**Time-dependent density functional theory in attoscience: Promises and Challenges**

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http://dft.rutgers.edu/
(DFT book, TDDFT book, Benasque)

**Theme**

- DFT is method-of-choice for solids and large molecules
- TDDFT includes response to external TD fields
- Both enormously successful and popular
- So why aren’t all calculations DFT?
**Ground-state DFT**

What atoms, molecules, and solids exist, and what are their properties?

- DFT is an utterly ALIEN way to treat interacting electrons.
- Many users, few developers.
- Often misleading, sometimes downright nasty.
- But..
  - runs faster and is far more accurate than Hartree-Fock!
**DFT possibilities**

**Crambin**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS energy</td>
<td>7.40 h</td>
</tr>
<tr>
<td>GS gradient</td>
<td>1.56 h</td>
</tr>
<tr>
<td>TURBOMOLE V5-7-1, RIdFT/TPSS/SV(P), 1.5 GHz</td>
<td>i7 Itanium</td>
</tr>
</tbody>
</table>

645 atoms, 5587 basis functions


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**What are the Kohn-Sham equations?**

- The Kohn-Sham equations (1965) are just the Schrödinger equation for fictitious, independent electrons.
- In principle, they produce the exact density.
- All modern DFT calculations are for these fictitious electrons, so NEVER find true wavefunction.
Kohn-Sham equations (1965)

\[ \frac{1}{2} \nabla^2 \phi_i(r) + V_s(r) \phi_i(r) = \varepsilon_i \phi_i(r) \]

\[ \rho(r) = \sum_{i=1}^{N} \phi_i(r)^2 = \text{ground-state density of interacting system} \]

\[ V_s(r) = V_{\text{xc}}(\rho(r)) + \int \frac{\rho(r')}{|r-r'|} dr' \]

\[ \rho(r) = V_s(r) \]

He atom in Kohn-Sham DFT

Dashed-line: EXACT KS potential
**In reality...**

- Must approximate a small unknown piece of the functional, the exchange-correlation energy $E_{xc}[\rho]$.

- Early 90’s:
  - Approximations became accurate enough to be useful in chemistry
  - 98 Nobel to Kohn and Pople

**Functional soup**

- **Good:** choose one functional and stick with it (e.g., LDA or PBE or B3LYP).

- **Bad:** Run several functionals, and pick ‘best’ answer.

- **Ugly:** Design your own functional with 2300 parameters.
**Time-dependent DFT**

- New theorem (Runge-Gross 1984) applied to time-dependent Schrödinger equation, showing potential a functional of $\rho(r,t)$.

- Define TD Kohn-Sham equations for independent electrons producing right $\rho(r,t)$.

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**TDDFT publications in recent years**

Search ISI web of Science for topic ‘TDDFT’

- Warning! By 2300, entire mass of universe will be TTDFT papers
Recent reviews of TDDFT

Time-dependent density functional theory: Past, present, and future
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Time-dependent density functional theory (TDDFT) is presently enjoying ever-increased popularity in quantum chemistry, as a useful tool for making electronic excited state energies. This article discusses the TDDFT method and its advantages, as well as its limitations. Particular emphasis is given to the role of the exchange-correlation functional. The outlook for the future is also considered. © 2005 American Institute of Physics. [DOI: 10.1063/1.1852449]

Annual Reports in Comp Chem 1

Chapter XX. Time-dependent density functional theory in quantum chemistry

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Density functional methods for excited states: equilibrium structure and electronic spectra
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**TD Kohn-Sham equations**

- Time-dependent KS equations:

\[
\left\{ \frac{-1}{2} \nabla^2 + v_s(\mathbf{r}t) \right\} \phi_i(\mathbf{r}t) = i \frac{d \phi_i(\mathbf{r}t)}{dt}
\]

- Density:

\[
\rho(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2
\]

- XC potential:

\[
v_s(\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) + \int d^3r' \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[n, \Psi(0), \Phi(0)](\mathbf{r}t)
\]

- Depends on entire history (MEMORY)

- Initial state(s) dependence (MEMORY)

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**Overview of ALL TDDFT**

1. General Time-dependent Density Functional Theory
   - Any e⁻ system subjected to any $v_{\text{ext}}(\mathbf{r}t)$
   - Only unknown: $v_{\text{xc}}[\rho](\mathbf{r}t)$
   - Treat atoms and molecules in INTENSE laser fields

2. TDDFT linear response to weak fields
   - Linear response:

\[
\delta \rho(\mathbf{r}t) = \int d^3r' \int dt' \chi(\mathbf{r}, \mathbf{r}', t-t') \delta \rho(\mathbf{r}'t')
\]

- Only unknown:

\[
v_{\text{xc}}(\mathbf{r}t) \quad \text{near ground state}
\]

\[
v_{\text{xc}}[\rho_0 + \delta \rho](\mathbf{r} \omega) = v_{\text{xc}}[\rho_0](\mathbf{r}) + \int d^3r' f_{\text{xc}}[\rho_0](\mathbf{r} \omega) \delta \rho(\mathbf{r}' \omega)
\]

- Treat electronic excitations in atoms + molecules + solids

3. Ground-state Energy from TDDFT
   - Fluctuation-dissipation theorem: Exc from susceptibility
   - Van der Waals; seamless dissociation

**Basic approximation: ALDA** $v_{\text{xc}}^{\text{unif}}(\rho(\mathbf{r}t))$
**TDDFT linear response**

- Probe system with AC field of freq $\omega$
- Ask at what $\omega$ you find a self-sustaining response
- That’s a transition frequency!
- Need a new functional, the XC kernel, $f_{xc}[\rho_0](r,r',\omega)$
- Almost always ignore $\omega$-dependence (called adiabatic approximation)
- Can view as corrections to KS response

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**Linear response in TDDFT**

Key quantity is susceptibility

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

Dyson-like equation for a susceptibility:

$$\chi(rr',\omega) = \chi_{s}(rr',\omega) + \int d^3 r_1 \int d^3 r_2 \chi_{s}(rr,\omega) \left[ \frac{1}{|r_1 - r_2|} + f_{xc}[\rho_0](r_1, r_2, \omega) \right] \chi(r_2, r' \omega)$$

Two inputs: KS susceptibility

$$\chi_{s}(rr',\omega) = \sum_{jk} (f_k - f_j) \phi_j(r) \phi_k^*(r) \phi_k^*(r') \phi_j(r')$$

and XC kernel

$$f_{xc}(r,r',t-t') = \left. \frac{\delta n_{xc}(r,t)}{\delta p(r',t')} \right|$$
Methodology for TDDFT

- In general: Propagate TDKS equations forward in time, and then transform the dipole moment, eg. Octopus code

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
**TDDFT from exact KS potential**

Open symbols are triplet, closed are singlet.

**Strong fields: Promises and challenges**

1. HHG seems to work well, but need orbital dependent potentials.

2. Difficulty with eg multiple ionization.
**Simple problem with ground-state potential**

- Density functionals usually have bad potentials!

- Orbital-dependent functionals are much better.

**KS potential in LDA**
KS potential in LDA-SIC

He atom

HHG for He, Ullrich et al, 96

Figure 1: Harmonic spectrum for He at λ = 616nm and J = \(3.5 \times 10^{14}\) W/cm². The squares represent experimental data taken from Ref. [26] normalised to the value of the 33rd harmonic of the calculated spectrum. The experiment was performed with a peak intensity of \(1.4 \times 10^{14}\) W/cm².
**Improvement over SAE**

Tong and Chu, PRA 1998

HGH in He atom, $\lambda=246\text{nm}, I=3\times10^{15}\text{W/cm}^2$

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**Two key differences for multiple ionization**

- The XC potential, far from the ground-state, is not well-approximated by standard functionals.
- The KS wavefunction can be very different from the true wavefunction.
Pumping to an excited state

- Imagine exact TDKS in which He atom is pumped into 2p excited state.
- But ALWAYS stays in single doubly-occupied orbital.
- If stationary, KS potential is highly non-spherical (Maitra et al PRL 2002).

Exact KS potential for multiple ionization

- Do exact calculation, and invert TDKS equations (Hessler et al, PRL 99) to find \( v_s(r,t) \).
- See what’s going on, and try to approximate.
**TDKS potential during ionization**

From Lein and Kummel, PRL 05: Step in correlation potential as one electron leaves

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**Multiple ionization from model TDKS potential**

FIG. 3. Probabilities for laser-induced single- ionization (open symbols) and double ionization (filled symbols) from TDDFT (circles) and TDHF (squares) calculations.
**But...still not accurate!**

1D Helium atom (with soft Coulomb interaction)


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λ = 780 nm
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In the meantime...

- Margaret Murnane showed neat results for probing molecular vibrations using HHG.

- Zac Walters did calculation for intensities, using static-exchange for scattering in recombination step, showing how all modes comparable.
Ideas

- Build on good results from linear response, e.g., scattering theory. Where can they be used inside more demanding calculations?

- Use dipole matrix elements from lin. resp. in strong field calculations (Jan Werschnik, Berlin, for quantum control)

- A thought: almost always want evolution in same time-dependent field (an electric field).
Lessons

- DFT best when physics is understood, but computational accuracy is crucial.
- Whenever DFT used in new field, must take present approximations, and see what works and what doesn’t.
- For failures, usually can rationalize why they fail, but can take a while to see how to build physics into better functionals.
- But, most important, its absolutely necessary for interface with all other DFT calculations/experience.

Tricks: eg, double excitations

- In linear response, can show adiabatic approximation only includes single-excitations.
- We showed how to construct $f_{xc}(\omega)$ to yield doubles.
- New TDDFT ideas should be tested in linear regime.
Unlikely, but not impossible