

Time-Dependent Density-Functional Theory

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Outline



The Electronic Many-Body Problem

- Non-relativistic time-dependent many-electron problem:

$$i \frac{d}{dt} |\Phi(t)\rangle = \hat{\mathcal{H}}(t) |\Phi\rangle,$$

$$\hat{\mathcal{H}}(t) = \sum_{i=1}^N \hat{t}_i + \sum_{i=1}^N v_{\text{ext}}(\hat{\vec{r}}_i, t) + \sum_{i,j=1}^N \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|},$$

$$v_{\text{ext}}(\vec{r}) = \sum_{\alpha=1}^{N_{\text{nuclei}}} \frac{Z_{\alpha}}{|\vec{r} - \vec{R}_{\alpha}(t)|} + v_{\text{field}}(\mathbf{r}, t).$$



Time-dependent and time-independent pictures

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

- Time-independent picture: Solve the time-independent Schrödinger equation for as many states “as needed”:

$$\hat{H}_0|\Psi_K\rangle = E_K|\Psi_K\rangle.$$

- If the perturbation is small, use the $\{\Psi_K, E_K\}$ basis set as departing point for perturbation theory. For most properties, no explicit propagation is needed.
- If the perturbation is large, propagate the td Schrödinger equation in the $\{\Psi_K, E_K\}$ basis set.
- Time-dependent picture: propagate explicitly Schrödinger's eq.:

$$\begin{aligned}i \frac{d}{dt} |\Psi(t)\rangle &= \hat{H}(t) |\Psi(t)\rangle, \\ \Psi(t=0)\rangle &= |\Psi_{\text{initial}}\rangle.\end{aligned}$$



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Why extending ground-state DFT?

- Many interesting properties of atoms, molecules and solids can be obtained from the knowledge of their **total energies** at their **ground state**.

E.g.: equilibrium lattice constants of solids, geometrical arrangements of molecules, phonons or vibrational modes, activation barriers for chemical reactions, . . .

- But we also need to know how a quantum mechanical system **responds** to external perturbations \Rightarrow **response properties**.

E.g.: linear and non-linear optical properties (polarizabilities, photo-absorption . . .), magnetic susceptibilities, photoemission, . . .

These properties require the knowledge of not only the ground state of some electronic Hamiltonian, but also excited states, and transition matrix elements between them.



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Example: dynamical polarizability.

- Electric field, dipolar approximation:

$$\mathbf{E}(\mathbf{r}, t) = E_0(t)\hat{\mathbf{z}}.$$

$$v(\mathbf{r}, t) = -E_0(t)z.$$

- Ground-state electric dipole of a molecule:

$$Z_0 = -e\langle\Psi_0|\hat{Z}|\Psi_0\rangle.$$

- Problem: how does the irradiation of a molecule with a weak electric field affects the electric dipole?

$$Z(t) = \langle\Psi(t)|[-e\hat{Z}|\Psi(t)\rangle = Z_0 + \delta Z(t)$$



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Why extending ground-state DFT?

- We can expand the Fourier transform of $\delta Z(t)$, $\delta Z(\omega)$, in a power series of the Fourier transform of the field strength, $E_0(\omega)$:

$$\delta Z(\omega) = \alpha_{zz}(\omega)E_0(\omega) + \mathcal{O}(E_0^2)$$

- The first order coefficient is called the **dipole polarizability**:

$$\alpha_{zz}(\omega) = \frac{\delta Z(\omega)}{E_0(\omega)}.$$

- The polarizability has many properties and applications; e.g. it determines the photo-absorption cross section through a simple relationship:

$$\sigma_{zz}(\omega) = \frac{4\pi\omega}{c} \Im[\alpha_{zz}(\omega)]$$



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- Working in the “time-independent” picture, one can obtain α_{zz} directly from the unperturbed ground and excited states, through the so-called “sum-over-states” (SOS) formula.

$$\alpha_{zz}(\omega) = \frac{e^2}{\hbar} \sum_K |\langle \Psi_K | \hat{Z} | \Psi_0 \rangle|^2 \left[\frac{1}{-\omega + \omega_K - i\eta} + \frac{1}{\omega + \omega_K + i\eta} \right].$$

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- Let us rewrite this in a more “density-functional” language:

$$n_{\sigma}(\mathbf{r}, t) = \langle \Psi(t) | \sum_{k=1}^N \delta(\hat{\mathbf{r}}_k - \mathbf{r}) \delta_{\sigma\sigma_k} | \Psi(t) \rangle$$

- If we apply a small perturbation $\delta v_{\sigma}(\mathbf{r}, t)$,

$$\delta n_{\sigma}(\mathbf{r}, \omega) = \sum_{\sigma'} \int d^3r' \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\sigma'}(\mathbf{r}', \omega).$$

The object $\chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega)$ is the **response function** of the system.



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Why extending ground-state DFT?

- The polarizability is related to the response function through:

$$\alpha_{ij}(\omega) = - \int \int d^3r d^3r' x_i \chi(\mathbf{r}, \mathbf{r}', \omega) x_j'.$$

- The **response** functions contain all the information that is necessary to predict the reaction of a system to any external perturbation.
- Directly from its definition, it can be seen that the response function is a functional of the spin density:

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Why extending ground-state DFT?

Another example: interaction of very intense electromagnetic fields with atoms or molecules, and generation of high harmonics.

- If the perturbation is not weak, the study cannot be made perturbatively.
- From the explicit propagation of Schrödinger equation, we can get the evolution of the dipole moment in time:

$$\mathbf{D}(t) = -e\langle\Psi(t)|\hat{\mathbf{R}}|\Psi(t)\rangle,$$

which can be written in terms of the density alone:

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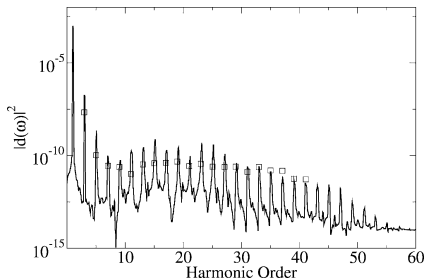
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- The atom/molecule re-emits part of the energy that it receives; the emission spectrum can be approximated as:

$$H(\omega) \propto \left| \int dt e^{i\omega t} \frac{d^2}{dt^2} \mathbf{D}(t) \right|^2$$



Why extending ground-state DFT?

- Summarizing: some important properties are, intrinsically, “excited-states properties”:

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- Everything is a functional of the ground-state density, including excited states, excited states transition, etc. So “standard” DFT should be enough. . .
- In practice, those functionals are unknown, and therefore it is better to look for an alternative theory.



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The time-dependent one-to-one mapping

- System \mathcal{S} : $\hat{H} = \hat{T} + \hat{W} + \hat{V}(t)$
 - $\hat{W} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$ is the electronic interaction.
 - $\hat{V}(t) = \sum_i v(\hat{r}_i, t)$ is the external field seen by the electrons.
 - $|\Phi(t=0)\rangle = |\Phi_0\rangle \Rightarrow n(\vec{r}, t) = \langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle$.
- System \mathcal{S}' : $\hat{H}' = \hat{T} + \hat{W}' + \hat{V}'(t)$
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The time-dependent one-to-one mapping

- Question: Given \hat{W}' , is there any $v'(\vec{r}, t)$ such that:

$$n'(\vec{r}, t) = \langle \Phi'(t) | \hat{n}(\vec{r}) | \Phi'(t) \rangle = n(\vec{r}, t) \quad ?$$

- Answer: Yes, and it is unique.

[R. van Leeuwen, Phys. Rev. Lett. **82** 3863 (1999).]



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The Runge-Gross theorem, and the TDKS system

- Now assume that $W'=W$.
- $v'(\vec{r}, t) = v(\vec{r}, t)$ obviously, but the theorem also tells us that **it is unique**:
There exists a unique relationship between time-dependent densities and external potentials.
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- And now assume that $W'=0$. I.e., we have a non-interacting system.
- There exists a potential $v'(\vec{r}, t)$ for this non-interacting system such that it reproduces the density of the interacting system.

This is the so-called time-dependent Kohn-Sham potential, $v_{\text{KS}}(\vec{r}, t)$. The evolution of the non-interacting system may be easily obtained by propagating single-particle equations (i.e. Runge-Gross or td Kohn-Sham equations):

$$i \frac{\partial}{\partial t} \varphi_i(\vec{r}, t) = -\frac{1}{2} \nabla^2 \varphi_i(\vec{r}, t) + v_{\text{KS}}(\vec{r}, t) \varphi_i(\vec{r}, t).$$

$$\varphi_i(\vec{r}, t=0) = \varphi_i^0(\vec{r})$$



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Retrieval of observables in TDDFT

- The density of the *real*, interacting system, may be retrieved from the single-particle orbitals that solve the *auxiliary*, non-interacting system:

$$n(\vec{r}, t) = \sum_{i=1}^N |\varphi_i(\vec{r}, t)|^2.$$

- The expectation value of any observable $\hat{Q}(t)$ is a unique functional of the time-dependent density by virtue of the Runge-Gross theorem:

$$Q(t) \equiv \langle \hat{Q}(t) \rangle \equiv Q(t)[n].$$

- For example, the dipole-dipole 1st order dynamical polarizability would be:

$$\alpha_{\sigma\mu}[n](\omega) = -\frac{1}{E_{\mu}(\omega)} \int d^3r r_{\sigma} \delta n(\vec{r}, \omega).$$



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- RG is an *existence* theorem that is non-constructive: we do not know v_{KS} .
- As in gs DFT, a smaller unknown part may be isolated:

$$v_{\text{KS}}(\vec{r}, t) = v(\vec{r}, t) + u_{\text{Hartree}}[n](\vec{r}, t) + v_{\text{xc}}[n](\vec{r}, t),$$

- Involving the so-called “adiabatic approximation”, one can use the GS functionals:

$$A_{\text{xc}}[n] = \int_{t_0}^{t_f} d\tau E_{\text{xc}}[n_\tau]; \quad (n_\tau(\vec{r}) = n(\vec{r}, \tau)).$$

$$v_{\text{xc}}(\vec{r}, t) = \frac{\delta A_{\text{xc}}}{\delta n(\vec{r}, t)}.$$

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However, strong-field phenomena have proven to be especially demanding in terms of the xc approximations. For many purposes, non-adiabatic approximations are probably needed.



- Yet another problem: not all observables are explicit functionals of the td density. Most of them are unknown and have to be approximated. For example, the ionization probabilities:

$$I_p = 1 - \lim_{t \rightarrow \infty} \sum_{i \in [\text{BoundStates}]} |\langle \Psi(t) | \Psi_i \rangle|^2.$$

How can write $\langle \Psi(t) | \Psi_i \rangle$ in terms only of the density?



Example: propagation for problems in the non-linear regime

For large external perturbations (non-linear, or non-perturbative regime), one can directly propagate in time the TDKS equations. This permits, to obtain, e.g., harmonic spectra:

$$\sigma_{\text{emission}} \propto \left| \int dt e^{i\omega t} \frac{d}{dt} d[n](t) \right|^2,$$

where $d[n](t)$ is the system dipole moment: $d[n](t) = \int d^3r n(\vec{r})(t)x$.



Outline



Polarizability from real-time propagations

- We “kick” an atom/molecule with a sudden electric perturbation:

$$\mathbf{E}(t) = E_0 \delta(t) \hat{\mathbf{z}} \Rightarrow$$

$$\mathbf{E}(\omega) = E_0 \hat{\mathbf{z}}$$

- If we calculate the evolution of the variation of the dipole moment, and obtain its Fourier transform, $\delta Z(\omega)$, we can easily obtain the dynamical polarizability:

$$\alpha_{zz}(\omega) = \frac{\delta Z(\omega)}{E_0} .$$



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Polarizability from real-time propagations

- The effect of this perturbation on the Kohn-Sham system is a phase shift at time zero:

$$\varphi_i(\vec{r}, t = 0^+) = e^{iE_0z} \varphi_i^{\text{GS}}(\vec{r}).$$

- The evolution, afterwards, can be following by propagating the td Kohn-Sham equations with zero field:

$$i \frac{\partial}{\partial t} \varphi_i(\vec{r}, t) = -\frac{1}{2} \nabla^2 \varphi_i(\vec{r}, t) + v_{\text{KS}}(\vec{r}, t) \varphi_i(\vec{r}, t).$$

- We retrieve the density...

$$n(\vec{r}, t) = \sum_{i=1}^N |\varphi_i(\vec{r}, t)|^2.$$



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Polarizability from real-time propagations

- Calculate the variation of the dipole moment. . .

$$\delta Z(t) = \int d^3r n(\vec{r}, t) z - Z_0$$

- Fourier transform. . .

$$\delta Z(\omega) = \int dt e^{i\omega t} \delta Z(t),$$

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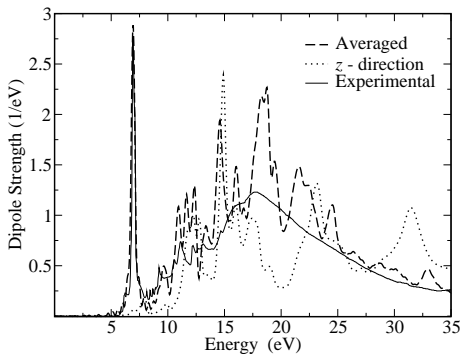
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Example: absorption spectrum of benzene



Outline



- If we assume small perturbations, one can derive a linearized form of the TDKS equations: the response density is a linear functional of the perturbation.
- The translation of the linear response theory formalism to TDDFT leads to a tractable set of equations that permits to obtain:
 - Excitation energies, $\omega_I = E_I - E_0$.
 - Transition matrix elements, oscillatory strengths – corresponding to transitions between the ground state and the excited states.
- It requires the *second functional derivative* of the exchange and correlation functional: the so-called kernel:

$$f_{xc}(\vec{r}t, \vec{r}'t') = \frac{\delta v_{xc}(\vec{r}, t)}{\delta n(\vec{r}', t')}.$$



$$\delta n_{\sigma}(\mathbf{r}, \omega) = \sum_{\sigma'} \int d^3 r' \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\sigma'}(\mathbf{r}', \omega).$$

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It is better to rewrite all this. . .

$$\Omega \mathbf{F}_I = \Omega_I \mathbf{F}_I$$

The dimension of the matrix is the number of **pairs** of occupied-unoccupied ground-state Kohn-Sham eigenstates ($ia\sigma$), for each spin component σ .

$$\Omega_{ia\sigma, jb\mu} = \delta_{ij} \delta_{ab} \delta_{\sigma\mu} (\varepsilon_{a\sigma} - \varepsilon_{i\sigma})^2 + 2\sqrt{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}} K_{ia\sigma, jb\mu} \sqrt{\varepsilon_{b\sigma} - \varepsilon_{j\sigma}}$$

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