Density functional theory

— an introduction

Anatole von Lilienfeld, Truman Fellow (1435)

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Abstract

We will review the basic foundations of Kohn-Sham density functional theory (DFT). Afterwards, applications of electronic ground-state, electronically excited states calculations, and *ab initio* molecular dynamics studies will be presented. The selected examples will include condensed as well as gas phase systems properties. Finally, we will discuss to which extent current DFT implementations are predictive.

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Overview

- Introduction
- Theory
- Electronic applications
- *Ab initio* molecular dynamics
- Excited states

Intro — Explicit electronic structure

- When does one have to solve the electron structure explicitly?
  - Chemical reactions: Breaking and creation of chemical bonds
  - Variable coordination
  - Changing type of interaction
  - Difficult chemistry of elements

  → whenever potentials are unknown — leverage Quantum Mechanics
  `The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.`
  P. Dirac

- Unfortunately, the complexity of the problem grows immensely: Nuclei localised (only coordinates needed), explicit electron structure means solving the full Schrödinger equation

⇒ Compromises, approximations

Intro — Many body electronic structure theory

Φ: Born-Oppenheimer *Ansatz* (Adiabaticity),

$$\Phi\left(\{\mathbf{R}_I\},\{\mathbf{r}_i\}\right) \approx \Psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) \times \chi(\{\mathbf{R}_I\}),$$

leads to electronic many-body eigenvalue equation (Schrödinger),

$$\mathcal{H}^e \Psi^{(n)}_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) = E^{(n)}_{\{\mathbf{R}_I\}} \Psi^{(n)}_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right)$$

with electronic Hamiltonian

$$\mathcal{H}^e \;=\; \widehat{T}_{ee} + \widehat{V}_{\text{ext}} + \widehat{V}_{ee} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{\text{ext}}\left(\mathbf{r}\right) + \frac{1}{4\pi\epsilon_0}\sum_{ij}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Ψ:
- depends on coordinates of electrons,

$$\Psi^{(n)}_{\{\mathbf{R}_I\}}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right),$$

- has to satisfy (Pauli),

$$\Psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j,\ldots\mathbf{r}_N\right) = -\Psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_i,\ldots\mathbf{r}_N\right),$$

- obtain ground state energy and wave function via minimisation (Ritz)

$$E_0 = \left\langle \Psi^{(0)} \middle| \mathcal{H}^e \middle| \Psi^{(0)} \right\rangle = \min_{\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \langle \Psi | \mathcal{H}^e | \Psi \rangle$$

- subject to the constraint on normalisation (Hilbert)

Intro — Many body wave function

Quantum chemistry approaches

- Hartree-Fock: Approximate wave function with a single determinant; anti-symmetric property automatically fulfilled
- Correlation:
  - MP2, MP3, MP4
  - MC-SCF
  - FCI
  - Coupled-cluster
  - ...

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Explicit presentation

- Imagine storing the full many body wave function, not even speaking of solving it
- For example 10 orbitals (20 electrons with spin degeneracy), 100 points per orbital
  - 100^{10} points, 4 bytes per point $\Rightarrow \approx 4 \times 10^{20} = 0.4$ mio PB

$\Rightarrow$ impossible data amount, simplification and/or approximations required

Theory — Alternative route

via density

- Density is a basic property of the system and the coordinate space does not grow with the number of particles (electrons)

- Is it enough to know only the (electron) density?

$$n_1(\mathbf{r}) = N \int \ldots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \ldots \, d\mathbf{r}_N$$

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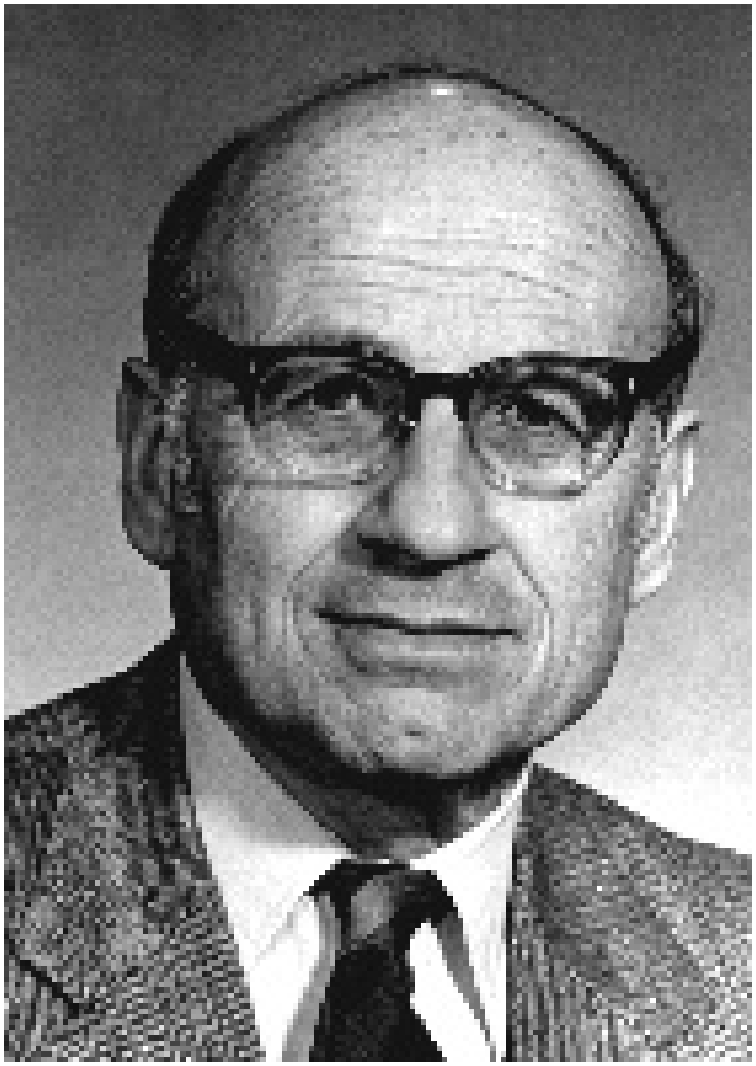
Hohenberg-Kohn theorem I

The exact electron many body (ground state) wave function Ψ — defined by external potential + N interacting electrons — is a unique functional of the electronic density n

Thus, all quantum mechanical observables are functionals of n, n can be used instead of the wavefunction to characterise all the properties of an electronic structure

Solution: Walter Kohn



$\frac{1}{2}$ Nobel prize Chemistry, 1998 (shared with Pople).

Theory — Hohenberg-Kohn theorem I: Proof

By *reductio ad absurdum*:

- Suppose there *were* two different potentials, v_1 and v_2, yielding the same density but different ground state wave functions Ψ_1 and Ψ_2

- Clearly, trial function Ψ_2 with potential v_1 would give,

$$\langle \Psi_2 | \, \hat{T}_{ee} + \hat{V}_{ee} + v_1 \, | \Psi_2 \rangle > \langle \Psi_1 | \, \hat{T}_{ee} + \hat{V}_{ee} + v_1 \, | \Psi_1 \rangle = E_0$$

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  Since $\langle \Psi | v_1 | \Psi \rangle = \int d\mathbf{r} n(\mathbf{r}) v_1(\mathbf{r})$, ($n$ is the same),

$$\langle \Psi_2 | \, \hat{T}_{ee} + \hat{V}_{ee} \, | \Psi_2 \rangle > \langle \Psi_1 | \, \hat{T}_{ee} + \hat{V}_{ee} \, | \Psi_1 \rangle$$

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  Swap 1 and 2,

$$\langle \Psi_1 | \, \hat{T}_{ee} + \hat{V}_{ee} \, | \Psi_1 \rangle > \langle \Psi_2 | \, \hat{T}_{ee} + \hat{V}_{ee} \, | \Psi_2 \rangle$$

$\Rightarrow$ *Absurdum*!

Theory — Hohenberg-Kohn theorem II

From all the densities, the one n that minimizes the energy functional with a given external potential is the ground state density, *i. e.* the density which corresponds to the solution of the Schrödinger equation; $E[\tilde{n}] \geq E_0$

Theory — Chemical potential

- All the variations with respect to density must be done at a constant number of electrons N

- This can be done applying a Lagrangean multiplier μ

$$E'[n] = E[n] - \mu \left[\int_{\mathbf{r}} n(\mathbf{r})\, d\mathbf{r} - N \right]$$

- Variation yields

$$\begin{aligned}
\delta E'[n] &= \delta \left\{ E[n] - \mu \int_{\mathbf{r}} n(\mathbf{r})\, d\mathbf{r} \right\} \\
&= \delta E[n] - \mu \int_{\mathbf{r}} \delta n(\mathbf{r})\, d\mathbf{r} \\
&= \int_{\mathbf{r}} \frac{\delta E[n]}{\delta n(\mathbf{r})} \delta n(\mathbf{r})\, d\mathbf{r} - \mu \int_{\mathbf{r}} \delta n(\mathbf{r})\, d\mathbf{r} \\
&= \int_{\mathbf{r}} \left\{ \frac{\delta E[n]}{\delta n(\mathbf{r})} - \mu \right\} \delta n(\mathbf{r})\, d\mathbf{r} \quad = \quad 0
\end{aligned}$$

$\Rightarrow$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = v_{\text{ext}}(\mathbf{r}) + \frac{\delta T[n]}{\delta n(\mathbf{r})} + \frac{\delta V_{ee}[n]}{\delta n(\mathbf{r})}$$

Theory — Kohn-Sham *Ansatz*

- Assume one electron orbitals $\{\phi_i\}$ in Slater determinant wave function (*i. e.* non-interacting),

$$\Psi_s = \frac{1}{N!} \,|\, \phi_1 \, \phi_2 \ldots \phi_N \,|.$$

- Kohn-Sham Equations

$$\hat{h}_s \phi_i = \epsilon_i \phi_i \qquad \hat{h}_s = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r})$$

Kohn-Sham orbitals ϕ_i are normalized orthonormal eigenstates of an effective Kohn-Sham potential v_s in the Kohn-Sham Hamiltonian,

$$\begin{aligned} \langle \phi_i | \phi_j \rangle &= \delta_{ij} \\ n(\mathbf{r}) &= \sum_i^N |\phi_i(\mathbf{r})|^2 \\ \int d\mathbf{r} \, n(\mathbf{r}) &= N \end{aligned}$$

Theory — Kohn-Sham scheme: Total energy

- This *Ansatz* leads to the total energy

$$E_{\mathsf{KS}}[n] = \int d\mathbf{r}\; n(\mathbf{r})\, v_{\mathsf{ext}}(\mathbf{r}) + T_s[n] + E_H[n] + E_{xc}[n] = \int d\mathbf{r}\; n(\mathbf{r})\, v_{\mathsf{ext}}(\mathbf{r}) + F_{\mathsf{ee}}[n].$$

- First term corresponds to interaction between electrons and external potential (ionic density + perturbations), and

$$T_s[n] = -\frac{1}{2} \min_{\{\phi_i\}\mapsto n} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle; \text{ kinetic energy of KS electrons}$$

$$E_H[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}; \text{ classical Coulomb interaction, aka Hartree term}$$

all the remainder goes into

$$E_{xc}[n] = (T[n] - T_s[n]) + (E_{ee} - E_H[n])$$

Theory — Kohn-Sham potential

Variational principle: for infinitesimally small variation $\delta n(\mathbf{r})$ (conserving N, *i. e.* $\int_{\mathbf{r}} \delta n(\mathbf{r})\, d\mathbf{r} = 0$),

$$\delta E_{\mathsf{KS}} = \delta T_s + \int_{\mathbf{r}} \frac{\delta \left[n(\mathbf{r})\, v_{\mathsf{ext}}(\mathbf{r}) + E_H + E_{xc} \right]}{\delta n(\mathbf{r})} \delta n(\mathbf{r})\, d\mathbf{r}$$

$$= \delta T_s + \int_{\mathbf{r}} \left[v_{\mathsf{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \delta n(\mathbf{r})\, d\mathbf{r} = 0$$

where

$$v_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r}')} = \int_{\mathbf{r}'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'; \text{ Hartree potential}$$

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})}; \text{ exchange-correlation potential}$$

And δT_s?

Theory — Kohn-Sham potential

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And δT_s? Use HK+KS,

$$\sum_i \langle \phi_i | -\frac{1}{2}\nabla^2 + v_s[n] | \phi_i \rangle = T_s[n] + \int_{\mathbf{r}} v_s(\mathbf{r}, [n])\, n(\mathbf{r})\, d\mathbf{r}$$

and, due to the variational principle,

$$\delta T_s + \int_{\mathbf{r}} v_s(\mathbf{r})\, \delta n(\mathbf{r})\, d\mathbf{r} = 0 \quad \longrightarrow \quad \delta T_s = -\int_{\mathbf{r}} v_s(\mathbf{r})\, \delta n(\mathbf{r})\, d\mathbf{r}$$

Theory — Kohn-Sham potential

- Substitute δT_s,

$$\delta E_{\mathsf{KS}} = -\int_{\mathbf{r}} v_s(\mathbf{r})\,\delta n(\mathbf{r})\,d\mathbf{r} + \int_{\mathbf{r}} [v_{\mathsf{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})]\,\delta n(\mathbf{r})\,d\mathbf{r} = 0$$

- The condition for n to be n_0, *i. e.* the density which minimizes E_{KS}, is that the integrands equate,

$$\rightarrow\ v_s[n_0](\mathbf{r}) := v_{\mathsf{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n_0\,(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_{xc}[n_0](\mathbf{r})$$

  evaluate n_0 *self-consistently*

- E_0 = minimal $E_{\mathsf{KS}}[n_0]$ is given by

$$E_0 = \int_{\mathbf{r}} v_{\mathsf{ext}}\,n_0\,d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0]$$

- While also,

$$T_s[n_0] + \int_{\mathbf{r}} v_s[n_0]\,n_0\,d\mathbf{r} = \sum_i^N \epsilon_i$$

Theory — Ground state energy

Alternative expression

$$
\begin{aligned}
E_0 &= \int_{\mathbf{r}} v_{\text{ext}}\, n_0\, d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0] \\
&= \int_{\mathbf{r}} v_{\text{ext}}\, n_0\, d\mathbf{r} - \int_{\mathbf{r}} v_s[n_0]\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \\
&= \int_{\mathbf{r}} (v_{\text{ext}} - v_s)\; n_0\, d\mathbf{r} + REST \\
&= \int_{\mathbf{r}} \left[v_{\text{ext}} - \left(v_{\text{ext}} + \int_{\mathbf{r}} \frac{n_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc} \right) \right] n_0\, d\mathbf{r} + REST \\
&= -\int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}') n_0(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'\, d\mathbf{r} - \int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + REST \\
&= -2E_H[n_0] - \int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + REST
\end{aligned}
$$

$$
\boxed{E_0 = -\int_{\mathbf{r}} v_{xc}\, n_0\, d\mathbf{r} + \sum_i^N \epsilon_i - E_H[n_0] + E_{xc}[n_0]}
$$

Theory — Kohn-Sham scheme

Lessons learned

- The Kohn-Sham equations must be solved *self-consistently*:

$$n(\mathbf{r}) \;\Rightarrow\; v_s[n] \;\Rightarrow\; \{\phi_i\} \;\Rightarrow\; n(\mathbf{r}) \;\Rightarrow\; \ldots$$

- There is an exact Kohn-Sham potential, albeit not known (2008)

- The eigenvalues are *not* physical, except for the one of the highest occupied orbital, which is represents the ionisation potential

- KS-DFT is a *ground state theory*

- There are other DFT flavors, orbital-free DFT (cheaper, less accurate), density matrix theory (more accurate, more expensive) ... KS-DFT most popular compromise

Theory — Approximations to v_{xc}

Climbing Jacob's ladder

- John Perdew's vision on the development of XC functionals

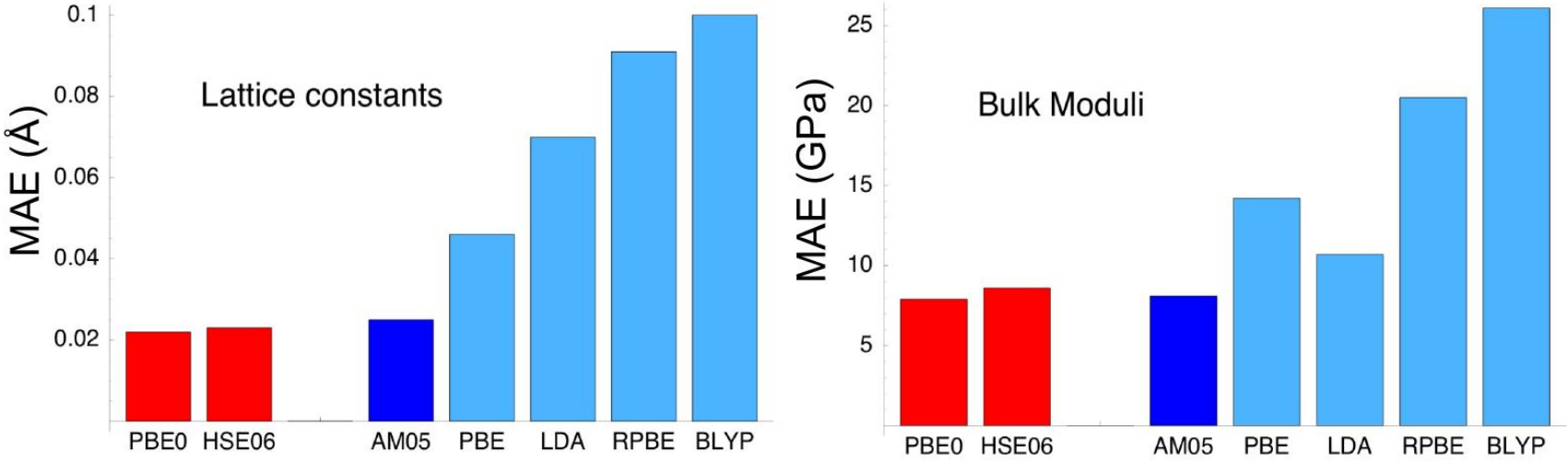
HEAVEN (chemical accuracy < kcal/mol)

explicit dependence on...		
unoccupied orbitals	rung 5	fully nonlocal (to come)
occupied orbitals	rung 4	*e. g.* hybrid functionals PBE0, HSE06, B3LYP
kinetic energy density	rung 3	meta-GGAs TPSS, B00, PKZB, BR89, LAP3
gradients of the density	rung 2	GGAs PBE, revPBE, PW91, BLYP, BP, HCTH93/407
local density only	rung 1	LDA

EARTH (Hartree theory)

Application — Electronic

Comparison of mean absolute errors (MAE) for properties of 20 solids calculated with seven different functionals.



Mattsson et al *JCP* (2008)

Application — Electronic

further performances

Property	LDA	GGA	meta or hybrid
Structures	slightly overbound	slightly underbound	ok
Energies	no	ok	good
Reaction barriers	no	strongly underest.	significantly underest.
Band gap	signific. underest.	strongly underest.	very good
Intermolecular	overbound	underbound	underbound
Electron transfer	no	sometimes	sometimes

Application — Ionic forces

Hellmann-Feynman forces in DFT

$$
\begin{aligned}
\mathbf{F_I} &= \frac{\partial E_0(\mathbf{R})}{\partial \mathbf{R_I}} = \frac{\partial}{\partial \mathbf{R_I}} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \langle \frac{\partial}{\partial \mathbf{R_I}} \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \frac{\partial}{\partial \mathbf{R_I}} \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} | \frac{\partial}{\partial \mathbf{R_I}} \Psi \rangle \\
&= E \langle \frac{\partial}{\partial \mathbf{R_I}} \Psi | \Psi \rangle + \langle \Psi | \frac{\partial}{\partial \mathbf{R_I}} \hat{H} | \Psi \rangle + E \langle \Psi | \frac{\partial}{\partial \mathbf{R_I}} \Psi \rangle \\
&= E \frac{\partial}{\partial \mathbf{R_I}} \langle \Psi | \Psi \rangle + \langle \Psi | \frac{\partial}{\partial \mathbf{R_I}} \hat{H} | \Psi \rangle \\
&= \langle \Psi | \frac{\partial}{\partial \mathbf{R_I}} \hat{H} | \Psi \rangle \\
&= \int d\mathbf{r}\, n(\mathbf{r}) \frac{\partial v_{\text{ext}}}{\partial \mathbf{R_I}} \quad = \quad \int d\mathbf{r}\, n(\mathbf{r}) \frac{Z_\mathbf{I} \times (\mathbf{r} - \mathbf{R_I})}{|\mathbf{r} - \mathbf{R_I}|^3}
\end{aligned}
$$

Basis for Verlet algorithm based *Ab Initio* Molecular Dynamics,

$$
\mathbf{R_I}(t + dt) = 2\mathbf{R_I}(t) - \mathbf{R_I}(t - dt) + \frac{\mathbf{F_I}(t)}{m_\mathbf{I}} dt^2
$$

$\rightarrow$ for a given stoichiometry physically meaningful ensembles can be generated and averaged (Movie @ `youtube.com`)

Car-Parrinello *vs* Born-Oppenheimer dynamics

Born-Oppenheimer MD	Car-Parrinello MD
Exactly on BO surface	Always slightly off BO surface
$\Delta t \approx$ ionic time scales, maximum time step possible	$\Delta t \ll$ ionic time scales, (much) shorter time step necessary
Expensive minimisation at each MD step	Orthogonalisation only, less expensive per MD step
Not stable against deviations from BO surface $\Rightarrow$ Energy/temperature drift, thermostatting of ions necessary	Stable against deviations from BO surface
Same machinery in zero-gap systems	Thermostatting of electrons to prevent energy exchange
Most applications in solids	Superior for liquids

CP *vs* BO

STABILITY OF BO AND CP MD COMPARED

CPMD results for the **8 Si atom model** system

Timings in cpu seconds and energy conservation in a.u. / ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	1×10^{7}	2310
CP	10	—	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

Why AIMD? — Free energy differences including reactions

- reaction coordinate ζ

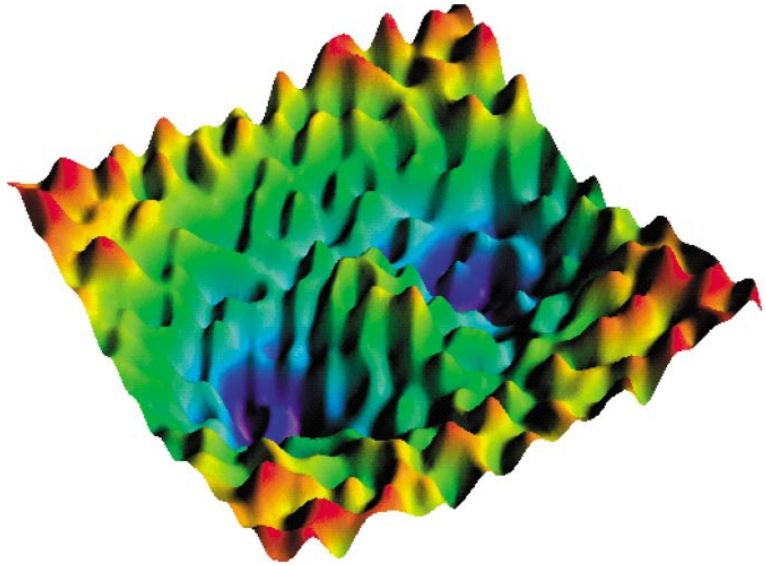
- probabilistic interpretation of free energy

$$W\left(\zeta'\right) = -kT \ln P_\zeta\left(\zeta'\right)$$

- Free energy difference

$$W\left(\zeta_2\right) - W\left(\zeta_1\right) = \int_{\zeta=\zeta_1}^{\zeta_2} d\zeta \left\langle \frac{\partial E}{\partial \zeta} \right\rangle_{\zeta'}^{\text{conditional}}$$

- Problematic rare events

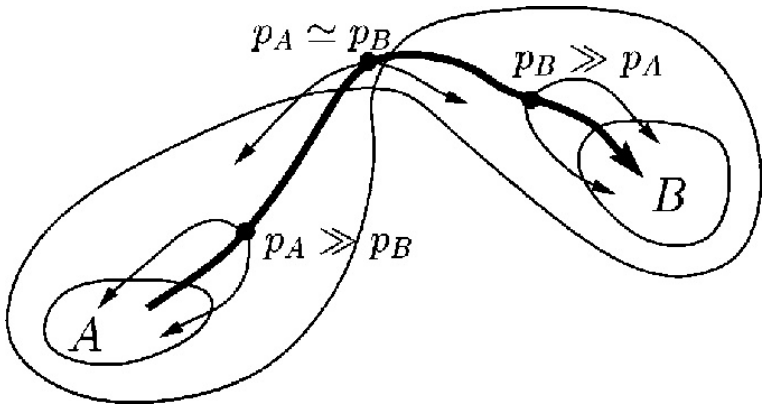


© D Chandler

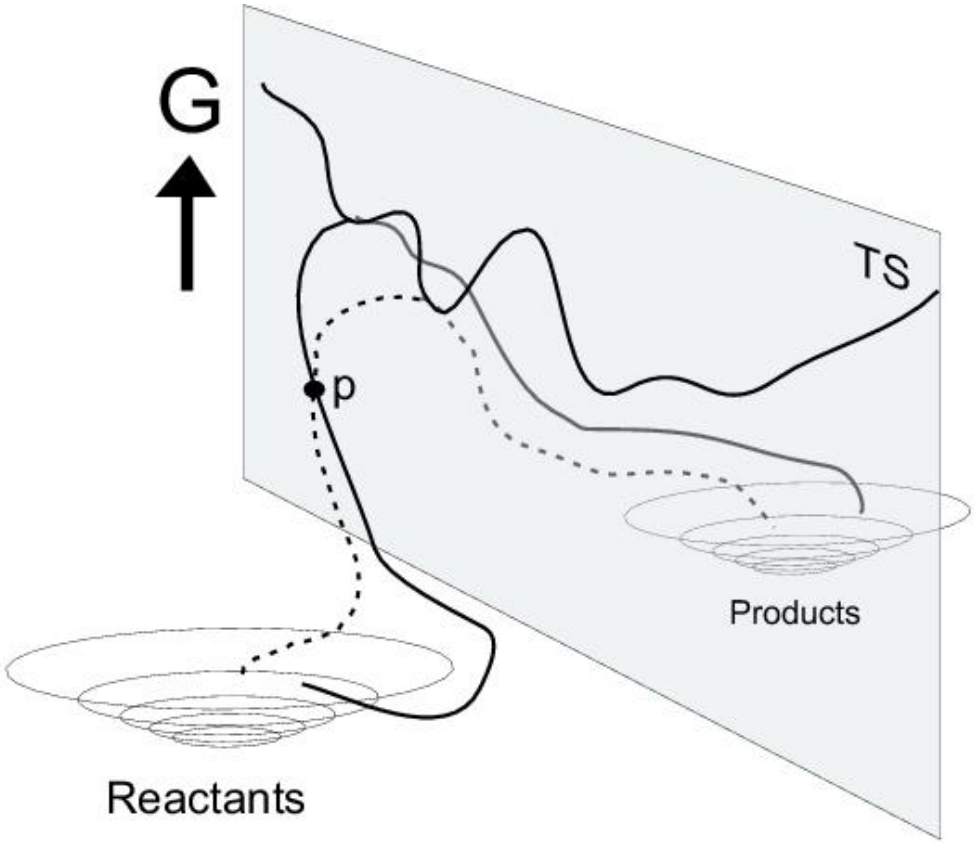
Transition path sampling

Or: Throwing ropes over rough mountains passes, in the dark

- Transition path sampling, idea:
  - Start with an initial reaction path
  - At a point along the present path start MDs with velocities $\dot{\mathbf{R}}_I$ and $-\dot{\mathbf{R}}_I$; if they lead to different end states, the state is probably close to a transition state



  - This way new reaction paths can be found, with a lower reaction barrier: Starting from a point "p" we might find another path with a lower barrier



- Reaction rates can be obtained, but with a large amount of statistics (different MD runs)

Electronic excitations

Time-dependent DFT

- Runge-Gross theorem (1984) extends the validity of KS to the time dependent domain. Time-dependent Kohn–Sham theory,

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r,t)\right]\Phi_i(r,t) = i\frac{\partial}{\partial t}\Phi_i(r,t)$$

$$V_{\text{eff}}(r,t) = V_{\text{H}}(r,t) + V_{\text{xc}}(r,t) + V_{\text{ext}}(r,t)$$

$$\rho(r,t) = \sum_i \mid \Phi_i(r,t) \mid^2$$

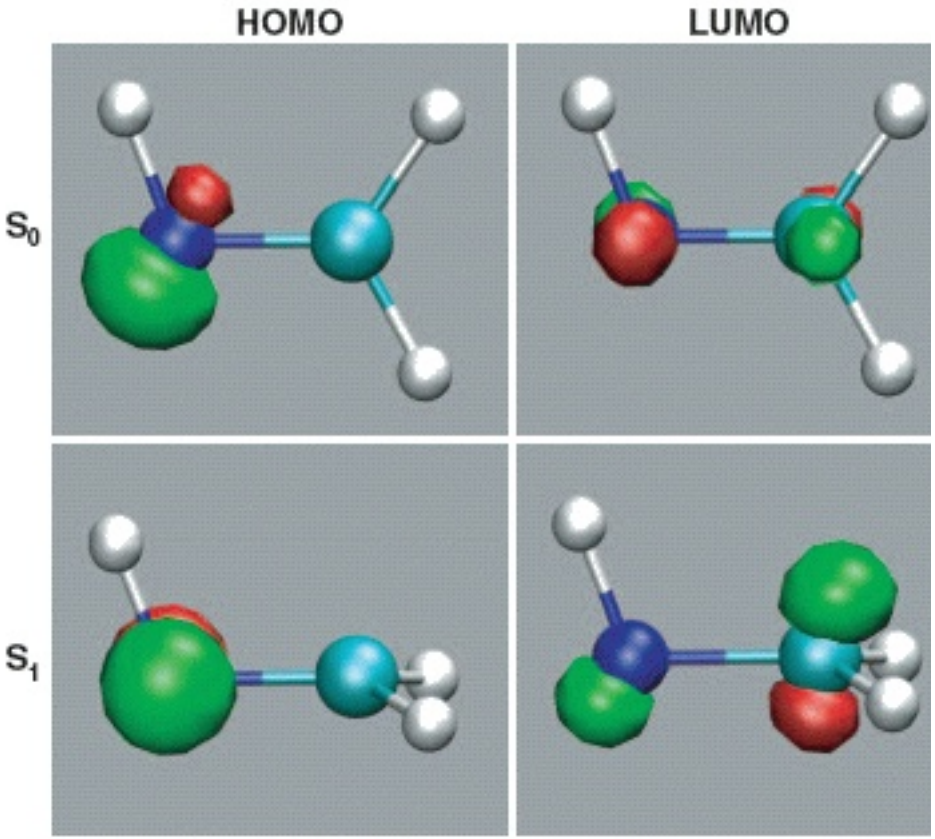
- Real time (small time step) and imaginary time (no electron dynamics) propagation

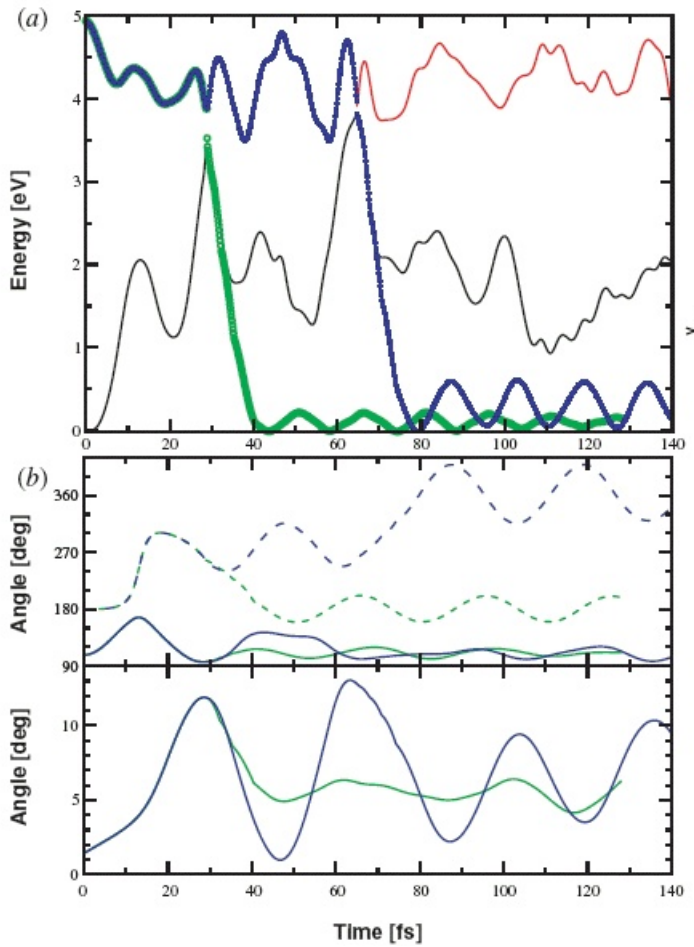
Linear response in TD Kohn–Sham scheme

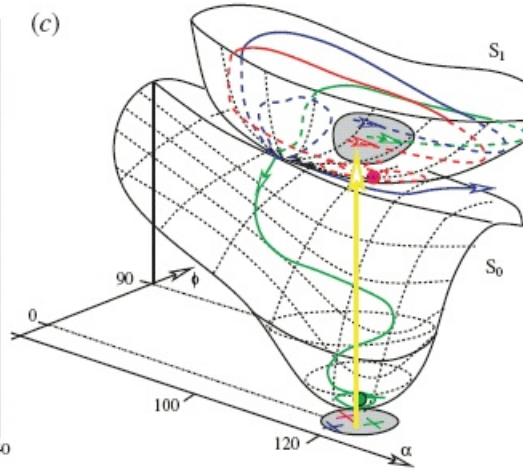
- *Excitation Energies from Time-Dependent Density-Functional Theory*, Petersilka, Gossmann & Hardy Gross, *PRL* **76**, 1212-1215 (1996)

- *Excited state nuclear forces from the Tamm–Dancoff approximation to time-dependent density functional theory within the plane wave basis set framework*, Jürg Hutter, *JPC* (2003)

Example for real time propagation: Formaldimine



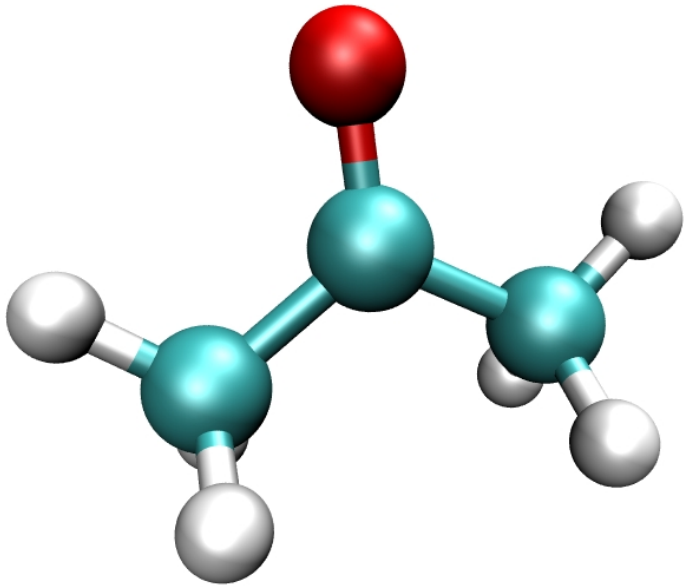




Ivano Tavernelli *Mol Phys* (2005)

Solvation: Acetone in water (full QM)

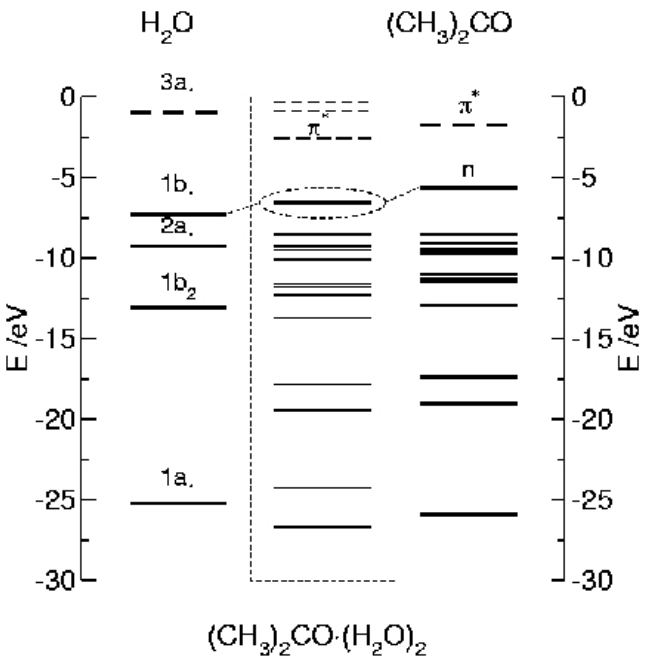
Bernasconi, Sprik & Hutter, JCP **119** (2003) 12417; CPL **394** (2004) 141

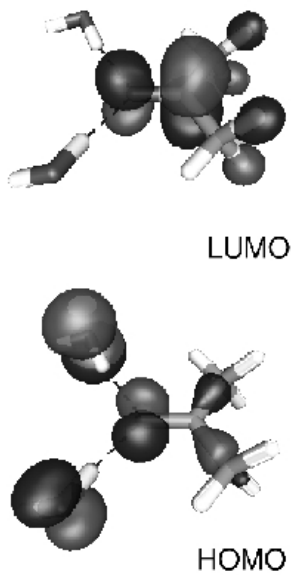


- Model system acetone for excited states in solvated systems
- acetone–water complexes and acetone in liquid water

Acetone in water

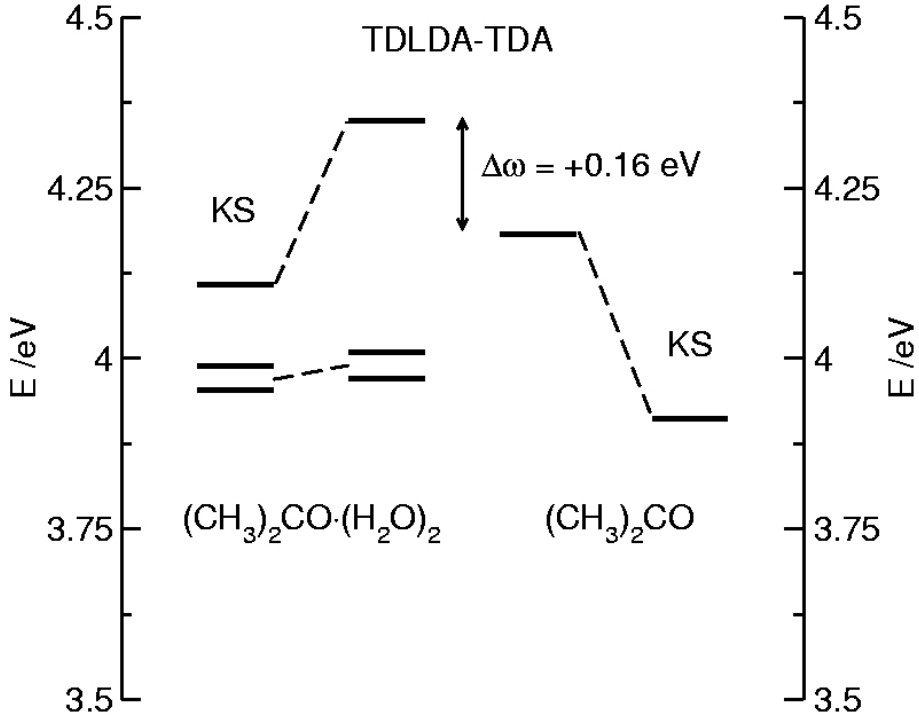
Acetone + water molecules





- Isolated $(CH_3)_2CO$: Lowest excitation symmetry-forbidden $n \rightarrow \pi^*$
- In TDA/TDDFT pure HOMO-LUMO transition at 4.18 eV
- Experimentally 4.3–4.5 eV
- With two water molecules mixing of HOMO, pure LUMO

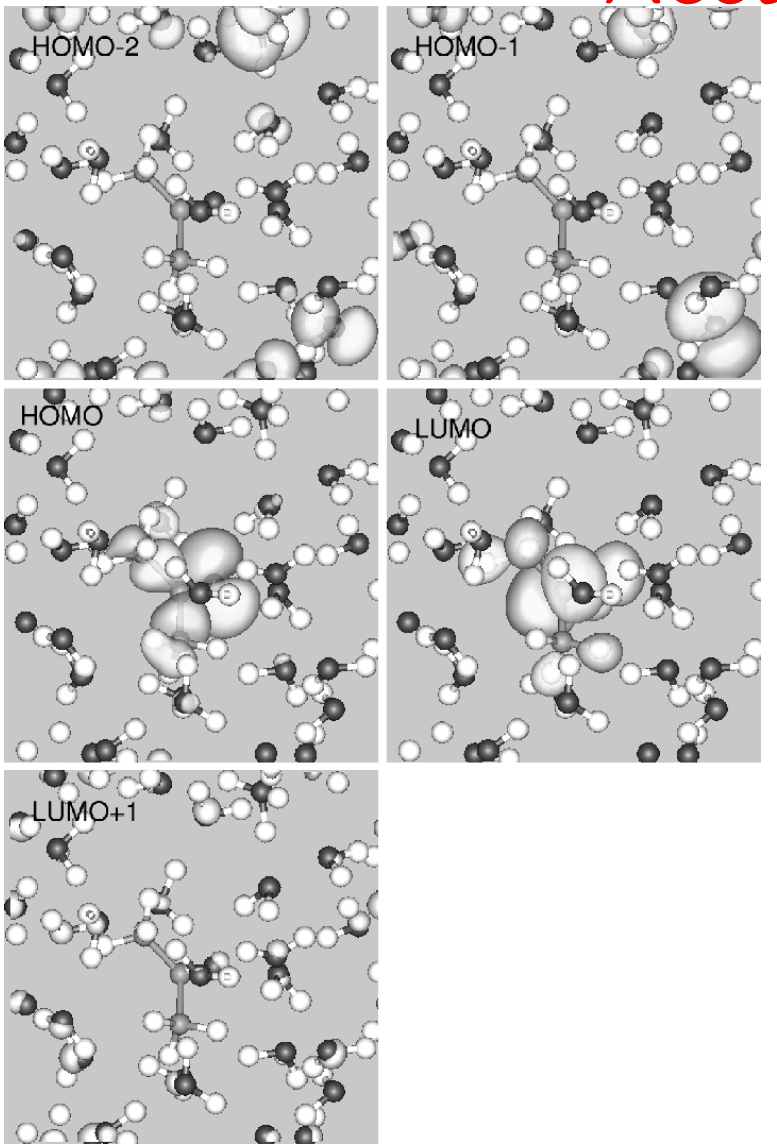
Acetone in water

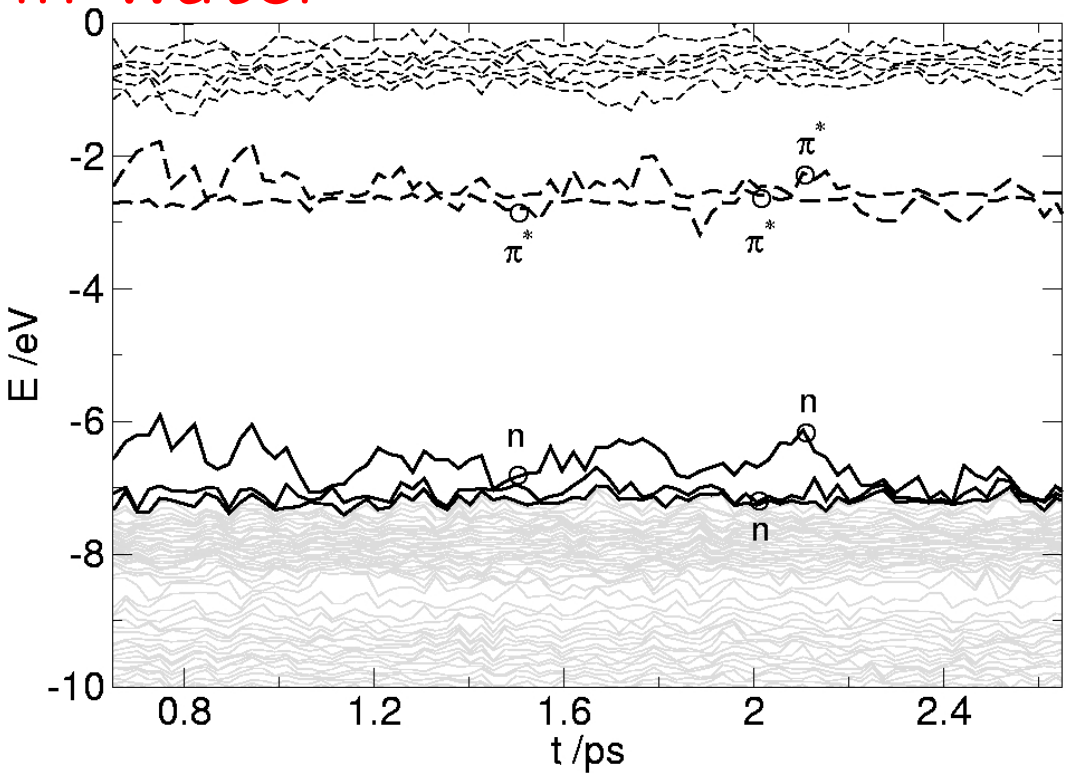


$(CH_3)_2CO \cdot 2H_2O$:

- In optimised structure: Solvation shift +0.16 eV

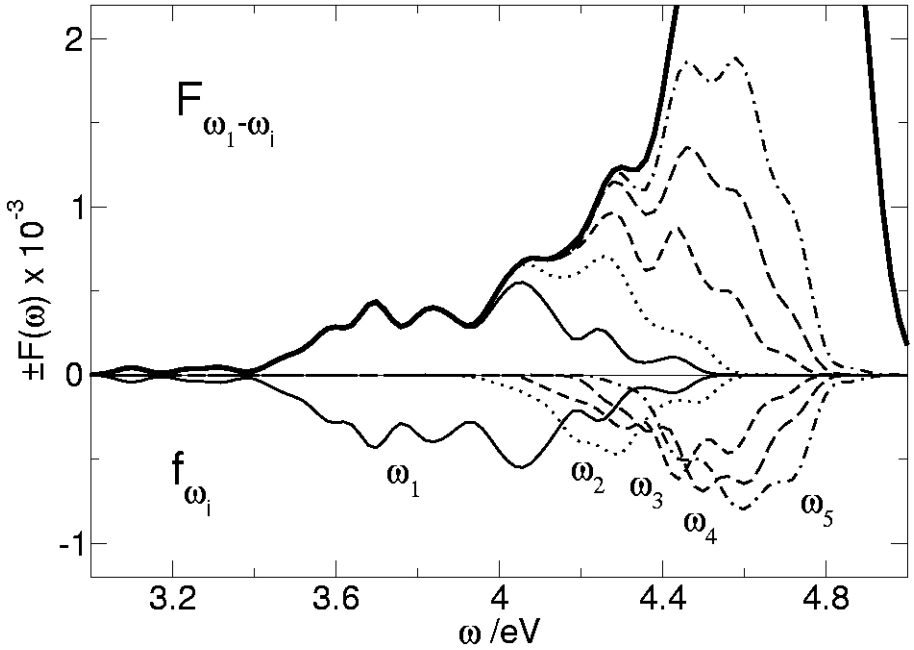
Acetone in water





- MD in liquid water: Occasional switching of states
- Water bands are wrong, water band gap is $\approx$ 8 eV !

Acetone in water



- $\omega_2 + \omega_3$ corresponds to excitation in acetone $\rightarrow$ solvation shift $+0.19$ eV
- Experimentally 0.19-0.21 eV
- However comparison difficult due to mixing of excitations — we need a better description

for more details,
Bernasconi, Sprik & Hutter, *JCP* (2003); *CPL* (2004)

(Another example: Movie @ `youtube.com`)

Applications — More properties

- diffusion, v-v autocorrelation spectrum
- T, displacement, fluctuations
- vibrations
- DOS, orbitals
- atomic charges, polarisation
- NMR chemical shifts
- Redox properties

Density functional theory: Summary

- All (ground state) properties can be derived from the ground state density
- The Kohn-Sham scheme yields a set of self-consistent equations; however the effective, or Kohn-Sham potential is local, the scaling with system size typically not worse than N^3.
- LDA yields in general good structural properties, less so for energetics. GGAs usually yield more accurate results than the local density approximation at a similar cost
- Method of choice for systems with $\simeq 10^2..10^4$ atoms in solid state, molecular liquids, gas phase, reactions, spectroscopy
- no systematic way to improve the results (so far, that is)
- Various implementations, linear scaling, QM/QM/MM, AIMD, properties, ...
- DFT @ SNL: Ann Mattsson (functional development), Peter Schultz (code development, Seqquest), Alan Wright (code development, Socorro), and many users
- Me: `http://www.sandia.gov/~oavonli`

Reminder: Kohn-Sham Equations

$$
\begin{aligned}
\left\{-\frac{1}{2}\nabla^2 + v_s\left[n\right]\left(\mathbf{r}\right)\right\}\phi_i\left(\mathbf{r}\right) &= \varepsilon_i\phi_i\left(\mathbf{r}\right) \\
v_s\left[n\right]\left(\mathbf{r}\right) &= v_{\text{ext}}\left(\mathbf{r}\right) + \int_{\mathbf{r}'}\frac{n\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}' + v_{xc}\left[n\right]\left(\mathbf{r}\right) \\
\langle\phi_i|\phi_j\rangle &= \delta_{ij} \\
n\left(\mathbf{r}\right) &= \sum_i\left|\phi_i\left(\mathbf{r}\right)\right|^2 \\
\int d\mathbf{r}\, n(\mathbf{r}) &= N
\end{aligned}
$$