The dynamical electronic problem

For any atom, molecule, cluster, solid...within Born-Oppenheimer,

\[ H \psi (r_1, r_2, ... r_N; t) = i \frac{\partial}{\partial t} \psi (r_1, r_2, ... r_N; t) \]

where

\[ H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{r_{ij}} + \sum_{i=1}^{N} v_{ext}(r_i; t) \]

Atomic units: \( e^2 = \hbar = m = 1 \)

- e-e interaction leads to exponential scaling with the number of electrons \( N \).
  - Prohibitively expensive for more than 2 or 3 electrons in intense fields.

From the Kohn-Sham non-interacting system, **exact** properties of the **interacting** dynamics can be extracted.
• Wide and varied applications, eg. dielectric functions, nanotube excitation spectra, spectra of large chemically interesting molecules, photosynthesis, spectra of DNA fragments, nano-tech - molecular wires ...

• In principle, all properties of the system are determined exactly but in practice approximations are required (more shortly)

• Strong-Field Physics – HHG, ATI, photo-dissociation, attosecond dynamics...

  – How well does TDDFT work here? What are the key issues involved? Can TDDFT help to understand the underlying mechanisms of the processes? What are possibilities for electronic quantum control?

Outline

• TDDFT Formalism

• Functional dependence: Memory

• Functional dependence: Importance, or not, of Coulomb tail

• Challenges for attosecond quantum control

• Phase-space-density functional theory

• Challenges for correlated electron-ion dynamics
**Time-Dependent DFT**

- Runge - Gross (1984) proved the 1-1 mapping:

  \[ n(r,t) \leftarrow n_{\psi_0}(r,t) \rightarrow n_{\psi}(r,t) \]

- For a given initial-state \( \psi_0 \), the time-evolving one-body density \( n(r,t) \) tells you everything about the time-evolving interacting electronic system, exactly.

  *i.e. you don’t need to know the far more complex \( (3N+1) \)-dimensional correlated wavefunction*

- Map interacting system onto a non-interacting Kohn-Sham (KS) system of orbitals, that reproduces the exact \( n(r,t) \)
  
  *(van Leeuwen, 1999: existence of KS)*

- Extract exact excitations and dynamics from KS system, much faster to solve

- Thus enables the quantum mechanical study of much larger systems than is possible using wavefunction methods.

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**TDDFT Formalism**

Time-dependent Kohn-Sham (KS) equation:

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

where

\[
n(r,t) = \sum_{i=1}^{N} |\phi_i(r,t)|^2 \quad \text{exact, interacting density}
\]

\[
v_s[n; \Phi_0](r,t) = v_{\text{ext}}(r,t) + \int \frac{d^3r'}{|r-r'|} n(r',t) + v_{\text{xc}}[n; \psi_0, \Phi_0](r,t)
\]

For initial KS state, choose any SSD that reproduces true initial \( n \) and \( \partial n/\partial t \)

\[
v_{\text{xc}}[n; \psi_0, \Phi_0](r,t) \quad \text{-- much more complicated object than in the ground-state case:}
\]

- depends on the entire history of the density, the true initial state \( \psi_0 \) and the choice of initial KS state \( \Phi_0 \).

  *Memory-dependence*
Functionals in TDDFT

Although the theory is formally exact, in practice approximations are needed for the exchange-correlation (xc) effects.

Almost all calculations today use an “adiabatic approximation”:
Just upgrade a ground-state functional,

\[ v_{xc}^A[n; \Psi_0, \Phi_0](rt) = v_{xc}^{GS}[n(rt)] \]

\[ \text{e.g. } v_{xc}^{ALDA}(rt) = v_{xc}^{LDA}[n(rt)] = \frac{d\epsilon_{xc}^\text{mnr}(n(rt))}{dn} \]

Completely forgetful: zero memory effects.

Development of memory-dependent functionals:
Orbital functionals also capture some memory

Memory-dependence

? How valid is the adiabatic approximation (AA) – can we really ignore memory?

- First, consider linear response – excitations and response properties:
  -- AA seems to work well – not entirely understood why.
  -- For some excitations, AA fails badly
    eg. double excitations (Maitra, Zhang, Cave, Burke, JCP 2004)
    eg. excitations of certain long-range molecules (including charge-transfer)
      (Maitra, JCP 2005, Maitra & Tempel sub. 2006)
    eg. interaction-induced chaos in wells (AA fails to give Wigner-Dyson level statistics) (Wasserman, Maitra, Heller, in prep. 2006)

- How about for strong-field dynamics? Not always easy to test, since exact solutions are hard to come by…
- Examples where exact solutions are available indicate memory plays a significant role and AA fails.
Memory-dependence

- Dependence on the history of the density:

\[ v_{xc}(n, \Psi_0, \Phi_0)(rt) \]

\[ n(rt'), t' < t \]

Eg. Time-dependent Hooke’s atom – exactly solvable

parametrizes density

\[ \int d^3r \, v_{xc}(rt') \, \dot{n}(rt') \]

2 electrons in parabolic well, time-varying force constant

\[ k(t) = 0.25 - 0.1 \cos(0.75 t) \]

Any adiabatic (or even semi-local-in-time) approximation would incorrectly predict the same \( v_c \) at both times.

Hessler, Maitra, Burke, JCP 117, 72 (2002).

Maitra, Burke, Woodward PRL 89, 023002 (2002) has other arguments showing \( xc \) potential is generally \textit{ultranonlocal} in time.

- Dependence on the initial-states:

A non-interacting example: Periodically driven HO

\[ v_{xc}[n; \Psi_0, \Phi_0](rt) \]

If we start in different \( \Psi_0 \)'s, can we get the same \( n(rt) \) by evolving in different potentials?

Yes!

Say this is the density of an interacting system. Both top and middle are possible KS systems.

\( \triangleright \) \( Vxc \) different for each. Cannot be captured by any adiabatic approximation

- Consequence for Floquet DFT: No 1-1 mapping between densities and time-periodic potentials.

Maitra & Burke, PRA 63, 042501 (2001); 64 039901 (E)

Eliminating initial-state dependence (ISD)

Evolve initial states backward in time, in some potential, to a ground-state $\rightarrow$ no ISD (due to Hohenberg-Kohn DFT) $\rightarrow$ instead, must tack on extra piece of "pseudo pre-history"

$$V_{xc}[\tilde{n}(r,t)] = V_{xc}[\tilde{n}(r,t)]$$

\[\text{Starts } t=0 \text{ in initial true state } \Psi_0 \text{ and KS evolves from initial state } \Phi_0\]

\[\text{This density is defined from time } -T:\]

- The pseudoprehistory is not unique – may find many ground-states that evolve to the same state at $t=0$, in different amounts of time, in different potentials.

- Eqn applies to all – and gives a strict exact test for approximate history-dependent functionals.

Ingredients for strong-field TDDFT calculations

(1) Approximation for $V_{xc}[\tilde{n};\Psi_0,\Phi_0] (r,t)$

- Adiabatic versus Non-Adiabatic? (Time-nonlocality i.e. memory)

- Long-range Coulomb tail needed or is short-range LDA OK? (Spatial non-locality)

- Derivative discontinuity? Important in NSDI (multi-e ionization) (Lein & Kuemmel, 2005)

(2) Observable as a functional of $n(r,t)$

- Is the relevant KS quantity physical? Certainly measurements involving only density (eg dipole moment) can be extracted directly KS.

  - HHG
  - ATI
  - NSDI
  - Attosecond Quantum Control
  - Correlated electron-ion dynamics

Harder: need functional approach
Long-range Coulomb tail needed or not?

- Most functionals, e.g., LDA, GGA's, lack the tail.
- Numerically more intensive functionals, e.g., SIC, OEP/KLI, do have \(-1/r\) tail (E.g., Nguyen, Bandrauk, Ullrich, PRA 2004, HHG/ATI spectra of Na-clusters)
- Sometimes not having a tail doesn’t matter!

Eg. Photo-absorption spectra accurate in LDA
(Wasserman, Maitra, Burke, PRL 2003)

- Suggests Starace’s QES/TDER analysis of HHG/ATI may be applied within TDDFT, with short-ranged LDA
  (Frolov, Khuskivadze, Manakov, Starace, J Phys B (2006))
- Could such analysis help to explain the extended plateaus of the TDDFT ATI in the Na-clusters?
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Electronic Quantum Control

What can theory predict? Electron correlation vital – use TDDFT!

Consider pumping He from ground to first accessible excited state (1s2p).

Problem!! The KS state remains doubly-occupied throughout – cannot evolve into a singly-excited KS state.

Simple model: evolve two electrons in a harmonic potential from ground-state (KS doubly-occupied \( \phi_0 \)) to the first excited state \( (\phi_0, \phi_1) \):

<table>
<thead>
<tr>
<th>Target density of singlet excited state</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Two orbitals of singly excited state of KS potential</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

Same density as that of target state

Doubly-occupied KS orbital reached by TDKS
• KS system can achieve the target density, but with a doubly-occupied orbital!!

• Yet this is how exact TDDFT describes the dynamics – the exact $v_{xc}$ is unnatural and difficult to approximate.

$v_s$ does not return to its initial value, as $v_{ext}$ does, after pumping complete.

• What functional to define the control target?
If try to optimize $\langle \Phi(T)|1s2p\rangle$ - max would be $\frac{1}{2}$ (c.f. close to 100% in the interacting He problem – Werschnik & Gross (2005))
i.e. the interacting system is controllable in this sense, but the non-interacting is not

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**An alternative approach...**

• Construct a *generalized density-functional theory* based on a phase-space density, eg Wigner function:

\[
W(\mathbf{r}, \mathbf{p}) = \int dy \rho_1(\mathbf{r} + y/2, \mathbf{r} - y/2)e^{i\mathbf{p} \cdot \mathbf{y}}
\]

The Wigner function for the two states in the harmonic oscillator control problem are distinct -

So although an adiabatic functional of the *density* predicts the same result for both states, an adiabatic functional of the *phase-space density* distinguishes them
TD Phase-Space FT

Currently under investigation

• Idea is that as more information is contained in the basic variable, functionals of it ought to be simpler – less non-local in time

• 1-1 mapping, $v_{\text{ext}} \leftrightarrow W(r,p,t)$, given $\Psi_0$, exists:
$W(r,p,t) \rightarrow n(r,t)$ by integration over $p \rightarrow v_{\text{ext}}(r,t)$ by RG thm

• Closely related to the first-order density matrix (1DM), $\rho_1(r,r',t)$
c.f. 1DM-FT in the ground-state (Lathiotakis, Helbig, & Gross (2005), Buijse
& Baerends, Mol. Phys. 2001)

• Deal directly with $W(r,p,t)$ – no KS system

• The kinetic part of the time-evolution can be done exactly (unlike in TDDFT)

• May help with some observable problems eg. directly gives momentum
distributions of ionized electrons in some region of space

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Coupled electron-ion dynamics

- A common approach: classical nuclei coupled to quantum electrons with Ehrenfest forces providing the quantum "backreaction".

Eg. Study of photo-dissociation in $N_2^+$ using TDDFT for the electrons: capturing Coulomb explosion following ionization

(Castro, Marques, Alonso, Bertsch, Rubio, 2004)

- Now programmed into freely-available octopus code

http://www.tddft.org,
Marques, Castro, Rubio, Yabana, Bertsch

- But Ehrenfest methods cannot capture correlations between nuclear and electronic motion eg. atomic collisions, amount of electronic excitation is correlated with resulting nuclear velocities – single averaged nuclear trajectory inadequate.

Eg. HHG in non-centrosymmetric diatomics: 1-d H—D

Exact quantum treatment of both electrons plus nuclei reveals even harmonics are generated. Must go beyond Born-Oppenheimer.

(Kreibich, Lein, Engel, Gross, PRL 2001)

- How well does approach with classical nuclei & Ehrenfest capture this?
Find even harmonics are produced but with dramatically less intensity. (Hardly detectable unless decrease nuclear masses by 100)

(Castro, Marques, Alonso, Bertsch, Rubio, 2004)
Correlated electron-ion dynamics using TDDFT?

- Prezhdo - first calculation of surface-hopping using TDDFT. 
  (Craig, Duncan, & Prezhdo PRL 2005)

- Showed significant improvement in calculations of nonradiative relaxation of GFP chromophore, and solar cell electron transfer

- Prezhdo's method: Evolve electrons via TDKS eqns, coupled to classical nuclei moving on KS potential energy surfaces (PES), making hops between them according “fewest-switches surface-hopping” scheme of Tully.

- But the KS PES’s are not true adiabatic PES’s → should use TDDFT-corrected ones (eg from linear response) to get correct forces on the nuclei.

Eg. PES of formaldehyde $^1A_1$ excited states along C-O bond:

Gradients of TDDFT curves (solid) quite different from bare KS curves (dashed).

- But, if correct adiabatic PES are obtained from TDDFT linear response, the trajectory hopping probabilities cannot be simply extracted:

  These depend on

  (i) coefficients of the time-evolving $\psi$ expanded in the e-states

  (ii) non-adiabatic couplings (NAC) between electronic PES

  *But DFT doesn't give $\psi$!

  *NAC density-functionals known for ground to excited states only

  Maitra, JCP (2006)
Summary

- TDDFT is an enticing method for the treatment of atomic and molecular dynamics in strong fields, scaling favorably with the system size while including electron correlation.
- Challenges remain in the development of memory-dependent exchange-correlation functionals, as well as density-dependence of physical observables.
- Impacts many important problems e.g. attosecond quantum control, coupled correlated nuclear-electron dynamics…
- These challenges raise lots of interesting fundamental questions!
- Addressing future challenges:

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- And to you all for listening!!