Time-dependent density functional theory

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What do we want to describe?

**System in laser field:**

**Generic situation**

\[
\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \sum_{j,\alpha} - \frac{Z_\alpha e^2}{|r_j-R_\alpha|} + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t
\]
What do we want to describe?

System in laser field: Generic situation

\[ \hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \sum_{j, \alpha} \left( -\frac{Z_{\alpha} e^2}{|r_j - R_{\alpha}|} \right) + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t \]

Electronic transport: Generic situation

Bias between L and R is turned on: \( U(t) \)
This Hamiltonian involves two approximations:

- Nuclei treated as clamped or moving on classical trajectories
- Photons treated as classical electromagnetic fields
Why don’t we just solve the many-body Schrödinger equation

Example: Oxygen atom (8 electrons)

\[ \Psi(\vec{r}_1, \ldots, \vec{r}_8) \] depends on 24 coordinates

**Rough table of the wavefunction**

- 10 entries per coordinate: \( \Rightarrow 10^{24} \) entries
- 1 byte per entry: \( \Rightarrow 10^{24} \) bytes
- 5\times10^9 \) bytes per DVD: \( \Rightarrow 2\times10^{14} \) DVDs
- 10 g per DVD: \( \Rightarrow 2\times10^{15} \) g of DVDs
  \[ = 2\times10^9 \) t of DVDs \]
Two fundamentally different classes of ab-initio approaches:

- **Wave function approaches**
  - Configuration interaction
    (also stochastic CI)
  - Tensor networks

- "**Functional Theories**"
Two fundamentally different classes of ab-initio approaches:

• **Wave function approaches**
  -- Configuration interaction  
    (also stochastic CI)  
  -- Tensor networks

• **“Functional Theories”**

  Write total energy as functional  
  of a simpler quantity and minimize
“Functional Theories”

MBPT  RDMFT  DFT

\[ G(r, r', t - t') \quad \gamma(r, r') = G(r, r', 0^+) \quad \rho(r) = \gamma(r, r) \]
## “Functional Theories”

<table>
<thead>
<tr>
<th>Method</th>
<th>Equation</th>
<th>Functional:</th>
<th>Functional:</th>
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</tr>
</thead>
<tbody>
<tr>
<td>MBPT</td>
<td>$G(r, r', t - t')$</td>
<td>$\Phi_{xc}[G]$</td>
<td>$\Sigma_{xc}[G]$</td>
<td></td>
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<tr>
<td>RDMFT</td>
<td>$\gamma(r, r') = G(r, r', 0^+)$</td>
<td>$E_{xc}[\gamma]$</td>
<td></td>
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<tr>
<td>DFT</td>
<td>$\rho(r) = \gamma(r, r)$</td>
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<td></td>
</tr>
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<td>DFT</td>
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<td></td>
<td></td>
</tr>
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<td>$\Phi_{\text{xc}}[G]$</td>
<td>$E_{\text{xc}}[\gamma]$</td>
<td>$E_{\text{xc}}[\varrho]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>or $\Sigma_{\text{xc}}[G]$</td>
<td>difficult</td>
<td>or $v_{\text{xc}}[\varrho]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>easy (e.g. GW)</td>
<td></td>
<td>very difficult</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Motivation

$(r, r') \ G(r, r', 0^-) + g = MBPT$'t t,'r,r( G

“Functional Theories”

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<tr>
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<td>$G(r, r', t - t')$</td>
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</tbody>
</table>

**Functional:**
- $\Phi_{xc}[G]$ or $\Sigma_{xc}[G]
- easy (e.g. GW)
- numerically heavy

**Functional:**
- $E_{xc}[\gamma]
- difficult
- moderate

**Functional:**
- $E_{xc}[\varrho]
- or $v_{xc}[\varrho]
- very difficult
- light
ESSENCE OF DENSITY-FUNCTIONAL THEORY

- Every observable quantity of a quantum system can be calculated from the density of the system ALONE.

- The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles.
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Hohenberg-Kohn theorem (1964)
Kohn-Sham theorem (1965)
(for the ground state)
\[
\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j, \alpha} - \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t
\]

**Strong laser** \(v_{\text{laser}}(t) \geq v_{\text{en}}\):  
Non-perturbative solution of full TDSE required

**Weak laser** \(v_{\text{laser}}(t) \ll v_{\text{en}}\):  
Calculate  
1. Linear density response \(\rho_1(\vec{r}, t)\) 
2. Dynamical polarizability \(\alpha(\omega) = -\frac{e}{E} \int z \rho_1(\vec{r}, \omega) d^3r\) 
3. Photo-absorption cross section \(\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im}\alpha\)
Photo-absorption in weak lasers

\[ \sigma(\omega) \]

Laser frequency \( \omega \)

- Continuum states
- Unoccupied bound states
- Occupied bound states

\( I_1 \)
\( I_2 \)
OUTLINE

• Basic theorems of TDDFT

• TDDFT in the linear response regime:
  -- Dyson equation for the response function
  -- Photo-absorption in molecules
  -- Photo-absorption in solids

• Beyond the linear regime:
  -- Transport through molecular junctions
  -- Laser-driven spin dynamics in solids
  -- Combination of TDDFT with Optimal Control Theory
1-1 correspondence (TD analogue of Hohenberg-Kohn theorem):

\[ v(rt) \leftrightarrow^{1-1} \rho(rt) \]

The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables for fixed initial state.

**TDKS theorem:**

The time-dependent density of the interacting system of interest can be calculated as density

\[
\rho(rt) = \sum_{j=1}^{N} \left| \varphi_j(rt) \right|^2
\]

of an auxiliary **non-interacting** (KS) system

\[
i\hbar \frac{\partial}{\partial t} \varphi_j(rt) = \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s[\rho](rt) \right) \varphi_j(rt)
\]

with the **local** potential

\[
v_s[\rho'(r't')] = v(rt) + \int d^3r' \frac{\rho(r't')}{|r-r'|} + v_{xc}[\rho'(r't')]\]

Basic theorems of TDDFT

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with the local potential

\[ v_s[\rho(r't')](rt) = v(rt) + \int d^3r' \frac{\rho(r't')}{|r-r'|} + v_{xc}[\rho(r't')](rt) \]
Proof of the 1-1 correspondence between $v(\vec{r}_t)$ and $\rho(\vec{r}_t)$

define maps $F: v(\vec{r}_t) \mapsto \Psi(t)$ and $\tilde{F}: \Psi(t) \mapsto \rho(\vec{r}_t)$

$$F: v(\vec{r}_t) \mapsto \Psi(t) \quad \tilde{F}: \Psi(t) \mapsto \rho(\vec{r}_t)$$

$$\rho(\vec{r}_t) = \langle \Psi(t)|\hat{\rho}(\vec{r})|\Psi(t)\rangle$$

$$\hat{\rho}(\vec{r}) = \sum_s \psi_s^+(\vec{r}) \psi_s(\vec{r})$$

$G: v(\vec{r}_t) \mapsto \rho(\vec{r}_t)$
to be shown that

\[ v(\vec{r} \ t) \neq v'(\vec{r} \ t) + c(t) \Rightarrow \rho(\vec{r} \ t) \neq \rho'(\vec{r} \ t) \]

i.e.

\[ v(\vec{r} \ t) \neq v'(\vec{r} \ t) + c(t) \]

proof (basic idea):

\[ v(\vec{r} \ t) \rightarrow \vec{j}(\vec{r} \ t) \rightarrow \rho(\vec{r} \ t) \]

\[ v'(\vec{r} \ t) \rightarrow \vec{j}'(\vec{r} \ t) \rightarrow \rho'(\vec{r} \ t) \]
use

\[ i \frac{\partial \mathbf{j}(\mathbf{r}, t)}{\partial t} = \langle \Psi(t) \left| \left[ \hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t) \right] \right| \Psi(t) \rangle \]

equation of motion for \( \mathbf{j} \)

and

\[ \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = - \text{div} \mathbf{j}(\mathbf{r}, t) \]

continuity equation

to show that there exists an integer \( k > 0 \) such that

\[ \left. \frac{\partial^k \rho}{\partial t^k} \right|_{t_0} \neq \left. \frac{\partial^k \rho'}{\partial t^k} \right|_{t_0} \]

\[ \Rightarrow \rho \text{ and } \rho' \text{ will become different from each other infinitesimally later than } t_0 \]
Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

$$V_{xc}^{ALDA}(\vec{r} \ t) := V_{xc,stat}^{hom}(n) \bigg|_{n=\rho(\vec{r} \ t)}$$

$V_{xc,stat}^{hom} = xc$ potential of static homogeneous e-gas
Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

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$v_{xc,\text{stat}}^{\text{hom}}$ = xc potential of static homogeneous e-gas

Any approximate ground-state-DFT xc functional can be used to generate an adiabatic approximation for TDDFT

$$v_{xc}^{\text{adiab}}(\vec{r} \ t) := v_{xc,\text{GS}}^{\text{approx}}[n] \bigg|_{n=\rho(\vec{r} \ t)}$$
LINEAR RESPONSE THEORY

t = t_0 : Interacting system in ground state of potential \( v_0(r) \) with density \( \rho_0(r) \)

\( t > t_0 \) : Switch on perturbation \( v_1(r, t) \) (with \( v_1(r, t_0) = 0 \)).

Density: \( \rho(r, t) = \rho_0(r) + \delta \rho(r, t) \)

Consider functional \( \rho[v](r, t) \) defined by solution of interacting TDSE

Functional Taylor expansion of \( \rho[v] \) around \( v_0 \):

\[
\rho[v](r, t) = \rho[v_0 + v_1](r, t) \\
= \rho[v_0](r, t) \\
+ \int \frac{\delta \rho[v](r, t)}{\delta v(r', t')} \bigg|_{v_0} v_1(r', t') d^3r' dt' \\
+ \frac{1}{2} \int \int \frac{\delta^2 \rho[v](r, t)}{\delta v(r', t') \delta v(r'', t'')} \bigg|_{v_0} v_1(r', t') v_1(r'', t'') d^3r' d^3r'' dt' dt'' \\
\vdots
\]

\( \longrightarrow \rho_o(r) \)

\( \longrightarrow \rho_1(r, t) \)

\( \longrightarrow \rho_2(r, t) \)
\[ \rho_1(r,t) = \text{linear density response of interacting system} \]

\[
\chi(r,t,r',t') := \left. \frac{\delta \rho[v](r,t)}{\delta v(r',t')} \right|_{v_0} = \text{density-density response function of interacting system}
\]

\[
\text{Lehmann representation of the full response function}
\]

\[
\chi(r,r';\omega) = \lim_{\eta \to 0^+} \sum_m \left( \frac{\langle 0|\hat{\rho}(r)|m\rangle\langle m|\hat{\rho}(r')|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{\rho}(r')|m\rangle\langle m|\hat{\rho}(r)|0\rangle}{\omega + (E_m - E_0) + i\eta} \right)
\]

with the exact many-body eigenfunctions and energies of the initial unperturbed interacting system Hamiltonian \( \hat{H}(t_0)|m\rangle = E_m|m\rangle \)

\[ \Rightarrow \text{The exact linear density response} \]

\[ \rho_1(\omega) = \chi(\omega) v_1 \]

has poles at the exact excitation energies \( \Omega = E_m - E_0 \)
Analogous functional $\rho_s[v_s](r\ t)$ for non-interacting system

$$\rho_s[v_s](r\ t) = \rho_s[v_{s,0} + v_{s,1}](r\ t) = \rho_s[v_{s,0}](r\ t) + \int \frac{\delta \rho_s[v_s](r\ t)}{\delta v_s(r' t')} \left. v_{s,1}(r' t') \right|_{v_{s,0}} d^3 r' dt' + \cdots$$

$$\chi_s(r, r', t') := \left. \frac{\delta \rho_s[v_s](r\ t)}{\delta v_s(r' t')} \right|_{v_{s,0}} = \text{density-density response function of non-interacting system}$$

$\chi_s(r, r', \omega)$ has also poles as function of $\omega$, but at the non-interacting single-particle (KS) excitation energies.
GOAL: Find a way to calculate $\rho_1(r\ t)$ without explicitly evaluating $\chi(r\ t, r'^t')$ of the interacting system

starting point: Definition of xc potential

$$v_{xc}[\rho](r\ t) := v_S[\rho](r\ t) - v_{ext}[\rho](r\ t) - v_H[\rho](r\ t)$$

$v_{xc}$ is well-defined through the non-interacting and the interacting 1-1 mapping.
\[
\left. \frac{\delta v_{xc}[\rho](r,t)}{\delta \rho(r') \delta \rho(t')} \right|_{\rho_0} = \left. \frac{\delta v_s[\rho](r,t)}{\delta \rho(r') \delta \rho(t')} \right|_{\rho_0} - \left. \frac{\delta v_{ext}[\rho](r,t)}{\delta \rho(r') \delta \rho(t')} \right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}
\]
\[
\left. \frac{\delta v_{xc} [\rho] (r \ t)}{\delta \rho(r' t')} \right|_{\rho_0} = \left. \frac{\delta v_s [\rho] (r \ t)}{\delta \rho(r' t')} \right|_{\rho_0} - \left. \frac{\delta v_{\text{ext}} [\rho] (r \ t)}{\delta \rho(r' t')} \right|_{\rho_0} - \frac{\delta (t - t')}{|r - r'|}
\]

\[
\uparrow \quad \uparrow \quad \uparrow \quad \uparrow
\]

\[
f_{xc} (r \ t, r' t') \quad \chi_s^{-1} (r \ t, r' t') \quad \chi^{-1} (r \ t, r' t') \quad W_C (r \ t, r' t')
\]
$$\frac{\delta v_{xc}[\rho](r,t)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_{s}[\rho](r,t)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](r,t)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

\[ f_{xc} (r,t,r't') \quad \chi_{s}^{-1}(r,t,r't') \quad \chi^{-1}(r,t,r't') \quad W_{C}(r,t,r't') \]

$$f_{xc} + W_{C} = \chi_{s}^{-1} - \chi^{-1}$$
\[
\frac{\delta v_{xc}[\rho](r, t)}{\delta \rho(r', t')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](r, t)}{\delta \rho(r', t')} \bigg|_{\rho_0} - \frac{\delta v_{\text{ext}}[\rho](r, t)}{\delta \rho(r', t')} \bigg|_{\rho_0} - \frac{\delta(t - t')}{|r - r'|}
\]

\[
f_{xc}(r, t, r', t') \quad \chi_S^{-1}(r, t, r', t') \quad \chi^{-1}(r, t, r', t') \quad W_C(r, t, r', t')
\]

\[
\chi_S \cdot f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \bigg| \cdot \chi
\]
\[
\frac{\delta v_{xc}[\rho](r\ t)}{\delta \rho(r' t')} \bigg|_{\rho_0} = \frac{\delta v_{s}[\rho](r\ t)}{\delta \rho(r' t')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](r\ t)}{\delta \rho(r' t')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}
\]

\[
\chi_S \cdot f_{xc} + W_C = \chi_s^{-1} - \chi^{-1} \cdot \chi
\]

\[
\chi_S \left( f_{xc} + W_C \right) \chi = \chi - \chi_S
\]
\[ \chi = \chi_s + \chi_s \left( W_{ee} + f_{xc} \right) \chi \]

Act with this operator equation on arbitrary \( v_1(r, t) \) and use \( \chi \, v_1 = \rho_1 : \)

\[ \rho_1(r, t) = \int d^3r' dt' \chi_s(r, t, r', t') \left[ v_1(r, t) + \int d^3r'' dt'' \left\{ W_{ee}(r', t', r'', t'') + f_{xc}(r', t', r'', t'') \right\} \rho_1(r'', t'') \right] \]

- Exact integral equation for \( \rho_1(r, t) \), to be solved iteratively

- Need approximation for \( f_{xc}(r', t', r'', t'') = \frac{\delta V_{xc}[\rho](r', t')}{\delta \rho(r'' t'')} \bigg|_{\rho_0} \)

(either for \( f_{xc} \) directly or for \( v_{xc} \))
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.

Photo-absorption in weak lasers

I_1

I_2

continuum states

unoccupied bound states

occupied bound states

photo-absorption cross section

σ(ω)

Laser frequency ω

Previous slide
Photo-absorption in weak lasers

\[ \begin{align*}
I_1 & \rightarrow I_2 \\
\text{continuum states} & \rightarrow \text{occupied bound states} \\
\text{unoccupied bound states} & \\
\text{occupied bound states} & \\
\end{align*} \]
Looking at those frequencies, $\Omega$, for which $q_1(\omega)$ has poles, leads to a (non-linear) eigenvalue equation

$$\sum_{q'} \left( A_{qq'}(\Omega) + \omega_q \delta_{qq'} \right) \beta_{q'} = \Omega \beta_q$$

where

$$A_{qq'} = \alpha_{q'} \int \Phi_q(r) \left( \frac{1}{|r-r'|} + f_{xc}(r, r', \Omega) \right) \Phi_{q'}(r')$$

$q = (j, a)$ double index

$$\alpha_q = f_a - f_j$$

$$\Phi_q(r) = \phi_a^*(r) \phi_j(r)$$

$$\omega_q = \varepsilon_a - \varepsilon_j$$
<table>
<thead>
<tr>
<th>Atom</th>
<th>Experimental Excitation Energies $^1S\rightarrow^1P$ (in Ry)</th>
<th>KS energy differences $\Delta \epsilon_{KS}$ (Ry)</th>
<th>TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.388</td>
<td>0.259</td>
<td>0.391</td>
</tr>
<tr>
<td>Mg</td>
<td>0.319</td>
<td>0.234</td>
<td>0.327</td>
</tr>
<tr>
<td>Ca</td>
<td>0.216</td>
<td>0.157</td>
<td>0.234</td>
</tr>
<tr>
<td>Zn</td>
<td>0.426</td>
<td>0.315</td>
<td>0.423</td>
</tr>
<tr>
<td>Sr</td>
<td>0.198</td>
<td>0.141</td>
<td>0.210</td>
</tr>
<tr>
<td>Cd</td>
<td>0.398</td>
<td>0.269</td>
<td>0.391</td>
</tr>
</tbody>
</table>

## Excitation energies of CO molecule [mH]

<table>
<thead>
<tr>
<th>State</th>
<th>( \Omega_{\text{expt KS}} )</th>
<th>KS-transition</th>
<th>( \Delta \epsilon_{\text{KS}} )</th>
<th>TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (^1\Pi)</td>
<td>312.7</td>
<td>5( \sigma \rightarrow 2\pi )</td>
<td>252.3</td>
<td>310.2</td>
</tr>
<tr>
<td>a (^3\Pi)</td>
<td>232.3</td>
<td></td>
<td></td>
<td>221.4</td>
</tr>
<tr>
<td>I (^1\Sigma^-)</td>
<td>363.1</td>
<td>1( \pi \rightarrow 2\pi )</td>
<td>362.6</td>
<td>362.6</td>
</tr>
<tr>
<td>e (^3\Sigma^-)</td>
<td>363.1</td>
<td></td>
<td></td>
<td>362.6</td>
</tr>
<tr>
<td>a' (^3\Sigma^+)</td>
<td>312.7</td>
<td></td>
<td></td>
<td>314.9</td>
</tr>
<tr>
<td>D (^1\Delta)</td>
<td>375.9</td>
<td></td>
<td></td>
<td>380.7</td>
</tr>
<tr>
<td>d (^3\Delta)</td>
<td>344.0</td>
<td></td>
<td></td>
<td>339.6</td>
</tr>
</tbody>
</table>

Molecular excitation energies from time-dependent density-functional theory
Failures of ALDA in the linear response regime

• \( \text{H}_2 \) dissociation is incorrect:

\[
E\left(1\Sigma_u^+\right) - E\left(1\Sigma_g^+\right) \xrightarrow{R \to \infty} 0 \quad (\text{in ALDA})
\]


• response of long chains strongly overestimated


• in periodic solids, \( f_{xc}^{\text{ALDA}}(q, \omega, \rho) = c(\rho) \) whereas, for insulators, \( f_{xc}^{\text{exact}} \xrightarrow{q \to 0} 1/q^2 \) divergent.

• charge-transfer excitations not properly described

Failures of ALDA in the linear response regime

- \( \text{H}_2 \) dissociation is incorrect:
  \[
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- in periodic solids,
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  \]
  for insulators,
  \[
  f_{xc}^{\text{exact}} \xrightarrow{q \to 0} \frac{1}{q^2} \quad \text{divergent.}
  \]

- charge-transfer excitations not properly described
  (see: Dreuw et al., J. Chem. Phys. 119, 2943 (2003))

These difficulties have largely been solved by xc functionals more advanced than ALDA