Advanced TDDFT II

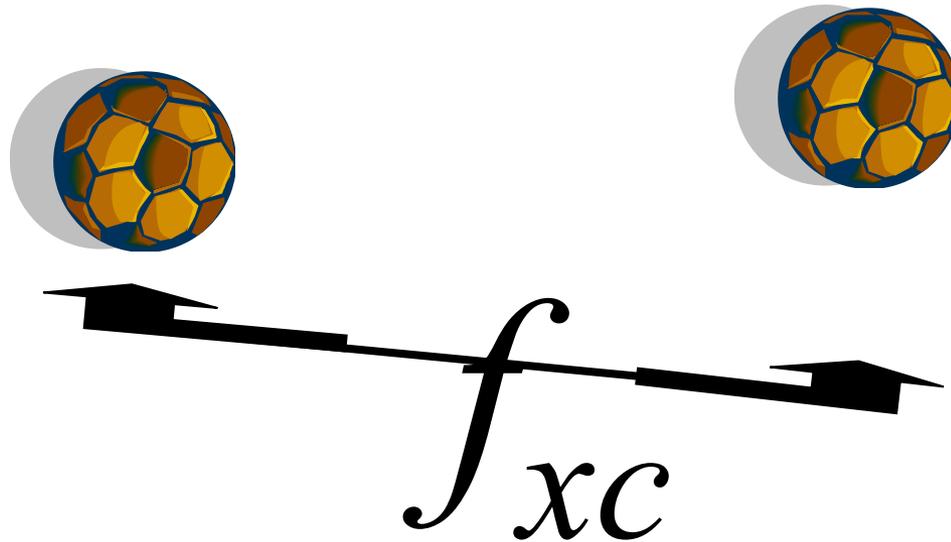## II. Frequency-Dependent Kernels: Double Excitations

$$f_{xc}$$

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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

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

*Casida, in Recent Advances in Comput. Chem. **1**,155, ed. Chong (1995)*

Poles at true excitations

Poles at KS excitations

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

$$\overleftrightarrow{\chi}^{-1}(\omega) = \overleftrightarrow{\chi}_{\mathrm{S}}^{-1}(\omega) - \overleftrightarrow{f}_{\mathrm{HXC}}(\omega)$$

adiabatic approx: no ω-dep

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

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

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

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

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 $\omega_q = \varepsilon_a - \varepsilon_i$, 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 → true frequencies of interacting system

Eigenvectors → oscillator strengths

Useful tool for analysis

Zoom in on a single KS excitation, q = i→ a

Well-separated single excitations: SMA $\quad \omega^2 = \omega_q^2 + 4\omega_q[q|f_{\text{HXC}}(\omega_q)|q]$
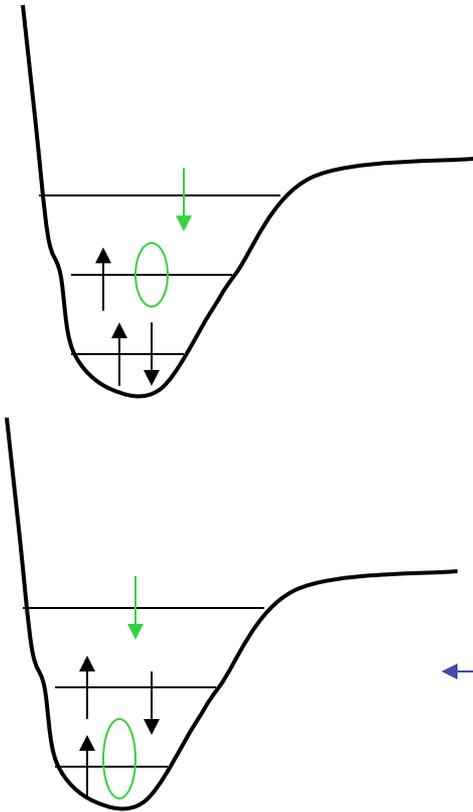
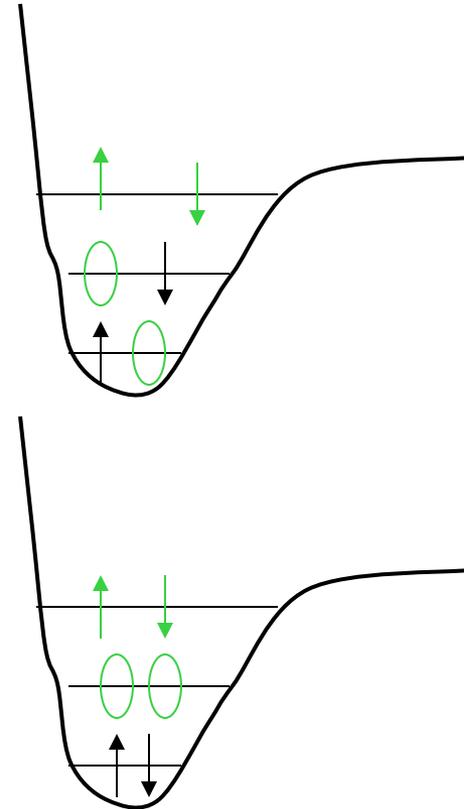When shift from bare KS small: SPA $\quad \omega = \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q]$

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:

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

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

$$\frac{1-m^2 : m^2}{} \omega_a$$

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

D - - - - -

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

$$\underline{}\omega_q$$

q

$$\frac{m^2 : 1-m^2}{} \omega_b$$

q : D

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

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

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

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

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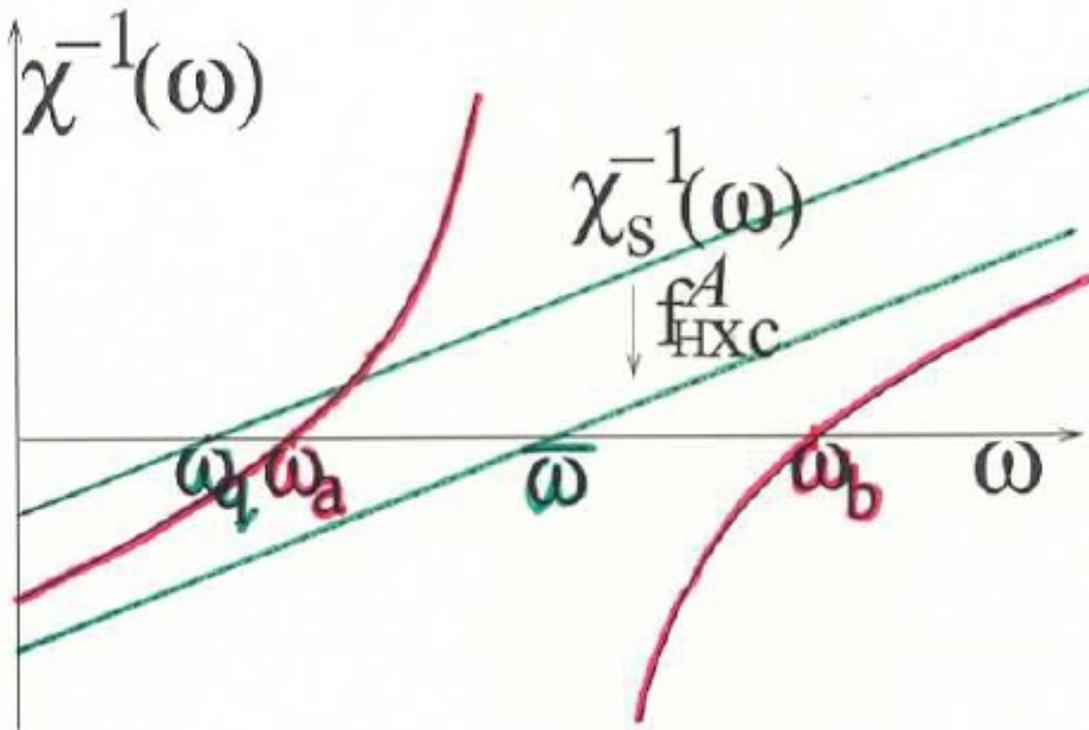
adiabatic

strong non-adiabaticity!

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

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

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

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

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

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

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)*

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

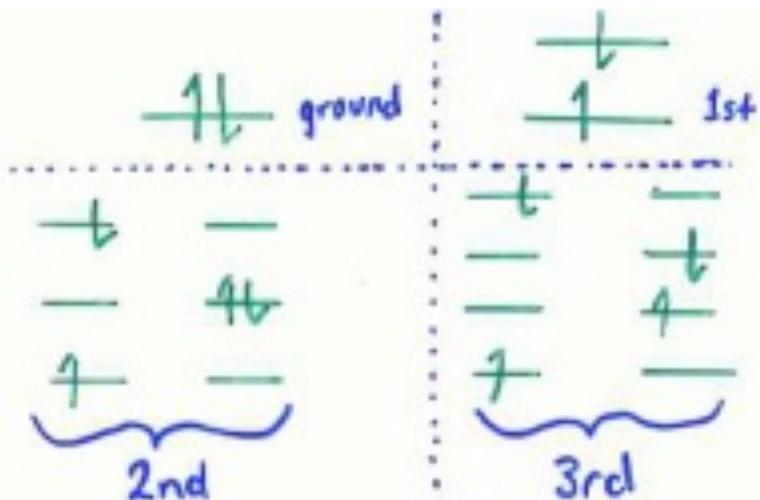-- from second-order polarization propagator (SOPPA) correction to ATDDFT

➢ P. Romaniello, D. Sangalli, J. A. Berger, F. Sottile, L. G. Molinari, L. Reining, and G. Onida, *JCP **130**, 044108 (2009)*

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

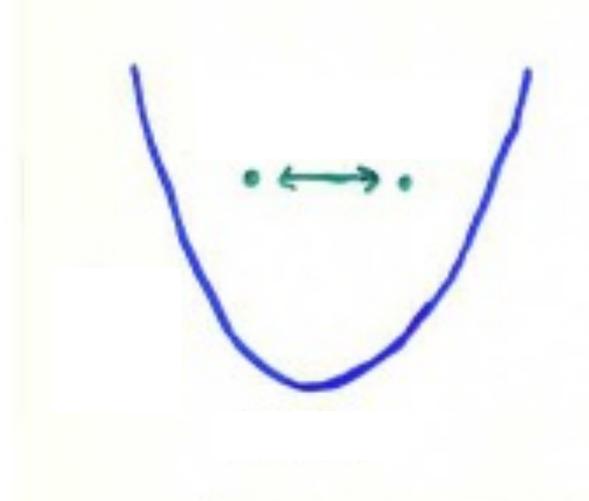➢ O. Gritsenko & E.J. Baerends, *PCCP **11**, 4640, (2009).*

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

Simple Model System: 2 el. in 1d

$Vext = x^2/2$

$Vee = \lambda \, \delta(x-x')$

Exact: $\frac{1}{2} : \frac{1}{2}$ Exact: $1/3 : 2/3$

$\frac{1}{2} : \frac{1}{2}$ $2/3 : 1/3$

$\lambda = 0.2$

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

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

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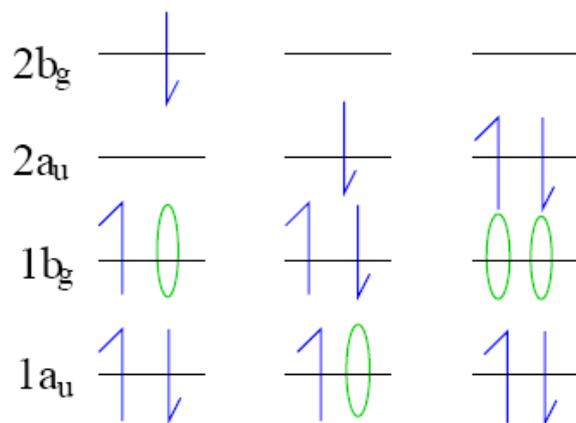
- 2^1A_g Vertical excitation energies (eV) for butadiene and hexatriene

System	CASPT2	ATDDFT	D-TD-TDDFT
C_4H_6	6.27	7.02	6.28
C_6H_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

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

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

Other implementations and tests:

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

M. Huix-Rotllant, A. Ipatov, A. Rubio, M. E. Casida, Chem. Phys. (2011) – extensive testing on 28 organic molecules, discussion of what's best for adiabatic part…

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

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

(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,
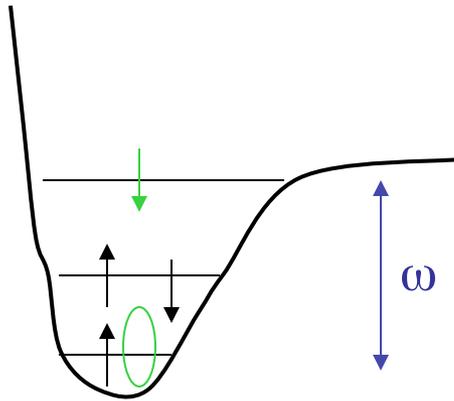i.e. no mixing between singly-excited states lying near a double-excitation

See analyses in
P. Elliott, S. Goldson, C. Canahui, N. T. Maitra, Chem. Phys. **135,** 104110 (2011), and
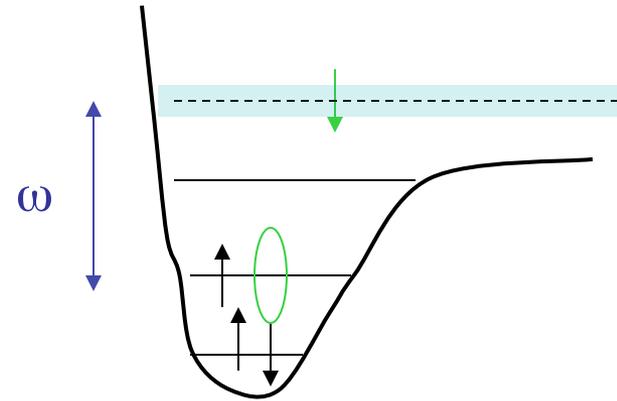*S. Tretiak and V. Chernyak, JCP* **119***, 8809 (2003).*

Autoizing Resonances

When energy of a bound excitation lies in the continuum:

KS (or another orbital) picture

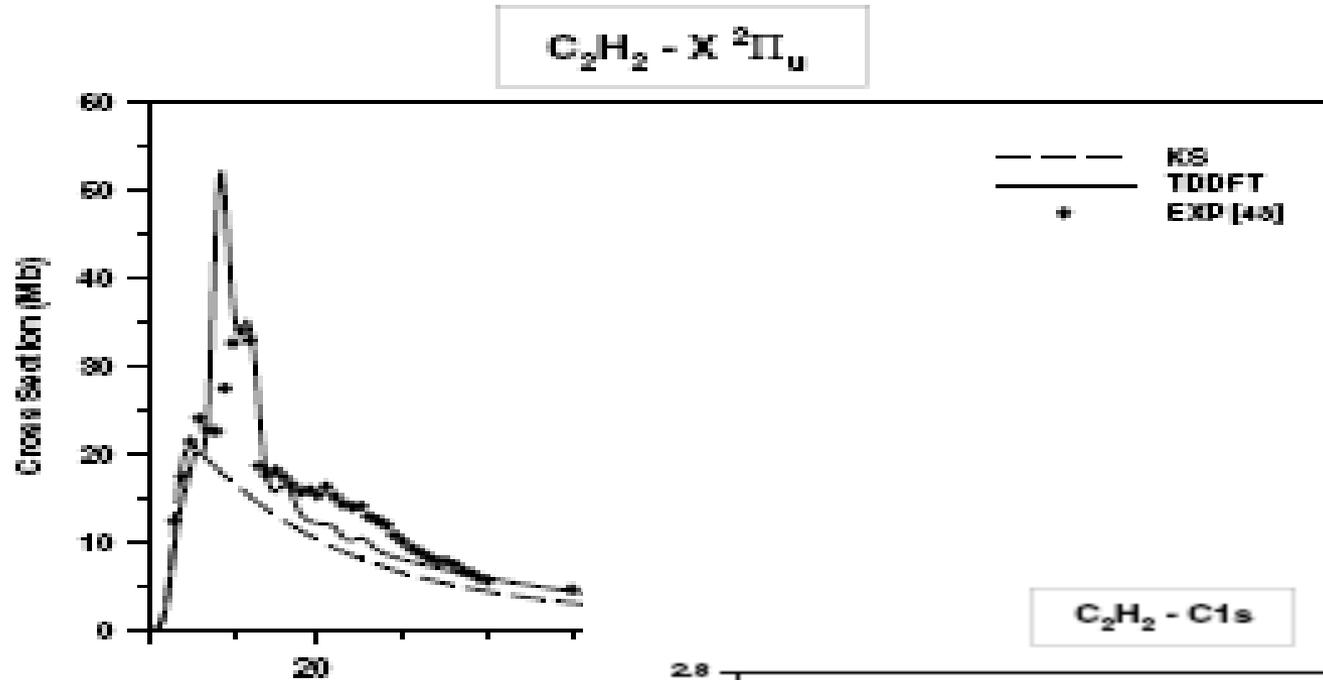bound, localized excitation   continuum excitation

True system: <u>Electron-interaction mixes these states → Fano resonance</u>

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

• *M. Hellgren & U. van Barth, JCP **131**, 044110 (2009)* → Fano parameters directly implied by Adiabatic TDDFT

•(Also note *Wasserman & Moiseyev, PRL **98,**093003 (2007), Whitenack & Wasserman, PRL **107,**163002 (2011)* -- complex-scaled DFT for lowest-energy resonance)
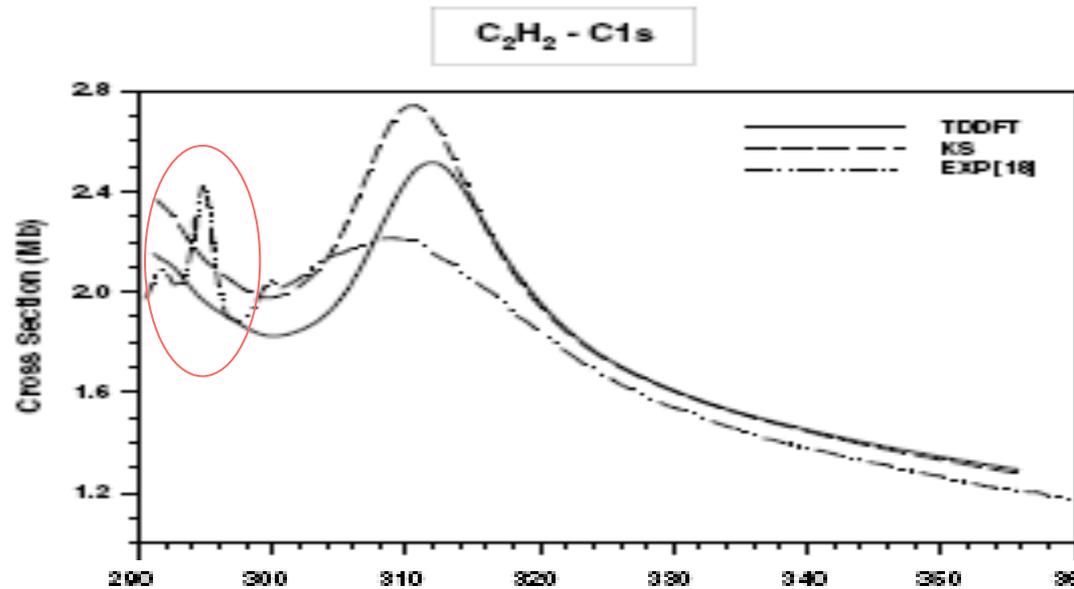
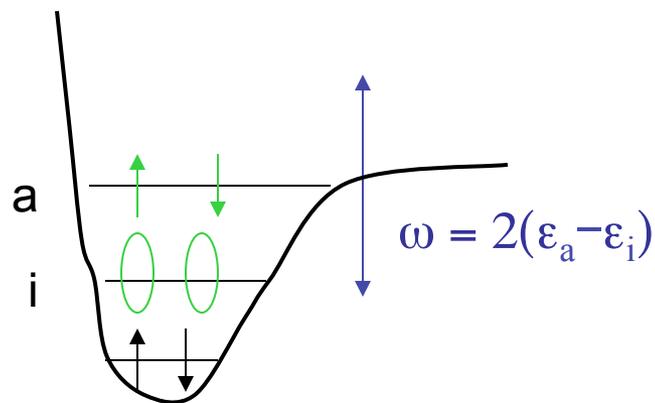# Auto-ionizing Resonances in TDDFT

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

$C_2H_2 - X\ ^2\Pi_u$

But here's a resonance that ATDDFT misses:

Why? It is due to a double excitation.

$C_2H_2 - C1s$

a

i

$\omega = 2(\varepsilon_a - \varepsilon_i)$

ω

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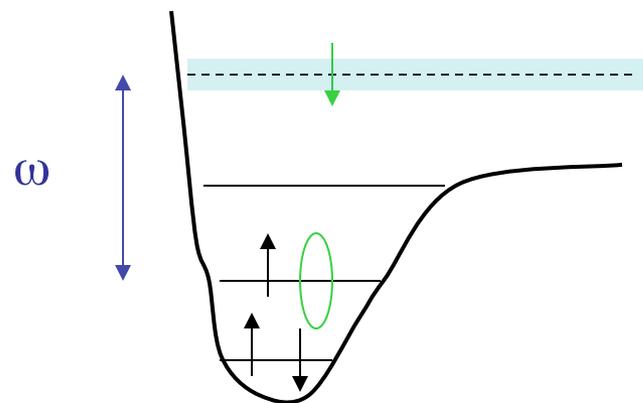
single excitation to continuum

Electron-interaction mixes these states → Fano resonance

✖ ATDDFT does not get these – double-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: $\sigma_{\alpha\beta}(\omega) = \frac{4\pi\omega}{c} \int d^3r\, d^3r'\, r_\alpha\, r'_\beta\, Im\chi(\mathbf{r}, \mathbf{r}', \omega)$

Where ,

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

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

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

Need 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

"pre-diagonalized"

Transition probability to continuum modified by the resonance due to Φ_b

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

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

$$E_r = E_b + \mathcal{P} \int dE' \frac{|V_{E'}|^2}{E - E'}$$

resonance position

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

resonance width

coupling Hamiltonian

q = asymmetry parameter…next slide

Ψ_E is the resonance-modified continuum state at energy $E = \omega + E_i$
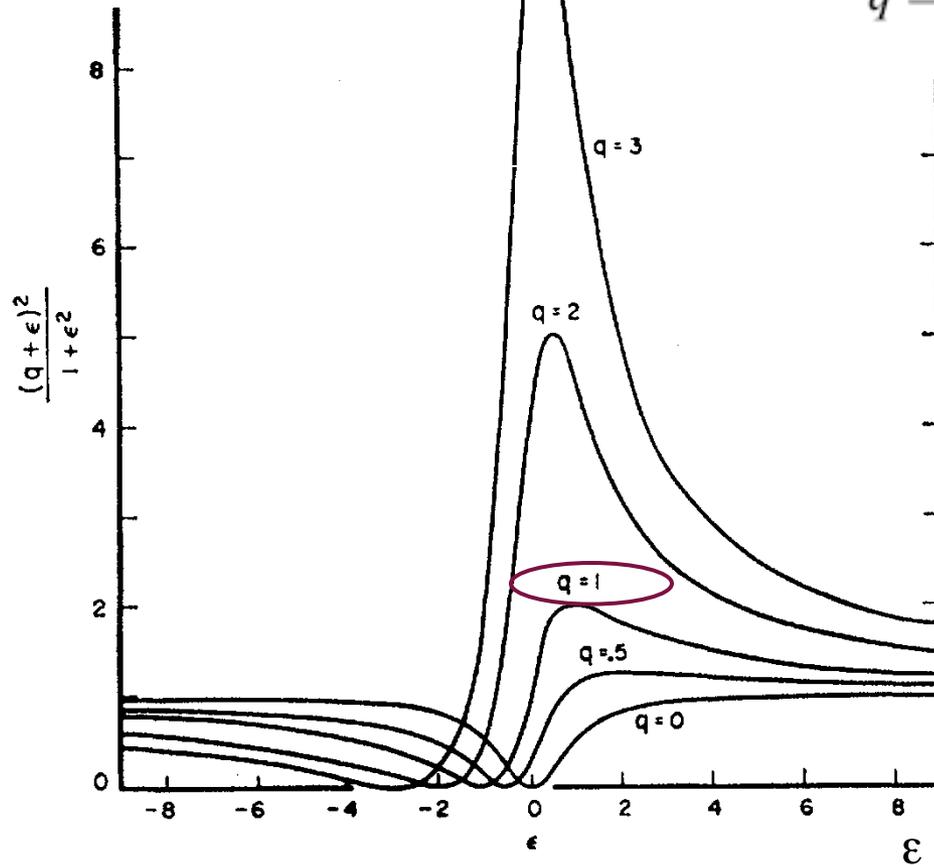
Φ_E is the unmodified continuum state at energy $E = \omega + E_i$

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

$\hat{T}$ is a transition operator

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:

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

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!*

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

Fano into TDDFT

Consider $|i>$, Φ_E and Φ_b (double-ex) to be *Kohn-Sham* states, and $\hat{T} = \hat{n}(r)$,

into Fano analysis:

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

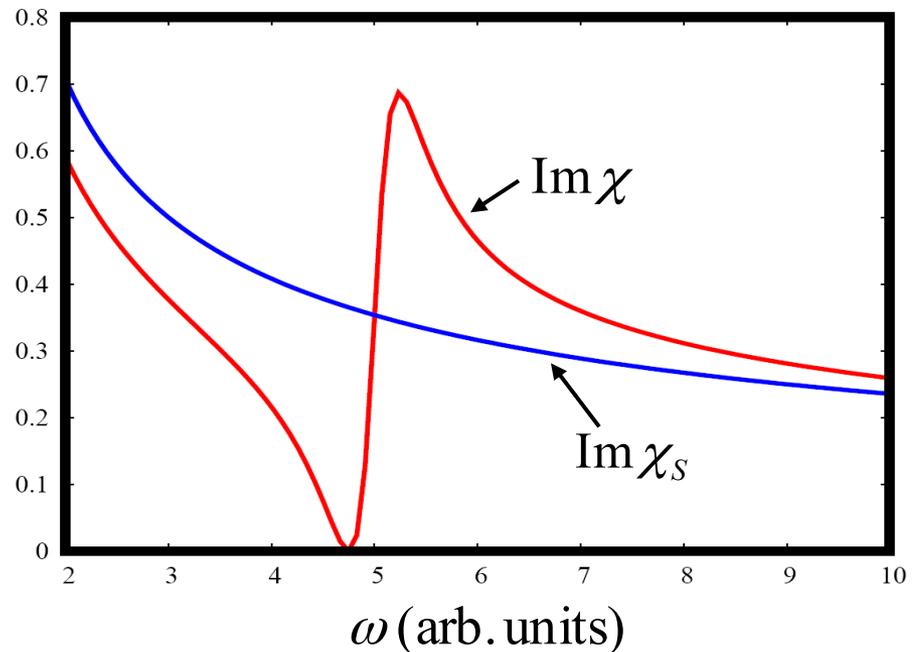$$\boxed{\text{Im}\,\chi(r,r',\omega) \approx \frac{(\omega - \omega_r + \Gamma/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2}\,\text{Im}\chi_S(r,r',\omega)}$$

For ω near resonance

Approximations:
 -- considered coupling between doubly-excited bound-state and continuum only

-- took Γ as the smallest energy scale in the system.

$\text{Im}\chi$

$\text{Im}\chi_S$

ω (arb. units)

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

Use Kramers-Kronig relation

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

… eventually get…

weak-interaction limit

ω near ω_r

$\omega_r \gg \Gamma$

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

$f_{HXC}(\omega)$

$\omega \,(\text{arb.\,units})$
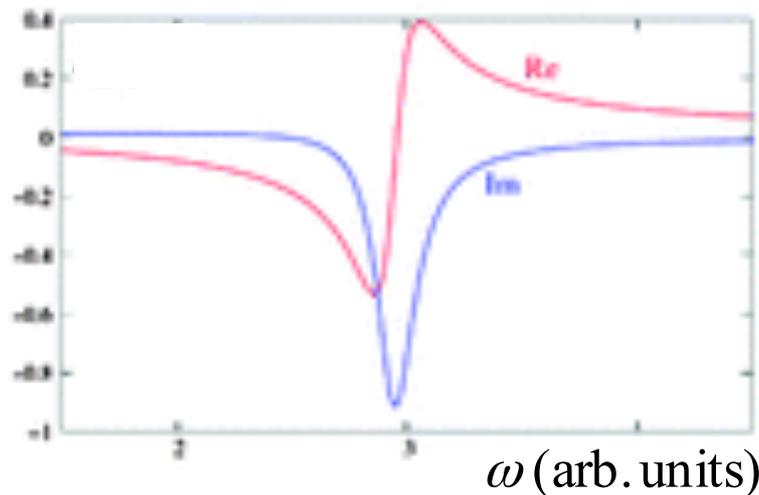
A. Krueger & N. T. Maitra, PCCP **11**, 4655 (2009);

P. Elliott, S. Goldson, C. Canahui, N. T. Maitra, Chem. Phys. **135**, 104110 (2011).

<u>Frequency-Dependent Kernels, more generally</u>

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

-- Exact-exchange kernel, *A. Görling, PRA **57**, 3433 (1998); Y. Shigeta, K. Hirao, and S. Hirata, PRA **73**, 010502(R) (2006); M. Hellgren & U. von Barth JCP **131** 044110 (2009)*

-- 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)*

 -- "Nanoquanta kernel", *M. Gatti, V. Olevano, L. Reining, I. V. Tokatly, PRL **99**, 057401 (2007), S.Botti, A. Schindlmayr, R. Del Sole, L. Reining, Rep. Prog. Phys. **70**, 357 (2007), and citations therein* – derive f_{xc} from Bethe-Salpeter equation.

• 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 <u>requires</u> f_{xc} to have an imaginary part.

Why?

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

$$\chi(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega) \star f_{Hxc}(\omega) \star \chi(\omega)$$

For ω inside the KS gap,

$$\mathfrak{Im}\, \chi_{KS}(\omega) = 0 \longrightarrow \left[\hat{1} - \mathfrak{Re}\, \chi_{KS}(\omega) \star f_{Hxc}(\omega)\right] \star \mathfrak{Im}\, \chi(\omega) = 0$$

While, analogously for ω inside the true gap,

$$\mathfrak{Im}\, \chi(\omega) = 0 \longrightarrow \mathfrak{Im}\, \chi_{KS}(\omega) \star \left[\hat{1} + f_{Hxc}(\omega) \star \mathfrak{Re}\, \chi(\omega)\right] = 0$$

Since [….]'s above cannot vanish identically in the *whole* true and KS gap regions →

wherever $\mathfrak{Im}\, \chi_{KS}(\omega) = 0 \longleftrightarrow \mathfrak{Im}\, \chi(\omega) = 0.$

$$\mathfrak{Im}\,\chi_{\mathrm{KS}}(\omega) = 0 \longleftrightarrow \mathfrak{Im}\,\chi(\omega) = 0.$$

i.e. the KS system and the true system have the same gap when a purely-real approximation for f_{xc} is used

➢ Having an imaginary part means f_{xc} cannot be frequency-independent.

Why? $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';t,t')$ must be real, since $f_{\mathrm{xc}}[n_0](\mathbf{r}t,\mathbf{r}'t') = \left.\dfrac{\delta v_{\mathrm{xc}}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n=n_0}$

→ its Fourier transform to ω-domain must then satisfy
$$f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';\omega) = f^*_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';-\omega)$$

→adiabatic approx means ω-independent (= $\left.\dfrac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(r)\delta n(r')}\right|_{n_{\mathrm{GS}}}$) and therefore f_{xc} real

→ adiabatic f_{xc} cannot open the gap

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

See more in eg. *"Quantum Theory of the Electron Liquid" by G.F. Guiliani and G. Vignale (Cambridge, 2005); also some discussion in Ch. 4 of your "Fundamentals of TDDFT" book.*

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.