TDDFT

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July 1, 2010
Outline

1. Time-dependent quantum mechanics
2. TDDFT: formalism
3. Linear response theory
4. Performance
5. Back to the ground state
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Time-dependent Schrödinger equation

\[ i \frac{\partial}{\partial t} \Psi(r_1, ..., r_N; t) = (\hat{T} + \hat{V}(t) + \hat{V}_{ee}) \Psi(r_1, ..., r_N; t) \]

with kinetic energy operator:

\[ \hat{T} = -\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 \]

and electron interaction:

\[ \hat{V}_{ee} = \frac{1}{2} \sum_{j \neq k} \frac{1}{|r_j - r_k|} \]

The TDSE describes the time evolution of a many-body state \( \Psi(t) \) starting from an initial state \( \Psi_0 = \Psi(t_0) \), under the influence of an external time-dependent potential:

\[ \hat{V}(t) = \sum_{j} v(r_j, t). \]
Two types of time-dependence: 1. Due to initial state

Initial wavefunction is not an eigenstate: e.g.

\[ \psi(x, t = 0) = \frac{1}{\sqrt{5}} \{2\phi_1(x) + \phi_2(x)\}. \]

Plasmonics: oscillations of nanoparticles


Ullrich and Maitra’s March 2010 APS TDDFT presentation
2nd type: Potential starts changing

Start in ground state, evolve in time-dependent potential $v(x, t)$:

Nonlinear response of molecules in strong laser fields:
Conservation of density in time-dependent problems

- Current operator:
  \[ \hat{j}(r) = \frac{1}{2} \sum_j \left( \hat{p}_j \delta(r-r_j) + \delta(r-r_j) \hat{p}_j \right) \]

- Acting on wavefunction:
  \[ j(r, t) = N \int d^3r_2 \cdots \int d^3r_N \Im\{ \Psi(r, r_2, \ldots, r_N; t) \nabla \Psi^*(r, r_2, \ldots, r_N; t) \} \]

- Continuity:
  \[ \frac{\partial n(r, t)}{\partial t} = -\nabla \cdot j(r, t) \]
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Recent reviews on TDDFT


- Any given current density, $j(r, t)$, initial wavefunction, statistics, and interaction, there’s only one external potential, $v(r, t)$, that can produce it.

- Imposing a boundary condition and using continuity, find also true for $n(r, t)$.

- Action in RG paper is **WRONG**.

- van Leeuwen gave a constructive proof (PRL98).
Basic points

TDDFT:

- is an addition to DFT, using a different theorem
- allows you to convert your KS orbitals into optical excitations of the system
- for excitations usually uses ground-state approximations that usually work OK
- has not been very useful for strong laser fields
- is in its expansion phase: Being extended to whole new areas, not much known about functionals
- with present approximations has problems for solids
- with currents is more powerful, but harder to follow
- yields a new expensive way to get ground-state $E_{XC}$. 
**TD Kohn–Sham equations**

- **Time-dependent KS equations:**
  \[
i \frac{\partial}{\partial t} \phi_j(r, t) = \left\{ -\frac{1}{2} \nabla^2 + v_s(r, t) \right\} \phi_j(r, t)
  \]

- **Density:**
  \[
n(r, t) = \sum_{j=1}^{N} |\phi_j(r, t)|^2
  \]

- The KS potential is
  \[
v_s(r, t) = v(r, t) + \int d^3 r' \frac{n(r, t)}{|r - r'|} + v_{XC}[n; \Psi_0, \Phi_0](r, t),
  \]
  where \(v_{XC}\) depends on memory:
  - entire history of \(n(r, t)\)
  - initial state \(\Psi_0\) and \(\Phi_0\).
Almost all calculations use adiabatic approximation
No standard improvement over this
Use ground state functional $v_{\text{XC}}^{\text{GS}}$ on time-dependent $n(r, t)$:

$$v_{\text{XC}}^{\text{adia}}[n](r, t) = v_{\text{XC}}^{\text{GS}}[n(t)](r).$$
Overview of *ALL* TDDFT

TDDFT is applied in 3 distinct regimes:

- **Strong fields**, where time-dependence is not perturbative.
  - Properties: double ionization probabilities, momentum distributions, high-harmonic generation
  - Methodology: Must be real time, usually on a grid in real space.
  - Performance: Several problems, including that $n(r, t)$ is not enough info to get the desired property, and that no good approximations when $n(r, t)$ is not close to ground state.

- **Excitations**: To extract excitations and optical absorption, only need linear response theory
  - Methodology: Either real time, fourier transform dipole moment, or response equations in frequency space.
  - Performance: Usually quite good (good properties of excited molecules) but growing list of deficiencies, e.g.:
    - Extended systems and non-locality
    - Charge transfer

- **Ground-state approximations**: Via fluctuation-dissipation theorem, can calculate the XC energy from TDDFT (very expensive - RPA cost)
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Many approaches to excitations in DFT

There is no HK theorem from excited-state density (PRL with Rene Gaudoin)

Would rather have variational approach (ensembles, constrained search, etc.)

TDDFT yields a response approach, i.e, looks at TD perturbations around ground-state
Linear response theory

We will need the density-density response function:

$$\delta n(r, t) = \int d^3 r' \int dt' \chi(rr', t-t') \delta v(r', t')$$

where

- $\delta v(r, t)$ is a perturbation to the potential,
- $\delta n(r, t)$ is the density response to this perturbation, and
- $\chi$ is the density-density response (susceptibility) function:

$$\chi(r, r', t-t') = \frac{\delta n(rt)}{\delta v(r't')}$$

(functional derivative)
Equate density change in reality with that of KS system (and Fourier transform):

\[ \delta n(r\omega) = \int d^3r' \chi[n](rr'\omega)\delta v(r'\omega) \]

\[ = \int d^3r' \chi_S[n](rr'\omega)\delta v_S[n](r'\omega) \]

which implies

\[ \delta v_S[n](r\omega) = \delta v(r\omega) + \int d^3r' \left\{ \frac{1}{|r - r'|} + f_{XC}[n](rr'\omega) \right\} \delta n(r'\omega) \]

and the XC kernel is defined in time as

\[ f_{XC}(rr', t - t') = \frac{\delta v_{XC}(rt)}{\delta n(r't')} \]
Dyson-like equation from equating density responses

Get the real response function from the \textit{ground-state} KS response function plus kernel:

\[
\chi(\mathbf{rr}'\omega) = \chi_S(\mathbf{rr}'\omega) + \\
\int d^3r_1 \int d^3r_2 \chi_S(\mathbf{rr}'\omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{XC}[n](\mathbf{r}_1\mathbf{r}_2\omega) \right\} \chi(\mathbf{rr}'\omega)
\]

with KS susceptibility

\[
\chi_S(\mathbf{rr}'\omega) = \sum_{jk} f_{jk} \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0_+}
\]

where \( f_{jk} = f_j - f_k \), \( \epsilon_j \) is the KS orbital energy and \( \phi_j(\mathbf{r}) \) is the orbital. If adiabatic approximation, the ground-state functional determines all.
Transitions

Look at KS transition frequencies $\omega_q = \epsilon_a - \epsilon_j$, where $j$ is an occupied and $a$ an unoccupied orbital. Thus $q$ is a double index $(j, a)$.

If we consider $\Phi_q(r) = \phi_j^*(r)\phi_a(r)$, we can rewrite

$$\chi_S(\mathbf{rr}'\omega) = 2 \sum_q \left\{ \frac{\Phi_q(r)\Phi_q^*(r')}{\omega - \omega_q + i0^+} - \frac{\Phi_q^*(r)\Phi_q(r')}{\omega + \omega_q - i0^+} \right\}.$$
TDDFT linear response

- Probe system with AC field of frequency $\omega$
- See at what $\omega$ you find a self-sustaining response
- That’s a transition frequency!
- Need a new functional, the XC kernel, $f_{\text{XC}}[\eta](r r \omega)$
- Almost always ignore $\omega$-dependence (called adiabatic approximation)
- Can view as corrections to KS response
Casida’s matrix formulation (1996)

Get true transition frequencies $\omega$ as eigenvalues of

$$
\sum_{q'} \Omega_{qq'}(\omega) \nu_{q'} = \omega^2 \nu_q,
$$

where $\nu_q = \_\_\_\_\_\_$,

$$
\Omega_{qq'} = \delta_{qq'} \omega_q^2 + 4 \sqrt{\omega_q \omega_{q'}} [q|f_{\text{HXC}}(\omega)|q']
$$

and

$$
[q|f_{\text{HXC}}(\omega)|q'] = \int \int d^3 r \ d^3 r' \ \Phi_q^*(r') f_{\text{HXC}}(rr'\omega) \Phi_{q'}(r)
$$
KS response

![Excitation Energies Diagram](image)

- Exact KS
- Exact TDDFT

Energy Levels:
- 6S
- 5S
- 4S
- 3P
- 3S
- 2P
- 2S

Energy Levels (eV):
- 24
- 23
- 22
- 21
- 20

States:
- singlet
- triplet

Continuum
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Benzene is the fruitfly of TDDFT

Case study: Naphthalene

Study of various functionals for Naphthalene. Variations in $\nu_{XC}(r)$ comparable to those in $f_{XC}(r, r')$.


### TABLE III: Performance of various density functionals for the first six singlet excitation energies (in eV) of naphthalene. An aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used. The “best” estimates of the true excitations were from experiment and calculations, as described in text.

<table>
<thead>
<tr>
<th>Method</th>
<th>$1^1B_{3u}$</th>
<th>$1^1B_{2u}$</th>
<th>$2^1A_g$</th>
<th>$1^1B_{1g}$</th>
<th>$2^1B_{3u}$</th>
<th>$1^1A_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSDA</td>
<td>4.191</td>
<td>4.026</td>
<td>5.751</td>
<td>4.940</td>
<td>5.623</td>
<td>5.332</td>
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<tr>
<td>B86</td>
<td>4.193</td>
<td>4.027</td>
<td>5.770</td>
<td>4.974</td>
<td>5.627</td>
<td>5.337</td>
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<tr>
<td>PBE</td>
<td>4.193</td>
<td>4.031</td>
<td>5.753</td>
<td>4.957</td>
<td>5.622</td>
<td>5.141</td>
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<tr>
<td>Hybrids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>4.393</td>
<td>4.282</td>
<td>6.062</td>
<td>5.422</td>
<td>5.794</td>
<td>5.311</td>
</tr>
<tr>
<td>PBE0</td>
<td>4.474</td>
<td>4.379</td>
<td>6.205</td>
<td>5.611</td>
<td>5.889</td>
<td>5.603</td>
</tr>
<tr>
<td>“best”</td>
<td>4.0</td>
<td>4.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

### TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/1ZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

<table>
<thead>
<tr>
<th>Method</th>
<th>$1^1B_{3u}$</th>
<th>$1^1B_{2u}$</th>
<th>$2^1A_g$</th>
<th>$1^1B_{1g}$</th>
<th>$2^1B_{3u}$</th>
<th>$1^1A_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS</td>
<td>5.139</td>
<td>4.984</td>
<td>7.038</td>
<td>6.251</td>
<td>6.770</td>
<td>5.862</td>
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<tr>
<td>CC2</td>
<td>4.376</td>
<td>4.758</td>
<td>6.068</td>
<td>5.388</td>
<td>6.018</td>
<td>5.736</td>
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<tr>
<td>CASPT2</td>
<td>4.03</td>
<td>4.56</td>
<td>5.39</td>
<td>5.53</td>
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<tr>
<td>“best”</td>
<td>4.07, 4.0</td>
<td>4.45, 4.7</td>
<td>5.50, 5.52</td>
<td>5.28, 5.22</td>
<td>5.93, 5.55</td>
<td>5.89</td>
</tr>
<tr>
<td>“best”</td>
<td>4.0</td>
<td>4.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Performance of functionals in TDDFT

Study of various functionals over a set of 500 organic compounds, 700 excited singlet states

Typical success of TDDFT for excited states

- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5
- Vibrational frequencies good to 5
- Cost scales as $N^2$, vs $N^5$ for CCSD
- Available now in your favorite quantum chemical code
Current challenges in TDDFT

- Rydberg states - know what to do
- Polarizabilities of long-chain molecules
- Optical response of solids
- Double excitations
- Long-range charge transfer
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Extracting $E_{XC}[n]$ from TDDFT

From the fluctuation-dissipation theorem:

$$E_{XC}[n] = -\frac{1}{2} \int_{0}^{1} d\lambda \int d^3r \int d^3r' \frac{1}{|r - r'|} \times$$

$$\int_{0}^{\infty} \frac{d\omega}{\pi} \left\{ \chi_{\lambda}[n](rr'\omega) + n(r)\delta(r - r') \right\}$$

Plug in ground-state $n(r)$ to obtain $E_{XC}$.

- Combine with TDDFT Dyson-like equation to get new approximations from old functionals, but demanding response calculation.
- For separated systems, gives van der Waals coefficients.
- Approximate frequency integration and factorization of response functions yields Langreth-Lunqvist van der Waals function—a non-local ground-state density functional.

Lessons about TDDFT

- A way to extract electronic excitations using new theorem, from ground-state DFT calculation.

- Only real game in town for excitations in chemistry for decent-sized molecules.

- Cost comparable to single-point ground-state calculation.

- Uses adiabatic approximation.

- Problems for large systems due to locality of approximate functionals.