TDDFT

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Outline

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

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

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:

Ullrich and Maitra’s March 2010 APS TDDFT presentation
Conservation of density in time-dependent problems

- Current operator:

\[ \hat{j}(\mathbf{r}) = \frac{1}{2} \sum_j (\hat{p}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \hat{p}_j) \]

- Acting on wavefunction:

\[ j(r, t) = N \int d^3 r_2 \cdots \int d^3 r_N \Im\{\psi(r, r_2, \ldots, r_N; t) \nabla \psi^*(r, r_2, \ldots, r_N; t)\} \]

- Continuity:

\[ \frac{\partial n(r, t)}{\partial t} = -\nabla \cdot j(r, t) \]
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
  - PRL 80, 1280, (1998)
  - but see
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 trickier
- yields a new expensive way to get ground-state $E_{XC}$, but see
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

\[
v_S(r, t) = v(r, t) + \int d^3r' \frac{n(r, t)}{|r - r'|} + v_{XC}[n; \Psi_0, \Phi_0](r, t),
\]

where \(v_{XC}\) depends on memory:

- entire history of \(n(r, t)\)
- initial state \(\Psi_0\) and \(\Phi_0\).
Adiabatic approximation

- Almost all calculations use adiabatic approximation

- No standard improvement over this

- Use ground state functional $\nu_{\text{xc}}^{\text{GS}}$ on time-dependent $n(r, t)$:

  $$\nu_{\text{xc}}^{\text{adia}}[n](r, t) = \nu_{\text{xc}}^{\text{GS}}[n(t)](r).$$

- Often, error is due to ground-state approximation, *not* missing frequency dependence.
  
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)
Excitations from DFT

- Many approaches to excitations in DFT

- There is no HK theorem from excited-state density

- 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:

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

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)
Linear response in TDDFT

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

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

which implies

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

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 ground-state KS response function plus kernel:

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

with KS susceptibility

\[
\chi_S(\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} f_{jk} \frac{\phi_j(\mathbf{r})\phi^*_k(\mathbf{r})\phi^*_j(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0^+}
\]

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

$$\chi_S(rr'\omega) = 2 \sum_q \left\{ \frac{\Phi_q(r)\Phi_q^*(r')}{\omega - \omega_q + i0^+} - \frac{\Phi_q^*(r)\Phi_q(r')}{\omega + \omega_q - i0^+} \right\}.$$
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, $f_{XC}[n](rr\omega)$
- 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

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

and

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

and the eigenvectors $\nu_q$ determine the optical strength.

KS response

![Graph showing excitation energies and their corresponding levels for KS and Exact TDDFT methods.](image-url)
Benzene is the fruitfly of TDDFT

**Case study: Naphthalene**

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


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**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>BP86</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>
</tr>
<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>
</tr>
<tr>
<td></td>
<td><strong>Pure density functionals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</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>
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<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/TZVP/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>
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</thead>
<tbody>
<tr>
<td>CIS</td>
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<td>7.038</td>
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<td>5.862</td>
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<td>CC2</td>
<td>4.376</td>
<td>4.758</td>
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<td>5.838</td>
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<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>exp.</td>
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<td>4.45, 4.7</td>
<td>5.50, 5.52</td>
<td>5.28, 5.22</td>
<td>5.63, 5.55</td>
<td>5.89</td>
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<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 (Turbomole)
Current challenges in TDDFT

- Rydberg states
  - Wasserman and Burke, PRL 95, 163006, (2005)
  - Wasserman, Maitra, and Burke, PRL 91, 263001, (2003)

- Double excitations

- Optical response of solids
  - Sharma et al., PRL 107, 186401 (2011)

- Long-range charge transfer
  - Stein, Kronik, and Baer, J. Am. Chem. Soc. 131, 2818 (2009)

- Polarizabilities of long-chain molecules
Extracting $E_{XC}[n]$ from TDDFT

From the fluctuation-dissipation theorem:

$$E_{XC}[n] = -\frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|r-r'|} \times$$

$$\int_0^\infty d\omega \frac{d\omega}{\pi} \left\{ \chi_\lambda[n](rr',\omega) + n(r)\delta(r-r') \right\}$$

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.