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

Frédéric Castet

f.castet@ism.u-bordeaux1.fr

Université Bordeaux 1
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 \( \hat{H} = \hat{T} + \hat{W} + \hat{V}_0 \)

\( T = \text{Kinetic energy}; \ W = \text{Coulomb interaction}; \ V_0 = \text{External potential} \)

*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:*

\[
\hat{T} = -\sum_{\mu=1}^{N} \frac{1}{2} \Delta_{\mu} \\
\hat{W} = \sum_{\mu=1}^{N} \sum_{\nu > 1}^{N} \frac{1}{r_{\mu\nu}} \\
\hat{V}_0 = -\sum_{\mu=1}^{N} \sum_{p=1}^{P} \frac{Z_p}{r_{\mu p}}
\]

*Kinetic energy* 

*2-electron Coulomb interactions* 

*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 $\rho(r)$. Therefore, the total electronic energy can be expressed as a functional of $\rho(r)$:

$$E[\rho(r)] = T[\rho(r)] + W[\rho(r)] + V_0[\rho(r)]$$

This holds true for every quantum mechanical observable.
TIME-INDEPENDENT DFT

SECOND HOHENBERG-KOHN THEOREM

The electron density $\rho(r)$ obeys a variational principle

Consequence:

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

Stationarity condition:

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

The ground-state density correspond to the minimum of the $E[\rho(r)]$ 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 $f$:

$$\frac{\delta f}{\delta x}
= \left. \frac{\delta f}{\delta g} \right|_{g(x)=g(x_0)} \frac{\delta g}{\delta x}
= \left. \frac{\delta f}{\delta g} \right|_{g(x)=g(x_0)} \frac{\delta g}{\delta x}
= \left. \frac{\delta g}{\delta x} \right|_{x=x_0}$$
Practically, $\rho$ 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:

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

Starting point:
We consider a fictitious system of non-interacting electrons that have for their overall ground-state density $\rho(r)$ the same density as some real system of interest where the electrons do interact
**TIME-INDEPENDENT Kohn-Sham Equations**

---

### real system
(interacting electrons)

- **Kinetic energy**
  \[ T[\rho] \]

- **Electron-electron interactions**
  \[ W[\rho] \]

### fictitious system
(non-interacting electrons)

- **Kinetic energy**
  \[ T_{KS}[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \int \psi_i(r) \Delta \psi_i(r) dr \]

- **Electron-electron interactions**
  \[ W_{KS}[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_2 - r_1|} dr_1 dr_2 \]

**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:**

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

*\(E_{XC}\) corrects the error made in using the non-interacting kinetic energy and in treating the electron-electron interactions classically*
Applying the variational theorem

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

\[
\left\{-\frac{1}{2} \Delta + \int \frac{\rho(r')}{|r-r'|} \, dr' + u_{xc}(r) + V_0(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r)
\]

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

\[
v_{KS}(r) = \int \frac{\rho(r')}{|r-r'|} \, dr' + u_{xc}(r) + V_0(r)
\]

Local exchange-correlation potential

\[
v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}
\]

The main difficulty of DFT is to find an appropriate description of \( E_{xc} \) as a function of \( \rho(r) \) → Many XC functionals
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-DEPENDENT PROBLEM

TIME-DEPENDENT SCHRODINGER EQUATION

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

Time-dependent electronic hamiltonian

\[ \hat{H}(t) = \hat{T} + \hat{W} + \hat{V}_{\text{ext}}(t) \]

- \( \hat{T} \) = kinetic energy
- \( \hat{W} \) = the Coulomb interaction
- \( \hat{V}_{\text{ext}} \) = time-dependent external potential

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

- \( V(\mathbf{r}, t) \) 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 \( \rho(r,t) \) and \( \rho'(r,t) \) of two systems evolving from the same initial state \( \Psi(t_0) \) under the influence of, respectively, the scalar potentials \( \nu(r,t) \) and \( \nu'(r,t) \), 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 \( \rho(r,t) \) is unique, up to a purely time-dependent function \( c(t) \). It determines the total time-dependent wavefunction \( \Psi \), which in turn is unique up to a time-dependent phase factor \( \alpha(t) \).

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

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

*Important note:*

In this treatment, only scalar potentials \( V_{\text{ext}}(r,t) \) are considered, thus excluding vector potentials \( V_{\text{ext}}(r,t) \). 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 \( \rho(r,t) \) and the current density \( j(r,t) \).
TIME-DEPENDENT DFT

SOLVING THE TIME-DEPENDENT SCHRODINGER EQUATION

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

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

The action is also a functional of the density:

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

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

$$\frac{\delta A[\rho]}{\delta \rho(r, t)} = 0$$
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 \( V_{\text{ext}}(r,t) \), of which the density at every time \( t \) is identical to the density of the real system

\[
i \frac{\partial}{\partial t} \psi_j(r,t) = \left\{ -\frac{1}{2} \Delta + \int \frac{\rho(r',t)}{|r-r'|} \, dr' + u_{\text{xc}}(r,t) + V_{\text{ext}}(r,t) \right\} \psi_j(r,t) - u_{\text{KS}}(r,t)
\]

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

\[
u_{\text{KS}}(r,t) = \int \frac{\rho(r',t)}{|r-r'|} \, dr' + u_{\text{xc}}(r,t) + V_{\text{ext}}(r,t)
\]

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

\[
u_{\text{xc}}(r,t) = \frac{\delta A_{\text{xc}}[\rho]}{\delta \rho(r,t)}
\]

where \( A_{\text{xc}} \) is the exchange-correlation action functional. \( A_{\text{xc}} \) is the analog of \( E_{\text{xc}} \) 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):

\[
v_{\text{XC}}(r,t) = \frac{\delta A_{\text{XC}}[\rho]}{\delta \rho(r,t)} \approx \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(r)} \bigg|_{\rho=\rho(r,t)}
\]

\(v_{\text{XC}}(r,t)\) is **local in time**. *It depends only on \(\rho\) at time \(t\).*

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

*All retardation effects are neglected.*
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
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:

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

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:

\[ \rho(r, t) = \rho_0(r) + \rho_1(r, t) + \ldots \] (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 \( V_0(r) \)
The first-order density change $\rho_1$ is related to the first-order potential via the linear response function $\chi$:

$$\rho_1(r,t) = \int \int \chi(r,t;r',t') V_1(r',t') \, dr' \, dt'$$

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

$$\chi(r,t;r',t') = \left. \frac{\delta \rho(r,t)}{\delta V_{\text{ext}}(r',t')} \right|_{V_0}$$

which has to be evaluated at the ground state initial potential.
LINEAR RESPONSE TDDFT

For the KS system of non-interacting electrons:

\[ \rho_1(r, t) = \int \int \chi_{KS}(r, t; r', t') u^{(1)}_{KS}(r', t') \, dr' \, dt' \]

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

\[ u^{(1)}_{KS}(r', t') = \int \frac{\rho_1(r', t)}{|r - r'|} \, dr' + \int \frac{\delta u_{XC}(r, t)}{\delta \rho(r', t')} \rho_1(r', t') \, dr' \, dt' + V_1(r, t) \]

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 1\(^{st}\)-order effective perturbation \( u_{KS} \).

Our objective is thus to determine the KS response function \( \chi_{KS} \).
**LINEAR RESPONSE TDDFT**

**Frequency-domain TD-DFT**

\[
\rho_1 (\mathbf{r}, t) = \int \int \chi_{KS} (\mathbf{r}, t; \mathbf{r}', t') \psi^{(i)}_{KS} (\mathbf{r}', t') \, d\mathbf{r}' \, dt'
\]

**Fourier transform**

\[
\rho_1 (\mathbf{r}, \omega) = \int \chi_{KS} (\mathbf{r}, \mathbf{r}', \omega) \psi^{(i)}_{KS} (\mathbf{r}', \omega) \, d\mathbf{r}'
\]

\[
\psi^{(i)}_{KS} (\mathbf{r}, \mathbf{r}', \omega) = \int \frac{\rho_1 (\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \int f_{XC} (\mathbf{r}, \mathbf{r}', \omega) \rho_1 (\mathbf{r}', \omega) \, d\mathbf{r}' + V_1 (\mathbf{r}, \omega)
\]

*The XC kernel is frequency independent in the adiabatic case*

**Note: Fourier transform convention**

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

\[
f(\omega) = \int \exp(i\omega t) f(t) \, dt
\]

**Convolution theorem**

\[
h(t) = \int g(t - t') f(t') \, dt' \Leftrightarrow h(\omega) = g(\omega) f(\omega)
\]
**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:*

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

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

$$\tilde{\mu}^{(i)}(t) = \tilde{\mu}^{(i)}_0 + \sum_{j=x,y,z} \alpha_{ij} F_0 \cos(\omega t) + ... \quad (1)$$

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 $\alpha$
LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

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

\[ \tilde{\mu}^{(i)}(t) = \int \rho(r, t) r^{(i)} \, dr = \int \rho_0(r) r^{(i)} \, dr + \int \rho_1(r, t) r^{(i)} \, dr \quad (2) \]

Identifying expressions (1) and (2):

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

\[ \rho_1(r, t) = \sum_{j=x,y,z} \rho_1^{(j)}(r, t) \]

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

\[ + \int \rho_1^{(j)}(r, -\omega) \exp(-i\omega t) r^{(i)} \, dr \]

\[ \alpha_{ij} = \frac{2}{F_0} \int \rho_1^{(j)}(r, \omega) r^{(i)} \, dr \]

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*

\[ \vec{\mu}_{0n} = \langle \psi_0 | \vec{\mu} | \psi_n \rangle = -|e| \langle \psi_0 | \vec{r} | \psi_n \rangle \]

Unit = C.m

1 a.u. of \( \mu \) = 8.478358 \( 10^{-30} \) C.m = 2.5415 D

*Oscillator strengths*

\[ f_{0n} = \frac{2}{3} \omega_n |\vec{\mu}_{0n}|^2 \]

Dimensionless (proportional to the absorption intensity)

Excitation coefficient \( \varepsilon \) \( f_{0n} \propto \int \varepsilon \, dv \)

with \( \varepsilon \) in mol\(^{-1}\).cm\(^{-1}\).L and \( \nu \) in cm\(^{-1}\), \( f_{0n} \approx 4.3 \times 10^{-9} \int \varepsilon \, dv \)
LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

What do we know?

The exact linear density response is written as

$$\rho_1 (r, \omega) = \int \chi_{KS} (r, r', \omega) v_{KS}^{(1)} (r', \omega) dr'$$

$$\chi_S (r; r', \omega) = 2 \sum_i \sum_a \psi_a (r) \psi_i (r) \psi_a (r') \psi_i (r') \frac{\varepsilon_a - \varepsilon_i}{\omega^2 + (\varepsilon_a - \varepsilon_i)^2}$$

$$v_{KS}^{(1)} (r, r', \omega) = \int \rho_1 (r', \omega) dr' + \int f_{XC} (r, r') \rho_1 (r', \omega) dr' + V_1 (r, \omega)$$

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

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

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

\(L\) and \(M\) are matrices of dimension \(N_{\text{occ}} \times N_{\text{virt}}\)

\(X\) and \(Y\) are vector-matrices

\(\Omega_q\) are the desired transition energies

\[
L_{ia,jb} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + K_{ia,jb} \quad M_{ia,jb} = K_{ia,jb} \quad \text{Tamm-Dancoff Approximation: } M = 0
\]

\[
K_{ia,jb} = \int \int \psi_i(r) \psi_a(r) \left( \frac{1}{|r - r'|} + f_{XC}(r,r') \right) \psi_j(r') \psi_b(r') dr dr'
\]

\(
X_{ia} = \frac{\int \psi_i(r') \psi_a(r') u_{KS}(r',\omega) dr'}{\omega - (\varepsilon_a - \varepsilon_i)}
\)

\(
Y_{ia} = \int \psi_i(r') \psi_a(r') u_{KS}(r',\omega) dr' - \left( \omega + (\varepsilon_a - \varepsilon_i) \right)
\)

LR-TDDFT APPLIED TO MOLECULAR SPECTROSCOPY

Matrix formulation of the TDDFT response equations

The matrix equations can be further reduced to an eigenvalue problem

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

\[WF_K = \Omega_K^2 F_K\]

\[W = (L - M)^{1/2} (L + M)(L - M)^{1/2}\]
\[F_K = (L - M)^{-1/2} (X + Y)_K\]

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 \( i \rightarrow a \)

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

The oscillator strengths are calculated from the normalized eigenvectors

\[
f_K = \frac{2}{3} \left( x^T S^{-1/2} F_K \right)^2 + \left( y^T S^{-1/2} F_K \right)^2 + \left( z^T S^{-1/2} F_K \right)^2 \right) \quad \text{with} \quad S_{qq'} = \delta_q \delta_{q'} / \omega_{q}
\]

\[
x_q = \int \psi_i(x) \psi_a(x) \, dx
\]

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 \( \{ \epsilon_i \} \)

- 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 \( F_q \) (interpretation):

\[
|\Psi_q\rangle = \sum_{jb} C_{jb}^q |\Psi^b_j\rangle \quad C_{jb}^q = \sqrt{\frac{\epsilon_b - \epsilon_i}{\Omega_q}} F_{jb}^q
\]

where \( |\Psi^b_j\rangle \) denotes the KS single determinant where the \( j^{th} \) occupied orbital has been replaced by the \( b^{th} \) unoccupied orbital.
Summary

- Time-Independent DFT
- Time-Dependent DFT
- Linear Response DFT
- Simulation of UV/Vis. Spectra using LR-DFT
  - **Which functional to use?**
- 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:**
\[
\omega_{CT} \approx IP^D - EA^A - 1/R
\]

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:

\[
L_{ia,jb} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + K_{ia,jb} \quad \Rightarrow L_{ia,ia} = \varepsilon_a - \varepsilon_i + K_{ia,ia}
\]

\[
M_{ia,jb} = K_{ia,bj} \quad \Rightarrow M_{ia,ia} = K_{ia,ia}
\]

**Nonhybrid (pure LDA or GGA) functionals:**

\[
K^{XC}_{ia,ia} = \int dr' dr \psi_a^*(r) \psi_i (r') f^{XC}_{ia} \psi_a (r) \psi_i (r') \approx 0 \quad \text{since } f^{XC} \text{ is a local operator (no asymptotic } -1/R \text{ dependence)}
\]

\[
\Rightarrow \omega^{\text{TDDFT}}_{CT} \approx \varepsilon^A_a - \varepsilon^D_i
\]

Nonhybrid functionals do not provide good estimates of CT state energies
**WHICH FUNCTIONAL SHOULD BE USED IN TDDFT CALCULATIONS?**

*Hybrid functionals:*

\[
K_{\text{XC}} = aK_{\text{DFT}}^{\text{XC}} + bK_{\text{HF}}^{\text{HF}}
\]

\[
K_{\text{HF}}^{\text{HF}} = \int \psi_a(r)\psi_b(r) \frac{1}{|r - r'|} \psi_i(r')\psi_j(r') \, dr \, dr'
\]

\[
\Rightarrow \omega_{\text{CT}}^{\text{TDDFT}} \approx \varepsilon_i^A - \varepsilon_i^D + f(-1/R)
\]

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:

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$

- **short range part** (combined with DFT-LDA exchange)
- **long-range part** (combined with HF exchange)

$\mu$ determines the balance of DFT to HF exchange at intermediate $r_{12}$

$\mu \rightarrow 0$ pure GGA calculation

$\mu \rightarrow \inf.$ pure HF calculation

Standard value in Gaussian09: $\mu = 0.47$

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 \( \mu = 0.33 \)

\[
\frac{1}{r_{12}} = \frac{1 - \left\{ \alpha + \beta \text{erf}(\mu r_{12}) \right\}}{r_{12}} + \frac{\alpha + \beta \text{erf}(\mu r_{12})}{r_{12}} \quad 0 \leq \alpha + \beta \leq 1; \\
0 \leq \alpha \leq 1; 0 \leq \beta \leq 1
\]

*short range part* (combined with DFT-LDA exchange) \[\rightarrow\] *long-range part* (combined with HF exchange)

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

![Graphs showing contributions to exchange](image)
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 \( \omega_{ct} \)
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.


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

Johannes Neugebauer, Oleg Gritsenko, and Evert Jan Baerends

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.


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

Michael J. G. Peach, Peter Benfield, Trygve Helgaker, and David J. Tozer

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, United Kingdom
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*

Jacquemin et al.
*TD-DFT Assessment of Functionals for Optical 0–0 Transitions in Solvated Dyes*

...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**

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

<table>
<thead>
<tr>
<th>Models</th>
<th>Explicit solvent models</th>
<th>Continuum solvation models</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Features</strong></td>
<td>All solvent molecules are explicitly represented.</td>
<td>Represent solvent as a continuous medium.</td>
</tr>
<tr>
<td><strong>Merits</strong></td>
<td>Detail information is provided. Generally more accurate.</td>
<td>Simple, inexpensive to calculate</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>Expensive for computation</td>
<td>Ignore specific short-range effects. Less accurate.</td>
</tr>
</tbody>
</table>
POLARIZABLE SOLVATION MODELS


ASC computed self-consistently:

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

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

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

\( D \): operator accounting for the electrical field generated by \( \sigma \) itself

IEF-PCM: default computation scheme of ASC in Gaussian 09
**Polarizable Solvation Models**


Hamiltonian operator for a solvated molecule

\[
\hat{H} = \hat{H}_0 + \hat{V}_{MS}
\]

\[
\hat{V}_{MS} = \sum_k \sum_i \hat{V}(i,k)q(k) \quad V(i,k): \text{electronic potential operator at tessera } k
\]
**POLARIZABLE SOLVATION MODELS**


Hamiltonian operator for a solvated molecule perturbed by an oscillating field

\[
\hat{H} = \hat{H}_0 + \hat{V}_\text{MS} + \hat{V}_\text{FIELD}(t) \\
\hat{F} = \hat{F}^\omega \cos(\omega t) + \hat{F}^0
\]

\[
\hat{V}_\text{FIELD}(t) = \sum_i \hat{\mu}_\alpha(i) \left[ F^\omega_\alpha \cos(\omega t) + F^0_\alpha \right] + \sum_i \sum_k \hat{V}(i,k) \left[ \frac{\partial q^\text{ex}_\alpha}{\partial F^\omega_\alpha} F^\omega_\alpha \cos(\omega t) + \frac{\partial q^\text{ex}_0}{\partial F^0_\alpha} F^0_\alpha \right]
\]

\(\mu\): dipole moment operator

\(q^\text{ex}\): 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.

<table>
<thead>
<tr>
<th>Gas-phase</th>
<th>Continuum</th>
<th>Mixed</th>
<th>Explicit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Realistic description &amp; computational cost</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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-$\pi$-A structure

$\rightarrow$ efficient tuning of both HOMO and LUMO with intramolecular charge separation.
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:

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>&lt;S^2&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2.2197</td>
<td>558.55</td>
<td>2.1548</td>
<td>0.000</td>
</tr>
<tr>
<td>159 -&gt; 161</td>
<td>0.26234</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 161</td>
<td>0.62396</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 162</td>
<td>-0.16926</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>&lt;S^2&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>3.0015</td>
<td>413.08</td>
<td>0.2846</td>
<td>0.000</td>
</tr>
<tr>
<td>157 -&gt; 161</td>
<td>0.18292</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>159 -&gt; 161</td>
<td>0.52264</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 161</td>
<td>-0.11966</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 162</td>
<td>0.40539</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>&lt;S^2&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td></td>
<td>3.2462</td>
<td>381.93</td>
<td>0.2733</td>
<td>0.000</td>
</tr>
<tr>
<td>159 -&gt; 161</td>
<td>-0.33459</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>159 -&gt; 162</td>
<td>0.15006</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 161</td>
<td>0.28693</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt; 162</td>
<td>0.51572</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$S_0 \rightarrow S_1$

Dominated by a HOMO-to-LUMO transition

Intramolecular charge transfer

*Large spatial separation of the orbitals*

$$\Lambda = \int \left| \psi_{HOMO}(r) \right| \left| \psi_{LUMO}(r) \right| \, dr = 0.57$$
**APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE**

Excitation energies and oscillator strengths:

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Excitation Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>$&lt;S^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Singlet-A</td>
<td>2.2197</td>
<td>558.55</td>
<td>2.1548</td>
<td>0.000</td>
</tr>
<tr>
<td>159 -&gt;161</td>
<td></td>
<td>0.2623</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;161</td>
<td></td>
<td>0.6239</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;162</td>
<td></td>
<td>-0.1692</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Excitation Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>$&lt;S^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Singlet-A</td>
<td>3.0015</td>
<td>413.08</td>
<td>0.2846</td>
<td>0.000</td>
</tr>
<tr>
<td>157 -&gt;161</td>
<td></td>
<td>0.1829</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>159 -&gt;161</td>
<td></td>
<td>0.5226</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;161</td>
<td></td>
<td>-0.1196</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;162</td>
<td></td>
<td>0.4053</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Excitation Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (f)</th>
<th>$&lt;S^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Singlet-A</td>
<td>3.2462</td>
<td>381.93</td>
<td>0.2733</td>
<td>0.000</td>
</tr>
<tr>
<td>159 -&gt;161</td>
<td></td>
<td>-0.3345</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>159 -&gt;162</td>
<td></td>
<td>0.1500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;161</td>
<td></td>
<td>0.2869</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160 -&gt;162</td>
<td></td>
<td>0.5157</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$S_0 \rightarrow S_1$

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

\[ \Delta \rho = \Delta \rho^+ + \Delta \rho^- \]

\[ q_{CT} = \int \Delta \rho^+ \, dr = \int \Delta \rho^- \, dr \]

\[ q_{CT} = 0.71|e| \]

\[ d_{CT} = 6.0 \text{ Å} \]
**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 \(<S^2>=0.000\)
- 159 \(\rightarrow\) 161 0.26234
- 160 \(\rightarrow\) 161 0.62396
- 160 \(\rightarrow\) 162 -0.16926

This state for optimization and/or second-order correction.

Total Energy, \(E(\text{TD-HF/TD-KS}) = -2609.62644420\)

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 \(\rightarrow\) 161 0.18292
- 159 \(\rightarrow\) 161 0.52264
- 160 \(\rightarrow\) 161 -0.11966
- 160 \(\rightarrow\) 162 0.40539

Excited State 3: Singlet-A 3.2462 eV 381.93 nm f=0.2733 \(<S^2>=0.000\)
- 159 \(\rightarrow\) 161 -0.33459
- 159 \(\rightarrow\) 162 0.15006
- 160 \(\rightarrow\) 161 0.28693
- 160 \(\rightarrow\) 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) $\Gamma=0.5$ eV.*

$$S(\omega) = \sum_{i} f_{i} \exp \left( \frac{(-\omega - \omega_{i})^{2}}{\Gamma^{2}} \right)$$
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) $\rightarrow$ completely out
APPLICATION: TDDFT CALCULATION OF THE ABSORPTION SPECTRA OF THE C212 DYE IN DICHLOROMETHANE

Impact of the XC functional

BLYP (pure GGA) $\rightarrow$ completely out
B3LYP (hybrid) $\rightarrow$ 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)