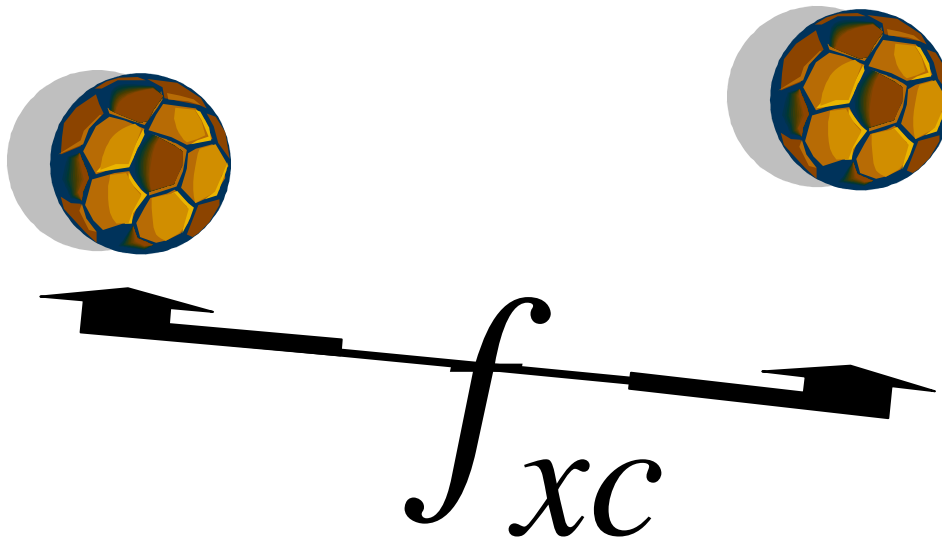


Advanced TDDFT

II. Frequency-Dependent Kernels: Double Excitations



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First, quick recall of how we get excitations in TDDFT: Linear response

Petersilka, Gossmann & Gross 76, 1212 (1996)

Casida, in Th. and Comput. Chem. 4, 391 (1996)

Poles at true excitations Poles at KS excitations

$$\vec{\chi}^{-1}(\omega) = \vec{\chi}_S^{-1}(\omega) - \vec{f}_{\text{HXC}}(\omega)$$

$1/|\mathbf{r}-\mathbf{r}'| + f_{\text{XC}}[n_0](\mathbf{r}, \mathbf{r}', \omega)$

adiabatic approx: no ω -dep

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

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

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

TDDFT linear response in quantum chemistry codes:

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

$q = (i \rightarrow a)$ labels a **single** excitation of the KS system, with transition frequency $\omega_q = \epsilon_a - \epsilon_i$, and

$$[q | f_{\text{HXC}}(\omega) | q'] = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \phi_{i'}(\mathbf{r}') \phi_{a'}^*(\mathbf{r}')$$

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

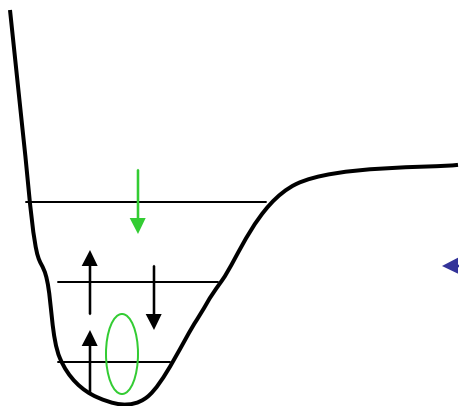
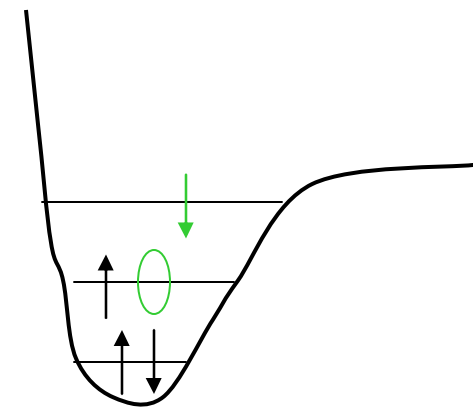
When shift from bare KS small:

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

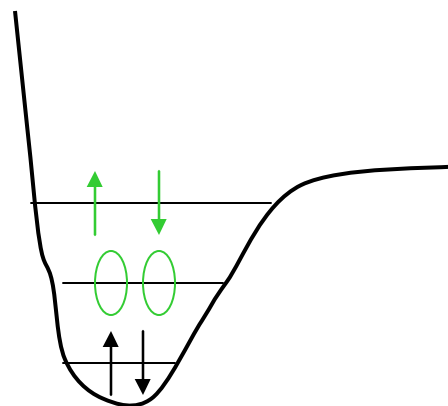
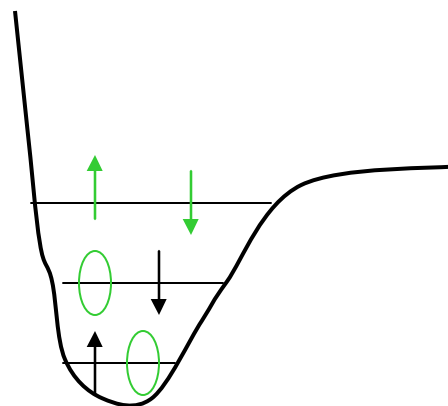
Types of Excitations

Non-interacting systems eg. 4-electron atom

Eg. single excitations



Eg. double excitations



← near-degenerate →

Interacting 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:

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

χ – poles at true states that are mixtures of singles, doubles, and higher excitations

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

➡ χ has more poles than χ_s

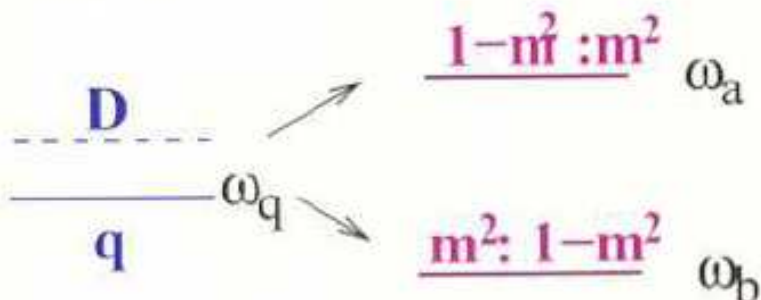
? How does f_{xc} generate more poles to get states of multiple excitation character?

Simplest Model:

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

KS

Exact



$$\Psi_a = m\Phi_D + \sqrt{1-m^2}\Phi_q,$$

$$\Psi_b = \sqrt{1-m^2}\Phi_D - m\Phi_q, \quad 0 < m < 1$$

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) \approx \frac{A(\mathbf{r}, \mathbf{r}', (\omega))}{\omega - \omega_q}$$

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

Invert and insert into Dyson-like eqn for kernel \rightarrow **dressed SPA** (i.e. ω -dependent):

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

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

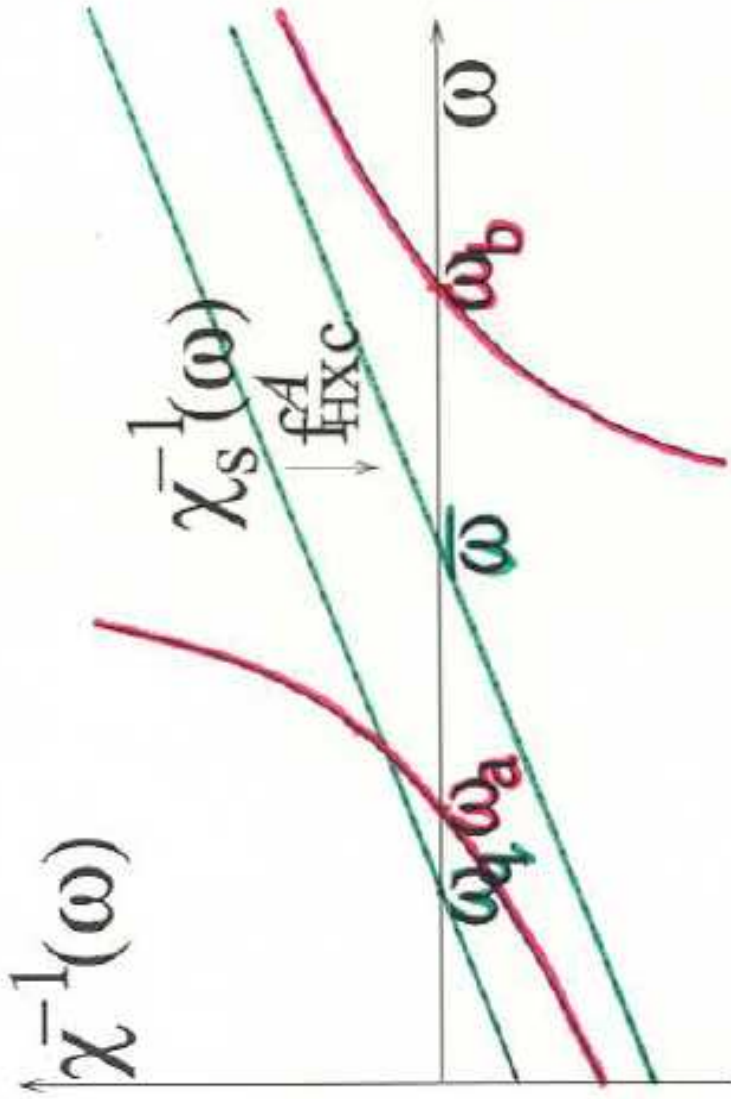
adiabatic

strong non-adiabaticity!

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

This kernel matrix element, by construction, yields the exact true ω 's when used in the Dressed SPA,

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



$$\chi^{-1} = \chi_s^{-1} - f_{HXC}$$

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

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


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:

usual adiabatic matrix element


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

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
JCP 120, 5932 (2004)*

Alternate Derivations

M.E. Casida

JCP 122, 054111 (2005)

-- Equation of motion superoperator formulation of propagator theory

Miguel Huix-Rottlant & M.E. Casida – see poster downstairs!

P. Romaniello, et. al.

JCP 130, 044108 (2009)

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

O. Gritsenko & E.J. Baerends

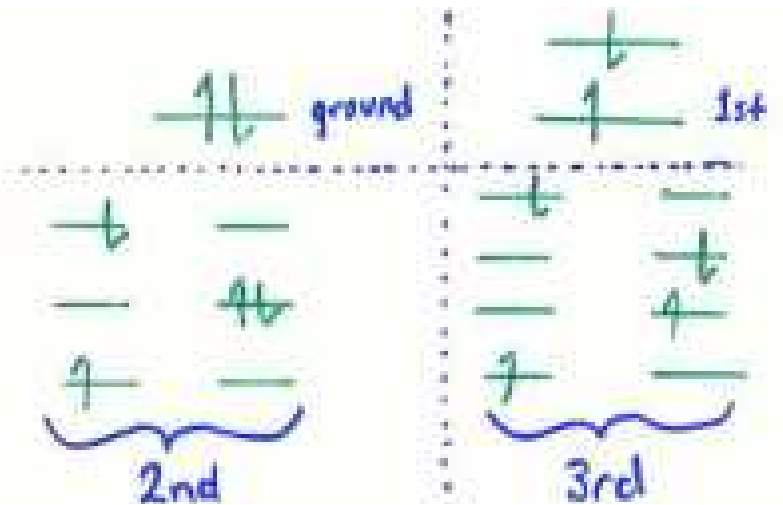
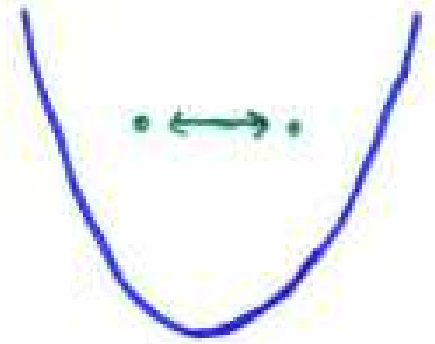
PCCP 11, 4640, (2009).

-- Use CEDA (Common Energy Denominator Approximation) to account for the effect of the other states on the inverse kernels, and obtain spatial dependence of fxc-kernel as well.

Simple Model System: 2 el. in 1d

$$V_{\text{ext}} = x^2/2$$

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



Exact: $\begin{cases} 1/2 : 1/2 \\ 1/2 : 1/2 \end{cases}$

Exact: $\begin{cases} 1/3 : 2/3 \\ 2/3 : 1/3 \end{cases}$

$$\lambda = 0.2$$

3rd	$\frac{3.0000}{2.9640}$	$\frac{2.9483}{2.9148}$	$\frac{2.9734}{2.9622}$	$\frac{3.0016}{2.9622}$
2nd	$\frac{2.0000}{1.9640}$	$\frac{1.9532}{1.9232}$	$\frac{1.9833}{1.9621}$	$\frac{2.0022}{1.9621}$
1st	1.0000	0.9616	1.0014	1.0014
	Exact	KS	SPA	DSPA

$$f_{\text{HXC}}^A \approx f_{\text{HX}} = \frac{1}{2} f_{\text{H}} = \frac{\lambda}{2} \delta(x_1 - x_2)$$

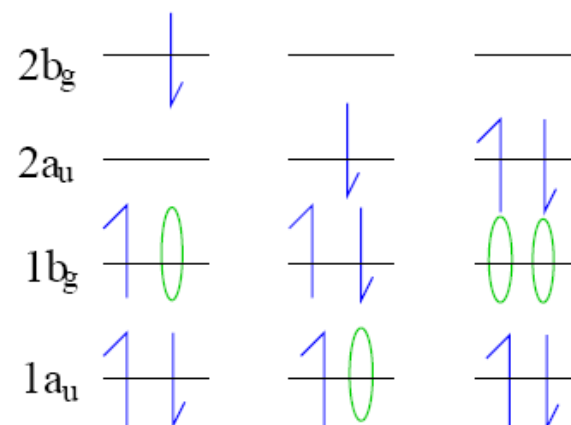
Dressed TDDFT
in SPA, $f_{\text{xc}}(\omega)$

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.

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



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

System	CASPT2	ATDDFT	D-TD-TDDFT
C ₄ H ₆	6.27	7.02	6.28
C ₆ H ₈	5.20	5.83	5.16

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

ΔE	CASPT2	ATDDFT	D-TD-TDDFT
Vertical	4.3	5.8	4.16
0-0	5.2	6.8	5.28

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

G. Mazur, R. Wlodarczyk, *J. Comp. Chem.* **30**, 811, (2008) – fuller analysis, implementation in *Niedoda*

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 PES

Levine, Ko, Quenneville, Martinez, Mol. Phys. 104, 1039 (2006)

(iii) Certain long-range charge transfer states!

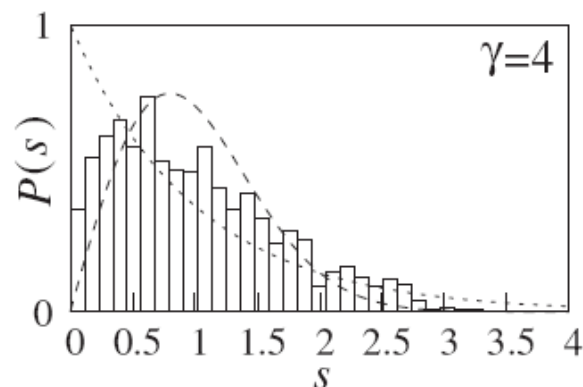
Stay tuned for next lecture!

(iv) Electron-induced quantum chaos in quantum wells

Wasserman, Maitra, Heller, PRA 77, 042503 (2008)

(v) Certain autoionizing resonances

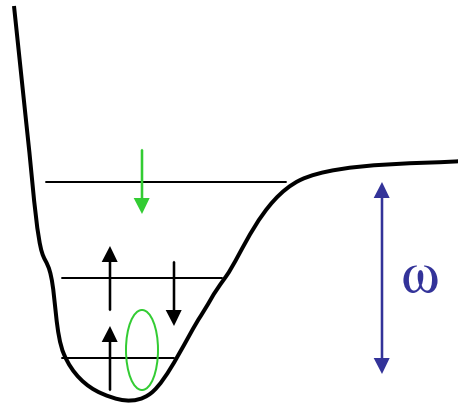
Next!



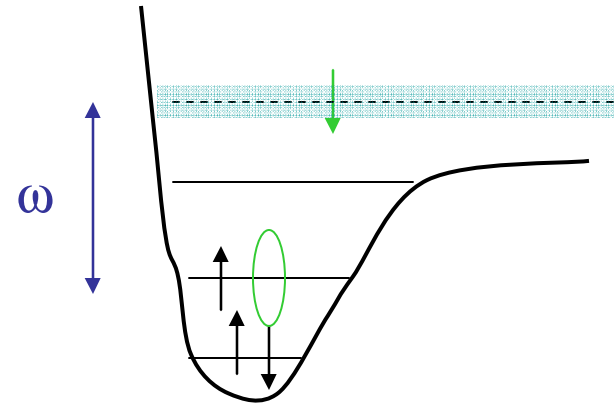
Autoionizing Resonances

When energy of a bound excitation lies in the continuum:

KS (or another orbital) picture



bound, localized excitation



continuum excitation

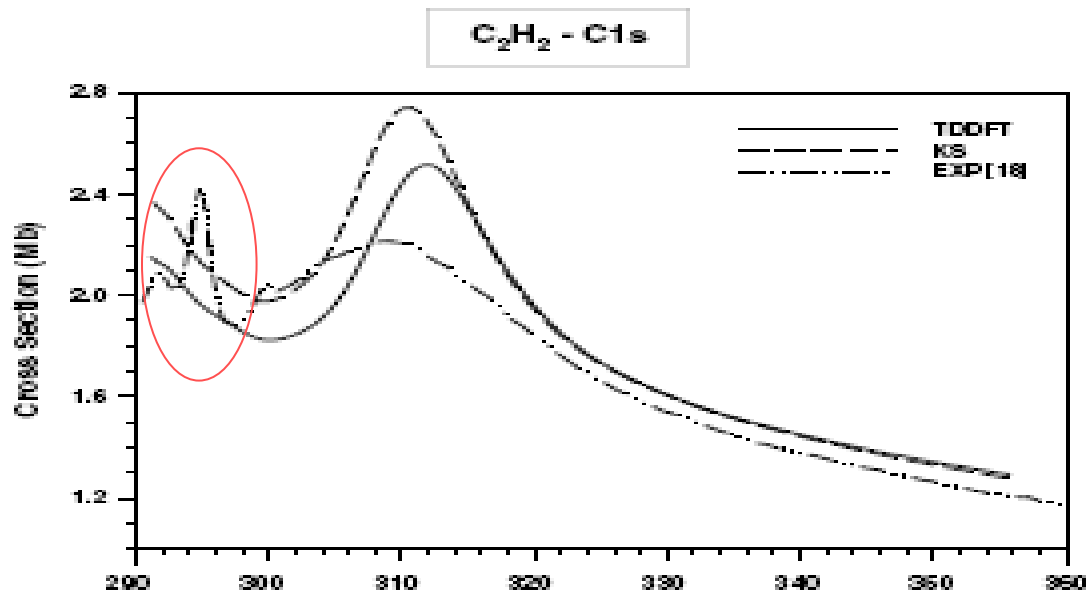
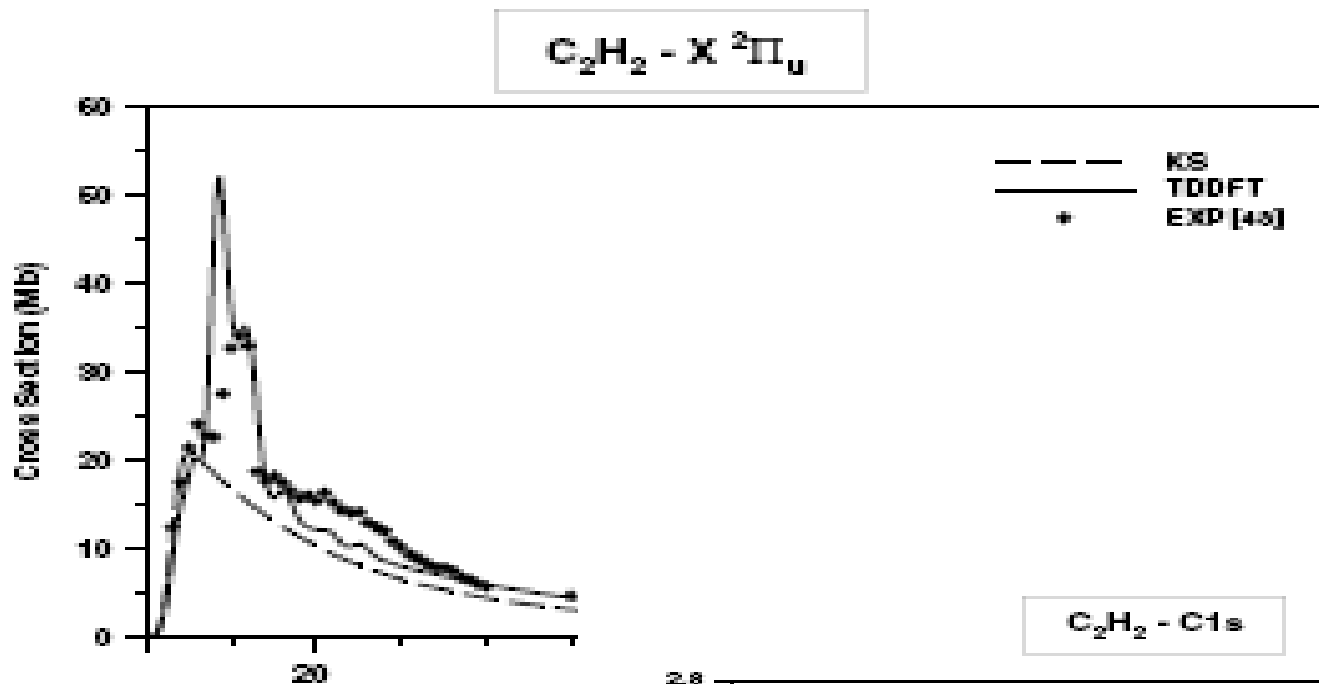
True system: Electron-interaction mixes these states → Fano resonance

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

M. Hellgren and U. van Barth, JCP 131, 044110 (2009) – gives Fano parameters directly implied by Adiabatic TDDFT (for resonances arising from single excitations)

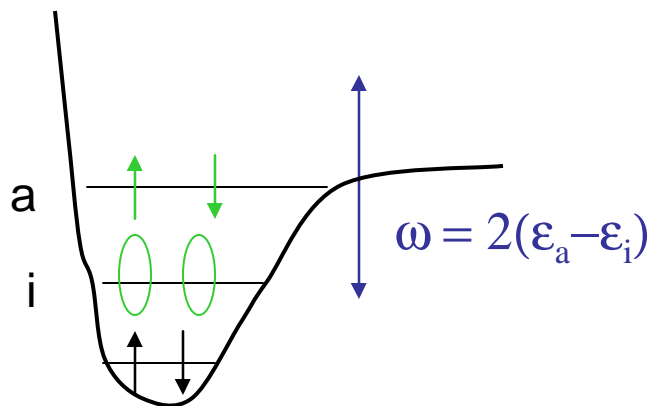
Auto-ionizing Resonances in TDDFT

Eg. Acetylene: G. Fronzoni, M. Stener, P. Decleva, *Chem. Phys.* **298**, 141 (2004)

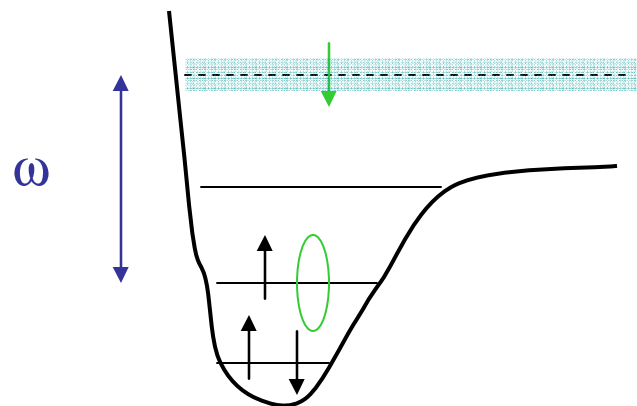


But here's a resonance that ATDDFT misses:

Why? It is due to a double excitation.



bound, localized **double** excitation with energy in the continuum



single excitation to continuum

Electron-interaction mixes these states → Fano resonance

✘ ATDDFT does not get these – double-ex

Getting the cross-section in TDDFT

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

Where ,

$$\text{Im}\chi(r, r', \omega) = -\pi \sum_I \langle 0 | \hat{n}(\mathbf{r}) | I \rangle \langle I | \hat{n}(\mathbf{r}') | 0 \rangle (\delta(\omega - \Omega_I) - \delta(\omega + \Omega_I))$$

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

How does the exact kernel add the resonant bump to χ_s ?

Need to do 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. Fano, Phys. Rev. 124, 1866 (1961)

Gives ratio of transition probability to continuum modified by the resonance, i.e.

$$\frac{|\langle \Psi_E | \hat{T} | i \rangle|^2}{|\langle \Phi_E | \hat{T} | i \rangle|^2} = \frac{(\omega - \omega_r + \Gamma q/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2}$$

Take $\hat{T} = \hat{n}(r)$

Kohn Sham states

where

Ψ_E is the interacting continuum state at energy $E = \omega + E_i$

Φ_E is the non-interacting continuum state at energy $E = \omega + E_i$

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

\hat{T} is a transition operator

$\omega_r = E_r - E_i = E_b - E_i + P \int \frac{|V_{E'}|^2}{E - E'} dE'$ is resonance position due to bound state

$V_E = \langle \Phi_E | V_{\text{cpl}} | \Phi_b \rangle$ is coupling Hamiltonian matrix elt – our case $V_{\text{cpl}} = V_{\text{ee}} - V_{\text{Hxc}}$

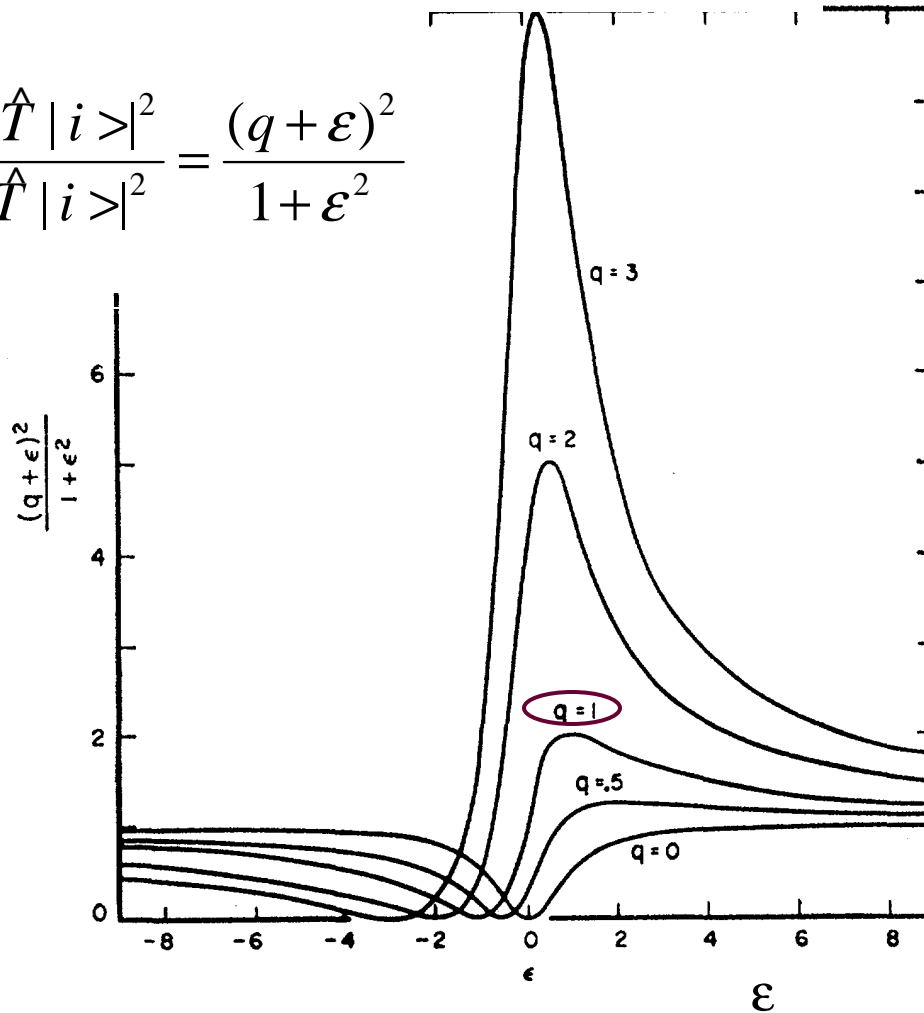
$\Gamma = 2\pi |V_E|^2$ is resonance width and q is asymmetry parameter...next slide

The expression for q looks complicated:

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

– but for our case, it is just 1 !!

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



because the double-excitation does not contribute to the KS cross-section, and the oscillator strength sum rule must be conserved, line-shape factor must be purely antisymmetric.

$q=1$

Figure from U. Fano, Phys. Rev. **124**,1866 (1961)

Fano into TDDFT

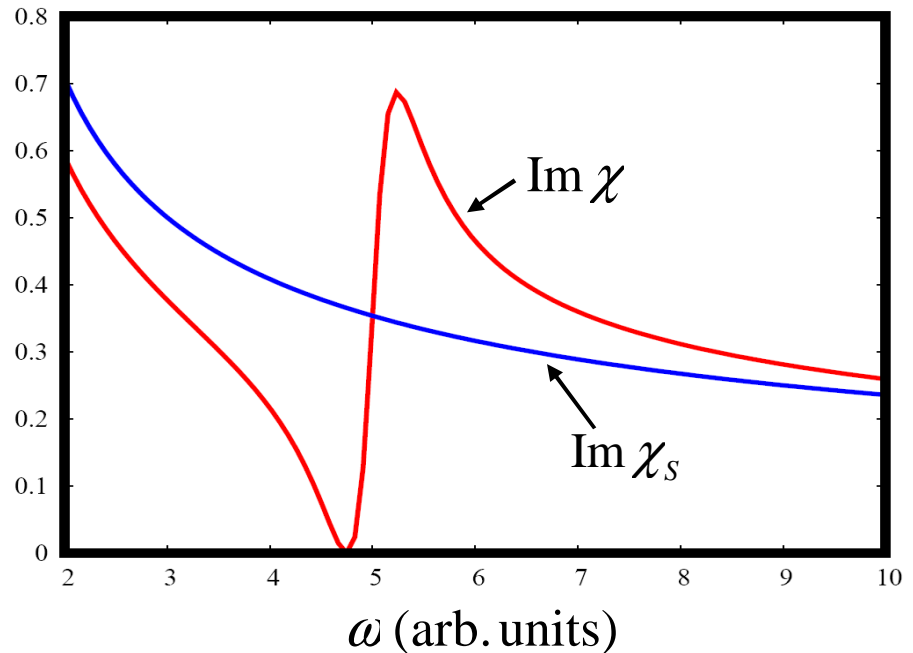
Consider $|i\rangle$, ϕ_E , and ϕ_{bound} (doubly excited) to be Kohn Sham states

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

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

For ω near resonance

In this approx, we considered coupling between doubly-excited to continuum only, and took Γ as the smallest energy scale in the system.



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

Use Kramers-Kronig relation

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

·
·
·
·

Assuming $2\omega_r \gg \Gamma$

$$\Re \chi(\omega) = \Re \chi_S(\omega) + \frac{\Gamma^2/2}{(\omega - \omega_r)^2 + (\frac{\Gamma}{2})^2} \Im \chi_S(\omega)$$

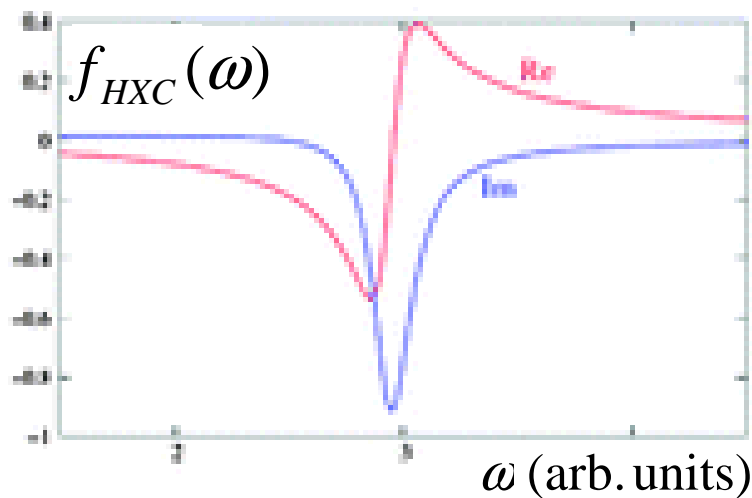
Putting real and imaginary together, we get:

$$\chi = \chi_S + \frac{\Gamma(\Gamma/2 + i(\omega - \omega_r))}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \Im \chi_S$$

So $f_{HXC}(r, r', \omega) = \chi_S^{-1} - \chi^{-1}$ looks like

$$\omega \text{ near } \omega_r$$

$$\omega_r \gg \Gamma$$



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

See also: M. Hellgren and U. van Barth, *JCP* **131**, 044110 (2009) – Fano parameters directly implied by adiabatic TDDFT (for resonances arising from *single* excitations)

Frequency-Dependent Kernels, more generally

- Note some other recent ω -dep kernels have been developed for calculations of spectra (*but not for capturing doubles correctly*):
 - **Exact-exchange kernel**, A. Görling, *PRA* **57**, 3433 (1998); Y-H. Kim & A. Gorling *PRL* **89**, 096402 (2002) – excitons in solids; Y. Shigeta, K. Hirao, and S. Hirata, *PRA* **73**, 010502(R) (2006); M. Hellgren & U. von Barth *JCP* **131** 044110 (2009) – pole structure of f_x in discrete spectrum and its violence in the continuum of small atoms
 - **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) test it on atoms and small molecules
 - **“Nanoquanta kernel”**, M. Gatti, V. Olevano, L. Reining, I. Tokatly, *PRL* **99**, 057401 (2007) and citations therein – using N -body Green’s functions from many-body theory to derive f_{xc} kernel of TDDFT
- Main motivation behind these is capturing spatial ultranonlocality (recall \rightarrow 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

Valence-conduction band energy difference at zero Bloch wave-vector

- Typically KS gap \ll true gap
- Opening up the gap requires fxc to have an imaginary part.

Why? Spectrum measures $\text{Im } \chi(\omega)$

$$\text{Now } \text{Im } \chi_s(\omega \in \text{KS gap}) = 0 \rightarrow \text{Im } \chi_s^{-1}(\omega \in \text{KS gap}) = 0$$

Using a real fxc in $\vec{\chi}^{-1}(\omega) = \vec{\chi}_s^{-1}(\omega) - \vec{f}_{\text{HXC}}(\omega)$

means that $\text{Im } \chi^{-1}(\omega) = \text{Im } \chi_s^{-1}(\omega) \rightarrow$ where one is zero, the other must be too.

\rightarrow both χ^{-1} and χ_s^{-1} are real at these $\omega \rightarrow \text{Im } \chi$ and $\text{Im } \chi_s$ have same gap

- Adiabatic fxc is real \rightarrow cannot open the gap
Note that long-ranged fxc $\sim 1/q^2$ is also required.

See more in eg. “*Quantum Theory of the Electron Liquid*” by G.F. Giuliani and G. Vignale (Cambridge, 2005)

Summary

- ATDDFT fundamentally fails to describe double-excitations as 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 (although more testing is needed).
- Likewise, in autoionization, resonances due to double-excitations are missed in ATDDFT.

A little more detail...

Diagonalizing in the 2 x 2 block of single and double state, gives

$$E = H_{qq} + \frac{|H_{qD}|^2}{E - H_{DD}} \quad \langle \Phi_q | H | \Phi_D \rangle$$

To get frequency, subtract E_0 , but instead we subtract H_{00} for consistency with 2x2 truncation:

$$\omega = (H_{qq} - H_{00}) + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{00})}$$

Replace freq-indep. part

$$H_{qq} - H_{00} \rightarrow \omega_q + 2[q|f_H + f_{XC}^d|q]$$