

Memory in TDDFT II: Linear-Response Regime



Neepa T. Maitra

Rutgers University at Newark



TDDFT for Linear Response



Unprecedented balance between accuracy and efficiency for electronic excitations

.... E.g. examples in Hardy's lecture yesterday...



But with the usual approximations, it doesn't always work!

Plan

- ❖ Brief recall of linear response TDDFT for excitations and response
- ❖ Cases where the usual approximations fail
- ❖ Memory in linear response: double-excitations

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

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

adiabatic approx: no ω -dep

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

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).

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

TDDFT linear response in matrix form (discrete spectra):

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

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

Where & why the *usual* approxs give poor excitations

i.e. the usual xc approxs that are semi-local in space and local in time

● Rydberg states

A little diversion: asymptotic behavior of the xc potential

Question for you! What is $v_{xc}(r \rightarrow \infty)$ for an atom ?

Far from nucleus of charge Z , electron sees an effective charge of $Z - (N-1)$

So, $v_s(r \rightarrow \infty) \rightarrow \frac{-Z+(N-1)}{r}$ while

$v_{ext}(r) \rightarrow \frac{-Z}{r}$ and $v_H(r \rightarrow \infty) \rightarrow \frac{N}{r}$ hence

$v_{xc}(r \rightarrow \infty) = v_s - v_{ext} - v_H \rightarrow \frac{-1}{r}$ (true for any finite system)

Another Question for you: What about in LDA? Or GGA?

Since $v_{xc}(r)$ depends locally on the $n(r)$, and $n(r)$ decays exponentially, then $v_{xc}(r)$ decays exponentially with r

This has some grave consequences!

A little diversion: asymptotic behavior of the xc potential

... recall Adam's lecture this morning!!

Without $-1/r$ tail, there's no Rydberg series.

Not only that, but while exact $\epsilon_H = -I$ (Koopman's thm)

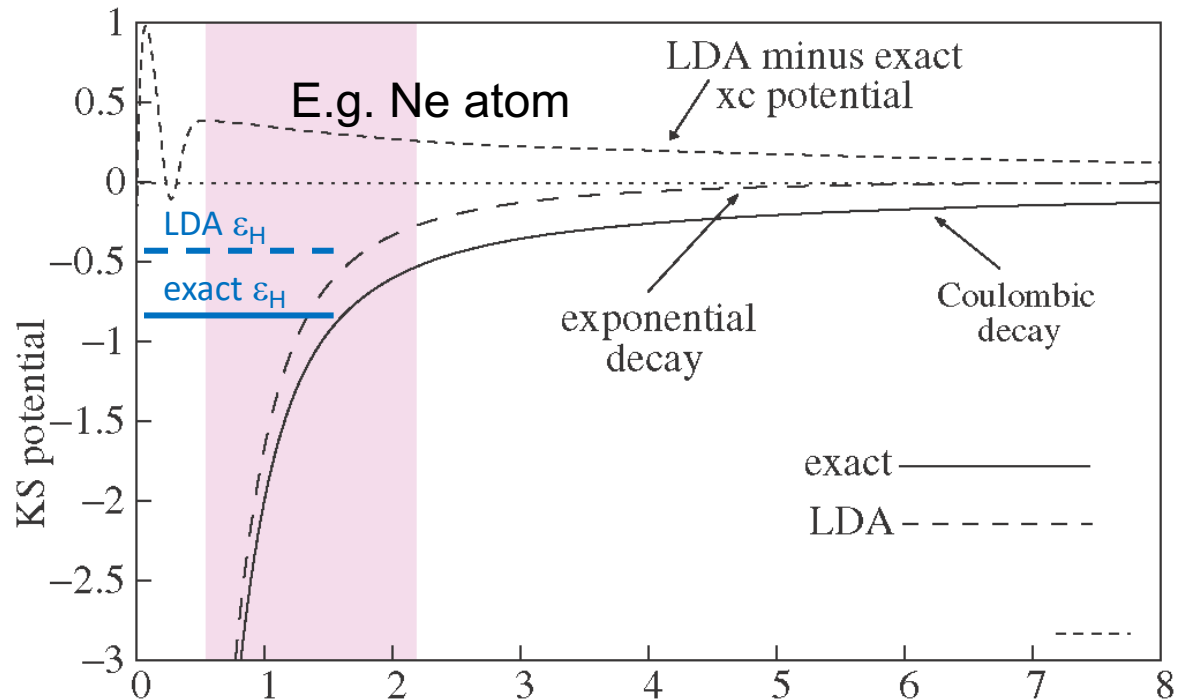
the LDA's wrong decay pushes up the HOMO \rightarrow

LDA ϵ_H underestimates $-I$



This is *one* aspect that leads to underestimate of charge-transfer excitations.

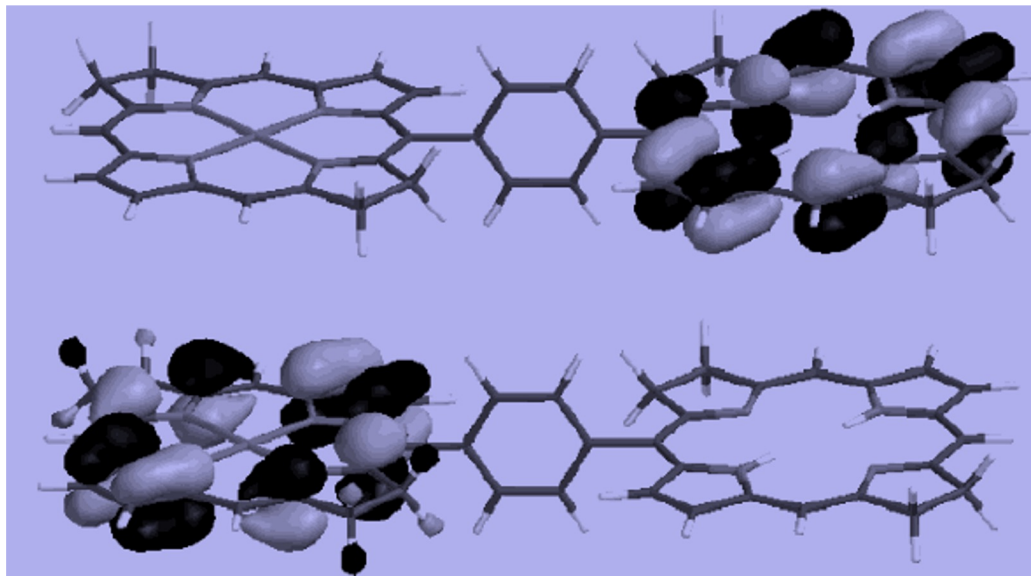
... see Christine's lecture...



Wasserman, Maitra, Burke, PRL **91**, 263001 (2003)

Semi-local TDDFT severely underestimates long-range CT energies

Eg. Zincbacteriochlorin-Bacteriochlorin complex (light-harvesting in plants and purple bacteria)



TDDFT predicts CT states energetically well below local fluorescing states. Predicts CT quenching of the fluorescence.

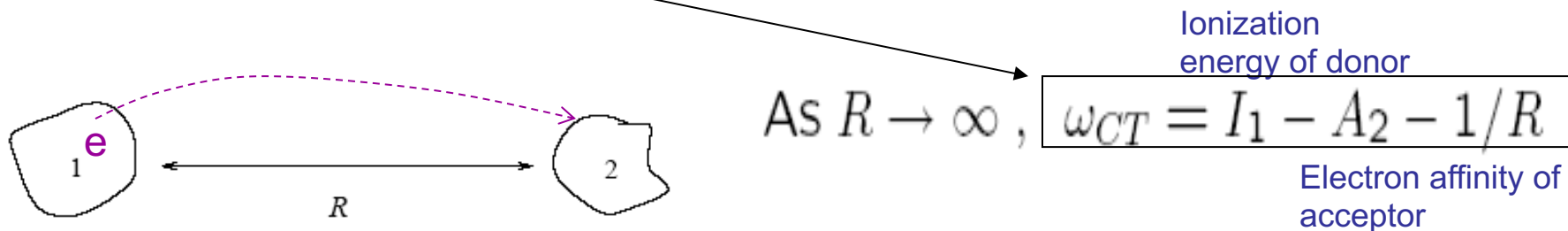
! Not observed !

TDDFT error $\sim 1.4\text{eV}$

Dreuw & Head-Gordon, JACS **126** 4007, (2004).

Why usual TDDFT approx's fail for long-range charge transfer

First, we know what the *exact* energy for charge transfer at long range should be:



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

Now to analyse TDDFT, use single-pole approximation (SPA):

$$\omega = \underbrace{\epsilon_2^L}_{-A_{s,2}} - \underbrace{\epsilon_1^H}_{-I_1} + \int \int dr dr' \underbrace{\phi_1^H(\mathbf{r})\phi_2^L(\mathbf{r})}_{\sim 0 \text{ overlap}} f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \underbrace{\phi_1^H(\mathbf{r}')\phi_2^L(\mathbf{r}')}_{\sim 0 \text{ overlap}}$$

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

- i.e. get just the **bare KS orbital energy difference**: missing xc contribution to acceptor's electron affinity, $A_{\text{xc},2}$, and $-1/R$
- And we just saw, the usual **ground-state approximations underestimate I**

Tozer, JCP **119**, 12697 (2003) ; Dreuw, J. Weisman, and M. Head-Gordon, JCP **119**, 2943 (2003)

Several work-arounds proposed, e.g. range-separated hybrids, Baer et al, Annu. Rev. Phys. Chem. **61**, 85 (2010)

Where & why the *usual* approxs give poor excitations

i.e. the usual xc approxs that are semi-local in space and local in time

- **Rydberg states**
 - GS v_{xc} decays $\sim e^{-2\sqrt{2I}r}$ instead of $-1/r$ at large r
 - ✓ Asymptotically corrected (“cut & splice”) functionals, (e.g. LB94, HCTH(AC)), EXX, or range-separated hybrids (eg CAM-B3LYP)...
e.g. Tozer & Handy Phys. Chem. Chem. Phys. **2**, 2117, (2000)
- **Polarizabilities of long-chain molecules**
 - GS v_{xc} needs non-local density-dependence
 - ✓ EXX, SIC-LDA, TD current-DFT
e.g. van Gisbergen et al. PRL **83**, 694 (1999),
van Faassen et al. PRL **88**, 186401 (2002).
- ❖ Primary problem above is the ground-state v_{xc} not primarily the adiabatic approximation ... what about cases where the problem is the f_{xc} ? We have...

Where the *usual* approxs give poor excitations, cont.

● Optical response of solids

Need “ultra-long-ranged” kernel $\sim 1/q^2$ to produce excitons and to open the gap

Reviews: G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)
S. Botti, A. Schindlmayr, R. D. Sole, and L. Reining, Rep. Prog. Phys. **70**, 357 (2007)
Y-M. Byun, J. Sun, C. A. Ullrich, Electron. Struct. **2** 023002 (2020)

See
Carsten's
lectures!

See
Christine's
lectures!

● Long-range charge transfer

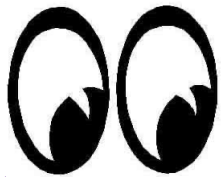
- Too fast decay of GS $v_{xc} \rightarrow \epsilon_H$ gives too small I , and exply-small donor-acceptor overlap $\rightarrow f_{xc}$ term ~ 0
- ✓ Range-separated hybrids, and other approaches, for *some* cases. Some cases need frequency-dependence.

Reviews with many refs:

Maitra, J. Phys. Condens. Matt. **29**, 423001 (2017)
Karolweski, Kronik, Kúmmel, JCP **138**, 204115 (2013)

- Adiabatic approx for f_{xc} fails.
- ✓ Frequency-dependent kernel developed \rightarrow “dressed TDDFT”

Maitra, Zhang, Cave, Burke, J. Chem. Phys. **120**, 5932 (2004)
Maitra, Ann. Rev. Chem. Phys. **73**, 117 (2022)



● Double excitations

Where the *usual* approxs give poor excitations, cont.

● Conical intersections

See Basile's lectures!

- Both the GS v_{xc} is poor due to near-degeneracy – “static correlation” – and adiabatic f_{xc} fails.

Levine et al. Mol. Phys. **104**, 1039 (2006);

Tapavicza et al, J. Chem. Phys. **129.**, 124108 (2008)

● Derivative Couplings

Needed in coupled electron-ion dynamics using surface-hopping – need quadratic response to get excited-to-excited state couplings, but adiabatic **quadratic response** gives divergences.

Parker, Roy, Furche J. Chem. Phys. **145**, 134105 (2016)

D. Dar, S. Roy, N. T. Maitra, J. Phys. Chem. Lett. **14**, 3186 (2023)

$$g_{xc,ijk}(t - t_i, t - t_k) = \frac{\delta^2 v_{xc}(r_i, t)}{\delta n(r_j, t_j) \delta n(r_k, t_k)} \quad \text{has linear } \omega\text{-dependence to cure this}$$

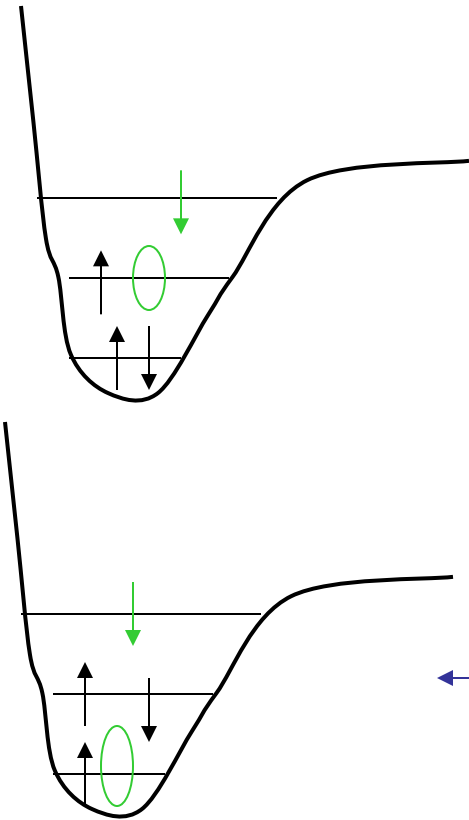
Plan

- ❖ Brief recall of linear response TDDFT for excitations and response
- ❖ Cases where the usual approximations fail
- ❖ Memory in linear response: double-excitations

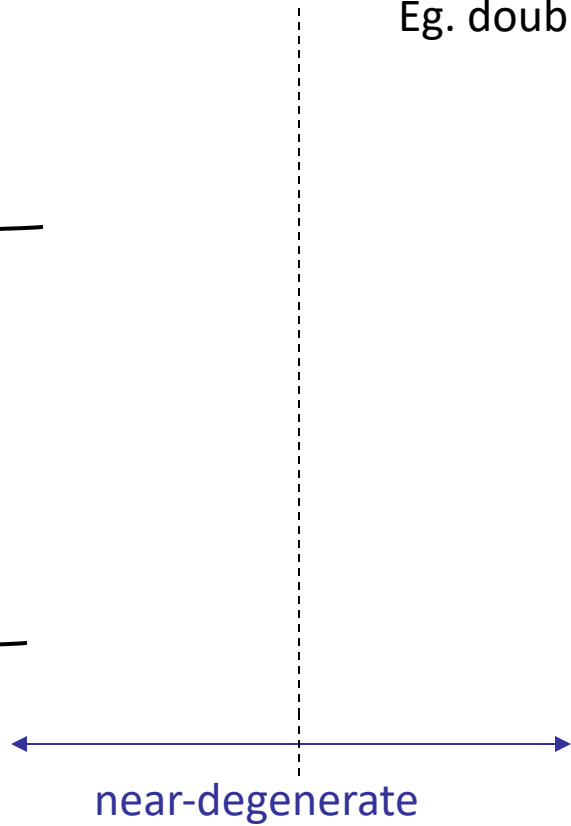
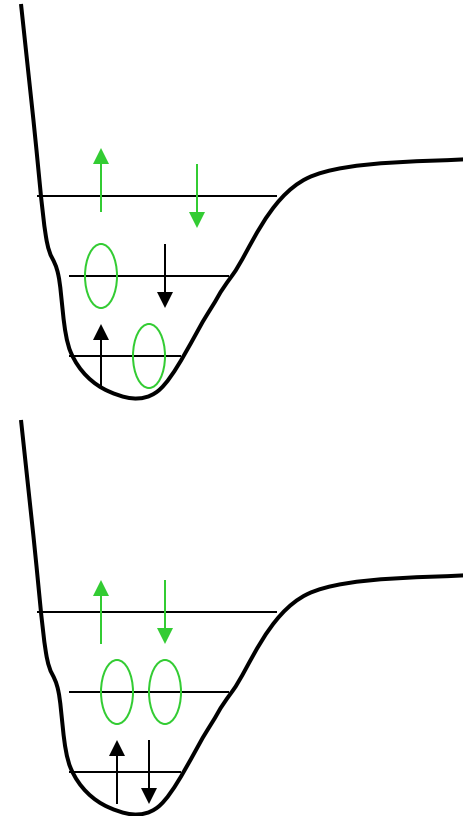
Types of Excitations

Non-interacting systems e.g. 4-electron atom

Eg. single excitations



Eg. double excitations



Interacting systems: generally involve combinations of (KS) determinants 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

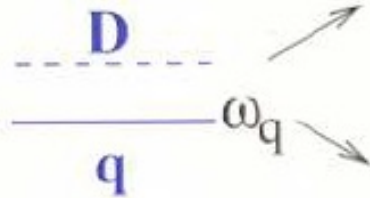
? How does f_{xc} generate more poles to get states of multiple excitation character?

Simplest Model:

Exactly solve for f_{xc} for one KS single (q) mixing with a nearby KS double (D)

KS

Exact



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

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

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

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

q : D

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

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

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

$$\begin{aligned} 2[q|f_{\text{HXC}}(\omega)|q] &= 2 \left([q|\chi_s^{-1}|q] - [q|\chi^{-1}|q] \right) \\ &= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')} \end{aligned}$$

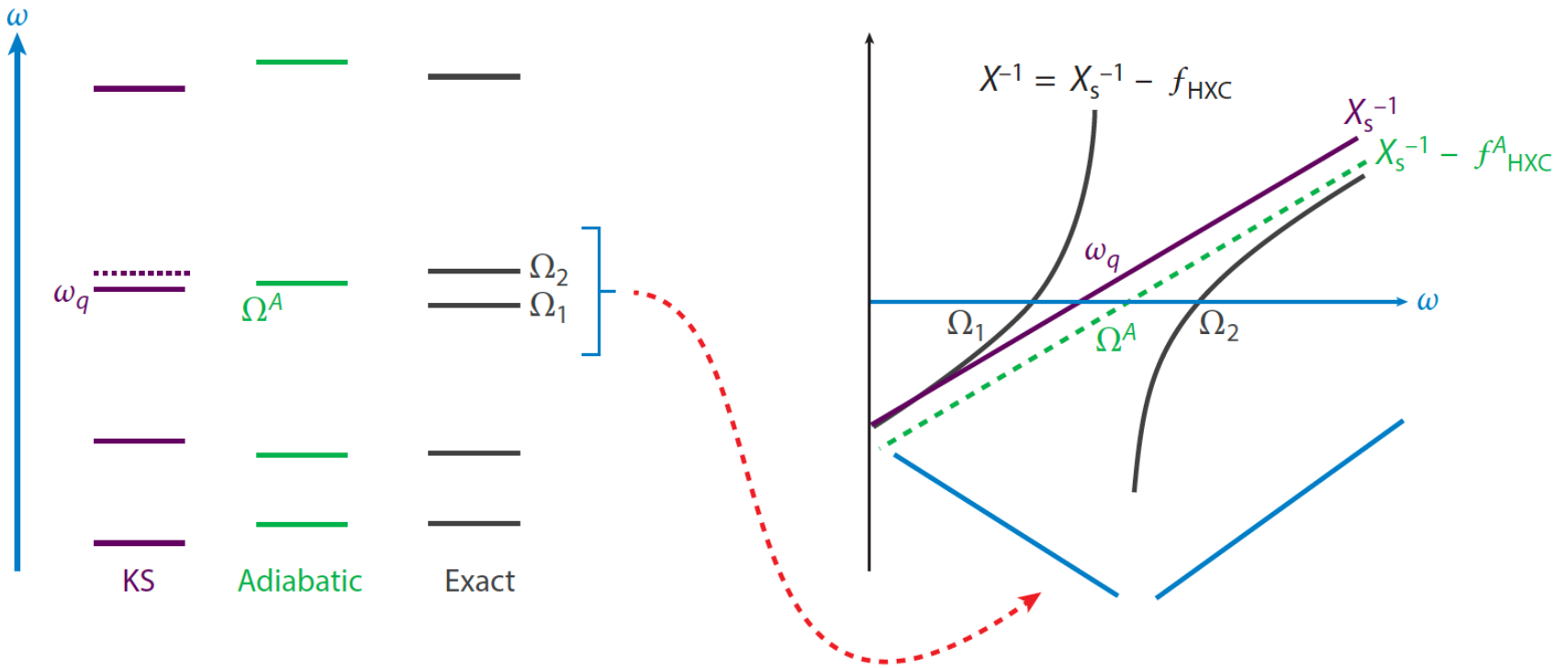
strongly non-adiabatic!

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

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

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

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




$$\begin{aligned}
 2[q|f_{\text{HXC}}(\omega)|q] &= 2 \left([q|\chi_s^{-1}|q] - [q|\chi^{-1}|q] \right) \\
 &= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')}
 \end{aligned}$$

Practical Approximation for the Dressed Kernel

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

Alternate Derivations

➤ M.E. Casida, *JCP* **122**, 054111 (2005)

M. Huix-Rotllant & M.E. Casida, in *Density-Functional Methods for Excited States*, ed. N. Ferre, M. Filatov, and M. Huix-Rotllant (Springer 2016)

-- 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.

Alternative DFT-based approach: ensemble DFT for excited states

A. Pribram-Jones et al, *JCP* (2014), Fromager & Loos & co-workers (2020), Pittalis & Gould & co-workers (2021)

(some talks next week!)

Example: short-chain polyenes

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

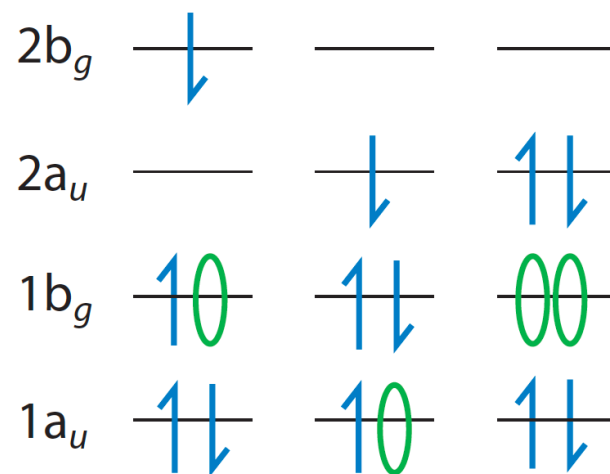
- 2^1A_g Vertical excitation energies (eV) for butadiene and hexatriene

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's dark 2^1A_g state



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

More implementations and tests:

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

M. Huix-Rotllant, A. Ipatov, A. Rubio, M. E. Casida, Chem. Phys. **391**, 120 (2011) – extensive testing on 28 organic molecules.

That's it for now about Memory in TDDFT!



Thanks so much for your attention!!!

Ask me any questions and I'll try to answer them!

And always feel free to reach out in email:
neepa.maitra@rutgers.edu

