Time-dependent density functional theory (TDDFT)

Ralph Gebauer

Isfahan and Freiburg (my home town in Germany) are twin cities!
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Electronic excitations … what’s that?

End of self-consistent calculation

\[ k = 0.0000 \ 0.0000 \ 0.0000 \ (8440 \ PWs) \ \text{bands (ev)}: \]

\[-29.5187 \ -13.9322 \ -11.7782 \ -11.7782 \ -8.8699 \ -1.8882 \ -1.8882 \ -0.2057 \ 0.9409 \ 1.0554 \]

highest occupied, lowest unoccupied level (ev): \[-8.8699 \ -1.8882 \]

! total energy \[=\] \[-43.17760726 \text{ Ry} \]

---

Why single-particle states?

\[\Rightarrow\] concept of quasi-particles
Excitations: Charged vs Neutral

**Charged Excitations**
N -> N+1 (or N-1)  
(Photoemission Spectroscopy)

**Neutral Excitations**
N -> N  
(Optical and Dielectric Spectroscopy)

Inverse Photoemission  
Optical Absorption
Photoemission Spectroscopy

Optical Spectroscopy
Ab-initio approaches to excited states:

TDDFT (Time-dependent density functional theory): Neutral excitations

Many-body perturbation theory:
- \( \rightarrow \) GW (charged excitations)
- \( \rightarrow \) BSE (Bethe Salpeter equation) (neutral excitations)

Rules of thumb for using TDDFT

<table>
<thead>
<tr>
<th></th>
<th>RPA</th>
<th>ALDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Loss</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Optical Prop</td>
<td>ok but..</td>
<td>ok but..</td>
</tr>
<tr>
<td>Energy Loss</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Optical Prop</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
Framework: What is TDDFT all about?

1964: Hohenberg and Kohn: Density Functional Theory (DFT)
work in terms of electron density (instead of many-particle wavefunctions)
DFT is a ground state theory

1984: Runge and Gross: Time-Dependent Density Functional Theory (TDDFT)

\[
\text{Given } |\Psi(t=0)\rangle : \hat{V}(r, t) \Leftrightarrow n(r, t)
\]

like DFT, TDDFT is formally exact

Recall: Basic ground-state DFT

For practical calculations: Kohn-Sham framework

\[
n_{\sigma}(r) = \sum_{i}^{N_{\sigma}} |\phi_{i\sigma}(r)|^2
\]

The density is written in terms of Kohn-Sham orbitals which satisfy

\[
\left[-\frac{\nabla^2}{2} + V_{KS}[n_\uparrow, n_\downarrow](r)\right] \phi_{i\sigma}(r) = \epsilon_{i\sigma} \phi_{i\sigma}(r)
\]

\[
F[n_\uparrow, n_\downarrow] = T_\uparrow[n_\uparrow, n_\downarrow] + E_{\text{Hartree}} + E_{\text{xc}}[n_\uparrow, n_\downarrow]
\]

\[
E_{\text{Hartree}} = \frac{1}{2} \int d^3r \int d^3r' n_\uparrow(r) n_\uparrow(r') \frac{1}{|r - r'|}
\]

\[
E_{\text{xc}}^{\text{LDA}} = \int d^3r \int d^3r' n_{\text{xc}}^{\text{LDA}}(n_\uparrow(r), n_\downarrow(r))
\]
The Runge-Gross Theorem

Generalizing the HK theorem to time-dependent systems

There exists a one-to-one correspondence between the external $v(r,t)$ and the electron density $n(r,t)$, for systems evolving from a fixed many-body state.

Proof:

\[
\begin{align*}
|\Psi(\mathbf{r}_0)\rangle &= |\Psi'(\mathbf{r}_0)\rangle \equiv |\Psi_0\rangle \\
n(\mathbf{r},t_0) &= n'(\mathbf{r},t_0) \equiv n'(\mathbf{r}) \\
j(\mathbf{r},t_0) &= j'(\mathbf{r},t_0) \equiv j'(\mathbf{r})
\end{align*}
\]

Step 1: Different potentials $v$ and $v'$ yield different current densities $j$ and $j'$

Step 2: Different current densities $j$ and $j'$ yield different densities $n$ and $n'$

\[v(\mathbf{r},t) \neq v'(\mathbf{r},t) + c(t) \quad \Rightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)\]

Using TDDFT in practice

Finding an equivalent of the Kohn-Sham formalism

\[i\frac{\partial}{\partial t} \varphi_{i\sigma}(\mathbf{r},t) = \tilde{H}_{KS}^\sigma(\mathbf{r},t) \varphi_{i\sigma}(\mathbf{r},t)\]

With a time-dependent Hamiltonian:

\[\tilde{H}_{KS}^\sigma(\mathbf{r},t) = -\frac{\nabla^2}{2} + v_{KS}[n_\uparrow, n_\downarrow](\mathbf{r},t)\]

Density and potentials are now defined like:

\[n_{\sigma}(\mathbf{r},t) = \sum_i^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r},t)|^2\]

\[v_{\sigma}^{KS}[n_\uparrow, n_\downarrow](\mathbf{r},t) = v_{\sigma}(\mathbf{r},t) + \int d^3r' \frac{n(\mathbf{r'},t)}{|\mathbf{r} - \mathbf{r'}|} + v_{\sigma}^{\text{ext}}[n_\uparrow, n_\downarrow](\mathbf{r},t)\]
Which functional to use?

The easiest and probably most widely used functional is the Adiabatic Local Density Approximation (ALDA)

\[ v^{\text{ALDA}}_{\sigma}(r, t) = \frac{\partial}{\partial n_{\sigma}} \left[ n \rho_{\text{xc}}^{\text{unif}}(n_{\uparrow}, n_{\downarrow}) \right]_{n_{\sigma}=n_{\sigma}(r, t)} \]

TDDFT in real time:
(1996:Bertsch; 2001: Octopus code)

- Consider a general time-dependent perturbation:
  \[ V_{\text{pert}}(r, t) \]
- Obtain orbitals, charge density, and potentials by solving the Schrödinger equation explicitly in real time:
  \[ \psi_j(t + \Delta) = \exp \left( -i H (t + \frac{\Delta}{2}) \right) \psi_j(t) \]
  \text{(Nonlinear TD Schrödinger equation)}
- Can be used for linear response calculations, or for general TD non-linear problems.
A first application: Photochemistry

- Recent experimental progress made it possible to produce ultra-short intense laser pulses (few fs)
- This allows one to probe bond breaking/formation, charge transfer, etc. on the relevant time scales
- Nonlinear real-time TDDFT calculations can be a valuable tool to understand the physics of this kind of probe.
- Visualizing chemical bonds: Electron localization function

Nonlinear optical response

- Electron localization function:

\[
ELF(r, t) = \frac{1}{1 + \left[ D_{\sigma}(r, t)/D_{\sigma}^0(r, t) \right]^2}
\]

\[
D_{\sigma}(r, t) = \tau_{\sigma}(r, t) - \frac{1}{4} \frac{[\nabla n_{\sigma}(r, t)]^2}{n_{\sigma}(r, t)} - \frac{j_{\sigma}^2(r, t)}{n_{\sigma}(r, t)}
\]
Example: Ethyne C$_2$H$_2$
How can we calculate optical spectra?

Consider a perturbation $\delta V$ applied to the ground-state system:

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

The induced dipole is given by the induced charge density:

$$d(t) = \int d^3r \delta n(r, t) \hat{r}$$

Consider the perturbation due to an electric field:

$$\delta V(r, t) = -eE_{\text{ext}}(t) \cdot \hat{r}$$

How can we calculate optical spectra?

The dipole susceptibility is then given by:

$$d(t) = \int dt' \alpha(t - t') E_{\text{ext}}(t')$$

The experimentally measured strength function $S$ is related to the Fourier transform of $\alpha$:

$$S(\omega) = \frac{2m}{\pi e^2 \hbar} \omega \text{Im} \alpha(\omega)$$

In practice: We take an E-field pulse $E_{\text{ext}} = E_0 \delta(t)$, calculate $d(t)$, and obtain the spectrum $S(\omega)$ by calculating

$$d(\omega) = \int_0^{\infty} dt e^{i\omega t - \delta t} d(t)$$
A typical dipole-function $d(t)$ …

… and the resulting spectrum
Linear response formalism in TDDFT:

- Calculate the system's ground state using DFT
- Consider a monochromatic perturbation:
  \[ V_{\text{pert}}(\mathbf{r}, t) = \psi_0(\mathbf{r}) (\exp(i\omega t) + \exp(-i\omega t)) \]
- Linear response: assume the time-dependent response:
  \[ \psi_j(t) = e^{-i\omega t} \left( \psi_j^0 + \delta \psi_j^+ e^{i\omega t} + \delta \psi_j^- e^{-i\omega t} \right) \]
  \[ \delta n(\mathbf{r}, t) = \delta n^+ (\mathbf{r}) e^{i\omega t} + \delta n^- (\mathbf{r}) e^{-i\omega t} \]
  \[ \delta V(\mathbf{r}, t) = V_{\text{pert}}(\mathbf{r}, t) + \delta V_{\text{SCF}}(\mathbf{r}) e^{i\omega t} + \delta V_{\text{SCF}}(\mathbf{r}) e^{-i\omega t} \]
- Put these expressions into the TD Schrödinger equation

\[ \omega \delta \psi_\uparrow^0(r) = \left( H_{KS}^0 - e_\uparrow^0 \right) \delta \psi_\uparrow(r) + \hat{P}_\rho \left( \delta V_{\text{SCF}}^+(\mathbf{r}) + V_{\text{pert}}(\mathbf{r}) \right) \psi_\uparrow^0(\mathbf{r}) \]
\[-\omega \delta \psi_\downarrow^0(r) = \left( H_{KS}^0 - e_\downarrow^0 \right) \delta \psi_\downarrow(r) + \hat{P}_\rho \left( \delta V_{\text{SCF}}^-(\mathbf{r}) + V_{\text{pert}}(\mathbf{r}) \right) \psi_\downarrow^0(\mathbf{r}) \]

Now define the following linear combinations:

\[ x_\uparrow(r) = \frac{1}{2} (\delta \psi_\uparrow(r) + \delta \psi_\downarrow(r)) \]
\[ y_\uparrow(r) = \frac{1}{2} (\delta \psi_\downarrow(r) - \delta \psi_\uparrow(r)) \]
Linear response TD-DFT essentially means solving a non-hermitean eigenvalue equation of dimension $2N_v \times N_c$.

**Standard way to proceed (Casida's equations):**

- Solve the time-independent problem to completely diagonalize the ground-state Hamiltonian.
  
  [Some computer time can be saved by limiting the diagonalization to the lower part of the spectrum]

- Obtain as many eigenstates/frequencies of the TD-DFT problem as needed (or as possible).
  
  [Some computer time can be saved by transforming the non-hermitean problem to a hermitean one (e.g. Tamm-Dancoff approx.)]
Eigenstates of very large matrices: Davidson methods

Let H be a hermitean matrix, or large dimension, and we look for few low-lying eigenstates.

1. Select a set of trial eigenvectors \( \{ \mathbf{b}_i \} \) (typically 2x the number of desired eigenstates)

2. Calculate the representation of H in the space of trial vectors:

\[
G_{ij} = \langle \mathbf{b}_i \mid H \mid \mathbf{b}_j \rangle
\]

3. Diagonalize G (M is the number of desired eigenstates):

\[
G \mathbf{X} = \mathbf{X} \Lambda
\]

4. Create new trial vectors \( \mathbf{c}^k \):

\[
\mathbf{c}^k = \sum_i \alpha_i^k \mathbf{b}_i
\]

5. Calculate the residue \( \mathbf{r}^k \):

\[
\mathbf{r}^k = \sum_i (H - \lambda^k) \mathbf{c}^k
\]

6. Using an approximation \( \tilde{H} \) for \( H \), calculate the correction vectors :

\[
\delta^k = (\lambda^k - \tilde{H})^{-1} \mathbf{r}^k
\]

7. Orthogonalize the \( \{ \delta^k \} \) to the \( \{ \mathbf{b}_i \} \) and get new trial eigenvectors.

Example: Benzene molecule

<table>
<thead>
<tr>
<th>#</th>
<th>Energy (Ry)</th>
<th>total</th>
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<tbody>
<tr>
<td>0.38112073E+00</td>
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<td>0.51361736E+00</td>
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</tbody>
</table>
Advantages:

One obtains not only the frequency (and oscillator strength), but the full eigenvector of each elementary excitation.

[Info can be used for spectroscopic assignments, to calculate forces, etc]

Disadvantages:

One obtains not only the frequency (and oscillator strength), but the full eigenvector of each elementary excitation.

[Info is often not needed, all the information is immediately destroyed after computation]

Computationally extremely demanding (large matrices to be diagonalized)

Time-dependent density functional perturbation theory (TDDFPT)

Remember: The photoabsorption is linked to the dipole polarizability $\alpha(\omega)$

$$d(t) = \int dt' \alpha(t - t') \mathcal{E}(t')$$

If we choose $\mathcal{E}(t') = \mathcal{E}_0 \delta(t')$, then knowing $d(t)$ gives us $\alpha(t)$ and thus $\alpha(\omega)$.

Therefore, we need a way to calculate the observable $d(t)$, given the electric field perturbation $\mathcal{E}_0 \delta(t)$. 
Consider an observable $A$:

$$A(t) = \sum_i \left( \langle \delta \psi_i(t) | \hat{A} | \psi_i^0 \rangle + \langle \psi_i^0 | \hat{A} | \delta \psi_i(t) \rangle \right)$$

Its Fourier transform is:

$$\hat{A}(\omega) = \sum_i \left( \langle \psi_i^0 | \hat{A} | \delta \psi_i^{-}(\omega) \rangle + \langle \psi_i^0 | \hat{A} | \delta \psi_i^{+}(\omega) \rangle \right)$$

$$= 2 \sum_i \langle \psi_i^0 | \hat{A} | x_i(\omega) \rangle$$

$$= 2 \langle \alpha, 0 | x, y \rangle$$

Recall: $$(\omega - \mathcal{L}) | x, y \rangle = | 0, v \rangle$$

Therefore:

$$\hat{A}(\omega) = 2 \langle \alpha, 0 | (\omega - \mathcal{L})^{-1} | 0, v \rangle$$

Thus in order to calculate the spectrum, we need to calculate one given matrix element of $(\omega - \mathcal{L})^{-1}$. 
In order to understand the method, look at the hermitian problem:

$$\langle \psi | (\omega - H)^{-1} | \psi \rangle$$

Build a Lanczos recursion chain:

$$\phi_{-1} = 0$$
$$\phi_0 = |\psi\rangle$$

$$b_{n+1}\phi_{n+1} = (H - a_n) \phi_n - b_n \phi_{n-1}$$

$$\langle \phi_{n+1} | \phi_{n+1} \rangle = 1$$

$$a_n = \langle \phi_n | H | \phi_n \rangle$$

$$H = \begin{pmatrix}
    a_0 & b_1 & 0 & \cdots & 0 \\
    b_1 & a_1 & b_2 & 0 & \cdots \\
    0 & b_2 & a_2 & \cdots & 0 \\
    \vdots & 0 & \cdots & \cdots & b_n \\
    0 & \cdots & 0 & b_n & a_n
\end{pmatrix}$$

$$\omega - H = \begin{pmatrix}
    \omega - a_0 & -b_1 & 0 & \cdots & 0 \\
    -b_1 & \omega - a_1 & -b_2 & 0 & \cdots \\
    0 & -b_2 & \omega - a_2 & \cdots & 0 \\
    \vdots & 0 & \cdots & \cdots & -b_n \\
    0 & \cdots & 0 & -b_n & \omega - a_n
\end{pmatrix}$$
Recall:

Therefore:

Use a recursion to represent $L$ as a tridiagonal matrix:

$$L = \begin{pmatrix} a_1 & b_1 & 0 & & \\ c_1 & a_2 & b_2 & & \\ 0 & c_2 & a_3 & b_3 & \\ & & \ddots & \ddots & \ddots \\ & & & c_{N-1} & a_N \end{pmatrix}$$

Back to the calculation of spectra:

Recall: 

$$\langle \omega - L | x, y \rangle = |0, v\rangle$$

Therefore:

$$\tilde{A}(\omega) = 2 \langle a, 0 | (\omega - L)^{-1} | 0, v \rangle$$

Use a recursion to represent $L$ as a tridiagonal matrix:
And the response can be written as a continued fraction!

\[ \tilde{A}(\omega) = 2 \langle a, 0 | (\omega - L)^{-1} | 0, v \rangle \]

\[ = \frac{1}{\omega - a_1 + b_2 \omega - c_2 + \cdots} \]

How does it work?
Benzene spectrum

Plum: 1000
Red: 2000
Green: 3000
Black: 6000
Spectrum of $\text{C}_{60}$

- Black: 4000
- Blue: 3000
- Green: 2000

Spectrum of $\text{C}_{60}$: Ultrasoft pseudopotentials

- Black: 2000
- Red: 1000
Speeding up convergence: Looking at the Lanczos coefficients

![Diagram showing Lanczos iteration and coefficients](image)

- Even coefficients
- Odd coefficients

04/05/16
Effect of the terminator:

No terminator:

Effect of the terminator:

No terminator:
Effect of the terminator:

No terminator:

![Graph showing the effect of terminator on absorption strength with energy in eV on the x-axis and absorption strength on the y-axis for 500, 1000, 1500, and 2500 iterations.]

Effect of the terminator:

No terminator:

![Graph showing the effect of terminator on absorption strength with energy in eV on the x-axis and absorption strength on the y-axis for 500, 1000, 1500, and 2500 iterations.]

Effect of the terminator:

No terminator:  
Terminator:

Energy [eV]  
Absorption strength

500 iterations  
1000 iterations  
1500 iterations  
2500 iterations

Effect of the terminator:

No terminator:  
Terminator:

Energy [eV]  
Absorption strength

800 iterations  
2500 iterations
Analyzing the spectrum

Example of a squaraine dye:

Can we analyze given features of the spectrum in terms of the electronic structure?

YES!

It is possible to compute the response charge density for any given frequency using a second recursion chain.

Convergence of the TDDFPT spectrum

Isolated squaraine molecule

- converged spectrum
- 500 Lanczos iterations
- 1000 Lanczos iterations
- 2000 Lanczos iterations
Conclusions

• TDDFT as a formally exact extension of ground-state DFT for electronic excitations
• Allows to follow the electronic dynamics in real time
• Using TDDFT in linear response allows one to calculate spectra
Thanks to:

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