Time-Dependent DFT: Basic Principle and Application to Molecular Spectroscopy

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Summary

- Time-Independent DFT
- Time-Dependent DFT
- Linear Response DFT
- Application to Molecular Spectroscopy
- Which functional to choose?
- Simulation of Solvent Effects
- A Practical Example: Simulation of a UV/Vis. Spectrum using LR-TDDFT

THE TIME-INDEPENDENT PROBLEM

TIME-INDEPENDENT SCHRÖDINGER EQUATION

$$\hat{H}\Psi = E\Psi$$

Electronic hamiltonian $\hat{H} = \hat{T} + \hat{W} + \hat{V}_0$

T = Kinetic energy; W = Coulomb interaction; V_0 = External potential

H is fully defined by the number of electrons N and the external potential V_0

For a molecule with N electrons and P nuclei:

$$\hat{T} = -\sum_{\mu=1}^{N} \frac{1}{2}\Delta_\mu$$ *Kinetic energy*

$$\hat{W} = \sum_{\mu=1}^{N}\sum_{\upsilon>1}^{N} \frac{1}{r_{\mu\upsilon}}$$ *2-electron Coulomb interactions*

$$\hat{V}_0 = -\sum_{\mu=1}^{N}\sum_{p=1}^{P} \frac{Z_p}{r_{\mu p}}$$ *External potential = static nuclear field*

TIME-INDEPENDENT DFT

FIRST HOHENBERG-KOHN THEOREM

The external potential V_0 is determined, within a trivial additive constant, by the electron density $\rho(r)$

Consequence:

The hamiltonian H, and thus the ground-state energy, are completely defined by the electron density $\rho(\mathbf{r})$. Therefore, the total electronic energy can be expressed as a functional of $\rho(\mathbf{r})$:

$$E\left[\rho\left(\mathbf{r}\right)\right]=T\left[\rho\left(\mathbf{r}\right)\right]+W\left[\rho\left(\mathbf{r}\right)\right]+V_0\left[\rho\left(\mathbf{r}\right)\right]$$

This holds true for every quantum mechanical observable.

TIME-INDEPENDENT DFT

SECOND HOHENBERG-KOHN THEOREM

The electron density ρ(r) obeys a variational principle

Consequence:

Among different densities $\rho(\mathbf{r})$, those that provide lower energies are closer to the exact one.

Stationarity condition:

$$\frac{\delta E\left[\rho\left(\mathbf{r}\right)\right]}{\delta\rho\left(\mathbf{r}\right)}=0$$

The ground-state density correspond to the minimum of the E[ρ(r)] functional

Note: a functional is a composite function f(g(x)) : the output of g is the argument of f
Chain rule for a derivative of a functional f:

$$\left.\frac{\delta f}{\delta x}\right|_{x=x_0}=\frac{\delta f}{\delta g}\times\frac{\delta g}{\delta x}\qquad\frac{\delta f}{\delta g}=\left.\frac{\delta f}{\delta g}\right|_{g(x)=g(x_0)}\qquad\frac{\delta g}{\delta x}=\left.\frac{\delta g}{\delta x}\right|_{x=x_0}$$

TIME-INDEPENDENT KOHN-SHAM EQUATIONS

Practically, ρ is determined by solving the Kohn-Sham equations

The Kohn-Sham formalism transforms the stationarity equation into a system of eigenvalue equations whose solutions are the *Khon-Sham orbitals*

The density is then calculated using the KS orbitals :

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} n_i \left|\psi_i(\mathbf{r})\right|^2$$

Starting point:

We consider a ***fictitious*** system of non-interacting electrons that have for their overall ground-state density $\rho(\mathbf{r})$ the same density as some ***real*** system of interest where the electrons do interact

TIME-INDEPENDENT KOHN-SHAM EQUATIONS

	real **system** (interacting electrons)	***fictitious*** **system** (non-interacting electrons)	
Kinetic energy	$T[\rho]$	$T_{KS}[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i(\mathbf{r})\Delta\psi_i(\mathbf{r})d\mathbf{r}$	
Electron-electron interactions	$W[\rho]$	$W_{KS}[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\lvert\mathbf{r}_2 - \mathbf{r}_1\rvert} d\mathbf{r}_1\, d\mathbf{r}_2$	*Hartree potential*

KS Energy functional for the real system:

$$E[\rho] = T_{KS}[\rho] + W_{KS}[\rho] + V_0[\rho] + E_{XC}[\rho]$$

Exchange-Correlation (XC) functional:

$$E_{XC}[\rho] = \left(T[\rho] - T_{KS}[\rho]\right) + \left(W[\rho] - W_{KS}[\rho]\right)$$

E_{XC} corrects the error made in using the non-interacting kinetic energy and in treating the electron-electron interactions classically

TIME-INDEPENDENT KOHN-SHAM EQUATIONS

Applying the variational theorem

The orbitals that minimize the energy satisfy the Khon-Sham equations, which have the same structure as the HF equations

$$\left\{-\frac{1}{2}\Delta+\underbrace{\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\upsilon_{XC}(\mathbf{r})+V_0(\mathbf{r})}_{\upsilon_{KS}(\mathbf{r})}\right\}\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})$$

The non-interacting electrons move in an effective KS potential depending on $\rho(\mathbf{r})$

$$\upsilon_{KS}(\mathbf{r})=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\upsilon_{XC}(\mathbf{r})+V_0(\mathbf{r})$$

Local exchange-correlation potential

$$\upsilon_{XC}(\mathbf{r})=\frac{\delta E_{XC}[\rho]}{\delta\rho}$$

The main difficulty of DFT is to find an appropriate description of E_{XC} as a function of $\rho(\mathbf{r})$ → *Many XC functionals*

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THE TIME-DEPENDENT PROBLEM

TIME-DEPENDENT SCHRÖDINGER EQUATION

$$i\frac{\partial\Psi(t)}{\partial t} = \hat{H}(t)\Psi(t)$$

Time-dependent electronic hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{W} + \hat{V}_{ext}(t)$$

T = kinetic energy
W = the Coulomb interaction
V_{ext} = ***time-dependent external potential***

$$\hat{V}_{ext}(\mathbf{r},t) = \begin{cases} V_0(\mathbf{r}) \text{ for } t < t_0 \\ V_0(\mathbf{r}) + V(\mathbf{r},t) \text{ for } t \geq t_0 \end{cases}$$

$V(\mathbf{r},t)$ *is required to be* ***expandable in Taylor series*** *around the finite time* t_0

The system evolves from a fixed initial state:

$$\Psi(t_0) = \Psi_0$$

TIME-DEPENDENT DFT

RUNGE-GROSS THEOREM [PRL 52 (1984) 997]

The densities ρ(r,t) and ρ'(r,t) of two systems evolving from the same initial state Ψ(t$_0$) under the influence of, respectively, the scalar potentials υ(r,t) and υ'(r,t), both Taylor expandable about t$_0$ and differing by more than a purely time-dependent function c(t), will always differ.

This is the time-dependent analog of the first Hohenberg-Kohn theorem

Consequence:

The time-dependent external potential associated to a time-dependent density ρ(r,t) is unique, up to a purely time-dependent function c(t). It determines the total time-dependent wavefunction Ψ, which in turn is unique up to a time-dependent phase factor α(t).

$$\Psi(\mathbf{r},t) = \tilde{\Psi}[\rho](t)e^{-i\alpha(t)}$$

TIME-DEPENDENT DFT

Another consequence:

The expectation value of a time-dependent operator (which does not contain derivative or integral operators on t) is a completely unique functional of the density

$$O[\rho](t) = \left\langle \tilde{\Psi}[\rho](t) \middle| \hat{O}(t) \middle| \tilde{\Psi}[\rho](t) \right\rangle$$

Important note:

In this treatment, only scalar potentials $V_{ext}(\mathbf{r},t)$ are considered, thus excluding vector potentials $\mathbf{V}_{\mathbf{ext}}(\mathbf{r},t)$. **This treatment thus allows describing perturbations due to electric fields, but not to magnetic fields**.

An extension of the present scheme is needed to treat magnetic effects. This is called *time-dependent current-density functional theory* (TDCDFT), because description of magnetic systems require determining both the time-dependent density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$.

TIME-DEPENDENT DFT

SOLVING THE TIME-DEPENDENT SCHRÖDINGER EQUATION

The analog of the second Hohenberg-Khon theorem, which introduces the variational principle, now involves the action:

$$A = \int \left\langle \Psi(t) \middle| i\frac{\partial}{\partial t} - \hat{H}(t) \middle| \Psi(t) \right\rangle dt$$

The action is also a functional of the density:

$$A[\rho] = \int \left\langle \Psi[\rho](t) \middle| i\frac{\partial}{\partial t} - \hat{H}(t) \middle| \Psi[\rho](t) \right\rangle dt$$

The true time-dependent density $\rho(\mathbf{r},t)$ is the one that makes the action stationary:

$$\frac{\delta A\left[\rho\right]}{\delta\rho(\mathbf{r},t)} = 0$$

TIME-DEPENDENT KOHN-SHAM EQUATIONS

As in the static case, we consider a ***fictitious*** system of non-interacting electrons moving in a local *time-dependent* potential $V_{ext}(\mathbf{r},t)$, of which ***the density at every time t is identical to the density of the real system***

$$i\frac{\partial}{\partial t}\psi_j(\mathbf{r},t)=\left\{-\frac{1}{2}\Delta+\underbrace{\int\frac{\rho(\mathbf{r}',t)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}'+\upsilon_{XC}(\mathbf{r},t)+V_{ext}(\mathbf{r},t)}_{\upsilon_{KS}(\mathbf{r},t)}\right\}\psi_j(\mathbf{r},t)$$

The non-interacting electrons move in an effective potential depending on $\rho(\mathbf{r},t)$

$$\upsilon_{KS}(\mathbf{r},t)=\int\frac{\rho(\mathbf{r}',t)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}'+\upsilon_{XC}(\mathbf{r},t)+V_{ext}(\mathbf{r},t)$$

The unknown is now the *local time-dependent exchange-correlation potential*

$$\upsilon_{XC}(\mathbf{r},t)=\frac{\delta A_{XC}[\rho]}{\delta\rho(\mathbf{r},t)}$$

where A_{xc} is the exchange-correlation action functional. *A_{xc} is the analog of E_{xc} in the static case. The exact A is not known, so approximations have to be made in order to perform calculations on real systems.*

ADIABATIC APPROXIMATION IN TDDFT

Within the adiabatic approximation (low frequency limit):

$$\upsilon_{XC}(\mathbf{r},t)=\frac{\delta A_{XC}[\rho]}{\delta\rho(\mathbf{r},t)}\approx\left.\frac{\delta E_{XC}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho(\mathbf{r},t)}$$

$\upsilon_{XC}(\mathbf{r},t)$ is <u>local in time</u>. ***It depends only on ρ at time t.***

The adiabatic approximation assumes that the XC potential changes instantaneously when the electron density is changed.

All retardation effects are neglected.

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LINEAR RESPONSE TDDFT

For the determination of properties like polarizabilities and excitation energies, only the knowledge of the linear density response is required

This implies that ***only a perturbative solution of the TDKS equations is required***

Time-dependent external potential:

small

$$\hat{V}_{\mathrm{ext}}(\mathbf{r},t) = \begin{cases} V_0(\mathbf{r}) \text{ for } t < t_0 \\ V_0(\mathbf{r}) + V_1(\mathbf{r},t) \text{ for } t \geq t_0 \end{cases}$$

In the case of ***small perturbations***, the TD density can be expanded as a Taylor series of the external potential, and truncated to first order:

$$\rho(\mathbf{r},t) = \rho_0(\mathbf{r}) + \rho_1(\mathbf{r},t) + \ldots \text{ (higher orders)}$$

First-order density change

Unperturbed density of $t<t_0$, which can be obtained from the ground state Kohn-Sham equation in the potential $V_0(\mathbf{r})$

LINEAR RESPONSE TDDFT

For the real system (interacting electrons)

The first-order density change ρ_1 is related to the first-order potential via the ***linear response function*** χ :

$$\rho_1(\mathbf{r},t) = \int\int \chi\left(\mathbf{r},t;\mathbf{r}',t'\right) V_1(\mathbf{r}',t')\, d\mathbf{r}'\, dt'$$

The ***exact*** response function is given by the functional derivative wrt V_{ext}:

$$\chi\left(\mathbf{r},t;\mathbf{r}',t'\right) = \left.\frac{\delta\rho(\mathbf{r},t)}{\delta V_{ext}(\mathbf{r}',t')}\right|_{V0}$$

which has to be evaluated at the *ground state initial potential*.

LINEAR RESPONSE TDDFT

For the KS system of non interacting electrons:

First order KS potential

$$\rho_1(\mathbf{r},t)=\int\!\!\int \chi_{KS}\left(\mathbf{r},t;\mathbf{r}',t'\right)\upsilon_{KS}^{(1)}(\mathbf{r}',t')\,d\mathbf{r}'\,dt'$$

where $\upsilon_{KS}^{(1)}(\mathbf{r}',t')$ is the KS potential in first-order of the external field:

$$\upsilon_{KS}^{(1)}(\mathbf{r}',t')=\int\frac{\rho_1(\mathbf{r}',t)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}'+\int\!\!\int\underbrace{\left.\frac{\delta\upsilon_{XC}\left(\mathbf{r},t\right)}{\delta\rho\left(\mathbf{r}',t'\right)}\right|_{\rho 0}}_{f_{XC}\left(\mathbf{r},t;\mathbf{r}',t'\right)}\rho_1(\mathbf{r}',t')\,d\mathbf{r}'\,dt'+V_1(\mathbf{r},t)$$

Exchange Correlation Kernel

The exact linear density response $\rho_1(r, t)$ of an interacting system can be written as the linear density response of a non-interacting system to the 1th-order effective perturbation υ_{KS}

Our objective is thus to determine the KS response function χ_{KS}

LINEAR RESPONSE TDDFT

Frequency-domain TD-DFT

$$\rho_1(\mathbf{r},\mathrm{t}) = \int\int \chi_{\mathrm{KS}}\left(\mathbf{r},\mathrm{t};\mathbf{r}',\mathrm{t}'\right)\upsilon_{\mathrm{KS}}^{(1)}(\mathbf{r}',\mathrm{t}')\,\mathrm{d}\mathbf{r}'\,\mathrm{dt}'$$

⇓ ***Fourier transform***

$$\rho_1(\mathbf{r},\omega) = \int \chi_{\mathrm{KS}}\left(\mathbf{r},\mathbf{r}',\omega\right)\upsilon_{\mathrm{KS}}^{(1)}(\mathbf{r}',\omega)\,\mathrm{d}\mathbf{r}'$$

$$\upsilon_{\mathrm{KS}}^{(1)}(\mathbf{r},\mathbf{r}',\omega) = \int \frac{\rho_1(\mathbf{r}',\omega)}{\left|\mathbf{r}-\mathbf{r}'\right|}\mathrm{d}\mathbf{r}' + \int f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}',\omega)\rho_1(\mathbf{r}',\omega)\,\mathrm{d}\mathbf{r}' + \mathrm{V}_1(\mathbf{r},\omega)$$

The XC kernel is frequency independent
in the adiabatic case

Note: Fourier transform convention

$$f(\mathrm{t}) = \frac{1}{2\pi}\int \exp(-\mathrm{i}\omega\mathrm{t})\,f(\omega)\,\mathrm{d}\omega$$

$$f(\omega) = \int \exp(\mathrm{i}\omega\mathrm{t})\,f(\mathrm{t})\,\mathrm{dt}$$

Convolution theorem

$$h(\mathrm{t}) = \int g(\mathrm{t}-\mathrm{t}')\,f(\mathrm{t}')\,\mathrm{dt}' \Leftrightarrow h(\omega) = g(\omega)\,f(\omega)$$

LINEAR RESPONSE TDDFT

Explicit formula for the response function

Using perturbation theory, the KS response function can be directly expressed in terms of the unperturbed KS orbitals:

$$\chi_{\mathrm{KS}}\left(\mathbf{r};\mathbf{r}',\omega\right)=2\sum_{\mathrm{i}}^{\mathrm{occ}}\sum_{\mathrm{a}}^{\mathrm{virt}}\psi_{\mathrm{a}}(\mathbf{r})\psi_{\mathrm{i}}(\mathbf{r})\psi_{\mathrm{a}}(\mathbf{r}')\psi_{\mathrm{i}}(\mathbf{r}')\frac{\varepsilon_{\mathrm{a}}-\varepsilon_{\mathrm{i}}}{\omega^{2}+(\varepsilon_{\mathrm{a}}-\varepsilon_{\mathrm{i}})^{2}}$$

Download the file Response_function_explicit_formula.pdf
for the details of the derivation

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LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

Time-dependent dipole moment

In the presence of an external oscillating electric field $F = F_0 \cos(\omega t)$ the *i*-component of the dipole moment of a molecule can be expanded as a Taylor series in the electric field amplitudes. To first-order:

$$\vec{\mu}^{(i)}(t) = \vec{\mu}_0^{(i)} + \underbrace{\sum_{j=x,y,z} \alpha_{ij} F_0 \cos(\omega t)}_{\vec{\mu}_1^{(i)}(t)} + \ldots \quad (1)$$

Dynamic polarizability = *response function that relates the external potential to the change in the dipole*

Permanent dipole

First-order field-induced dipole variation

Using perturbation theory, the dynamic polarizability can be expressed as a function of the vertical excitation energies and transition dipole moments of the molecule

$$\alpha_{ij} = 2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \mu^{(i)} | \Psi_n \rangle \langle \Psi_n | \mu^{(j)} | \Psi_0 \rangle}{\omega_n - \omega}$$

The frequency-dependent polarizability has poles at the excitation energies.
The residues determine the transition dipole moments.
Therefore, the optical absorption spectrum of a molecule is accessible from α

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

Alternatively, the time-dependent dipole moment can be expressed as a function of the time-dependent density:

i-component of **r**

$$\vec{\mu}^{(i)}(t) = \int \rho(\mathbf{r},t)\mathbf{r}^{(i)}\,d\mathbf{r} = \underbrace{\int \rho_0(\mathbf{r})\mathbf{r}^{(i)}\,d\mathbf{r}}_{\vec{\mu}_0^{(i)}} + \underbrace{\int \rho_1(\mathbf{r},t)\mathbf{r}^{(i)}\,d\mathbf{r}}_{\vec{\mu}_1^{(i)}(t)} \qquad (2)$$

Identifying expressions (1) and (2):

$$\sum_{j=x,y,z} \alpha_{ij}F_0\cos(\omega t) = \int \rho_1(\mathbf{r},t)\mathbf{r}^{(i)}\,d\mathbf{r} \xrightarrow[\rho_1(\mathbf{r},t)=\sum_{j=x,y,z}\rho_1^{(j)}(\mathbf{r},t)]{} \alpha_{ij}F_0\cos(\omega t) = \int \rho_1^{(j)}(\mathbf{r},t)\mathbf{r}^{(i)}\,d\mathbf{r}$$

*FT of ρ_1(**r**,t)*

$$\frac{1}{2}\alpha_{ij}F_0\left(\exp(i\omega t)+\exp(-i\omega t)\right) = \int \rho_1^{(j)}(\mathbf{r},\omega)\exp(i\omega t)\mathbf{r}^{(i)}\,d\mathbf{r} + \int \rho_1^{(j)}(\mathbf{r},-\omega)\exp(-i\omega t)\mathbf{r}^{(i)}\,d\mathbf{r}$$

Identifying the exponential terms

$$\alpha_{ij} = \frac{2}{F_0}\int \rho_1^{(j)}(\mathbf{r},\omega)\mathbf{r}^{(i)}\,d\mathbf{r}$$

The dynamic polarizability is directly related to the first-order density change.

This is what we obtain from LR-TDDFT!

ACCESSIBLE QUANTITIES FROM LR-TDDFT

Transition energies and wavelengths

$$\omega_n = E_n - E_0,\ \lambda_n$$

Transition dipoles

$$\vec{\mu}_{0n} = \left\langle \Psi_0 \middle| \vec{\mu} \middle| \Psi_n \right\rangle = -|e| \left\langle \Psi_0 \middle| \vec{r} \middle| \Psi_n \right\rangle$$

Unit = C.m

1 a.u. of μ = 8.478358 10^{-30} C.m = 2.5415 D

Oscillator strengths

$$f_{0n} = \frac{2}{3}\omega_n \left|\vec{\mu}_{0n}\right|^2$$

Dimensionless (proportional to the absorption intensity)

Exctinction coefficient ε $\quad f_{0n} \propto \int \varepsilon\, d\nu$

with ε in $mol^{-1}.cm^{-1}.L$ and ν in cm^{-1}, $\quad f_{0n} \approx 4.3 \times 10^{-9} \int \varepsilon\, d\nu$

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

What do we know?

The exact linear density response is written as

$$\rho_1(\mathbf{r},\omega) = \int \chi_{KS}\left(\mathbf{r},\mathbf{r}',\omega\right) \upsilon_{KS}^{(1)}(\mathbf{r}',\omega)\,d\mathbf{r}'$$

$$\chi_S\left(\mathbf{r};\mathbf{r}',\omega\right) = 2\sum_{i}^{occ}\sum_{a}^{virt} \psi_a(\mathbf{r})\psi_i(\mathbf{r})\psi_a(\mathbf{r}')\psi_i(\mathbf{r}')\frac{\varepsilon_a - \varepsilon_i}{\omega^2 + (\varepsilon_a - \varepsilon_i)^2}$$

$$\upsilon_{KS}^{(1)}(\mathbf{r},\mathbf{r}',\omega) = \int \frac{\rho_1(\mathbf{r}',\omega)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}' + \int f_{XC}(\mathbf{r},\mathbf{r}')\rho_1(\mathbf{r}',\omega)\,d\mathbf{r}' + V_1(\mathbf{r},\omega)$$

frequency independent XC kernel

What do we want?

- The **poles** of the response function (**excitation energies**)
- The **residues** of the response function (**transition dipole moments**)

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

Matrix formulation of the TDDFT response equations (Casida equations)

Excitation energies and transition dipole moments can be obtained by solving the matrix system

$$\begin{pmatrix} \mathbf{L} & \mathbf{M} \\ \mathbf{M} & \mathbf{L} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega_q \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Download the file
Matrix_Form_TDDFT.pdf
for the details of the derivation

L and **M** are matrices of dimension $N_{occ}xN_{virt}$
X and **Y** are vector-matrices
Ω_q are the desired transition energies

$$L_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + K_{ia,jb} \qquad M_{ia,jb} = K_{ia,jb}$$

Tamm-Dancoff Approximation: **M** = 0

$$K_{ia,jb} = \iint \psi_i(\mathbf{r})\psi_a(\mathbf{r})\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{XC}(\mathbf{r},\mathbf{r}')\right)\psi_j(\mathbf{r}')\psi_b(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Coupling matrix

$$X_{ia} = \frac{\int \psi_i(\mathbf{r}')\psi_a(\mathbf{r}')\upsilon_{KS}(\mathbf{r}',\omega)d\mathbf{r}'}{\omega - (\varepsilon_a - \varepsilon_i)} \qquad Y_{ia} = \frac{\int \psi_i(\mathbf{r}')\psi_a(\mathbf{r}')\upsilon_{KS}(\mathbf{r}',\omega)d\mathbf{r}'}{-\left(\omega + (\varepsilon_a - \varepsilon_i)\right)}$$

M. Casida, *Time-dependent density functional response theory for molecules*, Recent Advances in Density Functional Methods (D. E. Chong, ed.), World Scientific, Singapore, 1995

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

Matrix formulation of the TDDFT response equations

The matrix equations can be further reduced to an eigenvalue problem

$$\begin{pmatrix} \mathbf{L} & \mathbf{M} \\ \mathbf{M} & \mathbf{L} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega_K \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

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$$\boxed{\mathbf{W}\mathbf{F}_K = \boldsymbol{\Omega}_K^2 \mathbf{F}_K}$$

$$\mathbf{W} = (\mathbf{L}-\mathbf{M})^{1/2}(\mathbf{L}+\mathbf{M})(\mathbf{L}-\mathbf{M})^{1/2}$$

$$\mathbf{F}_K = (\mathbf{L}-\mathbf{M})^{-1/2}(\mathbf{X}+\mathbf{Y})_K$$

The eigenvalues of W are equivalent to the squares of the excitation energies

q are the index of the eigenvectors and denote an electron transition i→a

$$W_{q,q'} = \delta_q \delta_{q'} \omega_q^2 + 2\sqrt{\omega_q \omega_{q'}} K_{qq'} \qquad \omega_q = \varepsilon_a - \varepsilon_i$$

The oscillator strengths are calculated from the normalized eigenvectors

$$f_K = \frac{2}{3}\left(\left| \mathbf{x}^T \mathbf{S}^{-1/2} \mathbf{F}_K \right|^2 + \left| \mathbf{y}^T \mathbf{S}^{-1/2} \mathbf{F}_K \right|^2 + \left| \mathbf{z}^T \mathbf{S}^{-1/2} \mathbf{F}_K \right|^2 \right) \quad \text{with} \quad \begin{aligned} S_{qq'} &= \delta_q \delta_{q'} / \omega_q \\ x_q &= \int \psi_i x \psi_a \, d\mathbf{r} \end{aligned}$$

M. Casida, *Time-dependent density functional response theory for molecules*, Recent Advances in Density Functional Methods (D. E. Chong, ed.), World Scientific, Singapore, 1995

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

LR-TDDFT within the adiabatic approximation has become the most widely used implementation of TDDFT.

Within this approximation , the number of solutions of the LR-TDDFT equations is equal to the dimensions of Casida's matrices **L** and **M**. This corresponds exactly to the number of possible one-electron excitations in the system.

Hence, although the adiabatic approximation does include correlations effects, it is essentially a one-electron (CIS-like) theory.

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

How to get excitation energies using TD-DFT?

- Do a ground state Kohn-Sham calculation: obtain $\{\psi_i\}$ and the corresponding $\{\varepsilon_i\}$
- Form the matrices **L** and **M**
- Diagonalize the full matrices or use a specific algorithm to extract the first roots: obtain $\{\omega_i\}$ and $\{f_i\}$
- Information about the character of the excited states can be obtained from the vectors $\mathbf{F}_q$ (interpretation):

$$\left|\Psi_q\right\rangle = \sum_{jb} C_{jb}^{q} \left|\Psi_j^b\right\rangle \qquad C_{jb}^{q} = \sqrt{\frac{\varepsilon_b - \varepsilon_i}{\Omega_q}} F_{jb}^{q}$$

where $\left|\Psi_j^b\right\rangle$ denotes the KS single determinant where the *j*th occupied orbital has been replaced by the *b*th unoccupied orbital.

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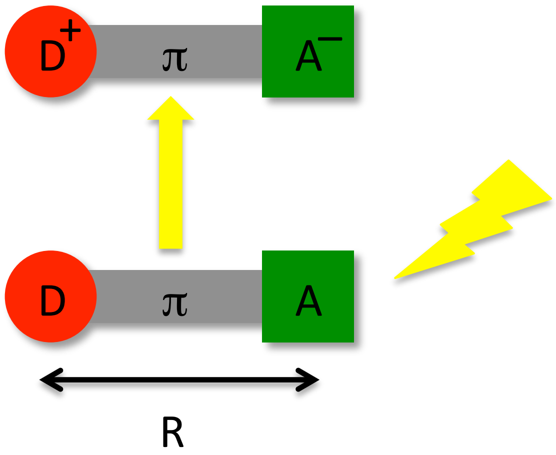
- Simulation of Solvent Effects
- Practical Examples

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

A common shortcoming of TD-DFT with popular functionals: the CT excitations



CT excitation energy:

$$\omega_{CT} \approx \mathrm{IP}^{D} - \mathrm{EA}^{A} - 1/R$$

At large separations R, the orbitals of D and A do not overlap. The leading terms in the **L** and **M** matrices are the diagonal terms:

$$L_{ia,jb} = \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + K_{ia,jb} \xrightarrow{ia=jb} L_{ia,ia} = \varepsilon_a - \varepsilon_i + K_{ia,ia}$$

$$M_{ia,jb} = K_{ia,bj} \xrightarrow{ia=jb} M_{ia,ia} = K_{ia,ai}$$

Nonhybrid (pure LDA or GGA) functionals:

$$K^{XC}_{ia,ia} = \int dr\,dr'\psi_a(\mathbf{r})\psi_i(\mathbf{r}')f_{XC}\psi_a(\mathbf{r})\psi_i(\mathbf{r}') \approx 0$$

*since f_{XC} is a **local** operator*
(no asymptotic –1/R dependence)

$$\Rightarrow \omega^{TDDFT}_{CT} \approx \varepsilon^{A}_{a} - \varepsilon^{D}_{i}$$

Nonhybrid functionals do not provide good estimates of CT state energies

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

Hybrid functionals:

$$K^{XC} = aK^{XC}_{DFT} + bK^{HF}$$

$$K^{HF}_{ai,bj} = \int \psi_a(\mathbf{r})\psi_b(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_i(\mathbf{r}')\psi_j(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

Asymptotic –1/R dependence

$$\Rightarrow \omega^{TDDFT}_{CT} \approx \varepsilon^{A}_{a} - \varepsilon^{D}_{i} + f(-1/R)$$

Hybrid functionals alleviate the CT errors of DFT, although a full compensation cannot be achieved (unless the functional contains 100% HF exchange).

If the charge separation is not complete (which is the case for many excitations formally labeled as CT) the errors from the functional may show up or not, or only to a certain degree.

→ Difficult to predict in which situation a computed excitation energy afford significant errors due to the CT problem, and when not.

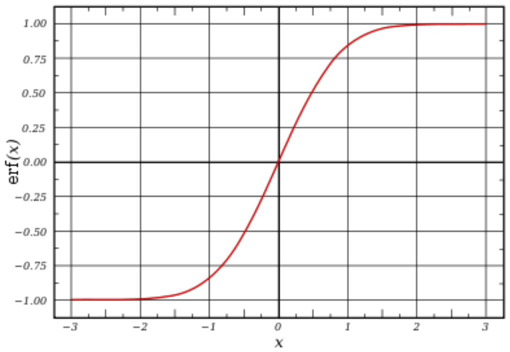
→ ***Spatial separation of the orbitals plays an important role***

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

Long-range corrected Hybrid Functionals

LC-BLYP: the electron repulsion operator $1/r_{12}$ is divided into short- and long-range parts by using a standard error function:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,\mathrm{d}t.$$



$$\frac{1}{r_{12}} = \underbrace{\frac{1-\mathrm{erf}\left(\mu r_{12}\right)}{r_{12}}} + \underbrace{\frac{\mathrm{erf}\left(\mu r_{12}\right)}{r_{12}}}$$

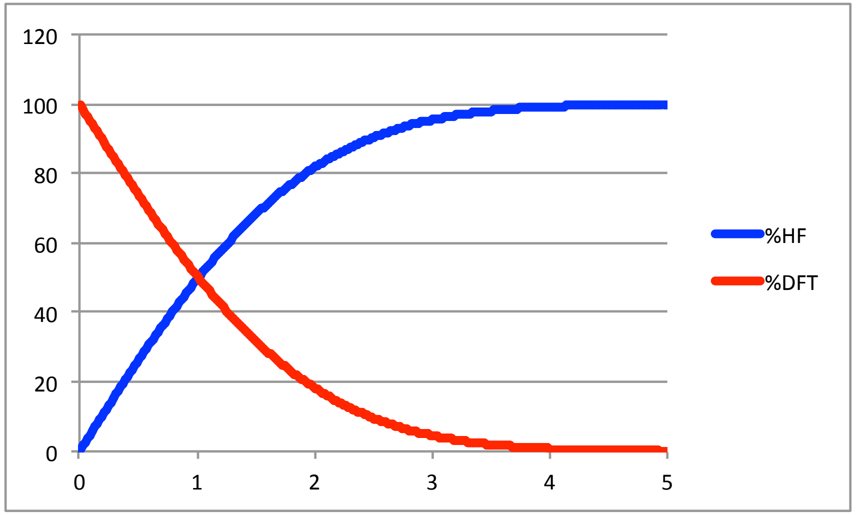
short range part (combined with DFT-LDA exchange)

long-range part (combined with HF exchange)

μ determines the balance of DFT to HF exchange at intermediate r_{12}

μ → 0 pure GGA calculation
μ → inf. pure HF calculation

Standard value in Gaussian09: μ = 0.47



Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K.
J. Chem. Phys., **2001**, *115,* 3540

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

Long-range corrected Hybrid Functionals

CAM-B3LYP: adds a long-range correction using the Coulomb-Attenuating Method
19% of HF exchange at short-range and 65% at long-range with μ = 0.33

$$\frac{1}{r_{12}} = \underbrace{\frac{1-\{\alpha+\beta \operatorname{erf}(\mu r_{12})\}}{r_{12}}} + \underbrace{\frac{\alpha+\beta \operatorname{erf}(\mu r_{12})}{r_{12}}}$$

$0 \le \alpha + \beta \le 1;$
$0 \le \alpha \le 1; 0 \le \beta \le 1$

short range part (combined with DFT-LDA exchange)

long-range part (combined with HF exchange)

The parameter α allows us to incorporate the HF exchange contribution over the whole range Yanai, T.; Tew, D.; Handy, N. *Chem. Phys. Lett*. **2004**, *393*, 51.

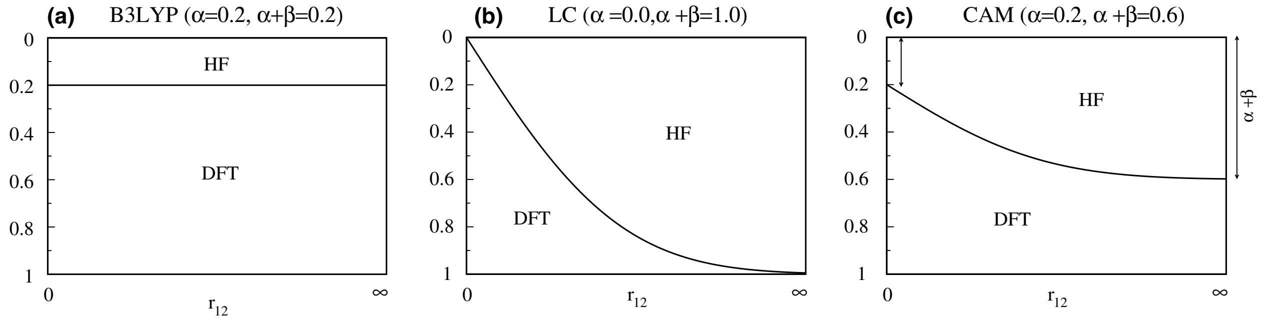


Fig. 2. Schematic plots of the contributions to exchange from r_{12}^{-1}, apportioned into DFT and HF, for: (a) B3LYP, (b) LC, and (c) CAM.

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

Using long-range corrected Hybrid Functionals

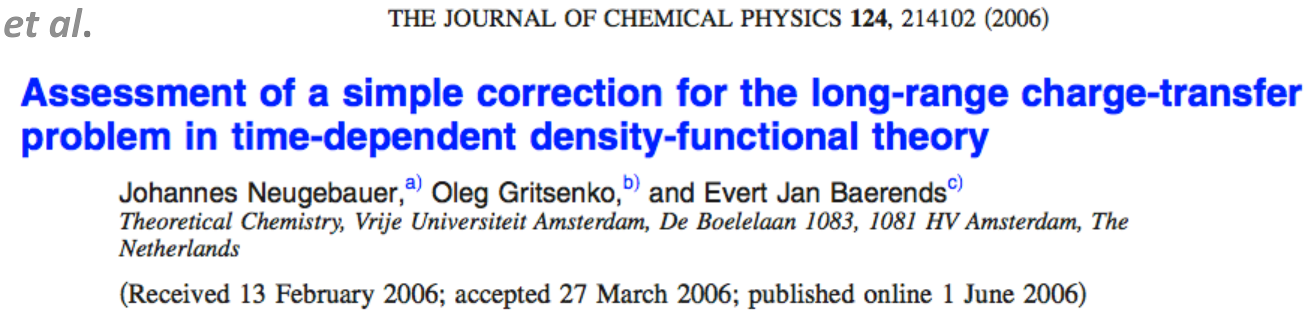
→ ***if an excitation involves a pair of orbitals that are spatially well separated, the exchange component in the K matrix is dominated by HF exchange***

→ ***This leads to a qualitatively correct behavior for ω_{CT}***

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

Several authors proposed some criteria based on the spatial separation of orbitals that might be able to warn users of TD-DFT about possible CT issues.

Baerends *et al*.



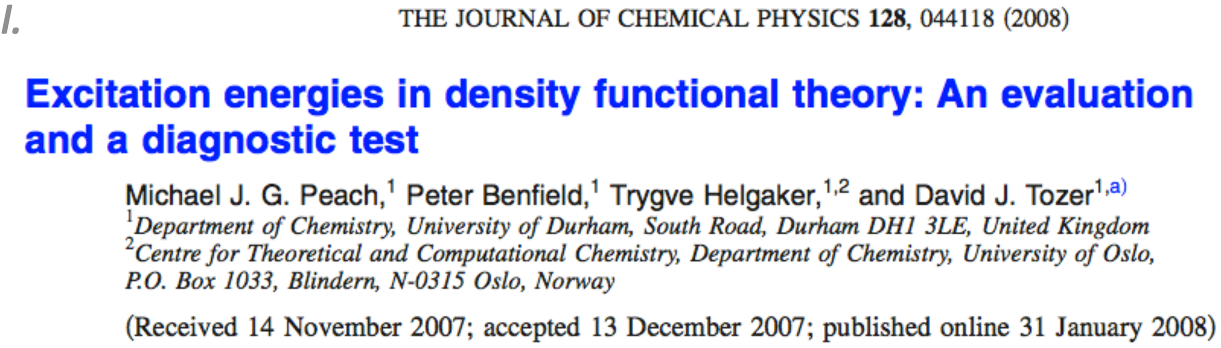
THE JOURNAL OF CHEMICAL PHYSICS **124**, 214102 (2006)

Assessment of a simple correction for the long-range charge-transfer problem in time-dependent density-functional theory

Johannes Neugebauer,[a] Oleg Gritsenko,[b] and Evert Jan Baerends[c]
Theoretical Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(Received 13 February 2006; accepted 27 March 2006; published online 1 June 2006)

Tozer *et al.*



THE JOURNAL OF CHEMICAL PHYSICS **128**, 044118 (2008)

Excitation energies in density functional theory: An evaluation and a diagnostic test

Michael J. G. Peach,[1] Peter Benfield,[1] Trygve Helgaker,[1,2] and David J. Tozer[1,a)]
[1]*Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, United Kingdom*
[2]*Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*

(Received 14 November 2007; accepted 13 December 2007; published online 31 January 2008)

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

The choice of the appropriate XC functional for TDDFT calculations remain however a difficult issue

TDDFT Benchmarks

Jacquemin et al.
Extensive TD-DFT Benchmark: Singlet-Excited States of Organic Molecules
J. Chem. Theor. Comput. **2009**, 5, 2420

Jacquemin et al.
TD-DFT Assessment of Functionals for Optical 0–0 Transitions in Solvated Dyes
J. Chem. Theor. Comput. **2012**, 8, 2359

…and many many others !

WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?

General advices

Avoid pure (i.e. exactexchange free) functionals as they tend to significantly undershoot the transition energies in the majority of organic and inorganic systems. **Use hybrids**.

For both **local n – π* and π – π* states**, hybrids such as **B3LYP, PBE0 or M06 generally provide accurate estimates**.

For **CT excited states**, use **range-separated hybrids** (CAM-B3LYP or ωB97X-D) to reach physically meaningful estimates.

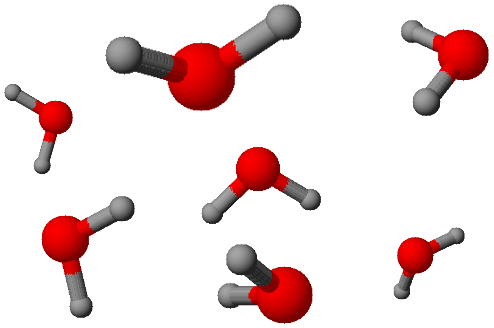
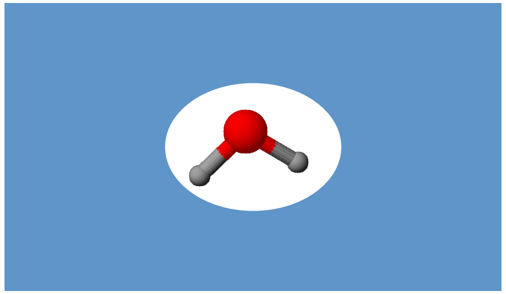
The calculations of excited-state properties with TDDFT
C. Adamo and D. Jacquemin, *Chem. Soc. Rev*. **2013**, *42*, 845-856 (tutorial review)

Autschbach, J., "Spectroscopic Properties obtained from Time-Dependent Density Functional Theory (TD-DFT)", in Computational Inorganic and Bioinorganic Chemistry, J. Solomon, E. I.; Scott, R. A. & King, R. B. (Eds.), John Wiley & Sons, 2009, 9, 71-90.

Summary

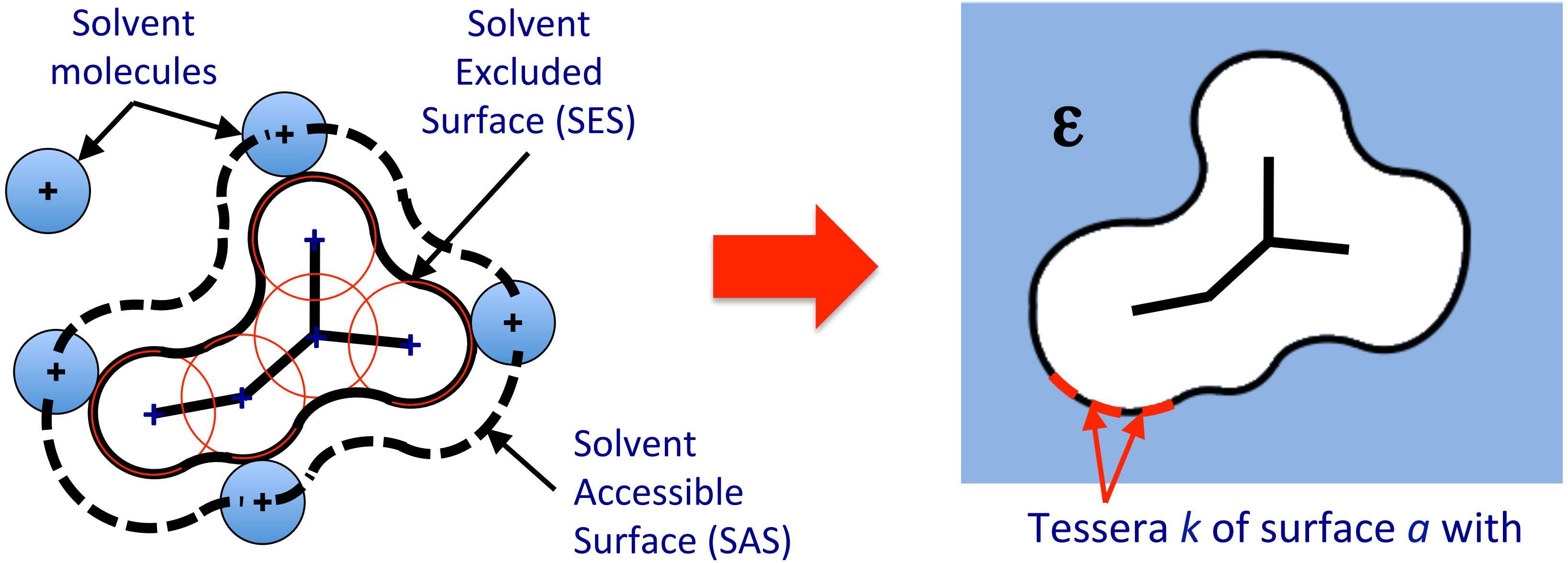
- Time-Independent DFT
- Time-Dependent DFT
- Linear Response DFT
- Application to Molecular Spectroscopy
- Which functional to choose?
- **Simulation of Solvent Effects**
- A Practical Example: Simulation of a UV/Vis. Spectrum using LR-TDDFT

SOLVATION MODELS

Models	Explicit solvent models	Continuum solvation models
Features	All solvent molecules are explicitly represented. 	Represent solvent as a continuous medium. 
Merits	Detail information is provided. Generally more accurate.	Simple, inexpensive to calculate
Disadvantages	Expensive for computation	Ignore specific short-range effects. Less accurate.

POLARIZABLE SOLVATION MODELS

Tomasi et al. *Chem. Rev.* **2005**, 105, 2999.



Solvent molecules

Solvent Excluded Surface (SES)

Solvent Accessible Surface (SAS)

Tessera *k* of surface *a* with Apparent Surface Charge (ASC):

$$\sigma(k) = q(k)/a$$

ASC computed self-consistently:

$$\left(\frac{\varepsilon+1}{\varepsilon-1} - \frac{1}{2\pi}D\right)\sigma(k) = -\frac{1}{2\pi}E(k)$$

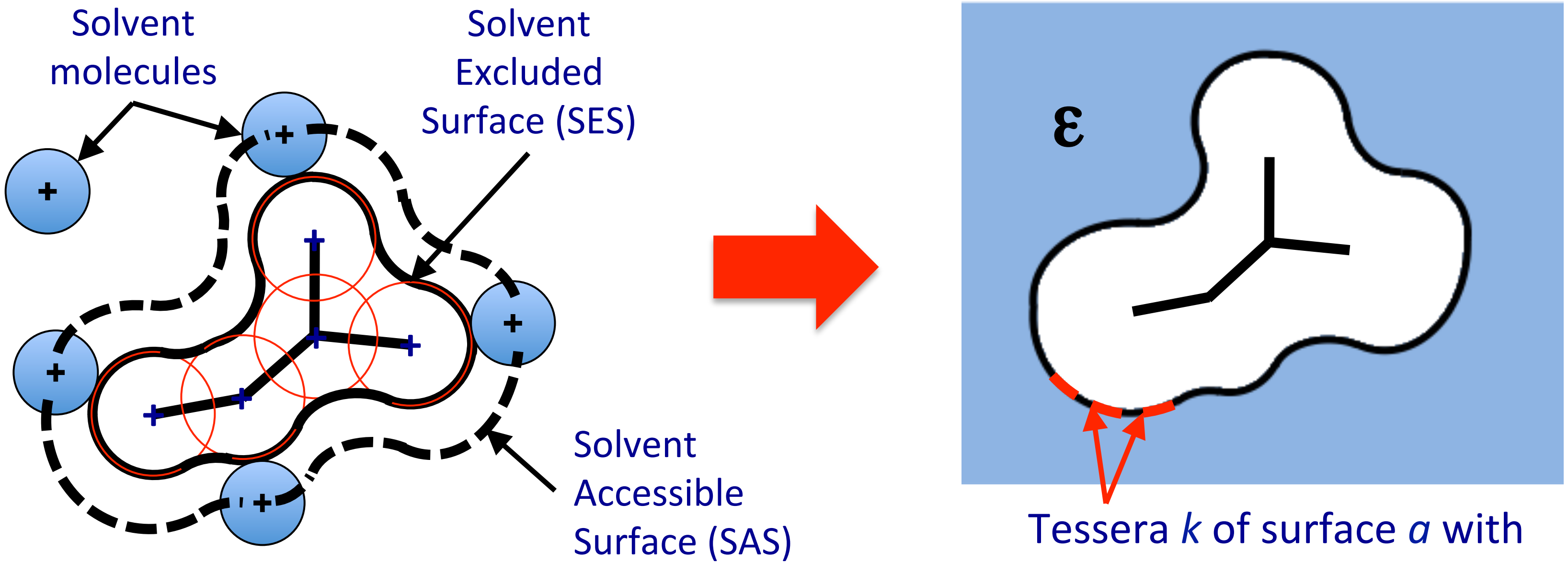
E(k): normal component of the electric field generated by the solute on the tessera k

D: operator accounting for the electrical field generated by σ itself

IEF-PCM: default computation scheme of ASC in Gaussian 09

POLARIZABLE SOLVATION MODELS

Tomasi et al. *Chem. Rev.* **2005**, 105, 2999.



Solvent molecules

Solvent Excluded Surface (SES)

Solvent Accessible Surface (SAS)

Tessera *k* of surface *a* with Apparent Surface Charge (ASC):

Hamiltonian operator for a solvated molecule

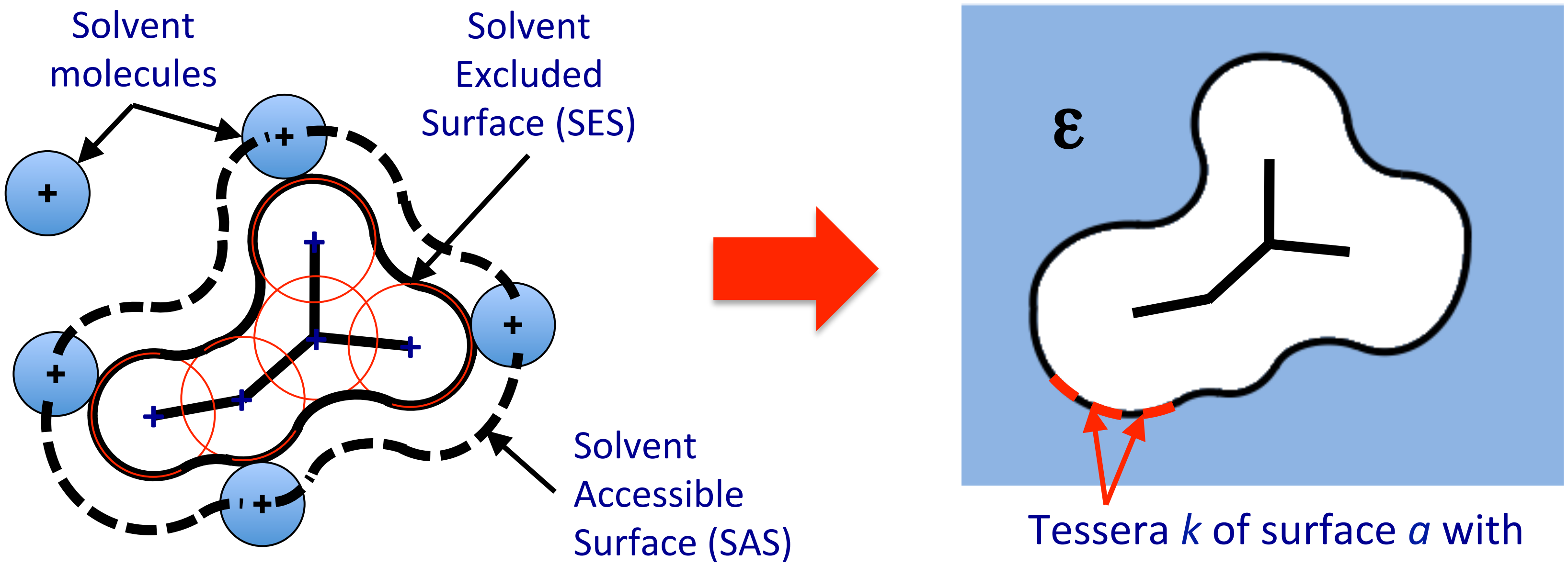
$$\hat{H} = \hat{H}_0 + \hat{V}_{MS}$$

$$\hat{V}_{MS} = \sum_k \sum_i \hat{V}(i,k)q(k)$$

V(i,k): *electronic potential operator at tessera k*

POLARIZABLE SOLVATION MODELS

Tomasi et al. *Chem. Rev.* **2005**, 105, 2999.



Solvent molecules

Solvent Excluded Surface (SES)

Solvent Accessible Surface (SAS)

Tessera *k* of surface *a* with Apparent Surface Charge (ASC):

Hamiltonian operator for a solvated molecule perturbed by an oscillating field

$$\hat{H} = \hat{H}_0 + \hat{V}_{MS} + \hat{V}_{FIELD}(t) \qquad \vec{F} = \vec{F}^{\omega}\cos(\omega t) + \vec{F}^{0}$$

$$\hat{V}_{FIELD}(t) = \sum_i \hat{\mu}_\alpha(i)\left[F_\alpha^\omega \cos(\omega t) + F_\alpha^0\right] + \sum_k \sum_i \hat{V}(i,k)\left[\frac{\partial q_\omega^{ex}}{\partial F_\alpha^\omega} F_\alpha^\omega \cos(\omega t) + \frac{\partial q_0^{ex}}{\partial F_\alpha^0} F_\alpha^0\right]$$

μ: *dipole moment operator*
q^{ex}: *apparent charge response of the solvent to the (static and oscillating) external fields*

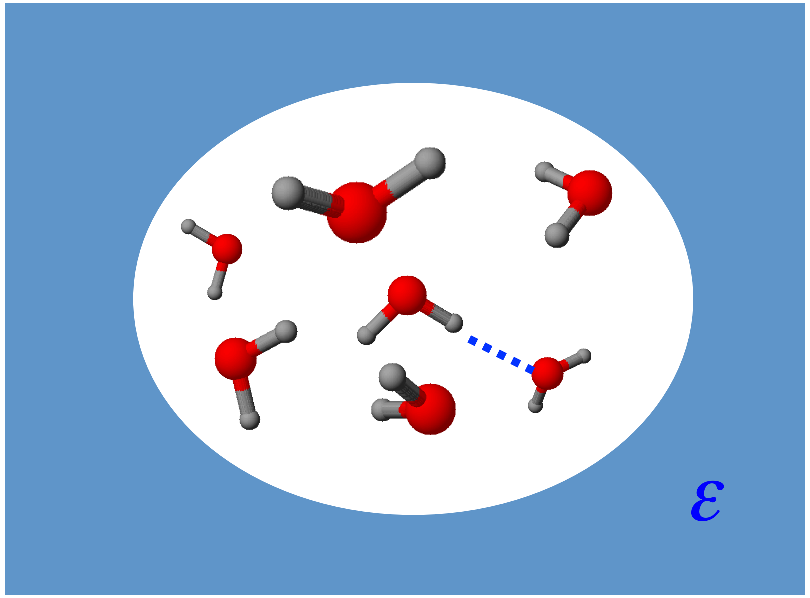
MIXED SOLVATION MODELS

- The first solvation sphere is explicitly described by a number of solvent molecules.
- The remaining solvent molecules are described by an uniform continuum medium with a dielectric constant.

- Advantage:
  Account for specific short-range effects (e.g., H-bonding).

- Disadvantage:
  Increase computational cost.

- Generally give substantial better results than pure continuum models.



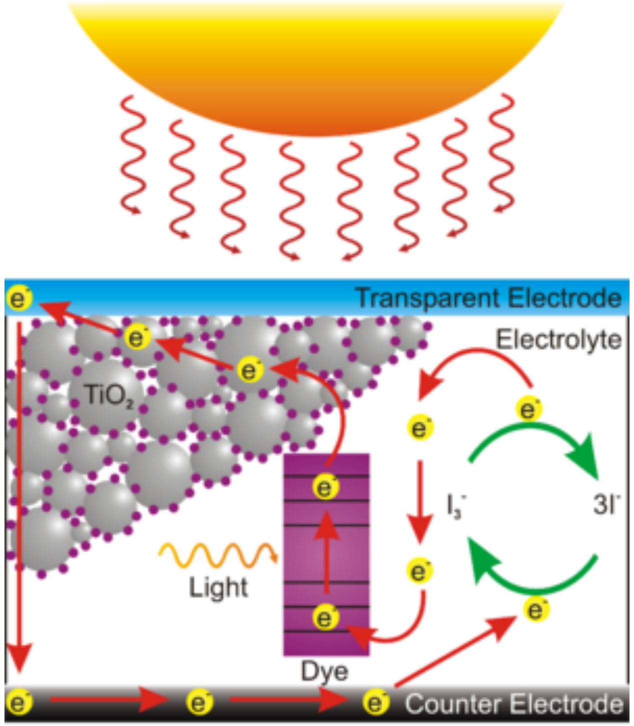
WHICH SOLVATION MODEL SHOULD BE USED?

- A compromise between accuracy and cost.
- Start with gas-phase model (without solvent) before you go for solvation models. Gas-phase calculations usually help to understand the quantum nature of the problem under study. Yet sometimes gas-phase models can be qualitatively wrong.
- Try continuum models before you go for explicit models. Continuum model calculations are unlikely to give you very accurate results, but they are informative in suggesting whether or not long-range solvation effects are important.
- Try mixed models before you go for explicit models. Mixed models are relatively easy to handle and much less expensive, with possibly reasonably good results.

Summary

- Time-Independent DFT
- Time-Dependent DFT
- Linear Response DFT
- Application to Molecular Spectroscopy
- Which functional to choose?
- Simulation of Solvent Effects
- **A Practical Example: Simulation of a UV/Vis. Spectrum using LR-TDDFT**

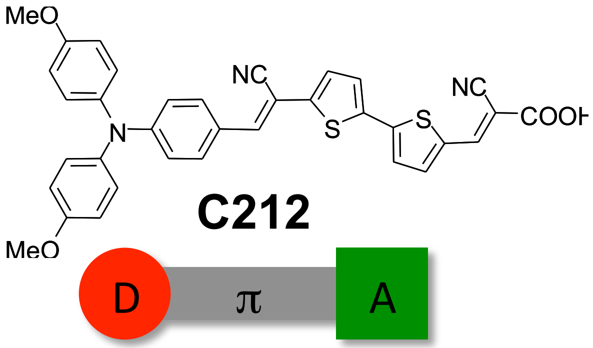
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



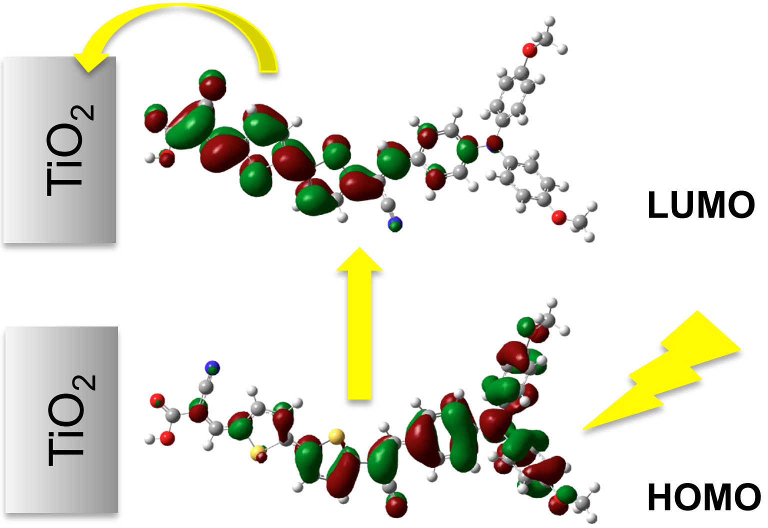
- Light-harvesting organic molecule anchored onto a mesoporous metal oxide semiconducting film (anatase TiO_2)
- In contact with a liquid electrolyte or a hole-transporting material to regenerate the system

Most efficient organic dyes = D-π-A structure

→ efficient tuning of both HOMO and LUMO with intramolecular charge separation.



C212



APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

Gaussian g09 input files

GEOMETRY

```
%chk=C212.chk
#P B3LYP/6-31g(d) opt freq SCRF=(IEFPCM,solvent=dichloromethane)

C212 – geometry optimisation

0 1
Input geometry
Blank line
```

SPECTRUM

```
%chk=C212.chk
#P td=(nstates=30) 6-31g(d) MPW1K density=all
SCRF=(IEFPCM,solvent=dichloromethane) geom=check

C212 – UV-Vis. spectrum

0 1
Blank line
```

Hybrid functional with 42% HF exchange

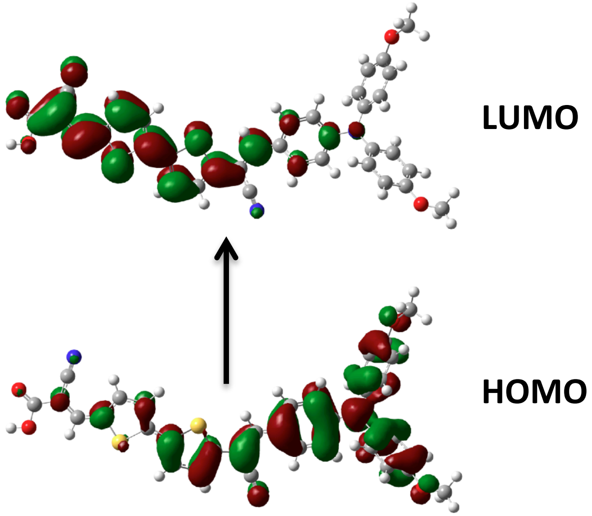
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      2.2197 eV  558.55 nm  f=2.1548  <S**2>=0.000
     159 ->161          0.26234
     160 ->161          0.62396
     160 ->162         -0.16926
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2609.62644420
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.0015 eV  413.08 nm  f=0.2846  <S**2>=0.000
     157 ->161          0.18292
     159 ->161          0.52264
     160 ->161         -0.11966
     160 ->162          0.40539

 Excited State   3:      Singlet-A      3.2462 eV  381.93 nm  f=0.2733  <S**2>=0.000
     159 ->161         -0.33459
     159 ->162          0.15006
     160 ->161          0.28693
     160 ->162          0.51572
```



$S_0 \rightarrow S_1$

Dominated by a HOMO-to-LUMO transition

Intramolecular charge transfer

Large spatial separation of the orbitals

$$\Lambda = \int \left|\psi_{\mathrm{HOMO}}(\mathbf{r})\right|\left|\psi_{\mathrm{LUMO}}(\mathbf{r})\right| d\mathbf{r} = 0.57$$

APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      2.2197 eV  558.55 nm  f=2.1548  <S**2>=0.000
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     159 ->161        -0.33459
     159 ->162         0.15006
     160 ->161         0.28693
     160 ->162         0.51572
```
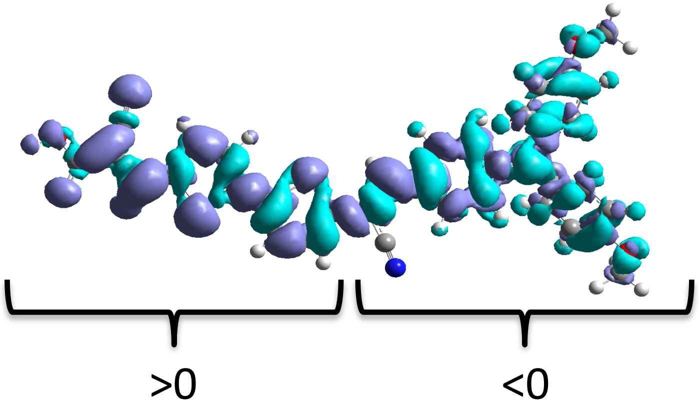
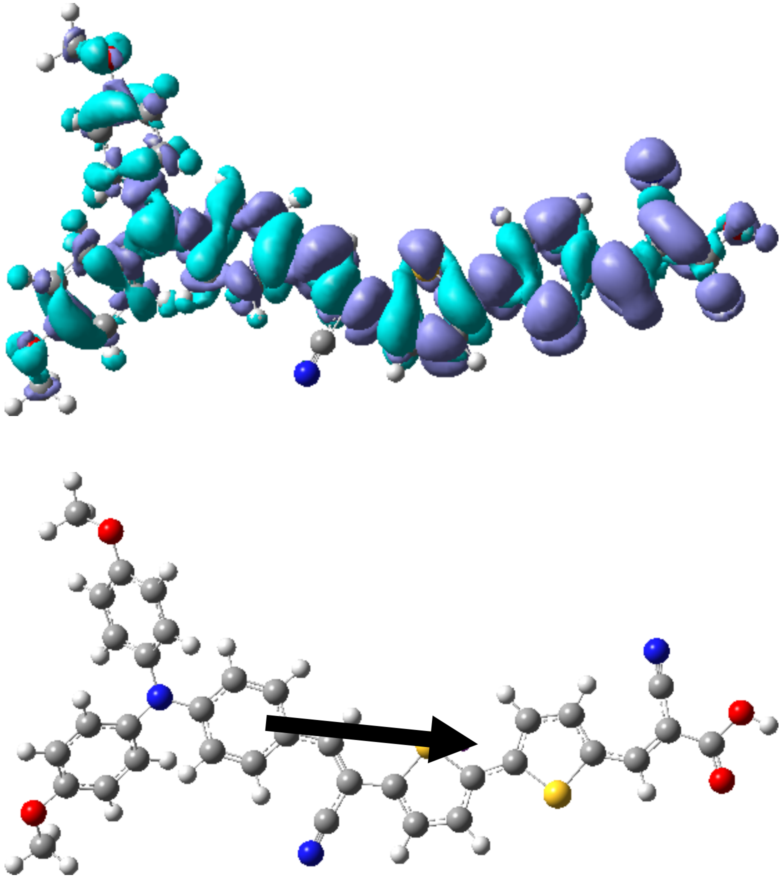

$S_0 \rightarrow S_1$

Dominated by a HOMO-to-LUMO transition
Intramolecular charge transfer



APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

Photoinduced charge-transfer: a more quantitative analyse



Le Bahers et al. JCTC **2011**, *7*, 2498
Jacquemin et al. PCCP **2012**, *14*, 5383

$$\Delta\rho = \Delta\rho^+ + \Delta\rho^-$$

$$q_{CT} = \int \Delta\rho^+ \, d\mathbf{r} = \int \Delta\rho^- \, d\mathbf{r}$$

$q_{CT} = 0.71|e|$
$d_{CT} = 6.0$ Å

APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

```
Excited State   1:      Singlet-A      2.2197 eV  558.55 nm  f=2.1548  <S**2>=0.000
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    157 ->161         0.18292
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    160 ->161        -0.11966
    160 ->162         0.40539

Excited State   3:      Singlet-A      3.2462 eV  381.93 nm  f=0.2733  <S**2>=0.000
    159 ->161        -0.33459
    159 ->162         0.15006
    160 ->161         0.28693
    160 ->162         0.51572
```
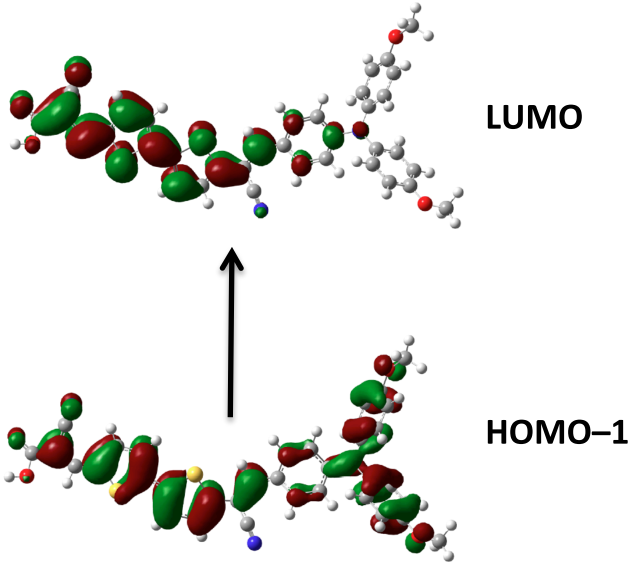

$S_0 \rightarrow S_2$

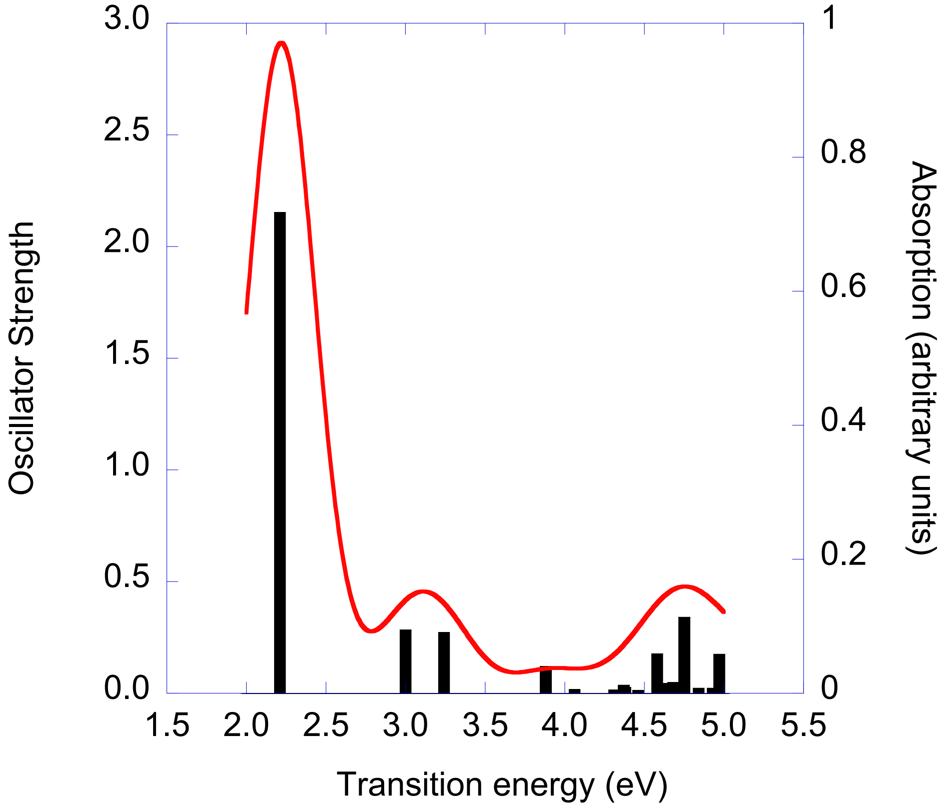
Dominated by a (HOMO–1)-to-LUMO transition

Less significant charge transfer

Higher transition energy



APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



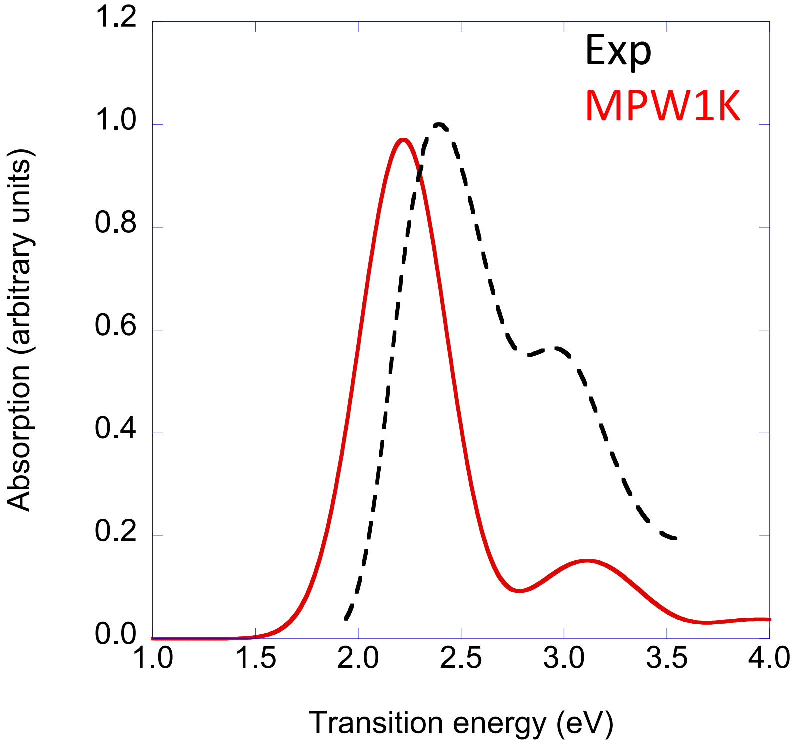
Geometry IEFPCM:B3LYP/6-31g(d)
Spectrum IEFPCM:MPW1K/6-31g(d)

Gaussian broadening

Theoretical absorption picks enlarged using Gaussian functions with a full width at half maximum (FWHM) Γ=0.5 eV.

$$S(\omega) = \sum_{i}^{\text{states}} f_i \exp\left(\frac{(\omega - \omega_i)^2}{\Gamma^2}\right)$$

APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



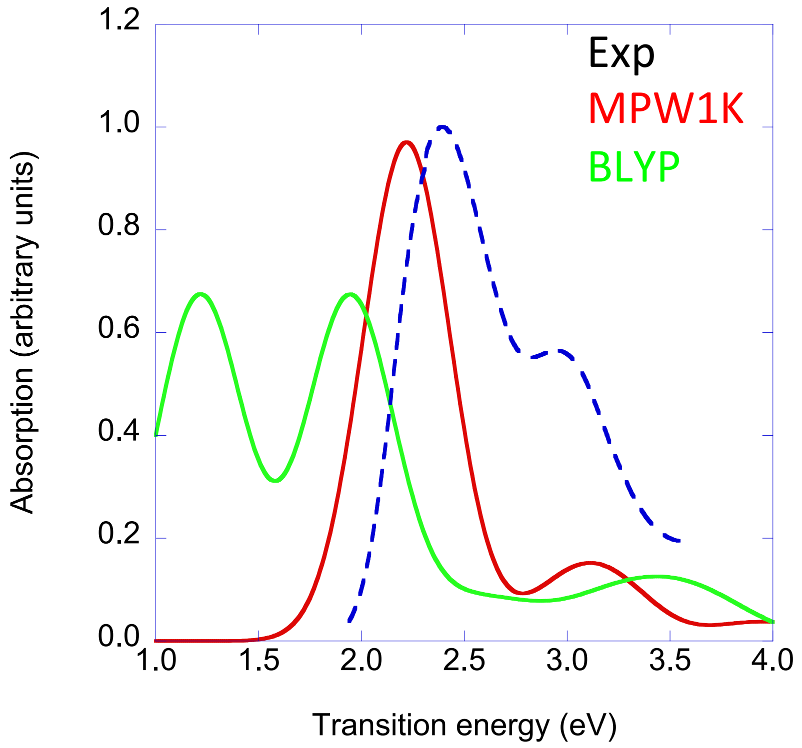
Comparison to experiment

MPW1K/6-31G(d)

Qualitative agreement, but:

- Underestimation of the $S_0 \rightarrow S_1$ transition energy
- Overestimation of the $S_0 \rightarrow S_2$ transition energy
- Underestimation of the intensity of the $S_0 \rightarrow S_2$ band

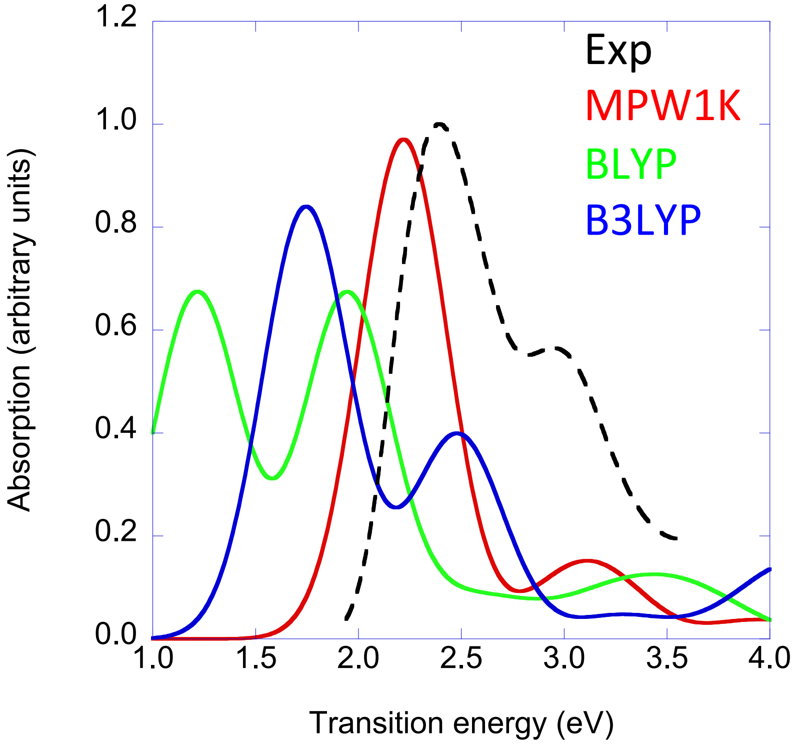
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



Impact of the XC functional

BLYP (pure GGA) → completely out

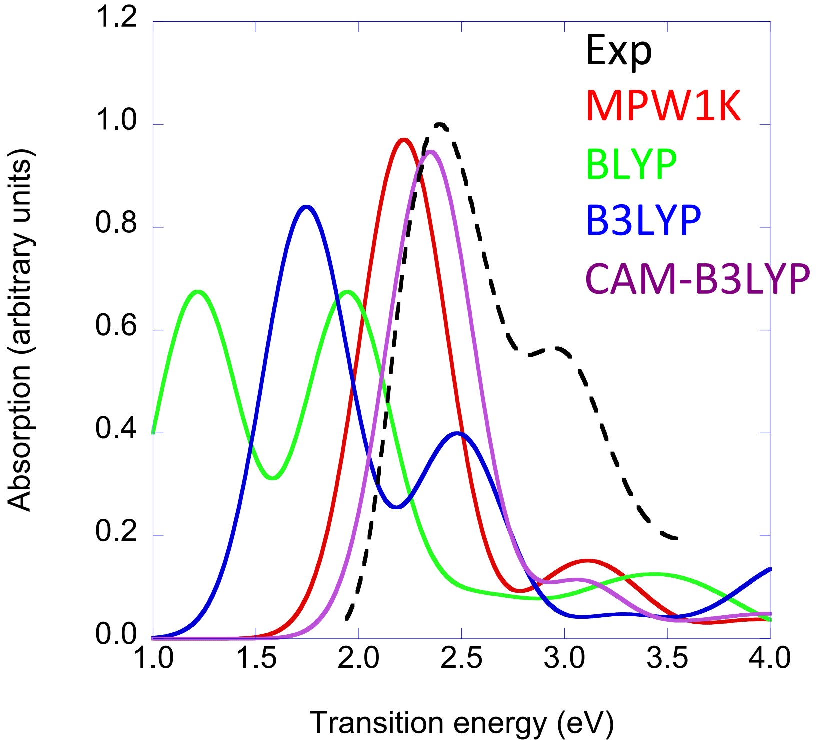
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



Impact of the XC functional

BLYP (pure GGA) → completely out
B3LYP (hybrid) → bad

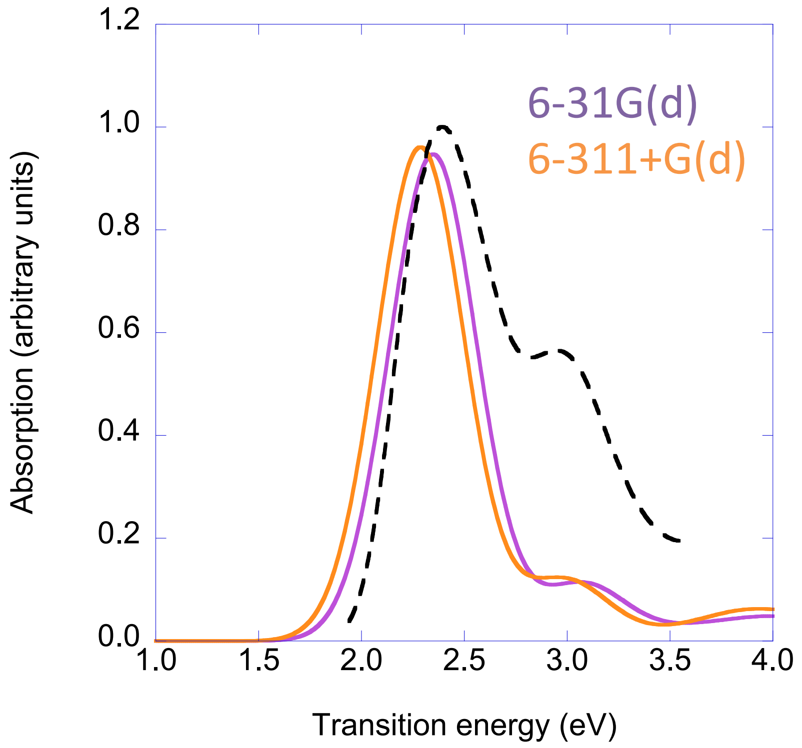
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



Impact of the XC functional

BLYP (pure GGA) → completely out
B3LYP (hybrid) → bad
CAM-B3LYP (long-range corrected) → OK!

APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE



Impact of the basis set (CAM-B3LYP)

Weak impact for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands (*in this particular case*)