# TD-DFT for electronic excitations

Electronic excitations
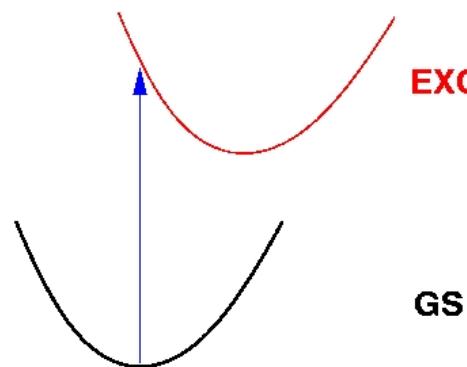
- Electronic absorption spectra
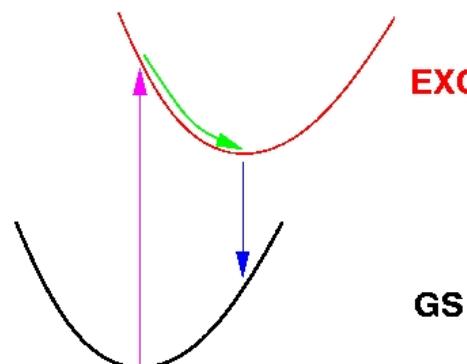
- Fluorescence spectra

- Photochemical reactions

Time-dependent density functional theory

- Exact theory analoguos to Hohenberg–Kohn density functional theory (Runge and Gross, 1984)

- Time-dependent Kohn–Sham theory

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

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

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

Two approaches to TDDFT

- Dynamics in real time: The envelope of the external, time-dependent potential varies in time; the transitions occur continuously
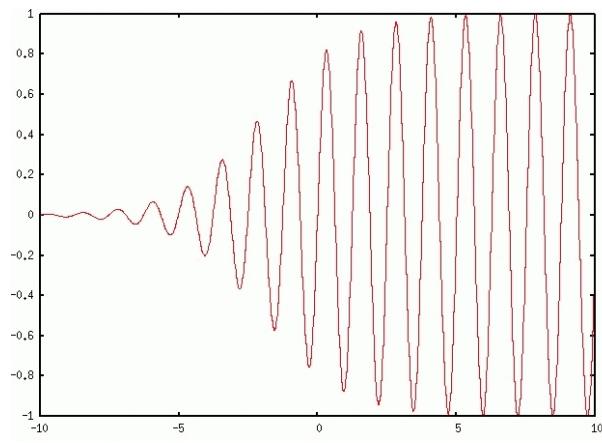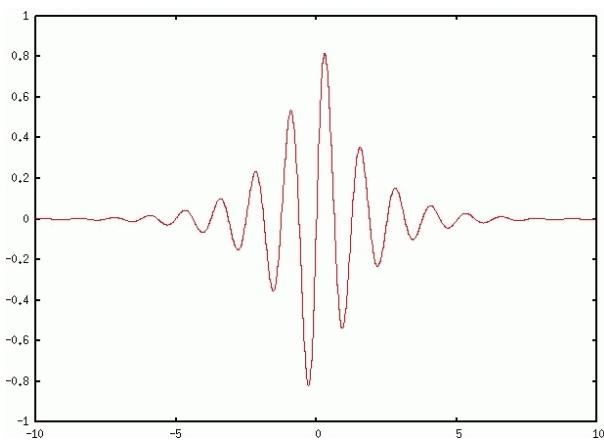
- "Dynamics" in imaginary time: The envelope remains constant; the transitions abruptly

Real time dynamics in TD Kohn–Sham scheme

- Propagation of the time-dependent Kohn-Sham equations:

$$\phi_i(t) = \mathcal{U}(t, t_0)\, \phi_i(t_0)$$

$$\mathcal{U}(t, t_0) = \hat{T} \exp\left[-\mathrm{i} \int_{t_0}^{t} \mathcal{K}_{\mathsf{KS}}(t')\, dt'\right]$$

- Since the real dynamics of the electrons has high frequencies, the time step for propagation is very small ($10^{-3} \ldots 10^{-3}$ atu)

- NOT included (yet) in official `CPMD` release

Propagators

- Alternatives

  - Split operator using Trotter factorisation

  $$e^{\mathrm{i}\hat{H}\Delta t} \approx e^{\mathrm{i}\hat{T}\Delta t/2} e^{\mathrm{i}\hat{v}[\phi,t]\Delta t} e^{\mathrm{i}\hat{T}\Delta t/2}$$

  - Cayley's finite difference form

  $$e^{i\hat{H}\Delta t} \approx \frac{1 - \frac{1}{2}\mathrm{i}\hat{H}\left[\phi,t\right]\Delta t}{1 + \frac{1}{2}\mathrm{i}\hat{H}\left[\phi,t\right]\Delta t}$$

  - Chebyshev quadrature

  $$\phi_i\left(t_m\right) = \phi_i\left(0\right) - \mathrm{i}T \sum_{l=0}^{N-1} \hat{H}\left[\phi\left(t_l\right), t_l\right] \phi_i\left(t_l\right) I_{lm}$$

  - Finite difference real space methods

- Two first are unitary; orthonormality automatically preserved

- Complication due to non-linearity in $\hat{H}$

Example: Formaldimine
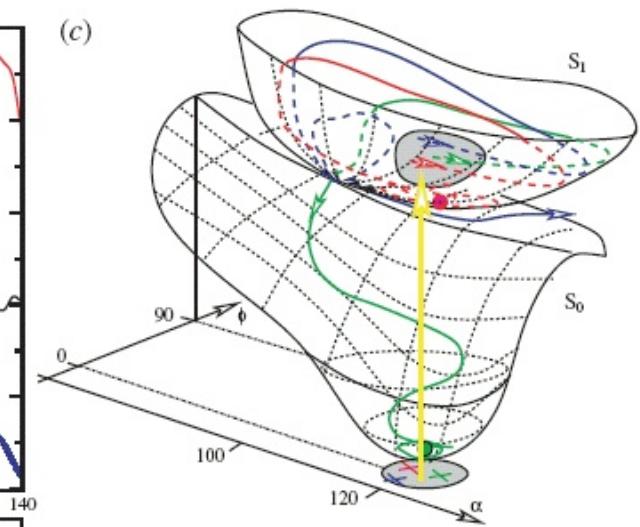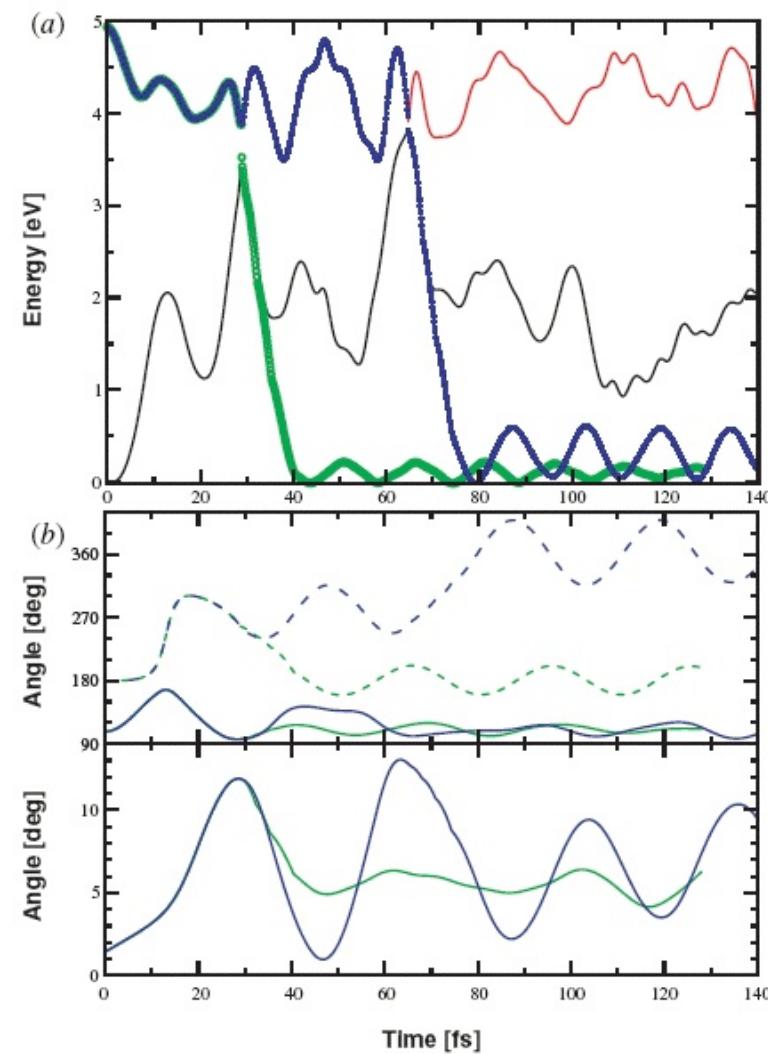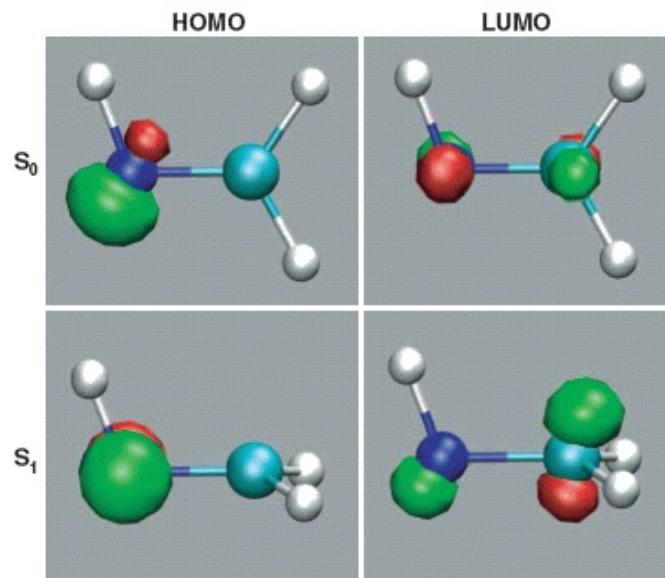
Linear response in TD Kohn–Sham scheme
Literature

- *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)

Imaginary-time TDDFT in CPMD
Ingredients

- Plane waves/pseudo potentials

  Periodic boundary conditions

- Molecular dynamics

  Temperature and pressure

- Density functional theory (DFT)

  Ground state electronic structure

- Linear response to time–dependent density functional theory (LR-TDDFT)

  Coupling to electro–magnetic fields and excited states

Code CPMD: http://www.cpmd.org/

Linear response in TD Kohn–Sham scheme

External perturbation: $\delta V(\mathbf{r}, t) = \delta V^{+}(\mathbf{r})e^{i\omega t} + \delta V^{-}(\mathbf{r})e^{-i\omega t}$

Self-consistent response:

$$\delta V_{\mathsf{SCF}}(\mathbf{r}, \pm\omega) = \int \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left.\frac{\delta^2 E_{\mathsf{xc}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n^{\{0\}}} \right\} n^{\{1\}}(\mathbf{r}', \pm\omega) \; d\mathbf{r}'$$

Perturbation theory:

$$\sum_{j=1}^{N} \left\{ \lambda_{ij} - (\hat{H} \pm \omega)\delta_{ij} \right\} \mid \Phi_j^{\{\pm\}}\rangle = Q \left\{ \delta V^{\{+\}} + \delta V_{\mathsf{SCF}}(\pm\omega) \right\} \mid \Phi_i^{\{0\}}\rangle$$

$$n^{\{1\}}(\mathbf{r}, \pm\omega) = \sum_{i=1}^{N} \Phi_i^{\{\mp\}}(\mathbf{r})\Phi_i^{\{0\}}(\mathbf{r}) + \Phi_i^{\{0\}}(\mathbf{r})\Phi_i^{\{\pm\}}(\mathbf{r})$$

$$Q = 1 - \sum_{k=1}^{N} |\Phi_k^{\{0\}}\rangle\langle\Phi_k^{\{0\}}|$$

Excitation energies are poles of the linear density response function

$$\chi(\omega) = [1 - \chi_0(\omega)K(\omega)]^{-1}\chi_0(\omega)$$

LR-TDKS equations — basis set

$$\sum_{i,j=1}^{N} \left(\hat{H}\delta_{ij} - \lambda_{ij} \right) |\Phi_j^{\{\pm\}}\rangle + Q\delta V_{\mathsf{SCF}}(\pm\omega)|\Phi_i^{\{0\}}\rangle = \mp\omega|\Phi_i^{\{\pm\}}\rangle$$

Define $\quad x_{pi} = \dfrac{1}{2}\left(c_{pi}^{\{+\}} + c_{pi}^{\{-\}} \right) \;, \quad y_{pi} = \dfrac{1}{2}\left(c_{pi}^{\{+\}} - c_{pi}^{\{-\}} \right) \;, \quad \mathbf{W}_{pq} = \langle \varphi_p \,|\, \delta V_{\mathsf{SCF}} \,|\, \varphi_q \rangle$

$$\Rightarrow \quad \sum_{qj} \left(\mathbf{F}_{pq}\delta_{ij} - \lambda_{ij}\delta_{pq} \right) x_{qj} + \sum_{qr} \mathbf{Q}_{pr}\mathbf{W}_{rq}[n^{\{1\}}]c_{qi}^{\{0\}} \;=\; -\omega y_{pi}$$

$$\sum_{qj} \left(\mathbf{F}_{pq}\delta_{ij} - \epsilon_{ij}\delta_{pq} \right) y_{qj} \;=\; -\omega x_{pi}$$

If we define *super-operators*

$$\mathcal{A}_{pi,qj} \;=\; \left(\mathbf{F}_{pq}\delta_{ij} - \epsilon_{ij}\delta_{pq} \right)$$

$$\mathcal{B}_{pi,qj} \;=\; \sum_{rsuv} \mathbf{Q}_{pr}\, c_{ui}^{\{0\}}\mathcal{K}_{ru,sv}c_{vj}^{\{0\}\star}\, \mathbf{Q}_{sq}$$

there follow two non-hermitian equations

$$\mathcal{A}\left(\mathcal{A}+\mathcal{B}\right)\mathbf{x} \;=\; \omega^2\mathbf{x}$$
$$\left(\mathcal{A}+\mathcal{B}\right)\mathcal{A}\mathbf{y} \;=\; \omega^2\mathbf{y}$$

Tamm–Dancoff Approximation

- TDA corresponds to the TD-HF/CIS method in quantum chemistry

Set $c_{pi}^{\{+\}} = 0 \ \Rightarrow x_{pi} = -y_{pi}$

$$\boxed{(\mathcal{A} + \mathcal{B})\, x = \omega x}$$

- Generally the excitation energies are close to full TDDFT results

- It is believed that oscillator strengths are bad

Variational Lagrangean

$$\mathcal{L}_{\mathsf{TDA}}[c^{\{0\}}, x, \omega] = \mathbf{x}^{\dagger}(\mathcal{A} + \mathcal{B})\,\mathbf{x} - \omega\left(\mathbf{x}^{\dagger}\mathbf{x} - 1\right)$$

Excitation Energies [eV]

	RPA	TDA	TDA(GTO)	Exp.
N_2	8.987	9.100	9.10	9.31
	9.524	9.524	9.60	9.97
	9.858	9.876	9.90	10.27
CH_2O	3.763	3.787	3.76	4.07
	5.680	5.685	5.63	7.11
	6.468	6.465	6.53	
Pyridine	4.296	4.342	4.39	4.59
	4.403	4.408	4.44	5.43
	5.318	5.383	5.29	4.99
Thiophene	5.328	5.328	5.64	5.33
	5.508	5.519	5.65	5.64
	5.694	5.695	5.67	
s-Tetrazine	1.825	1.901	1.90	2.25
	2.745	2.763	2.90	
	4.113	4.183	4.23	
Chrysazine	2.163	2.175	2.25	
	2.432	2.553	2.41	
	3.003	2.942	–	

Forces in TDA
Lagrangean technique

$$F_{\text{TDA}} = \frac{dE_{\text{KS}}}{dR_I} + \frac{dE_{\text{TDA}}}{dR_I} + \{ \text{ constraints } \}$$

- Construct a Lagrangean:

$$\mathcal{L}_{\text{KS}}[c^{\{0\}}, \Lambda] = E_{\text{KS}}[c^{\{0\}}] - \sum_{ij} \Lambda_{ij} \left\{ \sum_p (c_{pi}^{\{0\}})^\star c_{pj}^{\{0\}} - \delta_{ij} \right\}$$

$$\mathcal{L}_{\text{total}}[c^{\{0\}}, x, \Lambda, Z, \omega] = \mathcal{L}_{\text{KS}}[c^{\{0\}}, \Lambda] + \mathcal{L}_{\text{TDA}}[c^{\{0\}}, x, \omega]$$

$$+ \sum_{pi} \mathbf{Z}_{pi} \left\{ \sum_q \mathbf{F}_{pq} c_{qi}^{\{0\}} - \sum_j c_{qj}^{\{0\}} \Lambda_{ji} \right\} \ ,$$

- Variational in all wave function parameters

Forces: Generic variation in TDA

- Variation of $\mathcal{L}$ with respect to external parameter η:

$$\mathcal{L}_{\text{total}}^{(\eta)} = \frac{\partial E_{\text{KS}}}{\partial \eta} + \frac{\partial E_{\text{TDA}}}{\partial \eta} + \mathbf{Z}\,\frac{\partial \mathbf{F}}{\partial \eta}\,c^{\{0\}}$$

- Handy–Schaefer Z-vector equation (from $\frac{\partial \mathcal{L}}{\partial c^{\{0\}}} = 0$)

$$\left(F - \Lambda + \frac{\partial F}{\partial c^{\{0\}}}\right) Z = x^{\dagger}\,\frac{\partial\left(\mathcal{A} + \mathcal{B}\right)}{\partial c^{\{0\}}}\,x$$

Forces: Relaxed density matrix $\bar{P}$

$$\boxed{\frac{\partial \mathcal{L}_{\text{total}}}{\partial \eta} = \sum_{pq} \frac{\partial F_{pq}}{\partial \eta} \bar{P}_{qp}}$$

Relaxed density matrix

$$\bar{P}_{qp} = \sum_i c_{qi}^{\{0\}} c_{pi}^{\{0\}*} + \sum_i x_{qi} x_{pi}^*$$
$$- \sum_{rij} x_{rj} c_{pj}^{\{0\}} c_{qi}^{\{0\}*} x_{ri}^* + \sum_i Z_{pi} c_{qi}^{\{0\}}$$

Advantages of Lagrangean technique:

- $\bar{P}$ is independent of the perturbation! Thus only *one* calculation instead of *3N* in case of direct differentiation (in the case of forces)

- No terms involving $\frac{\partial c_{qi}^{\{0\}}}{\partial \eta}$, $\frac{\partial x_{qi}}{\partial \eta}$!

Generic variation: Possible applications

- Many properties of the excited state can be written as expectation values using $\bar{P}$

  - Nuclear coordinates: $\mathbf{R}_I \Rightarrow \mathbf{F}_I$

  - Electric field: $E_{\text{field}} \Rightarrow \mu$; polarisation

  - Coulomb potential: $V_{\text{Coulomb}} \Rightarrow n$

LR-TDDFT: Examples

- Small molecules: Accuracy

- Qualitative failure: Excited state proton transfer in chrysazin

- Solvation: Acetone in water (fully QM)

- Extended states: Pitfall of TDDFT within linear response

PBE

Perdew-Burke-Ernzerhof — Generalised gradient approximation; J Perdew, K Burke and M Ernzerhof, *Phys Rev Lett* **77** (1996) 3865

$$
\begin{aligned}
E_x^{\mathsf{PBE}}[n] &= \int n\left(\mathbf{r}\right) \epsilon_x^{\mathsf{unif}} F_x^{\mathsf{PBE}}(n, \nabla n) \; d\mathbf{r} \\
F_x^{\mathsf{PBE}}(n, \nabla n) &= 1 + \kappa - \frac{\kappa}{1 + \mu \, s(n, \nabla n)^2 / \kappa} \\
E_c^{\mathsf{PBE}}[n] &= \int n\left(\mathbf{r}\right) \epsilon_c^{\mathsf{PBE}}(n, \nabla n) \; d\mathbf{r} \\
\epsilon_c^{\mathsf{PBE}}(n, \nabla n) &= \epsilon_c^{\mathsf{unif}} + H(n, \nabla n)
\end{aligned}
$$

TPSS

Orbital function; Jianmin Tao, John P Perdew, Viktor N. Staroverov and Gustavo E Scuseria, *Phys Rev Lett* **91** (2003) 146401

$$
\begin{aligned}
E_x^{\mathsf{MGGA}}[n] &= \int n\left(\mathbf{r}\right) \epsilon_x^{\mathsf{unif}} F_x^{\mathsf{MGGA}}(n, \nabla n, \tau)\ d\mathbf{r} \\[2mm]
F_x^{\mathsf{MGGA}}(n, \nabla n, \tau) &= 1 + \kappa - \frac{\kappa}{1 + x(n, \nabla n, \tau)/\kappa} \\[2mm]
E_c^{\mathsf{TPSS}}[n] &= \int n\left(\mathbf{r}\right) \epsilon_c^{\mathsf{revPKZB}} \left[1 + d\epsilon_c^{\mathsf{revPKZB}} \left(\frac{\tau^W}{\tau}\right)^3\right]\ d\mathbf{r} \\[2mm]
\epsilon_c^{\mathsf{revPKZB}} &= \epsilon_c^{\mathsf{PBE}}(n, \nabla) \left[1 + C\left(\frac{\tau^W}{\tau}\right)^2\right] - [1 + C]\left(\frac{\tau^W}{\tau}\right)^2 \\[2mm]
&\quad \times \max[\epsilon_c^{\mathsf{PBE}}(n/2, 0, \nabla n/2, 0), \epsilon_c^{\mathsf{PBE}}(n, \nabla n)]
\end{aligned}
$$

SAOP

Statistical average of orbital potentials — correct asymptotic behaviour, shell structure; O V Gritsenko, P R T Schipper and E J Baerends, *Chem Phys Lett* **302** (1999) 199

$$V_{xci}^{SAOP}(\mathbf{r}) = \sum_{i}^{N} V_{xci}^{mod}(\mathbf{r}) \frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$V_{xci}^{mod}(\mathbf{r}) = e^{-2(\varepsilon_N - \varepsilon_i)^2} V_{xci}^{LB\alpha}(\mathbf{r}) + [1 - e^{-2(\varepsilon_N - \varepsilon_i)^2}] \, V_{xci}^{GLLB}(\mathbf{r})$$

$$V_{xc}^{LB\alpha}(\mathbf{r}) = \alpha V_{x}^{LDA}(\mathbf{r}) + V_{c}^{LDA}(\mathbf{r}) - \frac{\beta x^2(\mathbf{r}) n^{1/3}(\mathbf{r})}{1 + 3\beta x(\mathbf{r}) \ln[x(\mathbf{r}) + \sqrt{x^2(\mathbf{r}) + 1}]} \quad \to -\frac{1}{r}$$

$$V_{xci}^{GLLB}(\mathbf{r}) = \overline{V}_{xc}^{hole}(\mathbf{r}) + V_{resp}(\mathbf{r})$$

$$\overline{V}_{xc}^{hole}(\mathbf{r}) = 2\epsilon_{xc}^{GGA}(\mathbf{r})$$

$$V_{resp}(\mathbf{r}) = K \sum_{i}^{N} \sqrt{\varepsilon_N - \varepsilon_i} \, \frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})} \quad \approx \text{KLI}$$

PBE0

Hybrid functional; J P Perdew and M Ernzerhof, *J Chem Phys* **105** (1996) 9982; C Adamo and V Barone, *J Chem Phys* **110** (1999) 6158

$$E_{\mathrm{xc}}^{\mathrm{PBE0}} = E_{\mathrm{xc}}^{\mathrm{PBE}} + \frac{1}{4}\left(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{PBE}}\right)$$

	Symm.	TDA BLYP	TDDFT BLYP	CPMD PBE	TM PBE	CPMD PBE0	TM PBE0	CPMD TPSS	CPMD SAOP	Exp.
N_2	$V\Pi_g$	9.21	9.10	9.21	9.10	9.43	9.31	9.53	9.32	9.31
	$V\Sigma_u^-$	9.60	9.60	9.69	9.68	9.38	9.36	9.89	9.67	9.97
	$V\Delta_u$	9.91	9.90							10.27
CO	$V\Pi$	8.44	8.24	8.46	8.24	8.64	8.42	8.83	8.40	8.51
	$V\Sigma^+$	9.78	9.79	8.90	9.54	9.94	10.48	9.15	10.41	10.78
	$V\Sigma^+$			9.51	10.10	10.53	10.88	9.77	11.24	11.40
H_2O	RB_1	6.19	6.18	6.40	6.41	7.16	7.19	6.60	8.27	7.4
	RB_1	7.67	7.67	7.27	8.87	8.63	9.76	7.51	10.91	10.0
	RA_2	7.26	7.26	7.62	7.67	8.58	8.61	7.76	10.05	9.1
	RA_1	8.05	8.04	7.83	8.55		9.37	7.95	10.20	9.7
	RA_1	8.35	8.31	7.84	9.50		10.36	7.96	11.15	10.17
C_2H_4	RB_{3u}	6.16	6.16	6.31	6.48	6.76	6.87	6.39	7.21	7.11
	RB_{2g}	6.55	6.55	6.96	6.99	7.45	7.44	7.05	7.86	8.01
	RB_{1g}	6.60	6.60	6.98	7.03	7.42	7.44	7.07	7.89	7.80
	RB_{3u}	7.18	7.18	7.11	8.31		8.57	7.19		8.62
	RA_g	6.93	6.92	7.37	7.99		8.17	7.41	7.70	8.29
CH_2O	VA_2	3.78	3.76	3.58	3.55	3.67	3.68	3.90	4.32	4.07
	RB_2	5.63	5.63	5.76	5.84	6.71	6.79	5.98	7.83	7.11
	RB_2	6.37	6.37	6.44	6.84	7.47	7.68	6.63	8.66	7.97
	xA_1			6.56	6.64	7.54	7.62	6.75	8.91	
	xB_2			6.65	8.12	7.68	9.11	6.85	10.01	
	xA_2			6.74	7.26	7.75	8.18	6.92	9.12	
	RB_2	6.64	6.64	6.87	8.72	7.98	9.61	7.05		8.88
	RA_1	6.98	6.98	6.91	8.43		8.81	7.09		8.14

Example: Formaldehyde

Virtual orbitals:
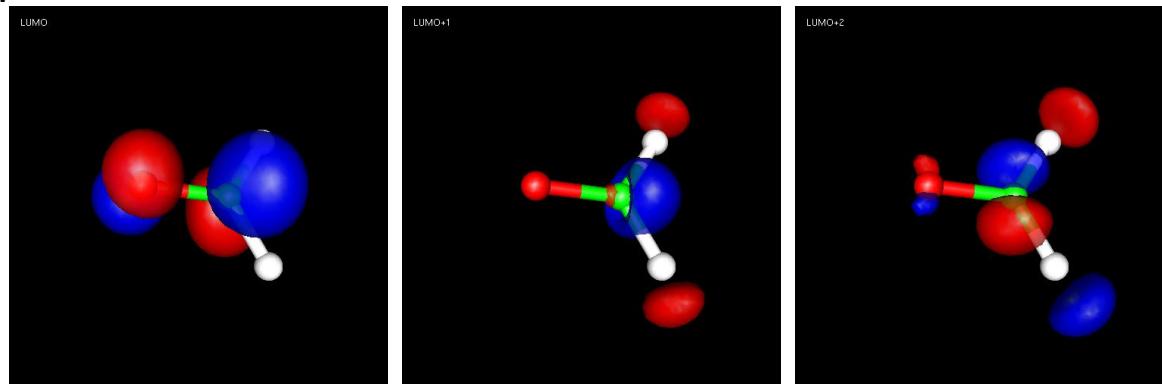
Occupied orbitals:
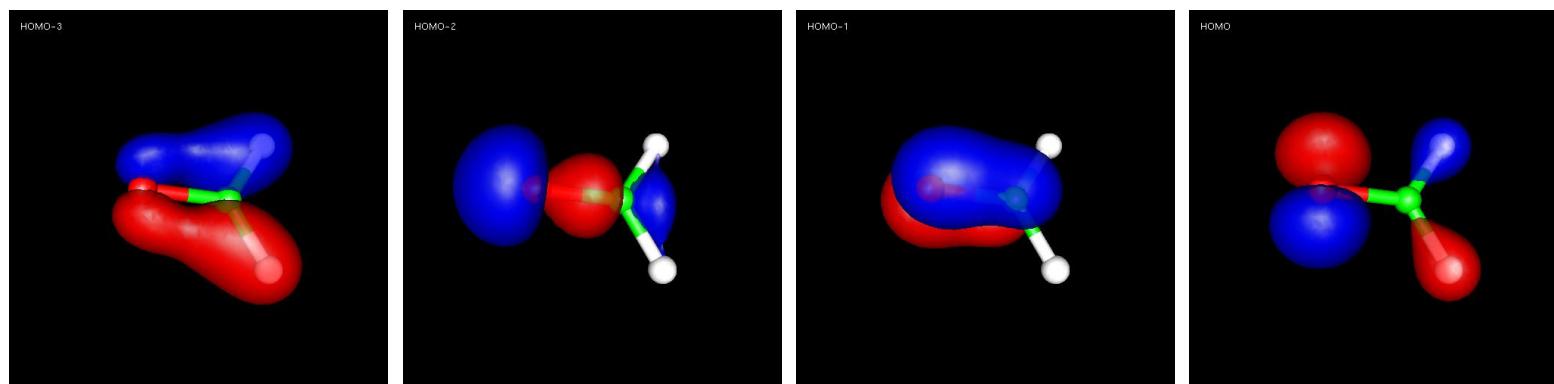
# Formaldehyde: Excitations

Excited state [n → π⋆] geometry

	TDA/PW PBE	LR-TDDFT PBE	MRDCI	EXP
R_{CO}	1.308	1.308	1.334	1.323
R_{CH}	1.103	1.106	1.111	1.098
Θ_{HCH}	116.8	116.2	120.2	118.4
Φ	30.0	34.3	34.5	34.0

Vibrational frequencies in the first excited state

		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
TDA/PW	PBE	524	1111	1230	1280	2910	3065
LR-TDDFT	PBE	619	853	1246	1288	2905	3008
Experiment			904	1183	1293	2846	2968

Formaldehyde: Molecular dynamics

Conserved Energy

CO Bond Length
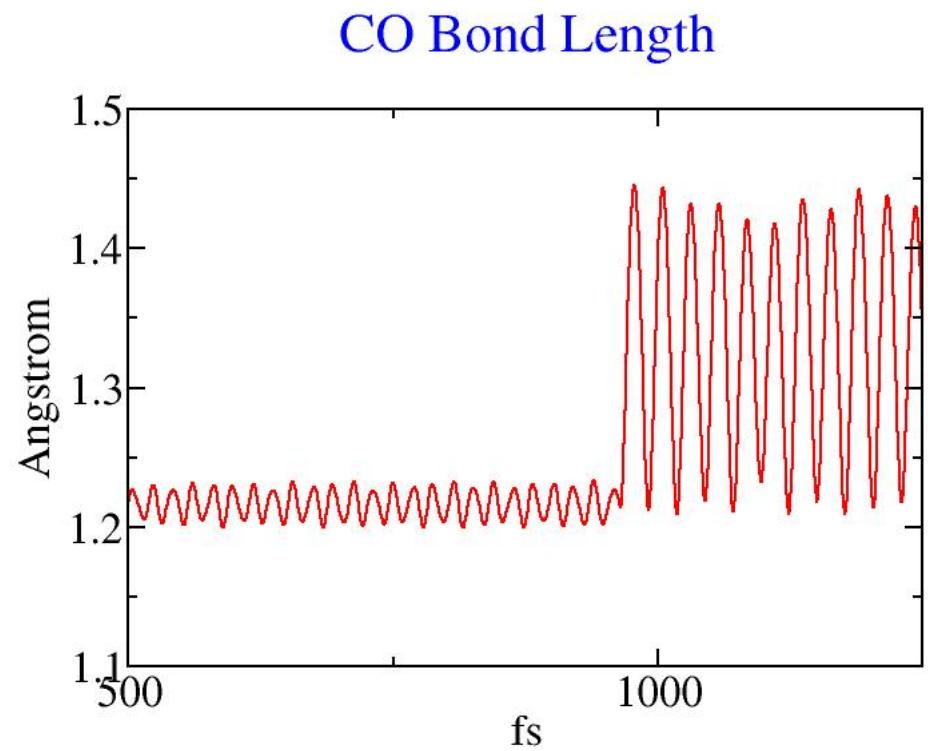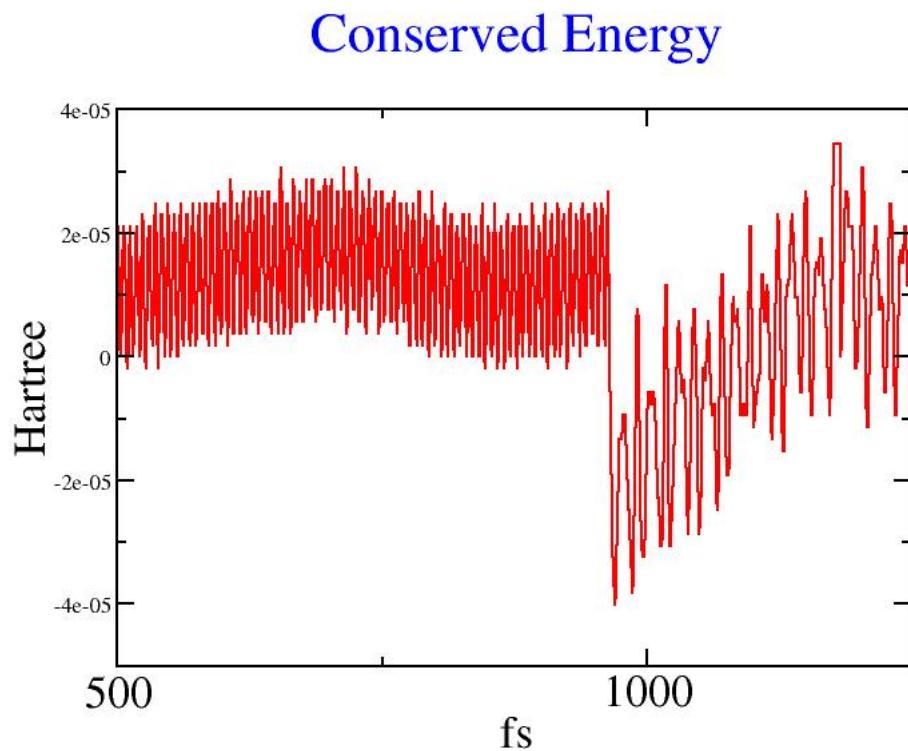
Excited state proton transfer

ESPT

Odelius, Laikov & Hutter, in preparation
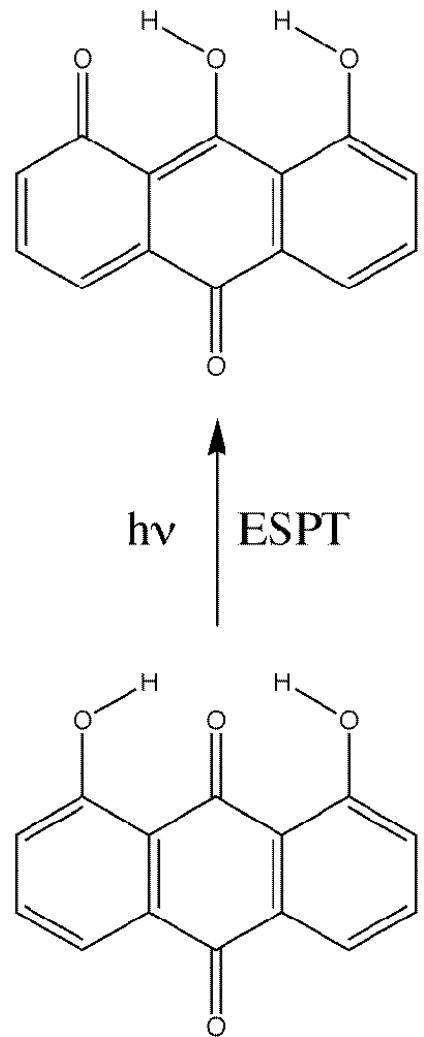
Example: **Chrysazin**

- Ground state: Symmetric, hydrogen-bonded structure

- Excited state: Asymmetric geometry

- Proton transfer upon excitation

ESPT: PES with ROKS
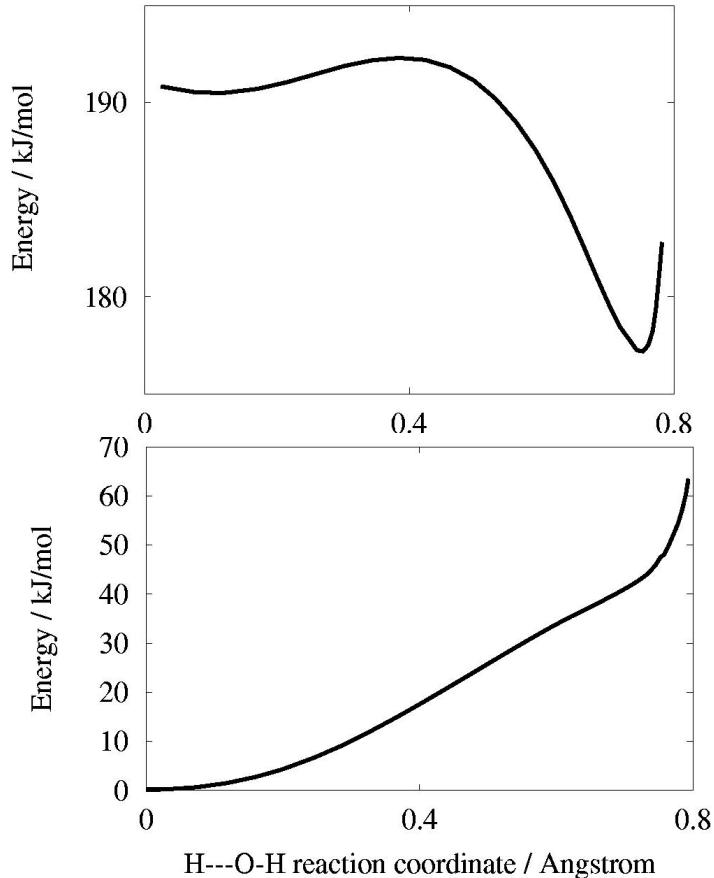
Example: **Chrysazin**

- ROKS: Proton transfer in the S_1 state

- TDDFT: Not even a local minimum at the proton-transferred geometry

- Even model solvent does not solve the problem for TDDFT

Extended states

Formaldehyde - triplets
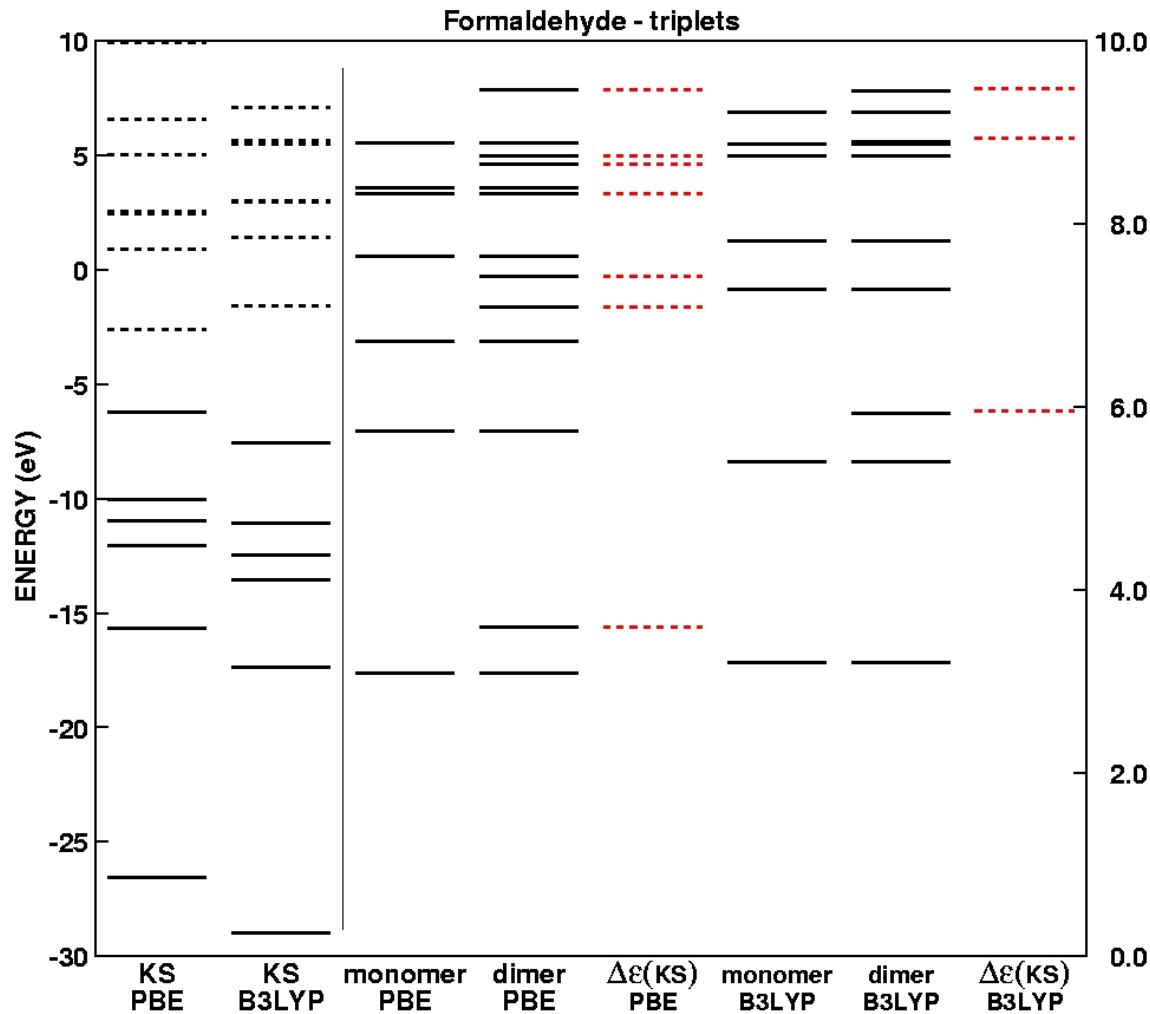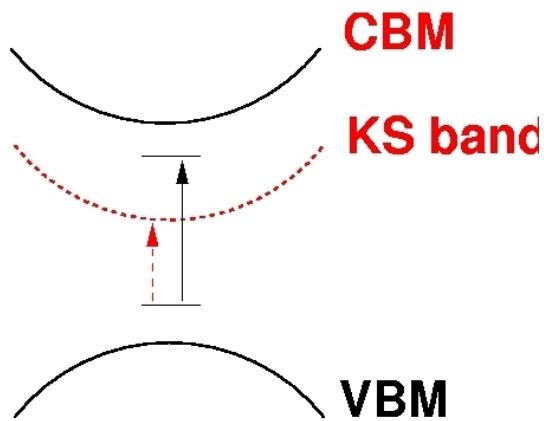
When the KS orbitals have negligible overlap $n^{\{1\}}(\mathbf{r}', \pm\omega)$ and thus $\delta V_{\mathsf{SCF}}(\mathbf{r}, \pm\omega)$ vanish $\Rightarrow \omega \to (\Delta\epsilon)_{ij}$

Solvation: Acetone in water (full QM)
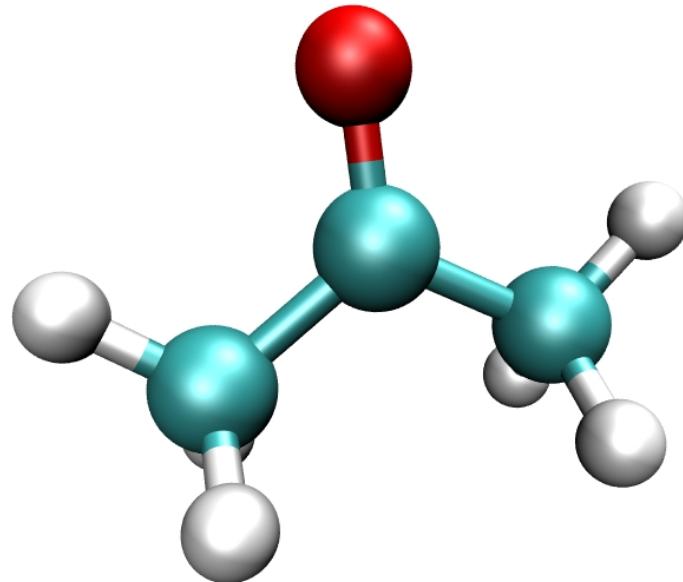
- Acetone will serve as a model system for excited states in solvated systems

- Three levels: Isolated acetone, acetone–water complexes and acetone in liquid water

Acetone in water
Acetone + water molecules
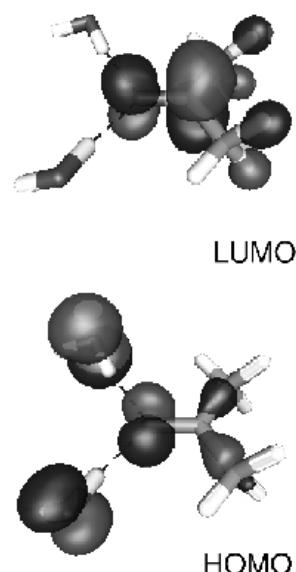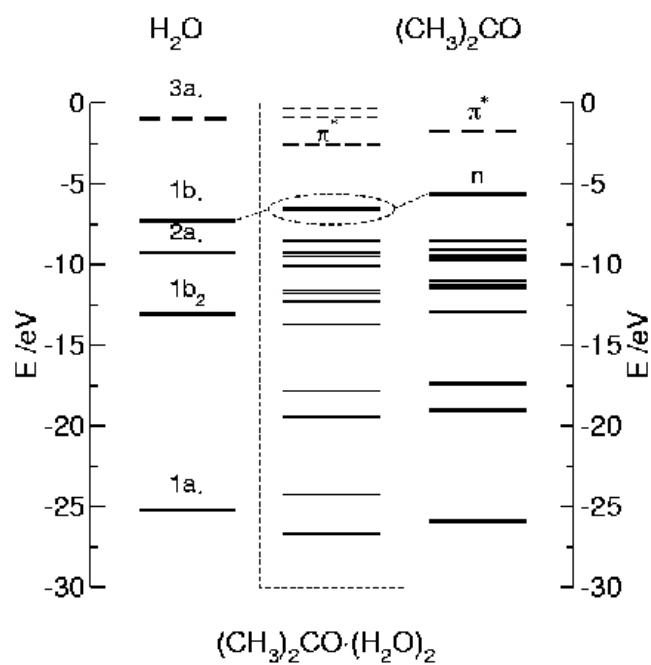
- Isolated $(CH_3)_2CO$: Lowest excitation symmetry-forbidden $n \to \pi^*$

- 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$_3$)$_2$CO · 2H$_2$O:

- In optimised structure: Solvation shift +0.16 eV
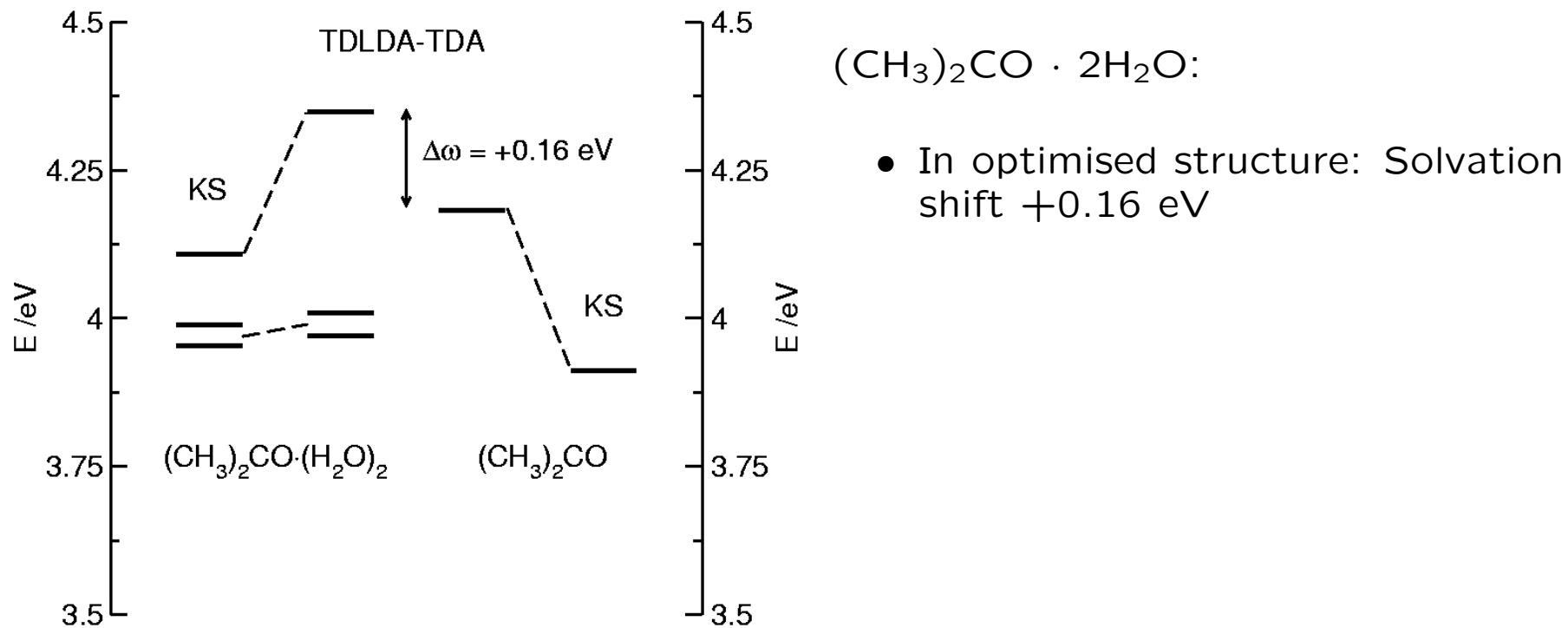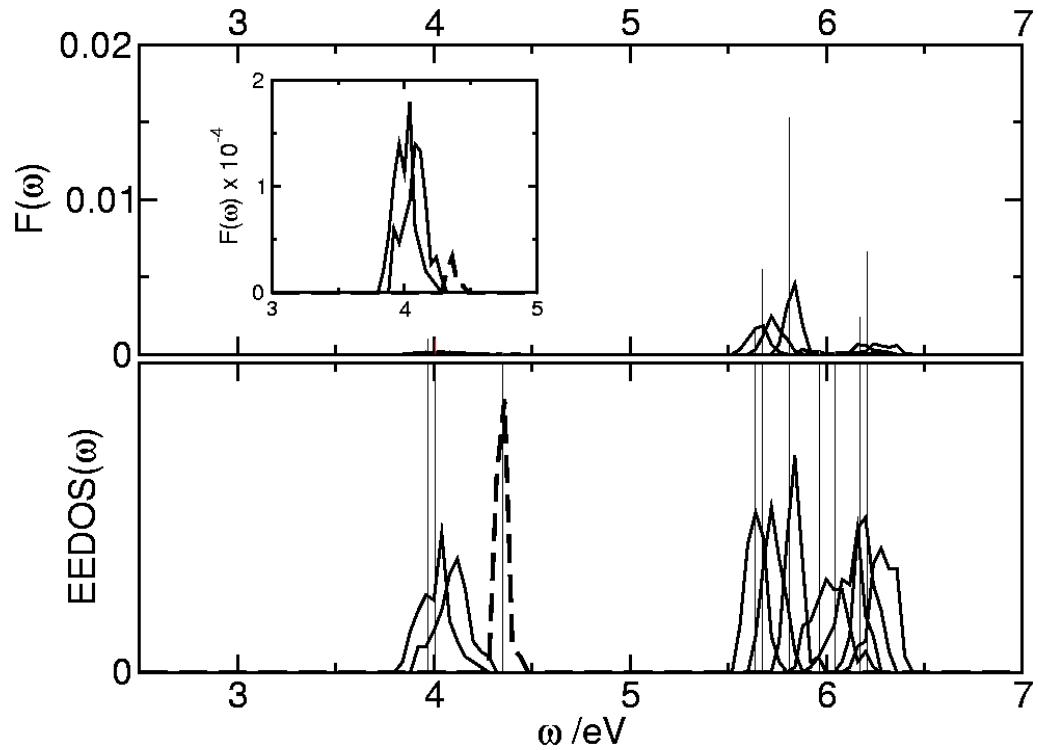
Acetone in water

- Molecular dynamics: Third excitation acetone $n \rightarrow \pi^*$

- Intensity included in $F(\omega)$ via oscillator strengths

- However the band gap of water should be ≈ 8 eV!!!

Acetone in water
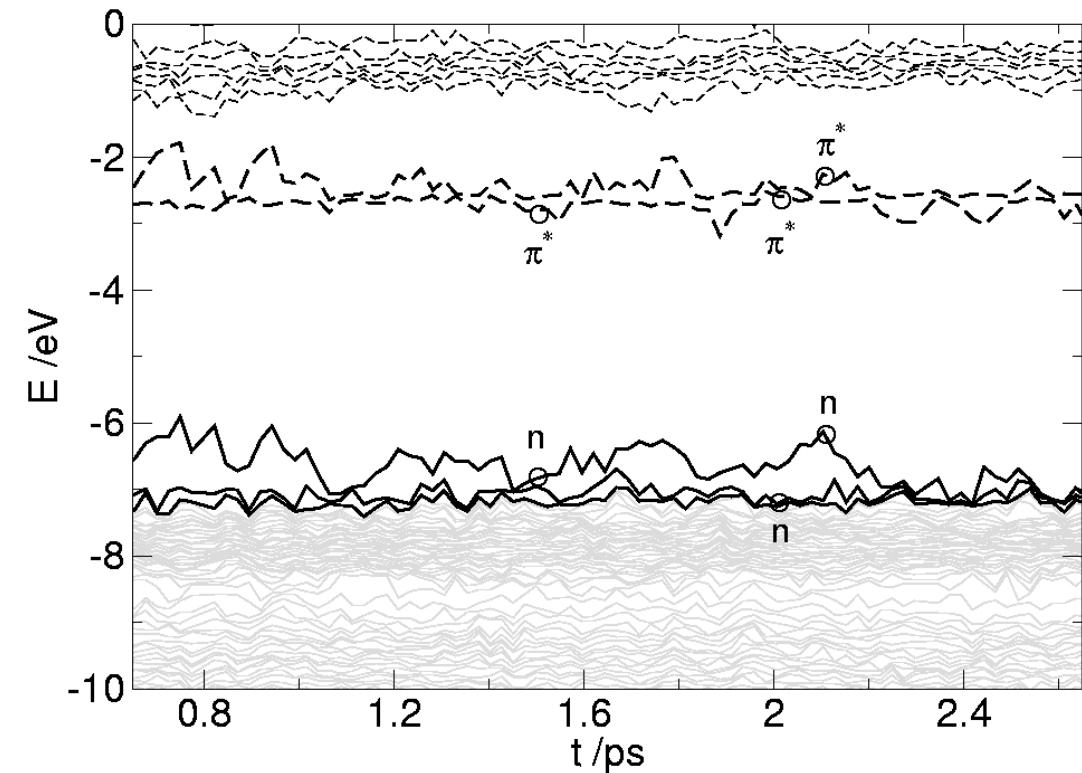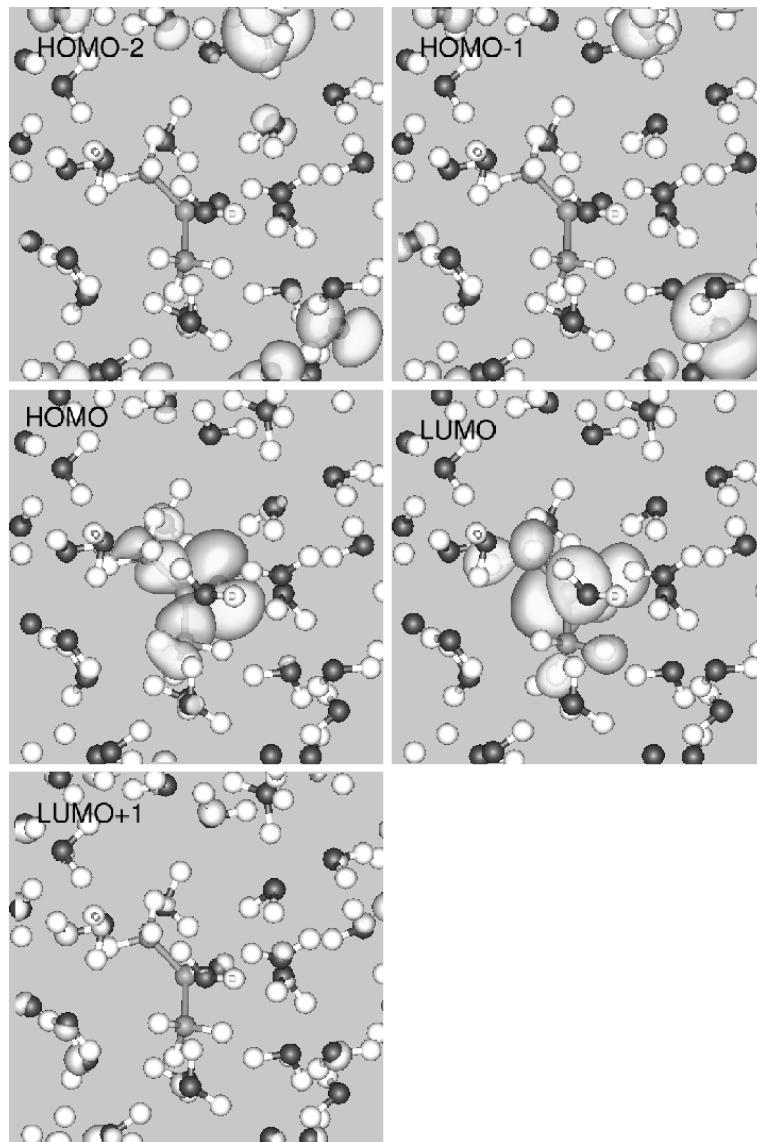
- MD in liquid water: Occasional switching of states

- Water bands are wrong!

Acetone in water
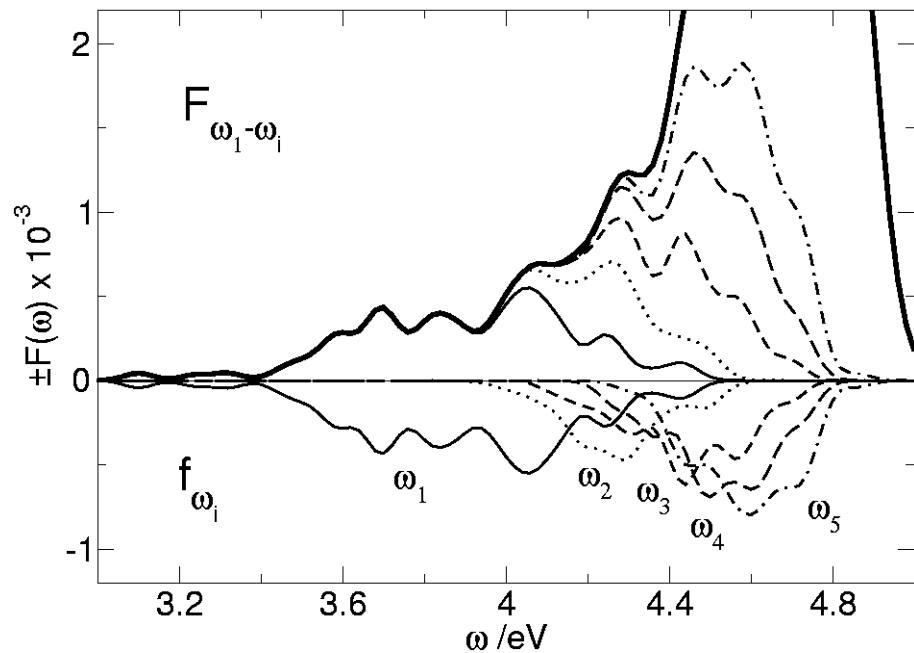
- $\omega_2 + \omega_3$ corresponds to excitation in acetone $\rightarrow$ solvation shift $+0.19$ eV

- Experimentally 0.19-0.21 eV

- However comparison difficult due to mixing of excitations — we need a better description

Acetone in water
Hybrid functionals

Instantaneous configuration (only 14
water molecules!), five lowest singlets

- In B3LYP and PBE0 the inter- and
  acetone-water transitions are
  pushed to higher energies

- The acetone intra-molecular
  transition is hardly changed!
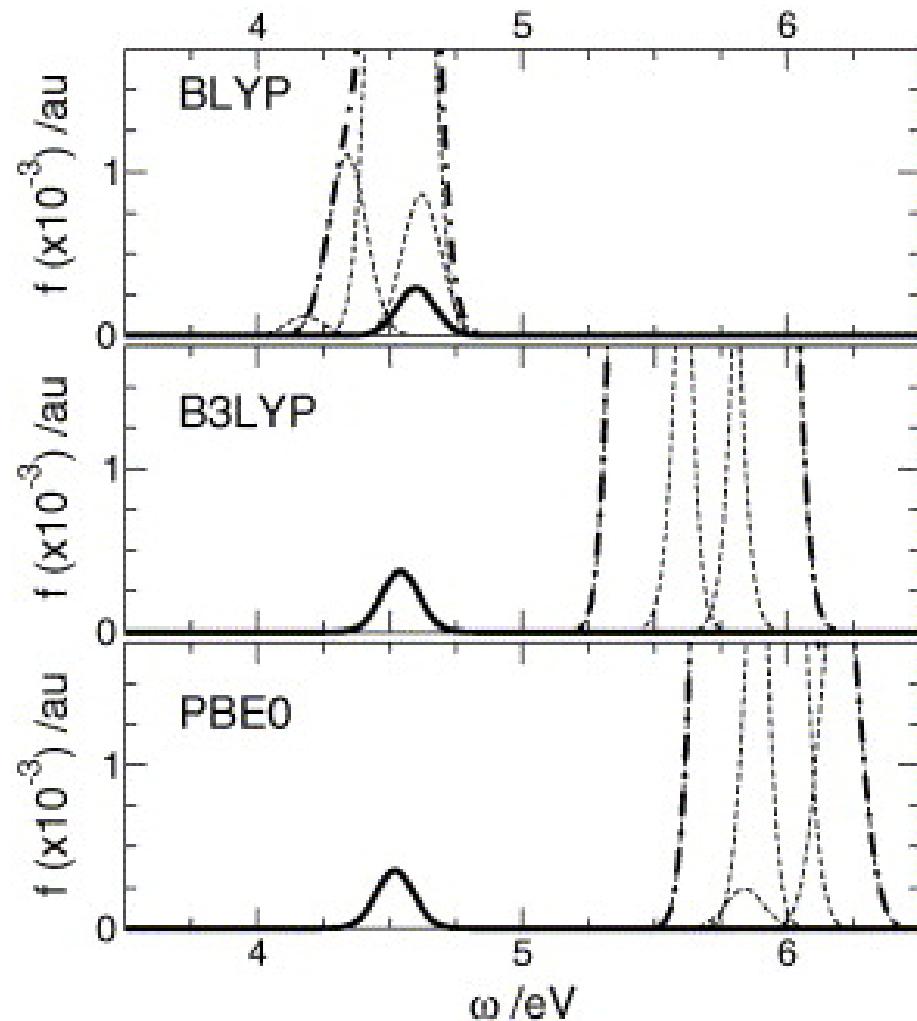
Acetone in water
Hybrid functionals
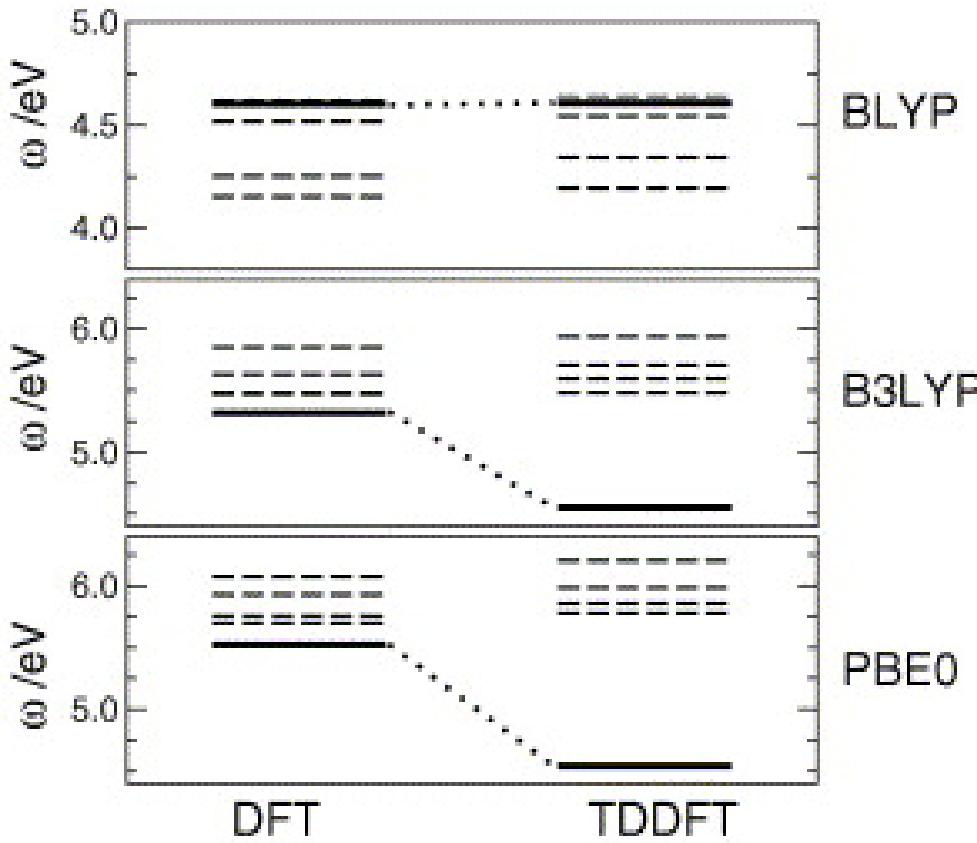
- In BLYP TDDFT hardly shifts any states — since they are delocalised

- Hybrid functionals i) shift Kohn-Sham eigenvalues and ii) change the excitation energy in the intra-molecular acetone excitation

- The change is a *decrease*

Acetone in water
Hybrid functionals

Solvation in water: MD at RT

- Excitation energies are broad both in the isolated molecule – dashed line – and solvated in water – solid line

- Averages marked with vertical arrows
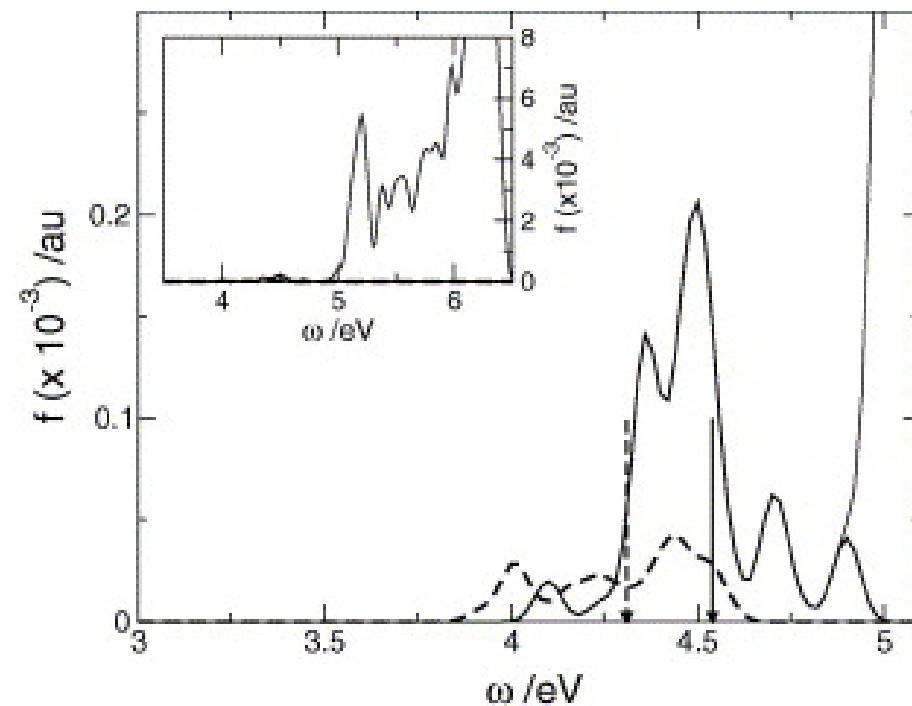
Acetone in water
Hybrid functionals

PBE0 gives a good description of the solvation shift and oscillator strength — the latter even with Tamm-Dancoff approximation

TDDFT BLYP and PBE0 $n \to \pi^*$ transition energy $\omega_n^{TD} \to \pi^*$ and intensity f in gas phase and solvated acetone

System	BLYP			PBE0			Exp.	
	$\omega_{n\to\pi^*}^{KS}$	$\omega_{n\to\pi^*}^{TD}$	f	$\omega_{n\to\pi^*}^{KS}$	$\omega_{n\to\pi^*}^{TD}$	f	$\omega_{n\to\pi^*}$	f
Gas phase $(CH_3)_2CO$								
(a) Optim. geom.	4.11	4.26	1×10^{-4}	5.74	4.41	1×10^{-4}		
(b) T = 298 K	3.91[a]	4.18[a]	2×10^{-4}[a]	5.60	4.31	3×10^{-4}	4.3–4.5	4×10^{-4}
Solvated $(CH_3)_2CO$								
(a) Instant. conf.	4.59	4.62	1×10^{-3}	5.52	4.54	1×10^{-3}		
(b) T = 298 K		4.37[a]	$\sim3\times10^{-4}$[a]		4.51	1×10^{-3}	4.5–4.7	$\sim6\times10^{-4}$

TDDFT: Summary

- TDDFT can be implemented either using real or imaginary time

- In real time progataion the electronic dynamics is realistically included

- Imaginary time TDDFT can straightforwardly be used to calculate the excitation energies, and forces on the ions *in the electronically excited state* are available (within Tamm-Dancoff approximation)

- Asymptotically corrected and hybrid functionals accurate, also for Rydberg states and resonances

- Remains

  - Charge transfer excitations

  - Delocalised excitations (solved?)