TDDFT as a tool in chemistry

Summer School on

“Time dependent Density-Functional Theory: Prospects and Applications”

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Definitions (chemistry, photochemistry and photophysics)

The Born-Oppenheimer approximation
potential energy surfaces (PES)

Methods for excited states in quantum chemistry
- HF, TDHF
- Configuration interaction, CI
- Coupled Cluster, CC
- MCSCF

TDDFT: Why TDDFT in chemistry and biology?

TDDFT: properties and applications in chemistry

TDDFT failures
- Accuracy and functionals
- charge transfer excitations
- topology of the PES

Program (lectures 1 and 2)

Lecture 1
- Definitions (chemistry, photochemistry and photophysics)
- The Born-Oppenheimer approximation
  potential energy surfaces (PES)
- Methods for excited states in quantum chemistry
  - HF, TDHF
  - Configuration interaction, CI
  - Coupled Cluster, CC
  - MCSCF
- TDDFT: Why TDDFT in chemistry and biology?

Lecture 2
- TDDFT: properties and applications in chemistry
- TDDFT failures
  - Accuracy and functionals
  - charge transfer excitations
  - topology of the PES

Lecture 3: Introduction to Non-adiabatic mixed-quantum classical molecular dynamics
Why TDDFT in chemistry?

All MR *ab-initio* methods are still computationally too expensive for large systems (they are limited to few tenths of atoms) and for mixed-quantum classical dynamics.

Among the SR (plus perturbation) methods:

- **CIS** is practically no longer used in the calculation of excitation energies in molecules. The error in the correlation energy is usually very large and give qualitatively wrong results. STILL good to gain insight on CT state energies! Largely replaced by TDDFT

- **CC2** is a quite recent development and therefore not widely available Accurate and fast, is the best alternative to TDDFT Good energies also for CT states

Among the MR methods, **CASSCF** is still widely used but is computationally very expensive and the quality of the excited state energies and properties are not necessarily better than the ones obtained from a TDDFT calculation. In addition, all SCF based methods need what is called “chemical intuition” in the construction of the active space.
Why TDDFT in chemistry?

Quantum chemists are developing interesting solutions for the efficient calculations of excited states properties.

CC2 is the most promising candidate for the calculation of accurate molecular potential energy surfaces for medium size molecules.

Nevertheless

TDDFT is formally exact and improvements of the xc-functionals is still possible.

Improvement of wavefunction based methods can only be done at huge costs in computational time.

TDDFT is still computationally more efficient and scales better than ab-initio methods.

\( O(N) \) DFT and \( \sim O(N^2) \) TDDFT scaling is possible [D. Foerster, PRB, 72, 073106 (2005)]

TDDFT can be used for large systems (up to thousand atoms)

TDDFT can be easily combined with MD (mixed quantum classical MD)
Why TDDFT in chemistry?

The desired electronic structure method to perform MQC Molecular Dynamics should offer the best possible compromise between accuracy and computational efficiency.

- We need accuracy in determining the PESs, which need to be at least qualitatively correct (obviously, the level of accuracy depends on the nature problem investigated)

- We need efficiency to

  > perform a reasonable scan of the PESs (statistics)
  > perform on-the-fly Molecular Dynamics

Sometimes, high level quantum calculations are performed with too small basis sets, while in other cases they are restricted to limited portions of the phase space (using constrains along reaction coordinates or enforcing the symmetry).
Why TDDFT in chemistry?

Hydrogen or proton transfer?

Experimental and theoretical evidences for an hydrogen transfer mechanism.

(C.Tanner, C Manca, S. Leutwyler, Science, 302, 1736 (2003))

CIS/CASSCF for the in-plane geometry.
Potential energy surfaces for GS, S_1, and S_2 along a reaction coordinate (fix C_s symmetry).
Why TDDFT in chemistry?

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Experimental and theoretical evidences for an hydrogen transfer mechanism.

(C. Tanner, C. Manca, S. Leutwyler, Science, 302, 1736 (2003))

CIS/CASSCF for the in-plane geometry.
Potential energy surfaces for GS, S₁, and S₂ along a reaction coordinate (fix C_s symmetry).
Why TDDFT in chemistry?

Hydrogen or proton transfer?

TDDFT/PBE/TDA combined with non-adiabatic molecular dynamics. Move to a reaction coordinate free description of the mechanism. (PW basis set)

We observe:

- Symmetry breaking (strong out of plane displacement)
- No crossing with the πσ* state
- Proton transfer instead of hydrogen transfer

Experimental and theoretical evidences of an hydrogen transfer mechanism.

(C.Tanner, C Manca, S. Leutwyler, Science, 302, 1736 (2003))
Why TDDFT in chemistry?

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TDDFT/PBE/TDA combined with non-adiabatic molecular dynamics. Move to a reaction coordinate free description of the mechanism. (PW basis set)
- Forcing in-plane (C₅ᵥ) symmetry gives a qualitatively similar energy profile like in the CIS study. Hydrogen transfer can occur.

- “Unconstrained” geometry optimization produces a completely different picture: The ammonia move out of plane and the πσ* remains high in energy and never gets populated. Proton transfer is observed.

With CASSCF: high barriers along the πσ* path.

At CASSCF/CASPT2 level of theory the proton transfer occurs almost barrierless.
Time dependent density functional theory

TDDFT in the linear response formulation

The basic quantity in LR-TDDFT is the density-density response function

$$\chi(r, t, r', t') = \frac{\delta \rho(r, t)}{\delta v_{ext}(r', t')} \bigg|_{v_0}$$

which relates the first order density response to the applied perturbation

$$\delta \rho(r, t) = \int d^3 r' dt' \chi(r, t, r', t') \delta v(r', t'),$$

The physical response function is related to the non-interacting KS response function via the Dyson-like equation

$$\chi(r, t, r', t') = \chi_s(r, t, r', t') +$$

$$+ \int d^3 r_1 dt_1 \int d^3 r_2 dt_2 \chi_s(r, t, r_1, t_1) \left( \frac{\delta(t_1 - t_2)}{|r_1 - r_2|} + \frac{\delta v_{xc}(r_1, t_1)}{\delta \rho(r_2, t_2)} \right) \chi(r_2, t_2, r, t_1),$$

or in Fourier space

$$\chi^{-1}(r, r', \omega) = \chi_s^{-1}(r, r', \omega) - \frac{1}{|r_1 - r_2|} - f_{xc}(r_1, r_2, \omega)$$

The KS response function can be computed (non-interacting system)

$$\chi_s(r, r', \omega) = \sum_{k,j} (f_k - f_j) \frac{\psi_k^*(r) \psi_j(r) \psi_j(r') \psi_k^*(r')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$
Time dependent density functional theory

TDDFT excitation energies and oscillator strengths

The dynamic dipole polarizability is the response functions that relates the external field to the change in the molecular dipole

\[ \delta \mu_x(\omega) = \alpha_{xz}(\omega) E_z(\omega) \]

where \( \alpha_{xz}(\omega) = - \sum_{ijkl} x_{ij} \chi_{ijkl}(\omega) z_{kl} \) and \( x_{ij} = \langle \psi_j | \hat{x} | \psi_j \rangle \).

According to the sum-over-states (SOS) relation (from your spectroscopy class)

\[ \overline{\alpha}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2} \]

\[ \omega_I = E_I - E_0 \]
\[ f_I = \frac{2}{3} \omega_I \left( |\langle \Psi_0 | \hat{x} | \Psi_I \rangle|^2 + |\langle \Psi_0 | \hat{y} | \Psi_I \rangle|^2 + |\langle \Psi_0 | \hat{z} | \Psi_I \rangle|^2 \right) \]

Therefore, the poles of the polarizability (which are the same as for \( \chi(\omega) \)) determines the excitations energies of the system.

Note that \( \chi_s(\omega) \) has poles at the Kohn-Sham energy differences. This zero order estimation of the excitation energies is modified by the second term in the Dyson-equation for \( \chi(\omega) \).
Time dependent density functional theory

TDDFT equations in practice: the Casida’s equations

After writing the dynamic polarizability in KS basis one gets

$$
\begin{bmatrix}
A(\omega) & B(\omega) \\
B^*(\omega) & A^*(\omega)
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix}
= \omega_I
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix}.
$$

with

$$A_{i\alpha\sigma,j\beta\tau}(\omega) = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb)$$

$$B_{i\alpha\sigma,j\beta\tau}(\omega) = (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb),$$

and

$$f_{xc}^{\sigma\tau}(r_1, r_2; \omega) = \int_{-\infty}^{+\infty} e^{i\omega(t_1 - t_2)} \frac{\delta^2 A_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\delta \rho_{\sigma}(r_1, t_1) \delta \rho_{\tau}(r_2, t_2)} d(t_1 - t_2).$$

In the adiabatic approximation the TDDFT kernel is time-independent (and its Fourier transform is independent from $\omega$) and therefore the number of solutions of Casida’s equations is equal to the dimensionality of the matrices.

$$
(\phi_p \phi_q | f | \phi_r \phi_s) = \int dr_1 dr_2 \phi_p^*(r_1) \phi_q(r_1) f(r_1, r_2) \phi_r^*(r_2) \phi_s(r_2)
$$
Time dependent density functional theory

The exact exchange formulation

Using a fraction of exact exchange in the functionals leads to

\[
\begin{bmatrix}
A(\omega) & B(\omega) \\
B(\omega) & A(\omega)
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix} = \omega I
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix}.
\]

where now

\[
A_{ia\sigma,jb\tau}(\omega) = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb) - c_x\delta_{\sigma,\tau}[((ij|f_H|ba) + (ia|f_x^{\sigma\sigma}|bj)]
\]

\[
B_{ia\sigma,jb\tau}(\omega) = (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb) - c_x\delta_{\sigma,\tau}[(ib|f_H|ia) + (ia|f_x^{\sigma\sigma}|jb)]
\]

\(c_x \) controls the degree of exact exchange in the TDDFT kernel.

Comments:

1. Due to the approximation of the TDDFT kernel and to failure of the ground state DFT triplet instabilities, \( \omega_T < 0 \), for \( c_x = 0 \) and singlet instabilities, \( \omega_S < 0 \), for \( c_x \neq 0 \) are possible. F. Cordova et al, JCP, 127, 164111 (2007)

2. Better kernels are needed OR use of the Tamm-Dancoff approximation (TDA)
Time dependent density functional theory

The Tamm-Dancoff approximation (TDA)

Note that the LR-TDDFT equations in the Tamm-Dancoff approximation ($B_{ia\sigma,jb\tau}(\omega) = 0$) are CIS-like, the only (but important) difference being the correlation effects brought in by the TDDFT kernel.

Time dependent density functional theory

Example: the 2 electrons two orbitals model.

TDDFT solutions:

\[
\omega_S = \sqrt{(\epsilon_a - \epsilon_i)[(\epsilon_a - \epsilon_i) + 4(ia|f_H|ai) + 2(ia|f_{xc}^{\uparrow\uparrow}(\omega_S) + f_{xc}^{\downarrow\downarrow}(\omega_S)|ai)]}
\]

\[
\omega_T = \sqrt{(\epsilon_a - \epsilon_i)[(\epsilon_a - \epsilon_i) + 2(ia|f_{xc}^{\uparrow\uparrow}(\omega_T) + f_{xc}^{\downarrow\downarrow}(\omega_T)|ai)]}
\]

TDDFT solutions in the TDA:

\[
\omega_{SDA} = A_{ia\uparrow,ia\downarrow}(\omega_S) + A_{ia\uparrow,ia\downarrow}(\omega_S)
\]

\[
= \epsilon_a - \epsilon_i + 2(ia|f_H|ai) + (ia|f_{xc}^{\uparrow\uparrow}(\omega_S) + f_{xc}^{\downarrow\downarrow}(\omega_S)|ia)
\]

\[
\omega_{TD} = A_{ia\uparrow,ia\uparrow}(\omega_T) - A_{ia\uparrow,ia\downarrow}(\omega_T)
\]

\[
= \epsilon_a - \epsilon_i + (ia|f_{xc}^{\uparrow\uparrow}(\omega_T) - f_{xc}^{\downarrow\downarrow}(\omega_T)|ia)
\]
**Time dependent density functional theory**

Naphthalene.

aug-TZVP basis set; PBE/TZVP/RI ground-state geometry.

<table>
<thead>
<tr>
<th>Method</th>
<th>$1^1B_{3u}$</th>
<th>$1^1B_{2u}$</th>
<th>$2^1A_g$</th>
<th>$1^1B_{1g}$</th>
<th>$2^1B_{3u}$</th>
<th>$1^1A_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSDA</td>
<td>4.191</td>
<td>4.026</td>
<td>5.751</td>
<td>4.940</td>
<td>5.623</td>
<td>5.332</td>
</tr>
<tr>
<td>BP86</td>
<td>4.193</td>
<td>4.027</td>
<td>5.770</td>
<td>4.974</td>
<td>5.627</td>
<td>5.337</td>
</tr>
<tr>
<td>PBE</td>
<td>4.193</td>
<td>4.031</td>
<td>5.753</td>
<td>4.957</td>
<td>5.622</td>
<td>5.141</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hybrids</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
</tr>
<tr>
<td>PBE0</td>
</tr>
</tbody>
</table>

**Wavefunction methods**

<table>
<thead>
<tr>
<th>Method</th>
<th>$1^1B_{3u}$</th>
<th>$1^1B_{2u}$</th>
<th>$2^1A_g$</th>
<th>$1^1B_{1g}$</th>
<th>$2^1B_{3u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS</td>
<td>5.139</td>
<td>4.984</td>
<td>7.038</td>
<td>6.251</td>
<td>6.770</td>
</tr>
<tr>
<td>CC2</td>
<td>4.376</td>
<td>4.758</td>
<td>6.068</td>
<td>5.838</td>
<td>6.018</td>
</tr>
<tr>
<td>CASPT2</td>
<td>4.03</td>
<td>4.56</td>
<td>5.39</td>
<td>5.53</td>
<td>5.54</td>
</tr>
</tbody>
</table>

expt. 5.63, 5.55 5.89

“best” 4.0 4.5 5.5 5.5 5.5 5.7

Adiabatic approximation
Examples

Calculations on Schiff bases and protonated Schiff bases

Basis: cc-pVDZ, functional B3LYP for DFT and TDDFT

(Aquino et al., ChemPhysChem, 7, 2006, 2089-2096)

Good agreement between the two methods, both for ground and excited state.
Examples

Calculations on Schiff bases and protonated Schiff bases

Basis: cc-pVDZ, functional B3LYP for DFT and TDDFT
(Aquino et al., ChemPhysChem, 7, 2006, 2089-2096)

Many differences are visible:
• RI-CC2 gives a much longer C4-C5 bond.
• For the bond C1-C2 we observe a clustering: MR-CI and CASSCF give shorter TDDFT and RI-CC2 longer bond lengths.
Time dependent density functional theory

TDDFT properties

> is size consistent (?)
> can produce pure spin states
> for valence excited states well below the ionization potential \((\pi\pi^*, n\pi^*, n\sigma^*)\):
  error between 0.2 and 0.6 eV.
  Good ordering and relative energies of the excited states (except for CT states)
> properties are also in general good, but they have to be derived from the excited state density.
> good also for transition metals (difficult for wavefunction based methods)
> analytic energy gradients are available (for optimization of structures and MD)
> scales \(\sim O(n^2)\) with \(n\) the number of electrons.
  Can deal with very large systems up to many hundreds of atoms (essential for biosystems)
> typical failures:
  - Topology of the excited surfaces is questioned: singlet and triplet instabilities and conical intersections.
  - problems to describe “double excitations” (see Maitra’s lecture), Rydberg excited states, ionic states of systems with large \(\pi\) systems.
  - standard adiabatic TDDFT fails for charge transfer (CT) states.
    Errors in the ordering of the excited PESs is deleterious for excited states MD.
Program (lectures 1 and 2)

- **Definitions** (chemistry, photochemistry and photophysics)

- The Born-Oppenheimer approximation
  potential energy surfaces (PES)

- Methods for excited states in quantum chemistry
  - HF, TDHF
  - CIS
  - CC
  - MCSCF

- TDDFT: Why TDDFT in chemistry and biology?

- TDDFT: properties and applications in chemistry

- TDDFT failures
  - Accuracy and functionals
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  - topology of the PES
TDDFT for chemical properties

A TDDFT study of the lowest excitation energies of polycyclic aromatic hydrocarbons


Comparison of experimental and theoretical (TDDFT) vertical excitation energies for PAH

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Exp. (eV)</th>
<th>PPP (eV)</th>
<th>TDDFT (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^3L_a$</td>
<td>2.70</td>
<td>3.82</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>$^1L_a$</td>
<td>3.76</td>
<td>4.34</td>
<td>3.97</td>
</tr>
<tr>
<td></td>
<td>$^3L_b$</td>
<td>4.24</td>
<td>5.84</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>$^1L_b$</td>
<td>4.53</td>
<td>5.15</td>
<td>4.91</td>
</tr>
<tr>
<td>2</td>
<td>$^3L_a$</td>
<td>2.08</td>
<td>2.85</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>$^1L_a$</td>
<td>3.53</td>
<td>4.31</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td>$^3L_b$</td>
<td>3.71</td>
<td>4.67</td>
<td>3.67</td>
</tr>
</tbody>
</table>

TDDFT underestimates the excitation energies for states with dominant ionic character ($L_a$), while for covalent states $^1L_b$ errors are significantly smaller.
In general TDDFT performs less well for transition metal complexes (errors ~ 0.2-0.4 eV) -
B3LYP for metals doesn’t perform necessary better than GGA functionals
- CASPT2 & TDDFT: all predict the same number of $^1T_2$ excited states. Assignment (in terms of orbital transitions) can however be different.
- None of the three methods put the highest intensity peak (larger oscillator strength) at the right energy (at ~ 6 eV).

Table 4  TDDFT/BP excitation energies (eV) and oscillator strengths (in parentheses) of the lowest allowed excited states of Ni(CO)$_4$, compared to CASPT2 and SAC-CI values and to experimental data

<table>
<thead>
<tr>
<th>State</th>
<th>TDDFT [68]</th>
<th>CASPT2 [70]</th>
<th>SAC-CI [72]</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1T_2$</td>
<td>4.70 (0.006)</td>
<td>4.34 (0.29)</td>
<td>4.79 (0.0023)</td>
<td>4.5$^a$; 4.54$^b$</td>
</tr>
<tr>
<td>$2^1T_2$</td>
<td>4.82 (0.099)</td>
<td>5.22 (0.38)</td>
<td>5.51 (0.0067)</td>
<td>5.4$^a$; 5.17$^b$; 5.24$^c$</td>
</tr>
<tr>
<td>$3^1T_2$</td>
<td>5.37 (0.123)</td>
<td>5.57 (0.29)</td>
<td>5.72 (0.0043)</td>
<td>5.52$^c$</td>
</tr>
<tr>
<td>$4^1T_2$</td>
<td>5.84 (0.086)</td>
<td>6.28 (0.47)</td>
<td>5.76 (0.0089)</td>
<td>6.0$^a$; 6.02$^c$</td>
</tr>
<tr>
<td>$5^1T_2$</td>
<td>6.74 (1.002)</td>
<td>6.97 (0.83)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Gas-phase spectrum from [65]; $^b$ matrix spectrum from [61]; $^c$ solution spectrum from [76]
TDDFT for chemical properties

Density functional calculations of the vibronic structure of electronic absorption spectra

Marc Dierksen and Stefan Grimme$^a$ (JCP, 120, 3544 (2004))

$\mu_{\epsilon', \epsilon''} = \langle v' (Q') | \mu_{\epsilon', \epsilon} (Q) | v (Q) \rangle$

"[...] the TDDFT/B3LYP approach to calculate vibronic structures seems to outperform both widely used ab initio methods based on configuration interaction singles or complete active space self-consistent field wave function and semiempirical treatments regarding accuracy, applicability, and computational effort."
TDDFT for chemical properties

Molecular dynamics in electronically excited states using time-dependent density functional theory

IVANO TAVERNELLI*, UTE F. RÖHRIG and URSULA ROTHISBERGER
(Molecular Physics, 103, 963 (2005))

- For simple molecules (no zwitterionic character, no charge transfer) TDDFT provides a good description of the first singlet excited state surface.
- The TDDFT molecular dynamics is in agreement with experimental observations and high level \textit{ab initio} wavefunction-based calculations.
- In formaldimine the lone pair on the nitrogen helps to stabilize the twisted geometry → better DFT and TDDFT energies and forces.
TDDFT for chemical properties

Other properties that can be computed with TDDFT:

- Calculation of frequency-dependent polarizability

  \[ \alpha_{ij}(\omega) = -2 \int d\mathbf{r} \delta \rho_i(\mathbf{r}, \omega) \mathbf{r}_j \]


- Electronic circular Dichroism Spectra

  \[ R_{L/R} = C \int_{\lambda_1}^{\lambda_2} \frac{\Delta_{L/R} \epsilon(\lambda)}{\lambda} d\lambda \]


- TDDFT based non-adiabatic mixed quantum classical dynamics

  … this is the main topic of the next lecture
Program (lectures 1 and 2)

- Definitions (chemistry, photochemistry and photophysics)
- The Born-Oppenheimer approximation potential energy surfaces (PES)
- Methods for excited states in quantum chemistry
  - HF, TDHF
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  - CC
  - MCSCF
- TDDFT: Why TDDFT in chemistry and biology?
- TDDFT: properties and applications in chemistry
  - TDDFT failures
    - Accuracy and functionals
    - charge transfer excitations
    - topology of the PES
TDDFT: accuracy and functionals

Limitations of the current Exchange and Correlation functionals

> Ground state DFT functionals

- Long history on ground state functionals
  LDA/GGA/Meta-GGA/Hybrid functional (with exact exchange)

- but still many problems to solve:
  → long-range asymptotic \((1/r)\)
  → biradical states
  → self-interaction correction (SIC)
  → non-locality/exact exchange

> TDDFT functionals

- Naturally the TDDFT functional retain all the problems of the ground state functionals.

- Especially important are the limitations introduced by the wrong asymptotic (charge transfer excitations / excitons) and the SIC correction (charge localization).

- Computational efficiency requires local kernels (adiabatic approximation).
Intramolecular charge transfer 1: dual fluorescence

(D. Rappoport, F. Furche, JACS, 126, 1277 (2004))

Dual fluorescence of DMABN in polar solvents is explained with the help of TDDFT. Involved is an intramolecular charge transfer.

There are two excited states: LE and ICT, that crosses at about 52° of twist.

For a correct modeling of the system it is crucial that both exited states (LE and ICT) are described with the same accuracy: B3LYP yields good agreement with experiment for the vertical excitation energies of the first two singlet states and for their energetic separation.
Intramolecular charge transfer 2: Photodissociation

Upon electronic excitation TrpH$^+$ undergoes rapid fragmentation (broad absorption band)

Microsolvation enhances dramatically the lifetime of the molecule (sharp UV absorption lines)

(S.R. Mercier et al, JACS, 128, 16938 (2006))

TDDFT predicts the correct dynamics for the two species: TrpH$^+$ and TrpH$^+$(H$_2$O)$_2$
**TDDFT: charge transfer problem**

Intramolecular charge transfer 3: D-B-A electron transfer

1. Intra-donor excitation

2. Charge-transfer excitation

TDDFT gives the wrong ordering of the excited state PESs.

There are 3 (dark) CT states very close in energy to the intra-donor excited state.

This error has deleterious consequences on the excited state MD:
States mix and PESs are crossing at the wrong geometries.

\[ \Delta \omega_{ij} \sim 1 - 2 \text{eV} \]

(TDDFT predicts too low excitation energies for the CT transition.)

(A. Dreuw, M. Head-Gordon, JACS, 126, 4007 (2004))

TDDFT/BLYP

TDDFT with HF x
TDDFT: charge transfer problem

What's wrong with CT excitations in TDDFT?

In a CT process the excitation energy can be approximated by

$$\omega_{CT}(R_{DA}) \sim I_D - A_A - 1/(R_{DA})$$

On the other end, in TDDFT (with no-exact exchange) the asymptotic behavior is wrong,

$$\omega_{CT}(R_{DA}) = (\epsilon_a - \epsilon_i) + 2(i\alpha|f_{HXC}|i\alpha) \quad \text{(dipole approximation)}$$

$$\simeq \epsilon_A^L - \epsilon_D^H = I_D + \epsilon_A^L$$

Solutions (some possible):

> Adding some exact exchange  \( \text{(Y.Tawada et al, JCP, 121, 8425 (2004), R. Baer et al, PRL, 94, 043002 (2005))} \)

> See also new hybrid meta functionals of Truhlar (MO5, MO6 families)  \( \text{(J.Chem.Theory Comput., 2, 364 (2006))} \)

> Derivative discontinuity  \( \text{(J. Tozer, JCP, 119, 12697 (2003))} \)

> long-range corrected xc-kernel  \( \text{(O. Gritsenko, E.J. Baerends, JCP, 121, 655 (2004))} \)

> Hybrid approach of Dreuw and Head-Gordon  \( \text{(A. Dreuw et al, JCP, 119, 2943 (2003))} \)

$$\omega_{CT}(R) = \omega_{CT}^{CIS}(R) - (\Delta DFT(R_0) - \omega_{CT}^{CIS}(R_0))$$

> Frequency dependent kernel \( \text{(N. T. Maitra, JCP, 122, 234104 (2005))} \)
TDDFT: Topology of the excited state PESs

Photochemistry and photophysics are strongly dependent on the topology of the PESs.

grey: singlet states
dark: triplet state

a) singlet excitations
b) energetic minimum
c) saddle point
d) avoided crossing
e) conical intersection
f) fluorescence
g) phosphorescence
TDDFT: Topology of the excited state PESs

Photochemistry/photophysics require a correct description of the topological properties of the most relevant potential energy surfaces involved.

Conical intersections are now recognized to play a critical role in the reaction dynamics of electronic excited states.

Molecular geometries where two electronic states are exactly degenerate

At a conical intersection two coordinates (over 3N):

- difference gradient, \( g_{I,J} = \nabla_R (E_I - E_J) \)
- non-adiabatic coupling vectors \( h_{I,J} = \langle \Psi_J | \nabla_R | \Psi_I \rangle \)

define the direction that lift the degeneracy between the PESs.
What about the topology of the TDDFT PESs close to a conical intersection?

Formally, TDDFT equations in the Tamm-Dancoff approximation (TDA) are similar to the CIS equations for the excited state energies.

From dimensional analysis (or alternatively by applying Brillouin’s theorem) one can show that restricted CIS (for closed shell systems) has the wrong dimensionality for the intersection with the $S_0$ PES: $f - 1$ (a seam of intersections instead of a conical intersection).

Is this also the case in TDDFT?
TDDFT: Topology of the excited state PESs

Topology of the $S_0$ and $S_1$ PESs of ethylene in the pyramidalization and torsion coordinates.

TDDFT: Topology of the excited state PESs

S₀/S₁ intersection in “linear” water

In CI there is one constraint less at the CI, because H₀₁ is zero by construction (Brillouin’s theorem). Therefore, at CI there is only one constraint left.

TDDFT: Topology of the excited state PESs

$S_0/S_1$ intersection in $H_2 + H$

TDDFT reproduces the correct splitting of the surfaces. These is because of the open-shell character of this system. (See E. Tapavicza et al, JCP (in press 2008)).

TDDFT: Topology of the excited state PESs

$S_0/S_1$ intersection in $H_2 + H$

TDDFT/PBE/TDA

\[ \chi = 1^\circ \]
TDDFT: Topology of the excited state PESs

Another case where TDDFT is at least qualitatively correct: Oxirane in the DG and CV coordinates

More during the workshop …
Quantum Chemistry Packages


Gaussian 03 is the most popular and widely-used computational chemistry packages, originally developed by Nobel prize winner John Pople.

CPMD The CPMD code is a parallelized plane wave/pseudopotential implementation of Density Functional Theory, particularly designed for ab-initio molecular dynamics.

Cp2k CP2K is a freely available (GPL) program, written in Fortran 95, to perform atomistic and molecular simulations of solid state, liquid, molecular and biological systems. It provides a general framework for different methods such as e.g. density functional theory (DFT) using a mixed Gaussian and plane waves approach (GPW), and classical pair and many-body potentials.

Octopus is a scientific program aimed at the ab initio virtual experimentation on a hopefully ever increasing range of systems types. Electrons are described quantum-mechanically within the Density-Functional Theory (DFT), in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles. Electron-nucleus interaction is described within the Pseudopotential approximation.

GAMESS - The General Atomic and Molecular Electronic Structure System is a general ab initio quantum chemistry package, free alternative to the Gaussian

GAMESS UK is an ab initio molecular electronic structure program for performing SCF-, DFT-, and MCSCF-gradient calculations, together with a variety of techniques for post Hartree Fock calculations

Molpro is a complete system of ab initio programs for molecular electronic structure calculations. As distinct from other commonly used quantum chemistry packages, the emphasis is on highly accurate computations, with extensive treatment of the electron correlation problem through the multiconfiguration-reference CI, coupled cluster and associated methods.

The Massively Parallel Quantum Chemistry Program (MPQCC) computes properties of atoms and molecules from first principles using the time independent Schrodinger equation. It runs on a wide range of architectures ranging from individual workstations to symmetric multiprocessors to massively parallel computers. Its design is object oriented, using the C++ programming language.

NWChem is a computational chemistry package that is designed to run on high-performance parallel supercomputers as well as conventional workstation clusters. It aims to be scalable both in its ability to treat large problems efficiently, and in its usage of available parallel computing resources

Q-Chem program exploits the latest developments in computer science, having adopted an Object Oriented approach to program design, which has been made possible by constructing a completely new program from the ground up. This decision is already proving invaluable in allowing developers to rapidly implement new methodologies with ease and reduce program code redundancy. The result is a highly efficient program with a flexible development base, making Q-Chem, Inc. the company of choice for quantum chemistry software.

ACES II implements the Coupled Cluster and Many Body Perturbation Theory methods
Quantum Chemistry Packages

**COLUMBUS** is a collection of programs for high-level ab initio molecular electronic structure calculations. The programs are designed primarily for extended multi-reference (MR) calculations on electronic ground and excited states of atoms and molecules. **Molcas** SCF/DFT, RASSCF, CASPT2, CC methods, Solvent models, QM/MM interface, Fast, accurate, and robust code. Free support and updates, Source code and tools for development.

**Dalton** is a powerful molecular electronic structure program, with an extensive functional for the calculation of molecular properties at the HF, DFT, MCSCF, and CC levels of theory.

**Psi 2.0** is a quantum chemistry program package developed by the Schaefer group. It is capable of evaluating SCF, MCSCF, CI, CCSD, and CCSD(T) energies and analytical gradients using expansions over Gaussian type basis functions.

**deMon** program allows to perform DFT calculations on large systems including transition metals with precision in a relatively short time.

**HyperChem** - Computational methods include molecular mechanics, molecular dynamics, and semi-empirical and ab-initio molecular orbital methods. HyperChem Data and HyperNMR have been migrated into HyperChem, and new features have been added. The new features include Open GL Rendering, DFT, TNDO, Charmm Protein Simulations, Molecules in Magnetic Fields, and much more.

**Jaguar** is a high-performance ab initio package for both gas and solution phase simulations, with particular strength in treating metal containing systems, making it the most practical quantum mechanical tool for solving real-world problems.

**Spartan** is a potent software tool that applies the power of molecular mechanics and quantum chemical calculations on your chemistry research. With state-of-the-art visualization and sophisticated computational algorithms, Spartan provides pharmaceutical and biotechnology organizations with key data supporting target identification and validation, lead selection and optimization, and process development.

**ArgusLab** - a freely licensed molecular modeling, graphics, and drug design program. Gaussian 98 & Gaussian 03 interfaces: easily set up and run Gaussian calculations on your local Windows PC. Outputs, surfaces plots, etc. are automatically added to the Calculation results in the Molecule Treeview. ArgusLab wraps the Gaussian calculation so effectively, you'll think it's a part of ArgusLab itself. You can also save ArgusLab-generated input files to run Gaussian offline or on another machine.

**CASTEP** is a software package which uses density functional theory to provide a good atomic-level description of all manner of materials and molecules. CASTEP can give information about total energies, forces and stresses on an atomic system, as well as calculating optimum geometries, band structures, optical spectra, phonon spectra and much more. It can also perform molecular dynamics simulations.

**Insight II** is a sophisticated molecular modeling environment that provides a powerful graphical interface to best-of-breed algorithms for molecular dynamics, homology modeling, de novo design, and electrostatics-making it the perfect solution for protein modelers, computational chemists, and structural biologists.
MOE is a comprehensive software system addressing the needs of today's research disciplines including Bioinformatics, Cheminformatics, Protein Modeling, Structure-Based Design, High Throughput Discovery and Molecular Modeling and Simulations. SYBYL is a suite of computational informatics software designed to enhance the drug discovery workflows and decision-making of today's computational chemists and molecular modelers. An industry standard for over 20 years and the basis for Tripos' expert molecular modeling environment, SYBYL provides the fundamental components for understanding molecular structure and properties with an emphasis on the discovery of lead candidates. Priroda 04 is a quantum-chemical program suite created by D. N. Laikov designed for the study of complex molecular systems by the density functional theory, at the MP2, MP3, and MP4 levels of multiparticle perturbation theory, and by the coupled-cluster single and double excitations method (CCSD) with the application of parallel computing. DMol3 is a unique, accurate, and reliable density functional theory (DFT) quantum mechanical code for research in the chemicals and pharmaceutical industries. Siesta (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is both a method and its computer program implementation, to perform electronic structure calculations and ab initio molecular dynamics simulations of molecules and solids. DGauss is a high-accuracy, high-performance computational chemistry package that uses density functional theory to predict molecular structures, properties and energetics. PyQuante - Python Quantum Chemistry is an open-source suite of programs for developing quantum chemistry methods. The program is written in the Python programming language, but has many "rate-determining" modules also written in C for speed. The resulting code is not nearly as fast as Jaguar, Gaussian, or GAMESS, but the resulting code is much easier to understand and modify. The goal of this software is not necessarily to provide a working quantum chemistry program (although it will hopefully do that), but rather to provide a well-engineered set of tools so that scientists can construct their own quantum chemistry programs without going through the tedium of having to write every low-level routine. Mopac 6 is the most widely distributed semiempirical quantum mechanics program in use throughout the world created by James JP Stewart. WinMopac is based on MOPAC, with addirional features and new methods, i.e. MNDO-d and PM5. AMPAC Semi-empirical Computational Program. It includes SAM1, AM1, MNDO, PM3, MNDO/C, MINDO/3 and MNDO/d semiempirical methods. MSINDO is a semiempirical molecular orbital program for the calculation of molecular properties of systems with first-, second- and third-row elements. It is a modification of the original SINDO1 method. The current version of MSINDO includes parameters for the following elements: H, Li-F, Na-Cl, K-Br.
PyMOL is an open-source, user-sponsored, molecular visualization system created by Warren Lyford DeLano. It is well suited to producing high quality 3D images of small molecules and biological macromolecules such as proteins. Almost a quarter of all published images of 3D protein structures in the scientific literature were made using PyMOL.

QC++ is a Linear Scaling Quantum Chemistry software based on the Divide and conquer method. The current version of QC++ supports the semi-empirical quantum models MNDO, AM1 and PM3. It allows to calculate the energy of a molecular configuration and its numerical gradient by some Self Consistent Field (SCF) algorithms: fixed point, optimal damping and level shifting.

Ascalaph is a Molecular Modelling Suite. Ascalaph Quantum is an interface for the quantum mechanics program PC GAMESS. Ascalaph Designer provides the generation and editing of molecular models. Ascalaph Graphics provides the window interface and 3D graphics.

PMViewMol - the program for fast viewing of molecules in OS/2 Warp. Based on the ViewMol3D.