

Properties

MD simulation: output

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

Mean square displacement, diffusion

- mean square displacement

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

- diffusion coefficient (Einstein relation)

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

alternative definition (Green-Kubo formula)

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

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

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

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 $E \dots E + \delta E$

- Can be evaluated via

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

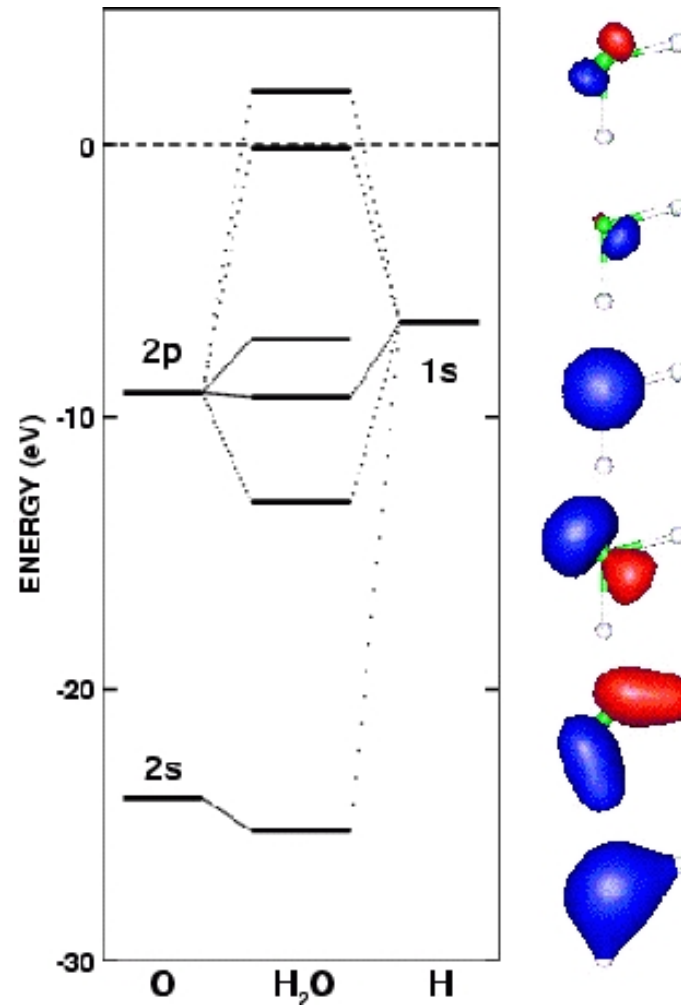
- in practise δ functions have to be broadened e. g. with Gaussian functions
- in CPMD: $E_{i,\mathbf{k}}$ can be obtained with **KOHN-SHAM ENERGIES**

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 **CUBEFIELD ORBITALS** or **RHOOUT BANDS**

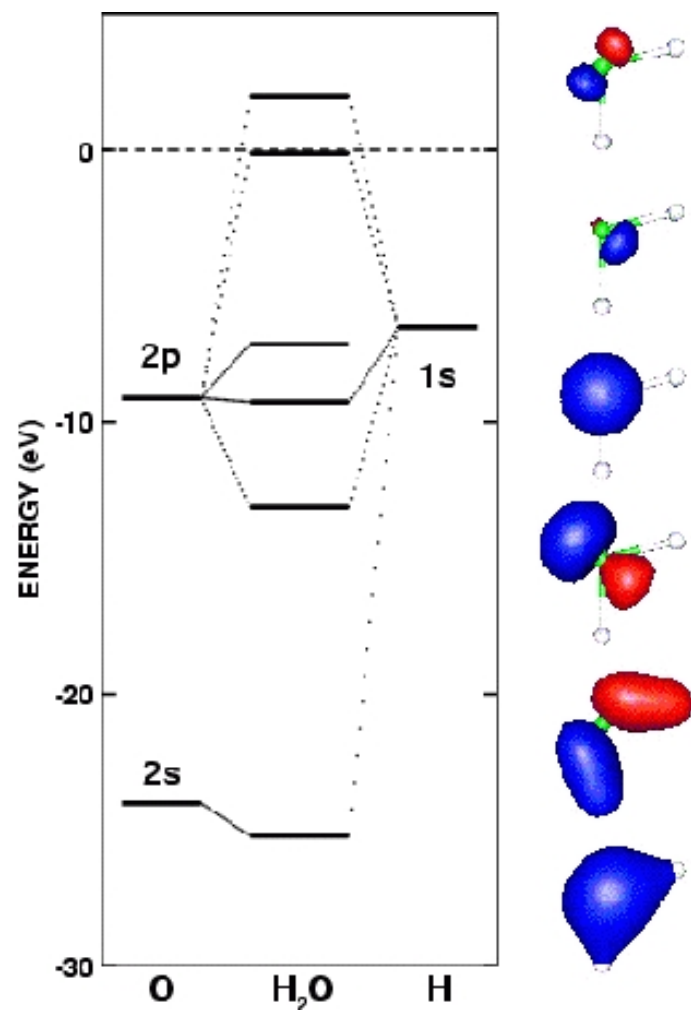
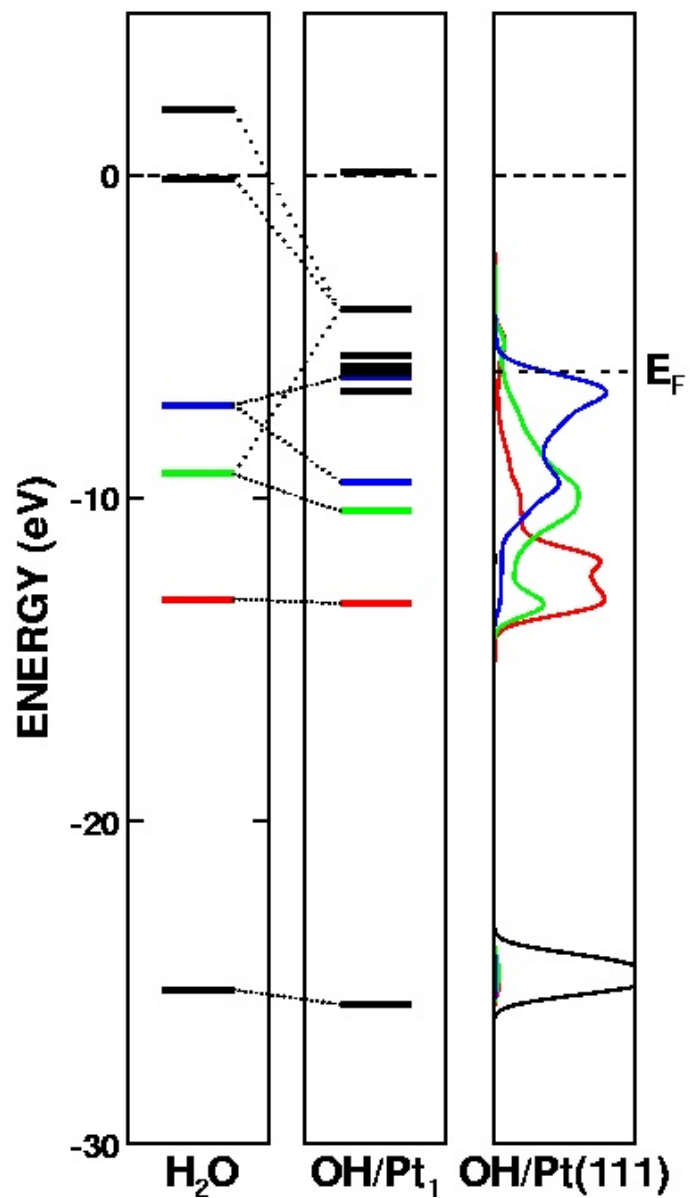
Energy level diagram

- 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



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

Conductivity

Optical conductivity

- The optical conductivity according to the Kubo-Greenwood formula

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

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

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

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

- 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{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

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

$\langle \hat{X} \rangle$ 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)

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

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

- infrared adsorption coefficient

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

- $n(\omega)$ = 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

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

- Leads to spread

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

where ω_I are weights depending on cell symmetry and

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

- Centre of orbital

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

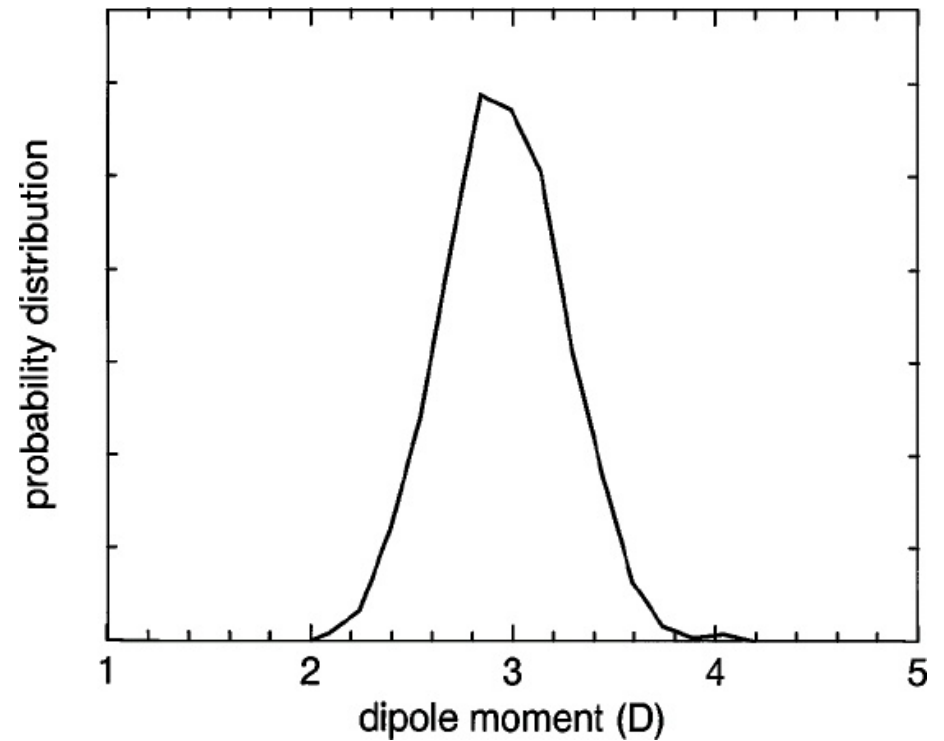
- Using the minimisation of Ω one obtains “maximally localised orbitals”

Wannier centres, orbitals

Example: Water

- Dipole moment of water molecules in different environments

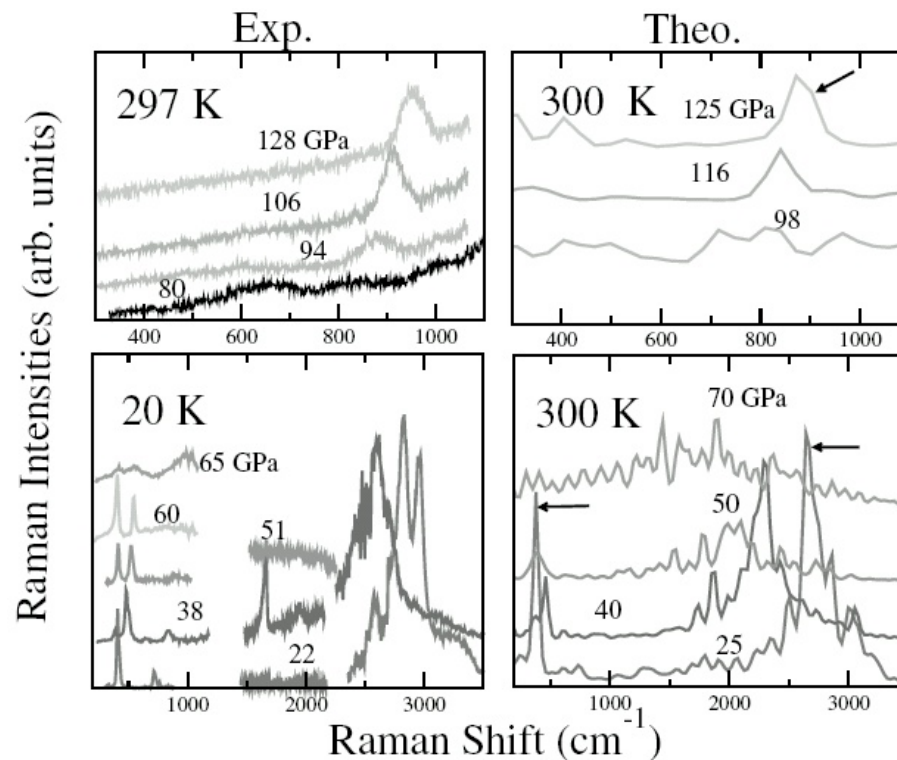
	d_{OO} (Å)	d_{OH} (Å)	μ (D)
Monomer		0.97	1.87
Dimer	2.94	0.98	2.15
Liquid	2.78	0.99	2.95



Raman spectrum

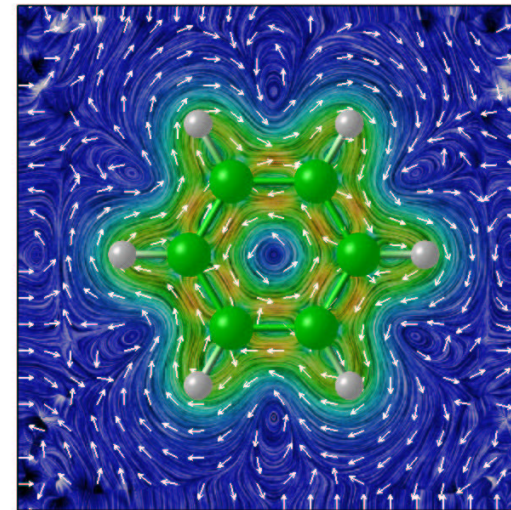
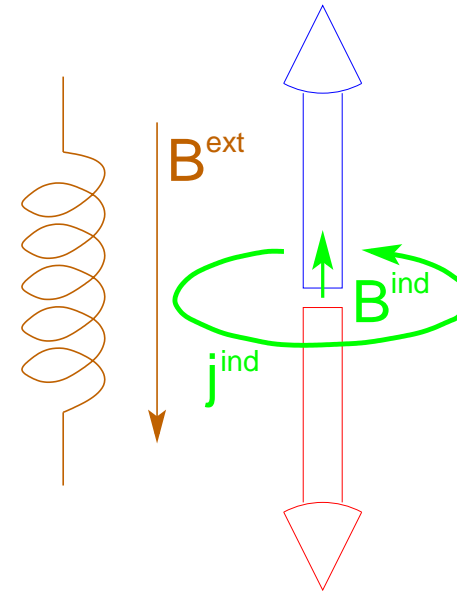
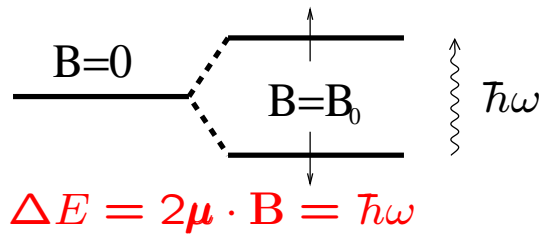
With CPMD Raman spectrum can be evaluated in two ways:

- Harmonic analysis: Calculate the vibrational normal modes (**VIBRATIONAL ANALYSIS**) and displace the ions along those modes; the Raman intensity would be proportional to the change in polarisability
- 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}^{ext}
- Electronic reaction: induced current $\mathbf{j}(\mathbf{r})$
- ⇒ *inhomogeneous* magnetic field $\mathbf{B}^{\text{ind}}(\mathbf{r})$
- Nuclear spin μ Up/Down
energy level splitting



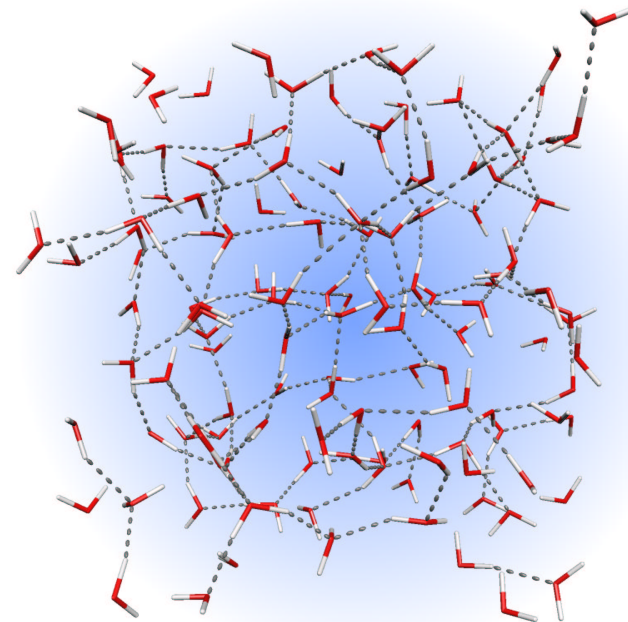
Chemical shifts – chemical bonding

- 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
⇒ NMR spectroscopy:
Unique characterization
of local microscopic structure



(liquid water)

Chemical shielding tensor

$$\sigma(R) = - \begin{pmatrix} \frac{\partial B_x^{\text{ind}}(R)}{\partial B_x^{\text{ext}}} & \frac{\partial B_x^{\text{ind}}(R)}{\partial B_y^{\text{ext}}} & \frac{\partial B_x^{\text{ind}}(R)}{\partial B_z^{\text{ext}}} \\ \frac{\partial B_y^{\text{ind}}(R)}{\partial B_x^{\text{ext}}} & \frac{\partial B_y^{\text{ind}}(R)}{\partial B_y^{\text{ext}}} & \frac{\partial B_y^{\text{ind}}(R)}{\partial B_z^{\text{ext}}} \\ \frac{\partial B_z^{\text{ind}}(R)}{\partial B_x^{\text{ext}}} & \frac{\partial B_z^{\text{ind}}(R)}{\partial B_y^{\text{ext}}} & \frac{\partial B_z^{\text{ind}}(R)}{\partial B_z^{\text{ext}}} \end{pmatrix}$$

- Tensor is *not* symmetric
⇒ symmetrization ⇒ diagonalization ⇒ Eigenvalues
- Isotropic shielding: $\text{Tr } \sigma(R)$
- Isotropic chemical shift: $\delta(R) = \text{Tr} \sigma^{\text{TMS}} - \text{Tr} \sigma(R)$

Magnetic field perturbation

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

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

- Cyclic variable: gauge origin \mathbf{R}_g
- Perturbation Hamiltonian purely imaginary $\implies n^\lambda = 0$

Magnetic field perturbation

Resulting electronic current density:

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

Dia- and paramagnetic contributions:
zero and first order wavefunctions

The Gauge origin problem

- Gauge origin \mathbf{R}_g theoretically not relevant
- In practice: very important: $\mathbf{j}^{\text{dia}}(\mathbf{r}') \propto \mathbf{R}_g^2$
- GIAO: Gauge Including Atomic Orbitals
- IGLO: Individual Gauges for Localised Orbitals
- CSGT: Continuous Set of Gauge Transformations: $\mathbf{R}_g = \mathbf{r}'$
- 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{r} not periodic
- non-periodic perturbation Hamiltonian $\hat{\mathcal{H}}^{\text{pert}}$

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

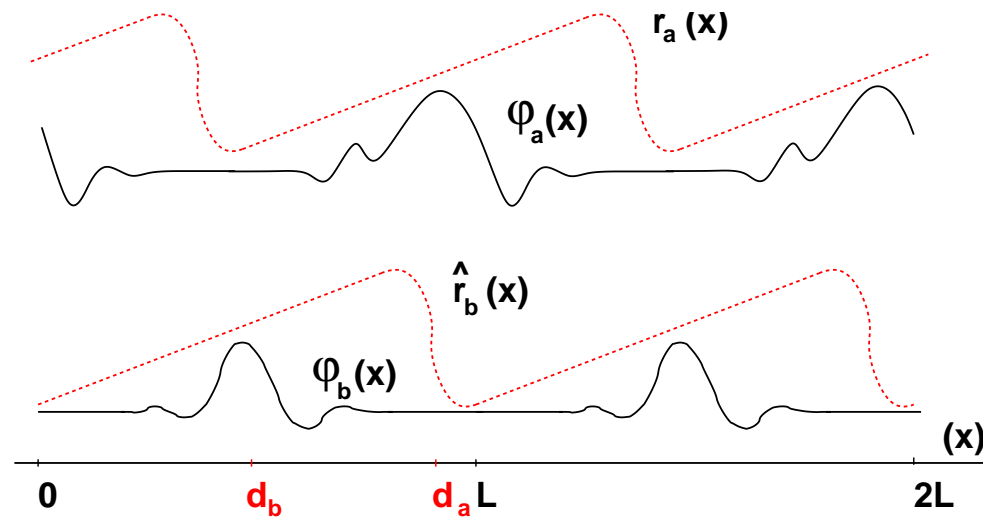
- Localised Wannier orbitals φ_i via unitary rotation:

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

orbital centers of charge \mathbf{d}_i

- Idea:

Individual operators
position

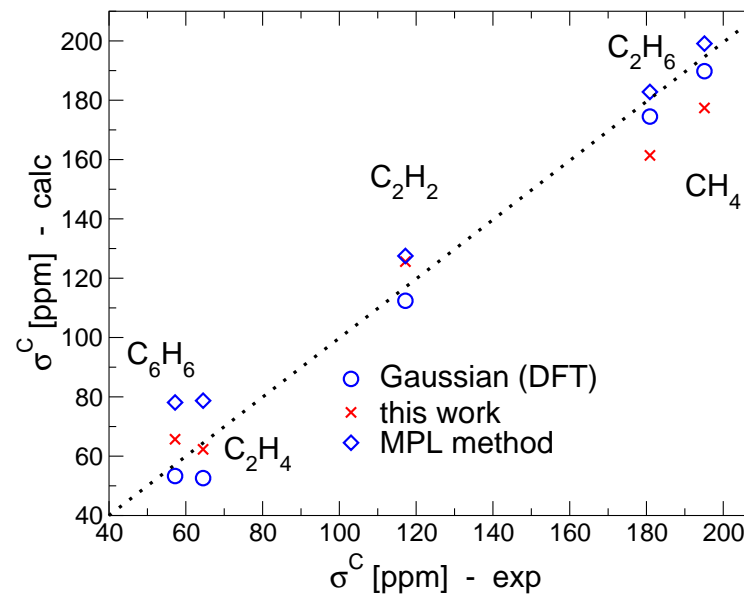
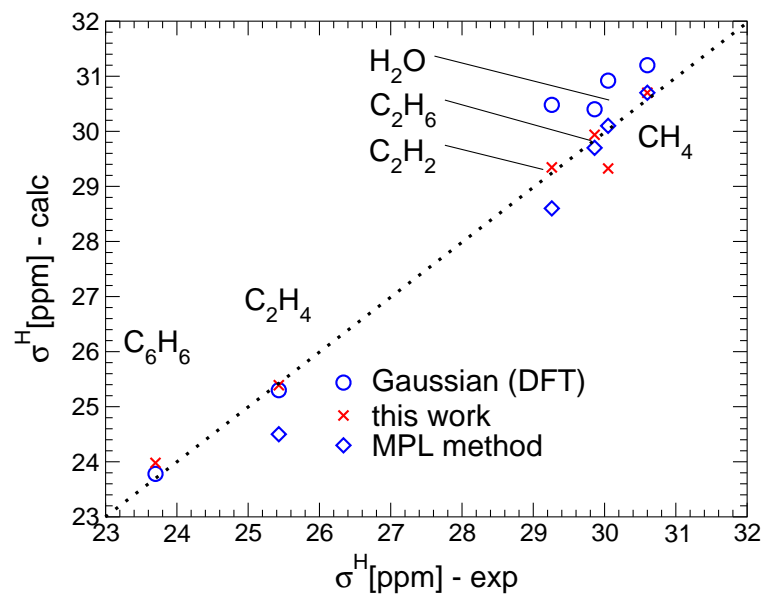


Magnetic fields in electronic structure

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

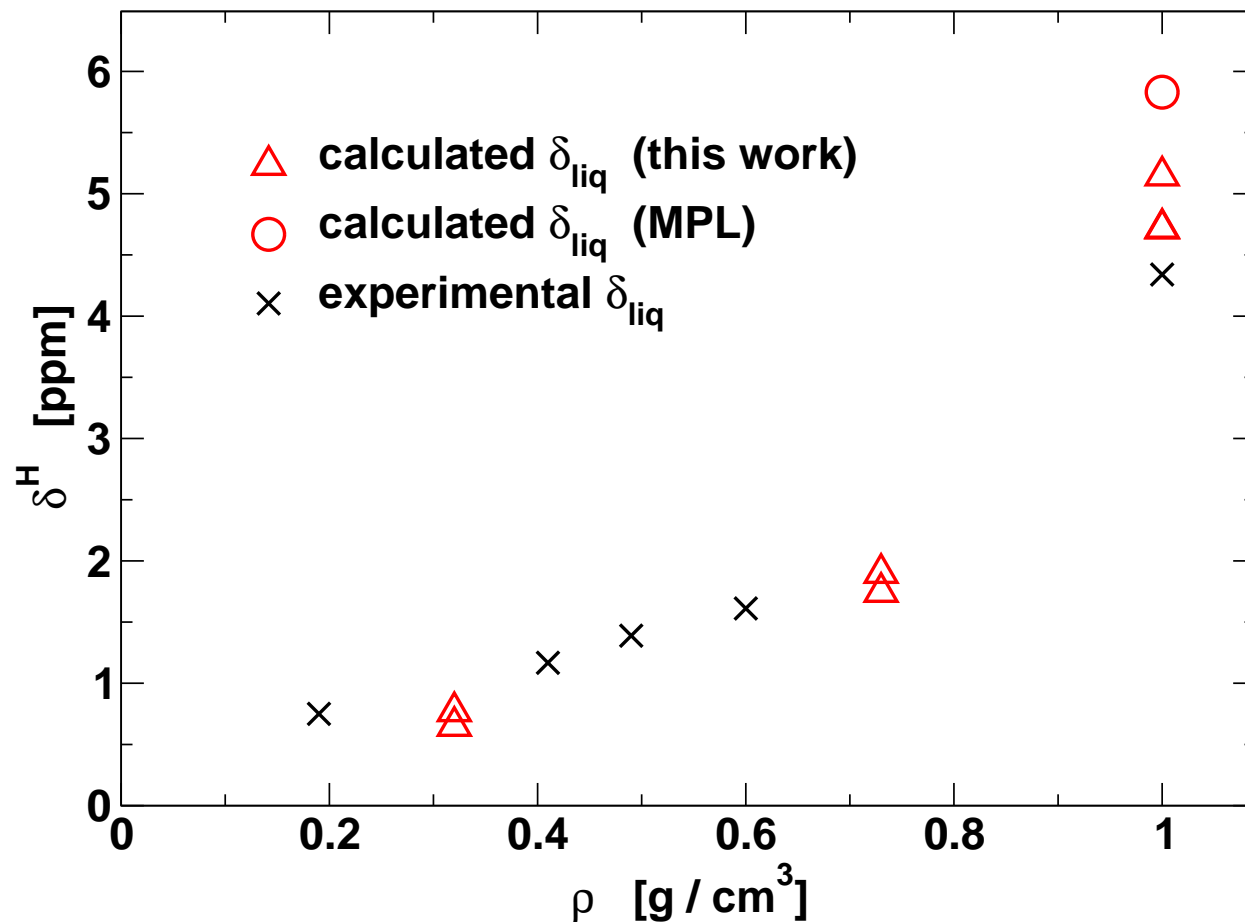
Isolated molecules

- Isolated organic molecules, ^1H 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 ?



⇒ confirmation of simulation

Properties: Summary

- CPMD provides many post-processing methods