Linear response time-dependent density-functional theory

Emmanuel Fromager

Laboratoire de Chimie Quantique, Université de Strasbourg, France

fromagere@unistra.fr

Time-dependent linear response regime

- *Time-dependent* Schrödinger equation:

$$\left(\hat{H} + 2\epsilon \cos(\omega t) \sum_{i=1}^{N} \mathcal{V}(\mathbf{r}_i) \times \right) \Psi(t) = i\frac{\partial \Psi(t)}{\partial t}$$

- *Perturbation expansion* through first order in ϵ (electric field *strength*, for example):

$$
\begin{aligned}
\Psi(t) &\equiv& \Psi(\epsilon, \omega, t) \\[2mm]
&=& \Psi(\epsilon = 0, \omega, t) + \epsilon \left.\frac{\partial \Psi(\epsilon, \omega, t)}{\partial \epsilon}\right|_{\epsilon=0} + \mathcal{O}(\epsilon^2) \\[2mm]
&=& e^{-iE_0 t}\Psi_0 \\[1mm]
&& -\epsilon \sum_{J>0} e^{-iE_J t}\Psi_J \left[\frac{e^{i(\omega+\omega_J)t} - 1}{\omega + \omega_J} + \frac{e^{-i(\omega-\omega_J)t} - 1}{-\omega + \omega_J}\right] \\[2mm]
&& \times \left\langle \Psi_J \left| \sum_{i=1}^{N} \mathcal{V}(\mathbf{r}_i) \times \right| \Psi_0 \right\rangle + \mathcal{O}(\epsilon^2)
\end{aligned}
$$

where $\omega_J = E_J - E_0$.

Linear response of the density

- Time-dependent density:

$$
\begin{aligned}
n(\mathbf{r}, t) &= N \sum_{\sigma = \pm \frac{1}{2}} \int d\mathbf{x}_2 \dots \int d\mathbf{x}_N \, |\Psi(\mathbf{r}, \sigma, \mathbf{x}_2, \dots, \mathbf{x}_N, t)|^2 \\
&\equiv n(\mathbf{r}, t, \omega, \epsilon).
\end{aligned}
$$

- The perturbation expansion of the density,

$$
n(\mathbf{r}, t, \omega, \epsilon) = n_{\Psi_0}(\mathbf{r}) + \epsilon \left. \frac{\partial n(\mathbf{r}, t, \omega, \epsilon)}{\partial \epsilon} \right|_{\epsilon=0} + \mathcal{O}(\epsilon^2),
$$

is obtained by expanding $\Psi^*(t) \times \Psi(t)$ in ϵ and integrating over $\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N$.

- The exact *excitation energies* are *poles* of the time-dependent electron density.

Time-dependent DFT

- Let us consider the time-dependent Hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{W}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i, t) \times$$

  and a fixed initial electronic wavefunction $\Psi(t = 0)$.

- For a given *time-dependent* potential $v(\mathbf{r}, t)$ we can solve the Schrödinger equation:

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

- By varying the time-dependent local potential $v(\mathbf{r}, t)$ we obtain a map of time-dependent densities $n_{\Psi[v](t)}(\mathbf{r})$ where $\Psi[v](t)$ is the solution to the time-dependent Schrödinger equation with potential $v(\mathbf{r}, t)$ and $\Psi[v](t = 0) = \Psi(t = 0)$.

- If two potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ differ by a time-dependent function, then $\Psi[v](t)$ and $\Psi[v'](t)$ will have the same density at any time.

Runge–Gross theorem

- According to the Runge–Gross theorem[*], the map of time-dependent densities can be inverted (up to an additive time-dependent function in the potential).

- This is nothing but the extension of the Hohenberg–Kohn theorem to the time-dependent regime.

- In the following, we will use the (already mentioned) potential

$$v(\mathbf{r}, t) = v_{\mathrm{ne}}(\mathbf{r}) + 2\epsilon \cos(\omega t)\mathcal{V}(\mathbf{r}).$$

- The potential $\mathcal{V}(\mathbf{r}) \equiv \mathcal{V}(x, y, z) = z$ describes the interaction with a uniform *electric field* along the z axis.

- We will assume that the system is in the ground state at time $t = 0$.

[*]E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

Time-dependent KS equations

- Like in the static case, the non-interacting N-electron time-dependent Schrödinger equation can be simplified into one-electron equations.

- For example, in the case of two electrons, the exact solution can be written as

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, t) = \varphi(\mathbf{r}_1, t)\varphi(\mathbf{r}_2, t)$$

where $\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v(\mathbf{r}, t) \right] \varphi(\mathbf{r}, t) = \mathrm{i}\frac{\partial}{\partial t}\varphi(\mathbf{r}, t)$.

- The basic idea in standard TD-DFT is to map in the time-dependent regime the real interacting (and therefore difficult to describe) system with Hamiltonian $\hat{H}(t)$ onto a non-interacting system, in complete analogy with KS-DFT.

- Therefore, by solving $\left[\hat{T} + \sum_{i=1}^N v^{\mathrm{KS}}(\mathbf{r}, t) \times \right] \Phi^{\mathrm{KS}}(t) = \mathrm{i}\frac{\partial}{\partial t}\Phi^{\mathrm{KS}}(t)$,

  where $\Phi^{\mathrm{KS}}(t)$ is a time-dependent Slater determinant, we should be able, in principle, to reproduce the exact time-dependent electron density $n(\mathbf{r}, t)$ of the molecule.

- Therefore, for two electrons, we should have $n(\mathbf{r}, t) = 2\left| \varphi^{\mathrm{KS}}(\mathbf{r}, t) \right|^2$.

Adiabatic approximation

- Consequently, if a time-dependent perturbation is applied to the molecule, the linear (and higher-order) response of the KS and real densities should be the same.

- In particular, the poles of the KS density (which correspond to the poles of the KS orbitals), should be the exact excitation energies of the true molecule (!).

- The exact time-dependent KS potential is in general (i.e. for "real" systems) *unknown* and difficult to model (memory effects).

- In the standard *adiabatic approximation*, it is simplified as follows:

$$v^{\mathrm{KS}}(\mathbf{r}, t) \to v_{\mathrm{ne}}(\mathbf{r}) + 2\epsilon \cos(\omega t) \mathcal{V}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n_{\Phi^{\mathrm{KS}}(t)}]}{\delta n(\mathbf{r})},$$

where $E_{\mathrm{Hxc}}[n]$ is the (time-independent) ground-state Hartree-exchange-correlation (Hxc) functional.

- Note that, within the adiabatic approximation, the KS potential is local in time (no memory effects are taken into account).

Linear response TD-DFT

- The unperturbed problem ($\epsilon = 0$) is the *regular* time-independent KS one.

- The linear response of the KS system describes explicitly *single excitations* only:

$$
\begin{aligned}
\varphi^{\mathrm{KS}}(\mathbf{r}_1, t, \epsilon)\varphi^{\mathrm{KS}}(\mathbf{r}_2, t, \epsilon) &= e^{-2\mathrm{i}\varepsilon_0 t}\varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2) \\
&\quad + \epsilon\, e^{-\mathrm{i}\varepsilon_0 t}\varphi_0(\mathbf{r}_1)\left.\frac{\partial \varphi^{\mathrm{KS}}(\mathbf{r}_2, t, \epsilon)}{\partial \epsilon}\right|_{\epsilon=0} \\
&\quad + \epsilon\, e^{-\mathrm{i}\varepsilon_0 t}\varphi_0(\mathbf{r}_2)\left.\frac{\partial \varphi^{\mathrm{KS}}(\mathbf{r}_1, t, \epsilon)}{\partial \epsilon}\right|_{\epsilon=0} \\
&\quad + \mathcal{O}(\epsilon^2).
\end{aligned}
$$

- If we were considering the true physical time-dependent perturbation *only*,

$$2\epsilon\cos(\omega t)\mathcal{V}(\mathbf{r}),$$

when solving the time-dependent KS equation, then the excitation energies (i.e. the poles) would reduce to

$$\varepsilon_j - \varepsilon_0 = \omega_{0\to j}.$$

Linear response TD-DFT

- But there is *another* (important) perturbation in the KS system.

- It relates to the *update* of the time-dependent density *in the Hxc potential*.

- Within the adiabatic approximation, this additional perturbation reads as follows:

$$\frac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi^{\mathrm{KS}}(\mathbf{r},t)\right|^2\right]}{\delta n(\mathbf{r})} - \frac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi_0(\mathbf{r})\right|^2\right]}{\delta n(\mathbf{r})}$$

$$= 2\int d\mathbf{r}'\, f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r}) \times \left(\left|\varphi^{\mathrm{KS}}(\mathbf{r},t)\right|^2 - \left|\varphi_0(\mathbf{r})\right|^2\right) + \mathcal{O}(\epsilon^2),$$

where $f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})$ is the so-called Hxc *kernel*.

- Note that *the perturbation depends on the linear response* of the KS orbital which itself depends on the perturbation... (self-consistent perturbation theory).

- The linear response TD-DFT equation (including the kernel) is referred to as *Casida's equation*[*].

[*]M. Casida in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, Singapore, 1995).

Mathematical interlude on functional derivatives

- Let $f : x \longmapsto f(x)$ be a function of x. The derivative of f at $x = x_0$ is obtained from the Taylor expansion (δx is a small variation of x around x_0)

$$f(x_0 + \delta x) = f(x_0) + \delta x \left. \frac{\mathrm{d}f(x)}{\mathrm{d}x} \right|_{x=x_0} + \frac{(\delta x)^2}{2} \left. \frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2} \right|_{x=x_0} + \ldots$$

- Let $S : n \longmapsto S[n]$ be a functional of the density n. The functional derivative of S at $n = n_0$ is by definition a function of $\mathbf{r}$ that is denoted $\frac{\delta S[n_0]}{\delta n(\mathbf{r})}$. The latter is obtained from the Taylor expansion [δn is a small deviation in density from n_0]:

$$S[n_0 + \delta n] = S[n_0] + \int \mathrm{d}\mathbf{r} \, \frac{\delta S[n_0]}{\delta n(\mathbf{r})} \times \delta n(\mathbf{r}) + \frac{1}{2} \int \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{\delta^2 S[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} \times \delta n(\mathbf{r}')\delta n(\mathbf{r}) + \ldots$$

- <u>Example:</u> for the Hartree (or Coulomb) functional $E_{\mathrm{H}}[n] = \frac{1}{2} \int \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid}$,

$$\frac{\delta E_{\mathrm{H}}[n_0]}{\delta n(\mathbf{r})} = \int \mathrm{d}\mathbf{r}' \, \frac{n_0(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \qquad \text{and} \qquad f_{\mathrm{H}}(\mathbf{r}', \mathbf{r}) = \frac{\delta^2 E_{\mathrm{H}}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} = \frac{1}{\mid \mathbf{r} - \mathbf{r}' \mid}$$

Multiple-electron excitations in TD-DFT

- Casida's equation is similar to an *eigenvalue equation*.
- The size of the matrix to diagonalize is essentially given by the number of *single excitations*.
- *Reducing* size *without* losing information:

$$
\begin{bmatrix} A & B \\ B & C \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \omega \begin{bmatrix} x \\ y \end{bmatrix} \quad \Leftrightarrow \quad \begin{cases} Ax + By = \omega x \\ (C - \omega)y = -Bx \end{cases}
$$

$$
\Leftrightarrow \quad \begin{cases} \boxed{A(\omega)x = \omega x} \\ A(\omega) = A - \dfrac{B^2}{C - \omega} \end{cases}
$$

$$
\Leftrightarrow \quad A(\omega) = \omega
$$

$$
\Leftrightarrow \quad (A - \omega)(C - \omega) - B^2 = 0 \quad \rightarrow \textit{two solutions!}
$$

- Multiple excitations can be described in principle in TD-DFT with a frequency-dependent Hxc kernel (i.e. *beyond the adiabatic approximation*).

H$_2$ molecule ($2^1\Sigma_g$, cc–pVQZ)

- exact (single excitation) ———
- exact (double excitation) ---------
- approximate TD–DFT ———

(y-axis) Excitation energy (atomic units)

(x-axis) Interatomic distance (atomic units)