Linear response time-dependent density functional theory

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Let us consider the time-dependent Hamiltonian \( \hat{H}(t) = \hat{T} + \hat{W}_{ee} + \sum_{i=1}^{N} \nu(r_i, t) \times \) and a fixed initial electronic wavefunction \( \Psi(t = 0) \).

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

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

According to the Runge and 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 first Hohenberg–Kohn theorem to the time-dependent regime.

In the following, we will consider that \( \nu(r, t) = \nu_{ne}(r) + \mathcal{V}(r, t) \) where \( \mathcal{V}(r, t) \) is a local time-dependent perturbation.

We will also assume that the system is in the ground state at time \( t = 0 \).

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
  \[
  \Phi(r_1, r_2, t) = \varphi(r_1, t)\varphi(r_2, t)
  \]
  where
  \[
  \left[- \frac{1}{2} \nabla_r^2 + v(r, t) \right] \varphi(r, t) = i \frac{d}{dt} \varphi(r, t).
  \]

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

- Therefore, by solving
  \[
  \left[ \hat{T} + \sum_{i=1}^{N} v^{KS}(r, t) \times \right] \Phi^{KS}(t) = i \frac{d}{dt} \Phi^{KS}(t),
  \]
  where $\Phi^{KS}(t)$ is a time-dependent Slater determinant, we should be able, in principle, to reproduce the exact time-dependent electron density $n(r, t)$ of the molecule.

- Therefore, for two electrons, we should have
  \[
  n(r, t) = 2 |\varphi^{KS}(r, t)|^2.
  \]
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 true molecule (!).

The exact time-dependent KS potential is in general unknown and difficult to model (memory effects).

In the standard adiabatic approximation, it is simplified as follows,

$$\nu_{\text{KS}}(r, t) \rightarrow \nu_{\text{ne}}(r) + \mathcal{V}(r, t) + \frac{\delta E_{\text{Hxc}}[n\Phi_{\text{KS}}(t)]}{\delta n(r)},$$

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

Note that, within the adiabatic approximation, the KS potential is local in time (no memory effects are taken into account).
Therefore, the (approximate) time-dependent KS equation to be solved for two electrons is

\[ \hat{h} \left[ \varphi^{\text{KS}} \right] (t) | \varphi^{\text{KS}}(t) \rangle = i \frac{d}{dt} | \varphi^{\text{KS}}(t) \rangle \]

where \( \hat{h} \left[ \varphi^{\text{KS}} \right] (t) \equiv -\frac{1}{2} \nabla_r^2 + \left[ v_{\text{ne}}(r) + V(r, t) + \frac{\delta E_{\text{Hxc}}}{\delta n(r)} \frac{2 | \varphi^{\text{KS}}(r, t) |^2}{\delta n(r)} \right] \times \)

Note that, in contrast to conventional wavefunction-based response theory, we have to solve a self-consistent time-dependent equation (time-dependent density functional perturbation theory).

In the following, the time-dependent local potential perturbation will be written as

\[ V(r, t) = 2\epsilon \cos(\omega t) V(r). \]

In the presence of a uniform electric field along the z axis, \( V(r) = z. \)
Let us first consider the KS system in the absence of perturbation ($\epsilon = 0$). The time-dependent KS orbital simply reads $\varphi_{KS}(r, t)|_{\epsilon=0} = e^{-i\epsilon_0 t} \varphi_0(r)$ where $\varphi_0(r)$ is the ground-state KS orbital with energy $\epsilon_0$:

$$
\left(-\frac{1}{2} \nabla_r^2 + \left[ \nu_{ne}(r) + \frac{\delta E_{Hxc} \left[ 2 |\varphi_0(r)|^2 \right]}{\delta n(r)} \right] \times \right) \varphi_0(r) = \epsilon_0 \varphi_0(r)
$$

Consequently, in TD-DFT, the unperturbed Hamiltonian is the KS Hamiltonian $\hat{h}$.

The perturbation in the KS system will be

$$
\mathcal{V}(r, t) + \frac{\delta E_{Hxc} \left[ 2 |\varphi_{KS}(r, t)|^2 \right]}{\delta n(r)} - \frac{\delta E_{Hxc} \left[ 2 |\varphi_0(r)|^2 \right]}{\delta n(r)}.
$$
In the following, we will use the ground (occupied) and excited (virtuals) KS orbitals \( \{ \phi_i(r) \}_{i=0,1,2,...} \) with energies \( \{ \varepsilon_i \}_{i=0,1,2,...} \) as a basis for expanding the time-dependent KS orbital in the presence of the perturbation. Note that \( \hat{h}\phi_i(r) = \varepsilon_i\phi_i(r) \).

By analogy with exact response theory, we therefore obtain

\[
|\varphi^{\text{KS}}(t)\rangle = \sum_i e^{-i\varepsilon_i t} C_i(t)|\phi_i\rangle.
\]

The derivation of the linear response TD-DFT equation (known as Casida equation) requires the expansion of the Hxc potential through first order in the perturbation strength \( \epsilon \).

By definition, the variation of the Hxc potential around a given density \( n_0(r) \) equals, through first order in \( \delta n(r') \),

\[
\frac{\delta E_{\text{Hxc}} [n_0 + \delta n]}{\delta n(r)} - \frac{\delta E_{\text{Hxc}} [n_0]}{\delta n(r)} = \int dr' \frac{\delta^2 E_{\text{Hxc}} [n_0]}{\delta n(r') \delta n(r)} \delta n(r')
\]

kernel ! \( f_{\text{Hxc}}(r', r) \)
Casida equation

In our case, \( n_0(r) = 2 |\varphi_0(r)|^2 \) and, by using \( C_i(t)|_{\epsilon=0} = \delta_{i0} \), we obtain

\[
\delta n(r') = 2 \left| \varphi^{KS}(r', t) \right|^2 - 2 \left| \varphi_0(r') \right|^2 \\
= 2 \sum_{ij} e^{-i(\epsilon_i - \epsilon_j)t} C_i(t) C_j^*(t) \varphi_i(r') \varphi_j^*(r') - 2 \left| \varphi_0(r') \right|^2 \\
= 2\epsilon \sum_i \left( e^{-i\Delta \epsilon_i t} \left. \frac{\partial C_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \varphi_i(r') \varphi_0^*(r') + e^{i\Delta \epsilon_i t} \left. \frac{\partial C_i^*(t)}{\partial \epsilon} \right|_{\epsilon=0} \varphi_0(r') \varphi_i^*(r') \right)
\]

where \( \Delta \epsilon_i = \epsilon_i - \epsilon_0 \).

Note that the two-electron KS wavefunction reads through first order

\[
\varphi^{KS}(r_1, t) \varphi^{KS}(r_2, t) = e^{-2i\epsilon_0 t} \varphi_0(r_1) \varphi_0(r_2) \\
+ \epsilon \sum_i e^{-i(\epsilon_i + \epsilon_0)t} \left. \frac{\partial C_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \left( \varphi_0(r_1) \varphi_i(r_2) + \varphi_i(r_1) \varphi_0(r_2) \right) \\
+ \ldots
\]

single electron excitation!
Finally, the (local) perturbation in the KS system equals through first order

\[ 2\epsilon \cos(\omega t) \mathcal{V}(\mathbf{r}) + 2\epsilon \sum_i e^{-i\Delta \epsilon_i t} \left. \frac{\partial C_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}', \mathbf{r}) \varphi_i(\mathbf{r}') \varphi^*_0(\mathbf{r}') \]

\[ + 2\epsilon \sum_i e^{i\Delta \epsilon_i t} \left. \frac{\partial C^*_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}', \mathbf{r}) \varphi_0(\mathbf{r}') \varphi^*_i(\mathbf{r}') \]

By analogy with exact response theory, we obtain

\[ \frac{d}{dt} \left. \frac{\partial C_j(t)}{\partial \epsilon} \right|_{\epsilon=0} = -i\mathcal{V}_{j0} \left[ e^{i(\omega+\Delta \epsilon_j)t} + e^{-i(\omega-\Delta \epsilon_j)t} \right] \]

\[ -2i\epsilon \sum_i e^{-i(\epsilon_i-\epsilon_j)t} \left. \frac{\partial C_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \langle j0| f_{\text{Hxc}} |0i \rangle \]

\[ -2i\epsilon \sum_i e^{i(\epsilon_i+\epsilon_j-2\epsilon_0)t} \left. \frac{\partial C^*_i(t)}{\partial \epsilon} \right|_{\epsilon=0} \langle ji| f_{\text{Hxc}} |00 \rangle \]

where \( \langle ij| f_{\text{Hxc}} |kl \rangle = \int d\mathbf{r} \int d\mathbf{r}' \varphi^*_i(\mathbf{r}) \varphi^*_j(\mathbf{r}') f_{\text{Hxc}}(\mathbf{r}', \mathbf{r}) \varphi_k(\mathbf{r}) \varphi_l(\mathbf{r}') \).
When the Hxc kernel is neglected, the TD-DFT linear response equation reduces to the exact linear response equation for the KS-DFT system. In this case, we obtain (approximate) excitation energies which are simply equal to the KS excitation energies $\varepsilon_j - \varepsilon_0$ with $j > 0$.

In a sense, KS excitation energies can be viewed as ”zeroth order” excitation energies if the Hxc kernel is considered as a perturbation.

We immediately see that, within the adiabatic approximation, multiple electron excitations (double excitations in particular) cannot be described. They are simply absent from the TD-DFT spectrum.

The Hxc kernel couples the time-dependent linear response coefficients. Consequently, there is no simple analytical solution to the problem.

Casida* has shown that a linear response equation can be written in matrix form for TD-DFT, exactly like in exact response theory. An important difference though is that the hessian matrix is not diagonal anymore. Moreover, within the adiabatic approximation, it is frequency-independent, which explains once again why multiple excitations cannot be described.

The only way to describe multiple excitations in TD-DFT is to use a frequency-dependent kernel, thus leading to a frequency-dependent hessian matrix. This would basically consists in introducing memory effects into the time-dependent KS potential.
Excitation energy (atomic units) vs. Interatomic distance (atomic units)

- H$_2$ molecule ($2^1\Sigma_g$, cc–pVQZ)
- Exact (single excitation)
- Exact (double excitation)
- Approximate TD–DFT

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