Advanced TDDFT II

II. Frequency-Dependent Kernels: Double Excitations

\[ \int fc \]

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Plan

-- Double-Excitations in TDDFT

-- Autoionizing Resonances

-- Opening the optical gap – also needs a frequency-dependent kernel
First, quick recall of how we get excitations in TDDFT: Linear response

\[ \chi^{-1}(\omega) = \chi_s^{-1}(\omega) - \tilde{f}_{\text{HXC}}(\omega) \]

Poles at true excitations

Poles at KS excitations

\[ 1/|r-r'| + f_{xc}[n_0](r, r', \omega) = \frac{\delta^2 E_{xc}[n]}{\delta n(r) \delta n(r')} \bigg|_{n_0} \]

adiabatic approx: no \( \omega \)-dep

Need (1) ground-state \( \nu_{S,0}[n_0](r) \), and its bare excitations

(2) XC kernel \( f_{xc}[n_0](r, r', t - t') = \delta v_{xc}(rt)/\delta n(rt')|_{n_0} \sim \delta(t-t') \)

Yields exact spectra in principle; in practice, approxs needed in (1) and (2).

\[ \chi(r, r'; \omega) = \sum_I \left\{ \frac{F_I(r)F_I^*(r')}{\omega - \omega_I + i0^+} - \frac{F_I^*(r)F_I(r')}{\omega + \omega_I + i0^+} \right\} F_I(r) = \langle \Psi_0 | \hat{n}(r) | \Psi_I \rangle \]

Petersilka, Gossmann & Gross, PRL 76, 1212 (1996)

TDDFT linear response in quantum chemistry codes:

\[
\tilde{\Omega}(\omega)_{qq'} = \delta_{qq'} \omega_q^2 + 4 \sqrt{\omega_q \omega_{q'}} [q \vert f_{\text{HXC}}(\omega) \vert q']
\]

\(q = (i \rightarrow a)\) labels a single excitation of the KS system, with transition frequency \(\omega_q = \varepsilon_a - \varepsilon_i\), and

\[
[q \vert f_{\text{HXC}}(\omega) \vert q'] = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \phi_i'(\mathbf{r'}) \phi_a^*(\mathbf{r'})
\]

Eigenvalues \(\rightarrow\) true frequencies of interacting system

Eigenvectors \(\rightarrow\) oscillator strengths

Useful tool for analysis

Zoom in on a single KS excitation, \(q = i \rightarrow a\)

Well-separated single excitations: SMA

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

When shift from bare KS small: SPA

\[
\omega = \omega_q + 2 [q \vert f_{\text{HXC}}(\omega_q) \vert q]
\]
Types of Excitations

Non-interacting systems eg. 4-electron atom

Eg. single excitations

Eg. double excitations

Interactive systems: generally involve mixtures of (KS) SSD’s that may have 1, 2, 3...electrons in excited orbitals.

single-, double-, triple- excitations
Double (Or Multiple) Excitations

How do these different types of excitations appear in the TDDFT response functions?

Consider:

$$\chi(r, r'; \omega) = \sum_I \left\{ \frac{F_I(r)F_I^*(r')}{\omega - \omega_I + i0^+} - \frac{F_I^*(r)F_I(r')}{\omega + \omega_I + i0^+} \right\} F_I(r) = \langle \Psi_0 | \hat{n}(r) | \Psi_I \rangle$$

$\chi$ – poles at true states that are mixtures of singles, doubles, and higher excitations

$\chi_S$ -- poles at single KS excitations only, since one-body operator $\hat{n}(r)$ can’t connect Slater determinants differing by more than one orbital.

$\Rightarrow \chi$ has more poles than $\chi_S$

**? How does $f_{xc}$ generate more poles to get states of multiple excitation character?**
Simplest Model:

Exactly solve one KS single (q) mixing with a nearby double (D)

\[ 
\Psi_a = m \Phi_D + \sqrt{1 - m^2} \Phi_q, \\
\Psi_b = \sqrt{1 - m^2} \Phi_D - m \Phi_q, \quad 0 < m < 1 
\]

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

\[ 
\chi(r, r'; \omega) \approx A(r, r'; \omega) \left( \frac{1 - m^2}{\omega - \omega_a} + \frac{m^2}{\omega - \omega_b} \right) 
\]
Invert and insert into Dyson-like eqn for kernel $\rightarrow$ **dressed SPA** (i.e. $\omega$-dependent):

$$2[q|f_{\text{HXC}}(\omega)|q] = 2\left([-q|x^{-1}_s|q| - [q|x^{-1}|q]\right)$$

$$= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}' \bar{\omega} - \omega_a \omega_b}{(\omega - \bar{\omega}')}$$

adiabatic

strong non-adiabaticity!

$$\bar{\omega} = (1 - m^2)\omega_a + m^2\omega_b$$

$$\bar{\omega}' = m^2\omega_a + (1 - m^2)\omega_b$$

This kernel matrix element, by construction, yields the **exact** true $\omega$'s when used in the Dressed SPA,

$$\omega = \omega_q + 2[q|f_{\text{HXC}}(\omega)|q]$$
\[
\chi^{-1} = \chi_s^{-1} - f_{\text{Hxc}}
\]

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

\[
= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')}
\]
An Exercise!

Deduce something about the frequency-dependence required for capturing states of triple excitation character – say, one triple excitation coupled to a single excitation.
Practical Approximation for the Dressed Kernel

**General case:** Diagonalize many-body $H$ in KS subspace near the double-ex of interest, and require reduction to adiabatic TDDFT in the limit of weak coupling of the single to the double:

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

usual adiabatic matrix element
dynamical (non-adiabatic) correction

So: (i) scan KS orbital energies to see if a double lies near a single,
(ii) apply this kernel just to that pair
(iii) apply usual ATDDFT to all other excitations

*N.T. Maitra, F. Zhang, R. Cave, & K. Burke*  
Alternate Derivations

  
  M. Huix-Rotllant & M.E. Casida, *arXiv*: 1008.1478v1

  -- from second-order polarization propagator (SOPPA) correction to ATDDFT


  -- from Bethe-Salpeter equation with dynamically screened interaction $W(\omega)$


  -- use CEDA (Common Energy Denominator Approximation) to account for the effect of the other states on the inverse kernels, and obtain spatial dependence of $f_{xc}$-kernel as well.
Simple Model System: 2 el. in 1d

\[ V_{\text{ext}} = x^2/2 \]

\[ V_{\text{ee}} = \lambda \delta(x-x') \]

\( \lambda = 0.2 \)

Exact: \[ \frac{1}{2} : \frac{1}{2} \]

\[ \frac{1}{2} : \frac{1}{2} \]

\[ \frac{1}{3} : \frac{2}{3} \]

\[ \frac{2}{3} : \frac{1}{3} \]

Dressed TDDFT in SPA, \( f_{xc}(\omega) \)
When are states of double-excitation character important?

(i) Some molecules eg short-chain polyenes

Lowest-lying excitations notoriously difficult to calculate due to significant double-excitation character.

- $2^1 A_g$ 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>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4H_6$</td>
<td>6.27</td>
<td>7.02</td>
<td>6.28</td>
</tr>
<tr>
<td>$C_6H_8$</td>
<td>5.20</td>
<td>5.83</td>
<td>5.16</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$\Delta E$</th>
<th>CASPT2</th>
<th>ATDDFT</th>
<th>D-TD-TDDFT</th>
</tr>
</thead>
<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>

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

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

Other implementations and tests:

R. Cave, F. Zhang, N.T. Maitra, K. Burke, CPL 389, 39 (2004);

G. Mazur, R. Wlodarczyk, J. Comp. Chem. 30, 811, (2008); Mazur, G., M. Makowski, R. Wlodarcyk, Y. Aoki, IJQC 111, 819 (2010);

When are states of double-excitation character important?

(ii) Coupled electron-ion dynamics

- propensity for curve-crossing means need accurate double-excitation description for global potential energy surfaces


(iii) Certain long-range charge transfer states!

Stay tuned for next lecture!

(iv) Near conical intersections

- near-degeneracy with ground-state (static correlation) gives double-excitation character to all excitations

(v) Certain autoionizing resonances

Coming up shortly!
How about Doubles in Adiabatic Quadratic Response?

Since two photons are required to excite two electrons, can we get away with the adiabatic approx in quadratic response?

*Not really:* The adiabatic quadratic response function does have poles at double excitations but they’re simply sums of linear-response-corrected single excitations, i.e. no mixing between singly-excited states lying near a double-excitation.

Autoionizing Resonances

When energy of a bound excitation lies in the continuum:

KS (or another orbital) picture

True system: Electron-interaction mixes these states $\rightarrow$ Fano resonance

✓ ATDDFT gets these – mixtures of single-ex’s

- M. Hellgren & U. van Barth, JCP 131, 044110 (2009) $\rightarrow$ Fano parameters directly implied by Adiabatic TDDFT

Auto-ionizing Resonances in TDDFT


But here’s a resonance that ATDDFT misses:

Why? It is due to a double excitation.
bound, localized **double** excitation with energy in the continuum

Electron-interaction mixes these states → Fano resonance

× ATDDFT does not get these – double-excitation

e.g. the lowest double-excitation in the He atom (1s^2 → 2s^2)
Getting the cross-section in TDDFT

Photo-absorption cross section:
\[
\sigma_{\alpha\beta}(\omega) = \frac{4\pi\omega}{c} \int d^3r d^3r' r_\alpha r'_\beta \text{Im}\chi(r, r', \omega)
\]

Where,
\[
\text{Im}\chi(r, r', \omega) = -\pi \sum_I <0|\hat{n}(r)|I><I|\hat{n}(r')|0>(\delta(\omega - \Omega_I) - \delta(\omega + \Omega_I))
\]

\[
\chi^{-1}(r, r', \omega) = \chi_s^{-1}(r, r', \omega) - f_{\text{HXC}}(r, r', \omega)
\]

How does the exact kernel add the resonant bump to \(\chi_s\) ?

Need a degenerate perturbation theory analysis in the continuum, diagonalizing the bound double-excitation with the continuum states.

Aha! Luckily this is closely along the lines of what Fano did in 1961…
Fano’s Universal Resonance Formula

\[ U. \text{ Fano, Phys. Rev. } 124, 1866 (1961) \]

“pre-diagonalized”

Transition probability to continuum modified by the resonance due to \( \Phi_b \)

\[
\left| \frac{\langle \Psi_E | \hat{T} | i \rangle}{\langle \Phi_E | \hat{T} | i \rangle} \right|^2 = \frac{(q + \epsilon)^2}{1 + \epsilon^2}
\]

\[ \epsilon = \frac{E - E_r}{\Gamma/2} \]

\[ E_r = E_b + \mathcal{P} \int dE' \frac{|V_E|^2}{E - E'} \]

\[ \Gamma = 2\pi |\langle \Phi_E | \hat{V}_{cpl} | \Phi_b \rangle|^2 = 2\pi |V_E|^2 \]

\( q = \) asymmetry parameter…next slide

\( \Psi_E \) is the resonance-modified continuum state at energy \( E = \omega + E_i \)

\( \Phi_E \) is the unmodified continuum state at energy \( E = \omega + E_i \)

\( |i\rangle \) is the initial (ground) state

\( \hat{T} \) is a transition operator

\( \mathcal{P} \) is a transition operator
Fano Lineshapes:

\[ \frac{|\langle \Psi_E | \hat{T} | i \rangle|^2}{|\langle \Phi_E | \hat{T} | i \rangle|^2} = \frac{(q + \epsilon)^2}{1 + \epsilon^2} \]

Asymmetry parameter:

\[ q = \frac{\Phi_b | \hat{T} | i \rangle + P \int V_{E'} \langle \Phi_{E'} | \hat{T} | i \rangle / (E - E') \, dE'}{\pi V_E \langle \Phi_E | \hat{T} | i \rangle} \]

Note \( q = \pm 1 \) means total integrated oscillator strength unchanged by resonance.

-This is the case when dressing the KS system with a resonance from a bound double-excitation!
Fano into TDDFT

Consider $|i\rangle$, $\Phi_E$ and $\Phi_b$ (double-ex) to be Kohn-Sham states, and $\hat{T} = \hat{n}(r)$, into Fano analysis:

$$\text{Im} \chi(r, r', \omega) \approx \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \text{Im} \chi_S(r, r', \omega), \text{with } q = 1$$

$$\text{Im} \chi(r, r', \omega) \approx \frac{(\omega - \omega_r + \Gamma/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \text{Im} \chi_S(r, r', \omega)$$

Approximations:
-- considered coupling between doubly-excited bound-state and continuum only
-- took $\Gamma$ as the smallest energy scale in the system.

For $\omega$ near resonance

For $\omega$ near resonance
To find \( f_{HXC}(r, r', \omega) = \chi_S^{-1} - \chi^{-1} \), we need \( \text{Re} \chi \).

Use the Kramers-Kronig relation:

\[
\text{Re} \chi(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im} \chi(\omega')}{(\omega')^2 - \omega^2} \, d\omega'
\]

… eventually get...

weak-interaction limit
\( \omega \) near \( \omega_r \)
\( \omega_r \gg \Gamma \)

\[
f_{HXC}(\omega) = \chi_S^{-1}(\omega) - \left( \chi_S(\omega) + \frac{\Gamma (\Gamma/2 + i(\omega - \omega_r))}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \chi_S(\omega) \right)^{-1}
\]

\( f_{HXC}(\omega) \)

A. Krueger & N. T. Maitra, PCCP 11, 4655 (2009);

Frequency-Dependent Kernels, more generally

• Note some other recent $\omega$-dep kernels have been developed for calculations of spectra (but not for capturing doubles):


-- VK kernel of TDCDFT, G. Vignale & W. Kohn (PRL 77, 20371996); C. A. Ullrich & K. Burke JCP 121, 28 (2004), and M. van Faassen & P. L. de Boeij JCP 120, 8353 (2004)


• Main motivation behind these is capturing spatial ultranonlocality (this implies time-nonlocality)

• Another place where the adiabatic approximation fails is the optical gap in semi-conductors – next slide!
The optical gap: Another place where adiabatic approx fundamentally fails

Meaning, onset of continuous absorption in spectrum (Im \( \chi(\omega) \))

- Typically KS gap << true gap
  -- even with the exact ground-state \( v_{xc} \)

- Opening the gap requires \( f_{xc} \) to have an imaginary part.
  Why?

Consider what happens if take a real approximate \( f_{xc} \) in imaginary part of:

\[
\chi(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega) \ast f_{Hxc}(\omega) \ast \chi(\omega)
\]

For \( \omega \) inside the KS gap,

\[
\text{Im} \chi_{KS}(\omega) = 0 \rightarrow [\hat{1} - \Re \chi_{KS}(\omega) \ast f_{Hxc}(\omega)] \ast \text{Im} \chi(\omega) = 0
\]

While, analogously for \( \omega \) inside the true gap,

\[
\text{Im} \chi(\omega) = 0 \rightarrow \text{Im} \chi_{KS}(\omega) \ast [\hat{1} + f_{Hxc}(\omega) \ast \Re \chi(\omega)] = 0
\]

Since [...]’s above cannot vanish identically in the whole true and KS gap regions \( \rightarrow \)

wherever \( \text{Im} \chi_{KS}(\omega) = 0 \iff \text{Im} \chi(\omega) = 0. \)
Having an imaginary part means $f_{xc}$ cannot be frequency-independent.

Why?

$$f_{xc}(\mathbf{r}, \mathbf{r}'; t, t')$$ must be real, since

$$f_{xc}[n_0](\mathbf{r} t, \mathbf{r}' t') = \frac{\delta v_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \bigg|_{n=n_0}$$

→ its Fourier transform to $\omega$-domain must then satisfy

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}^*(\mathbf{r}, \mathbf{r}'; -\omega)$$

→ adiabatic approx means $\omega$-independent ($= \frac{\delta^2 E_{xc}[n]}{\delta n(r) \delta n(r')} |_{n_{GS}}$) and therefore $f_{xc}$ real

→ adiabatic $f_{xc}$ cannot open the gap

Note that also a long-ranged $f_{xc} \sim 1/q^2$ is also required.

Summary

- ATDDFT fundamentally fails to describe double-excitations: strong frequency-dependence is essential.

- Diagonalizing in the (small) subspace where double excitations mix with singles, we can derive a practical frequency-dependent kernel that does the job. Shown to work well for simple model systems, as well as real molecules.

- Likewise, in autoionization, resonances due to double-excitations are missed in ATDDFT.