

Plan

- ❖ Introduction to what is memory in TDDFT
- ❖ Approximations including memory, and some exact conditions
- ❖ Some examples (including charge-transfer dynamics)
- ❖ Memory in linear response: double-excitations (after a short detour about asymptotics of v_{xc})

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

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

$= \left. \frac{\delta^2 E_{xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \right|_{n_0}$

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

adiabatic approx: no ω -dep

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

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

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 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 \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 the *usual* approxs give poor excitations

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

● Rydberg states

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 LDA? Or GGA?

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

This has some grave consequences!

Asymptotic behavior of the xc potential :

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

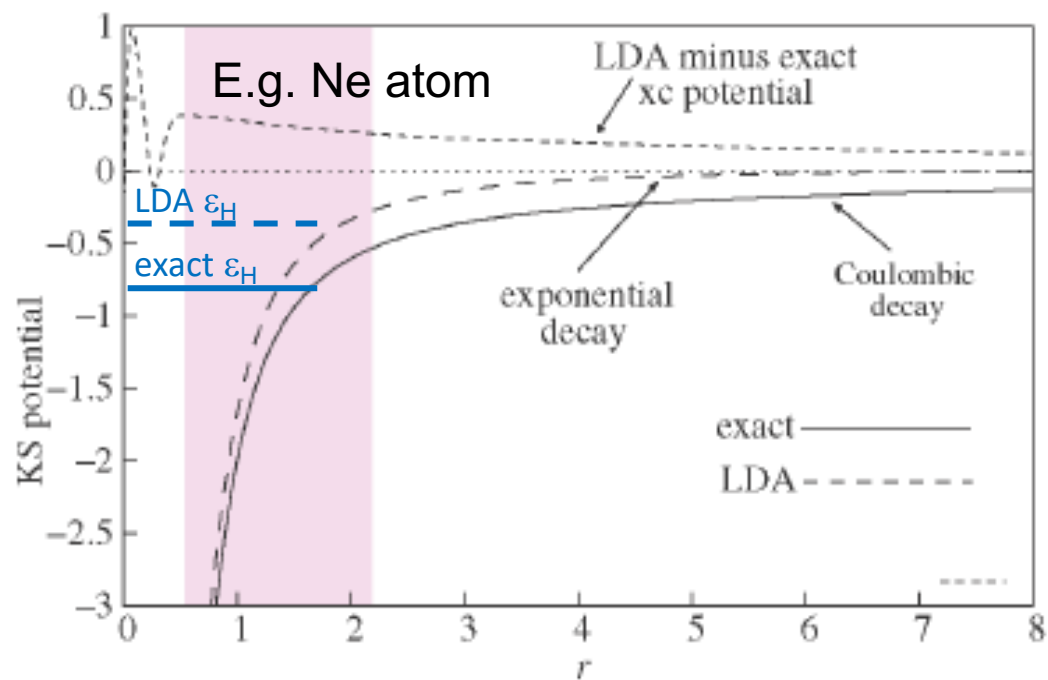
Moreover, while

exact: $\epsilon_H = -I$ (Koopman's thm)

but 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.



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

(Other problematic aspects: fxc correction vanishes due to vanishing orbital overlap, so cannot shift ϵ_L from being a neutral excitation to an affinity level, and cannot produce any electrostatic $-1/R$ behavior. Using hybrids within generalized KS, ϵ_L acquires affinity character itself, making fxc 's job easier).

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● Rydberg states

○ GS potential 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 fnal 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 xc potential....what about cases where the problem is the f_{xc} ? We have...

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● Optical response of solids

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

e.g. 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)

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

● Long-range charge transfer

- Exponentially-small overlap between donor and acceptor orbitals → fxc correction vanishes
- ✓ Range-separated hybrids in GKS, and other approaches, for *some* cases.

Review in, Maitra, J. Phys. Condens. Matt. **29**, 423001 (2017)

● Double excitations

- Adiabatic approx for fxc fails.
- ✓ Frequency-dependent kernel developed → “dressed TDDFT”

Maitra, Zhang, Cave, Burke, J. Chem. Phys. **120**, 5932 (2004)

● Conical intersections

- Both the GS fxc is poor due to near-degeneracy – static correlation – and adiabatic fxc fails.

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

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

● Derivative Couplings

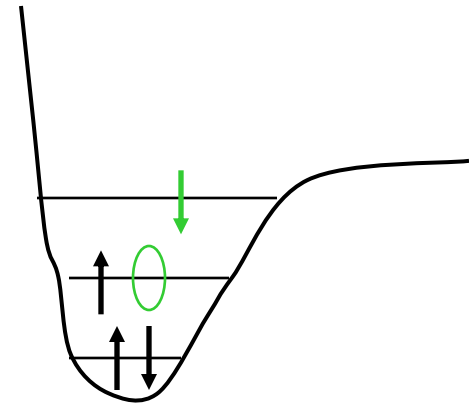
Needed in coupled electron-ion dynamics using surface-hopping – excited-to-excited non-adiabatic couplings are not accessible in linear resp, but adiabatic quadratic response gives divergences.

Ou, Bellchambers, Furche, Subotnik, J. Chem. Phys. **142**, 064114 (2015); Li, Liu, JCP **141**, 244105 (2014); Zhang, Herbert JCP **142**, 064109 (2015)

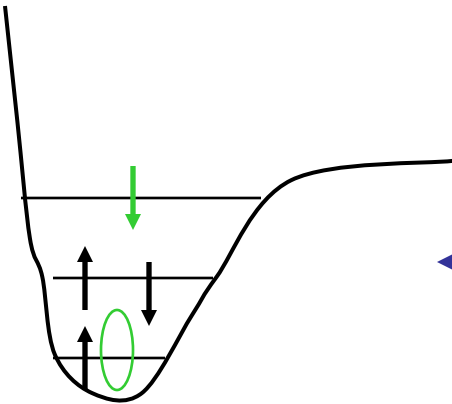
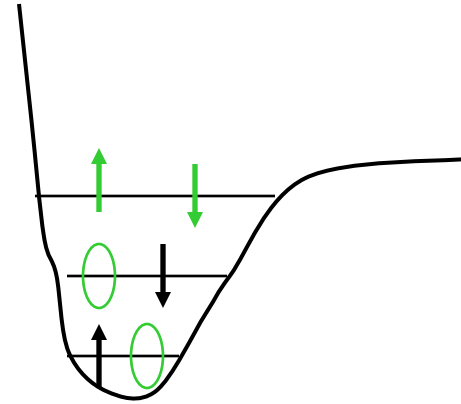
Types of Excitations

Non-interacting systems eg. 4-electron atom

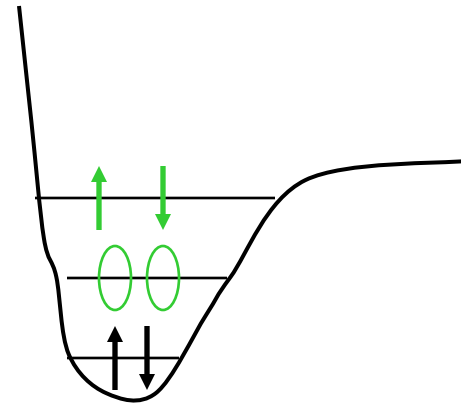
Eg. single excitations



Eg. double excitations



← near-degenerate →



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

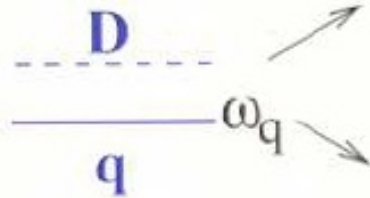
? How does f_{xc} generate more poles to get states of multiple excitation character?

Simplest Model:

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

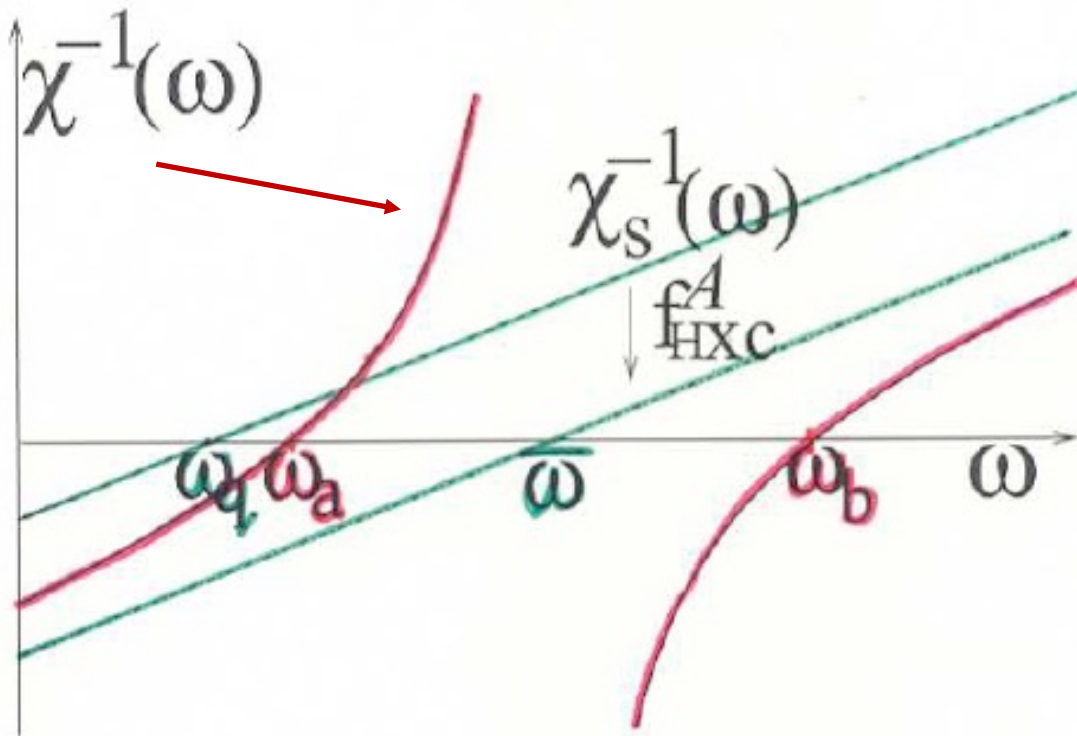
$$\begin{aligned} 2[q|f_{\text{HXC}}(\omega)|q] &= 2 \left([q|\chi_s^{-1}|q] - [q|\chi^{-1}|q] \right) \\ &= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')} \end{aligned}$$

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,

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




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

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

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


$$2[q|f_{XC}(\omega)|q] = 2[q|f_{XC}^A(\omega_q)|q] + \frac{|H_{qD}|^2}{\omega - \underbrace{(H_{DD} - H_{00})}_{\text{dynamical (non-adiabatic) correction}}}$$

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, 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.

Example: short-chain polyenes

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

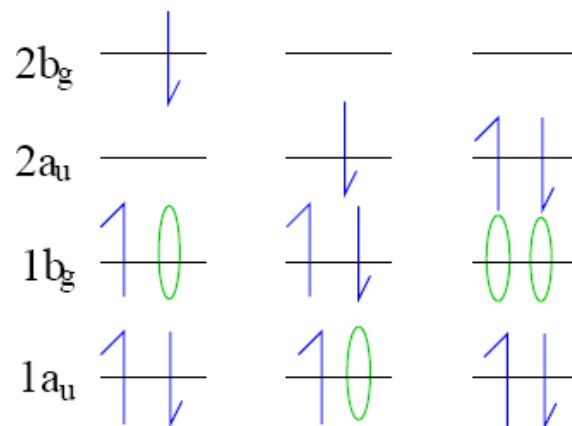
- 2^1A_g Vertical excitation energies (eV) for butadiene and hexatriene

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, dark 2^1A_g state



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

More implementations and tests:

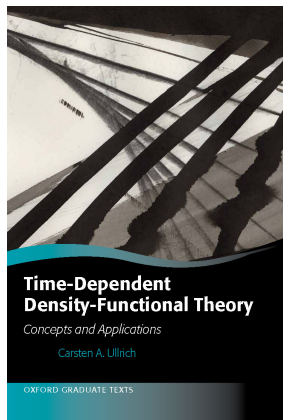
G. Mazur, R. Wlodarczyk, J. Comp. Chem. 30, 811, (2008); Mazur, G., M. Makowski, R. Wlodarczyk, Y. Aoki, IJQC 111, 819 (2010);

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

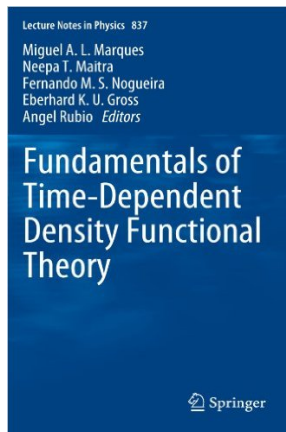
So that's a bit about memory in TDDFT

Ask me questions!

And, to find out more:



- TDDFT: Concepts and Applications, by Carsten Ullrich (Oxford University Press 2012)



- Fundamentals of TDDFT (Springer, 2012) **Ch.4**, "Introduction to TDDFT" and **Ch. 8** on Memory, both available from my website.

Recent reviews:

- N. T. Maitra, *Perspective* in J. Chem. Phys. **144**, 220901 (2016).
- M. R. Provorse and C. M. Isborn, Int. J. Quant. Chem. **116**, 739 (2016).
- C. A. Ullrich and Zeng-hui Yang, Brazilian J. of Phys. **44**, 154 (2014).

Thanks so much for your attention!!!