Introduction to CPMD

CPMD program

- *ab initio* electronic structure (DFT) and molecular dynamics program

- plane wave basis set (PBC), pseudopotentials

- massively parallelized, linear scaling up to thousands of CPU's

- WF, GEO, CPMD, BOMD, KS-orbitals, response functions, TDDFT, properties

- solids, liquids, gas-phase, materials, chemistry, biology

- `http://www.cpmd.org`, download, manual, mailing list, PP's

Installation and Running

more details in the manual or in the source

Installation

- Distribution of source *via* `http://www.cpmd.org/` for free for non-commercial users.

- `# mkconfig.sh` to see for which platforms a Makefile can be generated.

- `# mkconfig.sh platform` > `Makefile` to obtain Makefile for your platform.

- `# make` to get executable `cpmd.x`.

- frequent problem: libraries and paths are incorrect in Makefile, Makefile needs to be edited manually.

- if you change preprocessor flags type `# make clean`.

Running

`# cpmd.x input pseudopotentialdirectory > output`

- required files: executable, input, pseudopotentials

- `pseudopotentialdirectory` is either

    1 omitted and instead given by an environment variable called **PP_LIBRARY_PATH**,

    2 or explicitly given,

    3 or omitted and the pseudopotentials are in the running directory.

- other files: detailed/more condensed output is written to various files depending on the keyword.

- RESTART-files are written upon a proper ending of a run.

- runs can be properly ended by creating a file EXIT in the running directory.

Input

more details in the manual or in the source

Sections

- &CPMD ... &END
  $\hookrightarrow$ Control (mandatory)

- &DFT ... &END
  $\hookrightarrow$ Functional (mandatory)

- &SYSTEM ... &END
  $\hookrightarrow$ Cell (mandatory)

- &ATOMS ... &END
  $\hookrightarrow$ Pseudopotentials, Coordinates, Constraints (mandatory)

- &TDDFT ... &END
  $\hookrightarrow$ TDDFT

- &PIMD ... &END
  $\hookrightarrow$ Path Integral Molecular Dynamics

- &RESP ... &END
  $\hookrightarrow$ Response

- &VDW ... &END
  $\hookrightarrow$ Empirical van der Waals correction

Keywords

- Manual is incomplete by construction → only source is complete.

- Keywords relate to variables which trigger desired calculations, relations are often found in
  `control.F, sysin.F, pi_cnt1.F, ratom.F, recpnew.F, dftin.F, proppt.F, respin.F, lr_in.F`

- Order of keywords is arbitrary unless stated otherwise

- Only capital letters

- Choose one item from lists enclosed in {...}

- Choose any number of items from lists enclosed in [...]

- Arguments (for instance numbers) for keywords are given on following lines

- Keywords are read using FORTRAN `INDEX()`; order of keywords on a line is **USUALLY** irrelevant

- Abbreviations are allowed, **NOT** recommended

Most important parametres: Physical

- task (OPTIMISE GEOMETRY / WAVEFUNCTION / MOLECULAR DYNAMICS / ...)

- TIMESTEP (&CPMD)

- EMASS (&CPMD)

- CONVERGENCE (&CPMD)

- SYMMETRY (&SYSTEM)

- CELL (&SYSTEM)

- CUTOFF (&SYSTEM)

- atoms (&ATOM)

- ISOTOPE (&ATOM)

- FUNCTIONAL (&DFT)

- LSD (&CPMD)

- MULTIPLICITY (&SYSTEM)

Most important parametres: Practical

`&CPMD`

- FILEPATH (`CPMD_FILEPATH` as environmental variable)

- MAXCPUTIME

- MAXSTEP

- STORE

- RESTFILE

- REAL SPACE WFN KEEP

- MIRROR

Most important parametres: Analysis

- TRAJECTORY SAMPLE XYZ (&CPMD)

- STRUCTURE BONDS ANGLES ... (&CPMD)

- STRESS TENSOR (&CPMD)

- DIPOLE DYNAMICS WANNIER SAMPLE (&CPMD)

- CUBEFILE (RHOOUT [BANDS], ELECTROSTATIC POTENTIAL) (&PROP/&CPMD)

Examples

Tasks: Tuesday

- Optimise electron structure of H_2O

- Optimise geometry of H_2O
  - Visualise geometry [gOpenMol]

- Vibrational modes using displacements
  - Isotope effect? (RESTART VIBANALYSIS!)

- Perform BO and CP dynamics for H_2O
  - Visualise ENERGIES; what are constants of motion? Is there a drift?
  - What is the average temperature? Etc [xmgrace]
  - Visualise TRAJEC.xyz [gOpenMol]

- Vary time step, emass (in CP); when does the adiabatic approximation fail? When is the time step too large in BOMD?

- If you have time, optimise the geometry of $(H_2O)_2$. Calculate the binding energy, vibrational frequencies. How does the vibrational frequency of OH along the hydrogen bond change wrt monomer?

Tasks: Wednesday

- Perform CP dynamics for H_2O constraining the bending mode to the equilibrium value

- Perform simulated annealing for H_2O from the end of the previous trajectory; do you recover the geometry of Tuesday?

- Calculate the Kohn-Sham energies of H_2O; are the positive energies reliable?
  - Visualise orbitals (CUBEFILE) [gOpenMol]

- Mean square displacement of Tuesday's trajectory

- Vibrational spectrum of H_2O using Tuesday's trajectory

- Calculate charges on oxygen and hydrogen using Bader's method [charge]

- Calculate dipole moment of H_2O (DIPOLE MOMENT / &PROP)

- Calculate Wannier functions for H_2O; what is the hybridisation of H_2O?

- Calculate adsorption and emission spectrum of formaldehyde in the second excited state; how does the geometry look like? What is the fluoresence shift?