Time-dependent density-functional theory for strong-field electron dynamics

Outline

1. TDDFT in a nutshell
2. Observables and Applications
   - Atoms in strong fields
   - Nonlinear electron dynamics in metal clusters
   - The Heilme knee: worst-case scenario for TDDFT
3. The time-dependent xc potential
   - Asymptotic behavior
   - Discontinuity
   - Beyond the adiabatic approximation
Static and time-dependent density-functional theory

Hohenberg and Kohn (1964): \[ n(\vec{r}) \iff \nabla(\vec{r}) \]

All physical observables of a static many-body system are, in principle, functionals of the ground-state density \[ n(\vec{r}) \].

most modern electronic-structure calculations use DFT.

Runge and Gross (1984): \[ n(\vec{r}, t) \iff \nabla(\vec{r}, t) \]

Time-dependent density \[ n(\vec{r}, t) \] determines, in principle, all time-dependent observables.

TDDFT: universal approach for electron dynamics.

Time-dependent Kohn-Sham equations (1)

Instead of the full N-electron TDSE,

\[
i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, ..., \vec{r}_N, t) = \left( \hat{T} + \hat{V}_{\text{ext}}(t) + \hat{W}_{\text{e-e}} \right) \Psi(\vec{r}_1, ..., \vec{r}_N, t)
\]

one can solve N single-electron TDSE's,

\[
i\hbar \frac{\partial}{\partial t} \phi_j(\vec{r}, t) = \left( -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{KS}}(\vec{r}, t) \right) \phi_j(\vec{r}, t)
\]

such that the time-dependent densities agree:

\[
\int dr_2 ... \int dr_N |\Psi(\vec{r}, \vec{r}_2, ..., \vec{r}_N, t)|^2 = n(\vec{r}, t) = \sum_{j=1}^N |\phi_j(\vec{r}, t)|^2
\]
The TDKS single-particle effective potential is

$$V_{KS}(\vec{r}, t) = V_{ext}(\vec{r}, t) + \int d\vec{r}' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + V_{xc}[n](\vec{r}, t)$$

Hartree exchange-correlation

$$V_{xc}[n](\vec{r}, t)$$ is an (unknown) functional of the density, which needs to be approximated (more later).

The TDKS equations give the exact density, but not the wave function!

$$\Phi_{KS}(\vec{r}_1, ..., \vec{r}_N, t) = \frac{1}{\sqrt{N}} \det \{ \varphi_j(\vec{r}_j, t) \} \neq \Psi(\vec{r}_1, ..., \vec{r}_N, t)$$

---

**TDDFT: a 3-step process**

1. Prepare the initial state, usually the ground state, by a static DFT calculation. This gives the initial orbitals: $$\varphi_j(\vec{r}, 0)$$

2. Solve TDKS equations self-consistently, using an approximate time-dependent xc potential which matches the static one used in step 1. This gives the TDKS orbitals: $$\varphi_j(\vec{r}, t) \rightarrow n(\vec{r}, t)$$

3. Calculate the relevant observable(s) as a functional of $$n(\vec{r}, t)$$
“Easy” and “tough” observables in TDDFT

- Dipole moment: \( d(t) = \int dr \ z \ n(\vec{r}, t) \)

\[ \Rightarrow \text{HHG power spectrum: } |d(\omega)|^2 \]

- Total number of escaped electrons:

\[ N_{\text{esc}}(t) = N - \int_{\text{box}} dr \ n(\vec{r}, t) \]

**Easy**

- Photoelectron spectra and ATI
- Ion probabilities
- Transition probabilities \( |S_{i \rightarrow f}|^2 \) (J. Burgdörfer)

More difficult

HHG in Helium (3D)

\( \lambda = 616 \text{ nm} \)
\( I = 3.5 \times 10^{14} \text{ W/cm}^2 \)

Calculation: TDDFT exact exchange

Experiment: Miyazaki and Sakai (1992)
**HHG in Neon: all-electron calculation**

\[ \lambda = 248 \text{ nm} \]

Experiment: Sarukura et al., PRA 43, 1669 (1991) at \( 4 \times 10^{17} \text{ W/cm}^2 \)

**TDKS calculation for all outer-shell orbitals.**


---

**Neon: Kohn-Sham orbital norms**

\[ \lambda = 248 \text{ nm} \]

\[ I = 3 \times 10^{15} \text{ W/cm}^2 \]

\[ N_j(t) = \int_{box} dr |\varphi_j(\vec{r},t)|^2 \]

- **TDKI (“exact” exchange)**
- **ALDA**

The KS orbital norms have no rigorous physical meaning, but can be a useful diagnostic tool.
Neon: failure of the SAE approximation

2p₀ orbital dominates ionization and HHG, but gives spurious resonance

\[ N_{2p₀}(t) \]

Diatomie molecules

O₂, fixed nuclei, 800 nm pulses, 1x10¹⁴, 3x10¹⁴, 5x10¹⁴ W/cm²

X. Chu and S.-I Chu
PRA 63, 023411 (2001)
PRA 64, 063404 (2001)
PRB 70, 061402 (2004)

D. Dundas and J.M. Rost
PRA 71, 013421 (2005)
Na$_9^+$ cluster: the Mie plasmon


Na$_9^+$ in spherical jellium model

Cluster multiphoton ionization

Resonant ionization with Plasmon mode as “doorway” state


Na_{12} Coulomb explosion

Calvayrac, Reinhard, and Suraud (1998)

50 fs laser pulse

Na_{12} \rightarrow Na_{12}^{3+}

Non-BO dynamics

ions

electroes
**Photoelectron spectra and ATI**

A. Pohl, P.-G. Reinhard, E. Suraud, 
PRL 84, 5090 (2000)

\[ P_{KS}(E) = \sum_j \left| \varphi_j(\vec{r}_a, E) \right|^2 \]

(Fourier transform of KS orbitals)


\[ P(E, t) = n(t\sqrt{2(E \pm \Delta E)}) \]

(time-of-flight analysis of density at large t)

---

**ATI spectra of Na\(_4\) in two-color pulses**

H.S. Nguyen, A.D. Bandrauk, 

2-color 25 fs pulses:
- 1064 nm, 6x10\(^{12}\) W/cm\(^2\)
- 532 nm, 1.5x10\(^{12}\) W/cm\(^2\)

ATI cutoffs at 20-40 U\(_p\)
Ion probabilities

Exact definition:

\[ P^0(t) = \int_{box}^{box} d^3r_1 \cdots \int_{box}^{box} d^3r_N |\Psi(\vec{r}_1, \ldots, \vec{r}_N, t)|^2 \]

\[ P^{+1}(t) = N \int_{box}^{box} d^3r_1 \int_{box}^{box} d^3r_2 \cdots \int_{box}^{box} d^3r_N |\Psi(\vec{r}_1, \ldots, \vec{r}_N, t)|^2 \]

\[ \vdots \]

\[ P^{+n}(t) \] is the probability to find the system in charge state +n

\[ P^{+n}_{KS}(t) : \] evaluate the above formulas with \( \Phi_{KS}(\vec{r}_1, \ldots, \vec{r}_n, t) \)

A deadly sin in TDDFT!

KS Ion probabilities of a Na\textsubscript{9}+ cluster

25-fs pulses
0.87 eV photons

KS probabilities exact for

\( N_{\text{esc}} \rightarrow 0, \quad N_{\text{esc}} \rightarrow N \)
Ion probabilities for 2-electron systems

\[
P^0(t) = \frac{1}{2} \int_{\text{box}} d^3r_1 \int_{\text{box}} d^3r_2 \ n(\vec{r}_1, t)n(\vec{r}_2, t)g(\vec{r}_1, \vec{r}_2, t)
\]

\[
P^{+1}(t) = 2N(t) - 2P^0(t), \quad P^{+2}(t) = 1 - P^{+1}(t) - P^0(t)
\]

\[
N(t) = \frac{1}{2} \int_{\text{box}} d^3r \ n(\vec{r}, t), \quad g[n](\vec{r}_1, \vec{r}_2, t) = \frac{2|\Psi(\vec{r}_1, \vec{r}_2, t)|^2}{n(\vec{r}_1, t)n(\vec{r}_2, t)}
\]

pair correlation function

Using x-only limit, \(g(r_1, r_2, t) = 1/2\), gives the KS probabilities:

\[
P_{KS}^0 = N(t)^2, \quad P_{KS}^{+1}(t) = 2N(t)[1 - N(t)], \quad P_{KS}^{+2} = [1 - N(t)]^2
\]

Double ionization of He at 780 nm


![Graphs showing double ionization of He at 780 nm](image)

TDHF \hspace{1cm} KS ion probs. with exact density
Double ionization of He at 248 nm


- TDHF
- KS ion probs. with exact density

Nonsequential double ionization

- Worst-case scenario for TDDFT: highly correlated 2-electron dynamics described via 1-particle density

- Not a fundamental failure of TDDFT! Our present-day functionals are simply not good enough.

- TDDFT works better for sequential ionization.
The time-dependent xc potential

\[ i\hbar \frac{\partial}{\partial t} \varphi_j(t) = \left( -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ext}}(t) + V_H(t) + V_{xc}(t) \right) \varphi_j(t) \]

**Adiabatic approximation**: just take any xc potential from ground-state DFT and plug in time-dependent density.

\[ V_{xc}^{ALDA}(\vec{r}, t) = V_{xc}^{LDA}(n(\vec{r}, t)) \]

- depends only on density \( n \): same space-time point
- OK for **SLOW** variations in \( \vec{r} \) and \( t \).

The time-dependent xc potential: requirements

\[
\begin{aligned}
\text{quasi-static} & \quad \text{long-range asymptotic behavior} \\
\text{truly dynamic} & \quad \text{discontinuity as particle number changes} \\
& \quad \text{non-adiabatic: memory of previous history}
\end{aligned}
\]
Asymptotics of $V_{xc}$: ground state

C.J. Umrigar and X. Gonze, PRA 50, 3827 (1994)

Exchange–Correlation Potentials of Helium

Correct asymptotics:
- bound negative ions and KS Rydberg states
- $\varepsilon_{HOMO} = I_p$

Asymptotics of $V_{xc}$: excitation energies

| Atom | $\Delta \varepsilon_{\text{LDA}}$ | $\Omega_{\text{LDA/ALDA}}$ | $\Delta \varepsilon_{\text{EXX}}$ | $\Omega_{\text{EXX/PGG}}$ | $\Omega_{\text{exp}}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.129</td>
<td>0.200</td>
<td>0.130</td>
<td>0.196</td>
<td>0.194</td>
</tr>
<tr>
<td>Mg</td>
<td>0.125</td>
<td>0.176</td>
<td>0.117</td>
<td>0.164</td>
<td>0.160</td>
</tr>
<tr>
<td>Ca</td>
<td>0.088</td>
<td>0.132</td>
<td>0.079</td>
<td>0.117</td>
<td>0.108</td>
</tr>
<tr>
<td>Zn</td>
<td>0.176</td>
<td>0.239</td>
<td>0.157</td>
<td>0.211</td>
<td>0.213</td>
</tr>
<tr>
<td>Sr</td>
<td>0.082</td>
<td>0.121</td>
<td>0.071</td>
<td>0.105</td>
<td>0.099</td>
</tr>
<tr>
<td>Cd</td>
<td>0.152</td>
<td>0.214</td>
<td>0.135</td>
<td>0.188</td>
<td>0.199</td>
</tr>
</tbody>
</table>

Asymptotics of $V_{xc}$: strong-field properties


![Graph showing $N_{esc}(t=100\, \text{fs})$ vs. Photon Energy (eV)]

- minor quantitative differences between ALDA and SIC, EXX for multiphoton ionization or HHG

---

The time-dependent $xc$ potential: requirements

- long-range asymptotic behavior
- discontinuity as particle number changes
- non-adiabatic: memory of previous history
Discontinuity in $V_{xc}$: ground state

J.P. Perdew et al., PRL 49, 1691 (1982)

\[
\begin{align*}
V_{xc}(\vec{r}) & \quad V_{xc}(\vec{r}) + \Delta \\
N - \delta & \quad N & \quad N + \delta
\end{align*}
\]

- proper description of dissociation of heternuclear molecules
- band gap in solids include contribution from $\Delta$

Discontinuity in $V_{xc}$: ionization


Exact 1D Holium: $n(x, t) \Rightarrow V_{xc}(x, t)$

As the atom ionizes, a step develops in the correlation potential.
The time-dependent xc potential: requirements

- long-range asymptotic behavior
- discontinuity as particle number changes
- non-adiabatic: memory of previous history

\[ V_{xc}[n](\vec{r}, t) \text{ depends on previous history (} t' < t) \]

Nonadiabatic xc potentials

- **Linear response**: frequency-dependent xc kernel \( f_{xc}(\vec{r}, \vec{r}', \omega) \) required for double excitations
- **Beyond linear response**: ALDA invalid for rapid (nonadiabatic) changes of the density

E.g.: attosecond response to the removal of an electron

Nonadiabatic xc potentials

1. XC functionals using the language of hydrodynamics/elasticity

- Extension of LDA to dynamical regime: local in space, but nonlocal in time. The current is more natural variable.
- Dynamical xc effects: viscoelastic stresses in the electron liquid
- Frequency-dependent viscosity coefficients / elastic moduli

G. Vignale and W. Kohn, PRL 77, 2037 (1996)
I.V. Tokatly, PRB 71, 165105 (2005)

An xc potential with memory


For a quantum well:

\[ V_{xc} (z,t) = V_{xc}^{ALDA} (z,t) + V_{xc}^{M} (z,t) \]

\[ V_{xc}^{M} (z,t) = \int_{-\infty}^{z} \frac{dz'}{n(z',t)} \nabla_{z} \sigma_{xc} (z',t) \]

xc stress tensor: \[ \sigma_{xc} (z',t) = \int_{0}^{t} dt' Y(n(z',t), t-t') \nabla_{z} u_{xc} (z',t') \]

Memory kernel \( Y \)

Initial field = 0.01

Initial field = 0.5

\[ Y_{s} = 3 \]

GK

QV

\[
\begin{align*}
\text{Memory kernel } Y \\
\text{Initial field } = 0.01 \\
\text{Initial field } = 0.5 \\
Y_{s} = 3 \\
\text{GK} \\
\text{QV}
\end{align*}
\]
Breakdown of the ALDA


High-frequency, purely elastic limit ($\omega >> \omega_p$)

**Sloshing mode**: small deformation, minor corrections to ALDA

**Breathing mode**: large deformation, ALDA breaks down

---

Nonadiabatic xc potentials

(2) XC functionals using the KS orbitals:

Time-dependent optimized effective potential (TDOEP)


\[
\sum_{j=1}^{N} \int_{-\infty}^{t} dt' \int d^3 \vec{r}' \left[ V_{xc} (\vec{r}' t') - u_{xcj} (\vec{r}' t') \right] \phi_j (\vec{r} t) \phi_j^* (\vec{r}' t') K (\vec{r} t, \vec{r}' t) - c.c. = 0
\]

where

\[
K (\vec{r} t, \vec{r}' t') = \sum_{k=1}^{\infty} \phi_k^* (\vec{r} t) \phi_k (\vec{r}' t')
\]

\[
u_{xcj} (\vec{r} t) = \frac{1}{\phi_j^* (\vec{r} t)} \frac{\delta A_{xc} [\phi_j]}{\delta \phi_j (\vec{r} t)}
\]
Full TDOEP versus TDKLI: exact exchange
correct asymptotics, discontinuous as a new level is filled

Summary

- TDDFT is the most promising approach for the dynamics of large systems (molecules, materials).
- Quality of results depends on problem and functionals used.
- ALDA works well for processes that have an analog in the KS system (single excitations, sequential ionizations).
- Strongly correlated processes, multiple excitations, charge-transfer excitations, and ultrafast processes are much more challenging.
- Dynamical xc functionals are being developed and tested for simple model systems.
Acknowledgments

Group:
- Harshani Wijewardane
- Ednilson Orestes
- Scott Fines
- Dr. Fedir Kryuchenko
- Dr. Volodymyr Turkowski

Collaborators:
- Irene D’Amico (York)
- Klaus Capelle (Sao Paulo)
- Giovanni Vignale (MU)
- Ilya Tokatly (Erlangen/Germany)

Literature

Chapter 24: C.A. Ullrich and A.D. Bandrauk, Atoms and molecules in strong laser fields

TDDFT for atoms in strong fields:

TDDFT for metal clusters:

http://www.missouri.edu/~ullrichc