PIPEK. By default, the valence orbitals from the last energy calculation are localized using the Boys criterion. Only orbital subsets which leave the energy invariant are transformed. These defaults can be modified using the optional commands described in the following sections.

19.1 Defining the input orbitals (ORBITAL)

ORBITAL,*record.file*,*specifications*

The orbitals to be localized are read from dump record *record.file*. A state specific orbital set can be selected using *specifications*, as explained in section 4.11. Default are the orbitals calculated last.

19.2 Saving the localized orbitals (SAVE)

SAVE,*record.file*

This specifies the dump record where the localized orbitals are stored. If the dump record already exists, the localized orbitals are added to it. Default is the input record (cf. ORBITAL).

19.3 Choosing the localization method (METHOD)

METHOD,*method*

The localization method *method* can be either BOYS or PIPEK. This can also be specified as argument on the LOCALI card (see above).

19.4 Delocalization of orbitals (DELOCAL)

DELOCAL

If this card is present, the orbitals are delocalized.

19.5 Localizing AOs(LOCAO)

LOCAO

If this card is present, the number of AOs contributing to each MO is minimized. This can be useful to rotate degenerate orbitals (e.g., px, py, pz in an atom) so that pure orbitals (in this case px, py, pz) result.

This implies Pipek-Mezey localization.

19.6 Selecting the orbital space

By default, only the valence orbitals are localized, in order to ensure invariance of subsequent electron correlation treatments. This behaviour can be modified using the OCC and CORE directives.

19.6.1 Defining the occupied space (OCC)

OCC, o_1, $o_2 \ldots$

defines the highest orbital o_i in each symmetry i to be localized.

19.6.2 Defining the core orbitals (CORE)

CORE, c_1, $c_2 \ldots$

The first c_i orbitals in each symmetry are treated as core orbitals and not localized. Thus, orbitals $c_i + 1$ to o_i are localized in symmetry i.

19.6.3 Defining groups of orbitals (GROUP, OFFDIAG)

GROUP,*orb1,orb2,orb3,...*

This card defines groups of orbitals to be localized as follows:

`GROUP,1.1,2.1,3.1`	a group of orbitals 1-3 in symmetry 1
`GROUP,1.1,-3.1`	equivalent to previous example
`GROUP,3.1,5.1,-8.1`	this group includes orbitals 3,5,6,7,8 in symmetry 1

Orbitals in different groups are localized independently. Orbitals not included in any group are unchanged.

19.6.4 Localization between groups (OFFDIAG)

OFFDIAG

If this card is present, localize between groups instead of within groups.

19.7 Ordering of localized orbitals

ORDER,*type*

If *type*=CHARGE, the orbitals are ordered according to their charge centroids (default).

If *type*=FOCK, the orbitals are ordered according to increasing diagonal elements of the fock operator (PIPEK) or increasing Coulson-additive orbital energies (BOYS). This requires a Fock operator from the preceding energy calculation. For localization of Hartree-Fock orbitals, this operator is stored in the dump record and automatically found. For localization of MCSCF orbitals, an effective fock operator is computed from the MCSCF density matrix (see DENSITY option). Alternatively, a dump record of a previous SCF calculation can be specified on the FOCK card, and then the fock operator is read from this record. For degenerate orbitals, further ordering according to the the coordinates of charge centres is attempted (first according to largest z-coordinates, then according to x, then y).

19.7.1 No reordering (NOORDER)

NOORDER

If this card is present, the localized orbitals are not reordered. This is useful if localized orbitals are used as starting guess, and it is intended that their order remains unchanged.

19.7.2 Ordering using domains (SORT)

SORT,[THRCHCHG=*charge*][THREIG=*eps*],GROUP=*igrp*],[REVERT],*centrelist*

This directive only works for Pipek-Mezey localization. The orbitals are ordered according to domains and the given centrelist. The contributions of the centres to domains are determined by Löwdin charges. Only centres with charges greater than THRCHCHG (default 0.4) are included in these domains. The orbitals are reordered according to the following criteria:

1.) The primary centre in a domain is the one with largest charge, the secondary centre the one with the next largest charge. Orbitals are reordered separately within each localization group. First all orbitals are sorted so that the primary centres are in the order of the given *centrelist*. Orbitals with primary centres which are not in *centrelist* come last.

2.) Within each group of orbitals found for a given primary centre, those containing only one centre (lone pairs) are included first. The remaining ones are ordered so that the secondary atoms are in the order of *centrelist*. Orbitals with secondary centres which are not in *centrelist* come last.

3.) If REVERT is given, the order in each localization group is reverted.

4.) If GROUP is given, only the orbitals in the given group are reordered. *igrp* is 2 for closed shells and inactive orbitals, 1 for open-shells in single reference methods, and 3 for active orbitals in CASSCF calculations.

5.) If THREIG is given, only orbitals with energies larger than the given value are reordered. *eps* must be negative. The remaining orbitals come last (first if REVERT is given).

Note that core orbitals are neither localized nor reordered.

19.7.3 Defining reference orbitals (REFORB)

REFORB,*record.file*,*specifications*

The localized orbitals are reordered such that the overlap with the reference orbitals read from *record.file* is maximized. This is useful for local correlation treatments for keeping the order of the localized constant for different geometries. A state specific orbital set can be selected using *specifications*, as explained in section 4.11.

19.7.4 Selecting the fock matrix (FOCK)

FOCK,*record.file*

This specifies a record holding a Fock operator to be used for ordering the orbitals. Note that only SCF dump records hold fock operators. Default is the Fock operator from the energy calculation which produced the input orbitals.

19.7.5 Selecting a density matrix (DENSITY)

DENSITY,*record.file*,*specifications*

This specifies a record holding a density matrix for construction of a fock operator used for ordering the orbitals. This can be used if no fock operator is available, and has only an effect for MCSCF localizations. By default, the (state averaged) MCSCF density is used. A state specific density matrix can be selected using *specifications* as described in section 4.11.

19.8 Localization thresholds (THRESH)

THRESH,*thresh,eorder*

thresh is a threshold for localization (default 1.d-12). If *eorder* is nonzero (default 1.d-4), the orbitals whose energy difference is smaller then *eorder* are considered to be degenerate and reordered according to the position of their charge centres (see section 19.7).

19.9 Options for PM localization (PIPEK)

Some special options exist for Pipek-Mezey localization (all optional):

PIPEK,METHOD=*method*,DELETE=*ndel*,MAXDL=*maxdl*,THRESH=*thresh*,ORDER=*iorder*,STEP=*step*

METHOD:	*method=1*: use 2x2 rotation method (default); *method=2*: use Newton-Raphson method; *method=3*: Initial iterations using 2x2 rotation method , final convergence using NR method.
DELETE:	Delete the last *ndel* basis functions of each angular momentum type for each atom in PM localization. This can be useful to achieve proper localization with diffuse (augmented) basis sets.
MAXDL:	If *ndel*¿0 delete functions only up to angular momentum *maxdl*.
ORDER:	If *iorder=1*, order final orbitals according to increasing diagonal fock matrix elements; If *iorder=2*, order final orbitals according charge centres (default).
THRESH:	Localization threshold (same as on THRESH directive).
STEP:	Max step size in NR method (default 0.1d0).

19.10 Printing options (PRINT)

PRINT,[ORBITAL=]*pri* [,CHARGE] [,CENTRES] [,TEST] [,TRAN];

If ORB[ITAL] is given, the localized orbitals are printed.
If CHA[RGE] or CEN[TRES] is given, the charge centres of the localized orbitals are printed.
If TRAN is given, the transformation matrix is printed (Boys only).
If TEST is given, intermediate information is printed.

20 THE MCSCF PROGRAM MULTI

MULTI is a general MCSCF/CASSCF program written by
P. J. Knowles and H.-J. Werner (1984).

Bibliography:

H.-J. Werner and P. J. Knowles, J. Chem. Phys. 82, 5053 (1985).
P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. 115, 259 (1985).

All publications resulting from use of this program must acknowledge the above. See also:

H.-J. Werner and W. Meyer, J. Chem. Phys. 73, 2342 (1980).
H.-J. Werner and W. Meyer, J. Chem. Phys. 74, 5794 (1981).
H.-J. Werner, Adv. Chem. Phys. LXIX, 1 (1987).

This program allows one to perform CASSCF as well as general MCSCF calculations. For CASSCF calculations, one can optionally use Slater determinants or CSFs as a N-electron basis. In most cases, the use of Slater determinants is more efficient. General MCSCF calculations must use CSFs as a basis.

A quite sophisticated optimization method is used. The algorithm is second-order in the orbital and CI coefficient changes and is therefore quadratically convergent. Since important higher order terms in the independent orbital parameters are included, almost cubic convergence is often observed. For simple cases, convergence is usually achieved in 2-3 iterations. However, convergence problems can still occur in certain applications, and usually indicate that the active space is not adequately chosen. For instance, if two weakly occupied orbitals are of similar importance to the energy, but only one of them is included in the active set, the program might alternate between them. In such cases either reduction or enlargement of the active orbital space can solve the problem. In other cases difficulties can occur if two electronic states in the same symmetry are almost or exactly degenerate, since then the program can switch from one state to the other. This might happen near avoided crossings or near an asymptote. Problems of this sort can be avoided by optimizing the energy average of the particular states. It is also possible to force convergence to specific states by choosing a subset of configurations as primary space (`PSPACE`). The hamiltonian is constructed and diagonalized explicitly in this space; the coefficients of the remaining configurations are optimized iteratively using the P-space wavefunction as zeroth order approximation. For linear molecules, another possibility is to use the `LQUANT` option, which makes it possible to force convergence to states with definite Λ quantum number, i.e., Σ, Π, Δ, etc. states.

20.1 Structure of the input

All sub-commands known to *MULTI* may be abbreviated by four letters. The input commands fall into several logical groups; within each group commands may appear in any order, but the groups must come in correct order.

a) The program is invoked by the command `MULTI` or `MCSCF`

b) cards defining partitioning of orbitals spaces – `OCC`,`FROZEN`,`CLOSED`

c) general options (most commands not otherwise specified here)

d) a `WF` card defining a state symmetry

e) options pertaining to that state symmetry – `WEIGHT`,`STATE`,`LQUANT`

f) configuration specification for that state symmetry – SELECT,CON,RESTRICT

g) definition of the primary configurations for that state symmetry - PSPACE

h) further general options

Stages d) through to h) may be repeated several times; this is the way in which you specify an average energy of several states of different symmetry.

Many options can be specified on the MULTI command line:

MULTI,*options*

Selected options:

MAXIT	Max. number of iterations (default 10)
ENERGY	Convergence threshold for energy
GRADIENT	Convergence threshold for gradient
STEP	Convergence threshold for steplength
FAILSAFE	(logical) Use options for more robust convergence

Many further options and thresholds, which can also be given on the command line, are described in section 20.8.5.

20.2 Defining the orbital subspaces

20.2.1 Occupied orbitals

OCC,$n_1,n_2,\ldots,n_8$;

n_i specifies numbers of occupied orbitals (including FROZEN and CLOSED) in irreducible representation number i. In the absence of an OCC card, the information from the most recent MCSCF calculation is used, or, if there is none, those orbitals corresponding to a minimal valence set, i.e., full valence space, are used.

20.2.2 Frozen-core orbitals

FROZEN,$n_1,n_2,\ldots$,*record.file*;

n_i is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations and not optimized. Note that in earlier MOLPRO versions this directive was called CORE and has now been renamed to avoid confusion with CORE orbitals in the MRCI and CCSD programs.

record.file is the record name for frozen core orbitals; if not supplied, taken from *orb* on START card. *record.file* can be specified in any field after the last nonzero n_i. It should always be given if the orbital guess is from a neighbouring geometry and should then specify the SCF orbitals calculated at the present geometry. If a subsequent gradient calculation is performed with this wavefunction, *record.file* is mandatory and must specify closed-shell SCF orbitals at the present geometry. Note that *record* must be larger than 2000.

If the FROZEN card is omitted, then the numbers of core orbitals are taken from the most recent MCSCF calculation, or otherwise no orbitals are frozen. If the FROZEN card is given as

FROZEN,record.file, then the orbitals corresponding to atomic inner shells are taken, i.e., 1s for Li–Ne, 1s2s2p for Na–Ar, etc. A FROZEN card without any specification resets the number of frozen core orbitals to zero.

20.2.3 Closed-shell orbitals

CLOSED,$n_1, n_2, \ldots, n_8$

n_i is the number of closed-shell orbitals in irrep number i, inclusive of any FROZEN orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all CSFs. In contrast to the core orbitals (see FROZEN), these orbitals are fully optimized.

If the CLOSED card is omitted, then the data defaults to that of the most recent MCSCF calculation, or else the atomic inner shells as described above for FROZEN.

20.2.4 Freezing orbitals

FREEZE,*orb.sym*;

The specified orbital will not be optimized and will remain identical to the starting guess. *orb.sym* should be an active or closed-shell orbital. If *orb.sym* is a frozen core orbital, this card has no effect.

20.3 Defining the optimized states

Each state symmetry to be optimized is specified by one WF card, which may optionally be followed by STATE, WEIGHT, RESTRICT, SELECT, CON, and/or PSPACE cards. All cards belonging to a particular state symmetry as defined on the WF card must form a block which comes directly after the WF card. The cards can be in any order, however.

20.3.1 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF,*elec,sym,spin*

where

elec	is the number of electrons
sym	is the number of the irreducible representation
spin	defines the spin symmetry, *spin*$= 2S$ (singlet=0, doublet=1, triplet=2, etc.)

Note that these values take sensible defaults if any or all are not specified (see section 4.8).

The input directives STATE, WEIGHT, LQUANT, SELECT, PUNCSF always refer to the state symmetry as defined on the previous WF card. If such a directive is found before a WF card has been given, the current state symmetry is assumed, either from a previous calculation or from variables [MC]SYMMETRY(1) and [MC]SPIN(1) (if these are defined). If any of these cards or a WF card is given, the variables STATE, WEIGHT, LQUANT, SELECT are *not* used, and the number of state symmetries defaults to one, regardless of how many symmetries are specified in variable [MC]SYMMETRY.

20.3.2 Defining the number of states in the present symmetry

STATE,*nstate*;

nstate is the number of states in the present symmetry. By default, all states are optimized with weight 1 (see WEIGHT card).

20.3.3 Specifying weights in state-averaged calculations

WEIGHT,$w(1), w(2), \ldots, w(nstate)$;

$w(i)$ is the weight for the state i in the present symmetry. By default, all weights are 1.0. See also STATE card. If you want to optimize the second state of a particular state symmetry alone, specify

```
STATE,2;WEIGHT,0,1;
```

Note, however, that this might lead to root-flipping problems.

20.4 Defining the configuration space

By default, the program generates a complete configuration set (CAS) in the active space. The full space may be restricted to a certain occupation pattern using the RESTRICT option. Alternatively, configurations may be selected from the wavefunction of a previous calculation using SELECT, or explicitly specified on CON cards. Note that this program only allows to select or specify orbital configurations. For each orbital configuration, all spin couplings are always included. Possible RESTRICT, SELECT and CON cards must immediately follow the WF card which defines the corresponding state symmetry.

20.4.1 Occupation restrictions

RESTRICT,*nmin,nmax,*orb_1,orb_2,...orb_n;

This card can be used to restrict the occupation patterns. Only configurations containing between *nmin* and *nmax* electrons in the specified orbitals orb_1, orb_2,...,orb_n are included in the wavefunction. If *nmin* and *nmax* are negative, configurations with exactly abs(*nmin*) and abs(*nmax*) electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form *number.sym*, where *number* is the number of the orbital in irrep *sym*. Several RESTRICT cards may follow each other. RESTRICT only works if a CONFIG card is specified before the first WF card.

RESTRICT cards given before the first WF cards are global, i.e., are active for all state symmetries. If such a global restrict card is given, variable [MC]RESTRICT is *not* used.

Additional state-specific RESTRICT cards may be given after a WF card. These are used in addition to the global orbital restrictions.

If neither state-specific nor global RESTRICT cards are found, the values from the variable [MC]RESTRICT are used.

20.4.2 Selecting configurations

SELECT,*ref1,ref2,refthr,refstat,mxshrf*;

This card is used to specify a configuration set other than a CAS, which is the default. This option automatically triggers the CONFIG option, which selects CSFs rather than determinants. Configurations can be defined using CON cards, which must follow immediately the SELECT card. Alternatively, if *ref1* is an existing MOLPRO record name, the configurations are read in from that record and may be selected according to a given threshold.

ref1=rec1.file	(*rec1*> 2000) The configurations are read in from the specified record. If *ref1* is not specified, the program assumes that the configurations are read from subsequent CON cards (see CON).
ref2=rec2.file	(*rec2*> 2000) Additional configurations are read from the specified record. If *rec2* is negative, all records between *rec1* and abs(*rec2*) are read. All configurations found in this way are merged.
refthr	Selection threshold for configurations read from disc (records *rec1–rec2*). This applies to the norm of all CSFs for each orbital configuration.
refstat	Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If *refstat* is not specified, the configurations are selected from all states.
mxshrf	max. number of open shells in the selected or generated configurations.

20.4.3 Specifying orbital configurations

CON,$n_1,n_2,n_3,n_4,\ldots$

Specifies an orbital configuration to be included in the present symmetry. The first CON card must be preceded by a SELECT card. n_1, n_2 etc. are the occupation numbers of the active orbitals (0,1,or 2). For example, for
`OCC,5,2,2;CLOSED,2,1,1;`
n_1 is the occupation of orbital 3.1 (number.sym), n_2 is the occupation of orbital 4.1, n_3 of 5.1, n_4 of 2.2, and n_5 of 2.3 Any number of CON cards may follow each other.

Example for the BH molecule:

```
OCC,4,1,1;              ! four sigma, one pi orbitals are occupied
FROZEN,1;               ! first sigma orbital is doubly occupied and frozen
WF,6,1;                 ! 6 electrons, singlet Sigma+ state
SELECT                  ! triggers configuration input
CON,2,2                 ! 2sigma**2, 3sigma**2
CON,2,1,1               ! 2sigma**2, 3sigma, 4sigma
CON,2,0,2               ! 2sigma**2, 4sigma**2
CON,2,0,0,2             ! 2sigma**2, 1pi_x**2
CON,2,0,0,0,2           ! 2sigma**2, 1pi_y**2
```

20.4.4 Selecting the primary configuration set

PSPACE,*thresh*

The hamiltonian is constructed and diagonalized explicitly in the primary configuration space, which can be selected with the PSPACE card. The coefficients of the remaining configurations (Q-space) are optimized iteratively using the P-space wavefunction as zeroth order approximation.

If *thresh* is nonzero, it is a threshold for automatically selecting all configurations as P-space configurations which have energies less then $emin + thresh$, where *emin* is the lowest energy of all configurations. Further P-space configurations can be specified using CON cards, which must follow immediately after the PSPACE card. These are merged with the ones selected according to the threshold. Automatic selection can be avoided by specifying a very small threshold. There is a sensible default value for thresh (0.4), so you usually don't need a pspace card in your input. Furthermore, if the number of configurations in the MCSCF is less than 20, all configurations go into the P-space unless you give a PSPACE card in the input.

A P-space threshold defined on a PSPACE card before the first WF (or STATE, WEIGHT, SELECT, PUNCSF if WF is not given) card is global, i.e., valid for all state symmetries. State-specific thresholds can be defined by placing a PSPACE card after the corresponding WF card. In the latter case the PSPACE card can be followed by CON cards, which define state-specific P-space configurations.

20.4.5 Projection to specific Λ states in linear molecules

Since MOLPRO can only use Abelian point groups (e.g. C_{2v} instead of $C_{\infty v}$ for linear molecules), $\Delta_{x^2-y^2}$ states as well as Σ^+ states occur in the irreducible representation number 1, for example. Sometimes it is not possible to predict in advance to which state(s) the program will converge. In such cases the LQUANT option can be used to specify which states are desired.

LQUANT,*lam(1),lam(2),...,lam(nstate)*;

lam(i) is the Λ quantum number of state *i*, i.e., 0 for Σ states, 1 for Π states, 2 for Δ states, etc. The matrix over Λ^2 will be constructed and diagonalized in the P-space configuration basis. The eigenvectors are used to transform the P-space hamiltonian into a symmetry adapted basis, and the program then selects the eigenvectors of the correct symmetry. The states will be ordered by symmetry as specified on the LQUANT card; within each symmetry, the states will be ordered according to increasing energy.

20.5 Restoring and saving the orbitals and CI vectors

MULTI normally requires a starting orbital guess. In this section we describe how to define these orbitals, and how to save the optimized orbitals. In a CASSCF calculation, one has the choice of transforming the final orbitals to natural orbitals (the first order density matrix is diagonalized), to pseudo-canonical orbitals (an effective Fock-operator is diagonalized), or of localizing the orbitals.

20.5.1 Defining the starting guess

START,*record,[options]*;

record: dump record containing starting orbitals. As usual, *record* has the form *irec.ifil*, where *irec* is the record number (e.g., 2140), and *ifil* the file number (usually 2). The *options* can be used to select orbitals of a specific type; for details, see section 4.11.

If this card is missing, the program tries to find suitable starting orbitals as follows:

First:	Try to read orbitals from the record specified on the ORBITAL card (or the corresponding default, see ORBITAL). All files are searched.
Second:	Try to find orbitals from the most recent MCSCF calculation. All files are searched.
Third:	Try to find orbitals from the most recent SCF calculation. All files are searched.

If no orbitals are found, a starting orbital guess is generated.

It is often useful to employ MCSCF orbitals from a neighbouring geometry as starting guess (this will happen automatically if orbitals are found, see the above defaults). Note, however, that frozen-core orbitals should always be taken from an SCF or MCSCF calculation at the present geometry and must be specified separately on the FROZEN card. Otherwise the program is likely to stop with error "non-orthogonal core orbitals". The program remembers where to take the core orbitals from if these have been specified on a FROZEN card in a previous MCSCF calculation.

20.5.2 Rotating pairs of initial orbitals

ROTATE,*orb1.sym,orb2.sym,angle*

Performs a 2×2 rotation of the initial orbitals *orb1* and *orb2* in symmetry *sym* by *angle* degrees. With *angle*=0 the orbitals are exchanged. ROTATE is meaningful only after the START card. See MERGE for other possibilities to manipulate orbitals.

20.5.3 Saving the final orbitals

ORBITAL,*record.file*

The orbitals are dumped to record *record.file*. Default for *record* is 2140 and *file=2*. This default record number is incremented by one for each subsequent MCSCF calculation in the same job (see section 4.11). Therefore, if several different MCSCF calculations at several geometries are performed in one job, each MCSCF will normally start with appropriate orbitals even if no ORBITAL or START card is present.

The ORBITAL card can be omitted if a NATORB, CANORB or LOCORB card is present, since *orb* can also be specified on these cards (the same defaults for *orb* as above apply in these cases).

20.5.4 Saving the CI vectors and information for a gradient calculation

Old form (obsolete):

SAVE,*cidump,refsav,grdsav*;

New form:

SAVE,[CI=*cidump*,] [REF=*refsav*,] [GRD=*grdsav*];

This directive must be placed before any WF or STATE cards. The options can be given in any order.

cidump: record name for saving the CI vectors. By default, the vectors are only written to a scratch file. If NATORB, CANORB or LOCORB cards are present, *cidump* should be specified on these cards. At present, there is hardly any use of saved CI vectors, and therefore this option is rarely needed.

refsav: record name for saving the orbital configurations and their weights for use in subsequent MULTI or CI calculations using the SELECT directive. If wavefunctions for more than one state symmetry are optimized in a state-averaged calculation, the weights for each state symmetry are saved separately on records $refsav+(istsym-1)*100$, where *istsym* is the sequence number of the WF card in the input. If several NATORB, CANORB, or LOCORB cards are present, the record number is increased by 1000 for each subsequent orbital set. Note that this option implies the use of CSFs, even of no CONFIG card (see section 20.6.1) is present.

grdsav: record name for saving the information which is needed in a subsequent gradient calculation. This save is done automatically to record 5000.1 if the input contains a FORCE or OPTG card, and therefore the GRD option is normally not required.

20.5.5 Natural orbitals

NATORB,[*record*,] [*options*]

Request to calculate final natural orbitals and write them to record *record*. The default for *record* is 2140.2, or what else has been specified on an ORBITAL card, if present. By default, the orbitals are not printed and the hamiltonian is not diagonalized for the new orbitals The following *options* can be specified (in any order):

CI	Diagonalize the hamiltonian in the basis of the computed natural orbitals and print the configurations and their associated coefficients. This has the same effect as the GPRINT,CIVECTOR directive (see section 6.12. By default, only configurations with coefficients larger than 0.05 are printed. This threshold can be modified using the THRESH (see section 20.8.2) or GTHRESH (see section 6.11) options.
STATE=*state*	Compute natural orbitals for the specified state. *state* has the form *istate.isym*, e.g., 3.2 for the third state in symmetry 2. In contrast to earlier versions, *isym* refers to the number of the irreducible representation, and not the sequence number of the state symmetry. It is therefore independent of the order in which WF cards are given. The specified state must have been optimized. If STATE is not given and two or more states are averaged, the natural orbitals are calculated with the state-averaged density matrix (default).
SPIN=*ms2*	Compute natural orbitals for states with the specified spin. *ms2* equals $2*S$, i.e., 0 for singlet, 1 for doublet etc. This can be used to together with STATE to select a specific state in case that states of different spin are averaged. If STATE is not specified, the state-averaged density for all states of the given spin is used.

SAVE=*record*	Request to save the civector(s) to the specified record.
ORBITAL=*record*	Request to save the orbitals to the specified record (same effect as specifying *record* as first agrument (see above).
PRINT=*nvirt*	Request to print *nvirt* virtual orbitals in each symmetry. By default, the orbitals are not printed unless the ORBPRINT option (see section 20.8.1 is present or the global GPRINT,ORBITALS (see section 6.12) directive has been given before. The PRINT option on this card applies only to the current orbitals.

Several NATORB, CANORB, and LOCORB cards (for different states) may follow each other. In contrast to earlier versions of MOLPRO the different orbital sets can all be stored in one dump record (but different records still work). See section 4.11 for information about dump records and how specific orbital sets can be requested in a later calculation.

20.5.6 Pseudo-canonical orbitals

CANORB,[*record*,] [*options*]

or

CANONICAL,[*record*,] [*options*]

Request to canonicalize the final orbitals, and writing them to record *record*. All options have the same effect as described for NATORB.

20.5.7 Localized orbitals

LOCORB,[*record*,] [*options*]

or

LOCAL,[*record*,] [*options*]

Request to localize the final orbitals, and writing them to record *record*. All options have the same effect as described for NATORB.

Note: LOCAL is interpreted by MULTI, but LOCALI is a separate command which calls the localization program and not recognized by MULTI. In order to avoid confusion, it is recommended to use LOCORB rather then LOCAL as subcommand within MULTI.

20.5.8 Diabatic orbitals

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using using the new DIAB command in the MCSCF program. Only the active orbitals are transformed.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a DIAB directive to the input:

Old form (Molpro96, obsolete):

DIAB,*orbref, orbsav, orb1,orb2,pri*

New form:

DIAB,*orbref*[,TYPE=*orbtype*] [,STATE=*state*] [,SPIN=*spin*] [,*MS2=ms2*] [,SAVE=*orbsav*] [,ORB1=*orb1*, ORB2=*orb2*] [,*PRINT=pri*] [,*METHOD=method*]

Here *orbref* is the record holding the orbitals of the reference geometry, and *orbsav* is the record on which the new orbitals are stored. If *orbsav* is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the ORBITAL directive (see section 20.5.3). In contrast to earlier versions of MOLPRO it is possible that *orbref* and *orbsav* are the same. The specifications TYPE, STATE, SPIN can be used to select specific sets of reference orbitals, as described in section 4.11. *orb1, orb2* is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form *number.sym*, e.g. 3.1 means the third orbital in symmetry 1. If *orb1, orb2* are not given, the overlap of all active orbitals is maximized. *pri* is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each Jacobi iteration. *method* determines the diabatization method. *method=1* (default): use Jacobi rotations; *method=2*: use block diagonalization. Both methods yield very similar results. *method=2* must only be used for CASSCF wavefunctions. *method=-1* and *method=-2*: as the positive values, but AO overlap matrix of the current geometry is used. This minimizes the change of the MO coefficients, rather than maximizing the overlap to the neighbouring orbitals.

Using the defaults described above, the following input is sufficient in most cases:

DIAB,*orbref*

Using Molpro98 is is not necessary any more to give any GEOM and DISPL cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. **89**, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. **89**, 7367 (1988). Recently, an automatic procedure, as described in J. Chem. Phys. **102**, 0000, (1999) has been implemented into MOLPRO. This is available in Version 99.1 and later and is described in section 35.

Below we present an example for the first two excited states of H_2S, which have B_1 and A_2 symmetry in C_{2v}, and A'' symmetry in C_S. We first perform a reference calculation in C_{2v} symmetry, and then determine the diabatic orbitals for displaced geometries in C_S symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the C_{2v} calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets reforb=2141.2.

```
! $Revision: 2006.0 $
***,H2S diabatic A" states

basis=VDZ                                !use cc-pVDZ basis set
geometry={x;                             !use Cs symmetry
          planeyz;                       !fix orientation of the molecule
          noorient                       !dont allow automatic reorientation
          s;h1,s,r1;h2,s,r2,h1,theta}    !Z-matrix geometry input

gprint,orbitals,civector                 !global print options

text,reference calculation for C2V
theta=92.12,r1=2.3,r2=2.3                !reference geometry

{hf;occ,7,2;wf,18,1}                     !scf calculation for ground state

{multi;occ,9,2;closed,4,1;               !define active and inactive spaces
wf,18,2;state,2;                         !two A" states (1B1 and 1A2 in C2v)
orbital,2140.2}                          !save orbitals to 2140.2
reforb=2140.2

text,calculations at displaced geometries

rd=[2.4,2.5,2.6]                         !define a range of bond distances

do i=1,#rd                               !loop over displaced geometries

r2=rd(i)                                 !set r2 to current distance

{multi;occ,9,2;closed,4,1;               !same wavefunction definition as at reference geom.
wf,18,2;state,2;
orbital,2141.2                           !save new orbitals to record
diab,reforb}                             !compute diabatic orbitals using reference orbitals
                                         !stored on record reforb
reforb=2141.2                            !set variable reforb to the new orbitals.
enddo
```

examples/
h2s˙diab.com

See section 35 for the automatic generation of diabatic energies.

20.6 Selecting the optimization methods

By default, MULTI uses the non-linear optimization method developed by Werner, Meyer, and Knowles. Other methods, such as the Newton-Raphson procedure or the Augmented Hessian procedure, are also implemented and can be selected using the ITERATIONS directive (for state-averaged calculations, only the non-linear optimization method can be used). For CASSCF calculations, the CI problem is solved in a basis of Slater determinants, unless a CONFIG card is given. Some procedures may be disabled using the DONT directive.

20.6.1 Selecting the CI method

CONFIG,*key*;

key may be DET or CSF, and defaults to CSF. If no CONFIG or SELECT card is given, the default is determinants (CASSCF).

20.6.2 Selecting the orbital optimization method

The ITERATIONS directive can be use to modify the defaults for the optimization method. It consists of a sequence of several cards, ending with an END card.

```
ITERATIONS;
DO,method1,iter1[,TO,iter2];
DONT,method2,iter3[,TO,iter4];
...
END;
```

method can be one of the following:

DIAGCI	Diagonalize hamiltonian in the beginning of the specified iterations. This is the default for iteration 1.
INTERNAL	Optimize internal orbitals at the beginning of the specified iterations. This is default for second and subsequent iterations.
WERNER	use Werner-Meyer-Knowles non-linear optimization method for the specified iterations. This is the default for all iterations.
AUGMENT	Use step-restricted Augmented Hessian method for the specified iterations.
NEWTON	Use Newton-Raphson method for specified iterations.
UNCOUPLE	Do not optimize orbitals and CI coefficients simultaneously in the specified iterations. This option will set DIAGCI for these iterations.
NULL	No orbital optimization.

20.6.3 Disabling the optimization

In addition to the ITERATIONS directive described above, some procedures can be be disabled more simply using the DONT directive. DONT,*code*

code may be

ORBITAL	Do initial CI but don't optimize orbitals.
WAVEFUNC	Do not optimize the orbitals and CI coefficients (i.e. do only wavefunction analysis, provided the orbitals and CI coefficients are supplied (see START card)).
WVFN	Alias for WAVEFUNC.
ANAL	Do no wavefunction analysis.

20.6.4 Disabling the extra symmetry mechanism

NOEXTRA

This card disables the search for extra symmetries. By default, if extra symmetries are present, each orbital is assigned to such an extra symmetry and rotations between orbitals of different extra symmetry are not performed.

20.7 Calculating expectation values

By default, the program calculates the dipole expectation and transition moments. Further expectation values or transition properties can be computed using the TRAN, TRAN2 and EXPEC, EXPEC2 directives.

20.7.1 Matrix elements over one-electron operators

EXPEC,$oper_1, oper_2, \ldots, oper_n$
TRAN,$oper_1, oper_2, \ldots, oper_n$

Calculate expectation values and transition matrix elements for the given one-electron operators. With EXPEC only expectation values are calculated. $oper_i$ is a codeword for the operator. The available operators and their associated keywords are given in section 6.13.

20.7.2 Matrix elements over two-electron operators

EXPEC2,$oper_1, oper_2, \ldots, oper_n$
TRAN2,$oper_1, oper_2, \ldots, oper_n$

Calculate transition matrix elements for two-electron operators. This is presently only useful for angular momentum operators. With EXPEC2 only diagonal matrix elements will be computed. For instance

TRAN2,LXX	calculates matrix elements for L_x^2
TRAN2,LYY	calculates matrix elements for L_y^2
TRAN2,LXZ	calculates matrix elements for $\frac{1}{2}(L_xL_z + L_zL_x)$
TRAN2,LXX,LYY,LZZ	calculates matrix elements for L_x^2, L_y^2, and L_z^2. The matrix elements for the sum L^2 are also printed.

20.7.3 Saving the density matrix

DM,[*spindens*]

If the DM directive is given, the first order density matrix in AO basis is written to the dump record specified on the ORBITAL card (default 2140.2). If no ORBITAL card is present, but a record is specified on a NATORB, CANORB, or LOCORB card, the densities are saved to the first record occurring in the input. In a state-averaged calculation the SA-density, as well the individual state densities, are saved. See section 4.11 for information about how to recover any of these densities for use in later programs.

Of *spindens* is a number greater than zero, the spin density matrices are also saved. Note that a maximum of 50 density matrices can be saved in one dump record.

If no DM directive is given), the first order density matrix is saved in single-state calculations, and only the stage-averaged density matrix in state-averaged calculations.

20.8 Miscellaneous options

All commands described in this section are optional. Appropriate default values are normally used. Note that printing of the orbitals and civectors can also be requested using the global GPRINT command, or by giving NATORB or CANORB options.

20.8.1 Print options

ORBPRINT[,*nvirt*]

requests the occupied and *nvirt* virtual orbitals in each symmetry to be printed (default *nvirt*=0). By default, the program does not print the orbitals, unless the ORBPRINT directive or a global GPRINT,ORBITALS (see section 6.12) command is present. Specific orbital sets can be printed using the PRINT option on a NATORB, CANORB, or LOCORB card (see section 20.5.5). To print additional information at the end of the calculation, use

PRINT,*key1,key2,...*;

Printing is switched on for *key1*, *key2*,.... To print information in each iteration, use

IPRINT,*key1,key2,...*;

Possible print keys are:

MICRO	print details of "microiterations" — useful for finding out what's going wrong if no convergence
REF	print summary of configuration set (CSFs only)
REF1	print list of configuration set (CSFs only)
COR	print summary of intermediate spaces used in CSF calculation
COR1	print list of intermediate configuration sets (CSFs only)
PSPACE	print list of configurations making up the "primary" space
ORBITALS	print orbitals (see also ORBPRINT)
NATORB	print natural orbitals (see also ORBPRINT)
VIRTUALS	print virtual orbitals (see also ORBPRINT)
CIVECTOR	print CI vector (better use CANORB or NATORB)
INTEGRAL	print transformed integrals (for testing only!)
DENSITY	print density matrices
HESSIAN	print hessian
DIAGONAL	print diagonal elements of hessian
GRADIENT	print gradient
LAGRANGI	print Lagrangian
STEP	print update vector
ADDRESS	print addressing information (for testing only!)
DEBUG	print debugging information
CI2	print debugging information in routine ci2 (Warning: may be long!!)
IO	print debugging information in I/O routines

20.8.2 Convergence thresholds

Convergence thresholds can be modified using

ACCURACY,[GRADIENT=*conv*] [,STEP=*sconv*] [,ENERGY=*econv*]

where

conv	Threshold for orbital gradient (default 10^{-2}).)
econv	Threshold for change of total energy (default 10^{-6}).
`sconv`	Threshold for size of step (default 10^{-3}).

The default values can be modified using the global `GTHRESH` command (see section 6.11). Normally, the above default values are appropriate.

20.8.3 Maximum number of iterations

`MAXITER`,*maxit*;

maxit is maximum number of iterations (default 6). If the calculation does not converge in the default number of iterations, you should first think about the reason before increasing the limit. In most cases the choice of active orbitals or of the optimized states is not appropriate (see introduction of MULTI)

20.8.4 Test options

`TEST`,$i1, i2, i3, \ldots$;

Activate testing options numbered $i1$, $i2$, ... Please do not use unless you know what you are doing!

20.8.5 Special optimization parameters

The following parameters can also be given as options on the `MULTI` command line.

`STEP`,*radius,trust1,tfac1,trust2,tfac2*;

Special parameters for augmented hessian method. For experts only!

`GOPER`,*igop*;

Use G-operator technique in microiterations (Default). If igop.lt.0 do not use G-operators.

`COPT`,*ciacc,copvar,maxci,cishft,icimax,icimx1,icimx2,icstrt,icstep*;

Special parameters for the direct CI method. For experts only!

ciacc	grad threshold for CI diagonalization
copvar	start threshold for CI-optimization
maxci	max. number of CI-optimizations per microiteration
cishft	denominator shift for q-space
icimax	max. number of CI-optimizations in first macroiteration
icimx1	max. number of CI-optimizations in second and subsequent iterations
icimx2	max. number of CI-optimizations in internal absorption step
icstrt	first microiteration with CI-optimization
icstep	microiteration increment between CI-optimizations

INTOPT,*maxito,maxitc,maxrep,nitrep,iuprod*;

Special parameters for internal optimization scheme. For experts only!

NONLINEAR,*itmaxr,ipri,drmax,drdamp,gfak1,gfak2,gfak3,irdamp,ntexp*

Special parameters for non-linear optimization scheme. For experts only!

Old form (obsolete):

THRESH,*thrpri,thrpun,varmin,varmax,thrdiv,thrdoub*

New form:

THRESH [,THRPRI=*thrpri*] [,THRPUN=*thrpun*] [,VARMIN=*varmin*]
[,VARMAX=*varmax*] [,THRDIV=*thrdiv*] [,THRDOUB=*thrdoub*]

thrpri	threshold for printing CI coefficients (default 0.04)
thrpun	threshold for writing CI coefficients to the punch file. Default is no write to the punch file
varmin,varmax	thresholds for non-linear optimization scheme. For experts only!
thrdoub	threshold for detecting almost doubly occupied orbitals for inclusion into the pseudo canonical set (default 0, i.e. the feature is disabled).

DIIS,*disvar,augvar,maxdis,maxaug,idsci,igwgt,igvec,idstrt,idstep*;

Special parameters for DIIS convergence acceleration. For experts only!

20.8.6 Saving wavefunction information for CASVB

VBDUMP[,*vbdump*];

For users of the valence bond program *CASVB*, all wavefunction information that may subsequently be required is saved to the record *vbdump*. The default is not to write this information. If the keyword is specified without a value for *vbdump*, then record 4299.2 is used. This keyword is not needed prior to variational *CASVB* calculations.

20.8.7 Saving transformed integrals

TRNINT,*trnint*;

trnint specifies the record name for integrals in the basis of active CASSCF MOs. These are used for example by *CASVB* (see section 36.5). The default value for *trnint* is 1900.1.

20.9 Coupled-perturbed MCSCF

The coupled-perturbed MCSCF is required for computing gradients with state-averaged orbitals, non-adiabatic couplings, difference gradients or polarizabilities. We note that the present implementation is somewhat preliminary and not very efficient.

20.9.1 Gradients for SA-MCSCF

For computing state-averaged gradients, use

CPMCSCF,GRAD,*state*,[SPIN=*spin*],[MS2=*ms2*],[ACCU=*thresh*],[RECORD=*record*]

where *state* specifies the state (e.g., 2.1 for the second state in symmetry 1) for which the gradients will computed. *spin* specifies the spin of the state: this is half the value used in the corresponding WF card (e.g., 0=Singlet, 0.5=Doublet, 1=Triplet). Alternatively, MS2 can be used, where *ms2* = 2*spin, i.e., the same as specified on WF cards. The specification of SPIN or MS2 is only necessary if states with different spin are state-averaged. *record* specifies a record on which the gradient information is stored (the default is 5101.1). *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to FORCES or OPTG.

Note: if for some reason the gradients are to be computed numerically from finite energy differences, it is in state-averaged calculations necessary to give, instead of the CPMCSCF input, the following:

SAVE,GRAD=-1

Otherwise the program will stop with an error message.

20.9.2 Difference gradients for SA-MCSCF

For computing difference gradients, use

CPMCSCF,DGRAD,*state1*,*state2*,[ACCU=*thresh*],[RECORD=*record*]

where *state1* and *state2* specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) The gradient of the energy difference will be computed. Both states must have the same symmetry. *record* specifies a record on which the gradient information is stored (the default is 5101.1). *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to FORCES or OPTG.

20.9.3 Non-adiabatic coupling matrix elements for SA-MCSCF

For computing non-adiabatic coupling matrix elements analytically, use

CPMCSCF,NACM,*state1*,*state2*,[ACCU=*thresh*],[RECORD=*record*]

where *state1* and *state2* specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) Both states must have the same symmetry. *record* specifies a record on which the gradient information is stored (the default is 5101.1). This will be read in the subsequent gradient calculation. *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

NADC and NADK are an aliases for NADC, and SAVE is an alias for RECORD.

The matrix elements for each atom are computed by a subsequent call to FORCES.

Note: this program is not yet extensively tested and should be used with care!

20.10 Optimizing valence bond wavefunctions

VB={...}

Using this keyword, the optimization of the CI coefficients is carried out by *CASVB*. The VB keyword can be followed by any of the directives described in section 36. Energy-based optimization of the VB parameters is the default, and the output level for the main *CASVB* iterations is reduced to -1.

20.11 Hints and strategies

MCSCF is not a "black box" procedure like SCF! For simple cases, for example a simple CASSCF with no CLOSED orbitals, this program will converge in two or three iterations. For more complicated cases, you may have more trouble. In that case, consider the following:

- Always start from neighbouring geometry orbitals when available (this is the default).
- The convergence algorithm is more stable when there are no CLOSED orbitals, i.e., orbitals doubly occupied in all configurations, but fully optimized. Thus a reasonable approach is to make an initial calculation with CLOSED replaced by FROZEN (all doubly occ. frozen).
- If still no success, you can switch off the coupling between CI coefficients and orbital rotations for a few iterations, e.g.:

  ITERATIONS;UNCOUPLE,1,TO,2;END;

  and/or disable the simultaneous optimization of internal orbitals & CI, e.g.:

  ITERATIONS;DONT,INTERNAL,1,TO,2;END;

You can often get a clue about where the program starts to diverge if you include:

IPRINT,MICRO;

in the data. Also consider the general remarks at the beginning of this chapter. For the details of the algorithms used, see J. Chem. Phys 82, 5053 (1985); Chem. Phys. Letters 115, 259 (1985); Advan. Chem. Phys. 59, 1 (1987);

20.12 Examples

The simplest input for a CASSCF calculation for H_2O, C_{2v} symmetry, is simply:

```
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle                    examples/
hf                                    !do scf calculation            h2o˙casscf.com
multi                                 !do full valence casscf
```

This could be extended, for instance, by the following input cards

```
OCC,4,1,2;        !  specify occupied space
CLOSED,2          !  specify closed-shell (inactive) orbitals
FROZEN,1;         !  specify frozen core orbitals
WF,10,1;          !  define wavefunction symmetry
START,2100.2;     !  read guess orbitals from record 2100, file 2
ORBITAL,2140.2;   !  save final orbitals to record 2140, file 2
NATORB,PRINT,CI   !  print natural orbitals and diagonalize the hamiltonian
                  !  for the natural orbitals. The largest CI coefficients
                  !  are printed.
```

Example for a state-averaged calculation for CN, X and $B\ ^2\Sigma^+$ states, and $A\ ^2\Pi_x$, $^2\Pi_y$ states averaged. A full valence CASSCF calculation is performed

examples/cn˙sa˙casscf.com

```
! $Revision: 2006.0 $
***,cn
r=2.2                              !define bond length
geometry={c;n,c,r}
{rhf;occ,5,1,1;wf,13,1,1;             !RHF calculation for sigma state
orbital,2100.2}                      !save orbitals to record 2100.2 (default)

{multi;occ,6,2,2;closed,2;             !Define active and inactive orbitals
start,2100.2;                        !Start with RHF orbitals from above
save,ref=4000.2                      !Save configuration weights for CI in record 4000.2
wf,13,1,1;state,2;wf,13,2,1;wf,13,3,1;!Define the four states
natorb,ci,print;                     !Print natural orbitals and associated ci-coefficients
tran,lz                              !Compute matrix elements over LZ
expec2,lzz}                          !compute expectation values for LZZ
```

Example for an RASSCF (restricted active space) calculation for N_2, including SCF determinant plus all double excitations into valence orbitals. The single excitations are excluded. D_{2h} symmetry, CSF method used:

examples/n2˙rasscf.com

```
! $Revision: 2006.0 $
***,N2
geometry={N1;N2,N1,r}                !geometry input
r=2.2                                !bond length
{hf;occ,3,1,1,,2;wf,14,1;save,2100.2} !scf calculation

{multi;occ,3,1,1,,3,1,1;             !Define occupied orbitals
freeze,1,,,,1,2100.2;                  !Define frozen core scf orbitals
config;                              !Use CSF method
wf,14,1;                             !Define state symmetry
restrict,0,2,3.5,1.6,1.7;            !Restriction to singles and doubles
restrict,-1,-1,3.5,1.6,1.7;          !Take out singles
print,ref1                           !Print configurations
natorb,ci,print}                     !Print natural orbitals and CI coeffs
```

21 THE CI PROGRAM

Multiconfiguration reference internally contracted configuration interaction

Bibliography:

H.-J. Werner and P.J. Knowles, J. Chem. Phys. 89, 5803 (1988).
P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. 145, 514 (1988).

All publications resulting from use of this program must acknowledge the above. See also:

H.-J. Werner and E.A. Reinsch, J. Chem. Phys. 76, 3144 (1982).
H.-J. Werner, Adv. Chem. Phys. 59, 1 (1987).

The command `CI` or `CI-PRO` calls the program. The command `CISD` calls fast closed-shell CISD program. The command `QCI` calls closed-shell quadratic CI program. The command `CCSD` calls closed-shell coupled-cluster program.

The following options may be specified on the command line:

`NOCHECK`	Do not stop if no convergence.
`DIRECT`	Do calculation integral direct.
`NOSING`	Do not include singly external configurations.
`NOPAIR`	Do not include doubly external configurations (not valid for single reference methods).
`MAXIT=`*value*	Maximum number of iterations.
`MAXITI=`*value*	Maximum number of microiterations (for internals).
`SHIFTI=`*value*	Denominator shift for update of internal configurations.
`SHIFTS=`*value*	Denominator shift for update of singles.
`SHIFTP=`*value*	Denominator shift for update of doubles.
`THRDEN=`*value*	Convergence threshold for the energy.
`THRVAR=`*value*	Convergence threshold for the CI-vector. This applies to the square sum of the changes of the CI-coefficients.

21.1 Introduction

The internally contracted MRCI program is called by the CI command. This includes as special cases single reference CI, CEPA, ACPF, MR-ACPF and MR-AQCC. For closed-shell reference functions, a special faster code exists, which can be called using the CISD, QCI, or CCSD commands. This also allows to calculate Brueckner orbitals for all three cases (QCI and CCSD are identical in this case).

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the `OCC`, `CORE`, `CLOSED`, `WF`, `SELECT`, `CON`, and `RESTRICT` cards. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an `ORBITAL` directive is given. The wavefunction may be saved using the `SAVE` directive, and restarted using `START`. The `EXPEC` directive allows to compute expectation values over one-electron operators, and the `TRAN` directive can be used to compute transition matrix elements for one-electron properties. Natural orbitals can be printed and saved using the `NATORB` directive.

For excited state calculations see `STATE`, `REFSTATE`, and `PROJECT`.

21.2 Specifying the wavefunction

21.2.1 Occupied orbitals

OCC,$n_1,n_2,\ldots,n_8$;

n_i specifies numbers of occupied orbitals (including CORE and CLOSED) in irreducible representation number i. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation.

21.2.2 Frozen-core orbitals

CORE,$n_1,n_2,\ldots,n_8$;

n_i is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no CORE card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

CORE

21.2.3 Closed-shell orbitals

CLOSED,$n_1,n_2,\ldots,n_8$

n_i is the number of closed-shell orbitals in irrep number i, inclusive of any core orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all reference CSFs; however, in contrast to the core orbitals (see CORE), these orbitals are correlated through single and double excitations. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation. For calculations with closed-shell reference function (closed=occ), see CISD, QCI, and CCSD.

21.2.4 Defining the orbitals

ORBIT,*name.file*,[*specifications*];

name.file specifies the record from which orbitals are read. Optionally, various *specifications* can be given to select specific orbitals if *name.file* contains more than one orbital set. For details see section 4.11. Note that the IGNORE_ERROR option can be used to force MPn or triples calculations with non-canonical orbitals.

The default is the set of orbitals from the last SCF, MCSCF or CI calculation.

21.2.5 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF,*elec,sym,spin*

where

elec: is the number of electrons

sym:	is the number of the irreducible representation
spin:	defines the spin symmetry, *spin*$= 2S$ (singlet=0, doublet=1, triplet=2, etc.)

The WF card must be placed after any cards defining the orbital spaces (OCC, CORE, CLOSED.

The REF card can be used to define further reference symmetries used for generating the configuration space, see REF.

21.2.6 Additional reference symmetries

REF,*sym*;

This card, which must come after the WF directive, defines an additional reference symmetry used for generating the uncontracted internal and singly external configuration spaces. This is sometimes useful in order to obtain the same configuration spaces when different point group symmetries are used. For instance, if a calculation is done in C_s symmetry, it may happen that the two components of a Π state, one of which appears in A' and the other in A'', come out not exactly degenerate. This problem can be avoided as in the following example:

for a doublet A' state:

```
WF,15,1,1;      !define wavefunction symmetry (1)
REF,2;          !define additional reference symmetry (2)
```

and for the doublet A" state:

```
WF,15,2,1;      !define wavefunction symmetry (2)
REF,1;          !define additional reference symmetry (1)
```

For linear geometries the same results can be obtained more cheaply using C_{2v} symmetry,

```
WF,15,2,1;      !define wavefunction symmetry (2)
REF,1;          !define additional reference symmetry (1)
REF,3;          !define additional reference symmetry (3)
```

or

```
WF,15,3,1;      !define wavefunction symmetry (2)
REF,1;          !define additional reference symmetry (1)
REF,2;          !define additional reference symmetry (2)
```

Each REF card may be followed by RESTRICT, SELECT, and CON cards, in the given order.

21.2.7 Selecting configurations

SELECT,*ref1,ref2,refthr,refstat,mxshrf*;

This card is used to specify a reference configuration set other than a CAS, which is the default. Configurations can be defined using CON cards, which must appear after the *SELECT* card. Alternatively, if *ref1* is an existing MOLPRO record name, the configurations are read in from that record and may be selected according to a given threshold.

The select card should normally be placed directly after the *WF* or *REF* card(s), or, if present, the RESTRICT cards. The general order of these cards is

WF (or REF)
RESTRICT (optional)
SELECT (optional)
CON (optional)

ref1=rec1.file: (*rec1>2000*) The configurations are read in from the specified record. See section 20.5.4 about how to save the configurations in the MCSCF calculation. If *ref1* is not specified, the program assumes that the configurations are read from subsequent CON cards (see CON).

ref2=rec2.file: (*rec2>2000*) additional configurations are read from the specified record. If *rec2* is negative, all records between *rec1* and abs(*rec2*) are read. All configurations found in this way are merged.

refthr: Selection threshold for configurations read from disc (records *rec1–rec2*). This applies to the norm of all CSFs for each orbital configuration.

refstat: Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If *refstat* is zero or not specified, the configurations are selected from all states. If *refstat* is greater than zero, then the specified reference state is used. If *refstat* is less than zero, then all appropriate reference states are used. Lastly, if *refstat* is of the form *istat1.istat2*, states *istat1* through *istat2* are used.

mxshrf: maximum number of open shells in the selected or generated configurations.

21.2.8 Occupation restrictions

RESTRICT,*nmin,nmax,*orb_1,orb_2,...orb_n;

This card can be used to restrict the occupation patterns in the reference configurations. Only configurations containing between *nmin* and *nmax* electrons in the specified orbitals orb_1, orb_2, ..., orb_n are included in the reference function. If *nmin* and *nmax* are negative, configurations with exactly abs(*nmin*) and abs(*nmax*) electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form *number.sym*, where *number* is the number of the orbital in irrep *sym*. Several RESTRICT cards may follow each other.

The RESTRICT cards must follow the WF or REF cards to which they apply. The general order of these cards is

WF (or REF)
RESTRICT (optional)
SELECT (optional)
CON (optional)

If a RESTRICT cards precedes the WF card, it applies to all reference symmetries. Note that RESTRICT also affects the spaces generated by SELECT and/or CON cards.

21.2.9 Explicitly specifying reference configurations

CON,$n_1,n_2,n_3,n_4,\ldots$

Specifies an orbital configuration to be included in the reference function. n_1, n_2 etc. are the occupation numbers of the active orbitals (0,1,or 2). Any number of CON cards may follow each other, but they must all appear directly after a SELECT card.

21.2.10 Defining state numbers

STATE,*nstate,nroot(1),nroot(2),...,nroot(nstate)*;

nstate is the number of states treated simultaneously; *nroot(i)* are the root numbers to be calculated. These apply to the order of the states in the initial internal CI. If not specified, *nroot(i)=i*. Note that it is possible to leave out states, i.e.,

```
STATE,1,2;    ! calculates second state
STATE,2,1,3;  ! calculates first and third state
```

All states specified must be reasonably described by the internal configuration space. It is possible to have different convergence thresholds for each state (see ACCU card). It is also possible not to converge some lower roots which are included in the list *nroot(i)* (see REFSTATE card). For examples, see REFSTATE card.

21.2.11 Defining reference state numbers

REFSTATE,*nstatr,nrootr(1),nrootr(2),...,nrootr(nstatr)*;

nstatr is the number of reference states for generating contracted pairs. This may be larger or smaller than *nstate*. If this card is not present, *nstatr=nstate* and *nrootr(i)=nroot(i)*. Roots for which no reference states are specified but which are specified on the STATE card (or included by default if the *nroot(i)* are not specified explicitly on the STATE card) will not be converged, since the result will be bad anyway. However, it is often useful to include these states in the list *nroot(i)*, since it helps to avoid root flipping problems. Examples:

```
state,2;
```

will calculate two states with two reference states.

```
state,2;refstate,1,2;
```

will optimize second state with one reference state. One external expansion vector will be generated for the ground state in order to avoid root flipping. The results printed for state 1 are bad and should not be used (unless the pair space is complete, which might happen in very small calculations).

```
state,1,2;refstate,1,2;
```

As the second example, but no external expansion vectors will be generated for the ground state. This should give exactly the same energy for state 2 as before if there is no root flipping (which, however, frequently occurs).

```
state,2;accu,1,1,1;
```

Will calculate second state with two reference states. The ground state will not be converged (only one iteration is done for state 1) This should give exactly the same energy for state 2 as the first example.

21.2.12 Specifying correlation of orbital pairs

PAIR,*iorb1.isy1,iorb2.isy2,np*;

is a request to correlate a given orbital pair.

np=1:	singlet pair
np=-1:	triplet pair
np=0:	singlet and triplet pair (if possible)

Default is to correlate all electron pairs in active and closed orbitals. See also PAIRS card.

PAIRS,*iorb1.isy,iorb2.isy,np*;

Correlate all pairs which can be formed from orbitals *iorb1.isy1* through *iorb2.isy2*. Core orbitals are excluded. Either *iorb2* must be larger than *iorb1* or *isy2* larger than *isy1*. If *iorb1.isy1=iorb2.isy2* the PAIRS card has the same effect as a PAIR card. PAIR and PAIRS cards may be combined.

If no PAIR and no PAIRS card is specified, all valence orbitals are correlated. The created pair list restricts not only the doubly external configurations, but also the all internal and semi internals.

21.2.13 Restriction of classes of excitations

NOPAIR;

No doubly external configurations are included.

NOSINGLE;

No singly external configurations are included.

NOEXC;

Perform CI with the reference configurations only.

21.3 Options

21.3.1 Coupled Electron Pair Approximation

CEPA,*ncepa*;

Instead of diagonalizing the hamiltonian, perform CEPA calculation, CEPA type *ncepa*. This is currently available only for single configuration reference functions.

21.3.2 Coupled Pair Functional (ACPF, AQCC)

CPF,*ncpf,gacpfi,gacpfe*;
ACPF,*ncpf,gacpfi,gacpfe*;
AQCC,*ncpf,gacpfi,gacpfe*;

Instead of diagonalizing the hamiltonian, perform CPF calculation (*ncpf*=2) (not yet implemented) ACPF calculation (*ncpf*=0) or AQCC calculation (*ncpf*=1). For ACPF and AQCC, the

internal and external normalization factors *gacpfi*, *gacpfe* may be reset from their default values of 1, 2/*nelec* and 1, 1-(*nelec*-2)(*nelec*-3)/*nelec*(*nelec*-1), respectively.

The ACPF and related methods are currently not robustly working for excited states. Even though it sometimes works, we do not currently recommend and support these methods for excited state calculations.

21.3.3 Projected excited state calculations

PROJECT,*record,nprojc*;

Initiate or continue a projected excited state calculation, with information stored on *record*. If *nprojc*> 0, the internal CI vectors of *nprojc* previous calculations are used to make a projection operator. If *nprojc*$= -1$, this calculation is forced to be the first, i.e. ground state, with no projection. If *nprojc*$= 0$, then if *record* does not exist, the effect is the same as *nprojc*$= -1$; otherwise *nprojc* is recovered from the dump in *record*. Thus for the start up calculation, it is best to use `project`,*record*,-1; for the following excited calculations, use `project`,*record*; At the end of the calculation, the wavefunction is saved, and the information in the dump *record* updated. The project card also sets the `tranh` option, so by default, transition hamiltonian matrices are calculated.

For example, to do successive calculations for three states, use

```
ci;...;project,3000.3,-1;
ci;...;project,3000.3;
ci;...;project,3000.3;
```

21.3.4 Transition matrix element options

TRANH,*option*;

If *option*> -1, this forces calculation of transition hamiltonian matrix elements in a TRANS or PROJECT calculation. If *option*< 1, this forces calculation of one electron transition properties.

21.3.5 Convergence thresholds

ACCU,*istate,energy,coeff*;

Convergence thresholds for state *istate*. The actual thresholds for the energy and the CI coefficients are 10**(-*energy*) and 10**-(*coeff*). If this card is not present, the thresholds for all states are the default values or those specified on the THRESH card.

21.3.6 Level shifts

SHIFT,*shiftp,shifts,shifti*;

Denominator shifts for pairs, singles, and internals, respectively.

21.3.7 Maximum number of iterations

MAXITER,*maxit,maxiti*;

maxit: maximum number of macroiterations;

maxiti: maximum number of microiterations (internal CI).

21.3.8 Restricting numbers of expansion vectors

MAXDAV,*maxdav,maxvi*;

maxdav: maximum number of external expansion vectors in macroiterations;

maxvi: maximum number of internal expansion vectors in internal CI.

21.3.9 Selecting the primary configuration set

PSPACE,*select,npspac*;

select: energy criterion for selecting p-space configurations. If negative, a test for p-space H is performed.

npspac: minimum number of p-space configurations. Further configurations are added if either required by select or if configurations are found which are degenerate to the last p-space configuration. A minimum number of npspace is automatically determined from the state specifications.

21.3.10 Canonicalizing external orbitals

FOCK,$n_1,n_2,\ldots$;

External orbitals are obtained as eigenfunctions of a Fock operator with the specified occupation numbers n_i. Occupation numbers must be provided for all valence orbitals.

21.3.11 Saving the wavefunction

SAVE,*savecp,saveco,idelcg*;

or

SAVE [,CIVEC=*savecp*] [,CONFIG=*saveco*] [,DENSITY=*dumprec*] [,NATORB=*dumprec*] [,FILES]

savecp: record name for save of wavefunction. If negative the wavefunction is saved after each iteration, else at the end of the job. In case of coupled cluster methods (CCSD, QCISD, BCCD), the wavefunction is saved in each iteration in any case (presently only implemented for the closed-shell case).

saveco: record name for save of internal configurations and their maximum weight over all states for subsequent use as reference input (see SELECT card). If the record already exists, the record name is incremented by one until a new record is created.

idelcg: if nonzero or FILES is specified, don't erase icfil and igfil (holding CI and residual vectors) at the end of the calculation.

dumprec: Dump record for saving density matrix and natural orbitals. Only one dump record must be given. In any case the density matrix and the natural orbitals are saved. See also DM or NATORB cards.

21.3.12 Starting wavefunction

START,*readc1,irest*;

readc1: record name from which the wavefunction is restored for a restart. In the case of coupled cluster methods (CCSD, QCISD, BCCD), the amplitudes are read from record *readc1* and used for restart (presently only implemented for closed-shell methods)

irest: If nonzero, the CI coefficients are read and used for the restart; otherwise, only the wavefunction definition is read in.

21.3.13 One electron properties

EXPEC,$oper_1$,$oper_2$,$oper_3$,...;

After the wavefunction determination, calculate expectation values for one-electron operators $oper_i$. See section 6.13 for the available operators and their keywords. In multi-state calculations or in projected calculations, also the transition matrix elements are calculated.

21.3.14 Transition moment calculations

TRANS,*readc1,readc2*,[BIORTH],[$oper_1$,$oper_2$,$oper_3$,...];

Instead of performing an energy calculation, only calculate transition matrix elements between wavefunctions saved on records *readc1* and *readc2*. See section 6.13 for a list of available operators and their corresponding keywords. If no operator names are specified, the dipole transition moments are calculated.

If option BIORTH is given, the two wavefunctions may use different orbitals. However, the number of active and inactive orbitals must be the same in each case. Note that BIORTH is not working for spin-orbit matrix elements. Under certain conditions it may happen that biorthogonalization is not possible, and then an error message will be printed.

21.3.15 Saving the density matrix

DM,*record.ifil*,[*idip*];

The first order density matrices for all computed states are stored in record *record* on file *ifil*. If *idip* is not zero, the dipole moments are printed starting at iteration *idip*. See also NATORB. In case of transition moment calculation, the transition densities are also stored, provided both states involved have the same symmetry.

21.3.16 Natural orbitals

NATORB,[RECORD=]*record.ifil*,[PRINT=*nprint*],[CORE[=*natcor*]];

Calculate natural orbitals. The number of printed external orbitals in any given symmetry is *nprint*) (default 2). *nprint=-1* suppressed the printing. If *record* is nonzero, the natural orbitals and density matrices for all states are saved in a dump record *record* on file *ifil*. If *record.ifil* is specified on a DM card (see above), this record is used. If different records are specified on the DM and NATORB cards, an error will result. The record can also be given on the SAVE card. If CORE is specified, core orbitals are not printed.

Note: The dump record must not be the same as *savecp* or *saveco* on the SAVE card, or the record given on the PROJECT.

21.3.17 Miscellaneous options

OPTION,*code1=value,code2=value,...*

Can be used to specify program parameters and options. If no codes and values are specified, active values are displayed. The equal signs may be omitted. The following codes are allowed (max 7 per card):

NSTATE:	see state card
NSTATI:	number of states calculated in internal CI
NSTATR:	see refstat card
NCEPA:	see CEPA card
NOKOP:	if nonzero, skip integral transformation
ITRDM:	if .ge. 0 transition moments are calculated
ITRANS:	if nonzero, perform full integral transformation (not yet implemented)
IDIP:	Print dipole moments from iteration number *value*
REFOPT:	if nonzero, optimize reference coefficients; otherwise extract reference coefficients from internal CI
IAVDEN:	average HII and HSS denominators over spin couplings if nonzero
IDELCG:	if.ne.0 then destroy files icfil,igfil at end
IREST:	if nonzero, restart
NATORB:	if nonzero, natural orbitals are calculated and printed. The number of printed external orbitals per symmetry is min(*natorb*,2)
WFNAT:	if nonzero, natural orbitals are saved to this record
IPUNRF:	if nonzero, punch coefficients of reference configurations
NPUPD:	if nonzero, update pairs in nonorthogonal basis, otherwise in orthogonal basis.
MAXIT:	see maxiter card
MAXITI:	see maxiter card
MAXDAV:	see maxdav card
MAXVI:	see maxdav card

NOSING:	see nosing card
NOPAIR:	see nopair card
MXSHRF:	see select card
IKCPS=0:	In CIKEXT, only K(CP) is calculated; this option taken when and only when no singles.
IKCPS=1:	only K(CP') is calculated. Implies that modified coupling coefficients are used.
IKCPS=2:	K(CP) and K(CP') are calculated. Default is IKCPS=2 except when single reference configuration, when IKCPS=1.
IOPTGM:	Option for density matrix routines.
IOPTGM=0:	all quantities in density matrix routines are recalculated for each intermediate symmetry (max. CPU, min. core).
IOPTGM=1:	quantities precalculated and stored on disk (max. I/O, min. core).
IOPTGM=2:	quantities precalculated and kept in core (min. CPU, max. core).
IOPTOR:	If nonzero, calculate intermediate orbitals for each pair. Might improve convergence in some cases, in particular if localized orbitals are used.

21.3.18 Miscellaneous parameters

PARAM,*code1=value,code2=value...*

Redefine system parameters. If no codes are specified, the default values are displayed. The following codes are allowed:

LSEG:	disc sector length
INTREL:	number of integers per REAL*8 word
IVECT=0:	scalar machine
IVECT=1:	vector machine
MINVEC:	call MXMB in coupling coefficient routines if vector length larger than this value.
IBANK:	number of memory banks for vector machines. If IBANK>1, vector strides which are multiples of IBANK are avoided where appropriate.
LTRACK:	number of REAL*8 words per track or block (for file allocation)
LTR:	determines how matrices are stored on disc. If LTR=LSEG, all matrices start at sector boundaries (which optimizes I/O), but unused space is between matrices (both on disc and in core). With LTR=1 all matrices are stored dense. This might increase I/O if much paging is necessary, but reduce I/O if everything fits in core.
NCPUS:	Maximum number of CPUs to be used in multitasking.

21.4 Miscellaneous thresholds

THRESH,*code1=value,code2=value...*

If *value*=0, the corresponding threshold is set to zero, otherwise 10**(-*value*). The equal signs may be omitted. If no codes are specified, the default values are printed. The following codes are allowed (max 7 per card):

ZERO:	numerical zero
THRDLP:	delete pairs if eigenvalue of overlap matrix is smaller than this threshold.
PNORM:	delete pair if its norm is smaller than this threshold (all pairs are normalized to one for a closed shell case).
PRINT:	print CI coefficients which are larger than this value.
INTEG:	omit two-electron integrals which are smaller than this value.
ENERGY:	convergence threshold for energy; see also: ACCU card.
COEFF:	convergence threshold for coefficients; see also: ACCU card.
SPARSE:	omit coefficient changes which are smaller than this value.
EQUAL:	set values in the internal vector and the diagonal elements equal if they differ by less than this value. Useful for keeping track of symmetry.

21.5 Print options

PRINT,*code1=value,code2=value,...*

Print options. Generally, the value determines how much intermediate information is printed. *value*=-1 means no print (default for all codes). In some of the cases listed below the specification of higher values will generate even more output than described. The equal signs and zeros may be omitted. All codes may be truncated to three characters. The following codes are allowed (max 7 per card):

ORBITALS:	print orbitals
JOP=0:	print operator list
JOP=1:	print coulomb operators in MO basis
JOP=2:	print coulomb operators in AO and MO basis
KOP:	as JOP for internal exchange operators
KCP=0:	print paging information for CIKEXT
KCP=1:	print external exchange operators in MO basis
KCP=2:	print operators in AO and MO basis
DM=0:	print paging information for CIDIMA
DM=1:	print density matrix in MO basis
DM=2:	print density matrix in AO and MO basis
FPP=0:	print energy denominators for pairs
FPP=1:	in addition, print diagonal coupling coefficients in orthogonal basis.

FPP=2:	print operators FPP
CP=0:	print update information for pairs in each iteration
CP=1:	print pair matrix updates (MO basis)
CP=2:	in addition print pair matrices (MO basis)
CP=3:	print CP in AO basis (in CIKEXT)
CI=0:	print convergence information for internal CI
CI=1:	print internal CI coefficients and external expansion coefficients
CS:	as CP for singles
CPS=0:	print paging information for CICPS
CPS=1:	print matrices CPS in MO basis
GPP=0:	print paging information for CIGPQ
GPP=1:	print matrices GP at exit of CIGPQ
GPS=0:	print paging information for CIGPS
GPS=1:	print vectors GS at exit CIGPS
GSP=1:	print matrices GP at exit CIGPS
GPI=0:	print paging information for CIGPI
GPI=1:	print total GP in orthogonal basis
GPI=2:	print matrices GP and TP
GIP=0:	print paging information for CIGIP
GIP=1:	print GI at exit CIGIP
GSS=0:	print paging information for CIGSS
GSS=1:	print vectors GS at exit CIGSS
GSI=0:	print paging information for CIGSI
GSI=1:	print GS at exit CIGSI
GIS=0:	print paging information for CIGIS
GIS=1:	print GI at exit CIGIS
GII:	print intermediate information in internal CI
DPQ:	print coupling coefficients $\alpha(P,Q)$
EPQ:	print coupling coefficients $\beta(P,Q)$
HPQ:	print coupling coefficients $\gamma(P,Q)$
DPI:	print coupling coefficients for pair-internal interactions
DSS:	not yet used
DSI:	not yet used
LOG:	At end of each iteration, write summary to log file. Delete at end of job if LOG=0
CC=0:	print address lists for coupling coefficients
CC=1:	print coupling coefficients
DEN=1:	print internal first order density
DEN=2:	print internal second order density
DEN=3:	print internal third order density

DEN=4:	print first, second and third order densities
GAM=1:	print first order transition densities
GAM=2:	print second order transition densities
GAM=3:	print first and second order transition densities
PAIRS=0:	print list of non redundant pairs
PAIRS=1:	print list of all pairs
CORE=0:	print summary of internal configurations ($N, N-1$ and $N-2$ electron)
CORE=1:	print internal configurations ($N, N-1, N-2$)
REF=0:	print summary of reference configurations
REF=1:	print reference configurations and their coefficients
PSPACE:	print p-space configurations
HII:	print diagonal elements for internals
HSS:	print diagonal elements for singles
SPQ:	various levels of intermediate information in pair orthogonalization routine.
TEST=0:	print information at each subroutine call
TEST=1:	print in addition information about I/O in LESW, SREIBW
TEST=2:	print also information about I/O in FREAD, FWRITE
CPU:	print analysis of CPU and I/O times
ALL:	print everything at given level (be careful!)

21.6 Examples

examples/h2o˙cepa1.com

```
! $Revision: 2006.0 $
***,Single reference CISD and CEPA-1 for water
r=0.957,angstrom
theta=104.6,degree;
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
{hf;wf,10,1;}                          !TOTAL SCF ENERGY     -76.02680642
{ci;occ,3,1,1;core,1;wf,10,1;}         !TOTAL CI(SD) ENERGY  -76.22994348
{cepa(1);occ,3,1,1;core,1;wf,10,1;}    !TOTAL CEPA(1) ENERGY -76.23799334
```

examples/h2op˙mrci˙trans.com

```
! $Revision: 2006.0 $
***,Valence multireference CI for X and A states of H2O
gthresh,energy=1.d-8
r=0.957,angstrom,theta=104.6,degree;
geometry={O;              !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
{hf;wf,10,1;}          !TOTAL SCF ENERGY               -76.02680642
{multi;occ,4,1,2;closed,2;freeze,1;wf,9,2,1;wf,9,1,1;tran,ly}
                      !MCSCF ENERGY                   -75.66755631
                      !MCSCF ENERGY                   -75.56605896
{ci;occ,4,1,2;closed,2;core,1;wf,9,2,1;save,7300.1}
                      !TOTAL MRCI ENERGY              -75.79831209
{ci;occ,4,1,2;closed,2;core,1;wf,9,1,1;save,7100.1}
                      !TOTAL MRCI ENERGY              -75.71309879
{ci;trans,7300.1,7100.1,ly}
                      !Transition moment <1.3|X|1.1> = -0.14659810  a.u.
                      !Transition moment <1.3|LY|1.1> = 0.96200488i a.u.
```

examples/
bh˙mrci˙sigma˙delta.c

```
***,BH singlet Sigma and Delta states
r=2.1
geometry={b;h,b,r}
{hf;occ,3;wf,6,1;}
{multi;
occ,3,1,1;frozen,1;wf,6,1;state,3;lquant,0,2,0;wf,6,4;lquant,2;
tran,lz;
expec2,lzlz;}
! Sigma states -- energies -25.20509620 -24.94085861
{ci;occ,3,1,1;core,1;wf,6,1;state,2,1,3;}
! Delta states -- energies -24.98625171
{ci;occ,3,1,1;core,1;wf,6,1;state,1,2;}
! Delta state -- xy component
{ci;occ,3,1,1;core,1;wf,6,4;}
```

22 MULTIREFERENCE RAYLEIGH SCHRÖDINGER PERTURBATION THEORY

Bibliography:

Original RS2/RS3:

H.-J. Werner, Mol. Phys. 89, 645-661 (1996)

New internally contracted RS2C:

P. Celani and H.-J. Werner, J. Chem. Phys. 112, 5546 (2000)

All publications resulting from use of this program must acknowledge the above.

The commands

`RS2`,*options*
`RS2C`,*options*
`RS3`,*options*

are used to perform second or third-order perturbation calculations. `RS3` always includes `RS2` as a first step. For closed-shell single-reference cases, this is equivalent to `MP2` or `MP3` (but a different program is used). `RS2C` calls a new more efficient second-order program (see below), which should normally be used if third-order is not required (note that `RS3C` is not available).

Options can be the following:

`Gn`	Use modified zeroth order Hamiltonian, see section 22.4
`SHIFT`=*value*	Level shift, see section 22.5
`MIX`=*nstates*	Invokes multi-state (MS-CASPT2) treatment using *nstates* states. See section 22.3 for more details.
`ROOT`=*ioptroot*	Root number to be optimized in geometry optimization. This refers to the *nstates* included in the MS-CASPT2. See section 22.7 for more details.
`SAVEH`=*record*	Record for saving the effective Hamiltonian in MS-CASPT2 calculations. If this is not given, a default record will be used (recommended).
`INIT`	(logical) Initializes a MS-CASPT2 with single state reference functions, see section 22.3
`IGNORE`	(logical) Flags an approximate gradient calculation without CP-CASPT2; see section 22.7 for details.

In addition, all valid options for `MRCI` can be given (see Sect. 21).

22.1 Introduction

Multireference perturbation calculations are performed by the MRCI program as a special case. For RS2 (CASPT2,RASPT2) only matrix elements over a one-electron operator need to be computed, and therefore the computational effort is much smaller than for a corresponding MRCI. For RS3 (CASPT3) the energy expectation value for the first-order wavefunction must be computed and the computational effort is about the same as for one MRCI iteration. The

RS2 and RS3 programs use the same configuration spaces as the MRCI, i.e., only the doubly external configurations are internally contracted.

A new version of the program has been implemented in which also subspaces of the singly external and internal configuration spaces are internally contracted (see reference given above). This program, which is called using the keyword `RS2C`, is more efficient than `RS2`, in particular for large molecules with many closed-shell (inactive) orbitals. It is recommended to use this program for normal applications of second-order multireference perturbation theory (CASPT2, RASPT2). Note that it gives slightly different results than `RS2` due to the different contraction scheme. It should also be noted that neither `RS2` or `RS2C` are identical with the CASPT2 of Roos et al. [J. Chem. Phys. **96**, 1218 (1992)], since certain configuration subspaces are left uncontracted. However, the differences are normally very small. The last point that should be mentioned is that the calculation of CASPT2/RASPT2 density matrices (and therefore molecular properties) is presently possible only with the RS2 command and *not* with RS2C.

The results of multireference perturbation theory may be sensitive to the choice of the zeroth-order Hamiltonian. This dependence is more pronounced in second-order than in third-order. Several options are available, which will be described in the following sections. It may also happen that $(\hat{H}^{(0)} - E^{(0)})$ in the basis of the configuration state functions becomes (nearly) singular. This is known as "intruder state problem" and can cause convergence problems or lead to a blow-up of the wavefunction. Often, such problems can be eliminated by including more orbitals into the reference wavefunction, but of course this leads to an increase of the CPU time. The use of modified Fock operators (see below) or level shifts, as proposed by Roos and Andersson [Chem. Phys. Lett. **245**, 215 (1995)] may also be helpful. Presently, only "real" level shifts have been implemented.

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the `OCC`, `CORE`, `CLOSED`, `WF`, `SELECT`, `CON`, and `RESTRICT` cards, as described for the `CI` program. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an `ORBITAL` directive is given.

For a CASPT2 calculation, the zeroth-order Hamiltonian can be brought to a block-diagonal form when (pseudo)canonical orbitals are used. This leads to fastest convergence. It is therefore recommended that in the preceding `MULTI` calculation the orbitals are saved using the `CANONICAL` directive (note that the default is `NATORB`).

Most options for MRCI calculations (like `STATE`, `REFSTATE` etc.) apply also for RS2(C) and RS3 and are not described here again. Some additional options which specific for CASPT2/3 and are described below.

22.2 Excited state calculations

There are two possibilities to perform excited state calculations:

1) One can calculate each state separately. This is done using the card

`STATE`,1,*root*

where *root* is the desired root (i.e., 2 for the first excited state). In this case the Fock operator used in the zeroth-order Hamiltonian is computed using the density for the given state.

2) Alternatively, two or more states can be computed simultaneously, using

`STATE`, *n* [,*root1, root2, . . . , rootn*]

where *n* is the number of states to be computed. The default is to compute the lowest *n* roots. Optionally, this default can be modified by specifying the desired roots *rooti* as shown. One should note that this *does not* correspond to the multi-state CASPT2 as described in section 22.3.

In the case that several states are computed simultaneously, the fock operator employed in the zeroth-order Hamiltonian is computed from a state-averaged density matrix, and the zeroth-order Hamiltonians for all states are constructed from the same fock operator. By default, equal weights for all states are used. This default can be modified using the `WEIGHT` directive

`WEIGHT`,*w1, w2,...,wn.*

If a `REFSTATE` card is given (see section 21.2.11), the state-averaged fock operator is made for all reference states, and the `WEIGHT` card refers to the corresponding states.

22.3 Multi-State CASPT2

Multi-state CASPT2 is implemented as described by Finley et al. CPL **288**, 299 (1998). Currently this can only be used with the `RS2` program (i.e., not with `RS2C`). There are two different modes in which MS-CASPT2 calculations can be performed:

(i) Each of the states to be mixed is computed independently, and finally all states are mixed. In the following, such calculations will be denoted SS-SR-CASPT2 (single-state, single reference CASPT2). There is one contracted reference state for each CASPT2 calculation that is specific for the state under consideration. This is the cheapest method, but there are no gradients available in this case. It is the users responsibility to make sure that no state is computed twice.

(ii) All *nstates* states are treated together, with *nstates* contracted reference states. This is more expensive, but should give a more balanced description since the different reference states can mix in the CASPT2. It is required that *nstates* equals the number of states specified on the `STATE` directive. For this case, denoted "MS-MR-CASPT2" (multi-state multi reference CASPT2), analytical energy gradients are available, see section 22.7

22.3.1 Performing SS-SR-CASPT2 calculations

If one wants to mix together *nstates* CASPT2 wavefunctions, a *nstates* single-state, single-reference CASPT2 calculations must be run.

The first calculation must use

{`RS2,MIX=`*nstates*, `INIT`, *options*
`STATE,1,1;`}

and the subsequent ones

{`RS2,MIX=`*nstates*, *options*
`STATE,1,`*istate*;}

for $istate = 2,\ldots,nstates$. Further *options* can be given, for instance a level shift.

At the end of each calculation, the CASPT2 wavefunction is stored, and at the end of the last CASPT2 calculation the Bloch Hamiltonian and the corresponding overlap matrix are automatically assembled and printed. The Hamiltonian is diagonalized after symmetrization following Brandow IJQC 15, 207 (1979), as well as with simple half-sum (averaging). The MS-CASPT2 energy and mixing coefficients printed in each case.

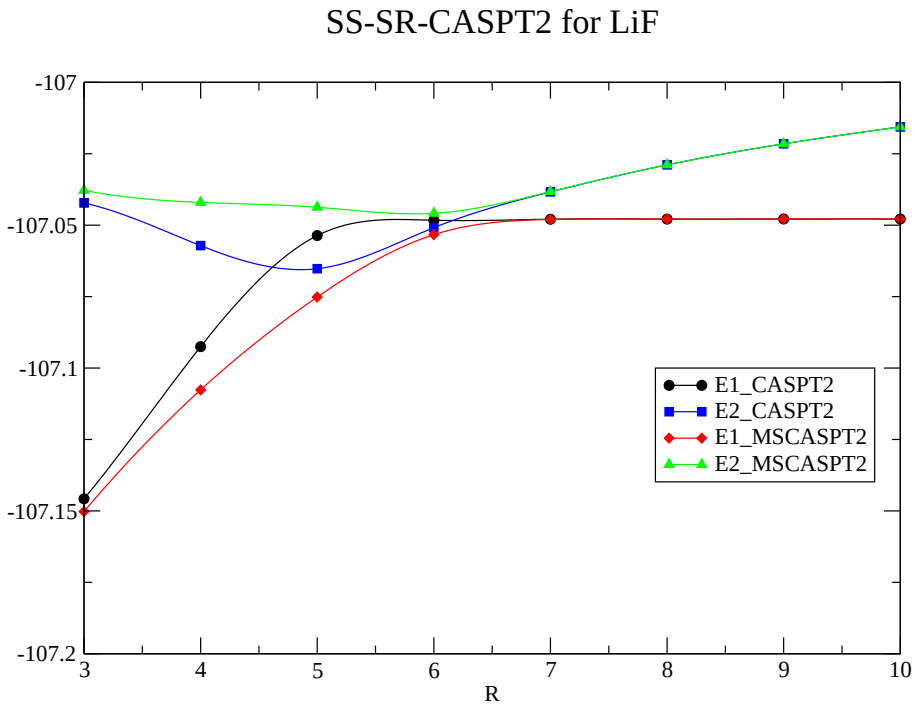
The variable MSENERGY(i) (with i=1,...nstates) is set to the multi-state energies obtained with half-sum diagonalization. If a Level Shift is present, MSENERGY(i) contains the multi-state energies obtained with half-sum diagonalization of the Bloch Hamiltonian whose diagonal elements (CASPT2 energies) have been corrected with the level shift.

Example: SS-SR-CASPT2 calculation for LiF

examples/
lif˙sr˙mscaspt2.com

```
! $Revision: 2006.1 $
r=[3,4,5,6,7,8,9,10] ang

i=1
geometry={Li
          F,1,r(i)}

basis=vtz,F=avtz

hf                      !Hartree-Fock

do i=1,#r               !loop over range of bond distances
{multi
closed,3,0,0,0
occ,   5,2,2,0
state,2                 !SA-CASSCF for 2 states
canonical,ci}

{rs2,MIX=2,INIT
state,1,1}              !single state CASPT2 for reference state 1

e1_caspt2(i)=energy     !unmixed caspt2 energy for ground state

{rs2,MIX=2
state,1,2}              !single state CASPT2 for reference state 2

e2_caspt2(i)=energy     !unmixed caspt2 energy for excited state
e1_mscaspt2(i)=msenergy(1)  !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2)  !ms-caspt2 energy for excited state
enddo

{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2
title,SS-SR-CASPT2 for LiF
plot,file='lif_sr_mscaspt2.plot'
}
```

This produces the plot



22.3.2 Performing MS-MR-CASPT2 calculations

In the case of multi-state multi-reference CASPT2 calculations, only a single run is needed:

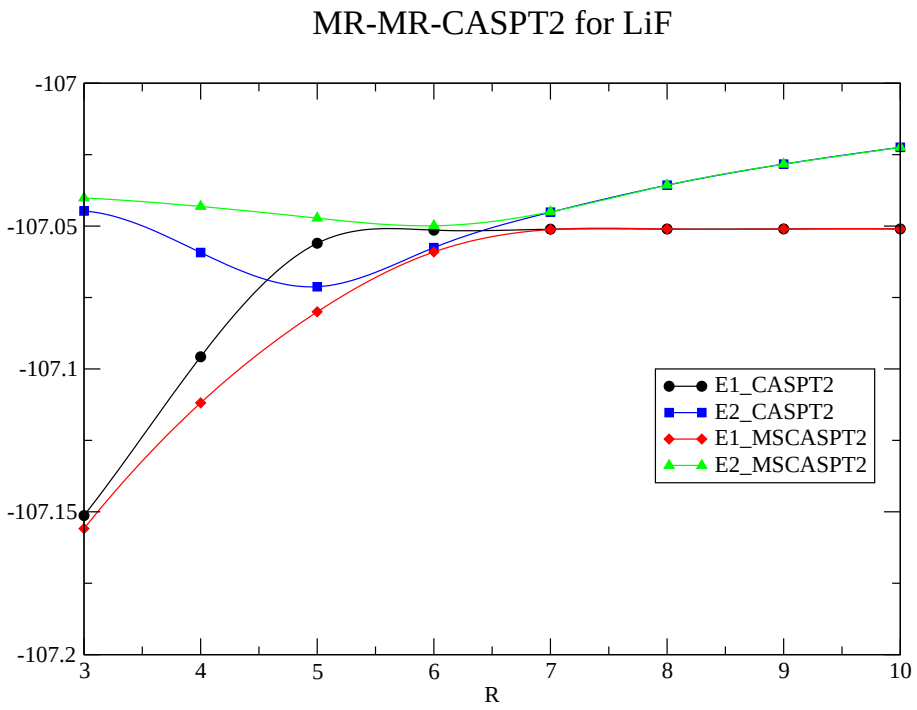
{`RS2,MIX=`*nstates*, *options*
`STATE,`*nstates*}

Example: MS-MR-CASPT2 calculation for LiF

examples/
lif˙mr˙mscaspt2.com

```
! $Revision: 2006.1 $
r=[3,4,5,6,7,8,9,10] ang

i=1
geometry={Li
          F,1,r(i)}

basis=vtz,F=avtz

hf                        !Hartree-Fock

do i=1,#r                 !loop over range of bond distances
{multi
closed,3,0,0,0
occ,   5,2,2,0
state,2                   !SA-CASSCF for 2 states
canonical,ci}

{rs2,MIX=2
state,2}                  !2-state CASPT2 with 2 reference states

e1_caspt2(i)=energy(1)       !unmixed caspt2 energy for ground state
e2_caspt2(i)=energy(2)       !unmixed caspt2 energy for ground state

e1_mscaspt2(i)=msenergy(1)   !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2)   !ms-caspt2 energy for excited state
enddo

{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2
title,MS-MR-CASPT2 for LiF
plot,file='lif_mr_mscaspt2.plot'
}
```

This produces the plot



One can clearly see that this gives smoother potentials than the SS-SR-CASPT2 calculation in the previous section. Also, the avoided crossing is shifted to longer distances, which is due to the improvement of the electron affinity of F.

22.4 Modified Fock-operators in the zeroth-order Hamiltonian.

The g_1, g_2, and g_3 operators proposed by Andersson [Theor. Chim. Acta **91**, 31 (1995)] as well as a further g_4 operator may be used. g_4 makes CASPT2 calculations size extensive for cases in which a molecule dissociates to high-spin open-shell (RHF) atoms.

The index *n* of the operator to be used is specified on the RS2, RS2C, or RS3 card:

RS2,*option*
RS2C,*option*
RS3,*option*

where *option* can be G1, G2, G3, or G4. This option can be followed or preceded by other valid options.

22.5 Level shifts

Level shifts are often useful to avoid intruder state problems in excited state calculations. MOLPRO allows the use of shifts as described by Roos and Andersson, [Chem. Phys. Lett. **245**, 215 (1995)]. The shift can be specified on the RS2 or RS2C card

RS2 [,G*n*] [,SHIFT=*shift*]
RS2C [,G*n*] [,SHIFT=*shift*]

Typical choices for the shift is are $0.1 - 0.3$. Only two figures after the decimal point are considered. The shift affects the results, the printed energies as well as the ENERGY variable include the energy correction for the shift as proposed by Roos and Andersson. At convergence, also the uncorrected energies are printed for comparison.

22.6 Integral direct calculations

RS2, RS2C, and RS3 calculations with very large basis sets can be performed in integral-direct mode. The calculation will be direct if a global DIRECT or GDIRECT card appears earlier in the input. Alternatively, (mainly for testing) DIRECT can be specified as an option on the RS*n*[C] card:

RS2 [,G*n*] [,SHIFT=*shift*] [,DIRECT]
RS2C [,G*n*] [,SHIFT=*shift*] [,DIRECT]

22.7 CASPT2 gradients

P. Celani and H.-J. Werner, J. Chem. Phys. **119**, 5044 (2003))

CASPT2 analytic energy gradients are computed automatically if a FORCE or OPTG command follows (see sections 38 and 39). Analytical gradients are presently only available for RS2 calculations (not RS2C), and only for the standard $\hat{H}^{(0)}$ (not G1, G2 etc). Gradients can be computed for single-state calculations, as well as multi-state MS-MR-CASPT2 (see section 22.3.

In single state calculations, the gradient is automatically computed for the state computed in CASPT2/RSPT2 (i.e., using STATE,1,2 the second state in the symmetry under consideration is computed, see section 22.2). In a multi-state MS-MR-CASPT2 calculation, the state for which the gradient is computed must be specified using the ROOT option (default ROOT=1), i.e.,

`RS2,MIX=`*nstates*, `ROOT=`*ioptroot*

where $1 \leq ioptroot \leq nstates$. The program works with state-averaged MCSCF (CASSCF) orbitals, and no `CPMCSCF` directive is needed. The RS2 gradient program can also be used to compute state-averaged MCSCF/CASSCF gradients using the `NOEXC` directive.

Level shifts can be used. By default, the exact gradient of the level-shift corrected energy is computed. For a non-zero shift, this requires to solve the CASPT2 Z-vector equations, which roughly doubles the computational effort. In single state calculations it is possible to ignore the effect of the level shift on the gradient and not to solve the Z-vector equation. This variant, which is described in the above paper, may be sufficiently accurate for many purposes. It is invoked using the `IGNORE` option, e.g.

```
RS2,SHIFT=0.2,IGNORE
OPTG
```

Any publications employing the CASPT2 gradients should cite the above paper. A citation for MS-CASPT2 gradient method is P. Celani and H.-J. Werner, *to be published*.

Example:

CASPT2 geometry optimizations for H_2O:

```
!$Revision: 2006.1 $
***
memory,8,m
gthresh,energy=1.d-10
!
basis=vdz
R=2.0
R0=R
Theta=100
geometry={O
          H1,O,R;
          H2,O,R,H1,THETA}

hf;accu,12

{multi;closed,2}

rs2,shift=0.3,ignoreshift      !ignore shift in computing gradient, i.e., no cp-caspt2
optg,gradient=1.d-5
e_opt(1)=energy
r_opt(1)=r
theta_opt(1)=theta
method(1)='rs2,analytical,ignore'
```

examples/
h2o˙caspt2˙opt.com

```
rs2,shift=0.3                  !exact gradient with shift
optg,gradient=1.d-5
e_opt(2)=energy
r_opt(2)=r
theta_opt(2)=theta
method(2)='rs2,analytical,exact'

rs2,shift=0.3                  !numerical gradient with shift
optg,gradient=1.d-5,numerical,fourpoint !use four-point numerical gradient
e_opt(3)=energy
r_opt(3)=r
theta_opt(3)=theta
method(3)='rs2,numerical'

rs2c,shift=0.3                 !numerical gradient of rs2c with shift
optg,gradient=1.d-5,fourpoint  !use four-point numerical gradient
e_opt(4)=energy
r_opt(4)=r
theta_opt(4)=theta
method(4)='rs2c,numerical'

table,method,r_opt,theta_opt,e_opt
digits,,4,4,8
```

This produces the Table

METHOD	R_OPT	THETA_OPT	E_OPT
rs2,analytical,ignore	1.8250	102.1069	-76.22789382
rs2,analytical,exact	1.8261	102.1168	-76.22789441
rs2,numerical	1.8261	102.1168	-76.22789441
rs2c,numerical	1.8260	102.1187	-76.22787681

MS-CASPT2 geometry optimization for the second excited $^3B_2$ state if H_2O:

```
!$Revision: 2006.1 $
***
memory,8,m
gthresh,energy=1.d-12
!
basis=vdz
R=2.0
R0=R
Theta=100
step=0.001
geometry={O
          H1,O,R;
          H2,O,R,H1,THETA}

hf;accu,12

multi        !state averaged casscf for various triplet states
closed,2
wf,10,1,2
state,3
wf,10,2,2
state,2
wf,10,3,2
state,3
canonical,2140.2                                                    examples/
                                                                    h2o˙mscaspt2˙opt.com

rs2,mix=3,root=2,shift=0.2   !optimized second 3B2 state
wf,10,3,2                    !3B2 wavefunction symmetry
state,3                      !include 3 states
optg,gradient=1.d-5          !geometry optimization using analytical gradients

e_opt(1)=msenergy(2)         !optimized ms-caspt2 energy
r_opt(1)=r                   !optimized bond distance
theta_opt(1)=theta           !optimized bond angle
method(1)='rs2,analytical'

rs2,mix=3,shift=0.2
wf,10,3,2                    !3B2 wavefunction symmetry
state,3                      !include 3 states
optg,variable=msenergy(2),gradient=1.d-5,fourpoint
                             !geometry optimization using numerical gradients

e_opt(2)=msenergy(2)         !optimized ms-caspt2 energy
r_opt(2)=r                   !optimized bond distance
theta_opt(2)=theta           !optimized bond angle
method(2)='rs2,numerical'

table,method,r_opt,theta_opt,e_opt
digits,,4,4,8
```

This produces the table

```
METHOD            R_OPT  THETA_OPT       E_OPT
rs2,analytical   2.4259    96.7213   -75.81630628
rs2,numerical    2.4259    96.7213   -75.81630628
```

22.8 Coupling MRCI and MRPT2: The CIPT2 method

P. Celani, H. Stoll, and H.-J. Werner, Mol. Phys. **102**, 2369 (2004).

For particularly difficult cases with strong intruder problems, or in which second-order perturbation theory fails to predict reliable results, a new method that couples MRCI and CASPT2 has been developed. This variant is invoked using the `CIPT2` directive:

`CIPT2`

In this case all excitations solely from active orbitals are treated by MRCI, while the remaining excitations involving inactive (closed-shell) orbitals are treated by second-order perturbation theory. Both methods are coupled by minimizing an appropriate energy functional. Of course, this method is much more expensive that MRPT2. The cost is comparable to the cost for an MRCI without correlating the inactive orbitals.

22.9 Further options for CASPT2 and CASPT3

Other options can be set using the `OPTION` command. These options are mainly used for testing purposes and should be used with care. It should be noted that the only option that can be modified in the RS2C program is `IFDIA`: all others only work with RS2/RS3.

`OPTION`,*code1=value,code2=value,...*

Of relevance for the CASPT2/3 program are the following options:

`IPROCS=0`	(Default). Calculation uses uncontracted singles with `RS2`.
`IPROCS=1`	Non-interacting singles are projected out during update. This is an approximate procedure which should be used with care.
`IPROCS=2`	The singles are fully internally contracted in `RS2`. This is achieved via a projection operator during the coefficient update and may be inefficient. G
`IPROCS=3`	Only singles with one or two holes in the closed-shells are internally contracted in `RS2` using a projection operator.
`IPROCI=0`	(Default). Calculation uses uncontracted internals with `RS2`.
`IPROCI=1`	Internals with two holes in the inactive space are internally contracted in `RS2` using a projection operator.
`IPROCS=3,IPROCI=1`	This combination of options reproduces with `RS2` the `RS2C` result using projection operators. This requires lot of memory and disk space and it is feasible only for small molecules.
`IFDIA=0`	(Default). All off-diagonal elements of the effective Fock matrix are included.
`IFDIA=1`	The internal-external block of the Fock-matrix is neglected. This eliminates the single-pair coupling.
`IFDIA=2`	All off-diagonal elements of the Fock matrix are neglected. This corresponds to CASPT2D of Andersson et al. Note: in this case the result is not invariant to rotations among active orbitals!
`IHINT=0`	(Default). Only one-electron integrals are used in the zeroth-order Hamiltonian for all interactions.
`IHINT=1`	The all-internal two-electron integrals are used in the zeroth-order Hamiltonian for the internal-internal and single-single interactions.
`IHINT=2`	The all-internal two-electron integrals in the zeroth-order Hamiltonian are used for the internal-internal, single-single, and pair-pair interactions. Using `IHINT=2` and `IDFIA=1` corresponds to Dyall's CAS/A method for the case that CASSCF references

with no closed-shells (inactive orbitals) are used. Note that this requires more CPU time than a standard CASPT2 calculation. Moreover, convergence of the CAS/A method is often slow (denominator shifts specified on a `SHIFT` card may be helpful in such cases). In general, we do not recommend the use of `IHINT` with nonzero values.

`NOREF=1` (Default). Interactions between reference configurations and singles are omitted.

`NOREF=0` Interactions between reference configurations and singles are included. This causes a relaxation of the reference coefficients but may lead to intruder-state problems.

`IMP3=2` After CASPT2 do variational CI using all internal configurations and the first-order wavefunctions of all states as a basis. In this case the second-order energy will correspond to the variational energy, and the third-order energy approximately to a Davidson-corrected energy. This is useful in excited state calculations with near-degeneracy situations.

23 MØLLER PLESSET PERTURBATION THEORY

Closed-shell Møller-Plesset perturbation theory up to full fourth order [MP4(SDTQ)] is part of the coupled-cluster program.

The commands `MP2, MP3, MP4` perform the MP calculations up to the specified order (lower orders are included).

`MP4;NOTRIPL;` performs MP4(SDQ) calculations.

Normally, no further input is needed if the `MPn` card directly follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. The resulting energies are stored in variables as explained in section 8.8.

23.1 Expectation values for MP2

One-electron properties can be computed as analytical energy derivatives for `MP2`. This calculation is much more expensive than a simple MP2, and therefore only done if an `EXPEC` card follows the `MP2` card (the `GEXPEC` directive has no effect in this case). The syntax of the `EXPEC` card is explained in section 6.13. For an example, see section 24.6.1. The density matrix can be saved using

`DM`,*record.ifil*];

See also sections 24.7 and 24.8.

23.2 Density-fitting MP2 (DF-MP2, RI-MP2)

`DF-MP2`,*options*

invokes the density fitted MP2 program. The present implementation works only without symmetry. `RI-MP2` is an alias for the command `DF-MP2`.

The following options can be specified:

`BASIS_MP2`=*basis*:	Fitting basis set. *basis* can either refer to a basis set defined in a `BASIS` block, or to a default fitting basis set (only available for correlation consistent basis sets). If a correlation consistent orbital basis set is used, the corresponding MP2 fitting basis is generated by default. In all other cases, the fitting basis must be defined.
`THRAO`=*value*:	Screening threshold for 3-index integrals in the AO basis
`THRMO`=*value*:	Screening threshold for 3-index integrals in the MO basis
`THROV`=*value*:	Screening threshold for 2-index integrals of fitting basis.
`THRPROD`=*value*:	Screening product threshold for first half transformation.
`SPARSE`=*value*:	If Non-zero, use sparse algorithm in second-half transformation (default).

See section 11 for a more general description of density fitting.

At present, expectation values and gradients cannot be computed with `DF-MP2`, but work with the local variant `DF-LMP2`.

23.3 Spin-component scaled MP2 (SCS-MP2)

The spin-component scaled MP2 energy as proposed by Grimme (J. Chem. Phys. **118**, 9095 (2003)) is printed automatically using the default scaling factors (1.2 for antiparallel spin, 1/3 for parallel spin). These factors can be modified using the options SCSFACS and SCSFACT, respectively, i.e.

MP2, SCSFACS=*facs*, SCSFACT=*fact*

The SCS-MP2 total energy is stored in the variable EMP2_SCS. Gradients can be computed for SCS-MP2 by setting the option SCSGRD=1. This only operational for density fitted MP2, i.e. using

DF-MP2,[DF_BASIS=*fitbasis*],SCSGRD=1,[SCSFACS=*facs*], [SCSFACT=*fact*]

followed by FORCES or OPTG. In the latter case, the geometry is optimized using the SCS-MP2 energy.

24 THE CLOSED SHELL CCSD PROGRAM

Bibliography:

C. Hampel, K. Peterson, and H.-J. Werner, Chem. Phys. Lett. 190, 1 (1992)

All publications resulting from use of this program must acknowledge the above.

The CCSD program is called by the CISD, CCSD, BCCD, or QCI directives. CID or CCD can be done as special cases using the NOSINGL directive. The code also allows to calculate Brueckner orbitals (QCI and CCSD are identical in this case). Normally, no further input is needed if the CCSD card follows the corresponding HF-SCF. Optional ORBITAL, OCC, CLOSED, CORE, SAVE, START, PRINT options work as described for the MRCI program in section 21. The only special input directives for this code are BRUECKNER and DIIS, as described below.

The following options may be specified on the command line:

NOCHECK	Ignore convergence checks.
DIRECT	Do calculation integral direct.
NOSING	Do not include singly external configurations.
MAXIT=*value*	Maximum number of iterations.
SHIFTS=*value*	Denominator shift for update of singles.
SHIFTP=*value*	Denominator shift for update of doubles.
THRDEN=*value*	Convergence threshold for the energy.
THRVAR=*value*	Convergence threshold for CC amplitudes. This applies to the square sum of the changes of the amplitudes.

The convergence thresholds can also be modified using

THRESH,ENERGY=*thrden*,COEFF=*thrvar*

Convergence is reached if the energy change is smaller than *thrden* (default 1.d-6) *and* the square sum of the amplitude changes is smaller than *thrvar* (default (1.d-10). The THRESH card must follow the command for the method (e.g., CCSD) and then overwrites the corresponding global options (see GTHRESH, sec. 6.11).

The computed energies are stored in variables as explained in section 8.8. As well as the energy, the T_1 diagnostic (T. J. Lee and P. R. Taylor, Int. J. Quant. Chem. S23 (1989) 199) is printed and stored in the variable T1DIAG for later analysis.

24.1 Coupled-cluster, CCSD

The command CCSD performs a closed-shell coupled-cluster calculation. Using the CCSD(T) command, the perturbative contributions of connected triple excitations are also computed.

If the CCSD is not converged, an error exit will occur if triples are requested. This can be avoided using the NOCHECK option:

```
CCSD(T),NOCHECK
```

In this case the (T) correction will be computed even if the CCSD did not converge. Note: NOCHECK has no effect in geometry optimizations or frequency calculations.

For further information on triples corrections see under RCCSD.

24.2 Quadratic configuration interaction, QCI

QCI or QCISD performs quadratic configuration interaction, QCISD. Using the QCI(T) or QCISD(T) commands, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the QCI card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. For modifying DIIS directives, see section 24.5

For avoiding error exits in case of no convergence, see CCSD(T).

24.3 Brueckner coupled-cluster calculations, BCCD

BCCD,[SAVE=*record*],[PRINT],[TYPE=,*type*]

BCCD performs a Brueckner coupled-cluster calculation and computes Brueckner orbitals. With these orbitals, the amplitudes of the singles vanish at convergence. Using the BCCD(T) command, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the BCCD card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. BRUECKNER parameters can be modified using the BRUECKNER directive.

The Brueckner orbitals and approximate density matrix can be saved on a MOLPRO dump record using the SAVE option. The orbitals are printed if the PRINT option is given. TYPE can be used to specify the type of the approximate density to be computed:

TYPE=REF	Compute and store density of reference determinant only (default). This corresponds to the BOX (Brueckner orbital expectation value) method of Chem. Phys. Lett. **315**, 248 (1999).
TYPE=TOT	Compute and store density with contribution of pair amplitudes (linear terms). Normally, this does not seem to lead to an improvement.
TYPE=ALL	Compute and store both densities

Note: The expectation variables are stored in variables as usual. In the case that both densities are made, the variables contain two values, the first corresponding to REF and the second to TOT (e.g., DMZ(1) and DMZ(2)). If TYPE=REF or TYPE=TOT is give, only the corresponding values are stored.

For avoiding error exits in case of no convergence, see CCSD(T).

24.3.1 The BRUECKNER directive

BRUECKNER,*orbbrk,ibrstr,ibrueck,brsfak*;

This directive allows the modification of options for Brueckner calculations. Normally, none of the options has to be specified, and the BCCD command can be used to perform a Brueckner CCD calculation.

orbbrk:	if nonzero, the Brueckner orbitals are saved on this record.
ibrstr:	First iteration in which orbitals are modified (default=3).
ibrueck:	Iteration increment between orbital updates (default=1).
brsfak:	Scaling factor for singles in orbital updates (default=1).

24.4 Singles-doubles configuration interaction, CISD

Performs closed-shell configuration interaction, CISD. The same results as with the CI program are obtained, but this code is somewhat faster. Normally, no further input is needed. For specifying DIIS directives, see section 24.5

24.5 The `DIIS` directive

`DIIS`,*itedis,incdis,maxdis,itydis*;

This directive allows to modify the DIIS parameters for CCSD, QCISD, or BCCD calculations.

itedis:	First iteration in which DIIS extrapolation may be performed (default=4).
incdis:	Increment between DIIS iterations (default=1).
maxdis:	Maximum number of expansion vectors to be used (default=6).
itydis:	DIIS extrapolation type. itedis=1 (default): residual is minimized. itedis=2: ΔT is minimized.

In addition, there is a threshold *THRDIS* which may be modified with the `THRESH` directive. DIIS extrapolation is only done if the variance is smaller than *THRDIS*.

24.6 Examples

24.6.1 Single-reference correlation treatments for H_2O

```
! $Revision: 2006.0 $
***,h2o test
memory,1,m                              !allocate 1 MW dynamic memory
geometry={o;h1,o,r;h2,o,r,h1,theta}     !Z-matrix geometry input
basis=vtz                               !cc-pVTZ basis set
r=1 ang                                 !bond length
theta=104                               !bond angle
hf                                      !do scf calculation

text,examples for single-reference correlation treatments

ci                                      !CISD using MRCI code
cepa(1)                                 !cepa-1 using MRCI code
mp2                                     !Second-order Moeller-Plesset
mp3                                     !Second and third-order MP
mp4                                     !Second, third, and fourth-order MP4(SDTQ)
mp4;notripl                             !MP4(SDQ)
cisd                                    !CISD using special closed-shell code
ccsd(t)                                 !coupled-cluster CCSD(T)
qci(t)                                  !quadratic configuration interaction QCISD(T)
bccd(t)                                 !Brueckner CCD(T) calculation
---
```

examples/
h2o˙ccsd.com

24.6.2 Single-reference correlation treatments for N_2F_2

examples/n2f2˙ccsd.com

```
! $Revision: 2006.0 $
***,N2F2 CIS GEOMETRY (C2h)
rnn=1.223,ang                          !define N-N distance
rnf=1.398,ang                          !define N-F distance
alpha=114.5;                           !define FNN angle
geometry={N1
          N2,N1,rnn
          F1,N1,rnf,N2,alpha
          F2,N2,rnf,N1,alpha,F1,180}
basis=vtz                              !cc-pVTZ basis set
$method=[hf,cisd,ccsd(t),qcisd(t),bccd(t)]  !all methods to use
do i=1,#method                         !loop over requested methods
$method(i)                             !perform calculation for given methods
e(i)=energy                            !save energy in variable e
enddo                                  !end loop over methods
table,method,e                         !print a table with results
title,Results for n2f2, basis=$basis   !title of table
```

This calculation produces the following table:

```
 Results for n2f2, basis=VTZ

 METHOD          E            E-ESCF
 CISD       -308.4634948   -0.78283137
 BCCD(T)    -308.6251173   -0.94445391
 CCSD(T)    -308.6257931   -0.94512967
 QCISD(T)   -308.6274755   -0.94681207
```

24.7 Saving the density matrix

DM,*record.ifil*];

The effective first order density matrix is computed an stored in record *record* on file *ifil*. This currently works for closed-shell MP2, QCISD, and CCSD. See also NATORB.

24.8 Natural orbitals

NATORB,[RECORD=]*record.ifil*,[PRINT=*nprint*],[CORE[=*natcor*]];

Calculate natural orbitals. This currently only works for closed-shell MP2 and QCISD. The number of printed external orbitals in any given symmetry is *nprint*) (default 2). *nprint=-1* suppressed the printing. The natural orbitals and the density matrix are saved in a dump record *record* on file *ifil*. If *record.ifil* is specified on a DM card (see above), this record is used. If different records are specified on the DM and NATORB cards, an error will result. The record can also be given on the SAVE card. Note that the effective density matrix of non-variational methods like MP2 or QCISD does not strictly behave as a density matrix. For instance, it has non-zero matrix elements between core and valence orbitals, and therefore core orbitals are affected by the natural orbital transformation. Also, occupation numbers of core orbitals can be larger than 2.0. If CORE is given (*natcor=1*), the core orbitals are frozen by excluding them from the natural orbital transformation.

25 EXCITED STATES WITH EQUATION-OF-MOTION CCSD (EOM-CCSD)

Excitation energies for singlet states can be computed using equation-of-motion (EOM) approach. For the excitation energies the EOM-CCSD method gives the same results as linear response CCSD (LR-CCSD) theory. Accurate results can only be expected for singly excited states. The states to be computed are specified on an EOM input card, which is a subcommand of CCSD. The following input forms are possible

EOM, *state1, state2, state3, ...*

Computes the given states. Each state is specified in the form *number.sym*, e.g., 5.3 means the fifth state in symmetry 3. Note that state 1.1 corresponds to the ground state CCSD wavefunction and is ignored if given.

EOM, $-n1.sym1,\ -n2,sym2,\ \ldots$

computes the first $n1$ states in symmetry *sym1*, $n2$ in *sym2* etc.

EOM, $n1.sym1,\ -n2,sym1,\ \ldots$

computes states $n1$ through $n2$ in symmetry *sym1*.

The different forms can be combined, e.g.,

EOM, -3.1, 2.2, 2.3, -5.3

computes states 1-3 in symmetry 1, the second excited state in symmetry 2, and the second through fifth excited states in symmetry 3. Note that state 1.1 is the ground-state CCSD wavefunction.

By default, an error exit will result if the CCSD did not converge and a subsequent EOM calculation is attempted. The error exit can be avoided using the NOCHECK option on the CCSD command (see also CCSD(T)).

25.1 Options for EOM

Normally, no further input is needed for the calculation of excitation energies.

EOM-CCSD amplitudes can be saved using SAVE=*record.ifil*. The vectors will be saved after every refreshing of the iteration space and at the end of the calculation. The calculation can be restarted from the saved vectors, if START=*record.ifil* is specified. The set of vectors to be computed can be different in old and restarted calculations. However, if both cards (SAVE and START) are specified and the records for saving and restarting are identical, the sets of vectors should be also identical, otherwise chaos. The identical SAVE and START records can be useful for potential energy surfaces calculations, see section 25.4.1.

By default, only excitation energies are calculated, since the calculation of properties is about two times as expensive, as the calculation of energies only. The one-electron properties and transition moments (expectation type, as defined in: J.F. Stanton and R.J. Bartlett, J. Chem. Phys., **98** 7029 (1993)) can be calculated by adding TRANS=1 to EOM card. The CCSD ground state is treated as a special case. If RELAX option is specified in EXPEC card, also the relaxed one-electron density matrix is calculated for the ground state. (Currently, the relaxed CCSD density matrix is available for all-electron calculations only.) By default, dipole moments are calculated. Other required properties can be specified using EXPEC card. Excited state densities are saved, if DM card is present. For an example see section 25.4.2. If TRANS=2, transition moments among excited states are also calculated.

It is possible to make the program to converge to a vector, which resembles a specified singles vector. This option is switched on by FOLLOW=*n* card (usually *n*=2 should be set). FOLLOW card should be always accompanied with EXFILE=*record.ifil* card, where *record.ifil* contains singles vectors from a previous calculation, see section 25.4.3.

25.2 Options for EOMPAR card

Normally, no further input is needed. However, some defaults can be changed using the EOMPAR directive:

EOMPAR, key1=*value1*, key2=*value2*,...

where the following keywords key are possible:

MAXDAV=*nv*	Maximum value of expansion vectors per state in Davidson procedure (default 20).
INISINGL=*ns*	Number of singly excited configurations to be included in initial Hamiltonian (default 20; the configurations are ordered according to their energy). Sometimes INISINGL should be put to zero in order to catch states dominated by double excitations.
INIDOUBL=*nd*	Number of doubly excited configurations to be included in initial Hamiltonian (default 10).
INIMAX=*nmax*	Maximum number of excited configurations to be included in initial Hamiltonian. By default, $nmax = ns + nd$.
MAXITER=*itmax*	Maximum number of iterations in EOM-CCSD (default 50).
MAXEXTRA=*maxex*	Maximum number of extra configurations allowed to be included in initial Hamiltonian (default 0). In the case of near degeneracy it is better to include a few extra configurations to avoid a slow convergence.
EOMLOCAL=*eoml*	If set to 0, non-local calculation (default). EOMLOCAL=1 switchs on the local module (experimental!).
INIMAX=*ini*	Number of CSFs included in initial Hamiltonian, used only if INISINGL and INIDOUBL are both zero.

All keywords can be abbreviated by at least four characters.

25.3 Options for EOMPRINT card

The following print options are mostly for testing purposes and for looking for the convergence problems.

EOMPRINT, key1=*value1*, key2=*value2*,...

where the following keywords key are possible:

DAVIDSON=*ipr*	Information about Davidson procedure: *ipr=1* print results of each "small diagonalization" *ipr=2* also print warning information about complex eigenvalues *ipr=3* also print hamiltonian and overlap matrix in trial space.

DIAGONAL=*ipr*	Information about configurations: *ipr=1* print the lowest approximate diagonal elements of the transformed hamiltonian *ipr=2* print orbital labels of important configurations *ipr=3* print all approximate diagonal elements *ipr=4* also print the long form of above.
PSPACE=*ipr*	Print information about the initial approximate hamiltonian: *ipr=2* print the approximate hamiltonian used to find the first approximation.
HEFF=*ipr*	Print information about effective Hamiltonian: *ipr=2* print columns of effective hamiltonian and overlap matrix in each iteration
RESIDUUM=*ipr*	Print information about residual vectors: *ipr=-1* no print in iteration *ipr=0* print energy values + residuum norm (squared) for each iteration (default) *ipr=1* also print warning about complex eigenvalue, and a warning when no new vectors is added to the trial space due to the too small norm of the residuum vector. *ipr=2* also print how many vectors are left
LOCEOM=*ipr*	*ipr=1* prints overlaps of sample and tested vectors in each iteration, if FOLLOW card is present. Increasing *ipr* switches on more and more printing, mostly related to the local EOM-CCSD method.
POPUL=*ipr*	if *ipr=1*, do a population analysis of the singles part of the rhs EOM-CCSD wave function. By default the Löwdin method is used. The Mulliken analysis can be forced by adding MULLPRINT=1 to EOM card. Note that a more correct (but more expensive) approach is to calculate and analyse the EOM-CCSD density matrix, see section 25.1.
INTERMED=*ipr*	Print intermediates dependent on ground state CCSD amplitudes: *ipr=0* no print (default) *ipr=1* print newly created intermediates *ipr=2* also print more intermediates-related information

25.4 Examples

25.4.1 PES for lowest excited states for hydrogen fluride

This example shows how to calculate potential energy surfaces for several excited states using restart from a previous calculation.

```
***, PES for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz                                          ! define basis set
geometry={h;f,h,r}                                  ! z-matrix
r=0.8 Ang                                           ! start from this distance
do n=1,100                                          ! loop over distances
rr(n)=r                                             ! save distance for table
hf                                                  ! do SCF calculation
ccsd                                                ! do CCSD calculation, try to restart
start,4000.2,save,4000.2                            ! and save final T amplitudes
eom,-2.1,-1.2,-1.4,start=6000.2,save=6000.2         ! do EOM-CCSD calculation, try to restart
                                                    ! and save final excited states' amplitudes
```

examples/hf_eom_pes.com

```
ebase(n)=energy(1)                                  ! save ground state energy for this geometry
e2(n)=energy(2)-energy(1)                           ! save excitation energies for this geometry
e3(n)=energy(3)-energy(1)
e4(n)=energy(4)-energy(1)
r=r+0.01                                            ! increment distance
enddo                                               ! end of do loop
table,rr,ebase,e2,e3,e4                             ! make table with results
digits,2,8,5,5,5,5,5,5,5,5                          ! modify number of digits
head,R(Ang),EGRST,E_EXC(2.1),E_EXC(1.2),E_EXC(1.4)! modify headers of table
! title of table
title,EOM-CCSD excitation energies for hydrogen fluoride (in hartree), basis $basis
save,hf_eom_ccsd.tab                                ! save table in file
```

This calculation produces the following table:

```
 EOM-CCSD excitation energies for hydrogen fluoride (in hartree), basis AVDZ

   R(ANG)         EGRST      E_EXC(2.1)   E_EXC(1.2)   E_EXC(1.4)
     0.80   -100.23687380      0.56664      0.41204      0.56934
     0.81   -100.24094256      0.56543      0.40952      0.56812
     0.82   -100.24451598      0.56422      0.40695      0.56690
```

etc.

25.4.2 EOM-CCSD transition moments for hydrogen fluoride

This example shows how to calculate and store CCSD and EOM-CCSD density matrices, calculate dipole and quadrupole moments (transition moments from the ground to excited states are calculated), and how to use the EOM-CCSD excited state density for Mulliken population analysis.

```
! $Revision: 2006.0 $
***, Properties and transition moments for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz                                          ! define basis set
geometry={h;f,h,r}                                  ! z-matrix
r=0.92 Ang                                          ! define distance
```

examples/hf_eom_prop.com

```
hf                                                  ! do SCF calculation
{ccsd                                               ! do CCSD calculation
dm,5600.2                                           ! density matrices will be stored here
expec,qm                                            ! require quadrupole moments
eom,-3.1,-2.2,-2.3,-2.4,trans=1}                    ! do EOM-CCSD calculation + properties

pop;density,5600.2,state=2.4                        ! make population analysis for state 2.4
```

This calculation produces the following table:

```
--------------------------------------------------------------------------------
                        Final Results for EOM-CCSD
                             (moments in a.u.)
--------------------------------------------------------------------------------

  State    Exc. Energy (eV)            X              Y              Z
   2.1         14.436

 Right transition moment           0.00000000     0.00000000     0.65349466
 Left  transition moment           0.00000000     0.00000000     0.68871635
 Dipole strength                   0.45007246
 Oscillator strength               0.15917669
 Dipole moment                     0.00000000     0.00000000     0.88758090
```

etc.

25.4.3 Calculate an EOM-CCSD state most similar to a given CIS state

This example shows how to force the convergence of the EOM-CCSD program to a state, which resembles at most a given CIS state.

```
***, EOM-CCSD, vector following procedure
memory,2,m
basis=avdz                                      ! define basis set
geometry={h;f,h,r}                              ! z-matrix
r=0.92 Ang                                      ! define distance
hf;save,2100.2                                  ! do SCF calculation, save orbitals
cis,-4.4,exfile=6000.2                          ! do CIS calculation, save amplitudes
ccsd;save,4000.2                                ! do CCSD calculation, save amplitudes
eom,-4.4,checkovlp=1,exfile=6000.2              ! do EOM-CCSD calculation,
                                                ! check overlap of singles with CIS vectors
                                                ! stored in record given in exfile  examples/
eompar,inisingl=200,inidoubl=0                  ! for first approximation take 200 singles  hf_eom_conv.com
                                                ! of approximate hamiltonian
ccsd;start,4000.2                               ! do CCSD calculation, try to restart
eom,2.4,follow=2,exfile=6000.2,checkovlp=1      ! do EOM-CCSD calculation for state closest
                                                ! to 2.4 CIS state, check overlap of singles
                                                ! with CIS vectors stored in exfile
eompar,inisingl=200,inidoubl=0
eomprint,loce=1                                 ! print overlaps of sample and EOM vectors in
                                                ! each iteration
```

In this example the CIS state 2.4 corresponds to the EOM-CCSD state 1.4!

25.5 Excited states with CIS

Excitation energies can also be calculated using the Configuration-Interaction Singles (CIS) method. This method cannot be expected to give accurate results, but can be used for quite large molecules. The states to be computed are specified similarly as for `EOM`, e.g.

```
hf
cis,-3.1,1.2,trans=1
```

26 OPEN-SHELL COUPLED CLUSTER THEORIES

Spin unrestricted (RHF-UCCSD) and partially spin restricted (RHF-RCCSD) open-shell coupled cluster theories as described in J. Chem. Phys. **99** (1993) 5219 (see also erratum , J. Chem. Phys., **112** (2000) 3106) are available in MOLPRO. In both cases a high-spin RHF reference wavefunction is used. No coupled cluster methods based on UHF orbitals are implemented in MOLPRO (the only correlation method in MOLPRO which uses UHF orbitals is UMP2). In the description that follows, the acronyms RCCSD and UCCSD are used, but the theories should normally be referred to as RHF-RCCSD, RHF-UCCSD, in order to distinguish them from alternative ansätze based on spin-unrestricted orbitals. The program will accept either the full or abbreviated acronyms as input commands.

In the RCCSD theory certain restrictions among the amplitudes are introduced, such that the linear part of the wavefunction becomes a spin eigenfunction (this is not the case in the UCCSD method, even if an RHF reference function is used). At present, the implementation of RCCSD is only preliminary, and no CPU time is saved by as compared to UCCSD. However, improved algorithms, as described in the above publication, are currently being implemented, and will be available in the near future.

The input is exactly the same as for closed-shell CCSD, except that RCCSD or UCCSD are used as keywords. By default, the open-shell orbitals are the same as used in the RHF reference function, but this can be modified using OCC, CLOSED, and WF cards.

Perturbative triples corrections are computed as follows:

RCCSD(T), UCCSD(T)	triples corrections are computed as defined by J. D. Watts, J. Gauss and R. J. Bartlett, J. Chem. Phys. **98** 8718 (1993).
RCCSD[T], UCCSD[T]	corrections are computed without contributions of single excitations (sometimes called CCSD+T(CCSD)) .
RCCSD-T, UCCSD-T	triples corrections are computed as defined by M. J. O. Deegan and P. J. Knowles, Chem. Phys. Letters 227 (1994) 321.

In fact, all three contributions are always computed and printed. The following variables are used to store the results (here CCSD stands for either UCCSD or RCCSD):

ENERGY	total energy for method specified in the input.
ENERGC	total CCSD energy without triples.
ENERGT(1)	total CCSD(T) energy.
ENERGT(2)	total CCSD[T] energy.
ENERGT(3)	total CCSD-T energy.

It should be noted that in open-shell cases the triples energy slightly depends on the treatment of core orbitals. In MOLPRO pseudo-canonical alpha and beta spin orbitals (http://dx.doi.org/10.1016/S0009-2614(91)85118-G) are generated by block-diagonalizing the corresponding Fock matrices in the space of valence orbitals, leaving frozen core orbitals untouched. Some other programs include the frozen core orbitals in the canonicalization and transformation. Because of core-valence mixing this leads to slightly different energies. Neither of the two methods can be regarded as better or more justified — it is just a matter of definition. However, the method in MOLPRO is more efficient since the subsequent integral transformation involves only valence orbitals and no core orbitals.

27 The MRCC program of M. Kallay (MRCC)

An interface exists to use the MRCC program of M. Kallay and J. Gauss within Molpro. The license and source code of the MRCC program must be obtained from Mihaly Kallay <kallay@mail.bme.hu>. Currently, only single reference methods with RHF reference functions are supported. Perturbative methods and CCn methods are only available for closed-shell. Furthermore, only serial execution is supported under MOLPRO, i.e. the mpp version cannot be used.

27.1 Installing MRCC

A file mrcc.tar.gz will be provided by by M. Kallay. This file should be copied into directory MRCC under the main MOLPRO directory. In this directory, a Makefile exists, and typing "make" will compile and install the MRCC program. The executables will be copied into the MOLPRO bin directory and are automatically called by MOLPRO. Orbitals and other input information are communicated via external files, transparent to the user. Once the program is installed, please run "make mrcctest" in testjobs directory.

27.2 Running MRCC

The MRCC program is invoked by the command

MRCC,*options*
directives

The available options summarized in Table 9. For a detailed description please refer to the MRCC manual of M. Kallay (file "manual" the mrcc directory)

In MOLPRO the method to be used can be given as a string (option METHOD=*string*). The available methods and the corresponding MRCC input parameters (see MRCC manual) as specified in Table 10.

Directives are usually not necessary, but the CORE, OCC, ORBITAL, MAXIT, directives work as in the MOLPRO CCSD program. In addition, the number of states can be given on a STATE directive and this has the same meaning as the EOM_NSTATES option.

Table 9: Options for MRCC

Option	Alias	Default value[a]	Meaning
METHOD	CALC	CC(n)	Computational method. See Table 10.
EXCITATION	LEVEL	-1	Excitation level in cluster operator
RESTART_CC	RESTART	0	Restart option. If 1, restart with previous amplitudes.
DIRECTORY	DIR	' '	Subdirectory in which MRCC runs (necessary for restart jobs)
EOM_NSING	NSING	-1	Number of excited singlet states in closed-shell case
EOM_NTRIP	NTRIP	0	Number of excited triplet states in closed-shell case
EOM_NSTATES	NDOUB	-1	Number of states in open shell case.
SYMM	SYMMETRY	-1	Symmetry of excited states
DENSITY	IDENS	0	Parameter for density calculation
HF		1	0 for UHF or ROHF, 1 for closed-shell
NACTO		0	Number of active occupied orbitals
NACTV		0	Number of active virtual orbitals
SACC		0	Spin-adapted coupled cluster
DBOC		0	Diagonal BO correction
MEMORY		-1	Memory
TOL	ENERGY	-1.0	Energy convergence threshold
FREQ		0.0	Frequency for dynamic polarizabilities
FILE		fort	Name for MRCC fortran files
CONVER	ICONV	0	See mrcc manual
CS		1	See mrcc manual
DIAG		0	See mrcc manual
MAXEX		0	See mrcc manual
SPATIAL		1	See mrcc manual

a) -1 means default value taken from MOLPRO

Table 10: Methods available in the MRCC program

Key	MRCC parameters METHOD	LEVEL	Notes
CI(n) configuration interaction methods			
CISD	0	2	
CISDT	0	3	
CISDTQ	0	4	
CI(N)	0	N	Specify excitation level N using LEVEL
CC(N) coupled cluster methods			
CCSD	1	2	
CCSDT	1	3	
CCSDTQ	1	4	
CC(N)	1	N	Specify excitation level N using LEVEL
CC(N-1)[N] coupled cluster methods			
CCSD[T]	2	3	
CCSDT[Q]	2	4	
CC(N-1)[N]	2	N	Specify excitation level N using LEVEL
CC(N-1)(N) coupled cluster methods. Also computes [n] corrections			
CCSD(T)	3	3	
CCSDT(Q)	3	4	
CC(N-1)(N)	3	N	Specify excitation level N using LEVEL
CC(n-1)(n)_L methods (also computes (n) and [n] corrections)			
CCSD(T)_L	4	3	
CCSDT(Q)_L	4	4	
CC(N-1)(N)_L	4	N	Specify excitation level N using LEVEL
CC(n)-1a methods			
CCSDT-1A	5	3	
CCSDTQ-1A	5	4	
CC(N)-1A	5	N	Specify excitation level N using LEVEL
CC(n)-1b methods			
CCSDT-1B	6	3	
CCSDTQ-1B	6	4	
CC(N)-1B	6	N	Specify excitation level N using LEVEL
CCn methods (only for ground states)			
CC3	7	3	
CC4	7	4	
CCN	7	N	Specify excitation level N using LEVEL
CC(n)-3 methods			
CCSDT-3	8	3	
CCSDTQ-3	8	4	
CC(N)-3	8	N	Specify excitation level N using LEVEL

Examples: Closed-shell ground-state calculations for H2O:

examples/h2o˙mrcc.com

```
***,mrcc calculations for h2o
memory,8,m
gthresh,energy=1.d-8

geometry={
o;h1,o,r;h2,o,r,h1,theta}
theta=104
r=1 ang
basis=vdz

hf
mrcc,method=cc3;                    !CC3 calculation
method(1)=program
e(1)=energy                         !the final energy is returned in variable energy

ccsd(t)                             !CCSD(T) calculation using Molpro
method(2)='CCSD(T) (MOLPRO)'
e(2)=energy

mrcc,method=ccsd(t)                 !CCSD(T) calculation using MRCC
method(3)='CCSD(T) (MRCC)'
e(3)=energy

mrcc,method=ccsdt,dir=mrccdir       !CCSDT calculation, run in directory mrccdir
method(4)=program
e(4)=energy

mrcc,method=ccsdt(q),restart=1,dir=mrccdir !CCSDT(Q) calculation
                                           !restart with previous amplitudes
method(5)=program
e(5)=energy

mrcc,method=CC(n),excitation=4,restart=1,dir=mrccdir !CCSDTQ calculation
method(6)=program
e(6)=energy

table,method,e
```

This yields

```
METHOD                  E
CC3                -76.23912734
CCSD(T)  (MOLPRO)  -76.23905150
CCSD(T)  (MRCC)    -76.23905150
CCSDT              -76.23922746
CCSDT(Q)           -76.23976632
CCSDTQ             -76.23973043
```

Excitation energies for H2O:

```
***,h2o excitation energies
memory,8,m
gthresh,energy=1.d-8
geometry={
o;h1,o,r;h2,o,r,h1,theta}
theta=104
r=1 ang
basis=vdz
hf

ii=0
s=2                          !number of states in each symmetry
do sym=1,4                   !loop over irreps
ccsd;eom,-(s+0.1*sym);$p=molpro;save_energy
mrcc,method=ccsd, symm=sym,nstates=2;$p=mrcc;save_energy
mrcc,method=ccsdt,symm=sym,nstates=2;$p=mrcc;save_energy
s=1
enddo

{table,method,prog,states,e,exc
 sort,3}

save_energy={       !procedure to save results in variables
!nogprint,variable
e1=energy(1)
do i=1,#energy
ii=ii+1
e(ii)=energy(i)
method(ii)=program
prog(ii)=p
states(ii)=i+0.1*sym
exc(ii)=(e(ii)-e1)*toev
end do
}
```

examples/
h2o˙mrcc˙eom.com

This yields

METHOD	PROG	STATES	E	EXC
CCSD	MOLPRO	1.1	-76.23580212	0.000
CCSD	MRCC	1.1	-76.23580212	0.000
CCSDT	MRCC	1.1	-76.23922746	0.000
CCSD	MOLPRO	1.2	-76.23580212	0.000
CCSD	MRCC	1.2	-76.23580212	0.000
CCSDT	MRCC	1.2	-76.23922746	0.000
CCSD	MOLPRO	1.3	-76.23580212	0.000
CCSD	MRCC	1.3	-76.23580212	0.000
CCSDT	MRCC	1.3	-76.23922746	0.000
CCSD	MOLPRO	1.4	-76.23580212	0.000
CCSD	MRCC	1.4	-76.23580212	0.000
CCSDT	MRCC	1.4	-76.23922746	0.000
CCSD	MOLPRO	2.1	-75.85033256	10.489
CCSD	MRCC	2.1	-75.85033257	10.489
CCSDT	MRCC	2.1	-75.85316687	10.505
CCSD	MOLPRO	2.2	-75.95093334	7.752
CCSD	MRCC	2.2	-75.95093335	7.752
CCSDT	MRCC	2.2	-75.95299013	7.789
CCSD	MOLPRO	2.3	-75.77630664	12.504
CCSD	MRCC	2.3	-75.77630665	12.504
CCSDT	MRCC	2.3	-75.77972816	12.504
CCSD	MOLPRO	2.4	-75.87776149	9.743
CCSD	MRCC	2.4	-75.87776150	9.743
CCSDT	MRCC	2.4	-75.88051189	9.761

Open-shell ground-state calculations for O2:

examples/
o2˙mrcc.com

```
***,O2 tests
memory,8,m
gthresh,energy=1.d-8

geometry={o1;o2,o1,r1}
r1=2.2
set,state=1,symmetry=4,spin=2  ! Triplet sigma- state
basis=vdz

rhf
uccsd(t)
method(1)='UCCSD(T) MOLPRO'
e(1)=energy

rccsd(t)
method(2)='RCCSD(T) MOLPRO'
e(2)=energy

mrcc,method=ccsdt,dir=mrccdir
method(3)='CCSDT MRCC'
e(3)=energy

mrcc,method=ccsdtq,restart=1,dir=mrccdir
method(4)='CCSDT MRCC'
e(4)=energy

table,method,e
```

This yields

```
METHOD                  E
UCCSD(T) MOLPRO   -149.9815472
RCCSD(T) MOLPRO   -149.9812566
CCSDT MRCC        -149.9816705
CCSDT MRCC        -149.9832255
```

28 LOCAL CORRELATION TREATMENTS

28.1 Introduction

The local correlation program of MOLPRO can currently perform closed-shell LMP2, LMP3, LMP4(SDTQ), LCISD, LQCISD(T), and LCCSD(T) calculations. For large molecules, all methods scale linearly with molecular size, provided very distant pairs are neglected, and the integral-direct algorithms are used.

Much higher efficiency is achieved by using density fitting (DF) approximations to compute the integrals. Density fitting is available for all local methods up to LCCSD(T), as well as for analytical LMP2 gradients. Only iterative triples methods like LCCSDT-1b can currently not be done with density fitting.

The errors introduced by DF are negligible, and the use of the DF methods is highly recommended. Linear scaling can be obtained in DF-LMP2 using the `LOCFIT` option (see Ref. 11); in DF-LCCSD(T), the most important parts also scale linearly, but some transformation steps scale quadratically.

Energy gradients are available for LMP2, DF-LMP2, DF-SCS-LMP2, and LQCISD (in the latter case only for `LOCAL=1`, i.e. the local calculation is simulated using the canonical program, and savings only result from the reduced number of pairs).

Local explicitly correlated methods (DF-LMP2-R12 and DF-LMP2-F12 are described in section 29.

Before using these methods, it is strongly recommended to read the literature in order to understand the basic concepts and approximations. A recent review [1] and Ref. [2] may be suitable for an introduction.

References:

Review:
[1] H.-J. Werner and K. Pflüger, *On the selection of domains and orbital pairs in local correlation treatments*, Ann. Rev. Comp. Chem., in press. (preprint available under `http://www.theochem.uni-stu`

General local Coupled Cluster:
[2] C. Hampel and H.-J. Werner, *Local Treatment of electron correlation in coupled cluster (CCSD) theory*, J. Chem. Phys. **104**, 6286 (1996).
[3] M. Schütz and H.-J. Werner, *Local perturbative triples correction (T) with linear cost scaling*, Chem. Phys. Letters **318**, 370 (2000).
[4] M. Schütz, *Low-order scaling local electron correlation methods. III. Linear scaling local perturbative triples correction (T)*, J. Chem. Phys. **113**, 9986 (2000).
[5] M. Schütz and H.-J. Werner, *Low-order scaling local electron correlation methods. IV. Linear scaling local coupled-cluster (LCCSD)*, J. Chem. Phys. **114**, 661 (2001).
[6] M. Schütz, *Low-order scaling local electron correlation methods. V. Connected Triples beyond (T): Linear scaling local CCSDT-1b*, J. Chem. Phys. **116**, 8772 (2002).
[7] M. Schütz, *A new, fast, semi-direct implementation of Linear Scaling Local Coupled Cluster Theory*, Phys. Chem. Chem. Phys. **4**, 3941 (2002).

Multipole treatment of distant pairs:
[8] G. Hetzer, P. Pulay, H.-J. Werner, *Multipole approximation of distant pair energies in local MP2 calculations*, Chem. Phys. Lett. **290**, 143 (1998).

Linear scaling local MP2:
[9] M. Schütz, G. Hetzer and H.-J. Werner, *Low-order scaling local electron correlation methods. I. Linear scaling local MP2*, J. Chem. Phys. **111**, 5691 (1999).

[10] G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, *Low-order scaling local electron correlation methods II: Splitting the Coulomb operator in linear scaling local MP2*, J. Chem. Phys. **113**, 9443 (2000).

Density fitted local methods:
[11] H.-J. Werner, F. R. Manby, and P. J. Knowles, *Fast linear scaling second-order Møller-Plesset perturbation theory (MP2) using local and density fitting approximations*, J. Chem. Phys. **118**, 8149 (2003). [12] M. Schütz and F.R. Manby, *Linear scaling local coupled cluster theory with density fitting. Part I: 4- external integrals*, Phys. Chem. Chem. Phys. **5**, 3349 (2003).
[13] Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, *Fast Hartree-Fock theory using local density fitting approximations*, Mol. Phys. **102**, 2311 (2004).
[14] H.-J. Werner and M. Schütz, *Low-order scaling coupled cluster methods (LCCSD(T)) with local density fitting approximations*, in preparation.

LMP2 Gradients and geometry optimization:
[15] A. El Azhary, G. Rauhut, P. Pulay and H.-J. Werner, *Analytical energy gradients for local second-order Møller-Plesset perturbation theory*, J. Chem. Phys. **108**, 5185 (1998).
[16] G. Rauhut and H.-J. Werner, *Analytical Energy Gradients for Local Coupled-Cluster Methods*, Phys. Chem. Chem. Phys. **3**, 4853 (2001).
[17] M. Schütz, H.-J. Werner, R. Lindh and F.R. Manby, *Analytical energy gradients for local second-order Møller-Plesset perturbation theory using density fitting approximations*, J. Chem. Phys. **121**, 737 (2004).

LMP2 vibrational frequencies:
[18] G. Rauhut, A. El Azhary, F. Eckert, U. Schumann and H.-J. Werner, *Impact of Local Approximations on MP2 Vibrational Frequencies*, Spectrochimica Acta **55**, 651 (1999).
[19] G. Rauhut and H.-J. Werner *The vibrational spectra of furoxan and dichlorofuroxan: a comparative theoretical study using density functional theory and Local Electron Correlation Methods*, Phys. Chem. Chem. Phys. **5**, 2001 (2003).
[20] T. Hrenar, G. Rauhut and H.-J. Werner, *Impact of local and density fitting approximations on harmonic vibrational frequencies*, J. Phys. Chem. A., **110**, 2060 (2006).

Intermolecular interactions and the BSSE problem:
[21] M. Schütz, G. Rauhut and H.-J. Werner, *Local Treatment of Electron Correlation in Molecular Clusters: Structures and Stabilities of* $(H_2O)_n$, $n = 2-4$, J. Phys. Chem. **102**, 5997 (1998). See also [2] and references therein.
[22] N. Runeberg, M. Schütz and H.-J. Werner, *The aurophilic attraction as interpreted by local correlation methods*, J. Chem. Phys. **110**, 7210 (1999).
[23] L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, and H.-J. Werner, *A Comparison of the metallophilic attraction in (X-M-*$PH_3)_2$ *(M=Cu, Ag, Au; X=H, Cl)*, Phys. Chem. Chem. Phys. **4**, 1006 (2002).

28.2 Getting started

The local correlation treatment is switched on by preceding the command name by an `L`, i.e., by using the `LMP2`, `LMP3`, `LMP4`, `LQCISD`, `LCCSD`, or `LCISD` commands.

The `LQCISD` and `LCCSD` commands can be appended by a specification for the perturbative treatment of triple excitations (e.g., `LCCSD(T0)`):

`(T)`	Use the default triples method. Currently this is T0.
`(T0)`	Non-iterative local triples. This is the fastest triples option. It is usually sufficiently accurate and recommended to be used in most cases.

(T1) T0 plus one perturbative update of the triples amplitudes. If the accuracy of T0 is insufficient (very rarely the case!), this can be used to improve the accuracy. The computational cost is at least twice as large as for T0. In contrast to T0, the triples amplitudes must be stored on disk, which can be a bottleneck in calculations for large molecules. Also the memory requirements are substantially larger than for T0.

(T1C) As T1, but a caching algorithm is used which avoids the simultaneous storage of all triples amplitudes on disk (as is the case for (T1) or (TF)). Hence, T1C requires less disk space but more CPU-time than T1. The more disk space is made available for the caching algorithm (using the T1DISK option on the local card, see below), the less CPU time is used.

(TF) Full iterative triples calculation. With full domains and without weak pair approximations this gives the same result as a canonical (T) calculation. Typically, 3-5 iterations are needed, and therefore the computational effort is 2-3 times larger than for (T1). The disk and memory requirements are the same as for T1. The T0 energy is also computed and printed. TFULL and FULL are aliases for TF.

(TA) As TF, but the T1 energy is also computed. Since the first iteration is different for T1, the convergence of the triples iterations is slightly different with TF and TA (TF being somewhat faster in most cases). TALL and ALL are aliases for TA.

Density fitting can be invoked by prepending the command name by DF-, e.g. DF-LMP2, DF-LCCSD(T0) etc. In density fitting calculations an additional auxiliary basis set is needed. Details about choosing such basis sets and other options for density fitting are described in sections 28.10 and 11.

The general input for local coupled LMP2 or coupled cluster calculations is:

LMP2,*options*	Local MP2 calculation
LCCSD,*options*	Local CCSD calculation
LCCSD(T0),*options*	Local CCSD(T0) calculation

The same options as on the command line can also be given on subsequent LOCAL and MULTP directives. Instead of using the MULTP directive, the MULTP option on the command line can also be used.

In the following, we will first give a summary of all options and directives. These will be described in more detail in the subsequent sections. For new users it is recommended to read section 28.9 at the end of this chapter before starting calculations.

28.3 Summary of options

Many options can be specified on the command line. For all options appropriate default values are set, and so these options must usually be modified only for special purposes. For convenience and historical reasons, alias names are available for various options, which often correspond to the variable name used in the program. Table 11 summarizes the options, aliases and default values. In the following, the parameters will be described in more detail.

Table 11: Summary of `local` (*multp*) options and their default values

Parameter	Alias	Default value	Meaning
General Parameters:			
LOCAL		4	determines which program to use.
MULTP		0	turns on multipole approximations for distant pairs.
SAVEDOM	SAVE	0	specifies record for saving domain info.
RESTDOM	START	0	specifies record for reading domain info.
PIPEK	LOCORB	0	activates or deactivates PM localization.
CANONICAL		0	allows to use canonical virtual orbitals (for testing).
PMDEL	CPLDEL	0	discards contributions of diffuse functions in PM localization.
SAVORB	SAVLOC	0	specifies record for saving local orbitals.
DOMONLY		0	if 1, only domains are made. if 2, only orbital domains are made.
Parameters to define domains:			
THRBP	DOMSEL	0.98	Boughton-Pulay selection criterion for orbital domains.
CHGMIN		0.01	determines the minimum allowed atomic charge in domains.
CHGMINH		0.03	as CHGMIN, but used for H-atoms (default 0.03).
CHGMAX		0.40	If the atomic charge is larger than this value, the atom is always included in the domain.
MAXANG	MAXL	99	angular momentum restriction for BP domain selection
MAXBP		0	determines how atoms are ranked in BP procedure.
MULLIKEN	LOCMUL	0	determines the method to determine atomic charges.
MERGEDOM		0	merges overlapping domains.
DELCOR	IDLCOR	2	delete projected core AOs up to certain shell.
DELBAS	IBASO	0	determines how to remove redundancies.
Distance criteria for domain extensions:			
REXT		0	criterion for all pair domains.
REXTS		0	criterion for strong pair domains.
REXTC		0	criterion for strong and close pair domains.
REXTW		0	criterion for strong, close, and weak pair domains.
Connectivity criteria for domain extensions:			
IEXT		0	criterion for all pair domains.
IEXTS		0	criterion for strong pair domains.
IEXTC		0	criterion for strong and close pair domains.
IEXTW		0	criterion for strong, close, and weak pair domains.
Parameters to select pair classes:			
USE_DIST		1	determines if distance of connectivity criteria are used.
RCLOSE	CLOSEP	1	distance criterion for selection of weak pairs.
RWEAK	WEAKP	3	distance criterion for selection of weak pairs.
RDIST	DISTP	8	distance criterion for selection of distant pairs.
RVDIST	VERYD	15	distance criterion for selection of very distant pairs.
ICLOSE		1	connectivity criterion for selection of weak pairs.
IWEAK		2	connectivity criterion for selection of weak pairs.
IDIST		5	connectivity criterion for selection of distant pairs.
IVDIST		8	connectivity criterion for selection of very distant pairs.
CHGMIN_PAIRS	CHGMINP	0.20	determines minimum charge of atoms used for pair classification.
KEEPCL		0	determines if close pairs are included in LCCSD.

Parameter	Alias	Default value	Meaning
Parameter for multipole treatment of exchange operators:			
DSTMLT		3	multipole expansion level for distant pairs
Parameters for energy partitioning:			
IEPART		0	If nonzero: do energy partitioning.
EPART		3.0	cutoff parameter for determining individual monomers.
Parameters for redundancy check using DELBAS=1 (not recommended)			
TYPECHECK	TYPECHK	1	activates basis function type restrictions.
DELSHL	IDLSHL	1	determines if whole shells are to be deleted.
DELEIG	IDLEIG	1	determines how to select redundant functions.
DELCMIN	CDELMIN	0.1	parameter for use with DELEIG=1
Parameters for choosing operator domains in LCCSD			
OPDOM	IOPDOM	5	determines how operator domains are determined for LCCSD
RMAXJ		8	distance criterion for J-operator list.
RMAXK		8	distance criterion for K-operator list.
RMAXL		15	distance criterion for L-operator list.
RMAX3X		5	distance criterion for 3-ext integral list.
RDOMJ		0	distance criterion for K-operator domains.
RDOMK		8	distance criterion for J-operator domains.
IMAXJ		5	connectivity criterion for J-operator list.
IMAXK		5	connectivity criterion for K-operator list.
IMAXL		8	connectivity criterion for L-operator list.
IMAX3X		3	connectivity criterion for 3-ext integral list.
IDOMJ		0	connectivity criterion for K-operator domains.
IDOMK		5	connectivity criterion for J-operator domains.
Miscellaneous options:			
SKIPDIST	SKIPD	3	determines at which stage weak and distant pairs are eliminated
ASYDOM	JITERM	0	parameter for use of asymmetric domains
LOCSING	LOCSNG	0	determines virtual space used for singles
PIPEKAO	LOCAO	0	activates AO localization criterion
NONORM		2	determines whether projected functions are normalized
LMP2ALGO	MP2ALGO	3	if nonzero, use low-order scaling method in LMP22 iterations
OLDDEF		0	allows to revert to older defaults
T1DISK		10	maximum disk space (in GByte) for T1 caching algorithm
Thresholds:			
THRBP		0.98	Threshold Boughton-Pulay method.
THRPIP		1.d-12	Threshold for Pipek-Mezey localization.
THRORB		1.d-6	Threshold for eliminating projected orbitals with small norm.
THRLOC		1.d-6	Threshold for eliminating redundant projected orbitals.
THRCOR		1.d-1	Threshold for eliminating projected core orbitals.
THRMP2		1.d-8	Threshold for neglecting small fock matrix elements in the LMP2 iteration.

28.4 Summary of directives

The same standard directives as in the canonical programs, e.g., OCC, CLOSED, CORE, WF, ORBITAL are also valid in the local methods. In addition, there are some directives which only apply to local calculations:

LOCAL	Invokes local methods and allows to specify the same options as on the command line.
MULTP	As LOCAL, but multipole approximations are used for distant pairs.
DOMAIN	Define domains manually (not recommended).
MERGEDOM	Allows to merge domains
REGION	Allows to select regions of a molecule to be treated at a certain level of theory.
ENEPART	Analysis of pair energies.
SAVE	Save domains and LCCSD amplitudes.
START	Restart with domains and LCCSD amplitudes from a previous calculation.

28.5 General Options

LOCAL=*local*	Determines which method is used: LOCAL=0: Conventional (non-local) calculation. LOCAL=1: Local method is simulated using canonical MOs. The local basis is used only at an intermediate stage to update the amplitudes in each iteration (only for testing). LOCAL=2: Calculation is done in local basis, but without using local blocking (i.e. full matrices are used). This is the most expensive method and only for testing. LOCAL=3: Fully local calculation (obsolete). LOCAL=4: Fully local calculation (default). This is the fastest method for large molecules with many weak pairs and requires minimum memory.
PIPEK=*option*	If this option is given and *option*>0, the orbitals are localized using the Pipek-Mezey technique. If this option is not given or *option*=0 (default), the orbitals are localized unless localized orbitals are found in the orbital record (cf. ORBITAL directive and LOCALI command). In the latter case, the most recent localized orbitals are used. Setting *option*=-1 switches the localization off. If *option*>1 the localized orbitals are printed. Note: Boys localization can only be performed using the LOCALI command. The program will use the Boys orbitals if they are found in the orbital record and the PIPEK option is absent or *option*≤ 0.
SAVORB=*record*	Allows the localized and projected orbitals to be saved in *record*=*name.ifil* for later use (e.g. plotting). The two orbital sets are stored in the same dump record and can be restored at later stages using ORBITAL,*record*,[TYPE=]LOCAL or ORBITAL,*record*,[TYPE=]PROJECTED, respectively.

DOMONLY=*value* If *value*> 0 only domains are made, but no energy is computed. This can be used to check and save the domains for later use.

DSTMLT=*level* Determines the expansion level of the multipole expansion of distant pairs (e.g. 1 means dipole approximation, 2 quadrupole approximation and so on). The default for MULTP is 3.

INTERACT Automatically determine individual molecules in a calculation and set appropriate pair lists for computing interaction energies. See section 28.9.8 for more details.

Parameters for energy partitioning:

IEPART=*value* enables/disables energy partitioning.
iepart=0: Energy partitioning is disabled.
iepart=1: Energy partitioning is enabled.
iepart=2: Energy partitioning is enabled. Additionally, a list of all pair energies and their components is printed.

EPART=*cutoff* Cutoff parameter to determine individual monomers in a cluster (i.e. centre groups). Should be somewhat larger than the largest intramolecular bond length (given in a.u.).

Miscellaneous options:

SKIPDIST=*skipdist* Test-parameter. Its value should only affect the efficiency but not influence the results.
skipdist=-1: Weak and distant pairs are set to zero after MP2 but are not eliminated from the pair list and not skipped in any loop.
skipdist=0: No pairs are deleted from pair list, but weak and distant pairs are skipped in the loops were appropriate.
skipdist=1: Very distant pairs are neglected from the beginning. Distant pairs are eliminated after MP2.
skipdist=2: As skipdist=1, but also weak pairs are eliminated after MP2.
skipdist=3: As skipdist=2, but distant pairs are eliminated from the operator list in case of LMP2 with multipole approximations for distant pairs. This is the default.

ASYDOM=*jiterm* Experimental test parameter. Enables the use of asymmetric domains for distant pairs. The asymmetric domain approximation supplements the multipole approximation for distant pairs, as it suppresses the treatment of configurations for which no integrals can be computed by multipole expansion. This leads to computational savings and improved numerical stability.
jiterm=0: Disable asymmetric domains.
jiterm=-1: Enable asymmetric domains (default).
jiterm=-2: Enable a variation of the asymmetric domain formalism: Exchange operators will initially be projected to the asymmetric domain instead of simply packed.

LOCSING=*locsing* If *locsing.ne.0*, the single excitations use the full space, i.e., they are not treated locally. This is only works for LOCAL=1.

MAXANG=*lmax* The purpose of this experimental option is to reduce the basis set sensitivity of the Boughton-Pulay (BP) method for domain selection. Only basis functions with angular momentum up to *lmax-1* are included when computing the overlap of the approximate and exact or-

bitals. For example, MAXANG=2 means to omit all contributions of d, f and higher angular momentum functions. To obtain reasonable domains, the value of THRBP must often be reduced (to 0.97 or so). This option should only be used with care!

PIPEKAO=*option* If *option*≥ 0, the orbitals are localized my maximizing the coefficients of basis functions of a given type at a given atom. Normally, this is only useful to uniquely define degenerate orbitals in atoms. For instance, when this option is used to localize the orbitals for a dimer like $(Ar)_2$ at a very long distance, clean s, p_x, p_y, and p_z atomic orbitals will be obtained. It is not recommended to use this option for molecular calculations!

NONORM=*value* Determines if projected functions are normalized (not recommended).
value=-1: projected orbitals are normalized before redundancy check.
value=0: projected orbitals are normalized after redundancy check (default).
value=1: projected orbitals are normalized in redundancy check, afterwards unnormalized.
value=2: projected orbitals are never normalized (default in gradient calculations).

LMP2ALGO=*value* If nonzero, use low-order scaling method in LMP2 iterations. Values can be 1, 2, or 3, and 3 is usually fastest if large basis sets are used.

OLDDEF=*value* For compatibility with older versions: if nonzero, revert to old defaults. Options set before this may be overwritten.

Thresholds:

THRPIP=*thresh* Threshold for Pipek-Mezey localization. The localization is assumed to be converged if all 2×2 rotation angles are smaller then *thresh*. The default is $1.d-12$. It can also be modified globally using GTHRESH, LOCALI=*thresh*.

THRORB=*thresh* Threshold for eliminating functions from pair domains whose norm is smaller then *thresh* after projecting out the occupied space. The default is *throrb=1.d-6*.

THRLOC=*thresh* Threshold for eliminating redundant basis functions from pair domains. For each eigenvalue of $\tilde{\mathbf{S}}^{ij} < thresh$ one function is deleted. The default is 1.d-6. The method used for deleting functions depends on the parameters IDLEIG and IBASO.

THRMP2=*thresh* Threshold for neglecting small fock matrix couplings in the LMP2 iterations (default 1.d-8). Specifying a larger threshold speeds up the iterations but may lead to small errors in the energy. In the initial iterations, a larger threshold is chosen automatically. It is gradually reduced to the specified final value during the iterations.

THRCOR=*thresh* Threshold for deleting projected core orbitals. The functions are only deleted if their norm is smaller than *thresh* (default 0.1)

The thresholds can also be specified on the THRESH directive.

28.6 Options for selection of domains

The following sections describe the most important options which affect the domains.

28.6.1 Standard domains

Standard domains are always determined first. They are used to define strong, close, weak, and distant pairs. More accurate results can be obtained with extended domains, as described in section 28.6.2.

`THRBP=`*value* Threshold for selecting the atoms contributing to orbital domains using the method of Boughton and Pulay (BP). As many atoms as needed to fulfill the BP criterion are included in a domain. The order in which atoms are considered depends on the parameter `MAXBP`, see below. The default is `THRBP=0.98`. `THRBP=1.0` includes all atoms into each orbital domain, i.e., leads to full domains. If no pairs are neglected, this should yield the canonical MP2 energy.

The criterion is somewhat basis dependent. See section 28.9.4 for recommended values of this threshold.

`CHGMIN=`*value* determines the minimum allowed Mulliken (or Löwdin) charge for an atom (except H) in a domain, i.e., atoms with a smaller (absolute) charge are not included, even if the `THRBP` criterion is not fulfilled (default 0.01).

`CHGMINH=`*value* as `CHGMIN`, but used for H-atoms (default 0.03).

`CHGMAX=`*value* If the atomic charge is larger than this value, the atom is included, independent of any ranking.

`MAXBP=`*maxbp* If *maxbp=1*, the atoms are ranked according to their contribution to the Boughton-Pulay overlap. If *maxbp=0* (default), the atoms are ranked according to atomic charges. In both cases atoms with charges greater than `CHGMAX` are always included, and atoms with the same charges are added as groups.

`MULLIKEN=`*option* Determines the method to determine atomic charges. `MULLIKEN=0` (default): squares of diagonal elements of $\mathbf{S}^{\frac{1}{2}}\mathbf{C}$ are used (Löwdin charges); `MULLIKEN=1`: Mulliken gross charges are used. The first choice is less basis set dependent and more reliable with diffuse basis sets.

`MERGEDOM=`*number* If *number* is greater than zero, all orbital domains containing *number* or more atoms in common are merged (*number=1* is treated as *number=2*, default 0). This is particularly useful for geometry optimizations of conjugated or aromatic systems like, e.g., benzene. In the latter case, `MERGEDOM=1` causes the generation of full π-domains, i.e., the domains for all three π-orbitals comprise all carbon basis functions. Note that the merged domains are generated after the above print of orbital domains, and information about merged domains is printed separately. See section 28.9.7 for further discussion of geometry optimizations.

There are some other options which should normally not be modified:

`DELBAS=`*ibaso* This parameter determines the method for eliminating redundant functions of pair domains.
ibaso=0: The space of normalized eigenvectors of $\tilde{\mathbf{S}}^{ij}$, which correspond to small eigenvalues, is eliminated (default). Any other

value is not recommended and not further documented.

DELCOR=*nshell* Activates elimination of basis functions corresponding to core orbitals. If *nshell=1*, only 1s-functions are eliminated from projected space. If *nshell=2* (default) 1s functions on first-row atoms, and 1s, 2s, and 2p-functions are eliminated on second-row atoms. Nothing is eliminated on H or He atoms. If effective core potentials are used, nothing is deleted at the corresponding atom. Also, functions are only deleted if the norm of the projected function is below THRCOR (default 0.1)

28.6.2 Extended domains

There are two alternative modes for domain extensions: either *distance criteria* REXT, REXTS, REXTC, or REXTW can be used. These are in Bohr and refer to the minimum distance between any atom in a standard orbital domain $[ij]$ and another atom. If an atom is found within the given distance, all PAOs at this atom are added to the domain $[ij]$. Alternatively, *connectivity criteria* IEXT, IEXTS, IEXTC, or IEXTW can be used. These refer to the number of bonds between any atom contained in the standard domain $[ij]$ and another atom. The advantage of distance criteria is that they select also atoms within the given radius which are not connected to the present domain by bonds. On the other hand, the connectivity criteria are independent of different bond lengths, e.g., for first and second-row atoms. Only one of the two possibilities can be used, i.e., they are mutually exclusive.

REXT=*value* Distance criterion for extension of all pair domains.

REXTS=*value* Distance criterion for extension of strong pair domains.

REXTC=*value* Distance criterion for extension of strong and close pair domains.

REXTW=*value* Distance criterion for extension of strong, close, and weak pair domains.

IEXT=*value* Connectivity criterion for extension of all pair domains.

IEXTS=*value* Connectivity criterion for extension of strong pair domains.

IEXTC=*value* Connectivity criterion for extension of strong and close pair domains.

IEXTW=*value* Connectivity criterion for extension of strong, close, and weak pair domains.

By default, domains are not extended, i.e., the default values of all parameters listed above are zero. Note that the pair classes are determined on the basis of the standard domains, and therefore domain extensions have no effect on the pair lists.

Also note that the computational effort increases with the fourth power of the domain sizes and can therefore increase quite dramatically when extending domains. This does not affect the linear scaling behaviour in the asymptotic limit.

28.6.3 Manually Defining orbital domains (DOMAIN)

It is possible to define the domains “by hand”, using the DOMAIN directive:

DOMAIN,*orbital*,*atom1*, *atom2* ...

where *orbital* has the form `iorb.isym`, e.g., 3.1 for the third orbital in symmetry 1, and *atomi* are the atomic labels as given in the Z-matrix geometry input, or, alternatively, the Z-matrix row numbers. All basis functions centred at the given atoms are included into the domain. For instance

```
DOMAIN,3.1,C1,C2
```

defines a domain for a bicentric bond between the carbon atoms `C1` and `C2`. The `DOMAIN` directive must be given after any `OCC`, `CLOSED`, or `CORE` directives. Note that the order of the localized orbitals depends on the localization procedure, and could even change as function of geometry, and therefore manual `DOMAIN` input should be used with great care. The domains of all orbitals which are not explicitly defined using `DOMAIN` directive are determined automatically as usual.

28.7 Options for selection of pair classes

There are two alternative modes for defining the pair classes: either *distance criteria* `RCLOSE`, `RWEAK`, `RDIST`, `RVDIST` can be used. These are in Bohr and refer for a given orbital pair (ij) to the minimum distance $R^{(ij)}$ between any atom in the standard orbital domains $[i]$ and any atom in the standard orbital domains $[j]$. Alternatively, the *connectivity criteria* `ICLOSE`, `IWEAK`, `IDIST`, `IVDIST` can be used. These refer to the minimum number of bonds between any atom contained in the standard domain $[i]$ and any atom contained in the standard domain $[j]$ The advantage of using connectivity criteria is the independence of the bond lengths, while the advantage of distance criteria (default) is that they are also effective in non-bonding situations. Only one of the two possibilities can be used, i.e., they are mutually exclusive. The use of distance criteria is the default. Using connectivity criteria for pair selection requires to set the option `USE_DIST=0`.

`USE_DIST`	(default 1) If nonzero, use distance criteria, otherwise connectivity criteria.
`CHGMIN_PAIRS`	Only atoms in the primary domains are considered for the pair classification if the atomic Löwdin charge is larger than `CHGMIN_PAIRS` (default value 0.2). This criterion was introduced in order to reduce the dependence of the pair selection on localization tails.
`RCLOSE`	(default 1) Strong pairs are defined by $0 \leq R^{(ij)} <$ `RCLOSE`. Close pairs are defined by `RCLOSE` $\leq R^{(ij)} <$ `RWEAK`.
`RWEAK`	(default 3) Weak pairs are defined by `RWEAK` $\leq R^{(ij)} <$ `RDIST`.
`RDIST`	(default 8) Distant pairs are defined by `RDIST` $\leq R^{(ij)} <$ `RVDIST`.
`RVDIST`	(default 15) Very distant pairs for which $R^{(ij)} \geq$`RVDIST` are neglected.
`ICLOSE`	(default 1) Strong pairs are separated by less that `ICLOSE` bonds. Close orbital pairs are separated by at least `ICLOSE` bonds but less than `IWEAK` bonds.
`IWEAK`	(default 2) Weak orbital pairs are separated by at least `IWEAK` bonds but less than `IDIST` bonds.
`IDIST`	(default 5) Distant orbital pairs are separated by at least `IDIST` bonds but less than `IVDIST` bonds.
`IVDIST`	(default 8) Very distant orbital pairs (neglected) are separated by at least `IVDIST` bonds.

KEEPCL (default 0) If KEEPCL=1, the LMP2 amplitudes of close pairs are included in the computation of the strong pair LCCSD residuals. If KEEPCL=2 all close pairs are fully included in the LCCSD (this does not affect the triples list). This option is not yet implemented as efficiently as it could, and can therefore lead to a significant increase of the CPU time.

Setting a distance criterion to zero means that all pairs up to the corresponding class are treated as strong pairs. For instance, RCLOSE=0 means that strong and close pairs are fully included in the LCCSD (in this case KEEPCL=1 has no effect). Note, however, that setting RCLOSE=0 increases the length of the triples list.

28.8 Directives

28.8.1 The LOCAL directive

The LOCAL directive can be used to specify options for local calculations. If this directive is inside the command block of a local calculation, the options are used only for the current calculation, and this is entirely equivalent as if they were specified on the command line. The LOCAL directive can also be given outside a command block, and in this case the options are used for all subsequent local correlation calculations in the same input.

Example:

```
DF-LMP2,THRBP=0.985
```

is equivalent to

```
{DF-LMP2
LOCAL,THRBP=0.985}
```

In the following example the LOCAL directive is global and acts on all subsequent local calculations, i.e. both calculations will use THRBP=0.985

```
LOCAL,THRBP=0.985
DF-LMP2       !local MP2 calculation
OPTG          !geometry optimization using the DF-LMP2 energy
DF-LCCSD(T)   !local coupled cluster at the optimized structure.
```

28.8.2 The MULTP directive

The MULTP directive turns on the multipole approximations for distant pairs, as described in Ref. [8]. Further options can be given as described above for the LOCAL directive.

LOCAL,MULTP,*options*

is equivalent to

MULTP,*options*

The level of the multipole approximation can be chosen using option DSTMLT (default 3) (1 means dipole approximation, 2 quadrupole approximation and so on).

The multipole approximation reduces the computational cost of LMP2 calculations for very large molecules, but leads to some additional errors, see Ref. [8]. It is normally not recommended to be used in coupled-cluster calculations and should never be used for computing intermolecular forces. It can also not be used in geometry optimizations or gradient calculations.

28.8.3 Saving the wavefunction (SAVE)

The wavefunction can be saved for later restart using

SAVE,*record*

where *record* has the usual form, e.g., 4000.2 means record 4000 on file 2. If this directive is given, the domain information as well as the amplitudes are saved (for MPn the amplitudes are not saved). If just the domain information should be stored, the SAVE option on the LOCAL directive must be used (cf. section 28.3).

28.8.4 Restarting a calculation (START)

Local CCSD or QCISD calculations can be restarted using

START,*record*

The record given must have been saved in a previous local calculation using the SAVE directive (otherwise this directive is ignored). If the START directive is given, the domain information as well as the amplitudes of the previous calculation are used for restart. It is possible, for instance, to start a local CCSD calculation with the amplitudes previously saved for a local QCISD calculation (but of course it is not possible to use a record saved for a non-local CCSD or QCISD calculation). If it is intended only to use the domain information but not the amplitudes for a restart, the START option on the command line or LOCAL directive must be used (cf. section 28.3).

28.8.5 Correlating subsets of electrons (REGION)

In large molecules, it may be sufficient to correlate only the electrons in the vicinity of an *active group*, and to treat the rest of the molecule at the SCF level. This approach can even be extended, different correlation levels may be used for different sections of the system. The REGION directive allows the specification of a subset of atoms:

REGION,METHOD=*method*,[DEFAULT=*default_method*], [TYPE=INCLUSIVE|EXCLUSIVE], *atom1*, *atom2* ...

The orbitals located at these atoms will be treated at the level specified in *method*. The remaining orbitals will be treated as defined in *default*. If not given by the user, the latter option will be set to HF.

The orbital selection can be done in two ways. If *type* is set to INCLUSIVE, any orbital containing one of the atoms in its domain centre list will be included. If type is set to EXCLUSIVE, the program will only add orbitals whose domains are exclusively covered by the given atoms. Any local correlation treatment can be given as *method*, with the restriction that only MP2 and HF can be used as *default_method*. Up to two REGION directives may be included in a single calculation, ordered according to the correlation level (*method*) specified for the region. The highest level region should be given last.

It is advisable to check the region orbital list and the orbital domains printed by the program. The use of regions may significantly reduce the computation time, and, provided the active atoms are sensibly chosen, may give still sufficiently accurate results for the *active group*, e.g. bond lengths and bond angles.

28.8.6 Domain Merging (MERGEDOM)

The restriction of the virtual space in local calculations may result in discontinuities for reaction path calculations due to changes of the geometry dependent domains. This may be avoided by the use of a MERGEDOM directive

MERGEDOM,[NEIGHBOUR=*value*],[CENTERS=[*atom1, atom2...*]], [RECORD=...],CHECK

This directive provides augmented domains, which can be saved (using option or directive SAVE, see section 28.8.3) for later use in reaction paths or in single point calculations (in cases where the orbital domain description is unbalanced). The use of the *neighbour* option works in the same way as the local option MERGEDOM, with *value* specifying the number of coincident centres. If the *centres* option is used, an atom list should be given (enclosed by square brackets). The domains of all orbitals located exclusively at these atoms will be merged, and the resulting merged domains will be used for all these orbitals.

One may also give a *record* number from a previously saved local calculation. The domain list contained in the record will be matched to the current one, and orbital domains augmented (merged) to include both sets. This domain definition should then be adequate for calculations on both points (and all those in between). This procedure can be repeated to include more geometries. In this way domains can be defined that are appropriate for a whole range of geometries (e.g. a reaction path), and if these domains are used in all calculations a strictly smooth potential energy surface is obtained.

28.8.7 Energy partitioning for molecular cluster calculations (ENEPART)

The local character of occupied and virtual orbitals in the local correlation treatment also offers the appealing possibility to decompose the intermolecular interaction energy of molecular clusters into individual contributions of different excitation classes. This allows to distinguish between intramolecular-, dispersive-, and ionic components of the correlation contribution to the interaction energy (cf. M. Schütz, G. Rauhut and H.J. Werner, J. Phys. Chem. **102**, 5197 (1998)). The energy partitioning algorithm is activated either by supplying the ENEPART directive:

ENEPART,[*epart*],[*iepart*]

or by giving the parameters as options on the command line.

The *epart* parameter determines the cutoff distance for (intramolecular) bond lengths (in a.u., default 3 a.u.) and is used to automatically determine the individual monomer subunits of the cluster. The *iepart* parameter enables the energy partitioning, if set to a value larger than zero (default 1). Additionally, if iepart is set to 2, a list of all intermolecular pair energies and their components is printed.

The output section produced by the energy partitioning algorithm will look similar to the following example:

```
energy partitioning enabled !
centre groups formed for cutoff [au] = 3.00
 1   :O1  H11 H12
```

```
 2   :O2  H21 H22
energy partitioning relative to centre groups:
intramolecular correlation:      -.43752663
exchange dispersion       :       .00000037
dispersion energy         :      -.00022425
ionic contributions       :      -.00007637
```

The centre groups correspond to the individual monomers determined for *epart=3*. In the present example, two water monomers were found. The correlation energy is partitioned into the four components shown above. The exchange dispersion, dispersion and ionic components reflect directly the related intermolecular components of the complex, while the intramolecular correlation contribution to the interaction energy has to be determined by a super-molecular calculation, i.e. by subtracting the (two) corresponding monomer correlation energies from the intramolecular correlation component of the complex given in the output.

Alternatively, the following form can be used:

`ENEPART,RMAX=[`*r1,r2,r3,...*`]`

and the program will then print the energy contributions of all pairs in the ranges between the given distances (in bohr, enclosed by square brackets, e.g., `enepart,rmax=[0,3,5,7,9,11]`). A second list in which the contributions are given as a function of the number of bonds between the pair domains will also be printed.

28.9 Doing it right

The local correlation methods in MOLPRO employ localized molecular orbitals (LMOs). Pipek-Mezey localization is recommended, but Boys localization is also possible. The virtual orbital space is spanned by non-orthogonal projected atomic orbitals (PAOs). The local character of this basis makes it possible to introduce two distinct approximations: first, excitations are restricted to *domains*, which are subspaces of (PAOs) that are spatially close to the orbitals from which the electrons are being excited. Secondly, the orbital pairs are classified according to their importance (based on distance or connectivity criteria), and only *strong pairs* are treated at the highest level (e.g. CCSD). The remaining *weak* and *distant* pairs are treated at the LMP2 level, and *very distant* pairs are neglected. These approximations lead to linear scaling of the computational resources as a function of the molecular size.

Naturally, such approximation can introduce some errors, and therefore the user has to be more careful than with standard black box methods. On the other hand, the low-order scaling makes it possible to treat much larger systems at high levels of theory than it was possible so far.

This section summarizes some important points to remember when performing local correlation calculations.

28.9.1 Basis sets

For numerical reasons, it is useful to eliminate projected core orbitals, since these may have a very small norm. By default, projected core orbitals are eliminated if their norm is smaller then 0.1 (this behaviour can be changed using the `DELCOR` and `THRCOR` options). For local calculations we recommend the use of generally contracted basis sets, e.g., the correlation consistent cc-pVnZ sets of Dunning and coworkers. For these basis sets the core basis functions are uniquely defined, and will always be eliminated if the defaults for `DELCOR` and `THRCOR` are used.

The correlation consistent basis sets are also recommended for all density fitting calculations, since optimized fitting basis sets are available for each basis.

28.9.2 Symmetry and Orientation

1. Turn off symmetry! Otherwise, you won't get appropriately localized orbitals (local orbitals will tend to be symmetry equivalent instead of symmetry adapted). Symmetry can be used only if all atoms are symmetry unique. This allows the local treatment of planar molecules in C_s symmetry. But note that neither the multipole program nor the density fitting programs support symmetry at all, so choose always C_1 symmetry for DF-calculations or with the `MULTP` option.

To turn off symmetry, specify `NOSYM` as the first line of your geometry input, e.g.

```
geometry={
  nosym
  O1
  H1,O1,roh
  H2,O1,roh,h1,hoh
}
```

Alternatively, add

```
SET,ZSYMEL=NOSYM
```

before the geometry block.

2. Use NOORIENT! We recommend to use the `NOORIENT` option in the geometry input, to avoid unintended rotations of the molecule when the geometry changes. This is particularly important for geometry optimizations and for domain restarts in calculations of interaction energies (see section 28.9.8).

28.9.3 Localization

By default, Pipek-Mezey localization is used and performed automatically in the beginning of a local correlation calculation. Thus

```
df-hf        !Hartree-Fock with density fitting
df-lmp2      !LMP2 using the Pipek-Mezey LMOs
```

is equivalent to

```
df-hf        !Hartree-Fock with density fitting
locali,pipek !Orbital localization using the Pipek-Mezey criterion
df-lmp2      !LMP2 using the Pipek-Mezey LMOs
```

Boys localization can be used as well, but in this case the localization must be done beforehand, e.g.

```
df-hf        !Hartree-Fock with density fitting
locali,boys  !Orbital localization using the Boys criterion
df-lmp2      !LMP2 using the Boys LMOs
```

Poor localization is sometimes an intrinsic problem, in particular for strongly conjugated systems or when diffuse basis sets are used. This is caused by localization tails due to the overlapping diffuse functions. The problem is particularly frequent in calculations of systems with short bonds, e.g., aromatic molecules. It can be avoided using directive

```
PIPEK,DELETE=n
```

with $n = 1$ or 2. This means that the contributions of the n most diffuse basis functions of each angular momentum type are ignored in the localization. This often yields much better localized orbitals when diffuse basis sets are used. For aug-cc-pVTZ, $n = 2$ has been found to work very well, while for aug-cc-pVDZ n=1

In rare cases it might also happen that the localization procedure does not converge. It is them possible to choose a second-order Newton-Raphson localization scheme, using the directive

```
PIPEK,METHOD=2,[DELETE=n]
```

28.9.4 Orbital domains

The orbital domains are determined automatically using the procedure of Boughton and Pulay, J. Comput. Chem., **14**, 736 (1993) and J. Chem. Phys. **104**, 6286 (1996). For higher accuracy the domains can be extended, and in this way the canonical result can be systematically approached (cf. Ref. [1] and section 28.6.2). Details are described in section 28.6.

In most cases, the domain selection is uncritical for saturated molecules. Nevertheless, in particular for delocalized systems, it is recommended always to check the orbital domains, which are printed in the beginning of each local calculation. For such checking, the option `DOMONLY=1` can be used to stop the calculation after the domain generation. The orbital domains consist of all basis functions for a subset of atoms. These atoms are selected so that the domain spans the corresponding localized orbital with a preset accuracy (alterable with option `THRBP`). A typical domain output, here for water, looks like this:

```
 Orbital domains

   Orb.    Atom    Charge       Crit.
   2.1     1 O1     1.17        0.00
           3 H2     0.84        1.00
   3.1     1 O1     2.02        1.00
   4.1     1 O1     1.96        1.00
   5.1     1 O1     1.17        0.00
           2 H1     0.84        1.00
```

This tells you that the domains for orbitals 2.1 and 5.1 comprise the basis functions of the oxygen atom and and one hydrogen atom, while the domains for orbitals 3.1 and 4.1 consist of the basis function on oxygen only. The latter ones correspond to the oxygen lone pairs, the former to the two OH bonds, and so this is exactly what one would expect. For each domain of AOs, corresponding projected atomic orbitals (PAOs) are generated, which span subspaces of the virtual space and into which excitations are made. Options which affect the domain selection are described in section 28.6. Improper domains can result from poorly localized orbitals (see section 28.9.3 or a forgotten `NOSYM` directive. This does not only negatively affect performance and memory requirements, but can also lead to unexpected results.

The default for the selection criterion `THRBP` is 0.98. This works usually well for small basis sets like cc-pVDZ. For larger basis sets like cc-pVTZ we recommend to use a slightly larger value of 0.985 to ensure that enough atoms are included in each domain. For cc-pVQZ recommend `THRBP=0.990` is recommended. In cases of doubt, compare the domains you get with a smaller basis (e.g., cc-pVDZ).

The choice of domains usually has only a weak effect on near-equilibrium properties like equilibrium geometries and harmonic vibrational frequencies. More critical are energy differences like reaction energies or barrier heights. In cases where the electronic structure strongly changes, e.g., when the number of double bonds changes, it is recommended to compare DF-LMP2 and DF-MP2 results before performing expensive LCCSD(T) calculations. More balanced results and smooth potentials can be obtained using the MERGEDOM directive, see section 28.8.6.

28.9.5 Freezing domains

In order to obtain smooth potential energy surfaces, domains must be frozen. The domain information can be stored using the SAVE option and recovered using the START option. Alternatively, the SAVE and START can be used, see section 28.8.3. In the latter case, also the CCSD amplitudes are saved/restarted. Freezing domains is particularly important in calculations of intermolecular interactions, see section 28.9.8. Domains that are appropriate for larger ranges of geometries, such as reaction pathways, can be generated using the MERGEDOM directive, section 28.8.6. The domains are automatically frozen in geometry optimizations and frequency calculations, see section 28.9.7.

28.9.6 Pair Classes

The *strong*, *close*, *weak* and *distant* pairs are selected using distance or connectivity criteria as described in more detail in section 28.7. *Strong* pairs are treated by CCSD, all other pairs by LMP2. In triples calculations, all orbital triples (ijk) are included for which (ij), (ik), and (jk) are *close pairs*. In addition, one of these pairs is restricted to be strong. The triples energy depends on the strong and close pair amplitudes. The close pair amplitudes are taken from the LMP2 calculation. Thus, increasing the distance or connectivity criteria for close and weak pairs will lead to more accurate triples energies. While for near equilibrium properties like geometries and harmonic vibrational frequencies the default values are normally appropriate, larger distance criteria are sometimes needed when computing energy differences, in particular barrier heights. In cases of doubt, RWEAK should first be increased until convergence is reached, and then RCLOSE can be varied as well. Such tests can be performed with small basis sets like cc-pVDZ, and the optimized values then be used in the final calculations with large basis sets.

28.9.7 Gradients and frequency calculations

Geometry optimizations [15-17] and numerical frequency calculations [18-20] can be performed using analytical energy gradients [15-17] for local MP2. LMP2 geometry optimizations are particularly attractive for weakly bound systems, since virtually BSSE free structures are obtained (see section 28.9.8 and Refs. [21-23]). For reasons of efficiency it is strongly advisable to use the DF-LMP2 Gradient [17] for all geometry optimizations. Setting SCSGRD=1 on the DF-LMP2 command or DFIT directive activates the gradient with respect to Grimmes SCS scaled MP2 energy functional (see also section DFIT). Analytical energy gradients are not yet available for the multipole approximation of distant pairs, and therefore MULTP cannot be used in geometry optimizations or frequency calculations.

In geometry optimizations, the domains are allowed to vary in the initial optimization steps. When the stepsize drops below a certain threshold (default 0.01) the domains are automatically frozen. In numerical Hessian or frequency calculations the domains are also frozen. It is therefore not necessary to include SAVE and START options.

Particular care must be taken in optimizations of highly symmetric aromatic systems, like, e.g., benzene. In D_{6h} symmetry, the localization of the π-orbitals is not unique, i.e., the localized orbitals can be rotated around the C_6 axis without changing the localization criterion. This redundancy is lost if the symmetry is slightly distorted, which can lead to sudden changes of the localized orbitals. If now the domains are kept fixed using the SAVE and START options, a large error in the energy might result. On the other hand, if the domains are not kept fixed, their size and quality might change during the optimization, again leading to spurious energy changes and divergence of the optimization.

The best way to avoid this problem is to use the MERGEDOM=1 option (see section 28.6). If this option is given, the domains for the π orbitals will comprise the basis functions of all six carbon atoms, and the energy will be invariant with respect to unitary transformations among the three π orbitals. Note that this problem does not occur if the symmetry of the aromatic system is lowered by a substituent.

Redundant orbital rotations can also lead to convergence difficulties of the Pipek-Mezey localization. This can be overcome by using

```
PIPEK,METHOD=2
```

With this option, the second derivatives of the localization criterion with respect to the orbital rotations is computed and diagonalized, and rotations corresponding to zero eigenvalues are eliminated.

Finally, we note that the LMP2 gradients are quite sensitive to the accuracy of the SCF convergence (as is also the case for MP2). If very accurate structures are required, or if numerical frequencies are computed from the gradients, the default SCF accuracy might be insufficient. We recommend in such cases to add an ACCU,14 directive (possibly even ACCU,16) after the HF command. Indicative of insufficient SCF accuracy are small positive energy changes near the end of the geometry optimization.

28.9.8 Intermolecular interactions

Local methods are particularly useful for the calculation of weak intermolecular interactions since the basis set superposition error (BSSE) is largely reduced [1,13,14] and counterpoise corrections are usually not necessary (provided the BSSE of the underlying Hartree-Fock is small). However, one must be careful to define the domains properly and to include all intermolecular pairs at the highest computational level. A convenient way to define appropriate domains and pair lists is to use the option INTERACT=1. If this option is given, individual molecules are identified automatically and all intermolecular pairs are automatically treated as strong pairs and included in the LCCSD. Similarly, appropriate triples lists are generated for LCCSD(T) calculations. It is required that all orbital domains are located on individual molecules. Note however that the inclusion of the intermolecular pairs strongly increases the number of strong pairs and triples, and therefore high-level calculations can become very expensive.

For calculations of interaction potentials of weakly interacting systems, the domains of the subsystems should be determined at a very large distance and saved using the SAVE=*record* option on the LOCAL or MULTP directive, or the SAVE directive (see section 28.8.3). If the asymptotic energy is not needed it is sufficient to do this initial calculation using option DOMONLY=1). These domains should then be reused in the subsequent calculations at all other intermolecular distances by using the START=*record* option or the START directive (see section 28.8.4). Only in this way the basis set superposition error is minimized and normally negligible (of course, this does not affect the BSSE for the SCF, and therefore the basis set should be sufficiently large to make the SCF BSSE negligible).

Usually, diffuse basis functions are important for obtaining accurate intermolecular interactions. When diffuse basis sets are used, it may happen that the Pipek-Mezey localization does not yield well localized orbitals. This problem can in most cases be overcome by using the directive

PIPEK,DELETE=*n*

as described in section 28.9.3

A final warning concerns local density fitting (see sections 28.10 and 11): local fitting must not be used in counterpoise calculations, since no fitting functions would be present on the dummy atoms and this can lead to large errors.

For examples and discussions of these aspects see Refs. [21-23]

28.10 Density-fitted LMP2 (DF-LMP2) and coupled cluster (DF-LCCSD(T0))

Density-fitting LMP2 and LCCSD calculations can be performed by adding the prefix DF- to the command name. The input is as follows:

DF-LMP2,[*options*]
DF-LCCSD(T),[*options*]

Options for density fitting can be mixed with any options for LOCAL. Options for density fitting can also be given on a DFIT directive (see section 11).

The most important options for density fitting in local methods are

BASIS_MP2=*string*	Fitting basis set used in LMP2 and in LCCSD for integrals with up to 2 external orbitals. If a correlation consistent basis set is used (e.g. cc-pVTZ) the corresponding fitting basis for MP2 us used by default (cc-pVTZ/MP2FIT). Otherwise the fitting basis set must be defined in a preceding basis block (see section 13).
BASIS_CCSD=*string*	Fitting basis set used in LCCSD for integrals over 3- and 4-external orbitals. The default is BASIS_MP2 and this is usually sufficient. However, the accurate approximation of 4-external integrals in LCCSD requires larger fitting basis sets than LMP2. Therefore, in order to minimize fitting errors, it is recommended to use the next larger fitting basis, e.g., BASIS_CCSD=VQZ for orbital basis VTZ.
LOCFIT=*value*:	If LOCFIT=1 local fitting is enabled. This is necessary to achieve linear scaling in DF-LMP2 (see Refs. [11-14]). The errors introduced by local fitting are usually very small, but there are some exceptions. For instance, LOCFIT=1 must not be used in counterpoise calculations, see section 28.9.8) Note that for small molecules LOCFIT=1 can be more expensive than LOCFIT=0.

For further details and options for density fitting see section 11.

29 EXPLICITLY CORRELATED METHODS

Explicitly correlated MP2-R12 and MP2-F12 calculations can be performed using density fitting for the necessary integrals. Currently the available Ansätze are restricted to the **2**A type. Methods are available in local (DF-LMP2-R12,DF-LMP2-F12) and canonical (DF-MP2-R12, DF-MP2-F12) versions, detailed below. Symmetry is not implemented for any of these methods, and therefore the NOSYM option must be given in the geometry block.

For DF-MP2-F12 the correlation factor is a frozen expansion f_{12} of Gaussian type geminals. By default the geminal is built from six Gaussian functions, and the exponents and coefficients are optimized to obtain the best least squares fit to $f_{12} = \exp(-\beta r_{12})$ using a suitable weight function. If correlation consistent basis sets are used, a suitable density fitting (DF) basis is automatically chosen. In the case of R12 methods, the default for the RI basis is the AO basis set, while for F12 methods Hartree-Fock JK-fitting bases are used by default (e.g., VTZ/JKFIT is used for orbital basis VTZ).

In general, only the F12 methods are recommended, since these lead to much more accurate results and converge better with respect to the AO, DF, and RI basis sets than the R12 methods.

Options for canonical and local versions:

DF_BASIS=*basis*	Select the basis for density fitting (see section 11 for details). *basis* can either refer to a set name defined in the basis block, or to a default MP2 fitting basis (e.g., DF_BASIS=VTZ generates the VTZ/MP2FIT basis). See section 11 for more details.
RI_BASIS=*basis*	Select the basis for the resolution of the identity (RI). In case of R12 methods, this should be chosen to be a large uncontracted AO basis (at least AVQZ). For F12 methods we have found that the Hartree-Fock JKFIT basis sets perform well for the RI, despite having been optimized for other purposes.
ANSATZ=*ansatz*	Select the explicitly correlated ansatz *ansatz* for the canonical methods. The ansatz takes the form 2A, 2*A, or 2A`. The optional * invokes additional approximations (based on the extended Brillouin approximation) that result in increased efficiency. The optional backward quote ` (standing in for 'prime') results in the inclusion of some small terms required for full orbital invariance. Since the terms are cheap to compute, the flexibility not to include them is provided for historical reasons. Whatever ansatz is chosen, all levels of theory are computed that do not entail the evaluation of additional integrals. Currently only ansatz **2***A is implemented in the local version, with the additional approximation that only "diagonal" $(ijij)$ pairs are included in the correlation factor.
GEM_BASIS	Basis set name for geminal expansion; atom labels are ignored. This can either be OPTFULL (full nonlinear fit of the geminal expansion), EVEN (even tempered fit), or refer to a set name defined in a previous BASIS block. Default is OPTFULL.
GEM_TYPE	Frozen geminal type: LINEAR or SLATER, default is SLATER.
GEM_NUMBER	Number of geminal functions (default 6).
GEM_CENTRE	Centre of even tempered geminal exponents, if GEM_BASIS=EVEN (default 1.0).

GEM_RATIO	Ratio of even tempered geminal exponents, if GEM_BASIS=EVEN (default 3.0).
GEM_BETA	Exponent for Slater-type frozen geminal, or parameter for weight function in other frozen geminal models (default 1.4).
GEM_OMEGA	Exponent for weighting function (default -1, which means a value derived from GEM_BETA.
GEM_MOM	Exponent for r in omega fitting (default 0).
GEM_M	Exponent for r in weighting function (default 0).
GEM_MAXIT	Max iteration in geminal optimization (default 200).
GEM_PRINT	Print parameter for geminal optimization (default 0).
GEM_DEBUG	Debug option for geminal optimization (default 0).
GEM_ACC	Convergence threshold for geminal line search (default 0.001).
GEM_FAC	Scaling factor for exponents in geminal optimization (default 1.0).
GEM_METHOD	Geminal optimization method (augmented Hessian (AH) or Newton-Raphson (NR), default AH).
GEM_TRUST	Trust ratio in AH geminal optimization (default 0.4).
GEM_SHIFT	Hessian shift in AH geminal optimization (default 0).
GEM_NUMERICAL	Flags numerical integration in geminal optimization (default 0).
GEM_PLOT	Geminal plot file (default blank).

Options only available for the canonical version:

PRINT=*ipri*	Select output level for canonical methods:	
	ipri=0	Standard output
	ipri=1	Standard output plus pair energies plus basis information
	ipri=2	Debugging output
THRBINV	Threshold below which non-physical eigenvalues are projected from approximate B matrices	
THRINT	Threshold for integral screening	

Local variants of the DF-MP2-F12 methods are available invoked by the commands DF-LMP2-F12 or DF-LMP2-R12.

Special options for these local variants are:

PAIRS	Specifies which pairs to be treated by R12 or F12 (STRONG|CLOSE|WEAK|ALL; pairs up to the given level are included). The default is STRONG.
DEBUG	Parameter for debug print
LOCFIT_F12	If set to one, use local fitting. Default is no local fitting (LOCFIT_F12=0)
LOCFIT_R12	Alias for LOCFIT_F12. Local fitting is not recommended in R12 calculations.

FITDOM	Determine how the base fitting domains are determined: 0: Fitdomains based on united operator domains; 1: Fitdomains based in orbital domains; 2: Fitdomains based on united pair domains using strong pairs; 3: Fitdomains based on united pair domains using strong, close and weak pairs (default);
RDOMAUX	Distance criterion for density fitting domain extensions in case of local fitting. The default depends on FITDOM.
IDOMAUX	Connectivity criterion for density fitting domain extensions in case of local fitting.
RAODOM	Distance criterion for RI domain extensions. Zero means full RI basis (default). If this parameter is chosen to be nonzero, it must be rather large to achieve sufficient accuracy. Values of at least 10 bohr have been found to work reasonably well (only for F12!).
IAODOM	Connectivity criterion for RI domain extensions. Zero means full RI basis (default). Values greater or equal to 6 should lead to sufficiently accurate results.
THRAO	Screening threshold for integrals in the AO or RI basis.
THRMO	Screening threshold for half transformed integrals.
THRPROD	Product screening threshold in the first half transformation.

Further options for density fitting are described in section 11. The use of local DF and RI domains is still experimental and is not recommended yet for general use.

Published work arising from these methods should cite the following:
F. R. Manby, J. Chem. Phys. **119** 4607 (2003) (for canonical DF-MP2-R12)
A. J. May and F R Manby, J. Chem. Phys. **121** 4479 (2004) (for canonical DF-MP2-F12)
H.-J. Werner and F R Manby, J. Chem. Phys. 124 054114 (2006) (for local DF-LMP2-R12)
F. R. Manby, H.-J. Werner, T. B. Adler and A. J. May, J. Chem. Phys. 124 094103 (2006) (for local DF-LMP2-F12).

30 THE FULL CI PROGRAM

This module is the determinant full CI program, as described in

P.J. Knowles and N.C. Handy, Chem. Phys. Letters 111 (1984) 315,
P.J. Knowles and N.C. Handy, Comp. Phys. Commun. 54 (1989) 75.

Published work resulting from the use of this program should cite these references.

The program in normal use finds the lowest eigenvector of the complete CI hamiltonian matrix; more sophisticated use is possible, but not documented here. The program is interfaced to free standing versions such as supplied in the CPC program library by use of the `DUMP` option.

The program is called with the command `FCI`.

30.1 Defining the orbitals

`ORBIT`,*name.file*;

name.file specifies the record from which orbitals are read. The default is the set of orbitals from the last SCF, MCSCF or CI calculation.

30.2 Occupied orbitals

`OCC`,$n_1,n_2,\ldots,n_8$;

n_i specifies numbers of occupied orbitals (including `CORE`) in irreducible representation number i. If not given, the default is the complete basis set.

30.3 Frozen-core orbitals

`CORE`,$n_1,n_2,\ldots,n_8$;

n_i is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no `CORE` card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

`CORE`

30.4 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the `WF` card:

`WF`,*elec,sym,spin*

where

elec:	is the number of electrons
sym:	is the number of the irreducible representation
spin:	defines the spin symmetry, *spin*$= 2S$ (singlet=0, doublet=1, triplet=2, etc.)

30.5 Printing options

PRINT,*code,value*;

Print options. Generally, the value determines how much intermediate information is printed. *value*=-1 means no print (default for all codes). if *value* is omitted, it is taken as zero, which is usually appropriate. Specification of higher values will generate more output. The following codes are allowed:

ORBITAL	Print molecular orbitals
INTEGRAL	Print integrals
TIMING	Print extra timing information
DIAGONAL	Print diagonal elements of Hamiltonian
HAMILTONIAN	Print much intermediate information

30.6 Interface to other programs

DUMP;

causes the FCI diagonalization to be bypassed, with input information and transformed integrals being written to a formatted file FCIDUMP. The format is as described in Comp. Phys. Commun. 54 (1989) 75.

31 SYMMETRY-ADAPTED INTERMOLECULAR PERTURBATION THEORY

31.1 Introduction

The SAPT (symmetry-adapted intermolecular perturbation theory) program calculates the total interaction energy between closed-shell molecules as a sum of individual first and second order interaction terms, namely electrostatic $E^{(1)}_{\rm pol}$, induction $E^{(2)}_{\rm ind}$ and dispersion $E^{(2)}_{\rm disp}$ accompanied by their respective exchange counterparts ($E^{(1)}_{\rm exch}$, $E^{(2)}_{\rm exch-ind}$ and $E^{(2)}_{\rm exch-disp}$). The latter ones arise due to electron exchange between the monomers when the molecules are close to each other and are sometimes denoted as Pauli repulsion. Since all above terms are accessible through static and (time-dependent) response density matrices of the monomers, in principle (see section 31.4) no calculation of the dimer wave function is required. Therefore SAPT is free from a zeroth-order basis set superposition error which occurs in the supermolecular approach.

References:

General Symmetry-adapted perturbation theory and many-body SAPT:
[1] B. Jeziorski, R. Moszynski and K. Szalewicz, Chem. Rev. **94**, 1887. (1994).

DFT-SAPT:
[2] G. Jansen and A. Heßelmann, J. Phys. Chem. A **105**, 646 (2001).
[3] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **357**, 464 (2002).
[4] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **362**, 319 (2002).
[5] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **367**, 778 (2003).
[6] A. Heßelmann and G. Jansen, Phys. Chem. Chem. Phys. **5**, 5010 (2003).

Density fitting DFT-SAPT (DF-DFT-SAPT):
[7] A. Heßelmann, G. Jansen and M. Schütz, J. Chem. Phys. **122**, 014103 (2005).

31.2 First example

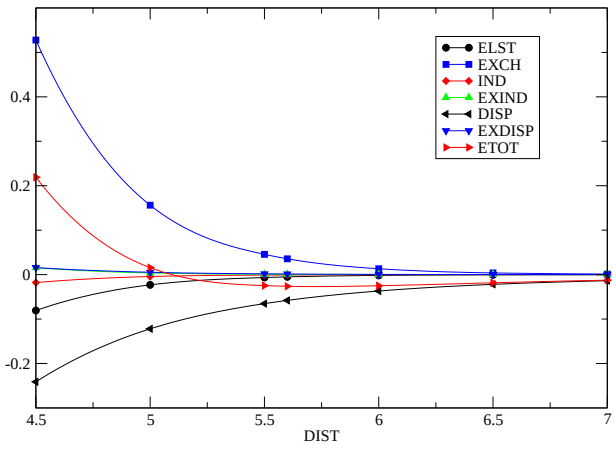
A typical input for SAPT has the following form:

```
r=5.6
geometry={nosym; he1; he2,he1,r}
basis=avqz

!wf records
ca=2101.2
cb=2102.2

!monomer A
dummy,he2
{hf; save,$ca}
sapt;monomerA

!monomer B
dummy,he1
{hf; start,atdens; save,$cb}
sapt;monomerB

!interaction contributions
sapt;intermol,ca=$ca,cb=$cb
```

Here the `sapt;monomerA/B` store some informations about the two monomers which are needed in the subsequent SAPT calculation invoked by `sapt;intermol`. The individual interaction energy terms are stored (in millihartree) in distinct variables and may be collected in arrays for producing potential energy surfaces. For example the input

```
geometry={nosym; he1; he2,he1,r}
basis=avtz

!wf records
ca=2101.2
cb=2102.2

!distances
dist=[4.5,5.0,5.5,5.6,6.0,6.5,7.0]

do i=1,#dist
   r=dist(i)

   !monomer A
   dummy,he2
   {hf; save,$ca}
   sapt;monomerA

   !monomer B
   dummy,he1
   {hf; start,atdens; save,$cb}
   sapt;monomerB

   !interaction contributions
   sapt;intermol,ca=$ca,cb=$cb

   elst(i)=E1pol;  exch(i)=E1ex
   ind(i)=E2ind;   exind(i)=E2exind
   disp(i)=E2disp; exdisp(i)=E2exdisp
   etot(i)=E12tot

   data,truncate,$ca
enddo

{table,dist,elst,exch,ind,exind,disp,exdisp,etot
ftyp,d,d,d,d,d,d,d,d
plot}
```

yields the plot



Currently SAPT only accepts single-determinant wave functions for the monomers, i.e. from Hartree-Fock or Kohn-Sham DFT (see next section) calculations. No point group symmetry can be exploited in a SAPT calculation.

31.3 DFT-SAPT

It is of crucial importance to account for the *intra*molecular correlation effects of the individual SAPT terms since Hartree-Fock theory often yields poor first- and second-order electrostatic properties. While this can be done using many-body perturbation theory [1] (in a double perturbation theory ansatz) a more efficient way is to use static and time-dependent DFT theory. This variant of SAPT, termed as DFT-SAPT [2-6], has in contrast to Hartree-Fock-SAPT the appealing feature that the polarisation terms ($E^{(1)}_{\rm pol}$, $E^{(2)}_{\rm ind}$, $E^{(2)}_{\rm disp}$) are potentially exact, i.e. they come out exactly if the exact exchange-correlation (xc) potential and the exact (frequency-dependent) xc response kernel of the monomers were known. On the other hand, this does not hold for the exchange terms since Kohn-Sham theory can at best give a good approximation to the exact density matrix of a many-body system. It has been shown [6] that this is indeed the the case and therefore DFT-SAPT has the potential to produce highly accurate interaction energies comparable to high-level supermolecular many-body perturbation or coupled cluster theory. However, in order to achieve this accuracy, it is of crucial importance to correct the wrong asymptotic behaviour of the xc potential in current DFT functionals [3-5]. This can be done by using e.g.:

```
{ks,lda; asymp,<shift>}
```

which activates the gradient-regulated asymptotic correction approach of Grüning *et al.* (J. Chem. Phys. **114**, 652 (2001)) for the respective monomer calculation. The user has to supply a `shift` parameter for the bulk potential which should approximate the difference between the exact ionisation potential of the monomer and the (negative) HOMO energy obtained from the respective standard Kohn-Sham calculation. Note that this needs to be done only once for each system.

Concerning the more technical parameters in the DFT monomer calculations it is recommended to use lower convergence thresholds and larger intergration grids compared to standard Kohn-Sham calculations.

31.4 High order terms

It has been found that third and higher-order terms become quite important if one or both monomers are polar. As no higher than second-order terms are currently implemented in SAPT, one may use a non-correlated estimation of those terms by using supermolecular Hartree-Fock (see e.g. [7]). This can be done by adapting the following template:

```
!dimer
hf
edm=energy

!monomer A
dummy,<monomer2>
{hf; save,$ca}
ema=energy
sapt;monomerA

!monomer B
```

```
dummy,<monomer1>
{hf; start,atdens; save,$cb}
emb=energy
sapt;monomerB

!interaction contributions
sapt,sapt_level=2;intermol,ca=$ca,cb=$cb

esup=(edm-ema-emb)*1000. mH
dHF=esup-e1pol-e1ex-e2ind-e2exind
```

which stores the resulting δ(HF) term in `dHF`.

31.5 Density fitting

In order to be able to study interactions between extended monomers one can use density fitting to approximate the integrals in SAPT [7]. For this one may use the input:

```
{sapt;intermol,ca=$ca,cb=$cb,fitlevel=3
dfit,basis_coul=jkfit,basis_exch=jkfit,basis_mp2=mp2fit,cfit_scf=3}
```

with in the basis section defined `jkfit` and `mp2fit` fitting basis sets (see section 11).

31.6 Options

`SAPT_LEVEL`	Set to 1 for first-order terms ($E^{(1)}_{\rm pol}$ and $E^{(1)}_{\rm exch}$), to 2 for additional second order (exchange-)induction terms ($E^{(2)}_{\rm ind}$ and $E^{(2)}_{\rm exch-ind}$) and 3 for all first- and second-order terms (including then also $E^{(2)}_{\rm disp}$ and $E^{(2)}_{\rm exch-disp}$) (default 3)
`SAPT_FITLEVEL`	Level of density fitting approximations in SAPT which can have values 0 to 3 (default 0)
`SAPT_ICPKS`	Switch between iterative (=1) and non-iterative (=0) solution of coupled-perturbed Kohn-Sham equations (default 0)
`SAPT_FROZENA`	Number of frozen electrons in the response calculations for monomer A (default 0)
`SAPT_FROZENB`	See above

The following parameters are of importance if `SAPT_FITLEVEL`>0:

`SAPT_NFRQ_DISP`	Number of frequencies for the Casimir-Polder integration (default 12)
`SAPT_NORM_DISP`	Norm for the density fitting which can be either `COULOMB` or `NATURAL` (default `COULOMB`)
`SAPT_DISP_N4`	Can speedup the calculation of the dispersion energy by N^4 scaling (default 1)
`THR_XCKERN`	Density threshold for the xc kernel matrix elements (default 1.d-8)
`FIT_XCKERN`	Fit both sides of the xc kernel (default 0)

SAPT_DISK	If 0 write all dimer amplitudes to file, if 1 write 3-index response propagators to file and if 2 write 3-index response propagators compressed to file. The latter two variants save disk space but need more CPU time to compute $E^{(2)}_{\mathrm{exch-disp}}$ (default 0)
COMPRESS_THR	If SAPT_DISK=2 this value determines the compression cutoff (default 1d-12)
UNCOUPLED	If SAPT_DISK>0 calculate also uncoupled (exchange-)dispersion energies (default false)
THRAO	Threshold for AO 3-index integrals (default 1.d-12)
THRMO	Threshold for MO 3-index integrals (default 1.d-8)
THROV	Threshold for AO 2-index integrals (default 1.d-10)
THRPROD	Product threshold for first half transformation (default 1.d-8)
THRSW	Threshold for Schwarz screening (default 1.d-5)

The last threshold values for the 2- and 3-index integrals should not be set higher in density fitting calculations as this can cause lower accuracies in the interaction terms. In addition SAPT knows the following subcommands:

MONOMERA	Stores informations (like number of electrons, etc.) about previous monomer A calculation
MONOMERB	See above
INTERMOL	Starts the SAPT calculation

INTERMOL may have the following subkeywords:

CA	Record number of wave function for monomer A (always needed)
CB	Record number of wave function for monomer B (always needed)
SAPTLEVEL	See above
FITLEVEL	See above
ICPKS	See above
FROZA	See above
FROZB	See above
NLEXFAC	Amount of nonlocal exact exchange in hybrid DFT-SAPT calculations

32 PROPERTIES AND EXPECTATION VALUES

32.1 The property program

The property program allows the evaluation of one-electron operators and expectation values. Normally, the operators are computed automatically when using the global GEXPEC directive (see section 6.13) or the EXPEC or TRAN commands in the SCF, MCSCF, and CI programs. The explicit use of the property program is only necessary in the rare case that the user is interested in an orbital analysis of the properties.

32.1.1 Calling the property program (PROPERTY)

PROPERTY

invokes the property program.

32.1.2 Expectation values (DENSITY)

DENSITY [,*record.file*] [,*specifications*]

If this card is present, the density matrix will be read from record *record.file* and property expectation values will be calculated. If the specification *record.file* is omitted, the last dump record is used. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.

32.1.3 Orbital analysis (ORBITAL)

ORBITAL [,*record.file*] [,*specifications*]

If this card is present, the orbitals are read from record *record.file* and an orbital analysis of the expectation values is printed (the density matrix must also be provided!). If *record.file* is omitted, the last dump record is used. This is only meaningful for diagonal density matrices (SCF or natural orbitals). Natural orbitals for specific states can be selected using *specifications*, as explained in section 4.11.

32.1.4 Specification of one-electron operators

The required operators are specified by code words. Optionally, the geometry or the nuclear centre at which the operator is computed can be specified.

For each operator, an input card of the following form is required:

code,centre,x,y,z,,factor

code specifies the property. The available operators are given in section 6.13.

The other parameters have the following meaning:

centre	row number of Z–matrix or atomic symbol defining the centre at which property shall be calculated; if *centre*$\neq$ 0 you need not read in coordinates.
x,y,z	cartesian coordinates of the point (only if *centre*=0).

factor the operator is multiplied by this factor. The default is *factor*=1 except for REL. In this cases proper factors for relativistic corrections are used unless *factor* is given. The two commas before factor are needed to preserve compatibility with Molpro96.

32.1.5 Printing options

PRINT,*print*

This card is used to control output, mainly for debugging purposes.

print= 0 no test output (default)

print> 0 operators are printed.

32.1.6 Examples

The following example computes the dipole quadrupole moments of water and prints an orbital analysis. By default, the origin is at the centre of mass, and this is taken as origin for the quadrupole moments.

```
! $Revision: 2006.0 $
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
hf                                    !do scf calculation
property                              !call property program
orbital                               !read scf orbitals
density                               !read scf density matrix
dm                                    !compute dipole moments and print orbital contributions
qm                                    !compute quadrupole moments and print orbital contributi
{multi;state,2;dm                     !do full-valence CASSCF
natorb,state=1.1                      !compute natural orbitals for state 1.1
natorb,state=2.1}                     !compute natural orbitals for state 2.1
                                                                          examples/
                                                                          h2o˙property.com
{property                             !call property program
orbital,state=1.1                     !read casscf natural orbitals for state 1.1
density,state=1.1                     !read casscf density matrix for state 1.1
dm                                    !compute dipole moments and print orbital contributions
qm}                                    !compute quadrupole moments and print orbital contribut

{property                             !call property program
orbital,state=2.1                     !read casscf natural orbitals for state 2.1
density,state=2.1                     !read casscf density matrix for state 2.1
dm                                    !compute dipole moments and print orbital contributions
qm}                                   !compute quadrupole moments and print orbital contributi
```

Alternatively, the dipole and quadrupole moments can be computed directly in the SCF and MCSCF programs, but in this case no orbital contributions are printed:

```
! $Revision: 2006.0 $
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
gexpec,dm,qm                          !global request of dipole and quadrupole moments
                                                                          examples/
                                                                          h2o˙gexpec1.com
hf                                    !do scf calculation
{multi;state,2                        !do full-valence CASSCF
natorb,state=1.1                      !compute natural orbitals for state 1.1
natorb,state=2.1}                     !compute natural orbitals for state 2.1
```

32.2 Distributed multipole analysis

Any density matrix can be analysed using the distributed multipole analysis described by Stone, Chem. Phys. Letters (1981), 83, 233. The multipole moments arising from the overlap of each pair of primitives are calculated with respect to the overlap centre, and then shifted to the nearest of a number of *multipole sites*. By default these comprise all atoms specified in the integral input. However the list of multipole sites can be modified by deleting and/or adding sites, and also by restricting the rank of multipole which may be transferred to any given site. The atomic charges are stored in the MOLPRO variable ATCHARGE. The i'th element in ATCHARGE corresponds to the i'th row of the Z-matrix input.

Options may appear in any order, except DENSITY, which must be first if given.

The present version does not allow generally contracted AO basis sets.

32.2.1 Calling the DMA program (DMA)

DMA;

This command initializes the DMA program.

32.2.2 Specifying the density matrix (DENSITY)

DENSITY,*record.file* [,*specifications*]

The density matrix to be analysed is that found in record *record* on file *file*. If omitted, *record.file* defaults to current orbital record. If specified, DENSITY must appear first in the input. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11.

32.2.3 Linear molecules (LINEAR, GENERAL)

GENERAL;

(default) invokes the normal program, which copes with any geometry.

LINEAR

invokes a faster program which can be used when all the atoms are arranged parallel to the z-axis and only the $m = 0$ components of the multipoles are required.

32.2.4 Maximum rank of multipoles (LIMIT)

LIMIT,*name,lmax*;

lmax is the highest rank of multipole that is to be calculated by the program. Default (and maximum) is 10 for the general program and 20 for the linear one. If *name* is specified, the limit applies only to multipole site *name*.

32.2.5 Omitting nuclear contributions (NONUCLEAR)

NONUCLEAR

The nuclear contributions to properties are not to be evaluated.

32.2.6 Specification of multipole sites (ADD, DELETE)

ADD,*name,x,y,z,lmax,radius*;

Add a new site at (x, y, z) with the *name* specified. The multipole rank is limited to *lmax* if a value is specified, otherwise the value of lmax specified by the LIMIT directive is used. No account is taken of symmetry; every site in a symmetry-equivalent set must be specified explicitly. The *radius* of the site may also be specified (default 1.0).

DELETE,*name*

Delete all atoms with the *name* given from consideration as a multipole site. Note that original atoms from the integral program have names $1, 2, 3, \ldots$ as printed in integral output. DELETE,ALL deletes all atoms and gives the multipoles with respect to the origin only.

32.2.7 Defining the radius of multipole sites (RADIUS)

RADIUS,*name,r*;

Assign radius r to all sites with the *name* given. The program moves multipoles at an overlap centre P to the site S for which the value of $|P-S|/r(S)$ is smallest. In the absence of a RADIUS directive, all sites are given radius 1.

32.2.8 Notes and references

The multipoles produced by this analysis are given in their spherical harmonic definitions. Explicit formulae for translating between the cartesian and spherical harmonic definitions of the multipole moments are given in, *Explicit formulae for the electrostatic energy, forces and torques between a pair of molecules of arbitrary symmetry*, S. L. Price, A. J. Stone, and M. Alderton, Molec. Phys., 52, 987 (1984).

For examples of the use of DMA analysis see, Price and Stone, Chem. Phys. Lett., 98, 419 (1983); Buckingham and Fowler, J. Chem. Phys., 79, 6426 (1983).

32.2.9 Examples

The following input calculates SCF multipole moments for water.

examples/
h2o˙dma.com

```
! $Revision: 2006.0 $
***,h2o distributed multipole analysis
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
basis=6-311g**
hf                                    !do scf calculation
{dma;limit,,4}                        !results for total multipoles are
```

32.3 Mulliken population analysis

32.3.1 Calling the population analysis program (POP)

POP;

Invokes Mulliken analysis program, which analyses any density matrix into its contributions from s,p,d,f... basis functions on each atom. The density matrix is taken from the last dump

record, unless overridden with the DENSITY card. The subcommands may be abbreviated by the first four characters. The atomic charges are stored in the MOLPRO variable ATCHARGE. The i'th element in ATCHARGE corresponds to the i'th row of the Z-matrix input.

32.3.2 Defining the density matrix (DENSITY)

DENSITY,*record,file* [,*specifications*]

Take density matrix to be analysed from record *record* on file *file*. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.

32.3.3 Populations of basis functions (INDIVIDUAL)

INDIVIDUAL;

32.3.4 Example

```
***,h2o population analysis
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
basis=6-311g**                                                    examples/
hf                                    !do scf calculation        h2o˙pop.com
pop;                                  !Mulliken population analysis using mcscf density
individual                            !give occupations of individual basis functions
```

If specified, the Mulliken populations of each individual basis function are printed.

32.4 Finite field calculations

Dipole moments, quadrupole moments etc. and the corresponding polarizabilities can be obtained as energy derivatives by the finite difference approximation. This is most easily done with the DIP, QUAD, or FIELD commands. An error will result if the added perturbation is not totally symmetric (symmetry 1). Note that the orbitals must be recomputed before performing a correlation calculation.

32.4.1 Dipole fields (DIP)

DIP,*xfield,yfield,zfield*;
DIP+,*xfield,yfield,zfield*;

Add a finite dipole field to the one electron Hamiltonian and the core energy. The field strength is given by *xfield,yfield,zfield*. DIP+ adds to any existing field, otherwise any previous field is removed.

32.4.2 Quadrupole fields (QUAD)

QUAD,*xxfield,yyfield,zzfield,xyfield,xzfield,yzfield*;
QUAD+,*xxfield,yyfield,zzfield,xyfield,xzfield,yzfield*;

Exactly as the DIP command, but adds a quadrupole field.

32.4.3 General fields (FIELD)

FIELD,*oper1*,*fac1, oper2*,*fac2, ...* ;
FIELD+,*oper1*,*fac1, oper2*,*fac2, ...* ;

Adds one-electron operators *oper1*, *oper2*, ... with the corresponding factors *fac1*, *fac2*, ... to the one-electron hamiltonian. The available operators are given in section 6.13. An error will result if the added perturbation is not totally symmetric (symmetry 1).

FIELD+ adds to any existing field, otherwise any previous field is removed.

Note that FIELD does currently not modify core polarization potentials (CPP). If CPPs are present, only DIP and QUAD should be used.

32.4.4 Examples

The first examples shows various possibilities to add perturbations to the one-electron hamiltonian.

examples/
field.com

```
! $Revision: 2006.0 $
***,H2O finite fields
memory,4,m
R     =    0.96488518 ANG
THETA =  101.90140469
geometry={H1
          O,H1,R;
          H2,O,R,H1,THETA}
{hf;wf,10,1}           !scf without field

f=0.05

dip,,,f                !add dipole (z) field to h0
hf                     !do scf with modified h0

field,dmz,f            !add dipole (z) field to H0
                       !same result as previous example
hf                     !do scf with modified h0

quad,,,f               !add quadrupole (qmzz) field to h0
hf                     !do scf with modified h0

field,qmzz,f           !add quadrupole (qmzz) field to h0;
                       !same result as previous example
hf                     !do scf with modified h0

field,zz,f,xx,-0.5*f,yy,-0.5*f
                       !add general field; same result as quad above
hf                     !do scf with modified h0

field,zz,f           !same as before with separate field commands
field+,xx,-0.5*f
field+,yy,-0.5*f
hf                     !do scf with modified h0

field                  !remove field
hf                     !scf without field
```

The second example shows how to compute dipole moments and polarizabilities using finite fields.

```
! $Revision: 2006.0 $
***,H2O finite field calculations

r=1.85,theta=104                    !set geometry parameters
geometry={O;                        !z-matrix input
          H1,O,r;
          H2,O,r,H1,theta}
basis=avtz                          !define default basis
field=[0,0.005,-0.005]              !define finite field strengths
$method=[hf,mp4,ccsd(t),casscf,mrci]

k=0
do i=1,#field                       !loop over fields
  dip,,,field(i)                    !add finite field to H
  do m=1,#method                    !loop over methods
    k=k+1
    $method(m)                      !calculate energy                    examples/
    e(k)=energy                     !save energy                        h2o˙field.com
  enddo
enddo

k=0
n=#method
do m=1,#method
  k=k+1
  energ(m)=e(k)
  dipmz(m)=(e(k+n)-e(k+2*n))/(field(2)-field(3))   !dipole moment as first energy derivative
  dpolz(m)=(e(k+n)+e(k+2*n)-2*e(k))/((field(2)-field(1))*(field(3)-field(1)))  !polarizability
enddo

table,method,energ,dipmz,dpolz
title,results for H2O, r=$R, theta=$theta, basis=$basis
---
```

32.5 Relativistic corrections

Relativistic corrections may be calculated within the Cowan-Griffin approach by computing expectation values of the mass-velocity and 1-electron Darwin integrals; these should be generated using the property integral program with keyword REL The expectation values can be computed within the SCF, MCSCF and CI programs in the usual way using the EXPECT command, again with the keyword REL. The mass-velocity and Darwin terms, and their sum are subsequently available through the MOLPRO variables MASSV, DARW and EREL respectively.

32.5.1 Example

```
***,ar2
geometry={ar1;ar2,ar1,r}   !geometry definition
r=2.5 ang                  !bond distance
{hf;                       !non-relativisitic scf calculation
expec,rel,darwin,massv}    !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy              !save non-relativistic energy in variable enrel
show,massv,darwin,erel     !show individual contribution and their sum
                                                                        examples/
dkroll=1                   !use douglas-kroll one-electron integrals   ar2˙rel.com
hf;                        !relativistic scf calculation
e_dk=energy                !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel     !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel           !show relativistic correction using Douglas-Kroll
```

32.6 CUBE — dump density or orbital values

CUBE,*filename,iflag,*n_1,n_2,n_3

calls a module which dumps the values of various properties on a spatial parallelopipedal grid to an external file. The purpose is to allow plotting of orbitals, densities and other quantities by external programs. The format of the file is intended to be the same as that produced by other programs.

filename	is the unix path name of the file to be written, and its specification is mandatory.
iflag	If *iflag* is negative (default), a formatted file will be written, otherwise unformatted fortran i/o will be used.
n_1,n_2,n_3	specify the number of grid points in each of three dimensions. If not specified, sensible defaults are chosen.

By default, the last density computed is evaluated on the grid, and written to *filename*. This behaviour can be modified by one or more of the following subcommands.

32.6.1 DENSITY — source of density

DENSITY,[*density-source*]
GRADIENT,[*density-source*]
LAPLACIAN,[*density-source*]

Compute the density and, optionally, its gradient and laplacian. *¡density-source¿* may be a record number containing the required density, and may contain further qualification, such as set number, in the usual way. By default, the last computed density is taken.

32.6.2 ORBITAL — source of orbitals

ORBITAL,[*orbital-list*],[*orbital-source*]

¡orbital-list¿ is a list of one or more orbital numbers of the form *number.symmetry* or keywords chosen from HOMO, LUMO, OCC, ALL. If nothing is specified, the default is HOMO. *¡orbital-source¿* may be a record number containing the required density, and may contain further qualification, such as set number, in the usual way. By default, the last computed orbitals are taken.

Note that the CUBE file format precludes simultaneous orbital and density dumps, but that this may be achieved in the GOPENMOL format (see 32.7).

32.6.3 AXIS — direction of grid axes

AXIS,*x,y,z*

x,y,z specify the unnormalised direction cosines of one of the three axes defining the grid. Up to three AXIS commands can be given, but none is required. Axes need not be orthogonal. By default, the first axis is the cartesian *x*, the second is orthogonal to the first and to the cartesian *z*, and the third is orthogonal to the first two.

32.6.4 BRAGG — spatial extent of grid

Based on the direction of the coordinate axes, a parallelopiped (in the usual case of orthogonal axes, a cuboid) is constructed to contain the molecule completely. The atoms are assumed to be spherical, with an extent proportional to their Bragg radii, and the constant of proportionality can be changed from the default value using

BRAGG,*scale*

After the parallelopiped has been constructed, the grid is laid out with equal spacing to cover it using the number of points specified on the CUBE command.

32.6.5 ORIGIN — centroid of grid

ORIGIN,*x,y,z*

x,y,z specify the centroid of the grid. It is usually not necessary to use this option, since the default should suffice for most purposes.

32.6.6 Format of cube file

The formatted cube file contains the following records

(A)	job title.
(A)	brief description of the file contents.
(I5,3F12.6)	number of atoms, coordinates of grid origin (bohr).
(I5,3F12.6)	number of grid points n_1, step vector for first grid dimension.
(I5,3F12.6)	number of grid points n_2, step vector for second grid dimension.
(I5,3F12.6)	number of grid points n_3, step vector for third grid dimension.
(I5,4F12.6)	atomic number, charge and coordinates; one such record for each atom.
(6E13.5)	$n_1 \times n_2$ records of length n_3 containing the values of the density or orbital at each grid point. In the case of a number of orbitals m, the record length is $m \times n_3$, with the data for a single grid point grouped together. In the case of the density gradient, there is first a record of length n_3 containing the density, then one of length $3n_3$ containing the gradient, with the three cartesian components contiguous. For the laplacian, there is a further record of length n_3.

32.7 GOPENMOL — calculate grids for visualization in gOpenMol

GOPENMOL,*filename,iflag,*n_1,n_2,n_3

The syntax and sub-options are exactly the same as for CUBE, except that the files produced are in a format that can be used directly in the gOpenMol visualization program. The following should be noted.

- Only the base name (up to the last '.') in *filename* is used, and is appended by different suffices to create several different files:

.crd — A CHARMm CRD-format file containing the coordinates is always produced, and may be used in the invocation of gOpenMol:

`rungOpenMol -i`*filename*`.crd`

`_density.plt` — If `DENSITY` is given, then the file *filename*`_density.plt` is produced and contains the density grid in gOpenMol internal format.

`_orbital_`*number*`.`*symmetry*`.plt` — If `ORBITAL` is given, then for each orbital *number*`.`*symmetry* specified, the file *filename*`_orbital_`*number*`.`*symmetry*`.plt` is produced and contains the orbital grid in gOpenMol internal format.

- The default is not to produce any orbitals or densities, and so only the atomic coordinates are dumped.
- The default is to use unformatted binary files, and this should not normally be changed.
- The `ORIGIN` and `AXIS` commands should not be used.
- If

  `INTERACT`

  is given in the input, when all the grids have been calculated, an attempt is made to start gOpenMol by executing the Unix command `rungOpenMol`. If `rungOpenMol` is not in `$PATH`, then nothing happens. Otherwise, gOpenMol should start and display the molecule. Any `.plt` files produced can be added to the display by following the `Plot;Contour` menu item. The name of the Unix command may be changed from the default `rungOpenMol` by specifying it as the first argument to the `INTERACT` directive. By default, gOpenMol is not started, and this is equivalent to giving the command `BATCH`.

33 DIABATIC ORBITALS

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using using the new `DIAB` command in the `MCSCF` program.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a `DIAB` directive to the input:

Old form (`Molpro96`, obsolete):

`DIAB`,*orbref, orbsav, orb1,orb2,pri*

New form:

`DIAB`,*orbref*[,`TYPE`=*orbtype*] [,`STATE`=*state*] [,`SPIN`=*spin*] [,*MS2=ms2*] [,`SAVE`=*orbsav*] [,`ORB1`=*orb1*, `ORB2`=*orb2*] [,*PRINT=pri*]

Here *orbref* is the record holding the orbitals of the reference geometry, and *orbsav* is the record on which the new orbitals are stored. If *orbsav* is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the `ORBITAL` directive (see section 20.5.3). In contrast to earlier versions of MOLPRO it is possible that *orbref* and *orbsav* are the same. The specifications `TYPE`, `STATE`, `SPIN` can be used to select specific sets of reference orbitals, as described in section 4.11. *orb1, orb2* is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form *number.sym*, e.g. 3.1 means the third orbital in symmetry 1. If *orb1, orb2* are not given, the overlap of all active orbitals is maximized. *pri* is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each jacobi iteration.

Using the defaults described above, the following input is sufficient in most cases:

`DIAB`,*orbref*

Using `Molpro98` is is not necessary any more to give any `GEOM` and `DISPL` cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. **89**, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. **89**, 7367 (1988).

Below we present an example for the first two excited states of H_2S, which have B_1 and A_2 symmetry in C_{2v}, and A'' symmetry in C_S. We first perform a reference calculation in C_{2v} symmetry, and then determine the diabatic orbitals for displaced geometries in C_S symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the C_{2v} calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets `reforb=2141.2`.

```
! $Revision: 2006.0 $
***,H2S diabatic A" states

basis=VDZ                                !use cc-pVDZ basis set
geometry={x;                             !use Cs symmetry
          planeyz;                       !fix orientation of the molecule
          noorient                       !dont allow automatic reorientation
          s;h1,s,r1;h2,s,r2,h1,theta}    !Z-matrix geometry input

gprint,orbitals,civector                 !global print options

text,reference calculation for C2V
theta=92.12,r1=2.3,r2=2.3                !reference geometry

{hf;occ,7,2;wf,18,1}                     !scf calculation for ground state

{multi;occ,9,2;closed,4,1;               !define active and inactive spaces
wf,18,2;state,2;                         !two A" states (1B1 and 1A2 in C2v)
orbital,2140.2}                          !save orbitals to 2140.2
reforb=2140.2

text,calculations at displaced geometries

rd=[2.4,2.5,2.6]                         !define a range of bond distances

do i=1,#rd                               !loop over displaced geometries

r2=rd(i)                                 !set r2 to current distance

{multi;occ,9,2;closed,4,1;               !same wavefunction definition as at reference geom.
wf,18,2;state,2;
orbital,2141.2                           !save new orbitals to record
diab,reforb}                             !compute diabatic orbitals using reference orbitals
                                         !stored on record reforb
reforb=2141.2                            !set variable reforb to the new orbitals.
enddo
```

examples/
h2s˙diab.com

34 NON ADIABATIC COUPLING MATRIX ELEMENTS

Non-adiabatic coupling matrix elements can be computed by finite differences for MCSCF or CI wavefunctions using the DDR program. For state-averaged MCSCF wavefunctions, they can also computed analytically (cf. section 20.9.2).

Note that present numerical procedure has been much simplified relative to Molpro96. No GEOM and DISPL input cards are needed any more, and the three necessary calculations can be done in any order.

34.1 The DDR procedure

In order to compute the coupling matrix elements by finite differences, one has to compute and store the wavefunctions at two (first-order algorithm) or three (second-order algorithm) slightly displaced geometries. The order of these calculations is arbitrary.

The typical strategy is as follows:

1.) Compute the wavefunction at the reference geometry. The wavefunctions for both states have to be stored using the SAVE command of the CI program. If the matrix elements are computed for MCSCF wavefunctions, it is necessary to recompute the wavefunction with the CI program, using the NOEXC option. The transition density matrix is stored using the DM directive of the CI program.

2.) Compute the wavefunctions at the (positively) displaced geometry and store the CI wavefunction in a second record.

3.) If the second-order (three-point) method is used, step (2) is repeated at a (negatively) displaced geometry.

4.) Compute the transition density matrices between the states at the reference geometry and the displaced geometr(ies). This is done with the TRANS directive of the CI program.

5.) Finally, the DDR program is used to assemble the matrix element. Using the first-order two-point method, only a single input line is needed:

DDR, *dr, orb1, orb2, trdm2*

where *dr* is the geometry increment used as denominator in the finite difference method, *orb1* is the record holding the orbitals of the reference geometry, *orb2* is the record holding the orbitals of the displaced geometry, and *trdm2* is the record holding the transition density matrix computed from the CI-vectors at *R* and *R+DR*.

If central differences (three points) are used, the input is as follows:

DDR,*2*dr*
ORBITAL,*orb1,orb2,orb3*
DENSITY,*trdm1,trdm2,trdm3*

where *dr, orb1, orb2* are as above, and *orb3* is the record holding the orbitals at the negatively displaced geometry.

trdm1, trdm2, trdm3 are the records holding the transition densities $\gamma(R|R)$, $\gamma(R|R+DR)$, and $\gamma(R|R-DR)$, respectively.

If more than two states are computed simultaneously, the transition density matrices for all pairs of states will be stored in the same record. In that case, and also when there are just two states

whose spatial symmetry is not 1, it is necessary to specify for which states the coupling is to be computed using the STATE directive:

STATE,$state_1$, $state_2$

where $state_i$ is of the form *istate.isym* (the symmetries of both states must be the same, and it is therefore sufficient to specify the symmetry of the first state).

As an example the input for first-order and second-order calculations is given below. The calculation is repeated for a range of geometries, and at the end of the calculation the results are printed using the TABLE command.

In the calculation shown, the "diabatic" CASSCF orbitals are generated in the two CASSCF calculations at the displaced geometries by maximizing the overlap with the orbitals at the reference geometry. This is optional, and (within the numerical accuacy) does not influence the final results. However, the relative contributions of the orbital, overlap and CI contributions to the NACME are modified. If diabatic orbitals are used, which change as little as possible as function of geometry, the sum of overlap and orbital contribution is minimized, and to a very good approximation the NACME could be obtained from the CI-vectors alone.

```
! $Revision: 2006.0 $
***,lif non-adiabatic coupling
memory,1,m

basis,f=avdz,li=vdz              !define basis
r=[10.0,10.5,11.0,11.5,12.0]     !define bond distances
dr=0.01                          !define increment
geometry={li;f,li,rlif}          !define geometry

rlif=3                           !first calculation at R=3
{hf;occ,4,1,1}                   !SCF
{multi;closed,3;                 !CASSCF, 3 inactive orbitals
wf,12,1;state,2;                 !Two 1A1 states
orbital,2140.2}                  !dump orbitals to record 2140.2

do i=1,#r                        !loop over geometries
rlif=r(i)                        !set bond distance
{multi;closed,3;                 !CASSCF, 3 inactive orbitals
wf,12,1;state,2;                 !Two 1A1 states
orbital,2140.2}                  !Overwrite previous orbitals by present ones

{ci;state,2;noexc;               !CI for 2 states, no excitations
save,6000.2;                     !save wavefunction to record 6000.2
dm,8000.2}                       !save (transition) densities to record 8000.2

rlif=r(i)+dr                     !increment bond distance by dr

{multi;closed,3;                 !same CASSCF as above
wf,12,1;state,2;                 !Two 1A1 states
start,2140.2;                    !start with orbitals from reference geometry
orbital,2141.2;                  !save orbitals to record 2141.2
diab,2140.2}                     !generate diabatic orbitals by maximizing the
                                 !overlap with the orbitals at the reference geometry

{ci;state,2;noexc;save,6001.2}   !CI for 2 states, wavefunction saved to record 6001.2

{ci;trans,6000.2,6001.2;         !Compute overlap and transition density <R|R+DR>
dm,8100.2}                       !Save transition density to record 8100.2

rlif=r(i)-dr                     !repeat at r-dr

{multi;closed,3;                 !same CASSCF as above
wf,12,1;state,2;                 !Two 1A1 states
start,2140.2;                    !start with orbitals from reference geometry
orbital,2142.2;                  !save orbitals to record 2142.2
diab,2140.2}                     !generate diabatic orbitals by maximizing the
                                 !overlap with the orbitals at the reference geometry

{ci;state,2;noexc;save,6002.2}   !CI for 2 states, wavefunction saved to record 6002.2

{ci;trans,6000.2,6002.2;         !Compute overlap and transition density <R|R-DR>
dm,8200.2}                       !Save transition density to record 8200.2

{ddr,dr,2140.2,2141.2,8100.2}    !compute NACME using 2-point formula (forward difference)
nacme1p(i)=nacme                 !store result in variable nacme1p
{ddr,-dr,2140.2,2142.2,8200.2}   !compute NACME using 2-point formula (backward difference)
nacme1m(i)=nacme                 !store result in variable nacme1m

{ddr,2*dr                        !compute NACME using 3-point formula
orbital,2140.2,2141.2,2142.2;    !orbital records for R, R+DR, R-DR
density,8000.2,8100.2,8200.2}    !transition density records for R, R+DR, R-DR
nacme2(i)=nacme                  !store result in variable nacme2

end do                           !end of loop over differend bond distances

nacmeav=(nacme1p+nacme1m)*0.5    !average the two results forward and backward differences
table,r,nacme1p,nacme1m,nacmeav,nacme2   !print a table with results
title,Non-adiabatic couplings for LiF    !title for table
```

This calculation produces the following table:

```
 Non-adiabatic couplings for LiF

      R       NACME1P       NACME1M       NACMEAV       NACME2
   10.0   -0.22828936   -0.22328949   -0.22578942   -0.22578942
   10.5   -0.51777034   -0.50728914   -0.51252974   -0.51252974
   11.0    0.76672943    0.76125391    0.76399167    0.76399167
   11.5    0.42565202    0.42750263    0.42657733    0.42657733
   12.0    0.19199878    0.19246799    0.19223338    0.19223338
```

Note that the sign changes because of a phase change of one of the wavefunctions. In order to keep track of the sign, one has to inspect both the orbitals and the ci-vectors.

35 QUASI-DIABATIZATION

The DDR procedure can also be used to generate quasi-diabatic states and energies for MRCI wavefucntions (CASSCF case can be treated as special case using the NOEXC directive in the MRCI). The quasi-diabatic states have the propery that they change as little as possible relative to a reference geometry; with other words, the overlap between the states at the current geometry with those at a reference geometry is maximized by performing a unitary transformation among the given states. Preferably, the adiabatic and diabatic states should be identical at the reference geometry, e.g., due to symmetry. For instance, in the examples given below for the $^1B_1$ and $^1A_2$ states of H_2S, C_{2v} geomtries are used as reference, and at these geometries the states are unmixed due to their different symmetry. At the displaced geometries the molecular symmetry is reduced to C_S. Both states now belong to the $^1A''$ irreducible representation and are strongly mixed. For a description and application of the procedure described below, see D. Simah, B. Hartke, and H.-J. Werner, J. Chem. Phys. **111**, 4523 (1999).

This diabatization can be done automatically and requires two steps: first, the active orbitals of a CASSCF calculation are rotated to maximize the overlap with the orbitals at the reference geometry. This is achieved using the DIAB procedure described in section 20.5.8. Secondly, the DDR procedure can be used to find the transformation among the CI vectors.

The following input is required:

DDR	calls the DDR procedure.
ORBITAL,*orb1, orb2*	*orb1* and *orb2* are the (diabatic) orbitals at the current and reference geometry, respectively.
DENSITY,*trdm1,trdm2*	*trdm1* are the transition densities computed at the current geometry, *trdm2* are transition densities computed using the wavefunctions of the current (bra) and reference (ket) geometries.
MIXING,*state1, state2, ...*	The given states are included in the diabatization.
ENERGY,*e1, e2, ...*	Adiabatic energies of the states. If this input card is present, the Hamiltonian in the basis of the diabatic states is computed and printed. Alternatively, the energies can be passed to DDR using the Molpro variable EADIA.

The results are printed and stored in the following Molpro variables, provided the ENERGY directive or the EADIA variable is found:

Results including the first-order orbital correction:

SMAT	The first $nstate \times nstate$ elements contain the state overlap matrix (bra index rans fastest).
UMAT	The first $nstate \times nstate$ elements contain the transformation matrix.
HDIA	The first $nstate \cdot (nstate+1)/2$ elements contain the lower triangle of the diabatic hamiltonian.
MIXANG	Non-adiabatic mixing angle in degree. This is available only in the two-state case.

The corresponding results obtained from the CI-vectors only (without orbital correction) are stored in the variables [SMATCI], UMATCI, HDIACI, and MIXANGCI.

The way it works is most easily demonstrated for some examples. In the following input, the wavefunction is first computed at the C_{2v} reference geometry, and then at displaced geometries.

examples/
h2s˙diab1.com

```
! $Revision: 2006.0 $
***,h2s Diabatization
memory,3,m

gprint,orbitals,civector

geometry={x;noorient         !noorient should always be used for diabatization
         s;
         h1,s,r1;
         h2,s,r2,h1,theta}

basis=avdz                   !This basis is too small for real application

r1=2.5                       !Reference geometry
theta=[92]

r=[2.50,2.55,2.60]           !Displaced geometries

reforb=2140.2                !Orbital dumprecord at reference geometry
refci=6000.2                 !MRCI record at reference geometry
savci=6100.2                 !MRCI record at displaced geometries

text,compute wavefunction at reference geometry (C2v)
r2=r1

{hf;occ,9,2;wf,18,2,4;
orbital,2100.2}

{multi;occ,9,2;closed,4,1;
wf,18,2;state,2;             !1B1 and 1A2 states
natorb,reforb                !Save reference orbitals on reforb
noextra}                     !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;      !MRCI at reference geometry
wf,18,2,0;state,2;           !1B1 and 1A2 states
orbital,reforb               !Use orbitals from previous CASSCF
save,refci}                  !Save MRCI wavefunction

Text,Displaced geometries

do i=1,#r                    !Loop over different r values
data,truncate,savci+1        !truncate dumpfile after reference
r2=r(i)                      !Set current r2

{multi;occ,9,2;closed,4,1;
wf,18,2,0;state,2;           !Wavefunction definition
start,reforb                 !Starting orbitals
orbital,3140.2;              !Dump record for orbitals
diab,reforb                  !Generate diabatic orbitals relative to reference geometry
noextra}                     !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;
wf,18,2,0;state,2;           !1B1 and 1A2 states
orbital,diabatic             !Use diabatic orbitals
save,savci}                  !Save MRCI for displaced geometries

e1(i)=energy(1)              !Save adiabatic energies
e2(i)=energy(2)

{ci;trans,savci,savci        !Compute transition densities at R2
dm,7000.2}                   !Save transition densities on this record
{ci;trans,savci,refci;       !Compute transition densities between R2 and R1
dm,7100.2}                   !Save transition densities on this record

{ddr
density,7000.2,7100.2        !Densities for <R2||R2> and <R2||R1>
orbital,3140.2,2140.2        !Orbitals for <R2||R2> and <R2||R1>
energy,e1(i),e2(i)           !Adiabatic energies
mixing,1.2,2.2}              !Compute mixing angle and diabatic energies

mixci(i)=mixangci(1)         !Mixing angle obtained from ci vectors only
```

This calculation produces the following results:

```
 Diabatic energies for H2S, obtained from CI-vectors

       R       E1            E2            H11CI         H22CI          H21CI          MIXCI
    2.50 -398.64296319 -398.63384782 -398.64296319 -398.63384782    0.00000000        0.00
    2.55 -398.64572746 -398.63666636 -398.64509901 -398.63729481   -0.00230207       15.27
    2.60 -398.64911752 -398.63771802 -398.64662578 -398.64020976   -0.00471125       27.87

 Diabatic energies for H2S, obtained from CI-vectors and orbital correction

       R       E1            E2            H11           H22           H21           MIXTOT
    2.50 -398.64296319 -398.63384782 -398.64296319 -398.63384782    0.00000000        0.00
    2.55 -398.64572746 -398.63666636 -398.64509941 -398.63729441   -0.00230139       15.26
    2.60 -398.64911752 -398.63771802 -398.64662526 -398.64021027   -0.00471160       27.88
```

The results in the first table are obtained from the CI-contribution to the state-overlap matrix only, while the ones in the second table include a first-order correction for the orbitals. In this case, both results are almost identical, since the `DIAB` procedure has been used to minimize the change of the active orbitals. This is the recommended procedure. If simply natural orbitals are used without orbital diabatization, the following results are obtained from the otherwise unchanged calculation:

```
 Diabatic energies for H2S, obtained from CI-vectors

       R       E1            E2            H11CI         H22CI          H21CI          MIXCI
    2.50 -398.64296319 -398.63384782 -398.64296319 -398.63384782    0.00000000        0.00
    2.55 -398.64572742 -398.63666630 -398.64475612 -398.63763760   -0.00280315       19.11
    2.60 -398.64911746 -398.63771803 -398.64521031 -398.64162518   -0.00541050       35.83

 Diabatic energies for H2S, obtained from CI-vectors and orbital correction

       R       E1            E2            H11           H22           H21           MIXTOT
    2.50 -398.64296319 -398.63384782 -398.64296319 -398.63384782    0.00000000        0.00
    2.55 -398.64572742 -398.63666630 -398.64509146 -398.63730226   -0.00231474       15.36
    2.60 -398.64911746 -398.63771803 -398.64648358 -398.64035190   -0.00480493       28.73
```

It is seen that the mixing obtained from the CI vectors only is now very different and meaningless, since the orbitals change significantly as function of geometry. However, the second calculations, which accounts for this change approximately, still gives results in quite good agreement with the calculation involving diabatic orbitals.

The final examples shows a more complicated input, which also computes the non-adiabatic coupling matrix elements. In a two-state model, the NACME should equal the first derivative of the mixing angle. In the example, the NACME is computed using the 3-point `DDR` method (NACMECI), and also by finite difference of the mixing angle (DCHI).

```
! $Revision: 2006.0 $
***,h2s Diabatization and NACME calculation
memory,3,m

gprint,orbitals,civector

geometry={x;noorient        !noorient should always be used for diabatization
         s;
         h1,s,r1;
         h2,s,r2,h1,theta}

basis=avdz                  !This basis is too small for real application

r1=2.5                      !Reference geometry
theta=[92]

r=[2.55,2.60]               !Displaced geometries
dr=[0,0.01,-0.01]           !Samll displacements for finite difference NACME calculation

reforb1=2140.2              !Orbital dumprecord at reference geometry
refci=6000.2                !MRCI record at reference geometry
savci=6100.2                !MRCI record at displaced geometries

text,compute wavefunction at reference geometry (C2v)
r2=r1

{hf;occ,9,2;wf,18,2,4;orbital,2100.2}

{multi;occ,9,2;closed,4,1;
wf,18,2;state,2;            !1B1 and 1A2 states
natorb,reforb1              !Save reference orbitals on reforb1
noextra}                    !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;      !MRCI at reference geometry
wf,18,2,0;state,2;          !1B1 and 1A2 states
orbital,reforb1             !Use orbitals from previous CASSCF
save,refci}                 !Save MRCI wavefunction

Text,Displaced geometries

do i=1,#r                   !Loop over different r values
data,truncate,savci+1       !truncate dumpfile after reference
reforb=reforb1

do j=1,3                    !Loop over small displacements for NACME
r2=r(i)+dr(j)               !Set current r2

{multi;occ,9,2;closed,4,1;
wf,18,2,0;state,2;          !Wavefunction definition
start,reforb                !Starting orbitals
orbital,3140.2+j;           !Dumprecord for orbitals
diab,reforb                 !Generate diabatic orbitals relative to reference geometry
noextra}                    !Dont use extra symmetries

reforb=3141.2               !Use orbitals for j=1 as reference for j=2,3

{ci;occ,9,2;closed,4,1;
wf,18,2,0;state,2;
orbital,diabatic            !Use diabatic orbitals
save,savci+j}               !Save MRCI for displaced geometries

eadia=energy                !Save adiabatic energies for use in ddr
if(j.eq.1) then
e1(i)=energy(1)             !Save adiabatic energies for table printing
e2(i)=energy(2)
end if

{ci;trans,savci+j,savci+j;  !Compute transition densities at R2+DR(j)
dm,7000.2+j}                !Save transition densities on this record
{ci;trans,savci+j,refci;    !Compute transition densities between R2+DR(j) and R1
dm,7100.2+j}                !Save transition densities on this record
```

examples/
h2s˙diab2.com

The calculation produces the following table

```
 Mixing angles and non-adiabatic coupling matrix elements for H2S

       R          MIXCI        MIXTOT          DCHI       NACMECI
    2.55       15.2694       15.2644       -5.2226       -5.2365
    2.60       27.8740       27.8772       -3.4702       -3.4794

 Diabatic energies for H2S, obtained from CI-vectors

       R       E1            E2            H11CI         H22CI         H21CI
    2.55 -398.64572746 -398.63666636 -398.64509901 -398.63729481   -0.00230207
    2.60 -398.64911752 -398.63771802 -398.64662578 -398.64020976   -0.00471125

 Diabatic energies for H2S, obtained from CI-vectors and orbital correction

       R       E1            E2            H11           H22           H21
    2.55 -398.64572746 -398.63666636 -398.64509941 -398.63729441   -0.00230139
    2.60 -398.64911752 -398.63771802 -398.64662526 -398.64021027   -0.00471160
```

As expected the coupling matrix elements obtained from the 3-point `DDR` calculation (NACMECI) and by differentiating the mixing angle (DCHI) are in close agreement.

36 THE VB PROGRAM CASVB

CASVB is a general program for valence bond calculations
written by T. Thorsteinsson and D. L. Cooper (1996–2005).

This program can be used in two basic modes:

a) variational optimization of quite general types of nonorthogonal MCSCF or modern valence bond wavefunctions

b) representation of CASSCF wavefunctions in modern valence form, using overlap- (*relatively inexpensive*) or energy-based criteria.

Bibliography:

T. Thorsteinsson, D. L. Cooper, J. Gerratt, P. B. Karadakov and M. Raimondi, Theor. Chim. Acta **93**, 343–66 (1996).
D. L. Cooper, T. Thorsteinsson and J. Gerratt, Int. J. Quant. Chem. **65**, 439–51 (1997).
D. L. Cooper, T. Thorsteinsson and J. Gerratt, Adv. Quant. Chem. **32**, 51–67 (1998).
T. Thorsteinsson and D. L. Cooper, in *Quantum Systems in Chemistry and Physics. Volume 1: Basic problems and models systems*, eds. A. Hernández-Laguna, J. Maruani, R. McWeeny, and S. Wilson (Kluwer, Dordrecht, 2000); pp 303–26.

All publications resulting from use of this program should acknowledge relevant publications. There is a more complete bibliography at http://www.liv.ac.uk/ dlc/CASVB.html

36.1 Structure of the input

All *CASVB* sub-commands may be abbreviated by four letters. The general input structure can be summarized as follows:

a) For generating representations of CASSCF wavefunctions, the program is invoked by the command `CASVB`. For variational optimization of wavefunctions it is normally invoked inside *MULTI* by the sub-command `VB` (see 20.10).

b) Definition of the CASSCF wavefunction (not generally required).

c) Definition of the valence bond wavefunction.

d) Recovery and/or storage of orbitals and vectors.

e) Manual input of starting guess (optional).

g) Optimization control.

f) Definition of molecular symmetry and possible constraints on the VB wavefunction.

h) Wavefunction analysis.

i) Further general options.

Items a) and b) should precede everything else in the input; apart from this, commands may come in any order.

36.2 Defining the CASSCF wavefunction

CASVB is interfaced with the determinant part of *MULTI* (i.e., `CONFIG,CSF;` must *not* be specified). When this program is run prior to *CASVB*, the CI vector must dumped using one of the directives `SAVE, NATORB, CANONICAL,` or `LOCALI` (see section 20.5.4). The three latter are recommended.

36.2.1 The VBDUMP directive

`VBDUMP`[,*vbdump*];

If present, the `VBDUMP` card must occur first in the *CASVB* input. It is *not* required for variational calculations.

Note that in the majority of cases (*e.g.*, if a *CASVB* run occurs immediately after *MULTI*, or for variational calculations), explicit specification of dump records with *vbdump* is not required.

Wavefunction definitions may be restored here using `VBDUMP` cards (see also Section 20.8.6). The default record name (*vbdump*) is 4299.2. If a `VBDUMP` card is not present and record 4299.2 does not exist, then *CASVB* will attempt to generate the wavefunction information automatically based on the latest MCSCF calculation (however, `STATE` and `WEIGHT` information will not be restored in such a case).

36.3 Other wavefunction directives

The definitions of the CASSCF wavefunction may also be specified manually using some or all of the directives:

`OCC`	Occupied orbitals.
`CLOSED`	Closed-shell orbitals.
`FROZEN`	Frozen-core orbitals.
`WF`	Wavefunction card.
`STATE`	Number of states for this wavefunction symmetry.
`WEIGHT`	Weights of states.

For the exact definition of these cards see sections 20.2 and 20.3. These commands may also be used to modify the values defined in `VBDUMP`. The information given on these cards should correspond to the CI vector saved in the CASSCF calculation. The cards, and their ordering, should therefore coincide with those used in *MULTI*, except for the `WEIGHT` cards which may differ. At present, the VB wavefunction must correspond to a well-defined number of electrons and total spin. Other states may be present, but an error condition will occur if non-zero weights are specified for wavefunction symmetries with varying values of *elec* or *spin*.

36.4 Defining the valence bond wavefunction

36.4.1 Specifying orbital configurations

The number of core and active orbitals (*mcore*, *mact*), active electrons (*Nact*), and the value of the total spin will be identical to that defined for the CASSCF wavefunction. The spatial VB

configurations are defined in terms of the active orbitals only, and may be specified using one or more CON cards (note that the RESTRICT and SELECT keywords are not used in *CASVB*):

CON,$n_1,n_2,n_3,n_4,\ldots$;

The configurations can be specified by occupation numbers, exactly as in *MULTI* (see section 20.4.3), so that n_i is the occupation of the ith valence bond orbital. Alternatively a list of *Nact* orbital numbers (in any order) may be provided – the program determines which definition applies. The two cards CON,1,0,1,2; and CON,1,3,4,4; are thus equivalent.

If no configurations are specified the single covalent configuration $\phi_1\phi_2\cdots\phi_{Nact}$ is assumed.

36.4.2 Selecting the spin basis

SPINBASIS,*key*;

key may be chosen from KOTANI (default), RUMER, PROJECT or LTRUMER, specifying the basis of spin eigenfunctions used in the definition of valence bond structures. PROJECT refers to spin functions generated using a spin projection operator, LTRUMER to Rumer functions with the so-called "leading term" phase convention.

36.5 Recovering CASSCF CI vector and VB wavefunction

The appropriate MOLPRO records may be specified explicitly using the START directive (an alternative is the *vbdump* mechanism described in section 36.2.1):

START,*ci,vb,orb,trnint*;

ci: record name for the CASSCF CI vector. The CI vector must have been dumped previously using either of the SAVE, NATORB, CANONICAL, or LOCALI directives (see section 20.5.4). A default value for *ci* is determined from the most recent *vbdump* record(s).

Note that if the *ci* record is not found, only an energy-based optimization of the VB wavefunction can be carried out.

vb: record name for the valence bond orbitals and structure coefficients, as saved by a previous CASVB calculation. If the VB wavefunction was previously saved in the AO basis the orbitals will be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (*orb* below) for this to be possible).

orb: record name for the molecular orbitals defining the CASSCF wavefunction. This information is necessary if one wants to output the valence bond orbitals in the atomic orbital basis.

trnint: record name for the transformed CASSCF integrals. These are required for the energy-based criteria (i.e., if CRIT,ENERGY is specified), and can be saved inside *MULTI* by the TRNINT sub-command (see 20.8.7). The default record name, both here and in *MULTI*, is 1900.1.

36.6 Saving the VB wavefunction

SAVE,*vb,civb,vbao*;

vb: record name for VB wavefunction (default is first available record after 3200.2), i.e., orbitals and structure coefficients.

civb: record name for valence bond full CI vector defined in terms of the CASSCF MOs (default is 3300.2). Saving this vector is necessary for the calculation of further properties, geometry optimization, etc.

vbao: record name for valence bond wavefunction in the AO basis. Note that specifying *orb* in the START directive is a precondition for this keyword. It may be useful for plotting of orbitals, or for providing a guess to be used in the interpretation of a CASSCF solution employing a different active space.

It is normally advisable to use records on file 2 for *vb*, *civb*, and *vbao*.

36.7 Specifying a guess

GUESS;*key-1,...*;*key-2,...*;...

The GUESS keyword initiates the input of a guess for the valence bond orbitals and structure coefficients. *key-i* can be either ORB, STRUC or READ. These keywords modify the guess provided by the program, or specified by the START directive. It is thus possible to modify individual orbitals in a previous solution to construct the starting guess.

36.7.1 Orbital guess

ORB,i, c_1, c_2,... c_{mact};

Specifies a starting guess for valence bond orbital number i. The guess is specified in terms of the *mact* active MOs defining the CASSCF wavefunction. (Note that the definition of these MOs will depend on how the CI vector was dumped – i.e. which of the SAVE, NATORB, CANONICAL, or LOCALI directives was used (see section 20.5.4). Use of one of the three latter keywords is recommended.)

36.7.2 Guess for structure coefficients

STRUC,c_1, c_2,... c_{NVB};

Specifies a starting guess for the *NVB* structure coefficients. If this card is not provided, and no guess specified by START, the perfect-pairing mode of spin coupling is assumed for the spatial configuration having the least number of doubly occupied orbitals. Note that the definition of structures depends on the value of SPINBASIS. Doubly occupied orbitals occur first in all configurations, and the spin eigenfunctions are based on the singly occupied orbitals being in ascending order.

36.7.3 Read orbitals or structure coefficients

The READ keyword can take one of the following forms:

READ,ORB,*iorb1*[,TO,*iorb2*] [,AS,*jorb1*[,TO,*jorb2*]] [,FROM,*record*];

READ,STRUC,*istruc1*[,TO,*istruc2*] [,AS,*jstruc1*[,TO,*jstruc2*]] [,FROM,*record*];

READ,ALL [,FROM,*record*];

In this way a subset of orbitals and/or structure coefficients may be picked out from a previous calculation. Renumbering of orbitals or structures can be done using the "AS" construct as outlined above. If the VB wavefunction was previously saved in the AO basis, the orbitals will

be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (*orb* in the START commmand) for this to be possible).

Default for *record* is the *vb* record name specified in keyword START (if applicable).

36.8 Permuting orbitals

ORBPERM,$i_1,\ldots,i_{mact}$;

Permutes the orbitals in the valence bond wavefunction and changes their phases according to $\phi'_j = \mathrm{sign}(i_j)\phi_{\mathrm{abs}(i_j)}$. The guess may be further modified using the GUESS keyword. Also the structure coefficients will be transformed according to the given permutation (note that the configuration list must be closed under the orbital permutation for this to be possible).

36.9 Optimization control

36.9.1 Optimization criterion

CRIT,*method*;

Specifies the criterion for the optimization. *method* can be OVERLAP or ENERGY (OVERLAP is default). The former maximizes the normalized overlap with the CASSCF wavefunction:

$$\max\left(\frac{\langle\Psi_{CAS}|\Psi_{VB}\rangle}{(\langle\Psi_{VB}|\Psi_{VB}\rangle)^{1/2}}\right)$$

and the latter simply minimizes the energy:

$$\min\left(\frac{\langle\Psi_{VB}|\hat{H}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle}\right).$$

36.9.2 Number of iterations

MAXITER,N_{iter};

Specifies the maximum number of iterations in the second order optimizations. Default is N_{iter}=50.

36.9.3 CASSCF-projected structure coefficients

(NO)CASPROJ;

With this keyword the structure coefficients are picked from the transformed CASSCF CI vector, leaving only the orbital variational parameters. For further details see the bibliography. This option may be useful to aid convergence.

36.9.4 Saddle-point optimization

SADDLE,n;

Defines optimization onto an n^{th}-order saddle point. See also T. Thorsteinsson and D. L. Cooper, Int. J. Quant. Chem. **70**, 637–50 (1998).

36.9.5 Defining several optimizations

More than one optimization may be performed in the same *CASVB* deck, by the use of `OPTIM` keywords:

`OPTIM`[;...;`FINOPTIM`];

The subcommands may be any optimization declarations defined in this section, as well as any symmetry or constraints specifications described in section 36.10. Commands given as arguments to `OPTIM` will be particular to this optimization step, whereas commands specified outside will act as default definitions for all subsequent `OPTIM` keywords.

If only one optimization step is required, the `OPTIM` keyword need not be specified.

When only a machine-generated guess is available, *CASVB* will attempt to define a sequence of optimization steps chosen such as to maximize the likelihood of successful convergence and to minimize CPU usage. To override this behaviour, simply specify one or more `OPTIM` cards.

36.9.6 Multi-step optimization

A loop over two or more optimization steps may be specified using:

`ALTERN`,*Niter*;...;`FINALTER`

With this specification the program will repeat the enclosed optimization steps until either all optimizations have converged, or the maximum iteration count, *Niter*, has been reached.

36.10 Point group symmetry and constraints

The problems associated with symmetry-adapting valence bond wavefunctions are considered, for example, in: T. Thorsteinsson, D. L. Cooper, J. Gerratt and M. Raimondi, Theor. Chim. Acta **95**, 131 (1997).

36.10.1 Symmetry operations

`SYMELM`,*label*,*sign*;

Initiates the definition of a symmetry operation referred to by *label* (any three characters). *sign* can be + or −; it specifies whether the total wavefunction is symmetric or antisymmetric under this operation, respectively. A value for *sign* is not always necessary but, if provided, constraints will be put on the structure coefficients to ensure that the wavefunction has the correct overall symmetry (note that the configuration list must be closed under the orbital permutation induced by *label* for this to be possible).

The operator is defined in terms of its action on the active MOs as specified by one or more of the keywords `IRREPS`, `COEFFS`, or `TRANS` (any other keyword will terminate the definition of this symmetry operator). If no further keyword is supplied, the identity is assumed for *label*. The alternative format `SYMELM`,*label*,*sign*;*key-1,*...;*key-2,*...;... may also be used.

36.10.2 The IRREPS keyword

`IRREPS`,i_1, i_2,...;

The list i_1, i_2,... specifies which irreducible representations (as defined in the CASSCF wavefunction) are antisymmetric with respect to the *label* operation. If an irreducible representation is not otherwise specified it is assumed to be symmetric under the symmetry operation.

36.10.3 The COEFFS keyword

COEFFS,i_1, i_2,...;

The list i_1, i_2,... specifies which individual CASSCF MOs are antisymmetric with respect to the *label* operation. If an MO is not otherwise specified, it is assumed to be symmetric under the symmetry operation. This specification may be useful if, for example, the molecule possesses symmetry higher than that exploited in the CASSCF calculation.

36.10.4 The TRANS keyword

TRANS,n_{dim}, i_1, ... $i_{n_{dim}}$, c_{11}, c_{12}, ... $c_{n_{dim}n_{dim}}$;

Specifies a general $n_{dim} \times n_{dim}$ transformation involving the MOs i_1, ... $i_{n_{dim}}$, specified by the c coefficients. This may be useful for systems with a two- or three-dimensional irreducible representation, or if localized orbitals define the CASSCF wavefunction. Note that the specified transformation must always be orthogonal.

36.10.5 Symmetry relations between orbitals

In general, for a VB wavefunction to be symmetry-pure, the orbitals must form a representation (not necessarily irreducible) of the symmetry group. Relations between orbitals under the symmetry operations defined by SYMELM may be specified according to:

ORBREL,i_1, i_2, *label1, label2,...*;

Orbital i_1 is related to orbital i_2 by the sequence of operations defined by the *label* specifications (defined previously using SYMELM). The operators operate right to left. Note that i_1 and i_2 may coincide. Only the minimum number of relations required to define all the orbitals should be provided; an error exit will occur if redundant ORBREL specifications are found.

36.10.6 The SYMPROJ keyword

As an alternative to incorporating constraints, one may also ensure correct symmetry of the wavefunction by use of a projection operator:

(NO)SYMPROJ[,$irrep_1$,$irrep_2$,...];

The effect of this keyword is to set to zero coefficients in unwanted irreducible representations. For this purpose the symmetry group defined for the CASSCF wavefunction is used (always a subgroup of D_{2h}). The list of irreps in the command specifies which components of the wavefunction should be kept. If no irreducible representations are given, the current wavefunction symmetry is assumed. In a state-averaged calculation, all irreps are retained for which a non-zero weight has been specified in the wavefunction definition. The SYMPROJ keyword may also be used in combination with constraints.

36.10.7 Freezing orbitals in the optimization

FIXORB,i_1, i_2,...;

This command freezes the orbitals specified in the list i_1, i_2,... to that of the starting guess. Alternatively the special keywords ALL or NONE may be used. These orbitals are eliminated from the optimization procedure, but will still be normalized and symmetry-adapted according to any ORBREL keywords given.

36.10.8 Freezing structure coefficients in the optimization

FIXSTRUC,i_1, i_2,...;

Freezes the coefficients for structures i_1, i_2,... . Alternatively the special keywords ALL or NONE may be used. The structures are eliminated from the optimization procedure, but may still be affected by normalization or any symmetry keywords present.

36.10.9 Deleting structures from the optimization

DELSTRUC,i_1, i_2,...,[ALL],[NONE];

Deletes the specified structures from the wavefunction. The special keywords ALL or NONE may be used. A structure coefficient may already be zero by symmetry (as defined by SYMELM and ORBREL), in which case deleting it has no effect.

36.10.10 Orthogonality constraints

ORTHCON;*key-1,...*;*key-2,...*;...

The ORTHCON keyword initiates the input of orthogonality constraints between pairs of valence bond orbitals. The sub-keywords *key-i* can be one of ORTH, PAIRS, GROUP, STRONG or FULL as described below. Orthogonality constraints should be used with discretion. Note that orthogonality constraints for an orbital generated from another by symmetry operations (using the ORBREL keyword) cannot in general be satisfied.

ORTH,i_1, i_2, ...;

Specifies a list of orbitals to be orthogonalized. All overlaps between pairs of orbitals in the list are set to zero.

PAIRS,i_1, i_2, ...;

Specifies a simple list of orthogonalization pairs. Orbital i_1 is made orthogonal to i_2, i_3 to i_4, etc.

GROUP,*label*,i_1, i_2, ...;

Defines an orbital group to be used with the ORTH or PAIRS keyword. The group is referred to by *label* which can be any three characters beginning with a letter a–z. Labels defining different groups can be used together or in combination with orbital numbers in ORTH or PAIRS. i_1, i_2, ... specifies the list of orbitals in the group. Thus the combination GROUP,AZZ,1,2; GROUP,BZZ,3,4; ORTH,AZZ,BZZ; will orthogonalize the pairs of orbitals 1-3, 1-4, 2-3 and 2-4.

STRONG;

This keyword is short-hand for strong orthogonality. The only allowed non-zero overlaps are between pairs of orbitals $(2n-1, 2n)$.

FULL;

This keyword is short-hand for full orthogonality. This is mainly likely to be useful for testing purposes.

36.11 Wavefunction analysis

36.11.1 Spin correlation analysis

(NO)SCORR;

With this option, expectation values of the spin operators $(\hat{s}_\mu + \hat{s}_\nu)^2$ are evaluated for all pairs of μ and ν. Default is NOSCORR. The procedure is described by: G. Raos, J. Gerratt, D. L. Cooper and M. Raimondi, Chem. Phys. **186**, 233–250 (1994); ibid, 251–273 (1994); D. L. Cooper, R. Ponec, T. Thorsteinsson and G. Raos, Int. J. Quant. Chem. **57**, 501–518 (1996).

At present this analysis is only implemented for spin-coupled wavefunctions.

36.11.2 Printing weights of the valence bond structures

For further details regarding the calculation of weights in CASVB, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. **23**, 105-26 (1998).

VBWEIGHTS,*key1*,*key2*,...

Calculates and outputs weights of the structures in the valence bond wavefunction Ψ_{VB}. *key* specifies the definition of nonorthogonal weights to be used, and can be one of:

CHIRGWIN	Evaluates Chirgwin-Coulson weights (see: B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. Lond. **A201**, 196 (1950)).
LOWDIN	Performs a symmetric orthogonalization of the structures and outputs the corresponding weights.
INVERSE	Outputs "inverse overlap populations" as in G. A. Gallup and J. M. Norbeck, Chem. Phys. Lett. **21**, 495–500 (1973).
ALL	All of the above.
NONE	Suspends calculation of structure weights.

The commands LOWDIN and INVERSE require the overlap matrix between valence bond structures, and some computational overhead is thus involved.

36.11.3 Printing weights of the CASSCF wavefunction in the VB basis

For further details regarding the calculation of weights in *CASVB*, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. **23**, 105-26 (1998).

CIWEIGHTS,*key1*,*key2*,... [,N_{conf}];

Prints weights of the CASSCF wavefunction transformed to the basis of nonorthogonal VB structures. For the *key* options see VBWEIGHTS above. Note that the evaluation of inverse overlap weights involves an extensive computational overhead for large active spaces. Weights are

given for the total CASSCF wavefunction, as well as the orthogonal complement to Ψ_{VB}. The default for the number of configurations requested, $N_{\rm conf}$, is 10. If $N_{\rm conf}$=-1 all configurations are included.

36.12 Controlling the amount of output

PRINT,i_1, i_2,...;

Each number specifies the level of output required at various stages of the execution, according to the following convention:

-1	No output except serious, or fatal, error messages.
0	Minimal output.
1	Standard level of output.
2	Extra output.

The areas for which output can be controlled are:

i_1	Print of input parameters, wavefunction definitions, etc.
i_2	Print of information associated with symmetry constraints.
i_3	General convergence progress.
i_4	Progress of the 2nd order optimization procedure.
i_5	Print of converged solution and analysis.
i_6	Progress of variational optimization.
i_7	Usage of record numbers on file 2.

For all, the default output level is +1. If $i_5 \geq 2$ VB orbitals will be printed in the AO basis (provided that the definition of MOs is available); such output may be especially useful for plotting of orbitals.

36.13 Further facilities

Calculations can also be performed for various types of direct product wavefunctions and/or with strictly localized orbitals. Details are available from the authors. These facilities will be documented in a later release.

36.14 Service mode

SERVICE;
This keyword takes precedence over any others previously defined to *CASVB*. It provides simple facilities for retrieving orbital coefficients and VB structure coefficients. It should not be used during a run of *CASVB* that has been invoked from inside *MULTI*.

START,*record.file*;
Coefficients are taken from *record.file*. The default value is *2100.2*.

WRITE,*iwrite*;
Vectors in the symmetry orbital basis are written to channel *iabs(iwrite)*. The default action is

to write these vectors to the standard output. If *iwrite* is negative, then the vectors are instead written to a binary file as a single record.

SPECIAL,*idim1,idim2,idim3,idim4*;
If present, this keyword must come last. The program attempts to retrieve from *record.file* a vector of length *idim1*idim2+idim3*, after first skipping *idim4* elements. The vector is written according to the setting of *iwrite*. (Default *idim* values are zero.)

36.15 Examples

```
***, ch2                      ! A1 singlet state
geometry={angstrom
c
h1,c,1.117
h2,c,1.117,h1,102.4}
int
hf
{multi;occ,4,1,2;closed,1      ! 6 in 6 CASSCF
natorb,,ci,save=3500.2;vbdump}
{casvb                         ! Overlap-based VB using
save,3200.2}                   ! the spin-coupled wavefunction
{casvb                         ! Energy-based VB calculation
start,,3200.2;save,3220.2
crit,energy}
{multi;occ,4,1,2;closed,1      ! Fully variational VB calculation
{vb;start,,3220.2;save,3240.2;print,,,,,2}}
---


memory,4,m
***,n2s2 (model a)             ! Variational calculation for N2S2.
geometry={x,y,z;
a1,n,-2.210137753,0,0;         ! NOTE: other choices of active space
a2,n,+2.210137753,0,0;         ! give alternative (competing) models.
a3,s,0,-2.210137753,0;
a4,s,0,+2.210137753,0}
basis=VTZ;
cartesian
{hf;wf,46,1}
{multi;occ,7,4,5,2,4,2,2,0;closed,7,4,5,2,1,0,1,0; natorb,,ci,save=3500.2}
{multi;occ,7,4,5,2,4,2,2,0;closed,7,4,5,2,1,0,1,0; vb}
---


***, lih                       ! Fully variational VB calculation
r=2.8,bohr                     ! and geometry optimization.
basis={
s,1,921.300000,138.700000,31.940000,9.353000,3.158000,1.157000;
k,1.6,0.001367,0.010425,0.049859,0.160701,0.344604,0.425197;
s,1,0.444600,0.076660,0.028640;
p,1,1.488000,0.266700,0.072010,0.023700;
k,1.2,0.038770,0.236257;
s,2,13.36,2.013,0.4538,.1233;
k,1.2,0.032828,0.231204;}
geometry={li;h,li,r}
int;
{hf;wf,4,1}
{multi
occ,4,0,0,0
closed,0,0,0,0
natorb,,ci,save=3500.2}
{multi;maxiter,20
vb}
```

```
optg
---
```

37 SPIN-ORBIT-COUPLING

37.1 Introduction

Spin-orbit matrix elements and eigenstates can be computed using either the Breit-Pauli (BP) operator or spin-orbit pseudopotentials (ECPs). The *state-interacting* method is employed, which means that the spin-orbit eigenstates are obtained by diagonalizing $\hat{H}_{el} + \hat{H}_{SO}$ in a basis of eigenfunctions of $\hat{H}_{el}$. The full Breit-Pauli SO-operator can be used only for MCSCF wavefunctions. For MRCI wavefunctions, the full BP operator is used for computing the matrix elements between *internal configurations* (no electrons in external orbitals), while for contributions of external configurations a mean-field one-electron fock operator is employed. The error caused by this approximation is usually smaller than 1 cm^{-1}.

The program allows either the computation of individual spin-orbit matrix elements for a given pair of states, or the automatic setting-up and diagonalization of the whole matrix for a given set of electronic states. In the latter case, matrix elements over one-electron operators are also computed and transformed to the spin-orbit eigenstates (by default, the dipole matrix elements are computed; other operators can be specified on the `GEXPEC` or `EXPEC` cards, see section 6.13). Since it may be often sufficient to compute the spin-orbit matrix elements in a smaller basis than the energies, it is possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable `HLSDIAG`.

37.2 Calculation of SO integrals

The one-and two-electron spin-orbit integrals over the BP Hamiltonian can be precomputed and stored on disk using the command

`LSINT` [,`X`] [,`Y`] [,`Z`]

`X`, `Y`, and `Z` specify the components to be computed. If none of these is given, all three are evaluated. The advantage of precomputing the integrals is that they can then be used in any number of subsequent SO calculations, but this may require a large amount of disk space (note that there are 6 times as many integrals as in an energy calculation). If the `LSINT` card is not given, the integrals are recomputed for one component at a time whenever needed, and destroyed at the end of the SO calculation. This reduces the disk space by a factor of 3, but may be expensive in terms of CPU if several SO calculations (e.g., for MCSCF and MRCI wavefunctions) are carried out.

The input for spin-orbit ECPs is described in section 14. Of course, in ECP-LS calculations the `LSINT` card is not needed.

37.3 Calculation of individual SO matrix elements

Individual spin-orbit matrix elements can be computed within the MRCI program using

`TRANLS`,*record1.file, record2.file, bra2ms, ket2ms, lsop*;

where

record1.file	Record holding the bra-wavefunction.
record2.file	Record holding the ket-wavefunction. Both records must have been generated using the `SAVE` directive of the MRCI program.

bra2ms	$2 \times M_S$ value of the bra-wavefunction.
ket2ms	$2 \times M_S$ value of the ket-wavefunction.
lsop	Cartesian component of the Spin-orbit Hamiltonian. This can be one of LSX, LSY, or LSZ in all electron calculations, and ECPLSX, ECPLSY, or ECPLSZ in ECP calculations.

Since the spin-orbit program is part of the MRCI program, the TRANLS card must be preceded by a [MR]CI card. For the case that the matrix elements are computed for MCSCF wavefunctions, one has to recompute and save the CI-vectors using the MRCI program (see chapter 21), using the NOEXC directive to avoid inclusion of any further excitations out of the MCSCF reference function. If in the MRCI step several states of the same symmetry are computed simultaneously using the STATE directive, the matrix elements are computed for all these states. Note that the OCC and CLOSED cards must be the same for all states used in a TRANLS calculation.

The selection rules for the M_S values are $\Delta M_S = \pm 1$ for the LSX and LSY operators, and $\Delta M_S = 0$ for the LSZ operator. Note that $2M_S$ has to be specified, and so the selection rules applying to the difference of the input values are 0 or 2.

In all-electron SO calculations the value of the calculated spin-orbit matrix element is saved (in atomic units) in the MOLPRO variables TRLSX, TRLSY and TRLSZ for the x, y, and z components respectively. For ECP-LS calculations the variables TRECPLSX, TRECPLSY, and TRECPLSZ are used. Note that for imaginary matrix elements (i.e., for the x and z components of the SO Hamiltonian) the matrix elements are imaginary and the stored real values have to be multiplied by i. If matrix elements for several states are computed, all values are stored in the respective variable-arrays with the bra-states running fastest.

37.4 Calculation and diagonalization of the entire SO-matrix

HLSMAT,*type*, *record1, record2, record3, ...*

Computes the entire SO matrix and diagonalizes it using all states which are contained in the records *record1, record2, record3, ...* All records must have been generated using the SAVE directive of the MRCI program. *type* may be either LS for Breit-Pauli calculations, or ECP for ECP-LS calculations. By default, the eigenvalues and dipole transition matrix elements between the ground and excited states are printed.

As with the TRANLS card, the HLSMAT is recognized only by the MRCI program and must be preceded by a CI card. Also, the OCC and CLOSED cards must be the same for all states used in a HLSMAT calculation.

37.5 Modifying the unperturbed energies

Often it may be sufficient to compute the spin-orbit matrix elements in a smaller basis or at a lower computational level than the energies. It is therefore possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable HLSDIAG. The energy values in HLSDIAG must be in exactly the same order as the states in the records given on the HLSMAT card. Before any spin-orbit calculation, the variable HLSDIAG must either be undefined or cleared (then the original energies are used), or must contain exactly the number of energies as the number of states treated in the subsequent spin-orbit calculation (use CLEAR,HLSDIAG to clear any previous values in the variable). It is the user's responsibility that the order of the energies in HLSDIAG is correct!

37.5.1 Print Options for spin-orbit calculations

PRINT,*option*$_1$=*value*$_1$, *option*$_2$=*value*$_2$,...

where option can be

HLS	HLS=−1 only the SO energies and transition matrix elements between ground and excited states are printed (default). HLS≥ 0: The SO matrix is printed. HLS≥ 1: The property matrices are printed. HLS≥ 2: The individual matrix elements are printed (same as OPTION,MATEL). HLS≥ 3: Debugging information is printed.
VLS	VLS=−1: No print of eigenvectors (default). VLS≥ 0: The eigenvectors are printed.

37.5.2 Options for spin-orbit calculations

Some options can be set using the OPTION directive (in any order)

OPTIONS [,WIGNER=*value*] [,HLSTRANS=*value*] [,MATEL=*value*]

where

WIGNER	This option determines whether the Wigner-Eckart theorem should be used when the SO matrix is determined. WIGNER=1 (default) uses the theorem, WIGNER=0 calculates each SO matrix element individually. This option is needed for test purposes only.
HLSTRANS	This option determines whether a SO matrix calculation should be performed in the not spin-symmetry adapted basis set (HLSTRANS=0), in the spin-symmetry adapted basis set (HLSTRANS=1, default) or with both basis sets (HLSTRANS=2). At present, symmetry adaption can only be performed for triplet states, where the following notation is used to indicate the symmetry adapted spin functions: $\|S,M_S\rangle_+ = \frac{1}{\sqrt{2}}(\|S,M_S\rangle + \|S,-M_S\rangle)$, $\|S,M_S\rangle_- = \frac{1}{\sqrt{2}}(\|S,M_S\rangle - \|S,-M_S\rangle)$. If only singlet and triplet states are considered, the spin-orbit matrix is blocked according to double-group symmetry and the eigenvalues for each each block are printed separately. In all other cases the HLSTRANS option is ignored.
MATEL	If the entire SO matrix is calculated using HLSMAT, the individual matrix elements are normally not shown. When the option MATEL=1 is given, the individual matrix elements and the contributions of the internal and external configuration classes are printed.

37.6 Examples

37.6.1 SO calculation for the S-atom using the BP operator

```
! $Revision: 2006.0 $
***,SO calculation for the S-atom
geometry={s}
basis={spd,s,vtz}                                   !use uncontracted basis

{rhf;occ,3,2,2,,2;wf,16,4,2}                        !rhf for 3P state

{multi                                              !casscf
wf,16,4,2;wf,16,6,2;wf,16,7,2;wf,16,1,0;state,3;    !1D and 1S states
wf,16,4,0;wf,16,6,0;wf,16,7,0}                      !3P states

{ci;wf,16,1,0;save,3010.1;state,3;noexc}            !save casscf wavefunctions using mrci
{ci;wf,16,4,0;save,3040.1;noexc}
{ci;wf,16,6,0;save,3060.1;noexc}
{ci;wf,16,7,0;save,3070.1;noexc}
{ci;wf,16,4,2;save,3042.1;noexc}
{ci;wf,16,6,2;save,3062.1;noexc}
{ci;wf,16,7,2;save,3072.1;noexc}

{ci;wf,16,1,0;save,4010.1;state,3}                  !mrci calculations for 1D, 1S states
ed=energy(1)                                        !save energy for 1D state in variable ed
es=energy(3)                                        !save energy for 1S state in variable es
{ci;wf,16,4,2;save,4042.1}                          !mrci calculations for 3P states
ep=energy                                           !save energy for 3P state in variable ep
{ci;wf,16,6,2;save,4062.1}                          !mrci calculations for 3P states
{ci;wf,16,7,2;save,4072.1}                          !mrci calculations for 3P states
text,only triplet states, casscf

lsint                                               !compute so integrals

text,3P states, casscf
{ci;hlsmat,ls,3042.1,3062.1,3072.1}                 !Only triplet states, casscf

text,3P states, mrci
{ci;hlsmat,ls,4042.1,4062.1,4072.1}                 !Only triplet states, mrci

text,3P, 1D, 1S states, casscf
{ci;hlsmat,ls,3010.1,3040.1,3060.1,3070.1,3042.1,3062.1,3072.1}       !All states, casscf

text,only triplet states, use mrci energies and casscf SO-matrix elements
hlsdiag=[ed,ed,es,ed,ed,ed,ep,ep,ep]             !set variable hlsdiag to mrci energies
{ci;hlsmat,ls,3010.1,3040.1,3060.1,3070.1,3042.1,3062.1,3072.1}
```

examples/
s so.com

37.6.2 SO calculation for the I-atom using ECPs

```
! $Revision: 2006.0 $
***,I
memory,5,M;
gprint,orbitals,civector,basis;
gthresh,energy=1.d-8,coeff=1.d-8;
geometry={I};

basis={
!
! Iodine-ECP (Dirac-Fock) with SO-coupling
!
ecp,I,46,4,3;
1; 2,   1.00000000,       0.00000000;                                          ! lokal term = 0
2; 2,   3.50642001,      83.09814545; 2,   1.74736492,       5.06370919;     ! s-terme
4; 2,   2.99860773, 1/3* 81.88444526; 2,   3.01690894, 2/3* 83.41280402;     ! p-terms with wei
   2,   1.59415934, 1/3*  2.32392477; 2,   1.19802939, 2/3*  2.72079843;
4; 2,   1.03813792, 2/5*  6.40131754; 2,   1.01158599, 3/5*  6.21328827;     ! d-terms with wei
   2,   2.04193864, 2/5* 19.11604172; 2,   1.99631017, 3/5* 19.08465909;
4; 2,   2.64971585,-3/7* 24.79106489; 2,   2.75335574,-4/7* 24.98147319;     ! f-terms with wei
   2,   0.49970082,-3/7*  0.27936581; 2,   0.79638982,-4/7*  0.70184261;
4; 2,   2.99860773,-2/3* 81.88444526; 2,   3.01690894, 2/3* 83.41280402;     ! ECP-SO for p-ter
   2,   1.59415934,-2/3*  2.32392477; 2,   1.19802939, 2/3*  2.72079843;
4; 2,   1.03813792,-2/5*  6.40131754; 2,   1.01158599, 2/5*  6.21328827;     ! ECP-SO for d-ter
   2,   2.04193864,-2/5* 19.11604172; 2,   1.99631017, 2/5* 19.08465909;
4; 2,   2.64971585, 2/7* 24.79106489; 2,   2.75335574,-2/7* 24.98147319;     ! ECP-SO for f-ter
   2,   0.49970082, 2/7*  0.27936581; 2,   0.79638982,-2/7*  0.70184261;
!
! Iodine-basis
!
s,I,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,-0.4782372,-0.5811680,0.2617769,0.4444120,-0.1596560;
s,I,0.05,0.1007509;
p,I,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,0.4251859,0.2995618,0.0303167,-0.2064228,0.0450858;
p,I,0.05,0.1007509,0.01;  ! diffuse p-Funktion wegen evt. neg. Part.Ldg
d,I,0.2,0.4;
f,I,0.3;
}
```

examples/
i˙ecp.com

```
{hf;occ,1,1,1,,1;wf,7,5,1}       !scf for 2Pz
{multi;occ,1,1,1,,1;             !casscf with minmal active space
wf,7,2,1;wf,7,3,1;wf,7,5,1}      !average 2P states
{ci;wf,7,2,1;noexc;save,5000.2}  !save casscf vector for 2Px state
{ci;wf,7,3,1;noexc;save,5100.2}  !save casscf vector for 2Py state
{ci;wf,7,5,1;noexc;save,5200.2}  !save casscf vector for 2Pz state
{ci;wf,7,2,1;save,6000.2}        !mrci for 2Px state
{ci;wf,7,3,1;save,6100.2}        !mrci for 2Py state
{ci;wf,7,5,1;save,6200.2}        !mrci for 2Pz state

{multi;occ,1,2,2,,2              !casscf with larger active space
wf,7,2,1;wf,7,3,1;wf,7,5,1}      !average 2P states
{ci;wf,7,2,1;noexc;save,5010.2}
{ci;wf,7,3,1;noexc;save,5110.2}
{ci;wf,7,5,1;noexc;save,5210.2}
{ci;wf,7,2,1;save,6010.2}
{ci;wf,7,3,1;save,6110.2}
{ci;wf,7,5,1;save,6210.2}

text,casscf,  occ,1,1,1,,1
{ci;hlsmat,ecp,5000.2,5100.2,5200.2}   !do spin-orbit calculations
text,casscf,  occ,1,2,2,,2
{ci;hlsmat,ecp,5010.2,5110.2,5210.2}

text,mrci, occ,1,1,1,,1
{ci;hlsmat,ecp,6000.2,6100.2,6200.2}
text,mrci, occ,1,2,2,,2
{ci;hlsmat,ecp,6010.2,6110.2,6210.2}
```

38 ENERGY GRADIENTS

38.1 Analytical energy gradients

MOLPRO uses two different gradient programs:

The CADPAC gradient program is based on the CADPAC integral routines by R. D. Amos. Currently, this program works for closed shell SCF, high spin RHF, and (state averaged) MCSCF. In the MCSCF case the wavefunction must either be fully optimized, or frozen core orbitals must be taken from a closed-shell SCF calculation (but this does not work in the case of state-averaged MCSCF). Note that CADPAC does not work with generally contracted basis functions.

The ALASKA gradient program is based on the SEWARD integral routines by R. Lindh. It allows the calculation of gradients of generally contracted basis functions for closed shell SCF, open shell RHF, UHF, RKS, UKS, MCSCF, MP2, LMP2, DF-LMP2, QCISD, QCISD(T), and RS2 (CASPT2). Gradients for state averaged MCSCF wave functions can be evaluated using the RS2 gradient program, see section 38.1.5. For details about CASPT2 gradients, see section 22.7.

By default, the program uses ALASKA gradients whenever possible. However, it is possible to force the use of a particular gradient program by defining the variable `GRADTYP` before calling the gradient program:

```
GRADTYP=ALASKA
GRADTYP=CADPAC
```

The gradient program is called using the `FORCE` command:

```
FORCE
```

Normally, the `FORCE` command is not needed, since geometry optimizations should be performed using the `OPTG` procedure. An exception is the optimization of counterpoise corrected energies, which requires several force calculations (cf. section 39.4.7).

If no further data cards are given, the default is to evaluate the gradient for the last optimized wavefunction. In this case no further input is needed for ordinary gradient cases (the program remembers the records on which the wavefunction information is stored). An exception is the unusual case that several different `CPMCSCF` calculations have been formed in a previous MCSCF calculation. In this case the `SAMC` directive must be used to select the desired record. If analytical gradients are not available for the last wavefunction, the gradient is computed numerically. For more details regarding numerical energy gradients see section 38.2.

38.1.1 Adding gradients (ADD)

`ADD`,*factor*,[`NOCHECK`];

If this card is present, the current gradient and energy are added to the previous ones using the given factor. This is useful for the optimization of counterpoise corrected energies (cf. 39.4.7). By default, the program will stop with an error message unless `NOORIENT` has been specified in the geometry input. This behaviour can be disabled by the `NOCHECK` option. This option should only be given if all gradients which are added are evaluated at exactly the same nuclear geometry; otherwise wrong results could result due to unintended rotations of the system.

38.1.2 Scaling gradients (SCALE)

`SCALE`,*factor*;

If this card is present, the current gradient and energy are scaled by the give factor. This is sometimes useful for the optimization of counterpoise corrected energies (cf. 39.4.7).

38.1.3 Defining the orbitals for SCF gradients (ORBITAL)

ORBITAL,*record.file*;

In the SCF case, *record.file* specifies the location of the orbitals, which are used for constructing density matrices, etc. This card is only needed if the SCF for which the gradient is to be computed was not the most recent energy calculation.

For MCSCF wavefunctions, the ORBITAL card is not needed, because the location of the orbitals is stored in the MCSCF dump record.

38.1.4 MCSCF gradients (MCSCF)

MCSCF,*record.file*;

Triggers code for MCSCF gradient. *record.file* specifies the location of information dumped from the MCSCF program, using a SAVE,GRD=*recmc.filmc* card. This card is not needed if the FORCE command appears directly after the corresponding MCSCF input, since the program automatically remembers where the MCSCF information was stored. The same is true if OPTG is used.

38.1.5 State-averaged MCSCF gradients with SEWARD

SA-MCSCF gradients can be computed using segmented or generally contracted basis sets using SEWARD and the RS2 gradient program. The NOEXC directive has to be used in the RS2 input, but no CPMCSCF card is required in MULTI. The RS2 gradient program does the CP-MCSCF automatically.

Example: compute SA-CASSCF gradients for $^2\Pi$ and $^2\Sigma^+$ state of OH.

```
geometry={o;h,o,r}
r=1.83
{multi;wf,9,2,1;wf,9,3,1;wf,9,1,1}      !state averaged casscf for X(2PI) and A(2SIGMA)
{rs2;noexc;wf,9,1,1}                    !compute A(2SIGMA) energy                    examples/
forces                                  !energy gradient for A(2SIGMA) state   oh˙samcforce.com
{rs2;noexc;wf,9,2,1}                    !compute A(2PI) energy
forces                                  !energy gradient for A(2PI) state
```

Without the NOEXC directive, the RS2 (CASPT2) gradient would be evaluated, using the state-averaged orbitals.

38.1.6 State-averaged MCSCF gradients with CADPAC

Normally, no further input is required for computing gradients for state-averaged MCSCF when CADPAC is used. Note, however, that a CPMCSCF,GRAD,*state* directive is required in the SA-MCSCF calculation (see Section 20.9). The gradients are then computed automatically for the *state* specified on the CPMCSCF card. The same is true for difference gradients (CPMCSCF,DGRAD,*state1, state2*) and non-adiabatic coupling matrix elements (CPMCSCF,NACM,*state1, state2*). It is possible to do several coupled-perturbed MCSCF calculations one after each other in the same MCSCF. In this case FORCE would use the last solution by default. The information from the

CPMCSCF is passed to the FORCE program in a certain records (default 5101.1, 5102.1, ...). If several CPMCSCF calculations are performed in the same MCSCF, several such records may be present, and a particular one can be accessed in the FORCE program using the SAMC directive:

SAMC,*record*.

An alias for SAMC is CPMC. For compatibility with earlier versions one can also use

NACM,*record*

for non-adiabatic couplings or

DEMC,*record*

for difference gradients.

Example:

```
multi;
....
state,3
cpmcscf,nacm,1.1,2.1,save=5101.1   !do cpmcscf for coupling of states 1.1 - 2.1
cpmcscf,nacm,1.1,3.1,save=5102.1   !do cpmcscf for coupling of states 1.1 - 3.1
cpmcscf,nacm,2.1,3.1,save=5103.1   !do cpmcscf for coupling of states 2.1 - 3.1

force;samc,5101.1;                 !compute NACME for states 1.1 - 2.1
force;samc,5102.1;                 !compute NACME for states 1.1 - 3.1
force;samc,5103.1;                 !compute NACME for states 2.1 - 3.1
```

See also test job lif_nacme.test.

38.1.7 Non-adiabatic coupling matrix elements (NACM)

see Section 38.1.6.

38.1.8 Difference gradients for SA-MCSCF (DEMC)

see Section 38.1.6.

38.1.9 Example

examples/h2o˙forces.com

```
***, Calculate Gradients for Water
alpha=104 degree           !set geometry parameters
r=1 ang
geometry={O;               !define z-matrix
          H1,o,r;
          H2,o,r,H1,alpha}
basis=vdz                  !basis set
hf                         !do scf
forces                     !compute gradient for SCF
mp2                        !mp2 calculation
forces                     !mp2 gradients
multi                      !casscf calculation
forces                     !casscf gradient
```

38.2 Numerical gradients

It is possible to compute gradients by finite differences using

FORCE,NUMERICAL,*options*

Numerical gradients are computed automatically if no analytical gradients are available for the last energy calculation. By default, no further input are needed, and the gradient will be computed for the last energy calculation. The following options can be given on the FORCE command or on subsequent directives (see subsequent sections):

STARTCMD=*command* The input between *command* and the current FORCE command defines the energy calculation for which the gradient is computed. This input section is executed for each displacement.

PROC=*procname* specifies a procedure to be executed for each displacement. This must define a complete energy calculation and must not contain gradient or Hessian calculations.

VARIABLE=*varname* Compute the gradient of the value of variable *varname*. This implies numerical gradients. The variable must be set in the corresponding energy calculation.

COORD=ZMAT|CART|3N coordinates with respect to which the gradient is evaluated. See section 38.2.1 for more information.

DISPLACE=ZMAT|SYM|UNIQUE|CART
Displacement coordinates to be used for numerical gradient. The default is ZMAT if the geometry is given as a zmatrix which depends on variables, and SYM (symmetrical displacement coordinates) otherwise. See section 38.2.1 for more information.

SYMMETRY=AUTO|NOSYM Symmetry to be used in wavefunction calculations of numerical gradients. This option is only relevant if DISPLACE=UNIQUE|CART. If AUTO is given, the maximum possible symmetry is used for each displacement. This implies that the energy is independent of the symmetry used. Note that this often not the case in MRCI or CASPT2 calculations. The option can also not be used in local correlation calculations.

AUTO (logical). Same as SYMMETRY=AUTO

ZMAT (logical). Same as COORD=ZMAT

OPT3N (logical). Same as COORD=3N

RSTEP=*rstep* Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.

DSTEP=*dstep* Step length for symmetrical displacements (in bohr). The default is 0.01.

ASTEP=*astep* Step length for angles in numerical gradient calculations (in degree). The default is 1.

CENTRAL (logical). Use 2-point central formula; needs $2M$ energy calculations for M degrees of freedom.

FORWARD (logical). Use forward gradients (needs only $M+1$ energy calculations, but less accurate)

FOURPOINT (logical). Use 4-point formula for accurate numerical gradient; needs $4M$ energy calculations.

NUMERICAL	(logical). Force the use of numerical gradients, even if gradients are available.
VARSAV	(logical). Save gradient in variables GRADX, GRADY, GRADZ.

Example

```
hf
ccsd(t)
forces,numerical
```

The program will then automatically repeat HF and CCSD(T) at as many geometries as needed for evaluating the gradient. This is equivalent to

```
hf
ccsd(t)
forces,numerical,startcmd=hf
```

or, using a procedure

```
forces,numerical,proc=runccsdt
...
runccsdt={
hf
ccsd(t)}
```

38.2.1 Choice of coordinates (COORD)

By default, the numerical gradients are computed relative to all variables on which the z-matrix depends. If the z-matrix depends on no variables or on 3*N* variables, the gradient is computed for all 3*N* coordinates and symmetrical displacement coordinates are used to evaluate the gradient. This yields the minimum computational effort.

These defaults can be modified using the COORD directive:

COORD,*coord_type*,[*displacement_type*]

where *coord_type* can be one of the following:

ZMAT	Compute the numerical gradients for all variables on which the geometry depends (default).
3N or CART	Compute the gradients for all 3*N* nuclear coordinates. This is the default if the z-matrix does not depend on variables or if the xyz input format is used. If this option is used and the original geometry is given in z-matrix form, the z-matrix is lost.

The specification of *displacement_type* is optional and only affects the numerical calculation of the gradient for 3*N* coordinates. It can also be given using

DISPLACE,*displacement_type*

displacement_type can be one of the following:

SYM Use symmetrical displacements. This yields the minimum number of displacements and always preserves the symmetry of the wavefunction. This is the default and only recommended option.

CART Displacements are generated for all 3*N* Cartesian coordinates. This is normally not recommended, since in cases in which molecular symmetry is present it generates far more displacements than needed. Also, the wavefunction symmetry is not preserved, and the calculation must be done in C1 symmetry.

UNIQUE As CART, but symmetry-equivalent displacements are eliminated. Not recommended either.

38.2.2 Numerical derivatives of a variable

Numerical derivatives of the value of a variable can be computed using

VARIABLE,*name*

The default is to compute the gradient of the current energy.

38.2.3 Step-sizes for numerical gradients

By default, the numerical step sizes are 0.01 bohr for distances or Cartesian coordinates, and 1 degree for angles. These defaults can be changed using

RSTEP,*dr*
ASTEP,*da*

where *dr* is the displacement for distances (or Cartesian coordinates) in bohr, and *da* is the displacement for angles in degree. The value of RSTEP is used for symmetrical displacements. The step sizes for individual variables can be modified using

VARSTEP,*varname*=*value*,...

where the *value* must be in atomic units for distances and in degree for angles.

38.2.4 Active and inactive coordinates

By default, numerical gradients are computed with respect to all variables on which the Z-matrix depends, or for all 3*N* coordinates if there are no variables or XYZ inputstyle is used. One can define subsets of active variables using

ACTIVE,*variables*

If this card is present, all variables which are not specified are inactive. Alternatively,

INACTIVE,*variables*

In this case all variables that are not given are active.

38.3 Saving the gradient in a variables

If the directive

VARSAV

is given, the gradient is saved in variables `GRADX`, `GRADY`, `GRADZ`. `GRADX(n)` is the derivative with respect to x for the n-th atom. The atoms are in the order as printed. This order can be different from the order in the input z-matrix, since the centres are reordered so that all atoms of the same type follow each other.

! optgeo.tex *Revision* : 2006.1

39 GEOMETRY OPTIMIZATION (OPTG)

Automatic geometry optimization is invoked using the OPTG command. The OPT command available in previous MOLPRO versions is no longer needed and not available any more.

OPTG[, *key1=value, key2=value,.....*]

The OPTG command can be used to perform automatic geometry optimizations for all kinds of wavefunctions. For minimum searches, it is usually sufficient to give just the OPTG command without further options or directives, but many options are available which are described in the following sections.

Various optimization methods can be selected as described in section 39.2.1. MOLPRO allows minimization (i.e. search for equilibrium geometries), transition state optimization (i.e. search for saddle points on energy surfaces), and reaction path following. The standard algorithms are based on the *rational function* approach and the *geometry DIIS* approach. Also available is the *quadratic steepest descent following* method of Sun and Ruedenberg (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5257 (1993)). This method is often advantageous in Transition State searches. For a detailed discussion of the various minimization algorithms see F. Eckert, P. Pulay and H.-J. Werner, *J. Comp. Chem* **18**, 1473 (1997). Reaction path following is described in F. Eckert and H.-J. Werner, *Theor. Chem. Acc.* **100**, 21, (1998). Please refer to the references section for citations of the analytic gradient methods.

When analytical gradients are available for the optimized energy these will be used. Otherwise the gradient will be computed numerically from finite energy differences. Normally, the last computed ground-state energy is used. But the VARIABLE directive or option can be used to optimize, e.g., Davidson corrected energies, excited states, or counterpoise corrected energies.

39.1 Options

Most parameters can be given as options on the OPTG command line, as described in this section. Alternatively, directives can be used, which will be described in section 39.2.

39.1.1 Options to select the wavefunction and energy to be optimized

By default, the last computed energy is optimized, and all commands on which the last energy calculation depends are automatically executed. For certain purposes, e.g., optimization of counter-poise corrected energies or Davdison corrected energies, the following options can be used to alter the default behaviour.

STARTCMD=*command* Specifies a start command. In each geometry optimization step all input beginning with *command* to the current OPTG is processed. This input must not include numerical gradient or Hessian calculations. If numerical gradients are needed, these will be computed for the final energy (or specified variable) by OPTG. It is assumed that these commands have been executed before entering the OPTG program.

PROC=*procname* specifies a procedure to be executed in each geometry optimization step. This must define a complete energy calculation (orbital optimization and correlation treatment), and must not include numerical

gradient of Hessian calculations (numerical gradients will be computed automatically for the optimized energy or variable). However, the procedure can include the calculation of analytical gradients, for instance for counter-poise corrected optimizations in which a linear combination of several gradient calculations is needed.

VARIABLE=*varname* Optimize the value of variable *varname*. This implies numerical gradients.

39.1.2 Options for optimization methods

METHOD=RF|AH|DIIS|QSD|QSTPATH|SRMIN|SRTRANS|STSTEEP
Optimization method to be used. See section 39.2.1 for details.

ROOT=1|2 Minimum search (1, default) or transition state search (2).

DIRECTION=idir Determines step length and direction in reaction path following, see section 39.2.16.

STEPMAX=*value* Max step length in one optimization step. For more detailed specifications see section 39.2.12.

TRUST=*value* Trust ratio for Augmented Hessian method (default 0.5).

AHMAX=*value* Maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5).

CUT=*value* Threshold for ortho-normalization used in conjugate gradient update of Hessian (default 1.d-3).

ROTATE (logical). If .true., the Cartesian coordinates are transformed to minimize rotations (default=.true.)

39.1.3 Options to modify convergence criteria

The standard MOLPRO convergency criterion requires the maximum component of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] and the maximum energy change to be less than $1 \cdot 10^{-6}$ [H] *or* the maximum component of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] and the maximum component of the step to be less then $3 \cdot 10^{-4}$ [a.u.].

It is also possible to use the convergency criterion of the Gaussian program package. It is somewhat weaker than the MOLPRO criterion and requires the maximum component of the gradient to be less then $4.5 \cdot 10^{-4}$ [a.u.] and the root mean square (RMS) of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] as well as the maximum component of the optimization step to be less then 0.0018 [a.u.] and the RMS of the optimization step to be less then 0.0012 [a.u.].

MAXIT=*maxit* maximum number of optimization cycles. The default is 50.

GRADIENT=*thrgrad* required accuracy of the optimized gradient. The default is $3 \cdot 10^{-4}$.

ENERGY=*threnerg* required accuracy of the optimized energy. The default is $1 \cdot 10^{-6}$.

STEP=*thrstep* convergence threshold for the geometry optimization step. The default is $3 \cdot 10^{-4}$.

BAKER (logical). Use Baker's convergency criteria (see J. Baker, *J. Comp. Chem.* **14**,1085 (1993)).

GAUSSIAN (logical). Use Gaussian convergency criteria.

SRMS=*thrsrms*	sets (for Gaussian convergency criterion) the required accuracy of the RMS of the optimization step. The default is 0.0012.
GRMS=*thrgrms*	sets (for Gaussian convergency criterion) the required accuracy of the RMS of the gradient. The default is $3 \cdot 10^{-4}$.
FREEZE=*thrfreez*	Freeze DFT grid and domains in local calculations if the step length is smaller than *thrfreez* (default 0.01).

Note: The defaults for the convergence parameters can also be changed by using a global GTHRESH directive, i.e.

GTHRESH, OPTSTEP=*step*, OPTGRAD=*grad*, ENERGY=*energy*;

39.1.4 Options to specify the optimization space

If the geometry is given as Z-matrix, the default is to optimize the variables on which the Z-matrix depends. In case of xyz input, always all 3N coordinates are optimized, even if the xyz input depends on fewer variables. If Cartesian z-matrix input is used, optimization in full space is only enforced if automatic orientation is requested using the ORIENT, MASS, or CHARGE options in the geometry block. See *opt_space* in section 39.2.2 for details.

SPACE=ZMAT|3N	Specifies the coordinates to be used in the optimization. Z-matrix optimization is only possible if the geometry is given as Z-matrix.
OPT3N|3N	(logical). Same as SPACE=3N
ZMAT	(logical). Same as SPACE=ZMAT

39.1.5 Options to specify the optimization coordinates

These options specify the coordinates in which the optimization takes place. The default is to use local normal coordinates. See *opt_coord* in section 39.2.2 for details.

COORD=NORMAL|NONORMAL|BMAT

NORMAL	(logical). Same as COORD=NORMAL.
NONORMAL	(logical). Same as COORD=NONORMAL.
BMAT	(logical). Same as COORD=BMAT.

39.1.6 Options for numerical gradients

Numerical gradients can be computed with respect to variables on which the Z-matrix depends or with respect to Cartesian coordinates. In the latter case, it is most efficient to use symmetrical displacement coordinates. These do not change the symmetry of the molecule and the number of displacements is minimal. Alternatively (mainly for testing purpose) the gradients can be computed using symmetry unique Cartesian displacements or all 3N Cartesian displacements. In these cases the symmetry of the molecule can be reduced by the displacements and using such displacements is normally not recommended.

DISPLACE=ZMAT|SYMM|UNIQUE|CART
: Displacement coordinates to be used for numerical gradient. The default is ZMAT if the geometry is given as a zmatrix which depends on variables, and SYMM (symmetrical displacement coordinates) otherwise. The use of UNIQUE or CART is not recommended.

SYMMETRY=AUTO|NOSYM
: Symmetry to be used in wavefunction calculations of numerical gradients. This option is only relevant if DISPLACE=UNIQUE|CART. If AUTO is given, the maximum possible symmetry is used for each displacement. This implies that the energy is independent of the symmetry used. Note that this often not the case in MRCI or CASPT2 calculations. The option can also not be used in local correlation calculations.

AUTO
: (logical). Same as SYMMETRY=AUTO

NOSYM
: (logical). Same as SYMMETRY=NOSYM

RSTEP=*rstep*
: Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.

DSTEP=*dstep*
: Step length for symmetrical displacements (in bohr). The default is 0.01.

ASTEP=*astep*
: Step length for angles in numerical gradient calculations (in degree). The default is 1.

FOURPOINT
: (logical). Use 4-point formula for accurate numerical gradient.

NUMERICAL
: (logical). Force the use of numerical gradients, even if gradients are available.

39.1.7 Options for computing Hessians

By default, an approximate Hessian (model Hessian) is used. Optionally, a Hessian can be computed in the optimization or read from a previous Hessian or frequency calculation.

NUMHESS=*hstep*
: If given, a numerical Hessian is computed in each *hstep'th* iteration. If *hstep=0* or not given, only an initial Hessian is computed.

HESSREC=*record*
: Read initial Hessian from the given record. If *record* is not given or zero, the last computed Hessian is used.

READHESS
: (logical). Same as HESSREC=0.

HESSPROC=*procname*
: specifies a procedure to be used for computing the Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy. For instance, an MP2 Hessian can be used for CCSD(T) optimizations, or a CASPT2 Hessian for MRCI optimizations. By default, the same procedure is used for the Hessian as for the optimized energy.

HESSVAR=*varname*
: Compute Hessian for variable *varname*. This implies numerical calculation of the Hessian from energies. The default is to use the same variable as for the energy and gradient.

HESSCENT
: Use central gradient differences for computing Hessian (only effective if gradients are available)

HESSFORW — Use forward gradient differences for computing Hessian (only effective if gradients are available). This effectively computes the Hessian at a slightly displaced geometry, but needs only half the number of displacements. This is the default.

UPDATE=BFGS|IBFGS|CGRD|PMS|POWELL|MS|NONE — Hessian update method to be used. See section 39.2.9 for details.

MAXUPD=*maxupd* — Max number of Hessian updates. The count is reset to zero each time a Hessian is computed.

39.1.8 Miscellaneous options:

VARSAVE — Save Cartesian gradients in variables GRADX, GRADY, GRADZ.

NONUC — Do not compute gradients at lattice points.

DEBUG — Set debug print options.

PRINT=*iprint* — Print option for optimization.

SAVEXYZ=*file* — Save optimized coordinates in an xyz-file. In case of reaction path following, one file is written for each step.

SAVEACT=*file* — Save optimized variables in given file. In case of reaction path following, the variables are saved in each step. The file can be read later using the READVAR command.

SAVEGRD=*file* — In case of reaction path following, write in each step the Cartesian coordinates and gradients to the given file.

APPEND — (logical). If given, existing SAVEACT and/or SAVEGRD files are appended.

39.2 Directives for OPTG

An alternative way to specify options is to use directives, as described in this section. In some cases this allows more detailed specifications than with the options on the OPTG command. In particular, directives ACTIVE or INACTICE can be used to define the optimization space in more detail.

39.2.1 Selecting the optimization method (METHOD)

METHOD,*key*;

key defines the optimization method.

For *minimization* the following options are valid for *key*:

RF — Rational Function method (default).

AH — Augmented Hessian method. This is similar to RF algorithm but uses a more sophisticated step restriction algorithm.

DIIS — Pulay's Geometry DIIS method. As an an additional option you may add the number of geometries to be used in GDIIS interpolation (default 5) and the interpolation type (i.e. the subspace in which the GDIIS interpolation is made.

	METHOD,DIIS, *number*, *type* *type* may be GRAD interpolation using the gradients (default), working good for rigid molecules, STEP interpolation using Quasi-Newton steps which could be advantageous in dealing with very floppy molecules, ENER interpolation using energies, which is an intermediate between the above two.
QSD	Quadratic steepest descent method of Sun and Ruedenberg.
SRMIN	Old version of QSD.

For *transition state* searches (invoked with the ROOT option, see section 39.2.11) *key* can be

RF	Rational Function method (default).
DIIS	Pulay's Geometry DIIS method (see above).
QSD	Quadratic Steepest Descent Transition State search using the image Hessian method (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **101**, 2157 (1994)) The use of this option is recommended for transition state searches – especially in complicated cases. The optimization step is checked and the Hessian is recalculated when approaching a troublesome region of the PES. Thus **this method is somewhat safer (and often faster) in reaching convergence than the RF or DIIS method**. The Hessian recalculation safeguard may be turned off using the METHOD,QSD,NOHESS input card.
SRTRANS	Old version of QSD.

For *reaction path following* the input *key* is

QSDPATH	Quadratic Steepest Descent reaction path following. This methods determines reaction paths (intrinsic reaction coordinates, IRCs) by following the exact steepest descent lines of subsequent quadratic approximations to the potential energy surface. The Hessian matrix is calculated numerically at the first optimization step and subsequently updated by Powell or BFGS update. If a given arc length of the steepest descent lines is exceeded, the Hessian is recalculated numerically (see OPTION section 39.2.16). For details see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5269 (1993) It is also possible to recalculate the Hessian after each *m* steps using the NUMHES,*m* command (see section 39.2.7). If the Hessian matrix is recalculated in every optimization step (NUMHES,1) a algorithm different to the one with updated Hessians is used, which is very accurate. Using the PRINT,OPT card, this algorithm prints in every optimization step a *reaction path point r* which is different from the point where the energy and the gradient is calculated but closer to the real reaction path (for further details of the algorithm see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5257 (1993)). For further input options of the QSD reaction path following see OPTION section 39.2.16.
SRSTEEP	Old Version of QSDPATH.

39.2.2 Optimization coordinates (COORD)

It is possible to use various coordinate types and algorithms for the optimization. This can be controlled by additional subcommands as described in this and the following subsections.

COORD,[*opt_space*],[*opt_coord*],[NOROT]

These options choose the optimization space and the coordinate system in which the optimization takes place.

opt_space defines the parameters to be optimized. By default, if the geometry input is given in Z-matrix format, all variables on which the Z-matrix depends are optimized. Subsets of the variables on which the Z-matrix depends can be chosen using the ACTIVE or INACTIVE subdirectives. If the Z-matrix depends on no variables or xyz input is used, all 3*N* cartesian coordinates are optimized.

opt_space can be one of the following:

ZMAT	Optimize all variables on which the Z-matrix depends (default if the geometry is given as Z-matrix).
3N	Optimize all 3*N* cartesian coordinates (default if the Z-matrix depends on no variables, or if xyz-input is used). Z-Matrix input coordinates will be destroyed if 3N is used..

opt_coord determines the coordinates in which the optimization takes place. By default, local normal coordinates are used. Optionally cartesian coordinates or natural internal coordinates can be used.

opt_coord can be one of the following:

NORMAL	Optimization in local normal coordinates. This is default if the Model Hessian is used to approximate the Hessian.
NONORM	Don't use local normal coordinates.
BMAT[=*filename*]	Use Pulay's *natural internal coordinates*, see G. Fogarasi, X. Zhou, P. W. Taylor and P. Pulay *J. Am. Chem. Soc.* **114**, 8191 (1992); P. Pulay, G. Fogarasi, F. Pang, J. E. Boggs *J. Am. Chem. Soc.* **101**, 2550 (1979)). Optionally, the created coordinates as well as additional informations about this optimization are written to the specified file. These coordinates resemble in part the valence coordinates used by vibrational spectroscopist, and have the advantage of decreasing coupling between different modes. This often increases the speed of convergence. The use of this option is highly recommended, especially in minimization of large organic molecules with rings. Nevertheless you should keep in mind that these coordinates are constructed automatically, and there exist exotic bond structures which might not be treated properly (e.g. weakly bonded species as in transition state optimizations). In such a case, if the BMAT optimization converges slowly or leads to symmetry-breaking errors, you should try another optimization method and/or cartesian or Z-Matrix coordinates.

If the option [NOROT] is given, the cartesian coordinates are not transformed to minimize rotations.

39.2.3 Displacement coordinates (DISPLACE)

DISPLACE,*displacement_type*

see section 38.2.1 for details.

39.2.4 Defining active geometry parameters (ACTIVE)

ACTIVE,*param*;

Declares variable name *param* to be active in the optimization. By default, initially all variables on which the geometry depends are active; inclusion of an ACTIVE card makes all parameters inactive unless explicitly declared active (see also INACTIVE).

39.2.5 Defining inactive geometry parameters (INACTIVE)

INACTIVE,*param*;

Declares variable name *param* to be inactive in the optimization. If any ACTIVE card appears in the input, this card is ignored! (see also ACTIVE)

39.2.6 Hessian approximations (HESSIAN)

By default, the MOLPRO geometry optimization utilizes a force field approximation to the hessian ("Model Hessian", see R. Lindh, A. Bernhardsson, G. Karlström and P. Malmqvist *Chem. Phys. Lett.* **241**, 423 (1995)), which speeds up convergence significantly. The Model Hessian is parameterized for the elements up to the third row. Alternatively, the model Hessian of Schlegel can be used, or the Hessian can be computed numerically (see also section 39.2.7).

HESSIAN,*options*

where *options* can be

MODEL	Use Lindh's Model Hessian in optimization (default).
MODEL=SCHLEGEL	Use Schlegel's Model Hessian.
MODEL=VDW	Add vdW terms to Lindh's Model Hessian.
SCHLEGEL	same as MODEL=SCHLEGEL.
VDW	same as MODEL=VDW.
NOMODEL	Don't use Model Hessian approximation to the hessian.
NUMERICAL=*hstep*	Recompute Hessian after *hstep* iterations. This disables the use of a model hessian. If *hstep*=0, the Hessian is only computed in the first iteration. Default parameters are used for computing the numerical Hessian, unless modified using options as described for the NUMHESS directive, see Sect. 39.2.7. Any option valid for the NUMHESS directive may also follow the NUMERICAL option on the HESSIAN directive.
READ|RECORD|HESSREC=*record*	Read Hessian from given *record*. If *record* is not given or zero, the last computed hessian will be read. See section 39.2.7 for more details about numerical Hessians.

UPDATE=*type*	Method used for hessian update. See section 39.2.9 for possibilities and details.
MAXUPD=*maxupd*	Max number of hessian updates. The count is reset to zero each time a hessian is computed.

If the Model Hessian is disabled (NOMODEL) and no Hessian is read or computed, the initial hessian is assumed to be diagonal, with values 1 hartree*bohr**(-2) for all lengths, 1 hartree*radian**(-2) for all angles. Additional matrix elements of the hessian can be defined using the HESSELEM directive, see section 39.2.8.

In transition state searches the Hessian is evaluated numerically in the first iteration by default. Alternatively, if READ is specified, a previously computed hessian is used.

39.2.7 Numerical Hessian (NUMHESS)

NUMHESS,*options*

or

NUMHESS,*hstep,options*

If this directive is present a numerical Hessian is computed using finite differences. If analytical gradients are available, one can use forward gradient differences (needs one gradient calculation for each coordinate) or central differences (more accurate, needs two gradient calculations for each coordinate). For transition state optimizations it is usually sufficient to use forward differences. If analytical gradients are not available for the optimized method, the energy is differentiated twice. In this case only central differences are possible.

The following options can be given:

HSTEP=*hstep*	*hstep*=-1: Don't calculate numerical hessian (default for minimization); *hstep*=0 Calculate numerical hessian only once at the start of the optimization (default for transition state searches). *hstep*=*n* Calculate numerical hessian after each *n* optimization steps. This is useful for difficult transition state optimizations (e.g. if the eigenvalue structure of the hessian changes during the optimization).
FORWARD	Use forward differences (default).
CENTRAL	Use the more accurate central differences.
RSTEP=*rstep*	Step length for distances (in bohr). The default is 0.01.
ASTEP=*astep*	Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.
DSTEP=*dstep*	Step length for symmetrical displacements (in bohr). The default is 0.01.
VARIABLE=*varname*	Use given variable for numerical calculation of the Hessian. Note that this disables the use of gradients, and Hessian evaluation can be very expensive.
PROCEDURE=*procname*	Procedure to be used for computing Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy. For instance, an MP2 hessian can be used for CCSD(T)

optimizations, or a CASPT2 hessian for MRCI optimizations. By default, the same procedure is used for the hessian as for the optimized energy.

DISPLACE=*type* *type* can be one of the following:

SYMM	Use symmetric displacement coordinates (default). This is the only recommended option.
CART	Use $3N$ cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry.
UNIQUE	Use symmetry-unique cartesian displacements (not recommended)

Note that the displacement type for gradient and hessian must be the same.

CALC=*icalc* *icalc*=0: Recalculate the complete Hessian matrix numerically after each *hstep* optimization steps (default).
icalc=1: Recalculate selected Hessian matrix elements if the relative deviation of this element before and after update (see UPDATE, section 39.2.9) is larger than *thresh*. If *thresh* is not specified, a default value of $thresh = 0.05$ (i.e. a maximum deviation of 5%) is used.
icalc=2: Recalculate complete Hessian matrix if the RMS deviation of the Hessian matrix before and after update is larger than *thresh*. If *thresh* is not specified a default value of

THRESH=*thresh* Threshold for partial or dynamical update of hessian, see above

39.2.8 Hessian elements (HESSELEM)

HESSELEM,*value*, *active1*,*active2*,...

sets the starting value for hessian matrix element between active variables *active1*, *active2* to *value*. If *active2* is omitted it defaults to *active1* (diagonal element). As many HESSELEM directives as needed may be given.

39.2.9 Hessian update (UPDATE)

UPDATE,[TYPE=]*type*,MAX=*maxupd*

This directive chooses the update type and limits the number of points used for the hessian update to *maxupd*. The default number of steps used in hessian update procedures is 5. If there are symmetry constraint in the coordinates of the optimization, the default number may be lower than five.

In minimizations *type* may be

BFGS	Use BFGS update of hessian (default).
IBFGS	Use BFGS update of the inverse hessian.
CGRD	Use Conjugate Gradient update (see also CUT,TRUST).
NONE	Don't do any update.

In transition state optimizations *type* may be

PMS	Combined Powell/Murtagh-Sargent update of hessian (default).
POWELL	Use Powell's update of the hessian.
MS	Use update procedure of Murtagh and Sargent.
NONE	Don't do any update.

39.2.10 Numerical gradients (NUMERICAL)

NUMERICAL,*options*,$active_1$=$step_1$, $active_2$=$step_2$ ... ;

With this directive the gradients are computed by finite differences. $step_i$ is the increment for the active geometry parameter $active_i$. For active parameters which are not specified, the default values are used. By default, the increment is 0.01 bohr for bond distances and 0.5 or 1 degree for angles less than or greater than 90 degrees, respectively. These defaults can be modified by specifying RSTEP or ASTEP. DSTEP is the length of symmetrical displacements, which are used if the optimization is performed in 3N coordinates.

For each active variable, two energy calculations are necessary in each geometry optimization step – so numerical optimizations may be expensive! In optimizations of 3N coordinates symmetrical displacement coordinates are normally used to minimize the number of energy calculations. (see section 38.2.1).

For optimization of special energies see VARIABLE section 39.2.17.

The following options can be given:

RSTEP=*rstep*	Step length for distances (in bohr). The default is 0.01.
ASTEP=*astep*	Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.
DSTEP=*dstep*	Step length for symmetrical displacements (in bohr). The default is 0.01.
CENTRAL	Use central differences for gradient (default)
FORWARD	Use forward differences (not recommended for gradient).
FOURPOINT	Use four-point formula for very accurate numerical gradients.
PROCEDURE=*procname*	Use given procedure for numerical calculation of the gradient. This procedure must define a complete energy calculation (orbital optimization and correlation treatment).
VARIABLE=*varname*	Use given variable for numerical calculation of the gradient.
DISPLACE=*type*	The displacement type. Note that the displacement type for gradient and hessian must be the same. *type* can be one of the following:

SYMM	Use symmetric displacement coordinates (default). This is the only recommended option.
CART	Use 3*N* cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry.
UNIQUE	Use symmetry-unique cartesian displacements (not recommended)

39.2.11 Transition state (saddle point) optimization (ROOT)

ROOT,*root*

Specifies the eigenvector of the hessian to be followed.

root=1	specifies a minimization (default).
root=2	specifies a transition state (saddle point) optimization.

In the present implementation a saddle point search is possible with the rational function method (METHOD,RF), the geometry DIIS method (METHOD,DIIS) and the quadratic steepest descent method of Sun and Ruedenberg (METHOD,SRTRANS).

Note that convergence is usually much more difficult to achieve than for minimizations. In particular, a good starting geometry and a good approximation to the hessian is needed. The latter is achieved by evaluating the hessian numerically (see section 39.2.7) or using a precomputed hessian (see section 39.2.6).

39.2.12 Setting a maximum step size (STEP)

STEP,*steplength*,*drmax*,*damax*,*drmax1*,*damax1*

steplength is the initial step length in the scaled parameter space (default 0.3). In the AH-method this is dynamically adjusted, and can have a maximum value *ahmax* (see TRUST).

drmax is the initial max change of distances (in bohr, default 0.3). In the AH-method this is dynamically adjusted up to a maximum value of *drmax1* (default 0.5 bohr).

damax is the initial max change of angles (in degree, default 2). In the AH-method this is dynamically adjusted up to a maximum value of *damax1* (default 10 degrees).

39.2.13 Redefining the trust ratio (TRUST)

TRUST,*ratio*,*ahmax*

ratio determines the radius around the current minimum in which points are used to update the Hessian with the conjugate gradient method (default 0.5; see also UPDATE).

ahmax is the maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5). The initial step size is *stepmx* (see STEP card).

39.2.14 Setting a cut parameter (CUT)

CUT,*threshold*

Specifies a threshold for ortho-normalization used in conjugate gradient update of hessian (default 1.d-3; see also UPDATE).

39.2.15 Line searching (LINESEARCH)

LINESEARCH,*iflag*,*thrlmin*,*thrlmax*

Interpolate the geometry of the stationary point (minimum or saddle point) by a quartic polynomial between the current and the previous geometry. If *iflag*=0 or no *iflag* is set, the next optimization step will be taken from the interpolated geometry using the interpolated energy and gradient. If *iflag*=1 the energy and gradient will be recalculated at the interpolated geometry before taking the new optimization step. Note though, that the additional effort of recalculating the energy and gradient is usually not met by the increase of the convergence rate of the optimization. *thrlmin* and *thrlmax* are min and max thresholds for the recalculation of the energy and the gradient in case *iflag*=1. I.e. the recalculation just takes place if the interpolated geometry isn't too close to the actual geometry *thrlmin* and isn't too remote from the actual geometry *thrlmax*. Default values are *thrlmin*=0.001 and *thrlmax*=0.05 in the scaled parameter space of the optimization.

39.2.16 Reaction path following options (OPTION)

OPTION,*key*=*param*;

where *key* can be

IDIR	If starting at a transition state (or near a transition state) determine where to take the first step. If IDIR=0 is chosen, the first step will be towards the transition state. This is the default. If IDIR=1 is given in the input the first optimization step will be along the "transition vector" i.e. the hessian eigenvector to the smallest eigenvalue which points down towards the minimum. If using a larger IDIR parameter, the first step will be larger; if using a negative value, the first step will be in the opposite direction.
STPTOL	If using an updated hessian matrix, this parameter determines what update to take. If the step size between two subsequent points on which the steepest decent lines are puzzled together is smaller than *stptol* (i.e. if we are close to a minimum) the BFGS update is used, otherwise it is Powell update. The default value of *stptol* is $1.d-6$.
SLMAX	This option is only valid with the old version of the reaction path following algorithm (i.e. METHOD,SRSTEEP). In this algorithm slmax determines the frequency of the recalculation of the numerical hessian. If the total step size of the last steps exceeds *slmax* the hessian will be recalculated, otherwise it will be updated. By default *slmax* is two times the maximum step size of the optimization step *steplength* (see STEP section 39.2.12). If you are using METHOD,QSD, the SLMAX option is obsolete and the NUMHES command (see above) should be used instead.

39.2.17 Optimizing energy variables (VARIABLE)

VARIABLE,*name*;

Defines a variable *name* which holds the energy value to be optimized in using finite differences. By default, this is ENERGY(1) as set by the most recent program. Other variables which can be used are

ENERGY(*i*)	holds last energy for state *i*.
ENERGR(*i*)	holds last reference energy for state *i*.
ENERGD(*i*)	holds last Davidson corrected energy for state *i*.
ENERGP(*i*)	holds last Pople corrected energy for state *i*.
ENERGC	holds CCSD (QCI, BCCD) energy in CCSD(T) [QCI(T), BCCD(T)] calculations (single state optimization).
ENERGT(1)	holds CCSD(T) energy in CCSD(T) calculations (single state)
ENERGT(2)	holds CCSD[T] energy in CCSD(T) calculations (single state).
ENERGT(3)	holds CCSD-T energy in CCSD(T) calculations (single state).

These variables are set automatically by the CI and/or CCSD programs. It is the user's responsibility to use the correct variable name; an error exit occurs if the specified variable has not been defined by the last program or the user.

Note: The use of the VARIABLE option triggers NUMERICAL, so optimization can be very inefficient!

39.2.18 Printing options (PRINT)

PRINT,*code*=*level*,...;

Enables printing options. Usually level should be omitted or 0; values of $level > 0$ produce output useful only for debugging. *code* can be

HESSIAN	prints the updated hessian matrix. Note that its diagonal elements are printed anyway.
HISTORY	prints the complete set of previous geometries, gradients and energies.
GRADIENT	prints extended gradient information
OPT	prints detailed information about the optimization process (mainly for debugging).

Several print options can be specified with one PRINT command.

39.2.19 Conical Intersection optimization (CONICAL)

To optimize a conical intersection between two electronic states having the same spin, three vectors must be evaluated at SA-CPMCSCF level:

1) Non-Adiabatic Derivative Coupling (DC).

2) Gradient of the lower state (LSG).

3) Gradient of the upper state (USG).

This requires three different CPMCSCF directives in the MULTI input:

CPMCSCF, NACM, S_i, S_j, ACCU=*1.0d-7*, record=*record1.file*
CPMCSCF, GRAD, S_i, SPIN=*Spin of state* S_i, ACCU=*1.0d-7*, record=*record2.file*
CPMCSCF, GRAD, S_j, SPIN=*Spin of state* S_j, ACCU=*1.0d-7*, record=*record3.file*

where S_i,S_j are the electronic states in the usual format *istate.istsym*, and *record[n].file* specifies the name and the file number where CPMCSCF solutions should be stored. Parameter SPIN is half of the value in the WF card used to define the electronic state.

Things to remember:

i) Specify always three different *record.file* on the CPMCSCF directives.

ii) Evaluate the CPMCSCF for USG always last.

iii) Skip the DC evaluation if the conical intersection involves states with different spin (e.g., a Singlet/Triplet crossing) because the coupling is then zero.

Three sets of FORCE commands (only two for Singlet/Triplet intersection) follow the MULTI input. They will be like:

FORCE
SAMC,*record[n].file*
CONICAL,*record4.file*[,NODC]

where *record.file* is one of the records containing CPMCSCF info and *record4.file* points to a free record used for internal storage by the CONICAL code. *record4.file* must be the same on all the CONICAL directives. Furthermore, the present implementation works properly only if *file=1* on the CONICAL directive. The optional keyword NODC must be used in case of different spins (e.g., S/T crossing) when DC is not needed.

The actual optimization is performed using OPTG,STARTCMD=MULTI The example below optimizes the conical intersection in LiH_2 (ground and excited states are both doublets).

```
!examples/lih2_D0D1.com $Revision: 2002.10 $
***, LiH2

basis=sto-3g
print,orbitals,civector

geometry={x            !use only molecular plane. Both states must be in the same symmetry.
          Li;
          h1,Li,r;
          h2,Li,r,h1,theta}

r=3.0
theta=35

{hf;wf,4,1,0}

{multi;occ,6,1;wf,5,1,1;state,2                       !state averaged casscf
CPMCSCF,NACM,1.1,2.1,accu=1.0d-7,record=5100.1        !cpmcscf for non-adiabatic coupling
CPMCSCF,GRAD,1.1,spin=0.5,accu=1.0d-7,record=5101.1   !gradient for state 1
CPMCSCF,GRAD,2.1,spin=0.5,accu=1.0d-7,record=5102.1}  !gradient for state 2

{Force
SAMC,5100.1             !compute coupling matrix element
CONICAL,6100.1}         !save information for optimization of conical intersection

{Force
SAMC,5101.1             !compute gradient for state 1
CONICAL,6100.1}         !save information for optimization of conical intersection

{Force
SAMC,5102.1             !compute gradient for state 2
CONICAL,6100.1}         !save information for optimization of conical intersection

optg,startcmd=multi     !find conical intersection
```

examples/lih2˙D0D1.com

This second example optimizes the singlet-triplet intersection in $LiH_2(+)$ (ground state is Singlet, excited state is Triplet).

examples/lih2+_S0T0.com

```
!examples/lih2+_S0T0.com $Revision: 2002.10 $
***, LiH2

basis=sto-3g

geometry={nosym
          Li;
          H1,Li,r;
          H2,Li,r,H1,theta}

r=3.7
theta=160

{hf;wf,4,1,0}

{multi;
 occ,7;
 wf,4,1,0;   !singlet state
 wf,4,1,2;   !triplet state
 CPMCSCF,GRAD,1.1,spin=0,accu=1.0d-7,record=5101.1   !cpmcscf for gradient of singlet state
 CPMCSCF,GRAD,1.1,spin=1,accu=1.0d-7,record=5100.1   !cpmcscf for gradient of triplet state
}

{Force
 SAMC,5101.1                !state averaged gradient for singlet state
 CONICAL,6100.1,NODC}       !save information for OPTCONICAL

{Force
 SAMC,5100.1                !state averaged gradient for triplet state
 CONICAL,6100.1,NODC}       !save information for OPTCONICAL

optg,startcmd=multi,gradient=1.d-6  !find singlet-triplet crossing point
```

39.3 Using the SLAPAF program for geometry optimization

It is optionally possible to use the SLAPAF program written by Roland Lindh for geometry optimizations. This is done by prepending the optimization method with 'SL'. The following methods are supported:

SLRF	Use the rational function approximation;
SLNR	Use the Newton-Raphson method;
SLC1	Use the C1-DIIS method;
SLC2	Use the C2-DIIS method.

When using DIIS methods (SLC1 or SLC2), the DIIS parameters are specified in the same way as in standard molpro optimizer.

There are some differences when using the SLAPAF program:

1) It is not possible to use Z-matrix coordinates in the optimization.

2) Instead, one can explicitly define internal coordinates to be varied or fixed.

3) Additional constraints can be imposed on the converged geometry in a flexible way.

39.3.1 Defining constraints

Constraints and internal coordinates (see below) can be linear combinations of bonds, angles etc. The latter, called here primitive internal coordinates, can be specified before the constraints definition, or directly inside. The general definition of a primitive coordinate is:

PRIMITIVE,[NAME=]*symbolic name*, *explicit definition;*

Here *symbolic name* is the name given to the primitive coordinate (if omitted, it will be generated automatically). This name is needed for further reference of this primitive coordinate.

explicit definition has the form:

type,atoms

type can be one of the following:

BOND	Bond length, defined by 2 atoms.
ANGLE	Bond angle, defined by 3 atoms (angle 1–2–3).
DIHEDRAL	Dihedral angle, defined by 4 atoms (angle between the planes formed by atoms 1,2,3 and 2,3,4, respectively).
OUTOFPLANE	Out-of-plane angle, defined by 4 atoms (angle between the plane formed by atoms 2,3,4 and the bond 1–4).
DISSOC	A dissociation coordinate, defined by two groups of atoms.
CARTESIAN	Cartesian coordinates of an atom.

For all types except DISSOC and CARTESIAN, atoms are given as:

ATOMS=[*a1,a2,a3,...*]

where the number of atoms required varies with *type* as specified above, and the atomic names *a1,a2,a3,...* can be either atomic tag names from the Z-matrix input, or integers corresponding to Z-matrix rows. Note that the square brackets are required here and do not indicate optional input.

For DISSOC the specification is as follows:

DISSOC,GROUP1=[*a1,a2,...*],GROUP2=[*b1,b2,...*];

The corresponding internal coordinate is the distance between the centres of mass of the two groups.

For CARTESIAN the definition is

CARTESIAN, *I, atom;*

where *I* can be one of X,Y,Z or 1,2,3 and *atom* can be a z-matrix atom name or an integer referring to the z-matrix row.

With this definition, the constraints are defined as

CONSTRAINT,[VALUE=]*value*,[*unit*],[[FACTOR=]*fac*,*prim*,[[FACTOR=]*fac*],*prim,...;*

where *value* is the value imposed to the constraint, and *prim* is either the name of the primitive defined before this constraint, or an explicit definition; and *fac* is a factor of the corresponding primitive in the constraint. If *fac* is omitted it is taken to be 1.

If *value* is specified in Angstrom or Radian, *unit* must be given.

Examples for H_2O in C_s symmetry:

Constraining the bond angle to 100 degrees:

```
constraint,100,deg,angle,atoms=[h1,o,h2];
```

which is equivalent to

```
primitive,a1,angle,atoms=[h1,o,h2];
constraint,100,a1;
```

Keeping the two OH distances equal:

```
constraint,0,bond,atoms=[h1,o],-1.,bond,atoms=[h2,o];
```

which is equivalent to

```
primitive,b1,bond,atoms=[h1,o];
primitive,b2,bond,atoms=[h2,o];
constraint,0,b1,-1.,b2;
```

39.3.2 Defining internal coordinates

By default SLAPAF optimizes in force-constant weighted normal coordinates that are determined automatically. However, the user can define his own coordinates. The definition of internal coordinates, similar to constraints, is based on primitive coordinates. The input is:

INTERNAL,[[NAME=]*name*],[[FACTOR=]*fac*],*prim*,[[FACTOR=]*fac*],*prim,...;*

FIX, [[NAME=]*name*],[[FACTOR=]*fac*],*prim*,[[FACTOR=]*fac*],*prim,...;*

Internal coordinates that are specified using INTERNAL are varied and those using FIX are fixed to their initial values.

An important point for the definition of internal coordinates is that their total number must be equal to the number of degrees of freedom of the molecule . Otherwise an error message is generated. Only symmetry independent coordinates need to be given.

39.3.3 Additional options for SLAPAF

Some options can be passed to the SLAPAF program. Options are specified with SLOPT subdirective:

{opt;method=slnr;{slopt;opt1;opt2,*par1,par2*;opt3;...}}

The available options are

CART	Use eigenvectors of the approximate Hessian, expressed in cartesian coordinates, as the definition of internal coordinates;
NOMA	Don't impose any restrictions on the step size;
UORD	Order the gradients and displacement vectors according to Schlegel prior to the update of the Hessian. Default is no reordering;
HWRS	Use force field weighted internal coordinates (default);
RS-P	Activate RS-P-RFO as default for transition state search; default is RS-I-RFO;

NOHW	Use unweighted internal coordinates;
PRBM	Print B-matrix;
RTHR, *Thra,Thrb,Thrt*	Thresholds for redundant coordinate selection for bonds, bends and torsions, respectively. Default 0.2, 0.2, 0.2
MODE, *index*	Hessian vector index for mode following when calculating transition states.
FIND	Enable unconstrained optimization for constrained cases, when looking for transition states (see MOLCAS manual).
GNRM, *thr*	Threshold for FIND, default 0.2 (see MOLCAS manual).
MEP-	Perform minimum energy path (MEP) search.
NMEP, *npoints*	Number of MEP points to find in MEP calculation.

For more information, please consult the MOLCAS manual.

39.4 Examples

39.4.1 Simple HF optimization using Z-matrix

examples/allene˙optscf.com

```
!examples/allene_optscf.com $Revision: 2002.10 $
 ***, Allene geometry optimization using Z-Matrix
 memory,1,m
 basis=sto-3g

 rcc=1.32 ang
 rch=1.08 ang
 acc=120  degree
 Geometry={C1                        !Z-matrix input
           C2,c1,rcc
           Q1,c1,rcc,c2,45
           C3,c2,rcc,c1,180,q1,0
           h1,c1,rch,c2,acc,q1,0
           h2,c1,rch,c2,acc,h1,180
           h3,c3,rch,c2,acc,h1,90
           h4,c3,rch,c2,acc,h2,90}
 hf
 optg,saveact=allene.dat,savexyz=allene.xyz    !default optimization using model hessian.
                                               !Save optimized variables in file allene.dat
                                               !Save optimized geometry in xyz style in in fil
```

39.4.2 Optimization using natural internal coordinates (BMAT)

```
!examples/allene_opt_bmat.com $Revision: 2002.10 $
 ***, Allene geometry optimization using natural internal coordinates
 memory,1,m
 basis=sto-3g

 rcc=1.32 ang
 rch=1.08 ang
 acc=120  degree
 Geometry={nosym;
           C1;                        !Z-matrix input
           C2,c1,rcc
           Q1,c1,rcc,c2,45
           C3,c2,rcc,c1,180,q1,0
           h1,c1,rch,c2,acc,q1,0
           h2,c1,rch,c2,acc,h1,180
           h3,c3,rch,c2,acc,h1,90
           h4,c3,rch,c2,acc,h2,90}
 hf;
 optg                !default optimization using model hessian
 coord,bmat          !use natural internal coordinates

 optg,coord=bmat     !same as above
```

examples/allene˙opt˙bmat.com

39.4.3 MP2 optimization using a procedure

```
!examples/allene_optmp2.com $Revision: 2002.10 $
 ***, Allene geometry optimization using Z-Matrix
 memory,2,m
 basis=vdz

 rcc=1.32 ang
 rch=1.08 ang
 acc=120  degree
 Geometry={C1                       !Z-matrix input
           C2,c1,rcc
           Q1,c1,rcc,c2,45
           C3,c2,rcc,c1,180,q1,0
           h1,c1,rch,c2,acc,q1,0
           h2,c1,rch,c2,acc,h1,180
           h3,c3,rch,c2,acc,h1,90
           h4,c3,rch,c2,acc,h2,90}

optg,procedure=runmp2     !use procedure optmp2

runmp2={hf;mp2}         !procedure definition
```

examples/allene˙optmp2.com

39.4.4 Optimization using geometry DIIS

examples/caffeine_opt_diis.com

```
!examples/caffeine_opt_diis.com $Revision: 2002.10 $
 ***, CAFFEINE cartesian coordinates (XYZ format)
 memory,1,m
 basis=sto-3g
 geomtyp=xyz
 geometry={
 24
            CAFFEINE CARTESIAN COORDINATES
 C           0.8423320060       -0.3654865620        0.0000000000
 C          -0.2841017540       -1.1961236000        0.0000000000
 N           2.0294818880       -1.1042264700        0.0000000000
 N           0.0774743850       -2.5357317920        0.0000000000
 N          -1.6472646000       -0.6177952290        0.0000000000
 C           1.4531962870       -2.3678913120        0.0000000000
 C           0.6373131870        1.1735112670        0.0000000000
 C          -1.7812691930        0.7688916330        0.0000000000
 N          -0.6771444680        1.6306355000        0.0000000000
 O           1.6106752160        1.9349693060        0.0000000000
 O          -2.9202890400        1.2510058880        0.0000000000
 C          -0.9202462430        3.1094501020        0.0000000000
 C          -2.8623938560       -1.4824503660        0.0000000000
 C           3.4552156930       -0.6811094280        0.0000000000
 H           2.0878150460       -3.2451913360        0.0000000000
 H          -1.4989252090        3.4222116470       -0.8897886280
 H          -1.4989252090        3.4222116470        0.8897886280
 H           0.0071905670        3.7148499490        0.0000000000
 H          -3.4903070930       -1.2888938190       -0.8907763360
 H          -3.4903070930       -1.2888938190        0.8907763360
 H          -2.6289534570       -2.5638654230        0.0000000000
 H           4.1360211370       -1.5529079440        0.0000000000
 H           3.6817059520       -0.0685850980        0.8931597470
 H           3.6817059520       -0.0685850980       -0.8931597470
 }

 hf
 optg,savexyz=caffeine.xyz   !save optimized geometry in file caffeine.xyz
 coord,bmat                  !Optimization in natural internal coordinates
 method,diis                 !Optimization method: Geometry DIIS

 optg,coord=bmat,method=diis,savexyz=caffeine.xyz   !same as above
```

39.4.5 Transition state of the HCN – HNC isomerization

The first example shows how to do a MP2 transition state optimization. The initial Hessian is taken from a previous HF frequency calculation.

```
!examples/hcn_mp2_ts.com $Revision: 2002.10 $
***, HCN <--> NHC Isomerization - Transition State Optimization and Frequencies

l1=1.18268242 ang
l2=1.40745082 ang
a1=55.05153416 degree

basis=3-21G

geometry={nosymm;
          C
          N,1,l1
          H,2,l2,1,a1}

hf                        ! HF-SCF

frequencies,analytical    ! Vibrational frequencies for HF-SCF (analytical Hessian)

mp2                       ! MP2

optg,root=2,method=rf,readhess     ! Transition State Search using Rational Function Optimizer

frequencies               ! Vibrational frequencies for MP2 (numerical Hessian)
---
```

examples/hcn˙mp2˙ts.com

The second example shows how to do a CCSD(T) optimization with an MP2 hessian. Note that currently the CCSD(T) gradient is computed numerically using finite energy differences, and this can take long time for larger molecules. The calculation of the MP2 hessian finite differences of analytical gradients.

```
!examples/hcn_ccsd_ts.com $Revision: 2002.10 $
***, HCN <--> NHC Transition State Optimization and Frequencies

rcn=1.18 ang
rnh=1.40 ang
alpha=55 degree

basis=vtz

geometry={
          C
          N,1,rcn
          H,2,rnh,1,alpha}

hf
ccsd(t)
optg,root=2,hessproc=runmp2  !Transition state optimization for ccsd(t) using mp2 hessian
frequencies                  !CCSD(T) frequencies (using numerical second derivatives)

runmp2={hf;mp2}    !procedure definition
---
```

examples/hcn˙ccsd˙ts.com

The last example shows how to do a MRCI+Q (MRCI with Davidson correction) optimization with an CASPT2 hessian. As for CCSD(T), the MRCI+Q gradient as computed numerically, while the CASPT2 hessian is obtained using finite differences of analytical CASPT2 gradients.

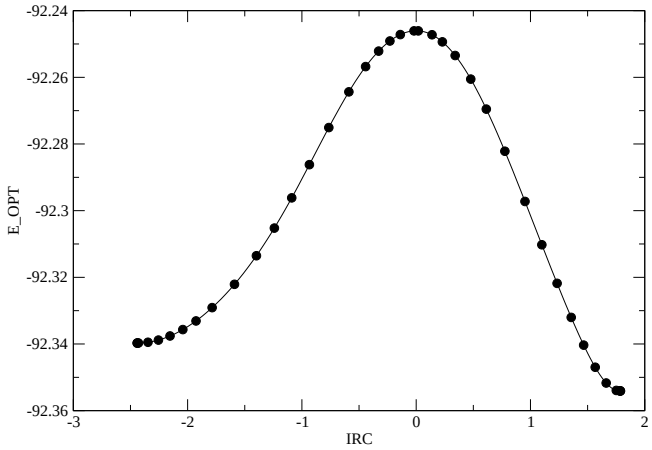
```
!examples/hcn_mrci_ts.com $Revision: 2002.10 $
***, HCN <--> NHC Isomerization - Transition State Optimization and Frequencies
print,orbitals,civector
rcn=1.18 ang
rnh=1.40 ang
alpha=55 degree

basis=vtz

geometry={
          C
          N,1,rcn                                                                    examples/
          H,2,rnh,1,alpha}                                                          hcn˙mrci˙ts.com

closed,4                ! global setting for casscf inactive space

hf                      ! HF-SCF
multi
mrci
optg,root=2,variable=energd,hessproc=runrs2   !optimize mrci+q transition state and caspt2 for

runrs2={multi;rs2}      !procedure definition for caspt2
---
```

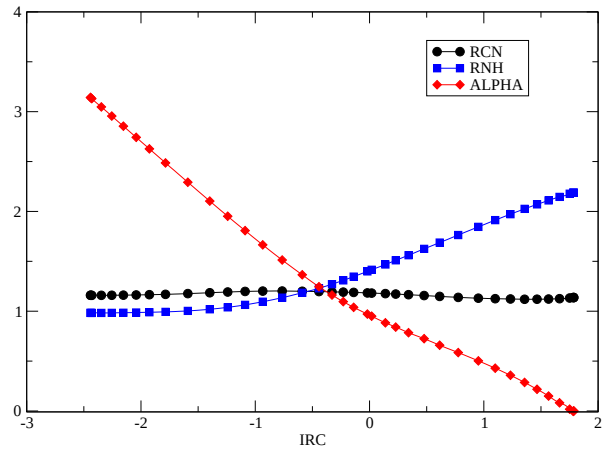
39.4.6 Reaction path of the HCN – HNC isomerization

The following input first optimizes the transition state, and then performs reaction path calculations in both directions. The results are plotted.

```
!examples/hcn_isomerization.com $Revision: 2002.10 $
 ***, HCN <---> NHC Isomerization Reaction Path
 memory,1,m
 basis=3-21G

 rcn=1.18282 ang      ! Starting geometry is transition state
 rnh=1.40745 ang
 alpha=55.05 degree

 geometry={x;           ! Cs Symmetry
           C
           N,1,rcn
           H,2,rnh,1,alpha}

 int
 rhf
 optg,root=2,saveact=hcn.ts                    ! Find the TS                    examples/
 {optg,method=qsdpath,dir=1, numhess=5,hesscentral,saveact=hcn.path}         ! find IRC in pos
                                                                            hcn˙isomerization.com

 readvar,hcn.ts                                ! Reset geometry to TS
 {optg,method=qsdpath,dir=-1,numhess=5,hesscentral,saveact=hcn.path,append} !find IRC in negat

 readvar,hcn.path

 alpha=alpha*pi/180    !convert angle to radian

 table,irc,rcn,rnh,alpha,e_opt   !tabulate results

 {table,irc,e_opt                !plot energy profile as function of irc
  plot,file='hcn_eopt.plot'}

 {table,irc,rcn,rnh,alpha        !plot distances and angle as function of irc
  plot,file='hcn_dist.plot'}
```

This produces the plots





39.4.7 Optimizing counterpoise corrected energies

Geometry optimization of counterpoise corrected energies is possible by performing for the total system as well as for each individual fragment separate `FORCE` calculations. The gradients and energies are added using the `ADD` directive. This requires that `NOORIENT` has been specified in the geometry input, in order to avoid errors due to unintended rotation of the system. This default can be disabled using the `NOCHECK` option, see `ADD` above.

The way a counterpoise corrected geometry optimization works is shown in the following example. Note that the total counterpoise corrected energy must be optimized, not just the interaction energy, since the interaction energy depends on the monomer geometries and has a different minimum than the total energy. The interaction energy could be optimized, however, if the monomer geometries were frozen. In any case, the last calculation before calling `OPTG` must be the calculation of the total system at the current geometry (in the example below the dimer calculation), since otherwise the optimizer gets confused.

```
!examples/hfdimer_cpcopt1.test $Revision: 2006.0 $
***,HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=      5.3
R1=       1.76
R2 =      1.75
THETA1 =  7.0
THETA2 = 111

geometry={x;noorient
      f1
      f2  f1  rff
      h1  f1  r1   f2  theta1
      h2  f2  r2   f1  theta2  h1  180.}

label:

text, CALCULATION AT LARGE SEPARATION

rff_save=rff            !save current rff distance
rff=1000                !dimer calculation at large separation

text, HF1

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1inf=energy          !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer

text, HF2

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2inf=energy          !save mp2 energy in variable
forces;                 !compute mp2 gradient for second monomer
add,1                   !add to previous gradient
einf=ehf1inf+ehf2inf    !total energy of unrelaxed momomers

rff=rff_save            !reset HF - HF distance to current value

text, CP calculation for HF1 MONOMER

dummy,f2,h2;            !second hf is now dummy                    examples/
{hf;accu,16}            !scf for first monomer                     hfdimer˙cpcopt1.com
mp2;                    !mp2 for first monomer
ehf1=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
add,-1                  !subtract from previous gradient

text, CP calculation for HF2 MONOMER

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
add,-1                  !subtract from previous gradient

text, DIMER CALCULATION
dummy                   !reset dummies
{hf;accu,16}            !scf for dimer
mp2;                    !mp2 for dimer
edimer=energy           !save mp2 energy in variable
forces;                 !compute mp2 gradient for dimer
```

The next example shows how the same calculations can be done using numerical gradients. In this case, first the total counter-poise corrected energy is formed and then optimized. Note that the ADD command does not work for numerical gradients.

```
!examples/hfdimer_cpcopt1_num.test $Revision: 2006.0 $
***,HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=      5.3
R1=       1.76
R2 =      1.75
THETA1 =  7.0
THETA2 = 111

geometry={x;noorient
      f1
      f2  f1  rff
      h1  f1  r1   f2  theta1
      h2  f2  r2   f1  theta2  h1  180.}

label:

text, CALCULATION AT LARGE SEPARATION

rff_save=rff            !save current rff distance
rff=1000                !dimer calculation at large separation

text, HF1

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1inf=energy          !save mp2 energy in variable

text, HF2

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2inf=energy          !save mp2 energy in variable
einf=ehf1inf+ehf2inf    !total energy of unrelaxed momomers

rff=rff_save            !reset HF - HF distance to current value

text, CP calculation for HF1 MONOMER

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1=energy             !save mp2 energy in variable

text, CP calculation for HF2 MONOMER

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2=energy             !save mp2 energy in variable

text, DIMER CALCULATION
dummy                   !reset dummies
{hf;accu,16}            !scf for dimer
mp2;                    !mp2 for dimer
edimer=energy           !save mp2 energy in variable
etot=edimer-ehf2-ehf1+ehf1inf+ehf2inf  !total BSSE corrected energy

optg,numerical,variable=etot,gradient=1.d-4,startcmd=label:   !optimize geometry


text, compute optimized monomer energy

rhf=r1
```

examples/
hfdimer˙cpcopt1˙num

In the last example the monomer structures are kept fixed, and the interaction energy is optimized.

examples/hfdimer_cpcopt2.com

```
!examples/hfdimer_cpcopt2.test $Revision: 2006.0 $
***,HF dimer MP2/CP optimization without monomer relaxation

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=      5.3
THETA1 =  7
THETA2 = 111

geometry={x;noorient
      f1
      f2  f1  rff
      h1  f1  1.74764059   f2  theta1
      h2  f2  1.74764059   f1  theta2  h1  180.}   !using fixed HF distances of isolated HF

label:

text, CP calculation for HF1 MONOMER

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
scale,-1                !multiply gradient by -1

text, CP calculation for HF2 MONOMER

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
add,-1                  !subtract from previous gradient

text, DIMER CALCULATION
dummy                   !reset dummies
{hf;accu,16}            !scf for dimer
mp2;                    !mp2 for dimer
edimer=energy           !save mp2 energy in variable
forces;                 !compute mp2 gradient for dimer
add,1                   !add to previous gradient

optg,gradient=.d-5,startcmd=label:   !find next energy

text,optimized geometry parameters
show,rhf,rff,theta1,theta2

text,computed interaction energies
de=(edimer-ehf1-ehf2)*tocm     !CPC corrected interaction energy with fixed monomers
```

40 VIBRATIONAL FREQUENCIES (FREQUENCIES)

FREQUENCIES,*method*,SYMM=*flag*,START=*rec.ifil*,DUMP=*dumprec.ifil*;

Calculate harmonic vibrational frequencies and normal modes. To get reasonable results it is necessary to do a geometry optimization before using the frequency calculation. This option uses a hessian matrix calculated numerically from $3N$ cartesian coordinates. Z-Matrix coordinates will be destroyed on this entry. The hessian is calculated analytically or numerically by finite differences from the input coordinates. In numerical differentiation, if analytic gradients are available, these are differentiated once to build the hessian, otherwise the energy is differentiated twice. Using numerical differentiation the dipole derivatives and the IR intensities are also calculated. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present.

The accuracy of the hessian is determined by *method*, which can be one of the following :

ANALYTICAL	use analytical second derivatives of the energy. At present, analytical second derivatives are only possible for closed shell Hartree-Fock (HF) and MCSCF wavefunctions without symmetry. It is not yet possible to calculate IR-intensities analytically. Note that, due to technical reasons, the analytical MCSCF second derivatives have to be computed in the MCSCF-program using e.g. `multi; cpmcscf,hess` (see MULTI) before they can be used in FREQUENCIES. If analytical MCSCF second derivatives are available, FREQUENCIES will use them by default.
CENTRAL	use central differences/high quality force constants (default).
NUMERICAL	differentiate the energy twice, using central differences.
FORWARD	use forward differences/low quality force constants.

During the numerical calculation of the hessian, the symmetry of the molecule may be lowered. Giving SYMM=AUTO the program uses the maximum possible symmetry of the molecular wavefunction in each energy/gradient calculation, and this option therefore minimizes the computational effort. With SYMM=NO no symmetry is used during the frequency calculation (default). For single reference calculations like HF, MP2, CCSD, RCCSD the AUTO option can be safely used and is recommended. However, it should be noted that SYMM=AUTO cannot be used for MRCI calculations, since the MRCI energy is slighly different with and without symmetry (this is due to first-order interacting space restrictions and can be avoided using `REF cards`, see secion 21.2.6). Furthermore, certain input, which depends on orbital occupations or symmetry labels, cannot be used in frequency calculations with symmetry: for instance, the use of RESTRICT, SELECT, REF, PROJECT, LOCAL, state-averaged MCSCF will lead on an error unless the calculation is performed in C_1 symmetry (NOSYM option in the geometry input).

If the energy second derivatives of a given wavefunction have been calculated numerically or analytically in a previous FREQUENCIES run, the frequency calculation can be restarted from a given frequencies-record *irec* on file *ifil* using the command FREQUENCIES,START=*irec.ifil*; If no *irec.ifil* is given, information is recovered from the latest FREQUENCIES calculation. By default frequency information is saved in record 5300 on file 2. After completion of the frequency calculation, the normal modes and frequencies are dumped to record 5400 on file 2. This default record can be changed using the DUMP option. The normal modes stored in this record can be visualized using MOLDEN (see PUT command, section 12.4). By default, imaginary and low frequency modes are not stored. By specifying DUMPALL rather than DUMP all modes are written out.

By default, all computed frequencies (including low and imaginary ones) are printed. The following options can be used to modify the print level

PRINT,HESSIAN	print the force constant matrix (hessian) i.e. the second derivative matrix of the energy and the mass weighted hessian matrix.
PRINT,LOW	print low vibrational frequencies (i.e. the 5 or 6 frequencies belonging to rotations and translations) and their normal modes (default; PRINT,LOW=-1 suppresses the print).
PRINT,IMAG	print imaginary vibrational frequencies and their normal modes (default; PRINT,IMAG=-1 suppresses the print). Imaginary frequencies appear at transition states. The normal mode of an imaginary frequency represents the transition vector of that state.

The threshold for low vibrations (default 150 cm^{-1} can be changed using

THRESH, LOW=*value*

where value is the threshold in cm^{-1}.

Other subcommands of FREQUENCIES are:

STEP,*rstep*	determines the step size of the numerical differentiation of the energy. Default step size *rstep*=0.001 [bohr].
NOPROJECT	don't project translations and rotations out of the hessian.
SAVE,*irec.ifil*	Save information of numerical frequency calculation to record *irec*. By default frequencies are saved on record 5300.2.
START,*irec.ifil*	Restart numerical frequency calculation from record *irec* on file *ifil* (usually the *.wfu*-file 2).
VARIABLE,*variable*	Name of a variable for which the hessian is computed
COORD=UNIQUE	Use symmetry-unique displacements in the numerical calculation of the hessian (default).
COORD=3N	Don't use symmetry-unique displacements (not recommended). using finite differences.

40.1 Numerical hessian using energy variables (VARIABLE)

VARIABLE,*name*;

Defines a variable *name* which holds the energy value to be used for computing the hessian using finite differences. By default, this is ENERGY(1) as set by the most recent program. For other other variables which can be used see section 39.2.17. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present.

40.2 Thermodynamical properties (THERMO)

It is also possible to calculate the thermodynamical properties of the molecule. Since MOLPRO can only handle Abelian point groups it is necessary to give the point group of the molecule in the input file:

THERMO,SYM=*pointgroup*

pointgroup has to be the Schoenflies Symbol (e.g. `C3v` for ammonia; linear molecules have to be `C*v` or `D*h` respectively). If no point group card is given, rotational degeneracy will be set to 1, eventually causing deviations in the rotational entropy. If no other input card is given the zero-point vibrational energy and the enthalpy $H(t) - H(0)$ [kJ/mol], heat capacity C_v [J/mol K] and entropy S [J/mol K] are calculated for standard Temperature and Pressure ($T = 298.150$ [K], $p = 1$ [atm]).

Subcommands of `THERMO` are

`PRINT,THERMO`	additional information (such as atomic masses, partition functions and thermodynamical function in calories) is printed to the output.
`SCALE,`*factor*	in calculating the thermodynamical properties use vibrational frequencies scaled with *factor*, in order to take account of systematic errors of the wavefunction (e.g. using SCF wavefunctions *factor*=0.89 is reasonable).
`TEMP,`*tmin*,*tmax*,*tstep*	calculate the thermodynamical properties at different temperatures, starting with *tmin* [K] up to *tmax* [K] in steps of *tstep* [K].
`PRESSURE,`*p*	calculate the thermodynamical properties at a given pressure of *p* [atm].

The `FREQUENCIES` program sets the variable *zpe* containing the zero-point-energy of the harmonic vibrations in atomic units. If the `THERMO` option is used, the variables *htotal* and *gtotal*, containing the enthalpy and the free enthalpy of the system in atomic units, are also set.

40.3 Examples

examples/form˙freq.com

```
! $Revision: 2006.0 $
***,formaldehyde freqency calculation
memory,8,m

basis=vdz
gthresh,energy=1.d-8

geomtyp=xyz
geometry={nosym;
   4
FORMALDEHYDE
C          0.0000000000        0.0000000000       -0.5265526741
O          0.0000000000        0.0000000000        0.6555124750
H          0.0000000000       -0.9325664988       -1.1133424527
H          0.0000000000        0.9325664988       -1.1133424527
}

hf;accu,14
optg;coord,3n;

{frequencies,analytic
thermo,sym=c2v
print,thermo}

mp2
optg;coord,3n
{frequencies
thermo,sym=c2v
print,thermo}
```

examples/
pf5˙freq.com

```
***, Phosphorous-pentafluoride Vibrational Frequencies
memory,1,m
basis=3-21G

geomtyp=xyz        ! use cartesian coordinates xmol style
geometry={nosym;   ! geometry input; don't use symmetry
6
  PF5
  P        0.00000        0.00000        0.00000
  F        0.00000        1.11100       -1.12400
  F        0.00000       -1.52800       -0.40100
  F        0.00000        0.41700        1.52500
  F       -1.60400        0.00000        0.00000
  F        1.60400        0.00000        0.00000}

rhf
optg               ! optimize geometry

frequencies        ! calculate vibrational frequencies
print,low          ! print frequencies+modes of zero frequencies
thermo,sym=d3h     ! calculate thermodynamical properties
temp,200,400,50    ! temperature range 200 - 400 [K]
---
```

41 THE COSMO MODEL

The Conductor-like Screening Model (COSMO) (A. Klamt and G. Schüürmann, J. Chem. Soc. Perkin Trans. II 799-805 (1993)) is currently available for HF (RHF, UHF) and DFT (RKS, UKS) energy calculations and the corresponding gradients.

The COSMO model is invoked by the COSMO card:

COSMO[,*option*$_1$=*value*$_1$, *option*$_2$=*value*$_2$,...]

where option can be

NPPA	size of the underlying basis grid. The value must satisfy: $value = 10 \times 3^k \times 4^l + 2$ (default = 1082; type integer).
NSPA	number of segments for non hydrogen atoms. The value must satisfy: $values = 10 \times 3^k \times 4^l + 2$ (default = 92; type integer).
CAVITY	the intersection seams of the molecular surface are closed (1) or open (0) (default = 1; type integer).
EPSILON	dielectric permittivity (default = -1.d0, which means $\varepsilon = \infty$; type real)
DISEX	distance criteria for the **A**-matrix setup. Short range interactions (segment centre distances ¡ DISEX $\times$ mean atomic diameter) are calculated using the underlying basis grid. Long range interactions are calculated via the segment centres (default = 10.d0; type float).
ROUTF	factor used for outer cavity construction. The radii of the outer cavity are defined as: $r_i^{out} = r_i + ROUTF \times RSOLV$ (default = 0.85d0; type float)
PHSRAN	phase offset of coordinate randomization (default = 0.d0; type float)
AMPRAN	amplitude factor of coordinate randomization (default = 1.0d-5; type float)
RSOLV	additional radius for cavity construction (default = -1d0, the optimized H radius is used; type float).
MAXNPS	maximal number of surface segments (default = -1, will be estimated; type integer).

It is recommended to change the default values for problematic cases only.

By default the program uses optimized radii if existent and 1.17$\times$vdW radius else. The optimized radii [Å] are: H=1.30, C=2.00, N=1.83, O=1.72, F=1.72, S=2.16, Cl=2.05, Br=2.16, I=2.32. Own proposals can be given directly subsequent to the cosmo card:

RAD,*symbol, radius*

where the *radius* has to be given in Å.

Example:

```
cosmo
rad,O,1.72
rad,H,1.3
```

Output file:

The COSMO output file will be written after every converged SCF calculation. The segment charges and potentials are corrected by the outlying charge correction. For the total charges and energies corrected and uncorrected values are given. The normal output file contains uncorrected values only. It is recommended to use the corrected values from the output file.

Optimizations:
It is recommended to use optimizer that operates with gradients exclusively. Line search techniques that use energies tends to fail, because of the energy discontinuities which may occur due to a reorganization of the segments after a geometry step. For the same reasons numerical gradients are not recommended.

41.1 BASIC THEORY

COSMO is a continuum solvation model, in which the solvent is represented as a dielectric continuum of permittivity ε. The solute molecule is placed in a cavity inside the continuum. The response of the continuum due to the charge distribution of the solute is described by the generation of a screening charge distribution on the cavity surface. This charge distribution can be calculated by solving the boundary equation of vanishing electrostatic potential on the surface of a conductor. After a discretization of the cavity surface into sufficiently small segments, the vector of the screening charges on the surface segments is

$$\mathbf{q}^* = -\mathbf{A}^{-1}\Phi$$

where Φ is the vector of the potential due to the solute charge distribution on the segments, and $\mathbf{A}$ is the interaction matrix of the screening charges on the segments. This solution is exact for an electric conductor. For finite dielectrics the true dielectric screening charges can be approximated very well by scaling the charge density of a conductor with $f(\varepsilon)$.

$$\mathbf{q} = f(\varepsilon)\mathbf{q}^*; \quad f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 0.5)$$

In every SCF step the screening charges $\mathbf{q}$ have to be generated from the potential Φ, and then added to the Hamiltonian as external point charges. The total energy of the system is

$$E_{tot} = E_0 + E_{diel}; \quad E_{diel} = \frac{1}{2}\Phi\mathbf{q}$$

where E_0 is the bare self-energy of the system and E_{diel} the dielectric energy.

Cavity construction:
First a surface of mutually excluding spheres of radius $R_i + rsolv$ is constructed, where the R_i are the radii of the atoms, defined as element specific radii and *rsolv* is some radius representing a typical maximum curvature of a solvent molecular surface. *rsolv* should not be misinterpreted as a mean solvent radius, nor modified for different solvents. Every atomic sphere is represented by an underlying basis grid of `nppa` points per full atom. Basis grid points which intersect a sphere of a different atom are neglected. In a second step the remainder of the basis grid points are projected to the surface defined by the radii R_i. As a third step of the cavity construction the remaining basis grid points are gathered to segments, which are the areas of constant screening charges in the numerical solution. Finally, the intersection seams between the atoms are filled with additional segments.
Now the A-matrix can be set up. The matrix elements will be calculated from the basis grid points of the segments for close and medium segment distances (governed by the `disex` value),

or using the segment centres for large segment distances.

Outlying charge correction:
The non vanishing electron density outside the cavity causes an error that can be corrected by the outlying charge correction. This correction uses the potential on the so called outer surface (defined by the radii $R_i + \text{rsolv} \times \text{routf}$) to estimate a correction term for the screening charges and the energies (A. Klamt and V. Jonas, J. Chem. Phys., 105, 9972-9981(1996)). The correction will be performed once at the end of a converged SCF calculation. All corrected values can be found in the COSMO output file.

42 ORBITAL MERGING

Orbitals can be manipulated using the MERGE facility. For instance, this allows the construction of molecular orbitals from atomic orbitals, to merge and orthogonalize different orbital sets, or to perform 2×2 rotations between individual orbitals. Other orbital manipulations can be performed using the LOCALI program (see section 19) or the MATROP program (section 43).

The merge program is called using

MERGE [,*namout.file*]

All subcommands described in the following sections may be abbreviated by three characters. *namout.file* specifies the output data set (see also SAVE command). If *namout.file* is omitted and no SAVE card is present, the new orbitals are not saved. All output orbitals must be supplied via ORBITAL and ADD, MOVE, EXTRA, or PROJECT directives before they can be saved.

42.1 Defining the input orbitals (ORBITAL)

ORBITAL,*namin.file*,*specifications*

Reads an input orbital set from a dump record. *specifications* can be used to select specific orbital sets, as described in section 4.11. Subsets of these orbitals can be added to the output set by the ADD, MOVE, or EXTRA commands.

42.2 Moving orbitals to the output set (MOVE)

MOVE,*orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend*

Moves orbitals *orb1.sym1* to *orb2.sym2* from the input set to the first vector of symmetry *sym3* in the output set which is undefined so far. The first *orb3-1* vectors in the output set are skipped regardless of whether they have been defined before or not. If *sym2* $>$ *sym1*, *sym3* will run from *sym1* to *sym2* and the input for *sym3* has no effect. If *orb1.sym1* is negative, abs(*orb1*) is the maximum number of orbitals to be moved, starting with orbital *1.sym1*, up to *orb2.sym2*. If *orb2.sym2* is negative, abs(*orb2*) is the maximum number of vectors to be moved, starting at *orb1.isym1* up to the last orbital in symmetry *sym2*.

Orbitals from the input set which have already been moved or added to the output set are generally skipped. If *orb1* and *orb2* are zero, the whole input set is moved to the output set. In this case the input and output dimensions must be identical. If *orb1* is nonzero but *orb2* is zero, *orb2* is set to the last orbital in symmetry *sym2*. If *sym2=0*, *sym2* is set to *sym1*. *ioff* is an offset in the output vector, relative to the global offset set by OFFSET directive. *fac* has no effect for move. The elements *istart* to *iend* of the input vector are moved. If *istart=0* and *iend=0*, the whole input vector is moved.

The usage of the MOVE directive is most easily understood by looking at the examples given below. See also ADD and EXTRA commands.

42.3 Adding orbitals to the output set (ADD)

ADD,*orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend*

This adds orbitals *orb1.sym1* to *orb2.sym2* to the output vectors, starting at *orb3.sym3*. The input vectors are scaled by the factor *fac*. If *fac=0*, *fac* is set to 1.0. For other details see

MOVE command. Note, however, that the output vectors which have already been defined are not skipped as for MOVE.

See also MOVE and EXTRA commands.

42.4 Defining extra symmetries (EXTRA)

EXTRA,*exsym,orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend*

Works exactly as MOVE, but only input vectors with extra symmetry *exsym* are considered. If *orb1.sym1* and *orb2.sym2* are zero, all input vectors are moved to the output set ordered according to increasing extra symmetries.

Examples:

EXTRA,1,-4.1	will move the next 4 orbitals in symmetry 1 which have extra symmetry 1. Orbitals which have been moved before are skipped.
EXTRA,2,1.1	will move all orbitals of symmetry 1 which have extra symmetry 2. Orbitals which have been moved before are skipped.
EXTRA	will move all orbitals (all symmetries) and order them according to extra symmetries.
EXTRA,3,1.1,0.8	Will move all orbitals which have extra symmetry 3 in all symmetries. Orbitals which have been moved before are skipped.

See also ADD and MOVE commands.

42.5 Defining offsets in the output set (OFFSET)

OFFSET,iof_1,iof_2,...,iof_8;

Sets offsets in the output vector for symmetries 1 to 8. In subsequent MOVE or ADD commands, the input vectors are moved to the locations iof_i+1 in the output vectors. The offset for individual ADD or MOVE commands can be modified by the parameter *ioff* on these cards. This card should immediately follow the orbital directive to which it applies. Generally, this card is only needed if the dimensions of input and output vectors are not identical.

If the dimensions of the input orbital sets are smaller than the current basis dimension, the offsets are determined automatically in the following way: each time an orbital set is read in, the previous input orbital dimensions are added to the offsets. Hence, this works correctly if the orbital sets are given in the correct order and if the individual dimensions add up to the current total dimension. If this is not the case, the offsets should be specified on an OFFSET card which must follow the orbital directive.

42.6 Projecting orbitals (PROJECT)

PROJECT,*namin.file*

This command will read vectors from record *namin.file*. These vectors must have the same dimension as those of the current calculation. All orbitals defined so far by the ORBITAL, MOVE, and ADD directives are projected out of the input set. The projected orbitals are then orthonormalized and moved to the undefined output vectors. This should always yield a complete set of vectors.

42.7 Symmetric orthonormalization (ORTH)

ORTH,$n_1,n_2,\ldots,n_8$

Symmetrically orthonormalizes the first n_i vectors in each symmetry i. These vectors must be supplied before by ORBITAL and MOVE or ADD directives.

42.8 Schmidt orthonormalization (SCHMIDT)

SCHMIDT,$n_1,n_2,\ldots,n_8$

Schmidt orthonormalizes the first n_i vectors in each symmetry i. These vectors must be supplied before by ORBITAL and MOVE or ADD directives.

42.9 Rotating orbitals (ROTATE)

ROTATE,*iorb1.sym,iorb2,angle*

Will perform 2×2 rotation of orbitals *iorb1* and *iorb2* in symmetry *sym* by the specified *angle* (in degree). *angle=0* means to swap the orbitals (equivalent to *angle=90*) These vectors must be supplied before by ORBITAL and MOVE or ADD directives.

42.10 Initialization of a new output set (INIT)

INIT,*namout.file*

Will initialize a new output set. All previous vectors in the output set are lost unless they have been saved by a SAVE directive!

42.11 Saving the merged orbitals

SAVE,*namout.file*

Saves the current output set to record *namout.file*. The current output set must be complete and will be Schmidt orthonormalized before it is saved. If the SAVE directive is not supplied, the output vectors will be saved after all valid commands have been processed to the record specified on the MERGE card.

42.12 Printing options (PRINT)

PRINT,*iprint,ideb*

Specifies print options.

$iprint = 0$	no print
$iprint \geq 1$:	orthonormalized orbitals specified on ORTH card are printed.
$iprint \geq 2$:	orbitals are also printed before this orthonormalization.
$iprint \geq 3$:	all final vectors are printed.
$ideb \neq 0$:	the overlap matrices are printed at various stages.

42.13 Examples

42.13.1 H_2F

This example merges the orbitals of H_2 and F

```
! $Revision: 2006.0 $
***,example for merge
print,orbitals,basis
rh2=1.4
rhf=300.
basis=vdz
geometry={x,y;F}                          !use C2v symmetry

text,F
{rhf;wf,9,1,1;occ,3,1,1;orbital,2130.2} !rhf for f-atom

text,H2
geometry={x,y;                            !use C2v symmetry
         H1,
         H2,H1,rh2}

{hf;orbital,2100.2}                       !scf for h2
{multi;occ,2;orbital,2101.2}              !mcscf for h2

text,FH2
geometry={F;                              !linear geometry for F+H2
         H1,F,rhf
         H2,H1,rh2,F,180}
```

examples/h2f˙merge.com

```
{merge
orbital,2130.2                            !rhf orbitals for F-atom
move,1.1,2.1,1.1                          !move orbitals 1.1, 2.1
move,3.1,0.4,4.1;                         !move all remaining, starting at 4.1
orbital,2100.2                            !hf orbitals for H2
move,1.1,0.4                              !move these to free positions
save,2131.2}                              !save merged orbitals

{rhf;occ,4,1,1;start,2131.2               !rhf for F+H2
orbital,2132.2}

{merge
orbital,2130.2                            !rhf orbitals for F-atom
move,1.1,2.1,1.1                          !move orbitals 1.1, 2.1
move,3.1,3.1,4.1;                         !move orbital 3.1 to 4.1
move,4.1,0.4,6.1                          !move all remaining, starting at 6.1
orbital,2101.2                            !mcscf orbitals for H2
move,1.1,0.4                              !move these to free positions
save,2141.2}                              !save merged orbitals

{multi;occ,5,1,1;start,2141.2}            !casscf for F+H2 using valence space
```

42.13.2 NO

This example merges the SCF orbitals of N and O to get a full valence space for NO. In the simplest case the atomic calculations are performed in the individual separate basis sets, but using the same symmetry (C_{2v}) as the molecular calculation.

```
! $Revision: 2006.0 $
***,NO merge
r=2.1

geometry={x,y;n}     !N-atom, c2v symmetry

{rhf;occ,3,1,1;       !rhf nitrogen
wf,7,4,3;            !4S state
orbital,2110.2}      !save orbitals to record 2110 on file 2

geometry={x,y;o}

{rhf;occ,3,1,1;       !rhf for oxygen
wf,8,4,2             !3P state
orbital,2120.2}      !save orbitals to record 2120 on file 2

geometry={n;o,n,r}   ! NO molecule, c2v symmetry

{MERGE
ORBITAL,2110.2       ! read orbitals of N atom
MOVE,1.1,1.1         ! move 1s orbital to output vector 1.1
MOVE,2.1,2.1,3.1     ! move 2s orbital to output vector 3.1
MOVE,3.1,3.1,5.1     ! move 2pz orbital to output vector 5.1
MOVE,1.2,1.2         ! move 2px orbital to output vector 1.2
MOVE,1.3,1.3         ! move 2py orbital to output vector 1.3
MOVE,4.1,,7.1        ! move virtual orbitals of symmetry 1
MOVE,2.2,,3.2        ! move virtual orbitals of symmetry 2
MOVE,2.3,,3.3        ! move virtual orbitals of symmetry 2
MOVE,1.4             ! move virtual orbitals of symmetry 2
ORBITAL,2120.2       ! read orbitals of O atom
MOVE,1.1,0.4         ! move all oxygen orbitals into place
ROT,3.1,4.1,45;      ! rotate 2s orbitals to make bonding and antibonding
                     ! linear combinations
ROT,5.1,6.1,-45;     ! rotate 2pz orbitals to make bonding and antibonding
                     ! linear combinations
PRINT,1              ! set print option
ORTH,6,2,2           ! symmetrically orthonormalize the valence orbitals
                     ! the resulting orbitals are printed
save,2150.2}         ! save merged orbitals to record 2150.2

{multi;occ,6,2,2      ! perform full valence casscf for NO
wf,15,2,1            ! 2Pix state
wf,15,3,1            ! 2Piy state
start,2150.2}        ! start with merged orbitals
```

examples/
no˙merge1.com

One can also do the atomic calculations in the total basis set, using dummy cards. In this case the procedure is more complicated, since the union of the two orbital spaces is over-complete. The calculation can be done as follows:

a) SCF for the total molecule, orbitals saved to 2100.2

b) SCF for the N atom with dummy basis on the O atom, orbitals saved on 2110.2

c) SCF for the O atom with dummy basis on the N atom, orbitals saved on 2120.2

d) Merge the atomic SCF orbitals. Finally, obtain the virtual orbitals by projecting the merge orbitals out of the SCF orbitals for NO.

examples/
no˙merge2.com

```
! $Revision: 2006.0 $
***,NO merge
geometry={n;o,n,r}
r=2.1

{rhf;occ,5,2,1     !rhf for NO
wf,15,2,1          !2Pi state
orbital,2100.2}    !save orbitals to record 2100 on file 2

dummy,o            !oxygen is dummy
{rhf;occ,3,1,1;     !rhf nitrogen
wf,7,4,3;          !4S state
orbital,2110.2}    !save orbitals to record 2110 on file 2

dummy,n            !nitrogen is dummy
{rhf;occ,3,1,1;    !rhf for oxygen
wf,8,4,2           !3P state
orbital,2120.2}    !save orbitals to record 2120 on file 2

{MERGE              !call merge program

ORBITAL,2110.2     ! read orbitals of N atom
MOVE,1.1,1.1       ! move input vector 1.1 to output vector 1.1
MOVE,2.1,3.1,3.1   ! move input vectors 2.1,3.1 to output vectors
                   ! 3.1 and 4.1
MOVE,1.2,1.2       ! move input vector 1.2  to output vector 1.2
MOVE,1.3,1.3       ! move input vector 1.3  to output vector 1.3
ORBITAL,2120.2     ! read orbitals of O atom
MOVE,1.1,3.1       ! move input vectors 1.1 to 3.1 to output vectors
                   ! 2.1, 5.1, 6.1
MOVE,1.2,1.2       ! move input vector 1.2 to output vector 2.2
MOVE,1.3,1.3       ! move input vector 1.3 to output vector 2.3
ROT,3.1,5.1,45;    ! rotate 2s orbitals to make bonding and antibonding
                   ! linear combinations
ROT,4.1,6.1,-45;   ! rotate 2pz orbitals to make bonding and antibonding
                   ! linear combinations
PRINT,1            ! set print option
ORTH,6,2,2         ! symmetrically orthonormalize the valence orbitals
                   ! the resulting orbitals are printed
PROJ,2100.2        ! Project valence orbitals out of scf orbitals of the
                   ! molecule and add virtual orbital set.
SAVE,2150.2        ! save merged orbitals to record 2150 on file 2
}

dummy              ! remove dummies
{multi;occ,6,2,2   ! perform full valence casscf for NO
wf,15,2,1          ! 2Pi state
wf,15,3,1          ! 2Pi state
start,2150.2}      ! start with merged orbitals
```

43 MATRIX OPERATIONS

MATROP;

MATROP performs simple matrix manipulations for matrices whose dimensions are those of the one particle basis set. To do so, first required matrices are loaded into memory using the LOAD command. To each matrix an internal *name* (an arbitrary user defined string) is assigned, by which it is referenced in further commands. After performing operations, the resulting matrices can be saved to a dump record using the SAVE directive. Numbers, e.g. traces or individual matrix elements, can be saved in variables.

code may be one of the following:

LOAD	Loads a matrix from a file
SAVE	Saves a matrix to a file
ADD	Adds matrices
TRACE	Forms the trace of a matrix or of the product of two matrices
MULT	Multiplies two matrices
TRAN	Transforms a matrix
DMO	Transforms density into MO basis
NATORB	Computes natural orbitals
DIAG	Diagonalizes a matrix
OPRD	Forms an outer product of two vectors
DENS	Forms a closed-shell density matrix
FOCK	Computes a closed-shell fock matrix
COUL	Computes a coulomb operator
EXCH	Computes an exchange operator
PRINT	Prints a matrix
PRID	Prints diagonal elements of a matrix
PRIO	Prints orbitals
ELEM	Assigns a matrix element to a variable
READ	Reads a square matrix from input
WRITE	Writes a square matrix from input
SET	Assigns a value to a variable

See the following subsections for explanations.

43.1 Calling the matrix facility (MATROP)

The program is called by the input card MATROP without further specifications.

MATROP

It can be followed by the following commands in any order, with the restriction that a maximum of 50 matrices can be handled. The first entry in each command line is a command keyword, followed by the name of the result matrix. If the specified result matrix *result* already exists, it

is overwritten, otherwise a new matrix is created. All matrices needed in the operations must must have been loaded or defined before, unless otherwise stated.

If a backquote (‘) is appended to a name, the matrix is transposed.

43.2 Loading matrices (LOAD)

All matrices which are needed in any of the subsequent commands must first be loaded into memory using the LOAD command. Depending on the matrix type, the LOAD command has slightly different options. In all forms of LOAD *name* is an arbitrary string (up to 16 characters long) by which the loaded matrix is denoted in subsequent commands.

43.2.1 Loading orbitals

LOAD,*name*,ORB [,*record*] [,*specifications*]

loads an orbital coefficient matrix from the given dump record. If the record is not specified, the last dump record is used. Specific orbitals sets can be selected using the optional *specifications*, as explained in section 4.11. The keyword ORB needs not to be given if *name*=ORB.

43.2.2 Loading density matrices

LOAD,*name*,DEN [,*record*] [,*specifications*]

loads a density matrix from the given dump record. If the record is not given, the last dump record is used. Specific orbitals sets can be selected using the optional *specifications*, as explained in section 4.11. The keyword DEN needs not to be given if *name*=DEN.

43.2.3 Loading the AO overlap matrix S

LOAD,*name*,S

loads the overlap matrix in the AO basis. The keyword S needs not to be given if *name*=S.

43.2.4 Loading $S^{-1/2}$

LOAD,*name*,SMH

loads $\mathbf{S}^{-1/2}$, where **S** is the overlap matrix in the AO basis. The keyword SMH needs not to be given if *name*=SMH.

43.2.5 Loading the one-electron hamiltonian

LOAD,*name*,H0

LOAD,*name*,H01

loads the one-electron hamiltonian in the AO basis. H01 differs from H0 by the addition of perturbations, if present (see sections 32.4.1, 32.4.2). The keyword H0 (H01) needs not to be given if *name*=H0 (H01). The nuclear energy associated to H0 or H01 is internally stored.

43.2.6 Loading the kinetic or potential energy operators

LOAD,*name*,EKIN

LOAD,*name*,EPOT

loads the individual parts of the one-electron hamiltonian in the AO basis. EPOT is summed for all atoms. The nuclear energy is associated to EPOT and internally stored. The keyword EKIN (EPOT) needs not to be given if *name*=EKIN (EPOT).

43.2.7 Loading one-electron property operators

LOAD,*name*,OPER,*opname*,[*isym*],*x,y,z*

loads one-electron operator *opname*, where *opname* is a keyword specifying the operator (a component must be given). See section 6.13 for valid keys. *isym* is the total symmetry of the operator (default 1), and *x,y,z* is the origin of the operator. If the operator is not available yet in the operator record, it is automatically computed. The nuclear value is associated internally to *name* and also stored in variable OPNUC (this variable is overwritten for each operator which is loaded, but can be copied to another variable using the SET command. Note that the electronic part of dipole and quadrupole operators are multiplied by -1.

43.2.8 Loading matrices from plain records

LOAD,*name*,TRIANG,*record*,[*isym*]
LOAD,*name*,SQUARE,*record*,[*isym*]

Loads a triangular or square matrix from a plain record (not a dump record or operator record). If *isym* is not given, 1 is assumed.

43.3 Saving matrices (SAVE)

SAVE,*name*,*record* [,*type*]

At present, *type* can be DENSITY, ORBITALS, FOCK, H0, ORBEN, OPER, TRIANG, SQUARE, or VECTOR. If type is not given but known from LOAD or another command, this is assumed. Orbitals, density matrices, fock matrices, and orbital energies are saved to a dump record (the same one should normally be used for all these quantities). If *type* is H0, the one-electron hamiltonian is overwritten by the current matrix and the nuclear energy is modified according to the value associated to *name*. The nuclear energy is also stored in the variable ENUC. All other matrices can be saved in triangular or square form to plain records using the TRIANG and SQUARE options, respectively (for triangular storage, the matrix is symmetrized before being stored). Eigenvectors can be saved in plain records using the VECTOR option. Only one matrix or vector can be stored in each plain record.

One-electron operators can be stored in the operator record using

SAVE,*name*,OPER, [PARITY=*np*], [NUC=*opnuc*], CENTRE=*icen*],[COORD=[*x,y,z*]]

The user-defined operator *name* can can then be used on subsequent EXPEC or GEXPEC cards. $np = 1, 0, -1$ for symmetric, square, antisymmetric operators, respectively (default 1). If CENTRE is specified, the operator is assumed to have its origin at the given centre, where *icen* refers to the row number of the z-matrix input. The coordinates can also be specified explicitly using COORD. By default, the coordinates of the last read operator are assumed, or otherwise zero.

If NATURAL orbitals are generated and saved in a dump record, the occupation numbers are automatically stored as well. This is convenient for later use, e.g., in MOLDEN.

43.4 Adding matrices (ADD)

ADD,*result* [,*fac1*],*mat1* [,*fac2*],mat2,...

calculates *result* = *fac1* · *mat1* + *fac2* · *mat2* + ...

The strings *result*, *mat1*, *mat2* are internal names specifying the matrices. *mat1*, *mat2* must exist, otherwise an error occurs. If *result* does not exist, it is created.

The factors *fac1*, *fac2* are optional (may be variables). If not given, one is assumed.

The nuclear values associated to the individual matrices are added accordingly and the result is associated to *result*.

43.5 Trace of a matrix or the product of two matrices (TRACE)

TRACE,*variable, mat1*,,[*factor*]

Computes *variable* = *factor**tr(*mat1*).

TRACE,*variable, mat1, mat2*,[*factor*]

Computes *variable* = *factor**trace(*mat1* · *mat2*).

The result of the trace operation is stored in the MOLPRO variable *variable*, which can be used in subsequent operations.

If *factor* is not given, one is assumed.

43.6 Setting variables (SET)

SET,*variable*,*value*

Assigns *value* to MOLPRO variable *variable*, where *value* can be an expression involving any number of variables or numbers. Indexing of *variable* is not possible, however.

43.7 Multiplying matrices (MULT)

MULT,*result, mat1, mat2*,[*fac1*],[*fac2*]

calculates *result* = *fac2* * *result* + *fac1* * *mat1* · *mat2*

The strings *result* , *mat1* , *mat2* are the internal names of the matrices. If *fac1* is not given, *fac1=1* is assumed. If *fac2* is not given, *fac2=0* is assumed. If a backquote (‘) is appended to *mat1* or *mat2* the corresponding matrix is transposed before the operation. If a backquote is appended to *result*, the resulting matrix is transposed.

43.8 Transforming operators (TRAN)

TRAN,*result*, *Op*, *C*

calculates *result* = *C(T)*Op*C*. The strings *result*, *C*, and *Op* are the internal names of the matrices. If a backquote (‘) is appended to *C* or *Op* the corresponding matrix is transposed before the operation. Thus,

TRAN,*result*, *Op*, *C‘*

computes *result* = *C*Op*C(T)*.

43.9 Transforming density matrices into the MO basis (DMO)

DMO,*result*, *D*, *C*

calculates *result* = *C(T)*S*D*S*C*. The strings *result*, *C*, and *D* are internal names.

43.10 Diagonalizing a matrix DIAG

DIAG,*eigvec*,*eigval*,*matrix* [,*iprint*]

Diagonalizes *matrix*. The eigenvectors and eigenvalues are stored internally with associated names *eigvec* and *eigval*, respectively (arbitrary strings of up to 16 characters). The if *iprint*.gt.0, the eigenvalues are printed. If *iprint.gt.1*, also the eigenvectors are printed.

43.11 Generating natural orbitals (NATORB)

NATORB,*name*,*dens*,*thresh*

computes natural orbitals for density matrix *dens*. Orbitals with occupation numbers greater or equal to *thresh* (default 1.d-4) are printed.

43.12 Forming an outer product of two vectors (OPRD)

OPRD,*result*,*matrix*,*orb1*,*orb2*,*factor*

Takes the column vectors *v1* and *v2* from *matrix* and adds their outer product to *result*. *v1* and *v2* must be given in the form *icol.isym*, e.g., 3.2 means the third vector in symmetry 2. The result is

$$result(a,b) = result(a,b) + factor * v1(a) * v2(b)$$

If *result* has not been used before, it is zeroed before performing the operation.

43.13 Forming a closed-shell density matrix (DENS)

DENS,*density*,*orbitals*,$iocc_1$, $iocc_2 \ldots$

Forms a closed-shell density matrix *density* from the given *orbitals*. The number of occupied orbitals in each symmetry *i* must be provided in $iocc_i$.

43.14 Computing a fock matrix (FOCK)

FOCK,*f*,*d*

computes a closed shell fock matrix using density *d*. The result is stored in *f*.

43.15 Computing a coulomb operator (COUL)

COUL,*J*,*d*

computes a coulomb operator J(d) using density *d*.

43.16 Computing an exchange operator (EXCH)

EXCH,*K*,*d*

computes an exchange operator K(d) using density *d*.

43.17 Printing matrices (PRINT)

PRINT,*name*,[*ncol(1), ncol(2),...*]

prints matrix *name*. *ncol(isym)* is the number of columns to be printed for row symmetry *isym* (if not given, all columns are printed). For printing orbitals one can also use ORB.

43.18 Printing diagonal elements of a matrix (PRID)

PRID,*name* prints the diagonal elements of matrix *name*.

43.19 Printing orbitals (PRIO)

PRIO,*name*,$n_1, n_2, n_3, \ldots, n_8$

prints orbitals *name*. The first n_i orbitals are printed in symmetry i. If $n_i = 0$, all orbitals of that symmetry are printed.

43.20 Assigning matrix elements to a variable (ELEM)

ELEM,*name*,*matrix*, *col*,*row*

assigns elements (col,row) of *matrix* to variable *name*. *col* and *row* must be given in the form *number.isym*, where *number* is the row or column number in symmetry *isym*. The product of the row and column symmetries must agree with the matrix symmetry.

43.21 Reading a matrix from the input file (READ)

READ,*name*,[[TYPE=]*type*],[[SUBTYPE=]*subtype*],[[SYM=]*symmetry*], [FILE=*file*]
{ *values* }

Reads a square matrix (symmetry 1) from input or an ASCII file. The *values* can be in free format, but their total number must be correct. Comment lines starting with '#', '*', or '!' are skipped. If the data are given in input, the data block must be enclosed either by curley brackets or the first linbe must be BEGIN_DATA and the last line END_DATA. If a *filename* is specified as option, the data are read from this file. In this case, the BEGIN_DATA, END_DATA lines in the file are optional, and no data block must follow.

For compatibility with older versions, the data can also be included in the input using the INCLUDE command (see section 3.1). In this case, the include file must contain the BEGIN_DATA and END_DATA lines (this is autopmatically the case if the file has been written using the MATROP,WRITE directive).

type is a string which can be used to assign a matrix type. If appropriate, this should be any of the ones used in the LOAD command. In addition, SUBTYPE can be specified if necessary. This describes, e.g., the type of orbitals or density matrices (e.g., for natural orbitals *TYPE*=ORB and *SUBTYPE*=NATURAL). The matrix symmetry needs to be given only if it is not equal to 1.

43.22 Writing a matrix to an ASCII file (WRITE)

WRITE,*name*,[*filename* [*status*]]

Writes a matrix to an ASCII file. If *filename* is not given the matrix is written to the output file, otherwise to the specified file (*filename* is converted to lower case). If *filename*=PUNCH it is written to the current punch file.

If *status*=NEW, ERASE or em REWIND, a new file is written, otherwise as existing file is appended.

43.23 Examples

The following example shows various uses of the MATROP commands.

```
! $Revision: 2006.0 $
***,h2o matrop examples
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
hf                                    !do scf calculation
{multi
natorb
canonical}
{matrop
load,D_ao,DEN,2140.2                  !load mcscf density matrix
load,Cnat,ORB,2140.2,natural          !load mcscf natural orbitals
load,Ccan,ORB,2140.2,canonical        !load mcscf canonical orbitals
load,Dscf,DEN,2100.2                  !load scf density matrix
load,S                                !load overlap matrix

prio,Cnat,4,1,2                       !prints occupied casscf orbitals

elem,d11,Dscf,1.1,1.1                 !print element D(1,1)
elem,d21,Dscf,2.1,1.1                 !print element D(2,1)
elem,d12,Dscf,1.1,2.1                 !print element D(1,2)

tran,S_mo,s,Cnat                      !transform s into MO basis (same as above)
print,S_mo                            !print result - should be unit matrix

trace,Nao,S_mo                        !trace of S_MO = number of basis functions
trace,Nel,D_ao,S                      !form trace(DS) = number of electrons

mult,SC,S,Cnat                        !form SC=S*Cnat
tran,D_nat,D_ao,SC                    !transform density to natural MO (could also be done usi

prid,D_nat                            !print diagonal elements (occupation numbers)

dmo,D_can,D_ao,Ccan                   !transform D_ao to canonical MO basis. Same as above sim
add,D_neg,-1,D_can                    !multiply d_can by -1
diag,U,EIG,D_neg                      !diagonalizes density D_can
mult,Cnat1,Ccan,U                     !transforms canonical orbitals to natural orbitals
prio,Cnat1,4,1,2                      !prints new natural orbitals

natorb,Cnat2,D_ao                     !make natural orbitals using MCSCF density D_ao directly
prio,Cnat2,4,1,2                      !prints new natural orbitals (should be the same as abov

add,diffden,D_ao,-1,Dscf              !form mcscf-scf difference density
natorb,C_diff,diffden                 !make natural orbitals for difference density

write,diffden,denfile                 !write difference density to ASCII file denfile
save,C_diff,2500.2                    !store natural orbitals for difference density in dump r
}
```

examples/
matrop.com

This second example adds a quadrupole field to `H0`. The result is exactly the same as using the `QUAD` command. `H0` is overwritten by the modified one-electron matrix, and the nuclear energy is automatically changed appropriately. The subsequent SCF calculations use the modified one-electron operator.

Note that it is usually recommended to add fields with the $\widehat{\text{DIP}}$, `QUAD`, or `FIELD` commands.

```
! $Revision: 2006.0 $
memory,2,m
R    =    0.96488518 ANG
THETA=  101.90140469
geometry={H1
          O,H1,R;
          H2,O,R,H1,THETA}
{hf;wf,10,1}

field=0.05             !define field strength

{matrop
load,h0,h0             !load one-electron hamiltonian
load,xx,oper,xx        !load second moments
load,yy,oper,yy
load,zz,oper,zz
add,h01,h0,field,zz,-0.5*field,xx,-0.5*field,yy   !add second moments to h0 and store in h01
save,h01,1210.1,h0}    !save h0
hf                     !do scf with modified h0
```

examples/
matropfield.com

```
{matrop
load,h0,h0             !load h0
load,qmzz,oper,qmzz    !load quadrupole moment qmzz
add,h01,h0,field,qmzz  !add quadrupole moment to h0  (same result as above with second moments
save,h01,1210.1,h0}    !save h0
hf                     !do scf with modified h0

quad,,,field           !add quadrupole field to h0
hf                     !do scf with modified h0 (same result as above with matrop)

field,zz,field,xx,-0.5*field,yy,-0.5*field   ! (add general field; same result as above)
hf                     !do scf with modified h0 (same result as above with matrop)

field,zz,field       !same as before with separate field commands
field+,xx,-0.5*field
field+,yy,-0.5*field
hf                     !do scf with modified h0 (same result as above with matrop)
```

43.24 Exercise: SCF program

Write a closed-shell SCF program for H_2O using MATROP!

Hints:

First generate a starting orbital guess by finding the eigenvectors of *h0*. Store the orbitals in a record. Basis and geometry are defined in the usual way before the first call to MATROP.

Then use a MOLPRO DO loop and call MATROP for each iteration. Save the current energy in a variable (note that the nuclear energy is stored in variable ENUC). Also, compute the dipole moment in each iteration. At the end of the iteration perform a convergence test on the energy change using the IF command. This must be done outside MATROP just before the ENDDO. At this stage, you can also store the iteration numbers, energies, and dipole moments in arrays, and print these after reaching convergence using TABLE. For the following geometry and basis set

```
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
basis=vdz                             !basis set
thresh=1.d-8                          !convergence threshold
```

the result could look as follows:

```
 SCF has converged in 24 iterations

    ITER       E             DIP
     1.0   -68.92227207    2.17407361
     2.0   -71.31376891   -5.06209922
     3.0   -73.73536433    2.10199751
     4.0   -74.64753557   -1.79658706
     5.0   -75.41652680    1.43669203
     6.0   -75.77903293    0.17616098
     7.0   -75.93094231    1.05644998
     8.0   -75.98812258    0.63401784
     9.0   -76.00939154    0.91637513
    10.0   -76.01708679    0.76319435
    11.0   -76.01988143    0.86107911
    12.0   -76.02088864    0.80513445
    13.0   -76.02125263    0.83990621
    14.0   -76.02138387    0.81956198
    15.0   -76.02143124    0.83202128
    16.0   -76.02144833    0.82464809
    17.0   -76.02145450    0.82912805
    18.0   -76.02145672    0.82646089
    19.0   -76.02145752    0.82807428
    20.0   -76.02145781    0.82711046
    21.0   -76.02145792    0.82769196
    22.0   -76.02145796    0.82734386
    23.0   -76.02145797    0.82755355
    24.0   -76.02145797    0.82742787
```

It does not converge terribly fast, but it works!

References

[1] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[2] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett **77**, 3865 (1996).

[4] C. Adamo and V. Barone, J. Chem. Phys **110**, 6158 (1999).

[5] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[6] R. Strange, F. R. Manby, and P. J. Knowles, Computer Physics Communications **136**, 310 (2001).

[7] B. Miehlich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).

[8] A. D. Becke, J. Chem. Phys **85**, 7184 (1986).

[9] A. D. Becke, J. Chem. Phys **107**, 8554 (1997).

[10] A. D. Becke, J. Chem. Phys **84**, 4524 (1986).

[11] A. D. Becke, J. Chem. Phys. **88**, 1053 (1998).

[12] A. D. Becke, J. Chem. Phys. **104**, 1040 (1995).

[13] F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, J. Chem. Phys **109**, 6264 (1998).

[14] P. A. Stewart and P. M. W. Gill, J. Chem. Faraday Trans. **91**, 4337 (1995).

[15] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[16] P. M. W. Gill, Mol. Phys. **89**, 433 (1996).

[17] A. D. Boese, N. L. Doltsinis, N. C. Handy, and M. Sprick, J. Chem. Phys **112**, 1670 (2000).

[18] M. Ernzerhof and G. Scuseria, J. Chem. Phys. **111**, 911 (1999).

[19] F. R. Manby and P. J. Knowles, J. Chem. Phys. **112**, 7002 (2000).

[20] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[21] Y. Zhang and W. Yang, Phys. Rev. Lett **80**, 890 (1998).

[22] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[23] D. J. Tozer and N. C. Handy, J. Chem. Phys. **108**, 2545 (1998).

[24] D. J. Tozer and N. C. Handy.

[25] D. J. Tozer and N. C. Handy, Mol. Phys. **94**, 707 (1998).

[26] D. J. Tozer, N. C. Handy, and W. H. Green, Chem. Phys. Lett. **273**, 183 (1997).

[27] T. V. Voorhis and G. E. Scusseria, J. Chem. Phys. **109**, 400 (1998).

[28] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

A Installation of MOLPRO

A.1 Obtaining the distribution materials

MOLPRO is distributed to licensees on a self-service basis using the world-wide web. Those entitled to the code should obtain it from http://www.molpro.net/download supplying the username and password given to them. The web pages contain both source code and binaries, although not everyone is entitled to source code, and binaries are not available for every platform.

Execution of MOLPRO, whether a supplied binary or built from source, requires a valid licence key. Note that the key consists of two components, namely a list of comma-separated key=value pairs, and a password string, and these are separated by '&'. In most cases the licence key will be automatically downloaded from the website when building or installing the software.

A.2 Installation of pre-built binaries

Binaries are given as RPM (see http://www.rpm.org) packages which are installed in the standard way. There are RPMs tuned for the Pentium III, Pentium 4 and Athlon architectures. These also support parallel execution. There is a generic serial rpm which should run on all IA32 architectures. You can install using the command:
`rpm -Uhv molpro-mpp-2006.1-0.p4.rpm`
where the filename of the rpm has the format:
`molpro-(mpp|serial)-2006.1-PATCHLEVEL.ARCH.rpm`
where `PATCHLEVEL` is a number denoting the patchlevel of the rpm and `ARCH` denotes the architecture. At present these RPMs are not relocatable, and will install under `/usr/local`. If a licence key is set in the `MOLPRO_KEY` environment variable or the rpm finds a licence key which has been cached in `$HOME/.molpro/token` from a previous install then that key will be installed with the software. If the rpm cannot find a key or automatically download it from the molpro website then the user will be prompted to run the post-install script: `/usr/local/bin/molpro-configure` which will download the key from the molpro website and place it in:
`/usr/local/lib/molpro-`*`mpptype-arch`*`/.token`

Other configuration options as described in section A.3.6 may also be specified in the script file: `/usr/local/bin/molpro`

A.3 Installation from source files

A.3.1 Overview

There are usually four distinct stages in installing MOLPRO from source files:

Configuration — A shell script that allows specification of configuration options is run, and creates a configuration file that drives subsequent installation steps.

Compilation — The program is compiled and linked, and other miscellaneous utilities and files, including the default options file, are built. The essential resulting components are

1. The `molpro` executable, which is a small front-end that parses options, performs housekeeping functions, and starts the one or more processes that do computation.

2. The `molpro.exe` executable, which is the main back-end. For parallel computation, multiple copies of `molpro.exe` are started by a single instance of `molpro` using the appropriate system utility (e.g. `mpirun`, `parallel`, `poe`, etc.).
3. The `molpro.rc` file which contains default options for `molpro` (cf. section A.3.6).
4. The `molproi.rc` file which contains MOLPRO-script procedures.
5. Machine-ready basis-set, and other utility, libraries.

Validation — A suite of self-checking test jobs is run to provide assurance that the code as built will run correctly.

Installation — The program can be run directly from the source tree in which it is built, but it is usually recommended to run the procedure that installs the essential components in standard system directories.

A.3.2 Prerequisites

The following are required or strongly recommended for installation from source code.

1. A Fortran 90 compiler. Fortran77-only compilers will not suffice. On most systems, the latest vendor-supplied compiler should be used.

   For IA32 Linux (for example Intel Pentium or AMD athlon) the recommended compilers are the Intel Compiler `ifort` version 9.0 or higher or the Portland `pgf90` compiler version 6.0 or higher. For Opteron and EM64T systems the recommended compilers are Portland version 6.0 or higher, Pathscale compiler `pathf90` version 2.3 or higher, or the Intel Compiler version 9.0 or higher. The full list of supported compilers can be found at http://www.molpro.net/supported.

2. GNU *make*, freely available from http://www.fsf.org and mirrors. GNU *make* must be used; most system-standard makes do not work. In order to avoid the use of a wrong *make*, and to suppress extensive output of GNU *make*, it may be useful to set an alias, e.g., `alias make='gmake -s'`.

3. The GNU *wget* utility for batch-mode http transfers, although not needed for installation, is essential for any subsequent application of patches that implement bug fixes.

4. About 10GB disk space (strongly system-dependent; more with large-blocksize file systems, and where binary files are large) during compilation. Typically 50Mb is needed for the finally installed program. Large calculations will require larger amounts of disk space.

5. One or more large scratch file systems, each containing a directory that users may write on. There are parts of the program in which demanding I/O is performed simultaneously on two different files, and it is therefore helpful to provide at least two filesystems on different physical disks if other solutions, such as striping, are not available. The directory names should be stored in the environment variables `$TMPDIR`, `$TMPDIR2`, `$TMPDIR3`,.... These variables should be set before the program is installed (preferably in `.profile` or `.cshrc`), since at some stages the installation procedures will check for them (cf. section A.3.6).

6. If the program is to be built for parallel execution then the Global Arrays toolkit is needed. We recommend version 4.0 or later (although earlier versions should also work). This is available from http://www.emsl.pnl.gov/docs/global and should be installed prior to compiling MOLPRO. In some installations, GA uses the *tcgmsg* parallel harness; on others, it sits on an existing MPI subsystem, and on others, it makes use of the native parallel subsystem (e.g., LAPI). MOLPRO can be built to use any of these, although it is not normally recommended to use MPI where other possibilities exist. For more information, see section

   A.3.3.

7. The source distribution of MOLPRO, which consists of a base compressed tar archive with a file name of the form `molpro.2006.1.tar.gz`, together, possibly, with one or more *module* archives with file names of the form `molpro.`*module*`.2006.1.tar.gz`. The modules contain code which is not generally distributed, or features which are not always required to install the code. An example is the program developers' kit (*module*=`develop`). The archives can be unpacked using `gunzip` and `tar`. All archives must be unpacked in the same directory. It is essential that the base archive is unpacked first, and advisable that any modules are unpacked before further installation.

   Under some circumstances, MOLPRO is delivered as a single tar file with a name of the form `molpro.all.2006.1.tar`. This archive contains all necessary base and module compressed tar archives, together with a shell script `unpack` which performs the unpacking described above.

A.3.3 Configuration

Once the distribution has been unpacked, identify the root directory that was created (normally `molpro2006.1`). In the following description, all directories are given relative to this root. Having changed to the root directory, you should check that the directory containing the Fortran compiler you want to use is in your PATH. Then run the command

```
./configure
```

which creates the file `CONFIG`. This file contains machine-dependent parameters, such as compiler options. Normally `CONFIG` will not need changing, but you should at the least examine it, and change any configuration parameters which you deem necessary. For further information, see any comments in the `CONFIG` file.

The `configure` procedure may be given command line options, and, normally, additionally prompts for a number of parameters:

1. On certain machines it is possible to compile the program to use either 32 or 64 bit integers, and in this case `configure` may be given a command-line option `-i4` or `-i8` respectively to override the default behaviour. Generally, the 64-bit choice allows larger calculations (files larger than 2Gb, more than 16 active orbitals), but can be slower if the underlying hardware does not support 64-bit integers (e.g., some IBM RS6000 hardware). Note that if `-i4` is used then large files (greater than 2Gb) are supported on most systems, but even then the sizes of MOLPRO records are restricted to 16 Gb since the internal addressing in MOLPRO uses 32-bit integers. If `-i8` is used, the record and file sizes are effectively unlimited.

2. In the case of building for parallel execution, the option -mpp or -mppx must be given on the command line. For the distinction between these two parallelism modes, please refer to the user manual, section 2.

   At present, Molpro supports several different cases: the GA library can be either built on top of tcgmsg, mpi, or myrinet; on the IBM SP platform, it can also be built with a GA library made with the LAPI target. configure prompts for the type (default tcgmsg), and then for the directory holding the associated libraries. Normally, tcgmsg is recommended, which is most efficient on most systems and also most easily installed. If a myrinet network is available, myrinet should be chosen. This requires in addition to the usual MPI libraries the gm library and mpirun_gm rather than mpirun. At present, the myrinet option has been tested only on Linux systems. The name of the MOLPRO executable is generated from the program version number, the library type and the machine architecture. It is then possible to install different versions simultaneously in the same MOLPRO tree; see section A.3.4.

   When building Global Arrays on Linux the default is *tcgmsg*. You should build with something similar to:

   ```
   make TARGET=...
   ```

   where TARGET is LINUX on a 32 bit Linux system, LINUX64 on a 64 bit system. On other platforms consult the README for a list of valid targets. The parallel job launcher needed to start molpro can be found at tcgmsg/ipcv4.0/parallel and should be copied into your PATH or it's location specified in configure

   In some cases you will need to specify the compiler you use when building molpro

   ```
   make TARGET=... FC=...
   ```

   where for example FC=ifort for the Intel compiler, FC=pgf90 for Portland or FC=pathf90 for Pathscale.

   When building with MPICH you should use something similar to:

   ```
   export MPI=/opt/mpich # or equivalent
   export PATH=$PATH:$MPI/bin
   export MPI_LIB=$MPI/lib
   export MPI_INCLUDE=$MPI/include
   export LIBMPI=-lmpich
   make TARGET=... FC=... USE_MPI=yes
   ```

   The details will vary from system to system. When running configure -mpp -mpptype mpi you should specify the location of the GA libraries and mpirun when prompted. When asked for the location of the MPI library

   ```
   Please give both the -L and -l loader options needed to access the MPI library
   ```

   it is necessary to give both the directory and library name even if the library would be found automatically by the linker, for example:

   ```
   -L/opt/mpich/lib -lmpich
   ```

   where the directory /opt/mpich/lib will vary between platforms. If any extra libraries are needed to link in the MPI library then they should not be specified here but manually added to the LIBS entry in CONFIG. After configure you should see something similar to this in your CONFIG file:

   ```
   MPI_LIB="-L/opt/mpich/lib -lmpich"
   MPPNAME="mpi"
   MPITYPE="mpich"
   MPIBASEDIR="/opt/mpich/"
   ```

3. If any system libraries are in unusual places, it may be necessary to specify them explicitly as the arguments to a `-L` command-line option.

4. `configure` asks whether you wish to use system BLAS subroutine libraries. MOLPRO has its own optimised Fortran version of these libraries, and this can safely be used. On most machines, however, it will be advantageous to use a system-tuned version instead. In the case of BLAS, you should enter a number between 1, 2 and 3; if, for example, you specify 2, the system libraries will be used for level 2 and level 1 BLAS, but MOLPRO's internal routines will be used for level 3 (i.e., matrix-matrix multiplication). Normally, however, one would choose either 0 or 3. If a system BLAS is chosen, you will be prompted to enter appropriate linker options (e.g. `-L/usr/lib -lblas`) to access the libraries.

   A special situation arises if 64-bit integers are in use (-i8), since on many platforms the system BLAS libraries only supports 32-bit integer arguments. In such cases (e.g., IBM, SGI, SUN) either 0 or 4 can be given for the BLAS level. BLAS=0 should always work and means that the MOLPRO Fortran BLAS routines are used. On some platforms (IBM, SGI, SUN) BLAS=4 will give better performance; in this case some 32-bit BLAS routines are used from the system library (these are then called from wrapper routines, which convert 64 to 32-bit integer arguments. Note that this might cause problems if more than 2 GB of memory is used).

   For good performance it is important to use appropriate BLAS libraries; in particular, a fast implementation of the matrix multiplication `dgemm` is very important for MOLPRO. Therefore you should use a system tuned BLAS library whenever available.

   Specification of BLAS libraries can be simplified by placing any relevant downloaded libraries in the directory `blaslibs`; `configure` searches this directory (and then, with lower priority, some potential system directories) for libraries relevant to the hardware, including that specified by a `-p3`, `-p4`, `-athlon`, `-amd64`, `-em64t` command line option.

   For Intel and AMD Linux systems we recommend the following BLAS libraries:

   mkl — The Intel Math Kernel Library (mkl), version 8.0 or higher http://www.intel.com/cd/software/products/asmo-na/eng/perflib/mkl

   atlas — The Atlas library http://math-atlas.sourceforge.net . You must use the atlas library specific to your processor:

Pentium III	`Linux_PIIISSE1`
Pentium 4,Xeon	`Linux_P4SSE2`
AMD Athlon	`Linux_ATHLON`
AMD Opteron	`Linux_HAMMER64SSE2_2` (64 bit)

   When using atlas MOLPRO will automatically compile in the extra lapack subroutines which do not come by default with the package and so the liblapack.a which comes with Atlas is sufficient. The appropriate linker options are:
   `-L` *`blasdir`* `-lcblas -lf77blas -latlas`

   acml — For Opteron systems then ACML http://developer.amd.com/acml.aspx is the preferred blas library.

   SGI Altix can use the `scsl` library is preferred. HP platforms can use the `mlib` math library. IBM Power platforms can use the `essl` package.

5. `configure` prompts for the destination directory (`INSTBIN`) for final installation of the MOLPRO executable. This directory should be one normally in the PATH of all users

who will access MOLPRO, and its specification will depend on whether the installation is private or public.

6. `configure` prompts for the destination directory (`INSTLIB`) for installation of ancillary files which are required for program execution.

7. `configure` will attempt to contact the molpro webserver and download an appropriate licence key if it does not a token in the file `$HOME/.molpro/token`. This token will be copied to `INSTLIB/.token` during installation.

8. `configure` prompts for the destination directory for documentation. This should normally be a directory that is mounted on a worldwide web server.

9. `configure` prompts for the destination directory for the CGI scripts that control the delivery of documentation. This might be the same directory as (h), but some web servers require a particular special directory to be used.

The latter two parameters are relevant only if the documentation is also going to be installed from this directory (see below).

The following command-line options are recognized by `configure`.

`-batch`	disables the prompting described above.
`-i8` |`-i4`	forces the use of 8- or 4-byte integers respectively.
`-L` *lib*	specifies any additional directories containing system libraries to be scanned at link time.
`-blas 0|1|2|3|4`	specifies system BLAS level, as described above.
`-mpp` |`-nompp`	controls whether compilation is to be for MPP parallelism (see above).
`-ifort` |`-pgf` |`-path`	controls whether the Intel (ifort), Portland (pgf) or Pathscale (path) compiler is to be used on Linux systems.
`-f` *ftcflag*	adds a token to the specifiers for the Fortran preprocessor *ftc*.
`-largefiles` |`-nolargefiles`	controls whether large file ($>$ 2Gb) support is wanted. This option is not relevant or used on all architectures. All modern Linux distributions should support large files.
`-p3` |`-p4` |`-athlon` |`-amd64` |`-em64t`	specifically identifies a particular hardware in order to force appropriate run-time libraries where possible. These options are supported only on Linux systems. If any of these options is given, the MOLPRO executable will be named `molpro_p3.exe`, `molpro_p4.exe`, or `molpro_athlon.exe` (in the mpp case, e.g., `molpro_p3_tcgmsg.exe`). It is possible to install different platform variants simultaneously in the same MOLPRO tree; see section A.3.4.

A.3.4 Configuration of multiple executables in the same MOLPRO tree

On Linux systems, it may be desirable to have optimized versions for different hardware architectures, like `p3`, `p4`, `athlon` or `x86_64` (see section A.3.3). Provided the compiler options are the same (i.e. neither `p4`, nor `athlon` specific), the different versions differ only by the use of specific BLAS libraries. It is then possible to install different executables for each case in the same MOLPRO tree, without the need to recompile the program. To do so, one first needs to run

configure for each case, and specify the appropriate libraries when configure prompts for them. These library paths are all stored in the file CONFIG, generated by configure. Subsequently,

make ARCH=*procname*

will link the desired version, where *procname* can be p3, p4, or athlon. This will generate the executable molpros_2006_0_i4_*procname*.exe. If the ARCH option is not given, the last one configured will be generated.

In addition, a file molpros_2006_0_i4_*procname*.rc will be generated for each case, which defines the running environment and may also contain system dependent tuning parameters (see section A.3.7). A specific executable can then be requested using

molpro -rcfile molpros_2006_0_i4_*procname*.rc input

More conveniently, one can set the Unix environment variable MOLPRO_RCFILE to molpros_2006_0_i4_*procname*.rc and then simply use molpro without an option. The recommended mechanism is to set the environment variable MOLPRO_RCFILE in the default environment (.cshrc, .profile) as appropriate on a given machine.

Similarly, different MPP version can also be installed in one MOLPRO tree (but the tree for parallel and serial versions must be distinct!). In this case, one can run configure for tcgmsg, mpi, and/or myrinet (and in addition with -p3, -p4, and/or -athlon), and then link using

make MPPLIB=*libname*

where *libname* can be tcgmsg, mpi, or myrinet. The ARCH and MPPLIB options can be combined, e.g.,

make MPPLIB=*libname* ARCH=*procname*

and this will generate the executable molprop_2006_0_i4_*procname_libname*.exe and the default file molprop_2006_0_i4_*procname_libname*.rc.

As described above, the different executables can then be chosen on a specific machine by setting the environment variable MOLPRO_RCFILE to molprop_2006_0_i4_*procname_libname*.rc.

Note that if MOLPRO_RCFILE is not set, molpro.rc will be used by default, which will correspond to the last molprop_2006_0_i4_*procname_libname*.rc generated.

A.3.5 Compilation and linking

After configuration, the remainder of the installation is accomplished using the GNU *make* command. Remember that the default *make* on many systems will not work, and that it is essential to use GNU *make* (cf. section A.3.2). Everything needed to make a functioning program together with all ancillary files is carried out by default simply by issuing the command

make

in the MOLPRO base directory. Most of the standard options for GNU *make* can be used safely; in particular, -j can be used to speed up compilation on a parallel machine. The program can then be accessed by making sure the bin/ directory is included in the PATH and issuing the command molpro.

A.3.6 Adjusting the default environment for MOLPRO

The default running options for MOLPRO are stored in the file `bin/molpro.rc`. After program installation, either using RPMs or from source files, this file should be reviewed and adjusted, if necessary. Particular attention should be payed to some or all of the following (see User's manual for full discussion of options).

`-d` *dir1:dir2:...* where *dir1:dir2:...* is a list of directories which may be used for creating scratch files. Each of the directories should be writable by those who will use the program, and the directory specification may contain embedded environment variables in shell form, for example `$TMPDIR` or `/tmp/$USER`; these will be expanded at run time. If multiple scratch file systems are available, it is advantageous to present a list of directories of which there is one in each file system. Some parts of MOLPRO present extreme I/O demands, and it is therefore important to be careful in optimizing the provision and specification of scratch directories.

Note that in the building of `bin/molpro.rc`, the environment variables `$TMPDIR`, `$TMPDIR2`, `$TMPDIR3`,... are used to construct the list of scratch directories for the `-d` option. Thus, these environment variables should at make time be filled with the names of directories on each available scratch file system (cf. section A.3.3).

`-I` *directory* This determines the destination of permanent integral files. At run time this file is located in the first directory specified after `-d`, (i.e., *dir1*, see above), but after completion of the job the file will be copied to the directory given after `-I`. Since the integral file can be very large, it is normally recommended that *directory* is identical to *dir1* (this is the default). Then no copying will take place. On some main frames, the scratch directory is erased automatically after a job has terminated, and in such cases a different `-I` directory, e.g., `$HOME/int`, can be specified (environment variables will be expanded at run time). In view of the large integral file sizes, this should be used with care, however. Note that in parallel runs with more than 1 processor the integral file will never be copied, and cannot be restarted.

`-W` *directory* This determines the destination of permanent wavefunction (dump) files used for storing information like orbitals or CI-vectors etc. These files are essential for restarting a job. As explained for the integral files above, permanent wavefunction files will be copied to *directory* after completion of the job. The default for *directory* is `$HOME/wfu`.

`-k` *key* where *key* is the licence key, obtainable as described in section A.1.

`-m, -G` The default local memory and GA memory should be checked to be appropriate for the hardware environment.

`-n, -N` The number of processors or their identity can be specified explicitly in the configuration file, but very often it is neither desirable nor necessary to do so. Where possible, the `molpro` program extracts a reasonable default for the node specification from the controlling batch system (e.g. LoadLeveler, PBS). Usually the user will want to either specify `-n` explicitly on the command line, or rely on `molpro`'s attempts to get it from the batch system.

A.3.7 Tuning

MOLPRO can be tuned for a particular system by running in the root directory the command

```
molpro tuning.com
```

This job automatically determines a number of tuning parameters and appends these to the file `bin/molpro.rc`. Using these parameters, MOLPRO will select the best BLAS routines depending on the problem size. This job should run on an empty system. It may typically take 10 minutes, depending on the processor speed, and you should wait for completion of this run before doing the next steps.

A.3.8 Testing

At this stage, it is essential to check that the program has compiled correctly. The makefile target *test* (i.e., command `make test`) will do this using the full suite of test jobs, and although this takes a significantly long time, it should always be done when porting for the first time. A much faster test, which checks the main routes through the program, can be done using `make quicktest`. For parallel installation, it is highly desirable to perform this validation with more than one running process. This can be done conveniently through the `make` command line as, for example,

```
make MOLPRO_OPTIONS=-n2 test
```

If any test jobs fail, the cause must be investigated. It may be helpful in such circumstances to compare the target platform with the lists of platforms on which MOLPRO is thought to function at http://www.molpro.net/supported. If, after due efforts to fix problems of a local origin, the problem cannot be resolved, the developers of MOLPRO would appreciate receiving a report. There is a web-based mechanism at http://www.molpro.net/bug at which as many details as possible should be filled in. `make test` produces a file of the form `testjobs/report.*.tar.gz` that contains some details of the MOLPRO installation, and the output files of the failing test jobs. You should normally attach this file to the bug report. Please note that the purpose of such bug reports is to help the developers improve the code, and not for providing advice on installation or running.

A.3.9 Installing the program for production

Although the program can be used in situ, it is usually convenient to copy only those files needed at run time into appropriate installation directories as specified at configuration time (see section A.3.3) and stored in the file `CONFIG`. To install the program in this way, do

```
make install
```

The complete source tree can then be archived and deleted. If multiple Linux executables have been generated (see section A.3.4), they can be installed using

`make MPPLIB=`*libname* `ARCH=`*procname* `install`

into the same `INSTBIN` and `INSTLIB` directories (but note that the `INSTLIB` directories must be distinct for i4 and i8 versions). The overall effect of this is to create in the `INSTBIN` directory an executable command file of the form *name_arch_mpplib*, where *name* is one of `molpros`, `molprop`, corresponding to serial or parallel execution. If the file `INSTBIN/`*name* does not already exist, or if the variable `DEFAULT` is set during `make install` (i.e., `make DEFAULT=1 install`), then a symbolic link is made to `INSTBIN/`*name*. Furthermore, If the file `INSTBIN/molpro` does not already exist, or if the variable `DEFAULT` is set to `molpro`

during `make install` then a symbolic link is made from `INSTBIN/`*name* to `INSTBIN/molpro`. The overall effect of this cascade of links is to provide, in the normal case, the commands `molpro` and one or both of `molpros` (serial) and `molprop` (parallel) for normal use, with the long names remaining available for explicit selection of particular variants. As with the uninstalled program, the environment variable `MOLPRO_RCFILE` can be used to override the choice of configuration file.

For normal single-variant installations, none of the above has to be worried about, and the `molpro` command will be available from directory `INSTLIB`.

During the install process the key from `$HOME/.molpro/token` is copied to `INSTLIB/.token` so that the key will work for all users of the installed version.

When the program has been verified and/or installed, the command `make clean` can be used to remove compilation logs. `make veryclean` will remove all binary and object files, retaining only those files included in the original distribution; it is usually recommended that this is not done, as it implies that to apply future updates and bug fixes, the whole program will have to be recompiled.

A.3.10 Getting and applying patches

Normally, the distribution when downloaded is fully up to date, and initial patching is not necessary. However, bug fixes and updates may be desired subsequently. The mechanism for updating MOLPRO source code with bug fixes and new features is through the provision of self-contained patch files, which, when applied, replace or add files, and store the replaced code in order to allow later reversion to the original. Those patches that are available can be seen at http://www.molpro.net/patch/2006.1 , whilst a list of those already installed is printed when running the program. Patch files automatically outdate any targets that need rebuilding as a result of the patch; for example, relevant object files are removed. Thus, after all patches have been applied, it is usually necessary to rebuild the program using `make`.

The order in which patches are applied and removed is important. Some patches are prerequisites of others, and some patches are 'parents' of one or more 'children': the parent and child patches have one or more files in common, but the parent is older than the child. Individual patch scripts will themselves refuse to apply or revert if rules based on these considerations would be violated. In order to deal with this issue smoothly, a program `patcher` is provided to manage the application and removal of one or more patches. `patcher` attempts to sort the order in which patches are applied or reverted so as to avoid such conflicts; it will also, if necessary, revert and reapply patches.

In order to run `patcher` you should issue the command:

```
make patch
```

This should be sufficient for most purposes. `patcher` will be built if has not yet been compiled and then it will contact the webserver, apply any available patches and then return the patchlevel that you have reached.

If it is necessary to pass arguments to the `patcher` program then in the top-level directory issue the command

```
./patcher  [--apply | --revert | --list]
           [--cache-directory] [--user] [--password]
           [--url] [--local]
           [--verbose] [--no-action] patch1 patch2 ....
```

It can operate in one of three possible modes according to the options

--apply, -a	(default) Apply (i.e. install) patches
--revert, -r	Revert (i.e. remove) patches
--list, -l	List available and installed patches

The list of patches to remove or install can be given on the command line after all options as an explicit list of either patch names or, in the case of application, patch files. Alternatively and usually, for the case of application, one can through options request either all patches that are in a local cache, or all patches that are available.

The MOLPRO patches from the central web server (default http://www.molpro.net), are cached by this program in a local directory (default `$HOME/.molpro/cache`). Access to the web server typically has to be authenticated; the first time you run this program, you can specify your username and password through command-line options, or else the program will prompt for them. They are then remembered in the file `CONFIG` in the cache directory.

In case of problems, first consult the file `patcher.log`, which contains the output from individual patch applications and reversions.

The following options can be given.

--cache-directory, -c d	location of cache directory.
--verbose, -v	Increase amount of information printed. Multiple –verbose options can be used.
--noverbose	Decrease amount of information printed.
--url	URL of web server.
--user, -u u	Username for web server.
--password, -p p	Password for web server.
--noaction, -n	No applications or reversions are actually done. Useful for seeing what would happen without doing it.
--local	Don't attempt to access the web server, but use only local files.
--token, -k	Download your licence key
--ssl, -s	Use SSL when contacting the webserver
--nossl, -i	Turn off SSL use

Examples:

```
patcher
```

Applies all patches that are available, but not yet installed. This is the normal use of the utility in bringing the copy of the source tree up to date with all available updates.

```
patcher -l
```

Lists installed and available patches.

```
patcher -r xx yy
```

Reverts patches xx and yy.

```
patcher -n
```

Loads all uninstalled patches into the cache for later use.

```
patcher --local
```

Applies all patches in the cache; no network connection needed.

A.3.11 Installation of documentation

The documentation is available on the web at http://www.molpro.net/info/users. It is also included with the source code. The PDF user's manual is found in the directory `molpro2006.1/doc/manual.pdf`, with the HTML version in the directory `molpro2006.1/doc/manual` (top level file is `manual.html`). The documentation can be copied to its final destination as specified in the `CONFIG` file generated by the `configure` command. To install the documentation and interactive basis set tool, issue `make install` in the `doc` directory. Numerous example input files are included in the manual, and can alternatively be seen in the directory `molpro2006.1/examples`.

B Recent Changes

B.1 New features of MOLPRO2006.1

There are very many new features and enhancements in MOLPRO version 2006.1, most notably efficient density fitting methods, explicitly correlated methods, local coupled cluster methods, and several new gradient programs: following:

1. More consistent input language and input pre-checking.
2. More flexible basis input, allowing to handle multiple basis sets
3. New more efficient density functional implementation, additional density functionals.
4. Low-order scaling local coupled cluster methods with perturbative treatment of triples excitations (LCCSD(T) and variants like LQCISD(T))
5. Efficient density fitting (DF) programs for Hartree-Fock (DF-HF), Density functional Kohn-Sham theory (DF-KS), Second-order Møller-Plesset perturbation theory (DF-MP2), as well as for all local methods (DF-LMP2, DF-LMP4, DF-LQCISD(T), DF-LCCSD(T))
6. Analytical QCISD(T) gradients
7. Analytical MRPT2 (CASPT2) and MS-CASPT2 gradients, using state averaged MCSCF reference functions
8. Analytical DF-HF, DF-KS, DF-LMP2, and DF-SCS-LMP2 gradients
9. Explicitly correlated methods with density fitting: DF-MP2-R12/2A', DF-MP2-F12/2A' as well as the local variants DF-LMP2-R12/2*A(loc) and DF-LMP2-F12/2*A(loc).
10. Coupling of multi-reference perturbation theory and configuration interaction (CIPT2)
11. DFT-SAPT
12. Transition moments and transition Hamiltonian between CASSCF and MRCI wavefunctions with different orbitals.
13. A new spin-orbit integral program for generally contracted basis sets.
14. Douglas-Kroll-Hess Hamiltonian up to arbitrary order.
15. Improved procedures for geometry optimization and numerical Hessian calculations, including constrained optimization.
16. Improved facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients.
17. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.
18. Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (`mppx Version`).
19. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).
20. Additional output formats for tables (XHTML, LaTeX, Maple, Mathematica, Matlab and comma-separated variables), orbitals and basis sets (XML), and an optional well-formed XML output stream with important results marked up.

B.2 New features of MOLPRO2002.6

Relative to version 2002.1, there are the following changes and additions:

1. Support for IA-64 Linux systems (HP and NEC) and HP-UX 11.22 for IA-64 (Itanium2).
2. Support for NEC-SX systems.
3. Support for IBM-power4 systems.
4. Modified handling of Molpro system variables. The `SET` command has changed (see sections 8 and 8.4).
5. The total charge of the molecule can be specified in a variable `CHARGE` or on the `WF` card, see section 4.9.
6. Improved numerical geometry optimization using symmetrical displacement coordinates (see sections 38.2 and 39).
7. Improved numerical frequency calculations using the symmetry (`AUTO` option, see section 40).

B.3 New features of MOLPRO2002

Relative to version 2000.1, there are the following principal changes and additions:

1. Modules direct and local are now included in the base version. This means that integral-direct procedures as described in

   M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999),

   linear-scaling local MP2, as described in

   G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998),
   M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999),
   G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, J. Chem. Phys. **113**, 9443 (2000),

   as well as LMP2 gradients as described in

   A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **108**, 5185 (1998)

   are now available without special license. The linear scaling LCCSD(T) methods as described in

   M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001),
   M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000),
   M. Schütz, J. Chem. Phys. **113**, 9986 (2000)

   will be made available at a later stage.
2. QCISD gradients as described in Phys. Chem. Chem. Phys. **3**, 4853 (2001) are now available.
3. Additional and more flexible options for computing numerical gradients and performing geometry optimizations.
4. A large number of additional density functionals have been added, together with support for the automated functional implementer described in Comp. Phys. Commun. **136** 310–318 (2001).

5. Multipole moments of arbitrary order can be computed.

6. Further modules have been parallelized, in particular the CCSD(T) and direct LMP2 codes. The parallel running procedures have been improved. The parallel version is available as an optional module.

7. The basis set library has been extended.

8. Some subtle changes in the basis set input: it is not possible any more that several one-line basis input cards with definitions for individual atoms follow each other. Each new basis card supercedes previous ones. Either all specifications must be given on *one* `BASIS` card, or a basis input block must be used. `BASIS,NAME` is now entirely equivalent to `BASIS=NAME`, i.e. a global default basis set is defined and the variable `BASIS` is set in both cases.

9. Pseudopotential energy calculations can now be performed with up to *i*-functions, gradients with up to *h*-functions.

10. Many internal changes have been made to make MOLPRO more modular and stable. Support has been added for recent operating systems on Compaq, HP, SGI, SUN, and Linux. The patching system has been improved.

B.4 Features that were new in MOLPRO2000

Relative to version 98.1, there are the following principal changes and additions:

1. There was a fundamental error in the derivation of the spin-restricted open-shell coupled-cluster equations in J. Chem. Phys. 99, 5129 (1993) that is also reflected in the RCCSD code in MOLPRO version 98.1 and earlier. This error has now been corrected, and an erratum has been published in J. Chem. Phys. **112**, 3106 (2000). Fortunately, the numerical implications of the error were small, and it is not anticipated that any computed properties will have been significantly in error.

2. There was a programming error in the transformation of gradients from Cartesian to internal coordinates, which in some cases resulted in slow convergence of geometry optimizations. The error is now fixed.

3. Vibrational frequencies formerly by default used average atomic masses, rather than those of the most common isotopes, which is now the default behaviour.

4. MCSCF second derivatives (author Riccardo Tarroni) added (preliminary version, only without symmetry). Frequency and geometry optimization programs are modified so that they can use the analytic Hessian.

5. New internally contracted multi-reference second-order perturbation theory code (author Paolo Celani) through command `RS2C`, as described in P. Celani and H.-J. Werner, J. Chem. Phys. **112**, 5546 (2000).

6. EOM-CCSD for excited states (author Tatiana Korona).

7. QCISD dipole moments as true analytical energy derivatives (author Guntram Rauhut).

8. Linear scaling (CPU and memory) LMP2 as described by G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998).
M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).

9. Improved handling of basis and geometry records. 98.1 and 99.1 dump files can be restarted, but in case of problems with restarting old files, add `RESTART,NOGEOM` immediately after the `file` card. Also, if there are unjustified messages coming up in very large cases about "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" try `ORBITAL,`*record*`,NOCHECK`. (This can happen for cases with more than 100 atoms, since the old version was limited to 100).
10. Reorganization and generalization of basis input. Increased basis library.
11. Counterpoise geometry optimizations.
12. Improved running procedures for MPP machines. Parallel direct scf and scf gradients are working. These features are only available with the MPP module, which is not yet being distributed.
13. Important bugfixes for DFT grids, CCSD with paging, finite field calculations without core orbitals, spin-orbit coupling.
14. Many other internal changes.

As an additional service to the MOLPRO community, an electronic mailing list has been set up to provide a forum for open discussion on all aspects of installing and using MOLPRO. The mailing list is intended as the primary means of disseminating hints and tips on how to use Molpro effectively. It is not a means of raising queries directly with the authors of the program. For clearly demonstrable program errors, reports should continue to be sent to molpro-support@molpro.net ; however, 'how-to' questions sent there will merely be redirected to this mailing list.

In order to subscribe to the list, send mail to molpro-user-request@molpro.net containing the text `subscribe`; for help, send mail containing the text `help`.

Messages can be sent to the list (molpro-user@molpro.net), but this can be done only by subscribers. Previous postings can be viewed in the archive at http://www.molpro.net/molpro-user/archive irrespective of whether or not you subscribe to the list. Experienced Molpro users are encouraged to post responses to queries raised. Please do contribute to make this resource mutually useful.

B.5 Facilities that were new in MOLPRO98

MOLPRO98 has the full functionality of MOLPRO96, but in order to make the code more modular and easier to use and maintain, a number of structural changes have been made. In particular, the number of different records has been significantly reduced. The information for a given wavefunction type, like orbitals, density matrices, fock matrices, occupation numbers and other information, is now stored in a single dump record. Even different orbital types, e.g., canonical, natural, or localized orbitals, are stored in the same record, and the user can subsequently access individual sets by keywords on the `ORBITAL` directive. New facilities allow the use of starting orbitals computed with different basis sets and/or different symmetries for SCF or MCSCF calculations. The default starting guess for SCF calculations has been much improved, which is most useful in calculations for large molecules. The use of special procedures for computing non-adiabatic couplings or diabatization of orbitals has been significantly simplified. We hope that these changes make the program easier to use and reduce the probability of input errors. However, in order to use the new facilities efficiently, even experienced MOLPRO users should read the sections *RECORDS* and *SELECTING ORBITALS AND DENSITY MATRICES* in the manual. It is likely that standard MOLPRO96 inputs still work, but changes may be required in more special cases involving particular records for orbitals, density matrices, or operators.

All one-electron operators needed to compute expectation values and transition quantities are now stored in a single record. Operators for which expectation values are requested can be selected globally for all programs of a given run using the global GEXPEC directive, or for a specific program using the EXPEC directive. All operators are computed automatically when needed, and the user does not have to give input for this any more. See section *ONE-ELECTRON OPERATORES AND EXPECTATION VALUES* of the manual for details.

Due to the changed structure of dump and operator records, the utility program MATROP has a new input syntax. MOLPRO96 inputs for MATROP do not work any more.

In addition to these organizational changes, a number of new programs have been added. Analytic energy gradients can now be evaluated for MP2 and DFT wavefunctions, and harmonic vibrational frequencies, intensities, and thermodynamic quantities can be computed automatically using finite differences of analytical gradients. Geometry optimization has been further improved, and new facilities for reaction path following have been added.

An interface to the graphics program MOLDEN has been added, which allows to visualize molecular structures, orbitals, electron densities, or vibrations.

Integral-direct calculations, in which the two-electron integrals in the AO basis are never stored on disk but always recomputed when needed, are now available for all kinds of wavefunctions, with the exception of perturbative triple excitations in MP4 and CCSD(T) calculations. This allows the use of significantly larger basis sets than was possible before. The direct option can be selected globally using the GDIRECT command, or for a specific program using the DIRECT directive. See section *INTEGRAL DIRECT METHODS* in the manual for details. Note that the DIRECT module is optional and not part of the basic MOLPRO distribution.

Local electron correlation methods have been further improved. In combination with the integral-direct modules, which implement efficient prescreening techniques, the scaling of the computational cost with molecular size is dramatically reduced, approaching now quadratic or even linear scaling for MP2 and higher correlation methods. This makes possible to perform correlated calculations for much larger molecules than were previously feasible. However, since these methods are subject of active current research and still under intense development, we decided not to include them in the current MOLPRO release. They will be optionally available in one of the next releases.

C Density functional descriptions

C.1 ALYP: Lee, Yang and Parr Correlation Functional

See reference [7] for more details.

$$K = 4\frac{A\rho_\alpha\rho_\beta Z}{\rho} + AB\omega\left(1/18\,\rho_\alpha\rho_\beta\left(47-7\,\delta\right)\sigma - 2/3\,\rho^2\sigma\right) + \sum_s AB\omega\left(\rho_s\rho_{\bar{s}}\left(8\,2^{2/3}e\left(\rho_s\right)^{8/3} - \left(5/2-1/18\,\delta\right)\sigma_{ss} - 1/9\,\frac{\left(\delta-11\right)\rho_s\sigma_{ss}}{\rho}\right) + \left(2/3\,\rho^2 - \left(\rho_s\right)^2\right)\sigma_{\bar{s}\bar{s}}\right), \tag{10}$$

where

$$\omega = e^{-\frac{c}{\sqrt[3]{\rho}}}Z\rho^{-11/3}, \tag{11}$$

$$\delta = \frac{c}{\sqrt[3]{\rho}} + \frac{dZ}{\sqrt[3]{\rho}}, \tag{12}$$

$$B = 0.04918, \tag{13}$$

$$A = 0.132, \tag{14}$$

$$c = 0.2533, \tag{15}$$

$$d = 0.349, \tag{16}$$

$$e = 3/10\,3^{2/3}\left(\pi^2\right)^{2/3} \tag{17}$$

and

$$Z = \left(1+\frac{d}{\sqrt[3]{\rho}}\right)^{-1}. \tag{18}$$

C.2 B86MGC: Xαβγ with Modified Gradient Correction

B86 with modified gradient correction for large density gradients. See reference [8] for more details.

$$K = \sum_s -c\left(\rho_s\right)^{4/3} - \frac{\beta\left(\chi_s\right)^2\left(\rho_s\right)^{4/3}}{\left(1+\lambda\left(\chi_s\right)^2\right)^{4/5}}, \tag{19}$$

where

$$c = 3/8\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}, \tag{20}$$

$$\beta = 0.00375 \tag{21}$$

and

$$\lambda = 0.007. \tag{22}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = -c\left(\rho_s\right)^{4/3} - \frac{\beta\left(\chi_s\right)^2\left(\rho_s\right)^{4/3}}{\left(1+\lambda\left(\chi_s\right)^2\right)^{4/5}}. \tag{23}$$

C.3 B86R: Xαβγ Re-optimised

Re-optimised β of B86 used in part 3 of Becke's 1997 paper. See reference [9] for more details.

$$K = \sum_s -\frac{c\left(\rho_s\right)^{4/3}\left(1+\beta\left(\chi_s\right)^2\right)}{1+\lambda\left(\chi_s\right)^2}, \tag{24}$$

where

$$c = 3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}, \tag{25}$$

$$\beta = 0.00787 \tag{26}$$

and

$$\lambda = 0.004. \tag{27}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = -\frac{c\left(\rho_s\right)^{4/3}\left(1+\beta\left(\chi_s\right)^2\right)}{1+\lambda\left(\chi_s\right)^2}. \tag{28}$$

C.4 B86: Xαβγ

Divergence free semiempirical gradient-corrected exchange energy functional. $\lambda = \gamma$ in ref. See reference [10] for more details.

$$K = \sum_s -\frac{c\left(\rho_s\right)^{4/3}\left(1+\beta\left(\chi_s\right)^2\right)}{1+\lambda\left(\chi_s\right)^2}, \tag{29}$$

where

$$c = 3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}, \tag{30}$$

$$\beta = 0.0076 \tag{31}$$

and

$$\lambda = 0.004. \tag{32}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = -\frac{c\left(\rho_s\right)^{4/3}\left(1+\beta\left(\chi_s\right)^2\right)}{1+\lambda\left(\chi_s\right)^2}. \tag{33}$$

C.5 B88CMASK:

Xq is the q component of an exchange functional with parameters t and u to be used in conjunction with B88C. See reference [11] for more details.

$$\begin{aligned} K = & -0.8\,\rho_\alpha\rho_\beta q^2\left(1-\frac{\ln\left(1+q\right)}{q}\right) \\ & +\sum_s -0.01\,\rho_s dz^4\left(1-2\,\frac{\ln\left(1+1/2\,z\right)}{z}\right), \end{aligned} \tag{34}$$

where

$$q = t\,(x+y)\,, \tag{35}$$

$$x = 0.5\,\frac{\rho_\alpha}{Xa}, \tag{36}$$

$$y = 0.5\,\frac{\rho_\beta}{Xb}, \tag{37}$$

$$online4, syntaxerror, \text{`} : \text{`} unexpected\ ::\text{`} \tag{38}$$

$$z = 2\,ur, \tag{39}$$

$$r = 0.5\,\frac{\rho_s}{Xs}, \tag{40}$$

$$online4, syntaxerror, \text{`} : \text{`} unexpected\ ::\text{`} \tag{41}$$

$$d = \tau_s - 1/4\,\frac{\sigma_{ss}}{\rho_s}, \tag{42}$$

$$c = 3/8\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}, \tag{43}$$

$$\beta = 0.00375 \tag{44}$$

and

$$\lambda = 0.007. \tag{45}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = -0.01\,\rho_s dz^4 \left(1 - 2\,\frac{\ln\left(1 + 1/2\,z\right)}{z}\right). \tag{46}$$

C.6 B88C: Becke88 Correlation Functional

Correlation functional depending on B86MGC exchange functional with empirical atomic parameters, t and u. The exchange functional that is used in conjunction with B88C should replace B88MGC here. See reference [11] for more details.

$$\begin{aligned} K = &-0.8\,\rho_\alpha\rho_\beta q^2 \left(1 - \frac{\ln\left(1+q\right)}{q}\right) \\ &+ \sum_s -0.01\,\rho_s dz^4 \left(1 - 2\,\frac{\ln\left(1 + 1/2\,z\right)}{z}\right), \end{aligned} \tag{47}$$

where

$$q = t\,(x+y)\,, \tag{48}$$

$$x = 0.5\,\left(c\sqrt[3]{\rho_\alpha} + \frac{\beta\,(\chi_\alpha)^2\sqrt[3]{\rho_\alpha}}{\left(1 + \lambda\,(\chi_\alpha)^2\right)^{4/5}}\right)^{-1}, \tag{49}$$

$$y = 0.5 \left(c \sqrt[3]{\rho_\beta} + \frac{\beta \left(\chi_\beta\right)^2 \sqrt[3]{\rho_\beta}}{\left(1 + \lambda \left(\chi_\beta\right)^2\right)^{4/5}} \right)^{-1}, \tag{50}$$

$$t = 0.63, \tag{51}$$

$$z = 2\,ur, \tag{52}$$

$$r = 0.5\,\rho_s \left(c \left(\rho_s\right)^{4/3} + \frac{\beta \left(\chi_s\right)^2 \left(\rho_s\right)^{4/3}}{\left(1 + \lambda \left(\chi_s\right)^2\right)^{4/5}} \right)^{-1}, \tag{53}$$

$$u = 0.96, \tag{54}$$

$$d = \tau_s - 1/4 \frac{\sigma_{ss}}{\rho_s}, \tag{55}$$

$$c = 3/8 \sqrt[3]{34}^{2/3} \sqrt[3]{\pi^{-1}}, \tag{56}$$

$$\beta = 0.00375 \tag{57}$$

and

$$\lambda = 0.007. \tag{58}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = -0.01\,\rho_s dz^4 \left(1 - 2 \frac{\ln\left(1 + 1/2\,z\right)}{z} \right). \tag{59}$$

C.7 B88: Becke88 Exchange Functional

See reference [1] for more details.

$$K = \sum_s -\left(\rho_s\right)^{4/3} \left(c + \frac{\beta \left(\chi_s\right)^2}{1 + 6\,\beta\,\chi_s \operatorname{arcsinh}\left(\chi_s\right)} \right), \tag{60}$$

where

$$c = 3/8 \sqrt[3]{34}^{2/3} \sqrt[3]{\pi^{-1}} \tag{61}$$

and

$$\beta = 0.0042. \tag{62}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = -\left(\rho_s\right)^{4/3} \left(c + \frac{\beta \left(\chi_s\right)^2}{1 + 6\,\beta\,\chi_s \operatorname{arcsinh}\left(\chi_s\right)} \right). \tag{63}$$

C.8 B95: Becke95 Correlation Functional

tau dependent Dynamical correlation functional. See reference [12] for more details.

$$K = \frac{E}{1 + l\left(\left(\chi_\alpha\right)^2 + \left(\chi_\beta\right)^2\right)} + \sum_s \frac{F\varepsilon\left(\rho_s, 0\right)}{H\left(1 + \nu\left(\chi_s\right)^2\right)^2}, \tag{64}$$

where

$$E = \varepsilon\left(\rho_\alpha, \rho_\beta\right) - \varepsilon\left(\rho_\alpha, 0\right) - \varepsilon\left(\rho_\beta, 0\right), \tag{65}$$

$$l = 0.0031, \tag{66}$$

$$F = \tau_s - 1/4\,\frac{\sigma_{ss}}{\rho_s}, \tag{67}$$

$$H = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho_s\right)^{5/3}, \tag{68}$$

$$\nu = 0.038, \tag{69}$$

$$\varepsilon\left(\alpha,\beta\right) = \left(\alpha+\beta\right)\left(e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right) - \frac{e\left(r\left(\alpha,\beta\right),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1-\left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c} + \left(e\left(r\left(\alpha,\beta\right),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right) - e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\right), \tag{70}$$

$$r\left(\alpha,\beta\right) = 1/4\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}}, \tag{71}$$

$$\zeta\left(\alpha,\beta\right) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{72}$$

$$\omega\left(z\right) = \frac{\left(1+z\right)^{4/3} + \left(1-z\right)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{73}$$

$$e\left(r,t,u,v,w,x,y,p\right) = -2t\left(1+ur\right)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{74}$$

$$c = 1.709921, \tag{75}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{76}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{77}$$

$$V = [7.5957, 14.1189, 10.357], \tag{78}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{79}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{80}$$

$$Y = [0.49294, 0.62517, 0.49671] \tag{81}$$

and

$$P = [1, 1, 1]. \tag{82}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = \frac{F\varepsilon(\rho_s, 0)}{H\left(1 + \nu\left(\chi_s\right)^2\right)^2}. \tag{83}$$

C.9 B97R: Density functional part of B97 Re-parameterized by Hamprecht et al

Re-parameterization of the B97 functional in a self-consistent procedure by Hamprecht et al. This functional needs to be mixed with 0.21*exact exchange. See reference [13] for more details.

$$\begin{aligned} K = & \left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) - \varepsilon\left(\rho_\alpha, 0\right) - \varepsilon\left(\rho_\beta, 0\right)\right)\left(A_0 + A_1\eta\left(d, \lambda_1\right) + A_2\left(\eta\left(d, \lambda_1\right)\right)^2\right) \\ & + \sum_s \varepsilon\left(\rho_s, 0\right)\left(B_0 + B_1\eta\left(\left(\chi_s\right)^2, \lambda_2\right) + B_2\left(\eta\left(\left(\chi_s\right)^2, \lambda_2\right)\right)^2\right) \\ & - 3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}\left(\rho_s\right)^{4/3}\left(C_0 + C_1\eta\left(\left(\chi_s\right)^2, \lambda_3\right) + C_2\left(\eta\left(\left(\chi_s\right)^2, \lambda_3\right)\right)^2\right), \end{aligned} \tag{84}$$

where

$$d = 1/2\left(\chi_\alpha\right)^2 + 1/2\left(\chi_\beta\right)^2, \tag{85}$$

$$\eta(\theta, \mu) = \frac{\mu\theta}{1 + \mu\theta}, \tag{86}$$

$$\begin{aligned} \varepsilon(\alpha, \beta) = (\alpha + \beta)\Bigg(& e\left(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right) \\ & - \frac{e\left(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right)\omega\left(\zeta(\alpha, \beta)\right)\left(1 - \left(\zeta(\alpha, \beta)\right)^4\right)}{c} \\ & + \left(e\left(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right) - e\left(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right)\omega\left(\zeta(\alpha, \beta)\right)\left(\zeta(\alpha, \beta)\right)^4\Bigg), \end{aligned} \tag{87}$$

$$r(\alpha, \beta) = 1/4\sqrt[3]{3}4^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha + \beta)}}, \tag{88}$$

$$\zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \tag{89}$$

$$\omega(z) = \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{90}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{91}$$

$$c = 1.709921, \tag{92}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{93}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{94}$$

$$V = [7.5957, 14.1189, 10.357], \tag{95}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{96}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{97}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{98}$$

$$P = [1, 1, 1], \tag{99}$$

$$A = [0.955689, 0.788552, -5.47869], \tag{100}$$

$$B = [0.0820011, 2.71681, -2.87103], \tag{101}$$

$$C = [0.789518, 0.573805, 0.660975] \tag{102}$$

and

$$\lambda = [0.006, 0.2, 0.004]. \tag{103}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$\begin{aligned} G = {} & \varepsilon(\rho_s, 0)\left(B_0 + B_1\eta\left((\chi_s)^2, \lambda_2\right) + B_2\left(\eta\left((\chi_s)^2, \lambda_2\right)\right)^2\right) \\ & - 3/8\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}\,(\rho_s)^{4/3}\left(C_0 + C_1\eta\left((\chi_s)^2, \lambda_3\right) + C_2\left(\eta\left((\chi_s)^2, \lambda_3\right)\right)^2\right). \end{aligned} \tag{104}$$

C.10 B97: Density functional part of B97

This functional needs to be mixed with 0.1943*exact exchange. See reference [9] for more details.

$$\begin{aligned} K = {} & \left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) - \varepsilon(\rho_\alpha, 0) - \varepsilon\left(\rho_\beta, 0\right)\right)\left(A_0 + A_1\eta(d, \lambda_1) + A_2\left(\eta(d, \lambda_1)\right)^2\right) \\ & + \sum_s \varepsilon(\rho_s, 0)\left(B_0 + B_1\eta\left((\chi_s)^2, \lambda_2\right) + B_2\left(\eta\left((\chi_s)^2, \lambda_2\right)\right)^2\right) \\ & - 3/8\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}\,(\rho_s)^{4/3}\left(C_0 + C_1\eta\left((\chi_s)^2, \lambda_3\right) + C_2\left(\eta\left((\chi_s)^2, \lambda_3\right)\right)^2\right), \end{aligned} \tag{105}$$

where

$$d = 1/2\,(\chi_\alpha)^2 + 1/2\,\left(\chi_\beta\right)^2, \tag{106}$$

$$\eta(\theta,\mu) = \frac{\mu\theta}{1+\mu\theta}, \tag{107}$$

$$\begin{aligned}\varepsilon(\alpha,\beta) = (\alpha+\beta)\Bigg(& e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1) \\ & - \frac{e(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3)\,\omega(\zeta(\alpha,\beta))\left(1-(\zeta(\alpha,\beta))^4\right)}{c} \\ & + (e(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2) - e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1))\,\omega(\zeta(\alpha,\beta))(\zeta(\alpha,\beta))^4\Bigg),\end{aligned} \tag{108}$$

$$r(\alpha,\beta) = 1/4\,\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}}, \tag{109}$$

$$\zeta(\alpha,\beta) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{110}$$

$$\omega(z) = \frac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{111}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1+1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right), \tag{112}$$

$$c = 1.709921, \tag{113}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{114}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{115}$$

$$V = [7.5957, 14.1189, 10.357], \tag{116}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{117}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{118}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{119}$$

$$P = [1,1,1], \tag{120}$$

$$A = [0.9454, 0.7471, -4.5961], \tag{121}$$

$$B = [0.1737, 2.3487, -2.4868], \tag{122}$$

$$C = [0.8094, 0.5073, 0.7481] \tag{123}$$

and

$$\lambda = [0.006, 0.2, 0.004]. \tag{124}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$\begin{aligned}G = {} & \varepsilon(\rho_s,0)\left(B_0 + B_1\eta\left((\chi_s)^2,\lambda_2\right) + B_2\left(\eta\left((\chi_s)^2,\lambda_2\right)\right)^2\right) \\ & - 3/8\,\sqrt[3]{34}^{2/3}\sqrt[3]{\pi^{-1}}\,(\rho_s)^{4/3}\left(C_0 + C_1\eta\left((\chi_s)^2,\lambda_3\right) + C_2\left(\eta\left((\chi_s)^2,\lambda_3\right)\right)^2\right).\end{aligned} \tag{125}$$

C.11 BR: Becke-Roussel Exchange Functional

A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

$$K = \frac{1}{2}\sum_s \rho_s U_s, \tag{126}$$

where

$$U_s = -(1 - e^{-x} - xe^{-x}/2)/b, \tag{127}$$

$$b = \frac{x^3 e^{-x}}{8\pi\rho_s} \tag{128}$$

and x is defined by the nonlinear equation

$$\frac{xe^{-2x/3}}{x-2} = \frac{2\pi^{2/3}\rho_s^{5/3}}{3Q_s}, \tag{129}$$

where

$$Q_s = (\upsilon_s - 2\gamma D_s)/6, \tag{130}$$

$$D_s = \tau_s - \frac{\sigma_{ss}}{4\rho_s} \tag{131}$$

and

$$\gamma = 1. \tag{132}$$

C.12 BRUEG: Becke-Roussel Exchange Functional — Uniform Electron Gas Limit

A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

As for BR but with $\gamma = 0.8$.

C.13 BW: Becke-Wigner Exchange-Correlation Functional

Hybrid exchange-correlation functional comprimising Becke's 1998 exchange and Wigner's spin-polarised correlation functionals. See reference [14] for more details.

$$\begin{aligned} K = &-4c\rho_\alpha\rho_\beta\rho^{-1}\left(1 + \frac{d}{\sqrt[3]{\rho}}\right)^{-1} \\ &+ \sum_s \alpha\left(\rho_s\right)^{4/3} - \frac{\beta\left(\rho_s\right)^{4/3}\left(\chi_s\right)^2}{1 + 6\beta\chi_s arcsinh\left(\chi_s\right)}, \end{aligned} \tag{133}$$

where

$$\alpha = -3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}, \tag{134}$$

$$\beta = 0.0042, \tag{135}$$

$$c = 0.04918 \tag{136}$$

and

$$d = 0.349. \tag{137}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \alpha\left(\rho_s\right)^{4/3} - \frac{\beta\left(\rho_s\right)^{4/3}\left(\chi_s\right)^2}{1 + 6\beta\chi_s arcsinh\left(\chi_s\right)}. \tag{138}$$

C.14 CS1: Colle-Salvetti correlation functional

R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

CS1 is formally identical to CS2, except for a reformulation in which the terms involving υ are eliminated by integration by parts. This makes the functional more economical to evaluate. In the limit of exact quadrature, CS1 and CS2 are identical, but small numerical differences appear with finite integration grids.

C.15 CS2: Colle-Salvetti correlation functional

R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

CS2 is defined through

$$K = -a\left(\frac{\rho + 2b\rho^{-5/3}\left[\rho_\alpha t_\alpha + \rho_\beta t_\beta - \rho t_W\right] e^{-c\rho^{-1/3}}}{1 + d\rho^{-1/3}}\right) \tag{139}$$

where

$$t_\alpha = \frac{\tau_\alpha}{2} - \frac{\upsilon_\alpha}{8} \tag{140}$$

$$t_\beta = \frac{\tau_\beta}{2} - \frac{\upsilon_\beta}{8} \tag{141}$$

$$t_W = \frac{1}{8}\frac{\sigma}{\rho} - \frac{1}{2}\upsilon \tag{142}$$

and the constants are $a = 0.04918, b = 0.132, c = 0.2533, d = 0.349$.

C.16 DIRAC: Slater-Dirac Exchange Energy

Automatically generated Slater-Dirac exchange. See reference [15] for more details.

$$K = \sum_s -c\left(\rho_s\right)^{4/3}, \tag{143}$$

where

$$c = 3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}. \tag{144}$$

C.17 G96: Gill's 1996 Gradient Corrected Exchange Functional

See reference [16] for more details.

$$K = \sum_s \left(\rho_s\right)^{4/3}\left(\alpha - \frac{1}{137}\left(\chi_s\right)^{3/2}\right), \tag{145}$$

where

$$\alpha = -3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}. \tag{146}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \left(\rho_s\right)^{4/3}\left(\alpha - \frac{1}{137}\left(\chi_s\right)^{3/2}\right). \tag{147}$$

C.18 HCTH120: Handy least squares fitted functional

See reference [17] for more details.

$$K = \left(\varepsilon\left(\rho_\alpha,\rho_\beta\right) - \varepsilon\left(\rho_\alpha,0\right) - \varepsilon\left(\rho_\beta,0\right)\right)\left(A_0 + A_1\eta\left(d,\lambda_1\right) + A_2\left(\eta\left(d,\lambda_1\right)\right)^2 + A_3\left(\eta\left(d,\lambda_1\right)\right)^3 + A_4\left(\eta\left(d,\lambda_1\right)\right)^4\right) + \sum_s \varepsilon\left(\rho_s,0\right)\left(B_0 + B_1\eta\left(\left(\chi_s\right)^2,\lambda_2\right) + B_2\left(\eta\left(\left(\chi_s\right)^2,\lambda_2\right)\right)^2 + B_3\left(\eta\left(\left(\chi_s\right)^2,\lambda_2\right)\right)^3 + B_4\left(\eta\left(\left(\chi_s\right)^2,\lambda_2\right)\right)^4\right) - 3/8\,\sqrt[3]{34}^{2/3}\sqrt[3]{\pi^{-1}}\left(\rho_s\right)^{4/3}\left(C_0 + C_1\eta\left(\left(\chi_s\right)^2,\lambda_3\right) + C_2\left(\eta\left(\left(\chi_s\right)^2,\lambda_3\right)\right)^2 + C_3\left(\eta\left(\left(\chi_s\right)^2,\lambda_3\right)\right)^3 + C_4\left(\eta\left(\left(\chi_s\right)^2,\lambda_3\right)\right)^4\right), \tag{148}$$

where

$$d = 1/2\left(\chi_\alpha\right)^2 + 1/2\left(\chi_\beta\right)^2, \tag{149}$$

$$\eta\left(\theta,\mu\right) = \frac{\mu\theta}{1+\mu\theta}, \tag{150}$$

$$\varepsilon\left(\alpha,\beta\right) = \left(\alpha+\beta\right)\left(e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right) - \frac{e\left(r\left(\alpha,\beta\right),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1-\left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c} + \left(e\left(r\left(\alpha,\beta\right),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right) - e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\right), \tag{151}$$

$$r\left(\alpha,\beta\right) = 1/4\,\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}}, \tag{152}$$

$$\zeta\left(\alpha,\beta\right) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{153}$$

$$\omega\left(z\right) = \frac{\left(1+z\right)^{4/3} + \left(1-z\right)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{154}$$

$$e\left(r,t,u,v,w,x,y,p\right) = -2t\left(1+ur\right)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{155}$$

$$c = 1.709921, \tag{156}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{157}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{158}$$

$$V = [7.5957, 14.1189, 10.357], \tag{159}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{160}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{161}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{162}$$

$$P = [1, 1, 1], \tag{163}$$

$$A = [0.51473, 6.9298, -24.707, 23.110, -11.323], \tag{164}$$

$$B = [0.48951, -0.2607, 0.4329, -1.9925, 2.4853], \tag{165}$$

$$C = [1.09163, -0.7472, 5.0783, -4.1075, 1.1717] \tag{166}$$

and

$$\lambda = [0.006, 0.2, 0.004]. \tag{167}$$

C.19 HCTH147: Handy least squares fitted functional

See reference [17] for more details.

$$\begin{aligned} K = {} & \left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) - \varepsilon\left(\rho_\alpha, 0\right) - \varepsilon\left(\rho_\beta, 0\right)\right)\left(A_0 + A_1\eta\left(d, \lambda_1\right) + A_2\left(\eta\left(d, \lambda_1\right)\right)^2 + A_3\left(\eta\left(d, \lambda_1\right)\right)^3\right. \\ & \left. + A_4\left(\eta\left(d, \lambda_1\right)\right)^4\right) \\ & + \sum_s \varepsilon\left(\rho_s, 0\right)\left(B_0 + B_1\eta\left(\left(\chi_s\right)^2, \lambda_2\right) + B_2\left(\eta\left(\left(\chi_s\right)^2, \lambda_2\right)\right)^2 + B_3\left(\eta\left(\left(\chi_s\right)^2, \lambda_2\right)\right)^3\right. \\ & \left. + B_4\left(\eta\left(\left(\chi_s\right)^2, \lambda_2\right)\right)^4\right) - 3/8\sqrt[3]{34}^{2/3}\sqrt[3]{\pi^{-1}}\left(\rho_s\right)^{4/3}\left(C_0 + C_1\eta\left(\left(\chi_s\right)^2, \lambda_3\right)\right. \\ & \left. + C_2\left(\eta\left(\left(\chi_s\right)^2, \lambda_3\right)\right)^2 + C_3\left(\eta\left(\left(\chi_s\right)^2, \lambda_3\right)\right)^3 + C_4\left(\eta\left(\left(\chi_s\right)^2, \lambda_3\right)\right)^4\right), \end{aligned} \tag{168}$$

where

$$d = 1/2\left(\chi_\alpha\right)^2 + 1/2\left(\chi_\beta\right)^2, \tag{169}$$

$$\eta\left(\theta, \mu\right) = \frac{\mu\theta}{1 + \mu\theta}, \tag{170}$$

$$\begin{aligned} \varepsilon\left(\alpha, \beta\right) = \left(\alpha + \beta\right)\Bigg(& e\left(r\left(\alpha, \beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right) \\ & - \frac{e\left(r\left(\alpha, \beta\right), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right)\omega\left(\zeta\left(\alpha, \beta\right)\right)\left(1 - \left(\zeta\left(\alpha, \beta\right)\right)^4\right)}{c} \\ & + \left(e\left(r\left(\alpha, \beta\right), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right) - e\left(r\left(\alpha, \beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right)\omega\left(\zeta\left(\alpha, \beta\right)\right)\left(\zeta\left(\alpha, \beta\right)\right)^4\Bigg), \end{aligned} \tag{171}$$

$$r\left(\alpha, \beta\right) = 1/4\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi\left(\alpha + \beta\right)}}, \tag{172}$$

$$\zeta\left(\alpha, \beta\right) = \frac{\alpha - \beta}{\alpha + \beta}, \tag{173}$$

$$\omega(z) = \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{174}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{175}$$

$$c = 1.709921, \tag{176}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{177}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{178}$$

$$V = [7.5957, 14.1189, 10.357], \tag{179}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{180}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{181}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{182}$$

$$P = [1, 1, 1], \tag{183}$$

$$A = [0.54235, 7.0146, -28.382, 35.033, -20.428], \tag{184}$$

$$B = [0.56258, -0.0171, -1.3064, 1.0575, 0.8854], \tag{185}$$

$$C = [1.09025, -0.7992, 5.5721, -5.8676, 3.0454] \tag{186}$$

and

$$\lambda = [0.006, 0.2, 0.004]. \tag{187}$$

C.20 HCTH93: Handy least squares fitted functional

See reference [13] for more details.

$$\begin{aligned} K = {} & \left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) - \varepsilon(\rho_\alpha, 0) - \varepsilon\left(\rho_\beta, 0\right)\right)\left(A_0 + A_1\eta(d,\lambda_1) + A_2\left(\eta(d,\lambda_1)\right)^2 + A_3\left(\eta(d,\lambda_1)\right)^3\right. \\ & \left. + A_4\left(\eta(d,\lambda_1)\right)^4\right) \\ & + \sum_s \varepsilon(\rho_s, 0)\left(B_0 + B_1\eta\left((\chi_s)^2, \lambda_2\right) + B_2\left(\eta\left((\chi_s)^2, \lambda_2\right)\right)^2 + B_3\left(\eta\left((\chi_s)^2, \lambda_2\right)\right)^3\right. \\ & \left. + B_4\left(\eta\left((\chi_s)^2, \lambda_2\right)\right)^4\right) - 3/8\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}\left(\rho_s\right)^{4/3}\left(C_0 + C_1\eta\left((\chi_s)^2, \lambda_3\right)\right. \\ & \left. + C_2\left(\eta\left((\chi_s)^2, \lambda_3\right)\right)^2 + C_3\left(\eta\left((\chi_s)^2, \lambda_3\right)\right)^3 + C_4\left(\eta\left((\chi_s)^2, \lambda_3\right)\right)^4\right), \end{aligned} \tag{188}$$

where

$$d = 1/2\,(\chi_\alpha)^2 + 1/2\,\left(\chi_\beta\right)^2, \tag{189}$$

$$\eta(\theta, \mu) = \frac{\mu\theta}{1 + \mu\theta}, \tag{190}$$

$$\varepsilon(\alpha,\beta) = (\alpha+\beta)\left(e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1)\right.$$
$$-\frac{e(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3)\,\omega(\zeta(\alpha,\beta))\left(1-(\zeta(\alpha,\beta))^4\right)}{c}$$
$$\left.+(e(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2)-e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1))\,\omega(\zeta(\alpha,\beta))(\zeta(\alpha,\beta))^4\right), \tag{191}$$

$$r(\alpha,\beta) = 1/4\,\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}}, \tag{192}$$

$$\zeta(\alpha,\beta) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{193}$$

$$\omega(z) = \frac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{194}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1+1/2\,\frac{1}{t(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1})}\right), \tag{195}$$

$$c = 1.709921, \tag{196}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{197}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{198}$$

$$V = [7.5957, 14.1189, 10.357], \tag{199}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{200}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{201}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{202}$$

$$P = [1,1,1], \tag{203}$$

$$A = [0.72997, 3.35287, -11.543, 8.08564, -4.47857], \tag{204}$$

$$B = [0.222601, -0.0338622, -0.012517, -0.802496, 1.55396], \tag{205}$$

$$C = [1.0932, -0.744056, 5.5992, -6.78549, 4.49357] \tag{206}$$

and

$$\lambda = [0.006, 0.2, 0.004]. \tag{207}$$

C.21 LTA: Local τ Approximation

LSDA exchange functional with density represented as a function of τ. See reference [18] for more details.

$$K = \sum_s 1/2\, E\left(2\tau_s\right), \tag{208}$$

where

$$E\left(\alpha\right) = 1/9\, c 5^{4/5} \sqrt[5]{9} \left(\frac{\alpha \sqrt[3]{3}}{\left(\pi^2\right)^{2/3}} \right)^{4/5} \tag{209}$$

and

$$c = -3/4\, \sqrt[3]{3} \sqrt[3]{\pi^{-1}}. \tag{210}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = 1/2\, E\left(2\tau_s\right). \tag{211}$$

C.22 LYP: Lee, Yang and Parr Correlation Functional

C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988); B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Letters 157, 200 (1989)

$$\begin{aligned} K &= 4\frac{A\rho_\alpha\rho_\beta Z}{\rho} + AB\omega\sigma\left(\rho_\alpha\rho_\beta\left(47-7\delta\right)/18 - 2\rho^2/3\right) \\ &+ \sum_s AB\omega\left(\rho_s\rho_{\bar{s}}\left(8\,2^{2/3} e \rho_s^{8/3} - \left(5/2-\delta/18\right)\sigma_{ss} - \frac{\left(\delta-11\right)\rho_s\sigma_{ss}}{9\rho}\right).\right. \\ &\left. + \left(2\rho^2/3 - \rho_s^2\right)\sigma_{\bar{s}\bar{s}}\right), \end{aligned} \tag{212}$$

where

$$\omega = e^{-\frac{c}{\rho^{1/3}}} Z \rho^{-11/3}, \tag{213}$$

$$\delta = \frac{c + dZ}{\rho^{1/3}}, \tag{214}$$

$$B = 0.04918, \tag{215}$$

$$A = 0.132, \tag{216}$$

$$c = 0.2533, \tag{217}$$

$$d = 0.349, \tag{218}$$

$$e = \frac{3}{10}\left(3\pi^2\right)^{2/3} \tag{219}$$

and

$$Z = \left(1 + \frac{d}{\rho^{1/3}}\right)^{-1}. \tag{220}$$

C.23 MK00B: Exchange Functional for Accurate Virtual Orbital Energies

MK00 with gradient correction of the form of B88X but with different empirical parameter. See reference [19] for more details.

$$K = \sum_s -3\,\frac{\pi\,(\rho_s)^3}{\tau_s - 1/4\,\upsilon_s} - \frac{\beta\,(\rho_s)^{4/3}\,(\chi_s)^2}{1 + 6\,\beta\,\chi_s\,\mathrm{arcsinh}\,(\chi_s)}, \tag{221}$$

where

$$\beta = 0.0016. \tag{222}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = -3\,\frac{\pi\,(\rho_s)^3}{\tau_s - 1/4\,\upsilon_s} - \frac{\beta\,(\rho_s)^{4/3}\,(\chi_s)^2}{1 + 6\,\beta\,\chi_s\,\mathrm{arcsinh}\,(\chi_s)}. \tag{223}$$

C.24 MK00: Exchange Functional for Accurate Virtual Orbital Energies

See reference [19] for more details.

$$K = \sum_s -3\,\frac{\pi\,(\rho_s)^3}{\tau_s - 1/4\,\upsilon_s}. \tag{224}$$

C.25 P86:

Gradient correction to VWN. See reference [20] for more details.

$$K = \rho\,e + \frac{e^{-\Phi} C\,(r)\,\sigma}{d\rho^{4/3}}, \tag{225}$$

where

$$r = 1/4\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\frac{1}{\pi\rho}}, \tag{226}$$

$$x = \sqrt{r}, \tag{227}$$

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho}, \tag{228}$$

$$e = \Lambda + \omega y\left(1 + h\zeta^4\right), \tag{229}$$

$$y = \frac{9}{8}\,(1+\zeta)^{4/3} + \frac{9}{8}\,(1-\zeta)^{4/3} - 9/4, \tag{230}$$

$$h = 4/9\,\frac{\lambda - \Lambda}{\left(\sqrt[3]{2} - 1\right)\omega} - 1, \tag{231}$$

$$\Lambda = q\,(k_1, l_1, m_1, n_1), \tag{232}$$

$$\lambda = q\,(k_2, l_2, m_2, n_2), \tag{233}$$

$$\omega = q\left(k_3, l_3, m_3, n_3\right), \tag{234}$$

$$q(A,p,c,d) = A\left(\ln\left(\frac{x^2}{X(x,c,d)}\right) + 2c\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1}\right.$$
$$\left. - cp\left(\ln\left(\frac{(x-p)^2}{X(x,c,d)}\right) + 2\left(c+2p\right)\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1}\right)\left(X(p,c,d)\right)^{-1}\right), \tag{235}$$

$$Q(c,d) = \sqrt{4d - c^2}, \tag{236}$$

$$X(i,c,d) = i^2 + ci + d, \tag{237}$$

$$\Phi = 0.007390075\,\frac{z\sqrt{\sigma}}{C(r)\,\rho^{7/6}}, \tag{238}$$

$$d = \sqrt[3]{2}\sqrt{\left(1/2 + 1/2\,\zeta\right)^{5/3} + \left(1/2 - 1/2\,\zeta\right)^{5/3}}, \tag{239}$$

$$C(r) = 0.001667 + \frac{0.002568 + \alpha r + \beta r^2}{1 + \xi r + \delta r^2 + 10000\,\beta r^3}, \tag{240}$$

$$z = 0.11, \tag{241}$$

$$\alpha = 0.023266, \tag{242}$$

$$\beta = 0.000007389, \tag{243}$$

$$\xi = 8.723, \tag{244}$$

$$\delta = 0.472, \tag{245}$$

$$k = [0.0310907, 0.01554535, -1/6\,\pi^{-2}], \tag{246}$$

$$l = [-0.10498, -0.325, -0.0047584], \tag{247}$$

$$m = [3.72744, 7.06042, 1.13107] \tag{248}$$

and

$$n = [12.9352, 18.0578, 13.0045]. \tag{249}$$

C.26 PBEC: PBE Correlation Functional

See reference [3] for more details.

$$K = \rho\left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) + H\left(d, \rho_\alpha, \rho_\beta\right)\right), \tag{250}$$

where

$$d = 1/12\,\frac{\sqrt{\sigma}3^{5/6}}{u\left(\rho_\alpha, \rho_\beta\right)\sqrt[6]{\pi^{-1}}\rho^{7/6}}, \tag{251}$$

$$u(\alpha,\beta) = 1/2\,(1+\zeta(\alpha,\beta))^{2/3} + 1/2\,(1-\zeta(\alpha,\beta))^{2/3}, \tag{252}$$

$$H(d,\alpha,\beta) = 1/2\,\left(u\left(\rho_\alpha,\rho_\beta\right)\right)^3\lambda^2\ln\left(1+2\,\frac{\iota\left(d^2+A(\alpha,\beta)\,d^4\right)}{\lambda\left(1+A(\alpha,\beta)\,d^2+(A(\alpha,\beta))^2d^4\right)}\right)\iota^{-1}, \tag{253}$$

$$A(\alpha,\beta) = 2\iota\lambda^{-1}\left(e^{-2\,\frac{\iota\varepsilon(\alpha,\beta)}{\left(u\left(\rho_\alpha,\rho_\beta\right)\right)^3\lambda^2}} - 1\right)^{-1}, \tag{254}$$

$$\iota = 0.0716, \tag{255}$$

$$\lambda = \nu\kappa, \tag{256}$$

$$\nu = 16\,\frac{\sqrt[3]{3}\sqrt[3]{\pi^2}}{\pi}, \tag{257}$$

$$\kappa = 0.004235, \tag{258}$$

$$Z = -0.001667, \tag{259}$$

$$\phi(r) = \theta(r) - Z, \tag{260}$$

$$\theta(r) = \frac{1}{1000}\,\frac{2.568+\Xi r+\Phi r^2}{1+\Lambda r+\Upsilon r^2+10\Phi r^3}, \tag{261}$$

$$\Xi = 23.266, \tag{262}$$

$$\Phi = 0.007389, \tag{263}$$

$$\Lambda = 8.723, \tag{264}$$

$$\Upsilon = 0.472, \tag{265}$$

$$\begin{aligned}\varepsilon(\alpha,\beta) = {} & e\left(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\\ & - \frac{e\left(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega(\zeta(\alpha,\beta))\left(1-(\zeta(\alpha,\beta))^4\right)}{c}\\ & + \left(e\left(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right)\right.\\ & \qquad \left. - e\left(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega(\zeta(\alpha,\beta))\left(\zeta(\alpha,\beta)\right)^4,\end{aligned} \tag{266}$$

$$r(\alpha,\beta) = 1/4\,\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi\,(\alpha+\beta)}}, \tag{267}$$

$$\zeta(\alpha,\beta) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{268}$$

$$\omega(z) = \frac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{269}$$

$$e(r,t,u,v,w,x,y,p) = -2t\,(1+ur)\ln\left(1+1/2\,\frac{1}{t\,(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1})}\right), \tag{270}$$

$$c = 1.709921, \tag{271}$$

$$C(d,\alpha,\beta) = K(Q,\alpha,\beta)+M(Q,\alpha,\beta), \tag{272}$$

$$M(d,\alpha,\beta) = 0.5\nu\,(\phi(r(\alpha,\beta))-\kappa-3/7Z)\,d^2e^{-335.9789467\,\frac{\sqrt[3]{2/3}d^2}{\sqrt[3]{\pi^5\rho}}}, \tag{273}$$

$$K(d,\alpha,\beta) = 0.2500000000\lambda^2\ln\left(1+2\,\frac{\iota\left(d^2+N(\alpha,\beta)\,d^4\right)}{\lambda\,(1+N(\alpha,\beta)\,d^2+(N(\alpha,\beta))^2d^4)}\right)\iota^{-1}, \tag{274}$$

$$N(\alpha,\beta) = 2\iota\lambda^{-1}\left(e^{-4\,\frac{\iota\varepsilon(\alpha,\beta)}{\lambda^2}}-1\right)^{-1}, \tag{275}$$

$$Q = 1/12\,\frac{\sqrt{\sigma_{ss}}\sqrt[3]{23}^{5/6}}{\sqrt[6]{\pi^{-1}}\rho^{7/6}}, \tag{276}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{277}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{278}$$

$$V = [7.5957, 14.1189, 10.357], \tag{279}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{280}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{281}$$

$$Y = [0.49294, 0.62517, 0.49671] \tag{282}$$

and

$$P = [1,1,1]. \tag{283}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \rho\,(\varepsilon(\rho_s,0)+C(Q,\rho_s,0))\,. \tag{284}$$

C.27 PBEXREV: Revised PBE Exchange Functional

Changes the value of the constant R from the original PBEX functional See reference [21] for more details.

$$K = \sum_s 1/2\, E\left(2\rho_s\right), \tag{285}$$

where

$$E\left(n\right) = -3/4\, \frac{\sqrt[3]{3}\sqrt[3]{\pi^2} n^{4/3} F\left(S\right)}{\pi}, \tag{286}$$

$$S = 1/12\, \frac{\chi_s 6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{287}$$

$$F\left(S\right) = 1 + R - R\left(1 + \frac{\mu S^2}{R}\right)^{-1}, \tag{288}$$

$$R = 1.245, \tag{289}$$

$$\mu = 1/3\, \delta \pi^2 \tag{290}$$

and

$$\delta = 0.066725. \tag{291}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = 1/2\, E\left(2\rho_s\right). \tag{292}$$

C.28 PBEX: PBE Exchange Functional

See reference [3] for more details.

$$K = \sum_s 1/2\, E\left(2\rho_s\right), \tag{293}$$

where

$$E\left(n\right) = -3/4\, \frac{\sqrt[3]{3}\sqrt[3]{\pi^2} n^{4/3} F\left(S\right)}{\pi}, \tag{294}$$

$$S = 1/12\, \frac{\chi_s 6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{295}$$

$$F\left(S\right) = 1 + R - R\left(1 + \frac{\mu S^2}{R}\right)^{-1}, \tag{296}$$

$$R = 0.804, \tag{297}$$

$$\mu = 1/3\, \delta \pi^2 \tag{298}$$

and

$$\delta = 0.066725. \tag{299}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = 1/2\, E\left(2\rho_s\right). \tag{300}$$

C.29 PW86:

GGA Exchange Functional. See reference [22] for more details.

$$K = \sum_s 1/2\, E\left(2\rho_s\right), \tag{301}$$

where

$$E\left(n\right) = -3/4\, \sqrt[3]{3}\sqrt[3]{\pi^{-1}} n^{4/3} F\left(S\right), \tag{302}$$

$$F\left(S\right) = \left(1 + 1.296 S^2 + 14 S^4 + 0.2 S^6\right)^{1/15} \tag{303}$$

and

$$S = 1/12\, \frac{\chi_s 6^{2/3}}{\sqrt[3]{\pi^2}}. \tag{304}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = 1/2\, E\left(2\rho_s\right). \tag{305}$$

C.30 PW91C: Perdew-Wang 1991 GGA Correlation Functional

See reference [5] for more details.

$$K = \rho\left(\varepsilon\left(\rho_\alpha, \rho_\beta\right) + H\left(d, \rho_\alpha, \rho_\beta\right)\right), \tag{306}$$

where

$$d = 1/12\, \frac{\sqrt{\sigma} 3^{5/6}}{u\left(\rho_\alpha, \rho_\beta\right) \sqrt[6]{\pi^{-1}} \rho^{7/6}}, \tag{307}$$

$$u\left(\alpha, \beta\right) = 1/2\, \left(1 + \zeta\left(\alpha, \beta\right)\right)^{2/3} + 1/2\, \left(1 - \zeta\left(\alpha, \beta\right)\right)^{2/3}, \tag{308}$$

$$H\left(d, \alpha, \beta\right) = L\left(d, \alpha, \beta\right) + J\left(d, \alpha, \beta\right), \tag{309}$$

$$L\left(d, \alpha, \beta\right) = 1/2\, \left(u\left(\rho_\alpha, \rho_\beta\right)\right)^3 \lambda^2 \ln\left(1 + 2\, \frac{\iota\left(d^2 + A\left(\alpha, \beta\right) d^4\right)}{\lambda\left(1 + A\left(\alpha, \beta\right) d^2 + \left(A\left(\alpha, \beta\right)\right)^2 d^4\right)}\right) \iota^{-1}, \tag{310}$$

$$J\left(d, \alpha, \beta\right) = \nu\left(\phi\left(r\left(\alpha, \beta\right)\right) - \kappa - 3/7 Z\right) \left(u\left(\rho_\alpha, \rho_\beta\right)\right)^3 d^2 e^{-\frac{400}{3}\, \frac{\left(u\left(\rho_\alpha, \rho_\beta\right)\right)^4 3^{2/3} d^2}{\sqrt[3]{\pi^5 \rho}}}, \tag{311}$$

$$A\left(\alpha, \beta\right) = 2\iota\lambda^{-1} \left(e^{-2\, \frac{\iota \varepsilon\left(\alpha, \beta\right)}{\left(u\left(\rho_\alpha, \rho_\beta\right)\right)^3 \lambda^2}} - 1\right)^{-1}, \tag{312}$$

$$\iota = 0.09, \tag{313}$$

$$\lambda = \nu\kappa, \tag{314}$$

$$\nu = 16\, \frac{\sqrt[3]{3}\sqrt[3]{\pi^2}}{\pi}, \tag{315}$$

$$\kappa = 0.004235, \tag{316}$$

$$Z = -0.001667, \tag{317}$$

$$\phi(r) = \theta(r) - Z, \tag{318}$$

$$\theta(r) = \frac{1}{1000}\frac{2.568 + \Xi r + \Phi r^2}{1 + \Lambda r + \Upsilon r^2 + 10\Phi r^3}, \tag{319}$$

$$\Xi = 23.266, \tag{320}$$

$$\Phi = 0.007389, \tag{321}$$

$$\Lambda = 8.723, \tag{322}$$

$$\Upsilon = 0.472, \tag{323}$$

$$\begin{aligned}\varepsilon(\alpha,\beta) = {} & e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1) \\ & - \frac{e(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3)\,\omega(\zeta(\alpha,\beta))\left(1-(\zeta(\alpha,\beta))^4\right)}{c} \\ & + (e(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2) \\ & \qquad - e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1))\,\omega(\zeta(\alpha,\beta))\,(\zeta(\alpha,\beta))^4,\end{aligned} \tag{324}$$

$$r(\alpha,\beta) = 1/4\,\sqrt[3]{34}^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}}, \tag{325}$$

$$\zeta(\alpha,\beta) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{326}$$

$$\omega(z) = \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{327}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{328}$$

$$c = 1.709921, \tag{329}$$

$$C(d,\alpha,\beta) = K(Q,\alpha,\beta) + M(Q,\alpha,\beta), \tag{330}$$

$$M(d,\alpha,\beta) = 0.5\nu\left(\phi(r(\alpha,\beta)) - \kappa - 3/7Z\right)d^2 e^{-335.9789467\,\frac{3^{2/3}d^2}{\sqrt[3]{\pi^5\rho}}}, \tag{331}$$

$$K(d,\alpha,\beta) = 0.2500000000\lambda^2\ln\left(1 + 2\,\frac{\iota\left(d^2 + N(\alpha,\beta)\,d^4\right)}{\lambda\left(1 + N(\alpha,\beta)\,d^2 + (N(\alpha,\beta))^2 d^4\right)}\right)\iota^{-1}, \tag{332}$$

$$N(\alpha,\beta) = 2\iota\lambda^{-1}\left(e^{-4\,\frac{\iota\varepsilon(\alpha,\beta)}{\lambda^2}} - 1\right)^{-1}, \tag{333}$$

$$Q = 1/12\,\frac{\sqrt{\sigma_{ss}}\sqrt[3]{2}3^{5/6}}{\sqrt[6]{\pi^{-1}}\rho^{7/6}}, \tag{334}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{335}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{336}$$

$$V = [7.5957, 14.1189, 10.357], \tag{337}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{338}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{339}$$

$$Y = [0.49294, 0.62517, 0.49671] \tag{340}$$

and

$$P = [1, 1, 1]. \tag{341}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \rho\left(\varepsilon(\rho_s, 0) + C(Q, \rho_s, 0)\right). \tag{342}$$

C.31 `PW91X`: Perdew-Wang 1991 GGA Exchange Functional

See reference [5] for more details.

$$K = \sum_s 1/2\,E(2\rho_s), \tag{343}$$

where

$$E(n) = -3/4\,\frac{\sqrt[3]{3}\sqrt[3]{\pi^2}n^{4/3}F(S)}{\pi}, \tag{344}$$

$$S = 1/12\,\frac{\chi_s 6^{2/3}}{\sqrt[3]{\pi^2}} \tag{345}$$

and

$$F(S) = \frac{1 + 0.19645\,S\,\mathrm{arcsinh}(7.7956\,S) + \left(0.2743 - 0.1508\,e^{-100S^2}\right)S^2}{1 + 0.19645\,S\,\mathrm{arcsinh}(7.7956\,S) + 0.004\,S^4}. \tag{346}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = 1/2\,E(2\rho_s). \tag{347}$$

C.32 PW92C: Perdew-Wang 1992 GGA Correlation Functional

Electron-gas correlation energy. See reference [2] for more details.

$$K = \rho\,\varepsilon\left(\rho_\alpha, \rho_\beta\right), \tag{348}$$

where

$$\begin{aligned}\varepsilon(\alpha,\beta) = {} & e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \\ & - \frac{e(r(\alpha,\beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3)\,\omega(\zeta(\alpha,\beta))\left(1 - (\zeta(\alpha,\beta))^4\right)}{c} \\ & + (e(r(\alpha,\beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \\ & \qquad - e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1))\,\omega(\zeta(\alpha,\beta))\,(\zeta(\alpha,\beta))^4,\end{aligned} \tag{349}$$

$$r(\alpha,\beta) = 1/4\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}}, \tag{350}$$

$$\zeta(\alpha,\beta) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{351}$$

$$\omega(z) = \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{352}$$

$$e(r,t,u,v,w,x,y,p) = -2t(1+ur)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{353}$$

$$c = 1.709921, \tag{354}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{355}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{356}$$

$$V = [7.5957, 14.1189, 10.357], \tag{357}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{358}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{359}$$

$$Y = [0.49294, 0.62517, 0.49671] \tag{360}$$

and

$$P = [1, 1, 1]. \tag{361}$$

C.33 STEST: Test for number of electrons

$$K = \sum_s \rho_s. \tag{362}$$

C.34 TH1: Tozer and Handy 1998

Density and gradient dependent first row exchange-correlation functional. See reference [23] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{363}$$

where

$$n = 21, \tag{364}$$

$$R_i = (\rho_\alpha)^{t_i} + \left(\rho_\beta\right)^{t_i}, \tag{365}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{366}$$

$$X_i = 1/2\,\frac{\left(\sqrt{\sigma_{\alpha\alpha}}\right)^{v_i} + \left(\sqrt{\sigma_{\beta\beta}}\right)^{v_i}}{\rho^{4/3\,v_i}}, \tag{367}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{368}$$

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, 1], \tag{369}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{370}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2,0,0,0,0,0,0,0,0,0], \tag{371}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0,0,0,0,0] \tag{372}$$

and

$$\begin{aligned}\omega = [&-0.728255, 0.331699, -1.02946, 0.235703, -0.0876221, 0.140854, 0.0336982,\\ &-0.0353615, 0.00497930, -0.0645900, 0.0461795, -0.00757191,\\ &-0.00242717, 0.0428140, -0.0744891, 0.0386577, -0.352519, 2.19805,\\ &-3.72927, 1.94441, 0.128877].\end{aligned} \tag{373}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{374}$$

C.35 TH2:

Density and gradient dependent first row exchange-correlation functional. See reference [24] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{375}$$

where

$$n = 19, \tag{376}$$

$$R_i = (\rho_\alpha)^{t_i} + \left(\rho_\beta\right)^{t_i}, \tag{377}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{378}$$

$$X_i = 1/2\,\frac{\left(\sqrt{\sigma_{\alpha\alpha}}\right)^{v_i} + \left(\sqrt{\sigma_{\beta\beta}}\right)^{v_i}}{\rho^{4/3\,v_i}}, \tag{379}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{380}$$

$$t = [\frac{13}{12}, 7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{381}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1], \tag{382}$$

$$v = [0,0,0,0,0,1,1,1,1,2,2,2,0,0,0,0,0,0,0], \tag{383}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,0,0,0,0] \tag{384}$$

and

$$\begin{aligned}\omega = [&0.678831, -1.75821, 1.27676, -1.60789, 0.365610, -0.181327, 0.146973, 0.147141,\\ &-0.0716917, -0.0407167, 0.0214625, -0.000768156, 0.0310377,\\ &-0.0720326, 0.0446562, -0.266802, 1.50822, -1.94515, 0.679078].\end{aligned} \tag{385}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{386}$$

C.36 TH3:

Density and gradient dependent first and second row exchange-correlation functional. See reference [25] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{387}$$

where

$$n = 19, \tag{388}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{389}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{390}$$

$$X_i = 1/2\,\frac{(\sqrt{\sigma_{\alpha\alpha}})^{v_i} + (\sqrt{\sigma_{\beta\beta}})^{v_i}}{\rho^{4/3\,v_i}}, \tag{391}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{392}$$

$$t = [7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, \frac{13}{12}], \tag{393}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{394}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,0,0,0,0,0,0,0,0], \tag{395}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,1,1,1,0,0,0,0,0] \tag{396}$$

and

$$\begin{aligned}\omega = [&-0.142542, -0.783603, -0.188875, 0.0426830, -0.304953, 0.430407,\\ &-0.0997699, 0.00355789, -0.0344374, 0.0192108,\\ &-0.00230906, 0.0235189, -0.0331157, 0.0121316, 0.441190, -2.27167, 4.03051,\\ &-2.28074, 0.0360204].\end{aligned} \tag{397}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{398}$$

C.37 TH4:

Density an gradient dependent first and second row exchange-correlation functional. See reference [25] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{399}$$

where

$$n = 19, \tag{400}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{401}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{402}$$

$$X_i = 1/2\,\frac{(\sqrt{\sigma_{\alpha\alpha}})^{v_i} + (\sqrt{\sigma_{\beta\beta}})^{v_i}}{\rho^{4/3\,v_i}}, \tag{403}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{404}$$

$$t = [7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, \frac{13}{12}], \tag{405}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{406}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,0,0,0,0,0,0,0,0], \tag{407}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,1,1,1,0,0,0,0,0] \tag{408}$$

and

$$\begin{aligned}\omega = [&0.0677353, -1.06763, -0.0419018, 0.0226313, -0.222478, 0.283432, -0.0165089,\\ &-0.0167204, -0.0332362, 0.0162254, -0.000984119, 0.0376713,\\ &-0.0653419, 0.0222835, 0.375782, -1.90675, 3.22494, -1.68698, -0.0235810].\end{aligned} \tag{409}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{410}$$

C.38 THGFCFO:

Density and gradient dependent first row exchange-correlation functional. FCFO = FC + open shell fitting. See reference [26] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{411}$$

where

$$n = 20, \tag{412}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{413}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{414}$$

$$X_i = 1/2\,\frac{(\sqrt{\sigma_{\alpha\alpha}})^{v_i} + (\sqrt{\sigma_{\beta\beta}})^{v_i}}{\rho^{4/3\,v_i}}, \tag{415}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{416}$$

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{417}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1], \tag{418}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2,0,0,0,0,0,0,0,0], \tag{419}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0,0,0,0] \tag{420}$$

and

$$\begin{aligned}\omega = [&-0.864448, 0.565130, -1.27306, 0.309681, -0.287658, 0.588767,\\ &-0.252700, 0.0223563, 0.0140131,\\ &-0.0826608, 0.0556080, -0.00936227, -0.00677146, 0.0515199,\\ &-0.0874213, 0.0423827, 0.431940, -0.691153, -0.637866, 1.07565].\end{aligned} \tag{421}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{422}$$

C.39 THGFCO:

Density and gradient dependent first row exchange-correlation functional. See reference [26] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{423}$$

where

$$n = 20, \tag{424}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{425}$$

$$S_i = \left(\frac{\rho_\alpha - \rho_\beta}{\rho}\right)^{2u_i}, \tag{426}$$

$$X_i = 1/2\,\frac{(\sqrt{\sigma_{\alpha\alpha}})^{v_i} + (\sqrt{\sigma_{\beta\beta}})^{v_i}}{\rho^{4/3\,v_i}}, \tag{427}$$

$$Y_i = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta} - 2\sqrt{\sigma_{\alpha\alpha}}\sqrt{\sigma_{\beta\beta}}}{\rho^{8/3}}\right)^{w_i}, \tag{428}$$

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{429}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1], \tag{430}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2,0,0,0,0,0,0,0,0], \tag{431}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0,0,0,0] \tag{432}$$

and

$$\begin{aligned}\omega = [&-0.962998, 0.860233, -1.54092, 0.381602, -0.210208, 0.391496, -0.107660,\\ &-0.0105324, 0.00837384, -0.0617859, 0.0383072, -0.00526905,\\ &-0.00381514, 0.0321541, -0.0568280, 0.0288585, 0.368326, -0.328799,\\ &-1.22595, 1.36412].\end{aligned} \tag{433}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho_s)^{t_i}\,(\sqrt{\sigma_{ss}})^{v_i}\left(\frac{\sigma_{ss}}{(\rho_s)^{8/3}}\right)^{w_i}\left((\rho_s)^{4/3\,v_i}\right)^{-1}. \tag{434}$$

C.40 THGFC:

Density and gradient dependent first row exchange-correlation functional for closed shell systems. Total energies are improved by adding DN, where N is the number of electrons and $D = 0.1863$. See reference [26] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i X_i, \tag{435}$$

where

$$n = 12, \tag{436}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{437}$$

$$X_i = 1/2 \frac{(\sqrt{\sigma_{\alpha\alpha}})^{v_i} + (\sqrt{\sigma_{\beta\beta}})^{v_i}}{\rho^{4/3\, v_i}}, \tag{438}$$

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2], \tag{439}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2] \tag{440}$$

and

$$\begin{aligned} \omega = [&-0.864448, 0.565130, -1.27306, 0.309681, -0.287658, 0.588767, \\ &-0.252700, 0.0223563, 0.0140131, -0.0826608, 0.0556080, \\ &-0.00936227]. \end{aligned} \tag{441}$$

To avoid singularities in the limit $\rho_{\bar{s}} \to 0$

$$G = \sum_{i=1}^{n} 1/2 \frac{\omega_i (\rho_s)^{t_i} (\sqrt{\sigma_{ss}})^{v_i}}{\rho^{4/3\, v_i}}. \tag{442}$$

C.41 THGFL:

Density dependent first row exchange-correlation functional for closed shell systems. See reference [26] for more details.

$$K = \sum_{i=1}^{n} \omega_i R_i, \tag{443}$$

where

$$n = 4, \tag{444}$$

$$R_i = (\rho_\alpha)^{t_i} + (\rho_\beta)^{t_i}, \tag{445}$$

$$t = [7/6, 4/3, 3/2, 5/3] \tag{446}$$

and

$$\omega = [-1.06141, 0.898203, -1.34439, 0.302369]. \tag{447}$$

C.42 VSXC:

See reference [27] for more details.

$$\begin{aligned} K = {} & F\left(x,z,p_3,q_3,r_3,t_3,u_3,v_3,\alpha_3\right)\left(\varepsilon\left(\rho_\alpha,\rho_\beta\right)-\varepsilon\left(\rho_\alpha,0\right)-\varepsilon\left(\rho_\beta,0\right)\right) \\ & +\sum_s \left(\rho_s\right)^{4/3} F\left(\chi_s,zs,p_1,q_1,r_1,t_1,u_1,v_1,\alpha_1\right) \\ & + ds\,\varepsilon\left(\rho_s,0\right) F\left(\chi_s,zs,p_2,q_2,r_2,t_2,u_2,v_2,\alpha_2\right), \end{aligned} \tag{448}$$

where

$$x = \left(\chi_\alpha\right)^2 + \left(\chi_\beta\right)^2, \tag{449}$$

$$zs = \frac{\tau_s}{\left(\rho_s\right)^{5/3}} - cf, \tag{450}$$

$$z = \frac{\tau_\alpha}{\left(\rho_\alpha\right)^{5/3}} + \frac{\tau_\beta}{\left(\rho_\beta\right)^{5/3}} - 2\,cf, \tag{451}$$

$$ds = 1 - \frac{\left(\chi_s\right)^2}{4\,zs + 4\,cf}, \tag{452}$$

$$F\left(x,z,p,q,c,d,e,f,\alpha\right) = \frac{p}{\lambda\left(x,z,\alpha\right)} + \frac{qx^2+cz}{\left(\lambda\left(x,z,\alpha\right)\right)^2} + \frac{dx^4+ex^2z+fz^2}{\left(\lambda\left(x,z,\alpha\right)\right)^3}, \tag{453}$$

$$\lambda\left(x,z,\alpha\right) = 1 + \alpha\left(x^2+z\right), \tag{454}$$

$$cf = 3/5\,3^{2/3}\left(\pi^2\right)^{2/3}, \tag{455}$$

$$\begin{aligned} \varepsilon\left(\alpha,\beta\right) = \left(\alpha+\beta\right)\Bigg(& e\left(l\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right) \\ & - \frac{e\left(l\left(\alpha,\beta\right),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1-\left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c} \\ & + \left(e\left(l\left(\alpha,\beta\right),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right) - e\left(l\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\Bigg), \end{aligned} \tag{456}$$

$$l\left(\alpha,\beta\right) = 1/4\,\sqrt[3]{3}4^{2/3}\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}}, \tag{457}$$

$$\zeta\left(\alpha,\beta\right) = \frac{\alpha-\beta}{\alpha+\beta}, \tag{458}$$

$$\omega\left(z\right) = \frac{\left(1+z\right)^{4/3}+\left(1-z\right)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{459}$$

$$e\left(r,t,u,v,w,x,y,p\right) = -2t\left(1+ur\right)\ln\left(1+1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right), \tag{460}$$

$$c = 1.709921, \tag{461}$$

$$p = [-0.98, 0.3271, 0.7035], \tag{462}$$

$$q = [-0.003557, -0.03229, 0.007695], \tag{463}$$

$$r = [0.00625, -0.02942, 0.05153], \tag{464}$$

$$t = [-0.00002354, 0.002134, 0.00003394], \tag{465}$$

$$u = [-0.0001283, -0.005452, -0.001269], \tag{466}$$

$$v = [0.0003575, 0.01578, 0.001296], \tag{467}$$

$$\alpha = [0.001867, 0.005151, 0.00305], \tag{468}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{469}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{470}$$

$$V = [7.5957, 14.1189, 10.357], \tag{471}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{472}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{473}$$

$$Y = [0.49294, 0.62517, 0.49671] \tag{474}$$

and

$$P = [1, 1, 1]. \tag{475}$$

To avoid singularities in the limit $\rho_{\bar{s}} \rightarrow 0$

$$G = (\rho_s)^{4/3} F(\chi_s, zs, p_1, q_1, r_1, t_1, u_1, v_1, \alpha_1) + ds\varepsilon(\rho_s, 0) F(\chi_s, zs, p_2, q_2, r_2, t_2, u_2, v_2, \alpha_2). \tag{476}$$

C.43 VWN3: Vosko-Wilk-Nusair (1980) III local correlation energy

VWN 1980(III) functional. The fitting parameters for $\Delta\varepsilon_c(r_s,\zeta)_{III}$ appear in the text shortly after equation 4.4 of the reference. See reference [28] for more details.

$$K = \rho\, e, \tag{477}$$

where

$$x = 1/4\,\sqrt[6]{3}4^{5/6}\sqrt[6]{\frac{1}{\pi\rho}}, \tag{478}$$

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho}, \tag{479}$$

$$e = \Lambda + \alpha y\left(1 + h\zeta^4\right), \tag{480}$$

$$y = \frac{9}{8}\left(1+\zeta\right)^{4/3} + \frac{9}{8}\left(1-\zeta\right)^{4/3} - 9/4, \tag{481}$$

$$h = 4/9\,\frac{\lambda - \Lambda}{\left(\sqrt[3]{2}-1\right)\alpha} - 1, \tag{482}$$

$$\Lambda = q\left(k_1, l_1, m_1, n_1\right), \tag{483}$$

$$\lambda = q\left(k_2, l_2, m_2, n_2\right), \tag{484}$$

$$\alpha = q\left(k_3, l_3, m_3, n_3\right), \tag{485}$$

$$\begin{aligned} q(A,p,c,d) = A\Bigg(&\ln\left(\frac{x^2}{X(x,c,d)}\right) + 2c\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1} \\ &- cp\left(\ln\left(\frac{(x-p)^2}{X(x,c,d)}\right) + 2\left(c+2p\right)\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1}\right)\left(X(p,c,d)\right)^{-1}\Bigg), \end{aligned} \tag{486}$$

$$Q(c,d) = \sqrt{4d - c^2}, \tag{487}$$

$$X(i,c,d) = i^2 + ci + d, \tag{488}$$

$$k = [0.0310907, 0.01554535, -1/6\,\pi^{-2}], \tag{489}$$

$$l = [-0.409286, -0.743294, -0.0047584], \tag{490}$$

$$m = [13.0720, 20.1231, 1.13107] \tag{491}$$

and

$$n = [42.7198, 101.578, 13.0045]. \tag{492}$$

C.44 VWN5: Vosko-Wilk-Nusair (1980) V local correlation energy

VWN 1980(V) functional. The fitting parameters for $\Delta\varepsilon_c(r_s,\zeta)_V$ appear in the caption of table 7 in the reference. See reference [28] for more details.

$$K = \rho\, e, \tag{493}$$

where

$$x = 1/4\,\sqrt[6]{3}4^{5/6}\sqrt[6]{\frac{1}{\pi\rho}}, \tag{494}$$

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho}, \tag{495}$$

$$e = \Lambda + \alpha y\left(1 + h\zeta^4\right), \tag{496}$$

$$y = \frac{9}{8}\left(1+\zeta\right)^{4/3} + \frac{9}{8}\left(1-\zeta\right)^{4/3} - 9/4, \tag{497}$$

$$h = 4/9\,\frac{\lambda - \Lambda}{\left(\sqrt[3]{2}-1\right)\alpha} - 1, \tag{498}$$

$$\Lambda = q\left(k_1, l_1, m_1, n_1\right), \tag{499}$$

$$\lambda = q\left(k_2, l_2, m_2, n_2\right), \tag{500}$$

$$\alpha = q\left(k_3, l_3, m_3, n_3\right), \tag{501}$$

$$\begin{aligned} q(A,p,c,d) = A\Bigg(&\ln\left(\frac{x^2}{X(x,c,d)}\right) + 2c\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1} \\ &- cp\left(\ln\left(\frac{(x-p)^2}{X(x,c,d)}\right) + 2\left(c+2p\right)\arctan\left(\frac{Q(c,d)}{2x+c}\right)\left(Q(c,d)\right)^{-1}\right)\left(X(p,c,d)\right)^{-1}\Bigg), \end{aligned} \tag{502}$$

$$Q(c,d) = \sqrt{4d - c^2}, \tag{503}$$

$$X(i,c,d) = i^2 + ci + d, \tag{504}$$

$$k = [0.0310907, 0.01554535, -1/6\,\pi^{-2}], \tag{505}$$

$$l = [-0.10498, -0.325, -0.0047584], \tag{506}$$

$$m = [3.72744, 7.06042, 1.13107] \tag{507}$$

and

$$n = [12.9352, 18.0578, 13.0045]. \tag{508}$$

Index