Aspects of Non-Adiabaticity in TDDFT

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Memory in TDDFT

Never forget...

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

(i) entire history of the density, \( n(r, t' < t) \)

and

(ii) initial states \( \Psi_0, \Phi_0 \)

Hessler, NTM, & Burke, JCP 117, 72 (2002);
NTM & Burke, PRA 63 042501 (2001); 64 039901 (E) (2001); CPL 359, 237 (2002);
NTM, Burke, & Woodward, PRL 89, 023002 (2002).
NTM, sub. to IJQC (2004).

- Linear response: only need to worry about (i)

- Almost all calculations are ”Adiabatic” - input only the instantaneous density into a ground-state functional: e.g. in ALDA, \( v_{xc}^{\text{unif}}[n(rt)](rt) \)
Neglect all memory-dependence.

- Functionals that include some non-adiabaticity:
  - Gross-Kohn (1990)
  - Vignale-Kohn (1996)
  - Dobson-Bünner-Gross (1997)
  - Tokatly-Pankratov (2003)
  - Kurzweil-Baer (2004)

- My talk today: focus on 3 situations where strong memory-dependence (non-adiabaticity) is essential.
Outline

- Memory in Quantum Control Problems

- Memory in Linear Response:
  - Double excitations
  - Long Range Charge Transfer between Open Shells
Significance of memory in quantum-control type problems
(from NTM, Burke, & Woodward, PRL 89, 023002 (2002))

(Interacting, true system)

Target state $\Psi_m$

$\nu_{\text{ext}}(t)$ where $\nu_{\text{ext, r}} = \nu_{\text{ext, 0}}$

Ground state $\Psi_0$

$\nu_{\text{ext, r}} = \nu_{\text{ext, 0}}$

and $n(rt > t^*) = n_m(r)$
How does the KS system describe this?

Consider the final KS state.

**Immediate observation:** Excited KS states of a fixed \( \nu_s \) do not have the same density as the excited states of the corresponding \( \nu_{\text{ext}} \rightarrow \nu_{s,1} \neq \nu_{s,0} \).
Scenario (i): Ground state $\Phi_0 \rightarrow \Phi_{m_8}$

$\Phi_{m_8}$ is a SSD with constant density $n_m(r)$, the $m_8$th excited state of a different KS potential, $v_{s,i} \neq v_{s,0}$.

$v_{s,i}(r) = v_s[n](r, t > t^*)$, a functional of the entire history of the density, necessarily including the early history $< t^*$.

(If it didn't, $v_{s,i}(r)$ would be e.g. the potential in which $n_m(r)$ is the ground-state density, rather than that of the $m_8$th excited state).

\[ \rightarrow v_s \text{ has 'infinite' memory!} \]

Alternatively, think of $v_{s,i}(r) = v_s[n_m;\Phi_{m_i}](r, t > t^*)$ (a special case of the exact condition in MBW02, with initial time $t^*$)

What would an adiabatic approximation give?

Const $n = n_m \rightarrow v_{s,i} \text{ const, but it will be the potential}$

where the ground-state has density $n_m$, $v_s[n_m]$, rather than the $m_8$th excited state of the corresponding $v_{ext}$ having density $n_m$.

Need infinite history-dependence to get it right.
Scenario (ii): Ground state $\Phi_0 \rightarrow \Phi(t)$

where $\Phi(t)$ and $v_s(t)$ continue to evolve forever in time, $t > t^*$, but with a constant density $\rightarrow v_s$ has infinite memory.

- The Kohn-Sham state is of a fundamentally different nature than the true state $\rightarrow$ challenging for TDDFT. An adiabatic approx. or anything not entirely non-local in time, can never get this as it would be constant in time, as the density is.

- Orbital functionals Incorporate "infinite KS memory", so most likely the best approach for these problems.
Hunt for the elephant....

Elephants never forget....
Linear response: Memory-dependence in excitation energy calculations

\[ \delta n(r\omega) = \int d^3r' \chi[n_0](rr')\delta v_{\text{ext}}(r') \]
\[ = \int d^3r' \chi_{s}[n_0](rr')\delta v_{s}(r') \]

Poles of \( \chi_s(r, r'; \omega) \rightarrow \) KS single excitation energies
Poles of \( \chi(r, r'; \omega) \rightarrow \) physical excitation energies

\[ \chi[n_0](\omega) = \chi_s[n_0](\omega) + \chi_s[n_0](\omega) * f_{\text{HXC}}(\omega) * \chi[n_0](\omega) \]
where
\[ f_{\text{HXC}}[n_0](r, r', \omega) = 1/|r - r'| + f_{\text{xc}}[n_0](r, r', \omega) \]

\( f_{\text{xc}} \) is the exchange-correlation kernel:
\[ f_{\text{xc}}[n_0](r, r', t - t') = \delta v_{\text{xc}}(rt)/\delta n(rt')|_{n_0} \]

- We note the single-pole approximation (SPA):
  \[ \omega = \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q] \]
  \[ [q|f_{\text{HXC}}(\omega)|q'] = \int drdr'\phi_i^*(r)\phi_a(r)f_{\text{xc}}(r, r', \omega)\phi_i(r')\phi_a^*(r') \]
valid when the excitation is "well-separated" from all others.

- Formally, memory shows up as frequency-dependence in \( f_{\text{xc}} \).

In the ubiquitous adiabatic approximations, \( f_{\text{xc}} \) is proportional to \( \delta(t - t') \), and its Fourier transform is frequency-independent – has no memory.

Yet often, but not always, this yields very good approximations for the interacting energies.

- When and why does the adiabatic approx work well? Well, I don’t know exactly, but I will instead show you two cases where it will fail - where strong \( \omega \)-dependence is essential.
Double excitations in TDDFT

NTM, Zhang, Cave, Burke, JCP 120, 5932 (2004)

\[ \chi(r, r'; \omega) = \sum I \left\{ \frac{F_I(r)F_I^*(r')}{\omega - \omega_I + i0^+} - \frac{F_I^*(r)F_I(r')}{\omega + \omega_I + i0^+} \right\}, \]

where \( F_I(r) = \langle 0 | \tilde{n}(r) | I \rangle \)

\( \chi_s \): Poles only at single KS excitations

\( \chi \): Poles at exact mixtures of singles, doubles, and higher.

\( \chi \) has more poles than \( \chi_s \)

Q: How does \( f_{xc} \) generate more poles, and include states of double-excitation character?

A: Exact \( f_{xc} \) has strong \( \omega \)-dependence near the double.

States of double-excitation character cannot be captured within an adiabatic approximation.
Consider simplest case: when a double excitation interacts with an otherwise isolated single,

\[ \text{KS} \quad \text{Exact} \]

\[ \frac{1 - m^2}{m^2} : m^2 \quad \omega_a \]

\[ \omega_q \quad m^2 : 1 - m^2 \quad \omega_b \]

\[ q : D \]

\[ \chi_s(r, r', \omega) \approx \frac{A(r, r', (\omega))}{\omega - \omega_q} \]

\[ \chi(r, r'; \omega) \approx A(r, r', (\omega)) \left( \frac{1 - m^2}{\omega - \omega_a} + \frac{m^2}{\omega - \omega_b} \right) \]

\[ 2 [q| f_{\text{HNC}}(\omega)|q] = 2 \left( [q| \chi_s^{-1} - [q| \chi^{-1} |q] \right) \]

\[ = (\bar{\omega} - \omega_q) + \frac{\bar{\omega}' \bar{\omega} - \omega_a \omega_b}{(\omega - \bar{\omega}') \quad \text{adiabatic approximates this term only} \}

\[ \bar{\omega}' = m^2 \omega_a + (1 - m^2) \omega_b \quad \text{strong non-adiabaticity Pole:} \]

Yields, in the dressed single-pole formula,

\[ \omega = \omega_q + 2 [q| f_{\text{HNC}}(\omega)|q] \]

the exact frequencies of the mixed single and double states, by construction.
\[ \chi^{-1}(\omega) = \chi_s^{-1} - f_{\text{Hxc}} \]
Dressed Single-Pole Approximation for Doubles

Diagonalize true H in the \((q, D)\) subspace (c.f. CI); then require reduction to Adiabatic TDDFT (ATDDFT) when the double lies far away.

\[
2[q| f_{XC}(\omega) | q] = 2[q| f_{XC}^A(\omega_q) | q] + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{00})}
\]

\(n\) Becomes exact in weakly-interacting limit.

* Practical scheme to calculate doubly-excited states:

(i) Solve TDDFT response equations with an adiabatic kernel

(ii) Determine whether doubles mix in by, e.g. scanning the KS singles to see if the sum of any two lies close to any of them, and

(iii) Apply DSPA correction above just to the single that is coupled to the double.

--- Good results, and, leaves largely single excitations unchanged from ATDDFT.

Can be generalized to when more than one single mixes with a double...see shortly...

- **New work by Casida**: shows the result above drops out of a superoperator calculation of non-adiabatic corrections.
Results I

Simple 1d model system

\[ V_{ce} = \lambda (x_1 - x_2) \]

\[ V_{ext} = \frac{1}{2} x^2 \]

\[ \lambda = 0.2 \]

<table>
<thead>
<tr>
<th></th>
<th>Exact</th>
<th>KS</th>
<th>SPA</th>
<th>DSPA</th>
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<td>0.9616</td>
<td>1.0014</td>
<td>1.0014</td>
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<tr>
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<td></td>
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<td></td>
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<td>2.9148</td>
<td></td>
<td>2.9622</td>
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</table>

\[ \text{Exact} \frac{1}{3} : \frac{2}{3} \text{mix} \]

Ground

1st

2nd

Exact 50:50 mix

3rd

\[ \text{Dressed TDOFT} \]

\[ f_{xc} = f_x \]

\[ f_{xc}(\omega) \]
Results II

Short-chain polyenes


Lowest-lying excitations are notoriously difficult to characterize and calculate, due to significant double character.

E.g. Butadiene, dark $2^1A_g$ state.

\[
\begin{array}{c}
2b_g \\
2a_u \\
1b_g \\
1a_u \\
\end{array}
\]

Apply dressing, now as a 2x2 matrix in KS singles space.

- $2^1A_g$ Vertical excitation energies (eV) for butadiene and hexatriene

<table>
<thead>
<tr>
<th>System</th>
<th>CASPT2</th>
<th>ATDDFT</th>
<th>D-TD-TDDFT</th>
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<tbody>
<tr>
<td>C_4H_6</td>
<td>6.27</td>
<td>7.02</td>
<td>6.28</td>
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<tr>
<td>C_6H_8</td>
<td>5.20</td>
<td>5.83</td>
<td>5.16</td>
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</tbody>
</table>

- $2^1A_g$ Vertical and 0-0 excitations for butadiene at the estimated planar stationary point for $2^1A_g$

<table>
<thead>
<tr>
<th>$\Delta E$</th>
<th>CASPT2</th>
<th>ATDDFT</th>
<th>D-TD-TDDFT</th>
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<tbody>
<tr>
<td>Vertical</td>
<td>4.3</td>
<td>5.8</td>
<td>4.16</td>
</tr>
<tr>
<td>0-0</td>
<td>5.2</td>
<td>6.8</td>
<td>5.28</td>
</tr>
</tbody>
</table>
More Acrobatics of $f_{xc}$ ....

$\sqrt{f_{xc}}$

...Long-Range Charge Transfer

between two open shell species & the effect of static correlation for TDDFT...
Long-range charge-transfer (CT) excited states

As $R \to \infty$, $\omega_{CT} = I_1 - A_2 - 1/R$

- TDDFT typically severely underestimates the energies of these states

$$\omega = \epsilon_2^l - \epsilon_1^H + \int \int dr dr' \phi_1^H(r) \phi_2^L(r) f_{\text{xc}}(r, r', \omega) \phi_1^H(r') \phi_2^L(r')$$

$$\approx I_1 - A_{5,2} - I_1$$

- Common approximations underestimate $I_1$, but,

  how does exact TDDFT retrieve $A_{xc,2}$?
Example: Zincbacteriochlorin-Bacteriochlorin complex
from Dreuw and Head-Gordon, JACS \textbf{126} 4007, (2004).
(light-harvesting in plants and purple bacteria)

TDDFT predicts CT states energetically well below individual tetrapyrrol $\pi \rightarrow \pi^*$ transitions (Q-states) $\rightarrow$ expect CT quenching of the excited state fluorescence.

\textbf{! Not observed !}

Dreuw & Head-Gordon mix in Hartree-Fock exchange to show that actually the CT states are much higher than the Q-states.
How does exact TDDFT get it right?

Simplest case: Electron-transfer between 1-electron species

Bare KS frequencies are those of the ground-state potential: To find $v_s$, invert KS eqn for the molecular ground-state:

$$\Phi_0 = \phi_0(r_1)\phi_0(r_2)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$$

↑
doubly-occupied bonding orbital. $\Phi_0 = (\Phi_1 + \Phi_2)/\sqrt{2}$

Find:

The step lines up the HOMO's !!

(It is necessary to prevent dissociation into fractionally charged species (Perdew) (Almbladh & von Barth)

- Degeneracies → zero KS energy for charge transfer!!!???
The electron interaction splits the degeneracy:

Three almost degenerate KS states:

\[
\begin{align*}
\Phi_0 &= \phi_0(r_1)\phi_0(r_2) \\
\Phi_q &= (\phi_0(r_1)\phi^*(r_2) + \phi^*(r_1)\phi_0(r_2))/\sqrt{2} \\
\Phi_D &= \phi^*(r_1)\phi^*(r_2)
\end{align*}
\]

Diagonalize \( H = H_s + V_{ee} - \nu_u - \nu_{xc} \) in this basis to get:

\[
(\text{atomic orbitals})
\]

Heitler-London \( \Psi_0 = (\phi_1(r)\phi_2(r') + \phi_2(r)\phi_1(r'))/\sqrt{2} \)

CT states \( \begin{cases} 
\Psi_{2\rightarrow 1} = \phi_1(r)\phi_1(r') & \omega = I_2 - A_1 - 1/R \\
\Psi_{1\rightarrow 2} = \phi_2(r)\phi_2(r') & \omega = I_1 - A_2 - 1/R
\end{cases} \)

where

\[
A = A_s + A_{xc}^{\text{approx}}, \text{ with}
\]

\[
A_{xc}^{\text{approx}} = -\int d^3r \int d^3r' \phi_H(r)^2\phi_H(r')^2V_{ee}(r-r')
\]

Notes: (a) Open-shell: \( A_s = I = -e^H \).

(b) Static correlation: HOMO's lining up makes the problem resemble somewhat homonuclear dissociation, well-known in ground-state DFT problems.

Large correlation: \( \nu_x = -\nu_u/2 \) (2 electrons) \( \sim O(\lambda) \) but \( \nu_c \) cancels this and adds the step, yielding

\[
\nu_{xc} = \frac{Z_2}{|r-R|} \text{ for } r \text{ near atom 1}
\]

\[
= I_2 - I_1 + \frac{Z_1}{|r|} \text{ for } r \text{ near atom 2}
\]
What is the approximate $A_{xc}$ like?

- It becomes exact in the weak interaction limit, when the 3x3 basis is effectively isolated.

- Example: Electron affinity of 1 fermion in a 1-d $\delta$-well, when fermions interact via $\delta$-fn repulsion:

$$H = -\sum_i^2 \frac{1}{2} \frac{d^2}{dx_i^2} - \sum_i^2 \delta(x_i) + \lambda \delta(x_1 - x_2)$$

- To bend the curve, would need e.g. Görling-Levy perturbation theory to include effect of higher excitations on the near-degenerate subspace, and so bend the curve...
TDDFT? $f_{xc}$ for CT between open-shells.

First, consider response functions:

$$\chi_s(r, r', \omega) = \sum_q \frac{F_q(r)F_q(r')}{\omega - \omega_q + i0^+} + c.c.(\omega \rightarrow -\omega) \text{ with } F_q = \phi_i \phi_u,$$

$$\approx \frac{2\omega^*}{\omega^2 - (\omega^*)^2} A_s(r, r', (\omega))$$

Similarly,

$$\chi(r, r', \omega) \approx \frac{2\omega_{2\rightarrow 1}}{\omega^2 - \omega_{2\rightarrow 1}^2} A_{2\rightarrow 1}(r, r', (\omega)) + \frac{2\omega_{1\rightarrow 2}}{\omega^2 - \omega_{1\rightarrow 2}^2} A_{1\rightarrow 2}(r, r', (\omega))$$

That the response fns vanish exponentially with separation, can also be understood from:

$$\chi_s(\omega) = \frac{\delta n}{\delta \omega}(\omega)$$ - perturbation at $\omega^*$ excites antibonding transition, whose density differs only exply smally from the bonding orbital's.

$$\chi(\omega) = \frac{\delta n}{\delta \text{ext}}(\omega)$$ - the CT transitions have very weak oscillator strength due to the widely separated spatial-regions.
Dressed Small Matrix Approximation

for CT transitions between open-shells:

\[ \omega^2 = \omega_q^2 + 4\omega_q[f_{\text{HXC}}(\omega)|q] \]

where \( f_{\text{HXC}}(\omega) = \chi_s^{-1}(\omega) - \chi^{-1}(\omega) \)

We find ...

\[ 4\omega^* [q|f_{\text{HXC}}(\omega)|q] = \overline{\omega^2} - \omega_0^2 - \frac{(\omega^2 - \omega_0^2 - \omega_1^2 - \omega_2^2)}{\omega^2 - \omega_0^2} \]

\[ q = (\phi_0 \rightarrow \phi^*) \]

**strong non-adiabaticity!**

\[ \overline{\omega^2} = \frac{1}{2} (\omega_{2-1}^2 + \omega_{1-2}^2) \]

**Note:**

The occ.– unocc. overlap is no longer zero:

\[ \phi_i(r)\phi_o(r) = \phi_0(r)\phi^*(r) = (\phi_1^2(r) - \phi_2^2(r))/2 \]

Rather, the matrix element \([q|f_{\text{HXC}}(\omega)|q]\) diverges with interatomic separation \( R \), as \( 1/\omega^* \sim e^{aR} \), inside each atomic region.

(c.f. Gritsenko & Baerends, JCP 120 8364, 2004; Gritsenko, van Gisbergen, Görling, & Baerends 2000)

Maybe this divergence is not present in velocity-velocity response functions.
Other excitations of a long-range heteroatomic molecule?

- The step in $v_s$ turns higher atomic excitations into KS resonances:

  Two "Eckart Atoms" in 1–d

![Graph showing two Eckart Atoms in 1–d with $I_1$, $I_2$, $I_{1-2}$, and $I_2$ labels.]

What acrobatics must $f_{\text{xc}}$ do to turn these KS resonances back into bound states of the true system?

- For every single excitation out of the HOMO bonding orbital, $(0 \rightarrow a)$, there is a near degenerate double-excitation, $(0,0) \rightarrow (0^*,a)$, absent in the KS response function, but essential for the true response $\rightarrow$ frequency-dependence, with ubiquitous poles of $f_{\text{xc}}$

Consequence of static correlation for TDDFT
Conclusions

- The role of memory often cannot be ignored without drastic consequences.

- In fully non-linear phenomena, e.g., quantum control, we encountered extreme non-locality in time, and challenges to deal with severe static correlation.

- In linear response, memory is essential for the treatment of double excitations where the exact kernel is strongly frequency-dependent. Our dressed SPA shows promising results and improved energies.

- For charge-transfer states between open-shells at long-range, frequency-dependence is also essential. The step in the ground-state KS potential renders the bare KS CT energies to be near 0. Static correlation leads to strong frequency-dependence in the kernel.

- Very interesting consequences of the step in the KS potential in a long-range heteroatomic molecule for TDDFT remain to be explored.
"This isn't right. This isn't even wrong."

- Wolfgang Pauli

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