Properties

MD simulation: output

- Energies
  - temperature
  - displacement
  - fluctuations
- Trajectory of atoms
  - positions: *e. g.* diffusion, mass transport
  - velocities: *e. g.* v-v–autocorrelation spectrum

MD simulation: Energetics

- Energies
  - temperature
  - displacement
  - fluctuations

File `ENERGY`

MD simulation: Trajectory

- Trajectory of atoms
  - positions: *e. g.* diffusion, mass transport
  - velocities: *e. g.* v-v–autocorrelation spectrum

Files `TRAJECTORY`, `TRAJEC.xyz`

Mean square displacement, diffusion

- mean square displacement

$$\mathrm{msd}(t) = \left\langle \Delta\mathbf{R}(t)^2 \right\rangle = \left\langle [\mathbf{R}(t) - \mathbf{R}(0)]^2 \right\rangle$$

- diffusion coefficient (Einstein relation)

$$D = \frac{1}{2d} \lim_{t\to\infty} \left\langle \Delta\mathbf{R}(t)^2 \right\rangle$$

  alternative definition (Green-Kubo formula)

$$D = \int_{t=0}^{\infty} \langle v_x(t)\, v_x(0) \rangle \, dt$$

- Attention with drift in centre of mass

- Many t_0's needed

Vibrational spectrum

- Velocity-velocity autocorrelation

$$C_v(t) = \int_{t=0}^{\infty} \langle v_x(t)\, v_x(0) \rangle \, dt$$

- Its cosine transform gives the vibrational, or power spectrum

$$I(\omega) = \int_t C_v(t)\, e^{\mathrm{i}\omega t}\, dt$$

- Many t_0's needed

Vibrational (harmonic) frequencies

- The vibrational frequencies can be evaluated either using the finite differences (**VIBRATIONAL ANALYSIS** in `CPMD`) or perturbation theory (see *e. g.* the work of Stefano Baroni for calculating phonon frequencies in solids)

- Always remember to relax the ionic structure first; the more better the convergence, the more accurate will your frequencies be, especially the lowest ones

Electronic density of states

- $n(E)$ is the number of electrons in the energy range $E \ldots E + \delta E$
- Can be evaluated via

$$n\left(E\right) = \sum_{i,\mathbf{k}} \delta\left(E - \varepsilon_{i,\mathbf{k}}\right)$$

- in practise δ functions have to be broadened *e. g.* with Gaussian functions
- `in CPMD`: $E_{i,\mathbf{k}}$ can be obtained with **KOHN-SHAM ENERGIES**

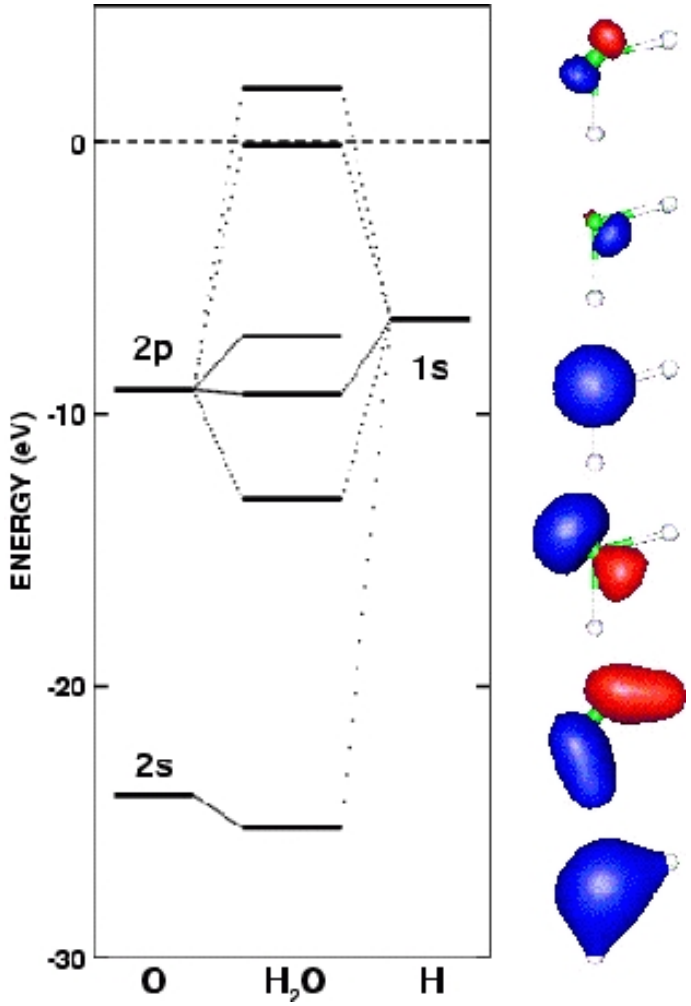
Kohn-Sham states

- Although not necessarily physical, it is often useful to plot them

- In `CPMD`: $\psi_{i,\mathbf{k}}$ can be obtained with **KOHN-SHAM ENERGIES** followed with a run employing either **CUBEFILE ORBITALS** of **RHOOUT BANDS**

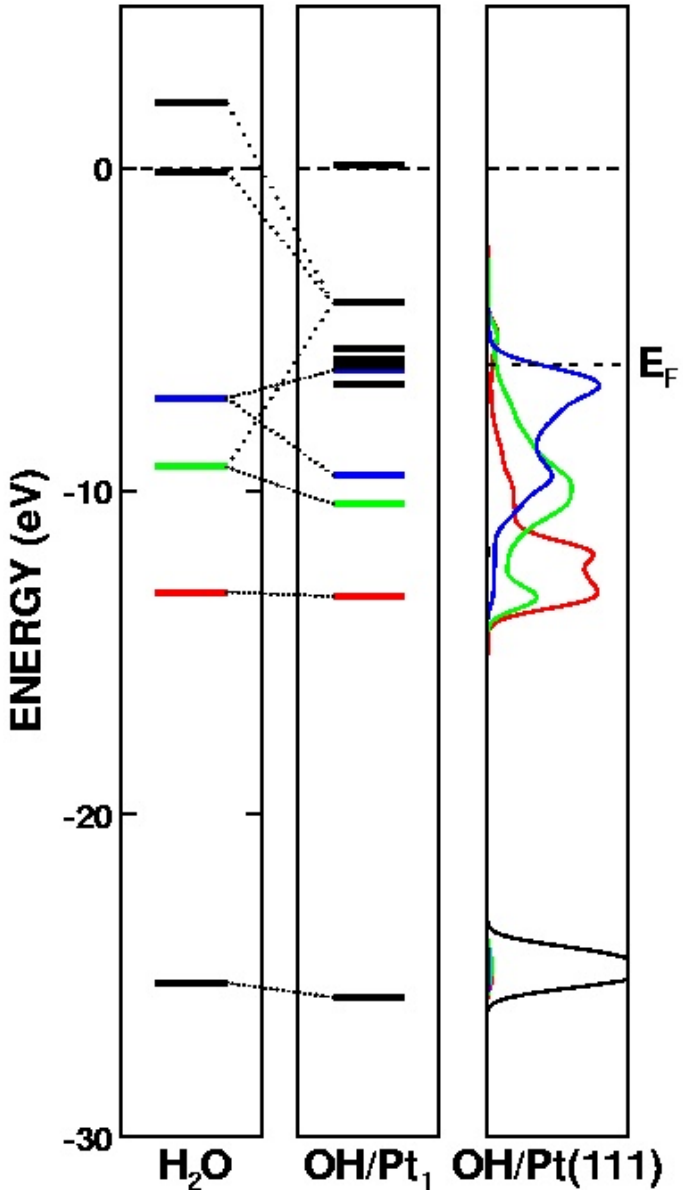
Energy level diagram

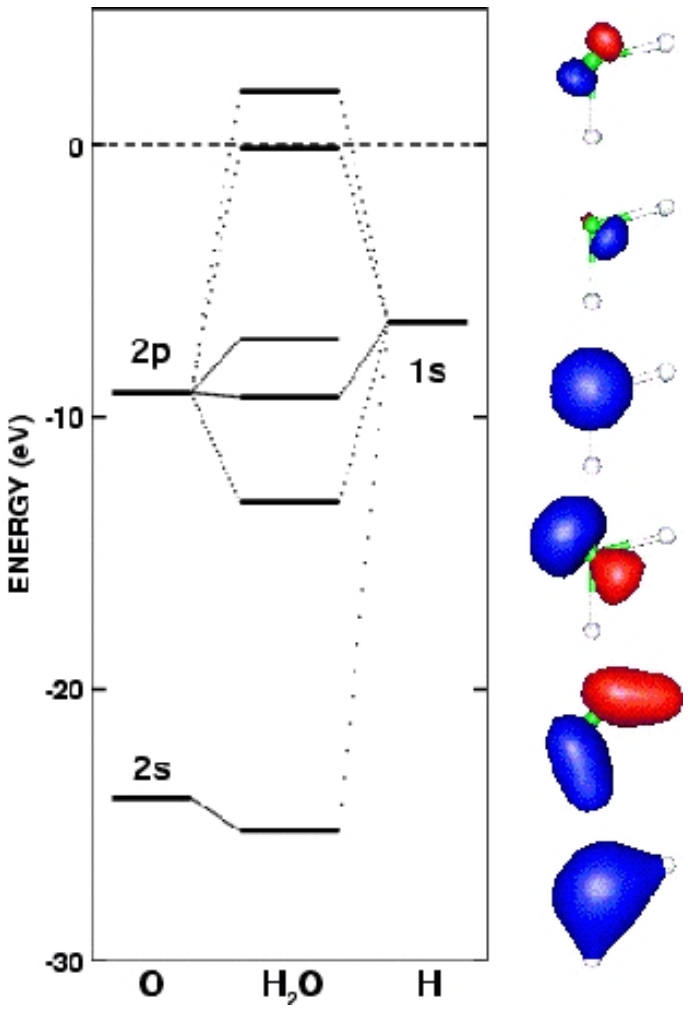
- Example: Water molecule



Local density of states

- Project the Kohn-Sham orbitals on the localised (pseudo) wave functions around the central atom
- Yields information about the energetic location of the orbitals and molecular hybrids formed by the atom
- Example: Hydroxyl on Pt(111) surface


ENERGY (eV)
0
-10
-20
-30
E_F
H_2O
OH/Pt_1
OH/Pt(111)


ENERGY (eV)
0
-10
-20
-30
2p
1s
2s
O
H_2O
H

Atoms In Molecules, AIM

Bader's zero flux surface

- Surface partitioning the charge to different atoms
- Based on the "zero flux", *i. e.* finding locations where $\nabla n \cdot \mathbf{u} = 0$, where $\mathbf{u}$ is the normal (unit) vector of the surface
- Based on the "zero flux", *i. e.* finding locations where $\nabla n \cdot$
- A freely-available code is available from Hannes Jónsson and co-workers (based on the file format "Gaussian cube")

Conductivity

Optical conductivity

- The optical conductivity according to the Kubo-Greenwood formula

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2 V_{\text{cell}}} \frac{1}{\omega} \sum_{i,j} \left(f_i - f_j\right) \left|\left\langle \psi_i \left|\hat{\mathbf{p}}\right| \psi_j \right\rangle\right|^2 \delta\left(\varepsilon_i - \varepsilon_j - \hbar\omega\right)$$

Electron localisation function

- Derived from Taylor expansion of the conditional probability of finding a second electron with the same spin close to a reference electron

- Normalised to the uniform electron gas

$$\boxed{\mathrm{ELF} = \frac{1}{1+\left(D_\sigma/D_\sigma^0\right)^2}}$$

$$D_\sigma = \tau_\sigma - \frac{1}{4}\frac{\left(\nabla n_\sigma\right)^2}{n_\sigma} \qquad \tau_\sigma = \sum_i |\nabla\psi_i|^2 \qquad D_\sigma^0 = \frac{3}{5}\left(6\pi^2\right)^{2/3} n_\sigma^{5/3}$$

- ELF is limited to $0 \leq ELF \leq 1$
  - ELF = 1: Perfect localisation
  - ELF = 1/2: Uniform electron gas

Modern theory of polarisation

- Recently large interest was paid to polarisation in crystals
- Problem: periodicity makes use of position operator $\hat{\mathbf{r}}$ impossible in solids
- Solution: Berry phases
- Yielded as "side products" *e. g.* Wannier centres, Wannier orbitals

Position operator in periodic systems

- Wave functions are periodic

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L})$$

- Result of operator acting on wave function has also to be periodic

$$\mathcal{O}\psi(\mathbf{r}) = \phi(\mathbf{r}) = \phi(\mathbf{r} + \mathbf{L})$$

- Result of operator acting on wave function has also to be periodic

$$\mathbf{r}\psi(\mathbf{r}) = (\mathbf{r} + \mathbf{L})\,\psi(\mathbf{r} + \mathbf{L})$$

- The expectation value of the position operator of a wave function using PBC

$$\langle \hat{X} \rangle = \frac{L}{2\pi} \Im \ln \left\langle \psi \left| e^{\mathrm{i}(2\pi/L)\hat{X}} \right| \psi \right\rangle$$

$\langle \hat{X} \rangle$ is defined only modulo $\mathbf{L}$

Polarisation in periodic systems

- Total polarisation

$$P_{\text{tot}} = P_{\text{nuc}} + P_{\text{el}}$$

- Electronic contribution (Γ-only)

$$P_{\text{el}}^{\alpha} = -\frac{2e}{2\pi\left|\mathbf{G}_{\alpha}\right|}\Im \ln \det S^{\alpha} \ ,$$

$$S_{mn}^{\alpha} = \left\langle \phi_m \left| e^{-\mathrm{i}\mathbf{G}_{\alpha}\mathbf{r}_{\alpha}} \right| \phi_n \right\rangle$$

- infrared adsorption coefficient

$$\alpha\left(\omega\right) = \frac{4\pi\omega \tanh(\beta\hbar\omega/2)}{3\hbar n\left(\omega\right) c\Omega} \int_{t=-\infty}^{\infty} \left\langle \mathbf{P}\left(t\right) \cdot \mathbf{P}\left(0\right)\right\rangle e^{\mathrm{i}\omega t}\, dt$$

- $n\left(\omega\right)$ = refractive index, c = speed of light, Ω = volume

Wannier orbitals

- Kohn-Sham energy is invariant upon a unitary rotation of the occupied orbitals

- Use this to define *localised* orbitals by minimising the spread Ω

$$\Omega = 2\sum_i \left(\left\langle \phi_i \left|\mathbf{r}^2\right| \phi_i \right\rangle - \left\langle \phi_i \left|\mathbf{r}\right| \phi_i \right\rangle^2\right)$$

- Leads to spread

$$\Omega_i = \frac{2}{(2\pi)^2}\sum_{I=1}^{6} \omega_I \left(1 - \left|z_{\alpha,i}\right|\right)$$

where ω_I are weights depending on cell symmetry and

$$z_{\alpha,i} = \int_{\mathbf{r}} \exp\left(\mathrm{i}\mathbf{G}_\alpha \cdot \mathbf{r}\right) \left|\phi_i\left(\mathbf{r}\right)\right|^2 d\mathbf{r}$$

- Centre of orbital

$$r_{\alpha,i} = -\sum_\beta \frac{\mathbf{h}_{\alpha\beta}}{2\pi} \Im \ln z_{\alpha,i}$$

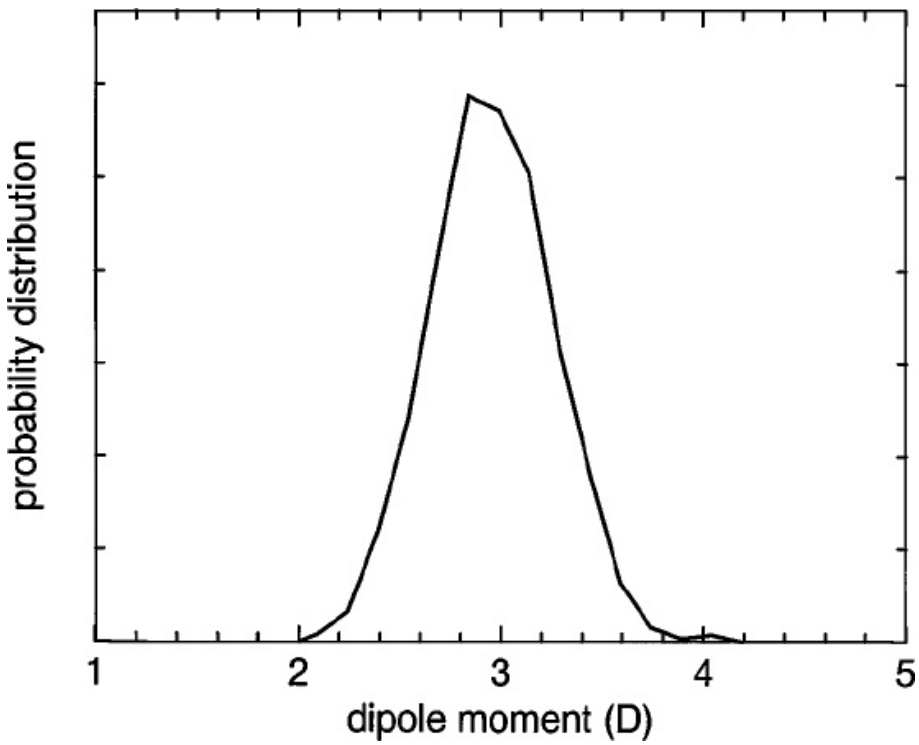
- Using the minimisation of Ω one obtains "maximally localised orbitals"

Wannier centres, orbitals

Example: Water

- Dipole moment of water molecules in different environments

	d_{OO} (Å)	d_{OH} (Å)	μ (D)
Monomer		0.97	1.87
Dimer	2.94	0.98	2.15
Liquid	2.78	0.99	2.95

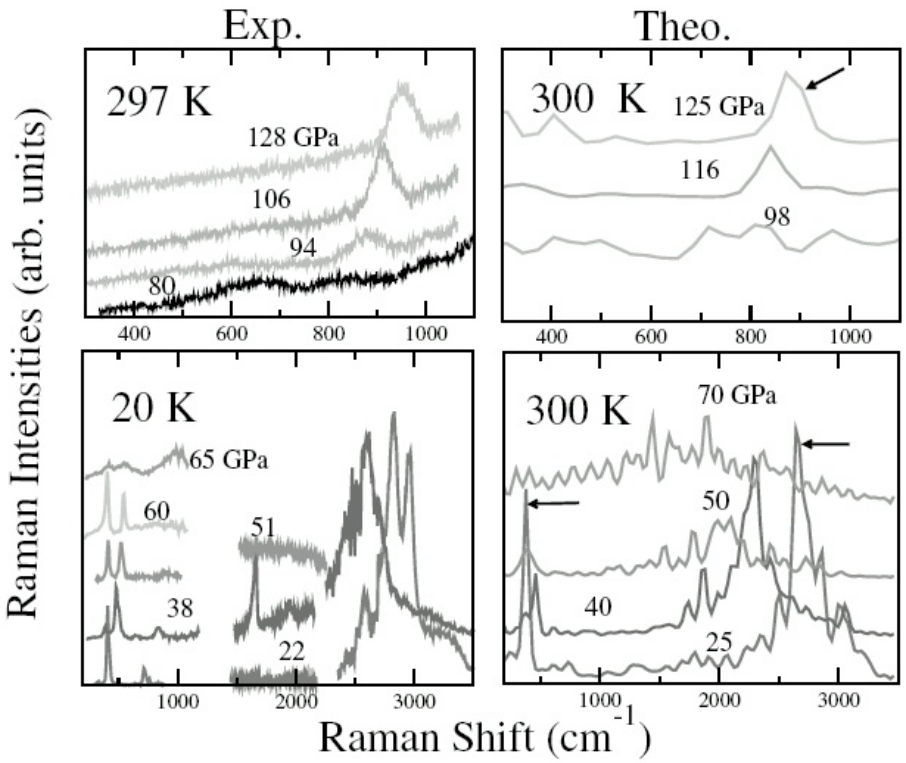


Raman spectrum

With `CPMD` Raman spectrum can be evaluated in two ways:

- Harmonic analyasis: Calculate the vibrational normal modes (**VIBRATIONAL ANALYSIS**) and displace the ions along those modes; the Raman intensity would be propotional to the change in polarisibility

- Perform molecular dynamics and every now and then evaluate the polarisability; the Raman intensity is related to its autocorrelation function

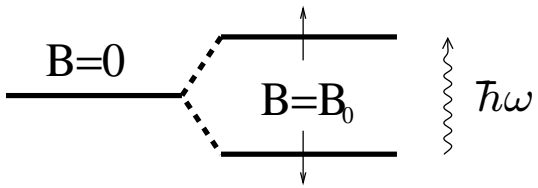


Nature of the chemical shielding

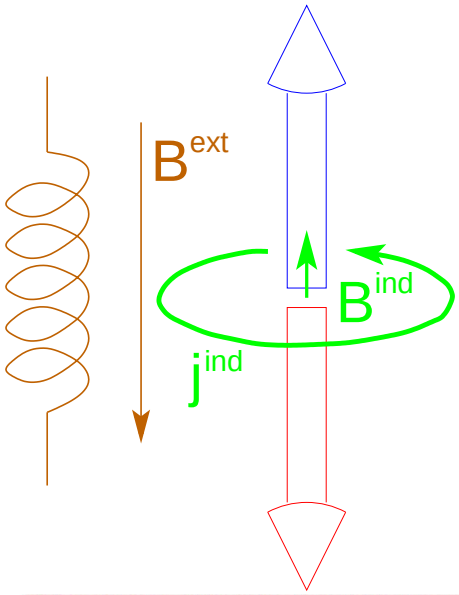
- External magnetic field $\mathbf{B}^{\text{ext}}$
- Electronic reaction: induced current $\mathbf{j}(\mathbf{r})$

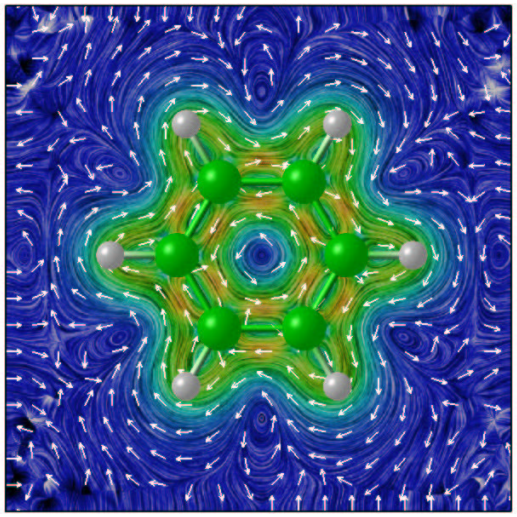
$\Rightarrow$ *inhomogeneous* magnetic field $\mathbf{B}^{\text{ind}}(\mathbf{r})$

- Nuclear spin $\boldsymbol{\mu}$ Up/Down
  energy level splitting



$$\Delta E = 2\boldsymbol{\mu} \cdot \mathbf{B} = \hbar\omega$$





Chemical shifts – chemical bonding

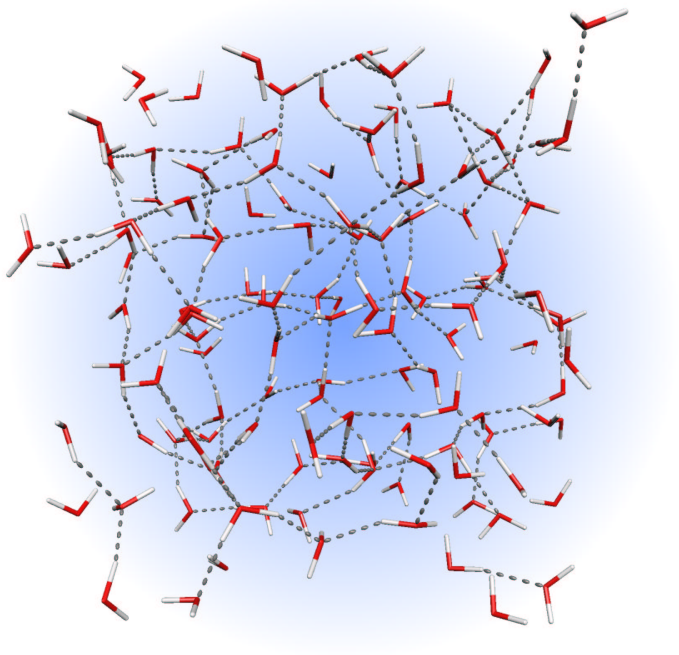
- NMR shielding tensor σ:
  definition through induced field

$$\mathbf{B}^{\text{tot}}(\mathbf{R}) = \mathbf{B}^{\text{ext}} + \mathbf{B}^{\text{ind}}(\mathbf{R})$$

$$\sigma(\mathbf{R}) = -\frac{\partial \mathbf{B}^{\text{ind}}(\mathbf{R})}{\partial \mathbf{B}^{\text{ext}}} \ll 1$$

- Strong effect of chemical bonding
  Hydrogen atoms: H-bonds

$\Rightarrow$ NMR spectroscopy:
Unique characterization
of local microscopic structure



(liquid water)

Magnetic field perturbation

- Magnetic field perturbation: vector potential $\mathbf{A}$

$$\begin{aligned}
\mathbf{A} &= -\frac{1}{2}\left(\mathbf{r} - \mathbf{R_g}\right) \times \mathbf{B} \\
\hat{\mathcal{H}}^{\text{pert}} &= -\frac{e}{m}\hat{\mathbf{p}} \cdot \hat{\mathbf{A}} \\
&= i\,\frac{\hbar e}{2m}\,\mathbf{B} \cdot \left(\hat{\mathbf{r}} - \mathbf{R_g}\right) \times \hat{\nabla}
\end{aligned}$$

- Cyclic variable: gauge origin $\mathbf{R_g}$

- Perturbation Hamiltonian purely imaginary $\Longrightarrow \quad n^{\lambda} = 0$

Magnetic field perturbation

Resulting electronic current density:

$$
\begin{aligned}
\hat{\mathbf{j}}_{\mathbf{r}'} &= \frac{e}{2m}\Big[\hat{\pi}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\hat{\pi}\Big] \\
&= \frac{e}{2m}\Big[(\hat{\mathbf{p}} - e\hat{\mathbf{A}})|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|(\hat{\mathbf{p}} - e\hat{\mathbf{A}})\Big] \\
\mathbf{j}(\mathbf{r}') &= \sum_k \langle\varphi_k^{(0)}|\,\hat{\mathbf{j}}_{\mathbf{r}'}^{(2)}\,|\varphi_k^{(0)}\rangle + 2\,\langle\varphi_k^{(0)}|\,\hat{\mathbf{j}}_{\mathbf{r}'}^{(1)}\,|\varphi_k^{(1)}\rangle \\
&= \mathbf{j}^{\text{dia}}(\mathbf{r}') + \mathbf{j}^{\text{para}}(\mathbf{r}')
\end{aligned}
$$

Dia- and paramagnetic contributions:
zero and first order wavefunctions

The Gauge origin problem

- Gauge origin $\mathbf{R}_\mathbf{g}$ theoretically not relevant
- In practice: very important: $\mathbf{j}^{\text{dia}}(\mathbf{r}') \propto \mathbf{R}_\mathbf{g}^2$
- GIAO: Gauge Including Atomic Orbitals
- IGLO: Individual Gauges for Localised Orbitals
- CSGT: Continuous Set of Gauge Transformations: $\mathbf{R}_\mathbf{g} = \mathbf{r}'$
- IGAIM: Individual Gauges for Atoms In Molecules

Magnetic field under periodic boundary conditions

- Basis set: plane waves
  (approach from condensed matter physics)

- Single unit cell (*window*)
  taken as a representative for the full crystal

- All quantities defined in reciprocal space (periodic operators)

- Position operator $\hat{\mathbf{r}}$ not periodic

- non-periodic perturbation Hamiltonian $\hat{\mathcal{H}}^{\text{pert}}$

PBC: Individual $\hat{r}$-operators for localized orbitals

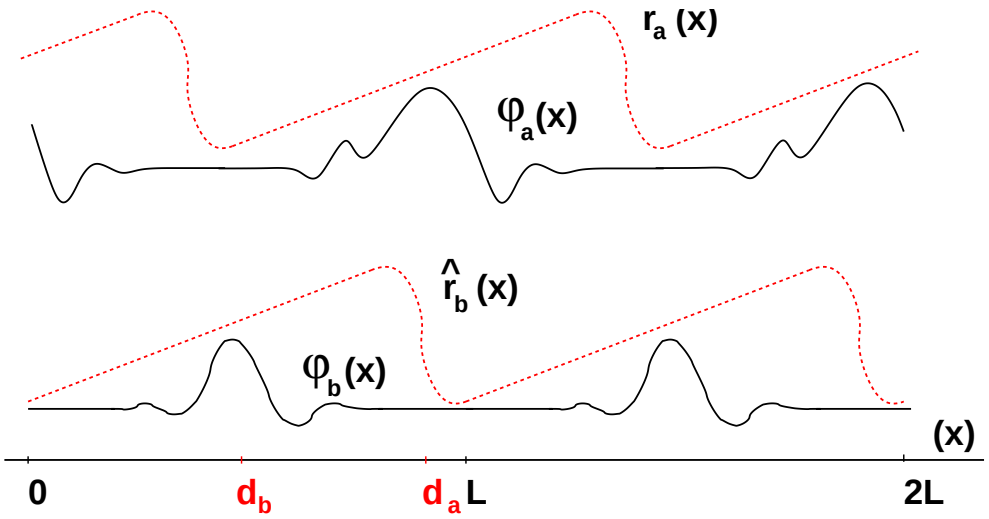
- Localised Wannier orbitals φ_i via unitary rotation:

$$\varphi_i \quad = \quad U_{ij}\, \psi_j$$

orbital centers of charge $\mathbf{d_i}$

- Idea:

Individual position operators



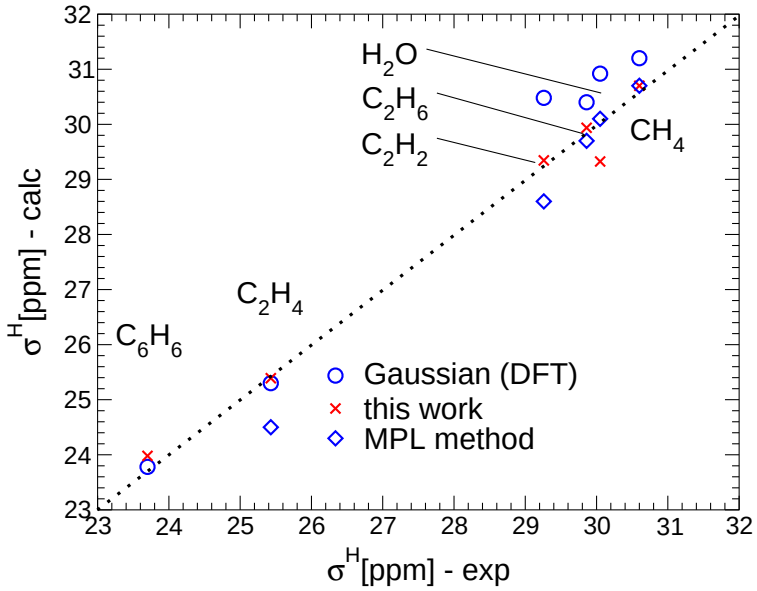
Magnetic fields in electronic structure

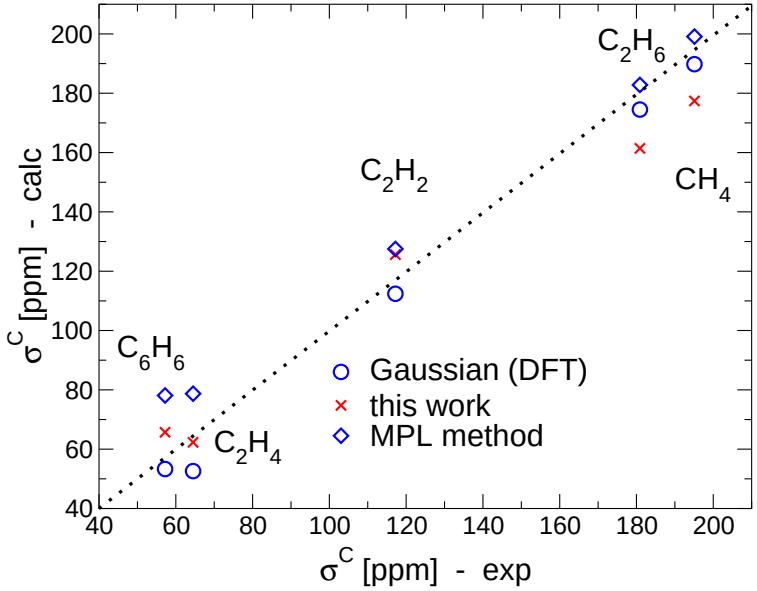
- Variational principle $\mapsto$ electronic response orbitals
- Perturbation Hamiltonian $\widehat{\mathcal{H}}^{\text{pert}}$: $\hat{\mathbf{A}} = -\frac{1}{2}\left(\hat{\mathbf{r}} - \mathbf{R}_{\mathrm{g}}\right) \times \mathbf{B}$
- Response orbitals $\mapsto$ electronic ring currents
- Ring currents $\mapsto$ NMR chemical shielding
- Reference to standard $\mapsto$ NMR chemical shift

Isolated molecules

- Isolated organic molecules, ^{1}H and ^{13}C chemical shifts

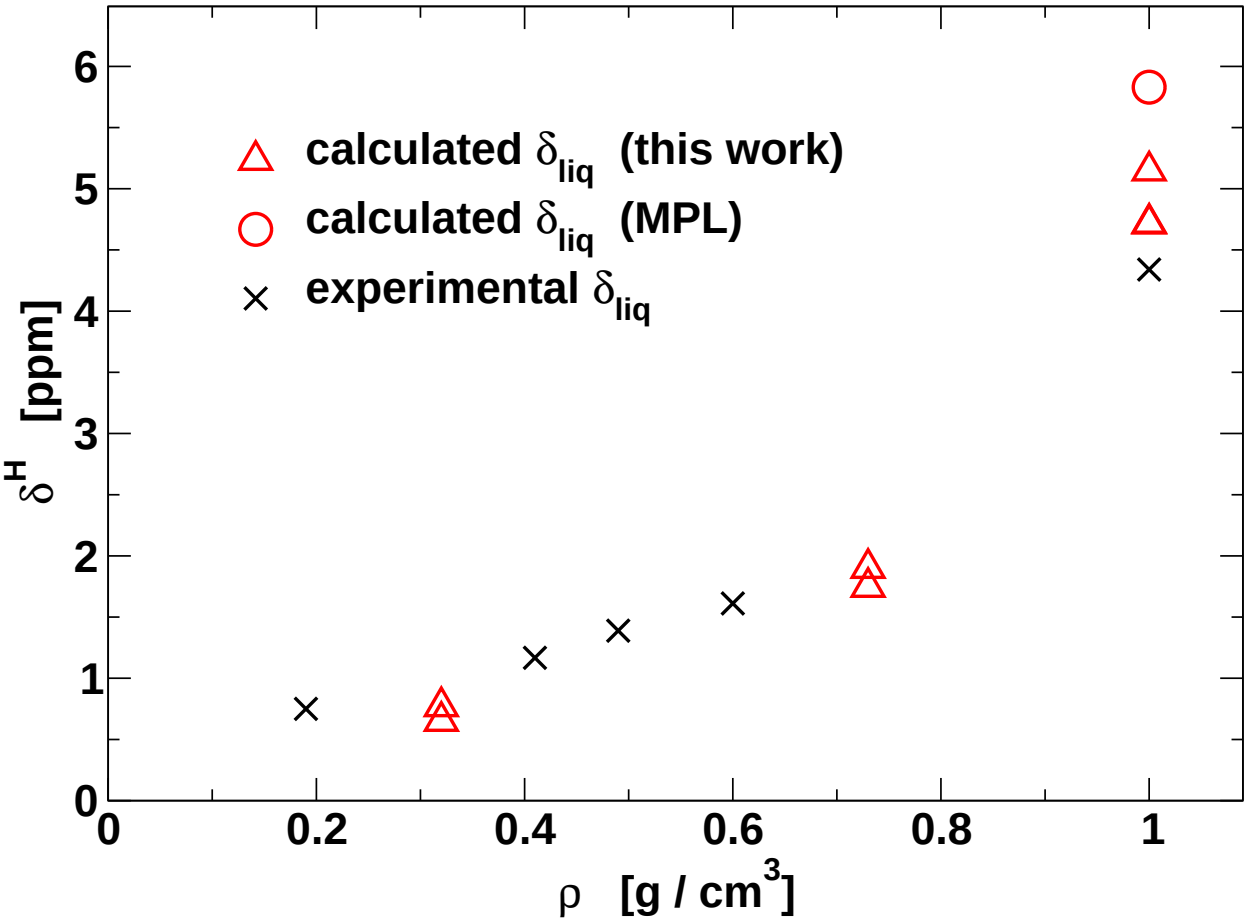
- Comparison with Gaussian 98 calculation,
  (converged basis set DFT/BLYP)





Supercritical water: gas − liquid shift

- Qualitatively reduced hydrogen bond network in supercritical water
- Excellent agreement with experiment
- Slight overestimation of H-bond strength at $T^{\ominus}$
  BLYP overbinding ?
  Insufficient relaxation ?



$\Longrightarrow$ confirmation of simulation

Properties: Summary

- `CPMD` provides many post-processing methods