

# Spuriously Shifting Resonances in TDDFT and Their Impact on Dynamics

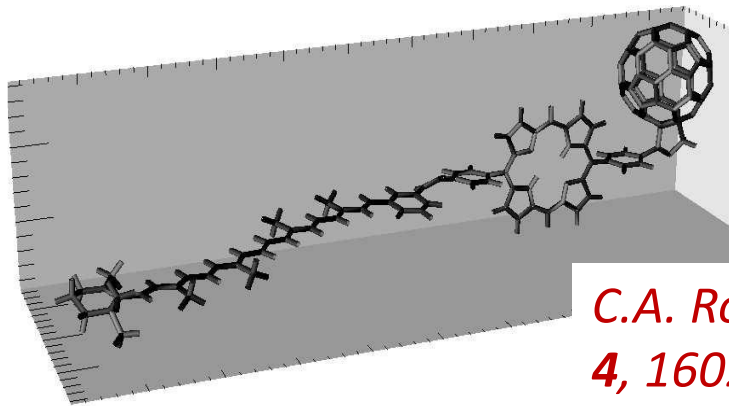
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City University of New York*

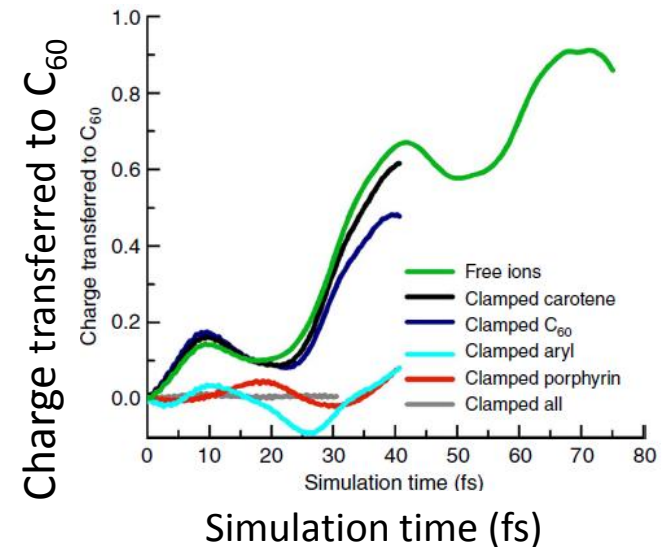


TDDFT has become popular for *fully time-resolved* studies...

e.g. Light-harvesting molecular triad:



*C.A. Rozzi et al, Nat. Comm  
4, 1602 (2013).*



**TDDFT (ALDA) + Ehrenfest** → good agreement with experimental time scales.

Coherent correlated electron-ion motion drives the charge-transfer.

***But why this work as well as it does ???!***

-- **electronic side:** charge-transfer with ALDA is expected to be very bad!

-- electron-ion side: Ehrenfest coupling should not be so good!

# Recall TDDFT...

$$i\partial_t\phi_i(\mathbf{r}, t) = (-\nabla^2/2 + v_s(\mathbf{r}, t))\phi_i(\mathbf{r}, t)$$

$$v_s[n; \Phi_0](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{XC}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$$

in practise  
approximated

Memory-dependence:  $n(\mathbf{r}, t' < t)$ ,  $\Psi_0$ ,  $\Phi_0$

**Adiabatic approximation**

$$v_{\text{XC}}^{\text{A}}[n; \Psi_0, \Phi_0](\mathbf{r}t) = v_{\text{XC}}^{\text{GS}}[n(\mathbf{r}t)]$$

E.g. ALDA, AGGA...

$$\text{e.g. } v_{\text{XC}}^{\text{ALDA}}(\mathbf{r}t) = v_{\text{XC}}^{\text{LDA}}[n(\mathbf{r}t)] = \frac{de_{\text{XC}}^{\text{unif}}(n(\mathbf{r}t))}{dn}$$

**Adiabatically-exact approximation:**  $v_{\text{XC}}^{\text{adia-ex}} = v_{\text{XC}}^{\text{exact-gs}}[n(t)](\mathbf{r})$

*What about the exact xc potential?*

# Outline

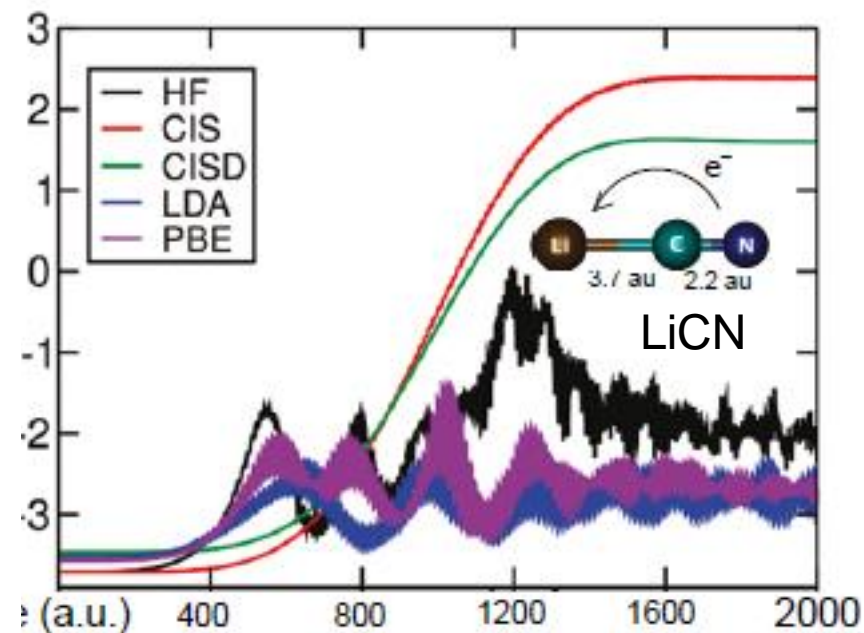
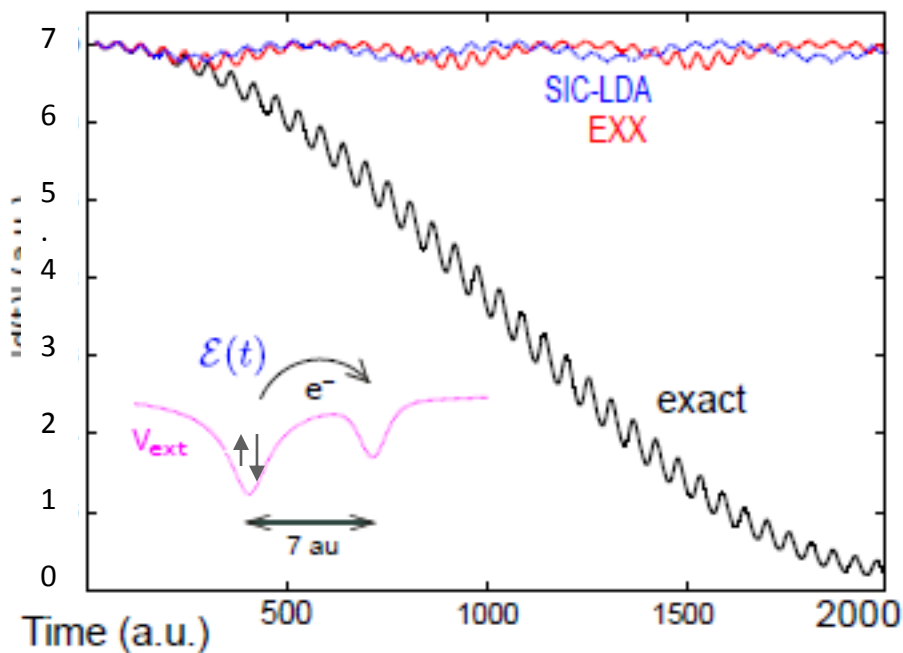
- ❖ **Charge-transfer dynamics in TDDFT : simple models**
  - CT from the ground-state: a landscape of steps and peaks
  - CT from an excited state
- **new exact condition(s) for *general* dynamics in TDDFT**

# Time-Resolved Charge-Transfer *Dynamics* from the ground state

particularly difficult for TDDFT approximations

$$v_{\text{mol}}(x) = -\frac{Z}{\sqrt{(x + \frac{R}{2})^2 + a}} - \frac{U_0}{\cosh^2(x - \frac{R}{2})}$$

Dipole moment during charge-transfer

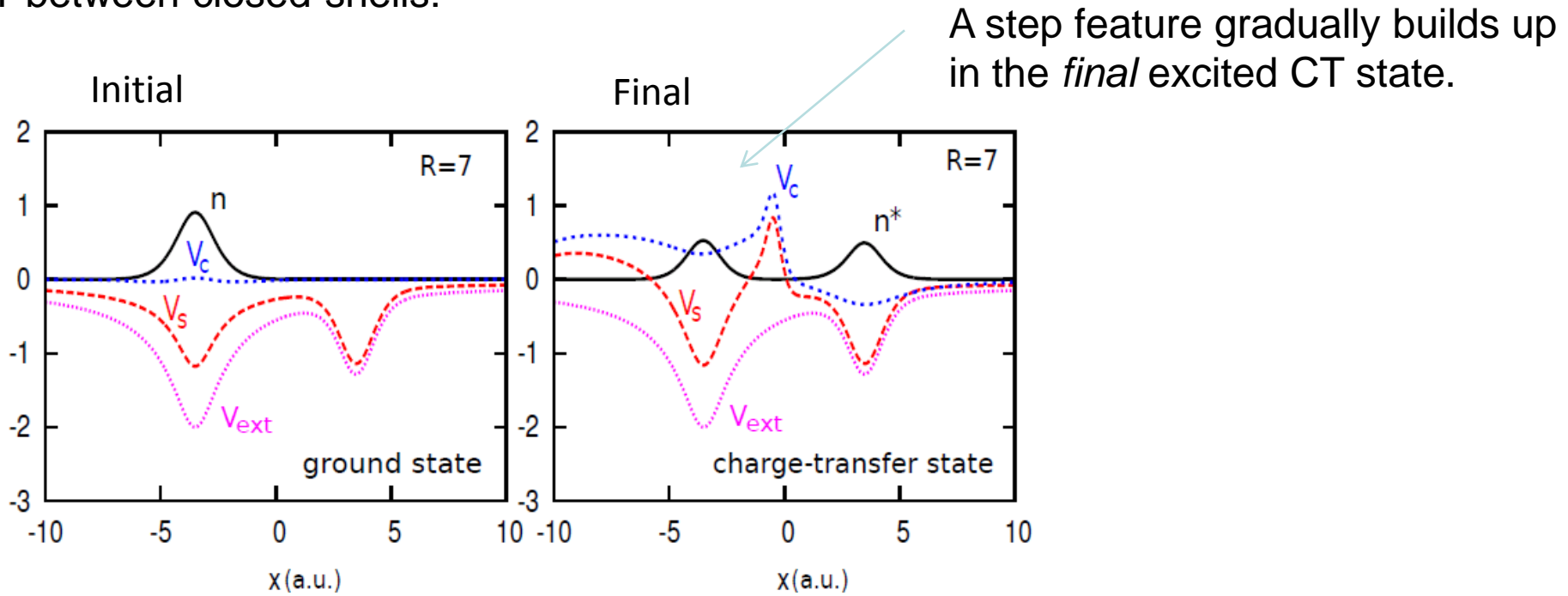


J. I. Fuks, P. Elliott, A Rubio, N. T. Maitra *J. Phys. Chem. Lett.* **4**, 735 (2013)

S. Raguathan, M. Nest, *J. Chem. Th. Comput.* **7** 2492 (2011).

# First ask, what is the final exact KS potential?

CT between closed-shells:



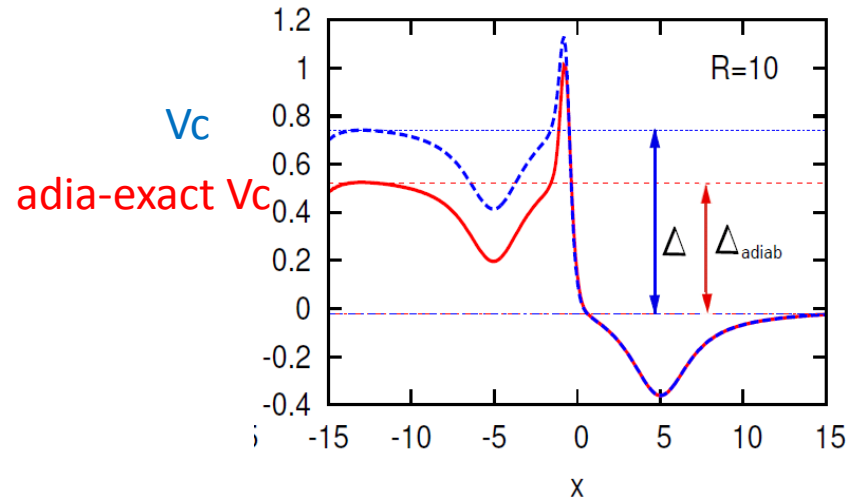
Certainly the step requires spatially non-local density-dependence, but can we get away with *time-local* density dependence, i.e. an adiabatic approx ?

- Adiabatically-exact approx predicts a CT step but of the wrong size!

Correlation potential in the final CT state, as  $R \rightarrow \infty$

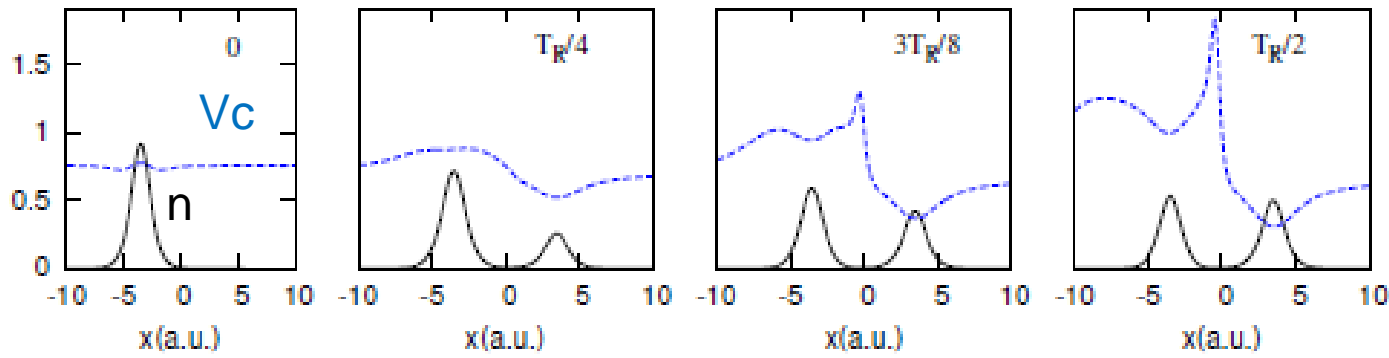
$$\Delta \equiv |I_D^{N_D-1} - I_A^{N_A+1}|$$

$$\Delta_{adia} \equiv |I_D^{N_D-1} - A_D^{N_D-1}|$$

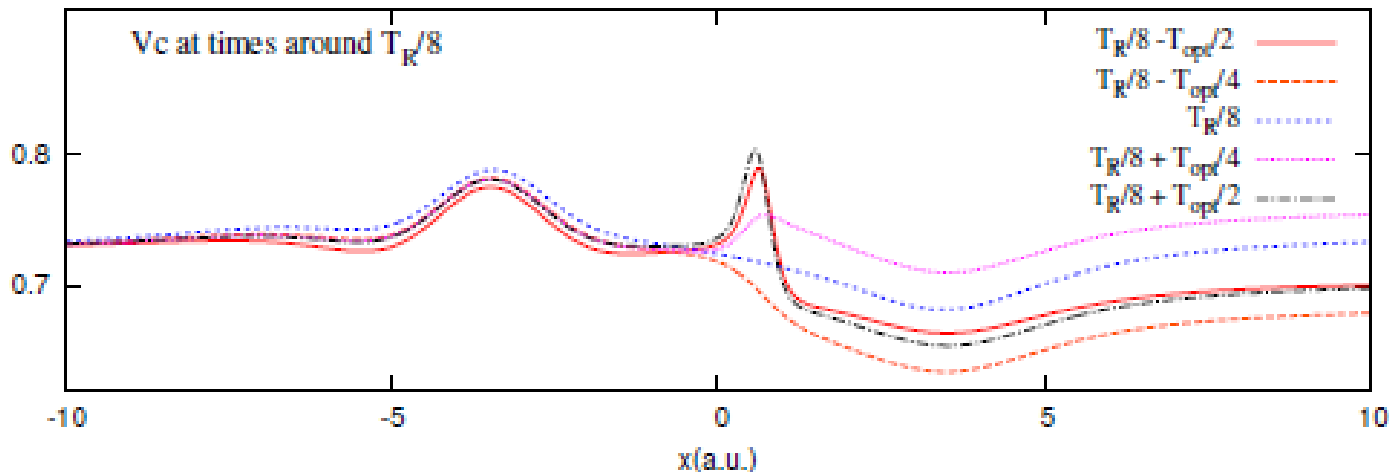


- This CT step gradually builds up during the resonantly-driven CT, accompanied by a faster oscillating dynamical step ...*(next slide)*

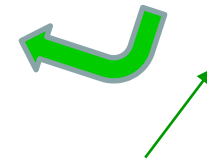
The **exact** correlation potential develops step and peak features ...



...gradual build-up of **step** associated with charge-transfer...



...on top of much faster “**dynamical step**” oscillating on the optical time-scale..

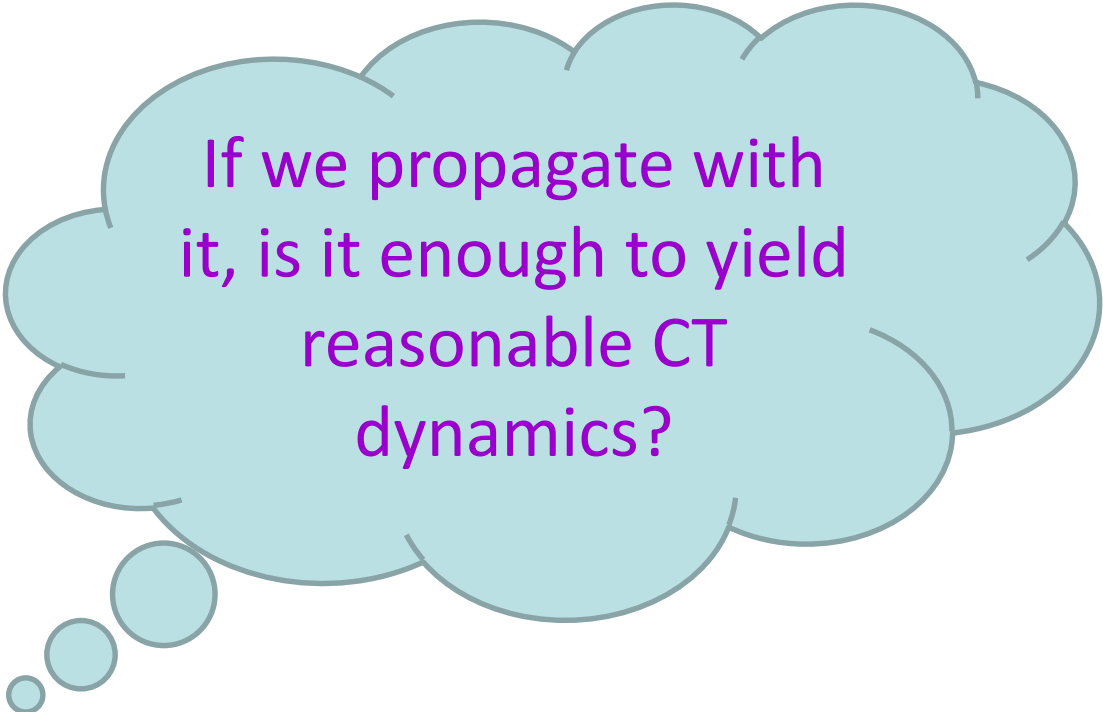


*Generically* appears in non-perturbative dynamics, completely missed in any adiabatic approximation,  
 e.g. J. D. Ramsden and R. W. Godby, Phys. Rev. Lett. **109**, 036402 (2012);  
 P. Elliott, J. I. Fuks, A Rubio, N. T. Maitra, Phys. Rev. Lett. **109**, 266404 (2012);

....

Approximations don't contain these steps and totally fail for CT dynamics starting in the ground-state

*But the adiabatically-exact approx does get a CT step, albeit with wrong size (& no dynamical step)...*

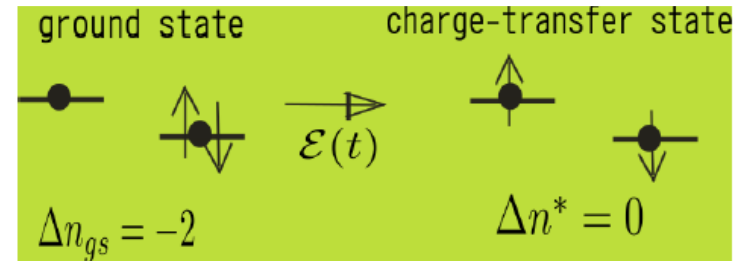


If we propagate with it, is it enough to yield reasonable CT dynamics?

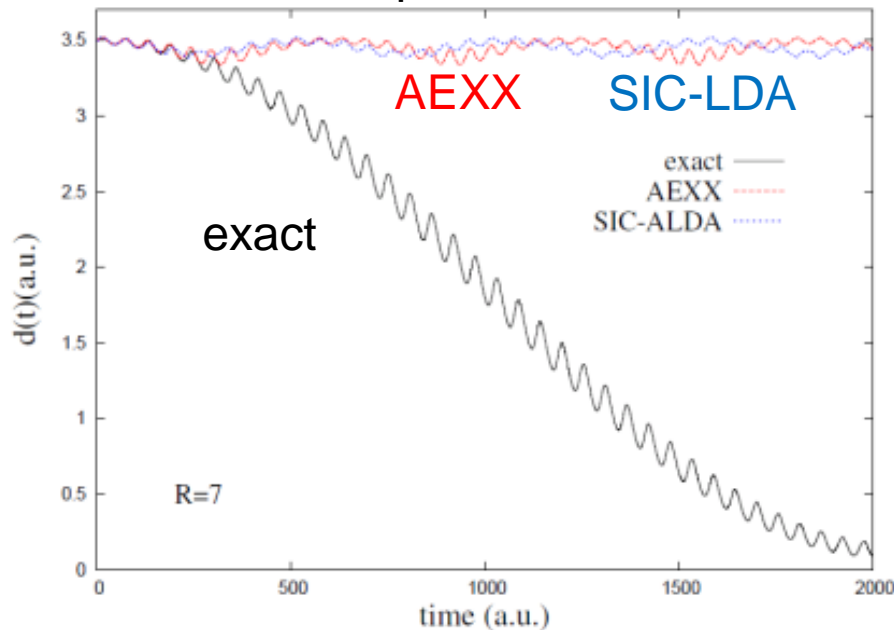
# Propagation with self-consistent exact-adiabatic $v_{xc}$ :

## 2-site asymmetric Hubbard model:

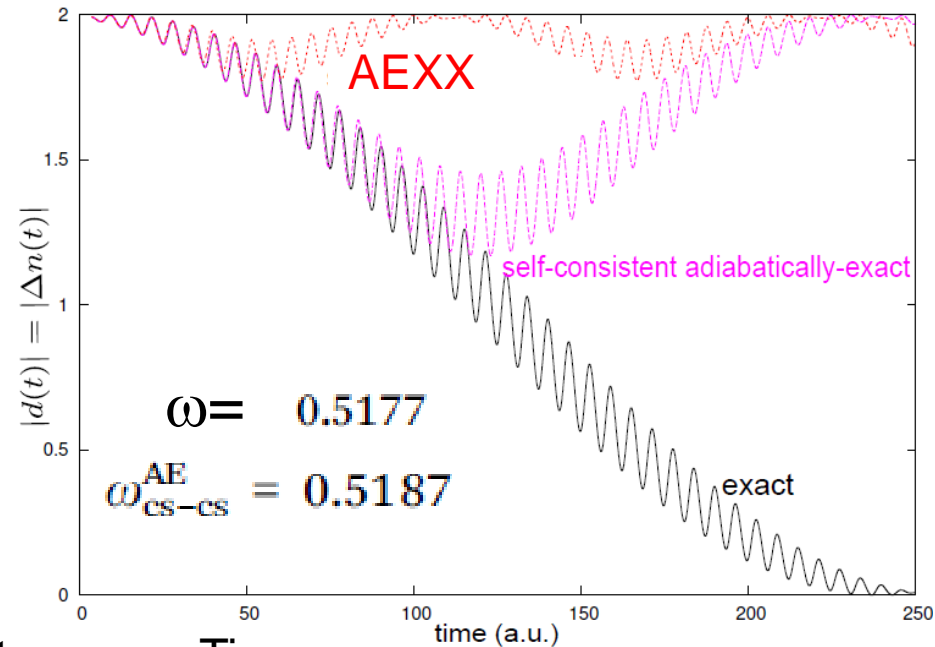
$$\hat{H} = -T \sum_{\sigma} \left( \hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + \hat{c}_{2\sigma}^{\dagger} \hat{c}_{1\sigma} \right) + U \left( \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} \right) + (\Delta v + \mathcal{E}(t)) (\hat{n}_1 - \hat{n}_2)$$



CT in real-space molecule



CT in Hubbard molecule



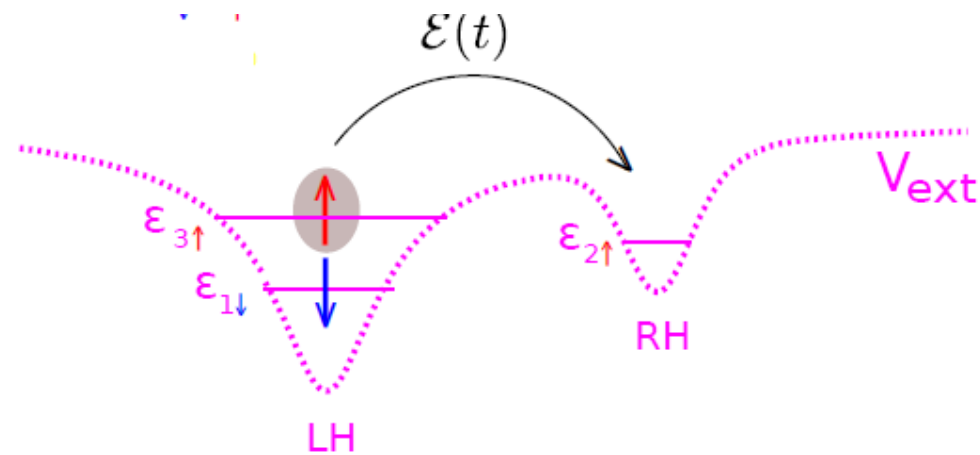
Dipole Moments versus Time

- Despite extremely accurate CT excitation energies, CT is not achieved by the adiabatically-exact approximation.

*Well, achieving the CT state from a KS ground state is hard: a single KS orbital must always describe both the transferring electron and one that stays...*



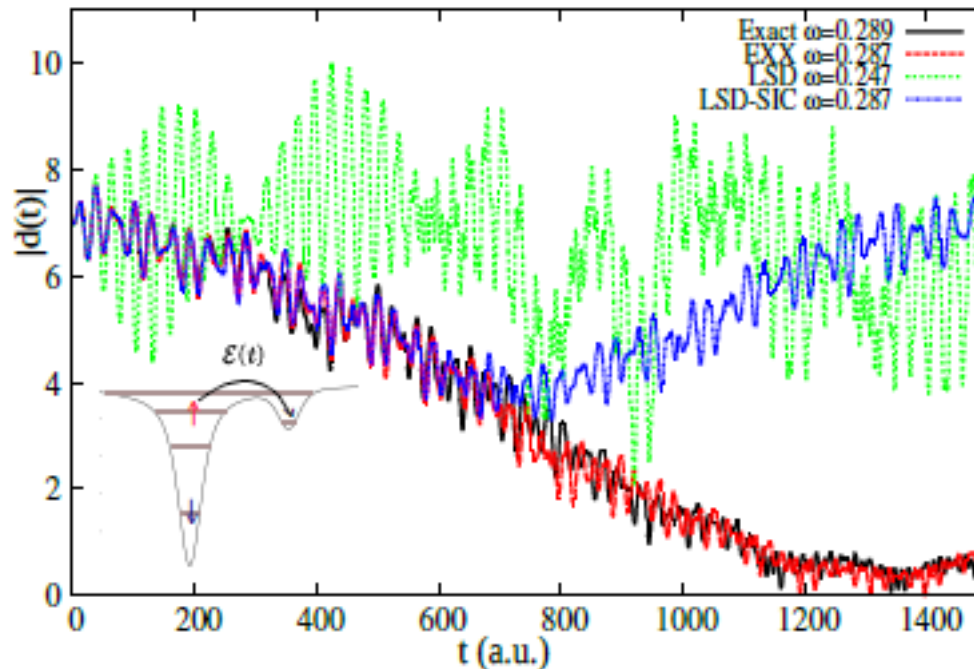
Break the restriction of having a single orbital describing both the transferring electron and an electron that stays.



*Actually this is how CT dynamics is run in many calculations e.g. photovoltaics...*

Adiabatic EXX fully charge-transfers the photo-excited electron!

*But not other functionals? Why?*



The ATDDFT frequencies typically change in time, unlike the exact.

time-dep.  $n(t) \rightarrow v_{xc}[n](t)$  time-dep

→ Bare KS frequencies change in time & fxc correction also time-dependent

These **two time-dependences** cancel with exact functional, but not with approximate functionals!

*Leads to a new exact condition...*

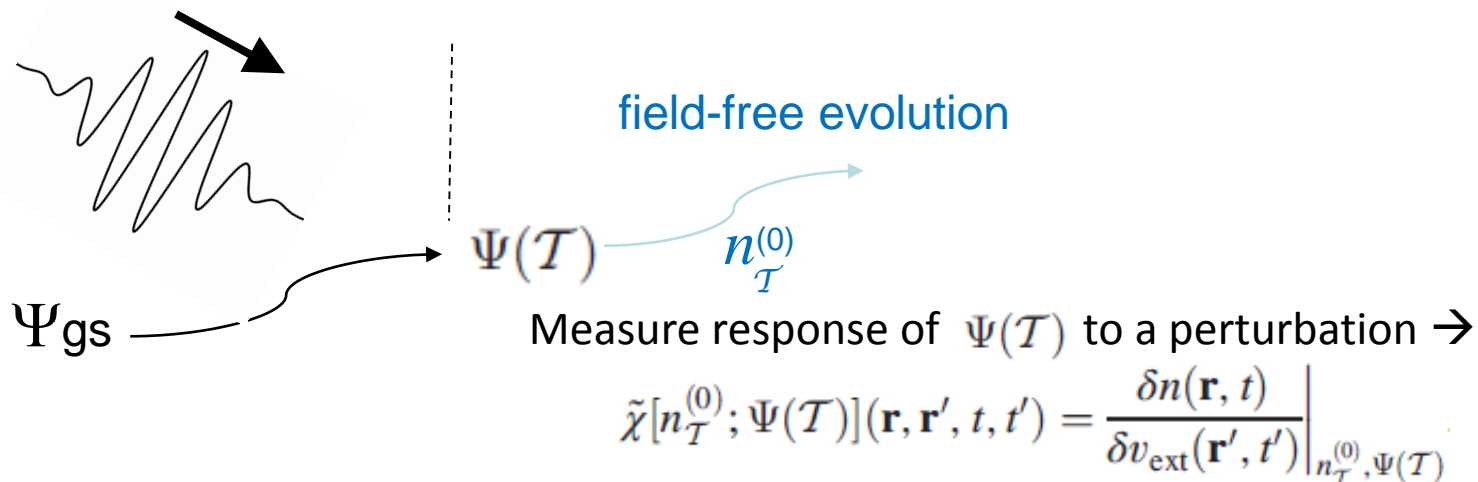
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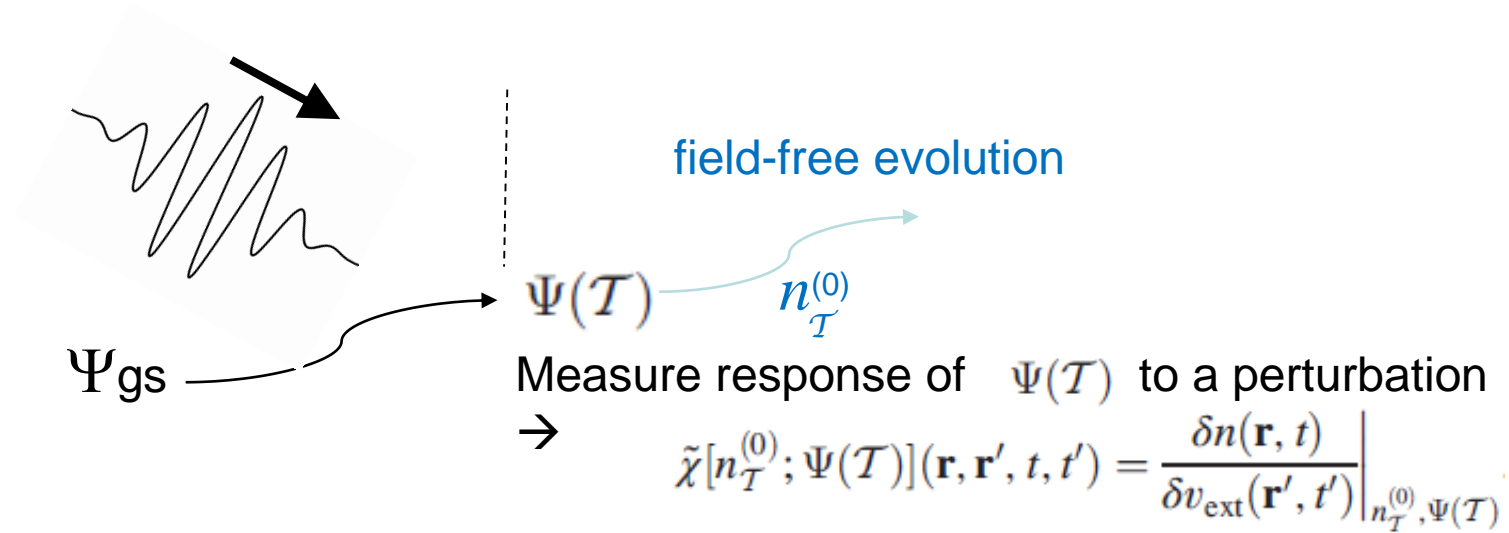
These **two time-dependences** cancel with exact functional, but not with approximate functionals!

→ Can be formalized as a new exact condition on the generalized xc kernel.

Generalized density-density response functions around the state at time when field is turned off,  $\mathcal{T}$ :



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



Let  $\omega_i$  be a pole of the Fourier transform w.r.t.  $(t-t')$  of

$$\tilde{\chi}[n_{\mathcal{T}}^{(0)}; \Psi(\mathcal{T})](\mathbf{r}, \mathbf{r}', t, t') = \left( \tilde{\chi}_{\text{S}}^{-1}[n_{\mathcal{T}}^{(0)}, \Phi(\mathcal{T})] - \tilde{f}_{\text{HXC}}[n_{\mathcal{T}}^{(0)}, \Psi(\mathcal{T}), \Phi(\mathcal{T})] \right)^{-1}$$

then

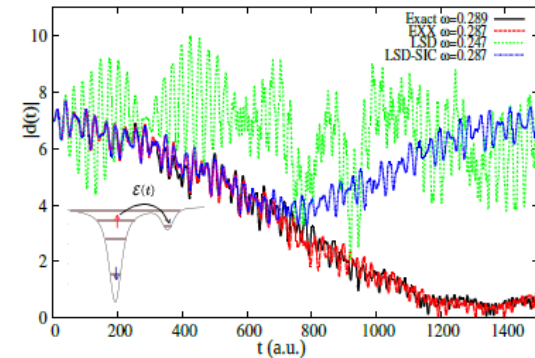
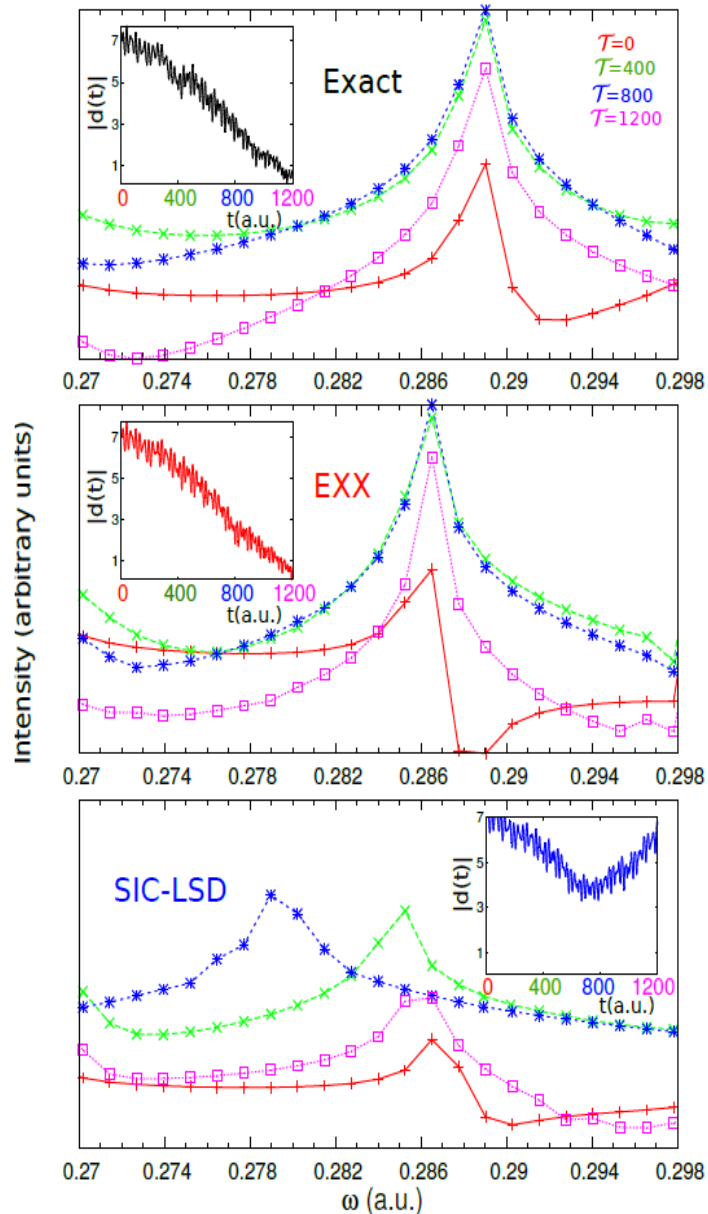
$$\boxed{\frac{d\omega_i}{d\mathcal{T}} = 0}$$

J. I. Fuks, K. Luo, E. Sandoval, N. T. Maitra, Phys. Rev. Lett. **114**, 183002 (2015).

K. Luo, J. I. Fuks, N. T. Maitra, J. Chem. Phys. **145**, 044101 (2016).

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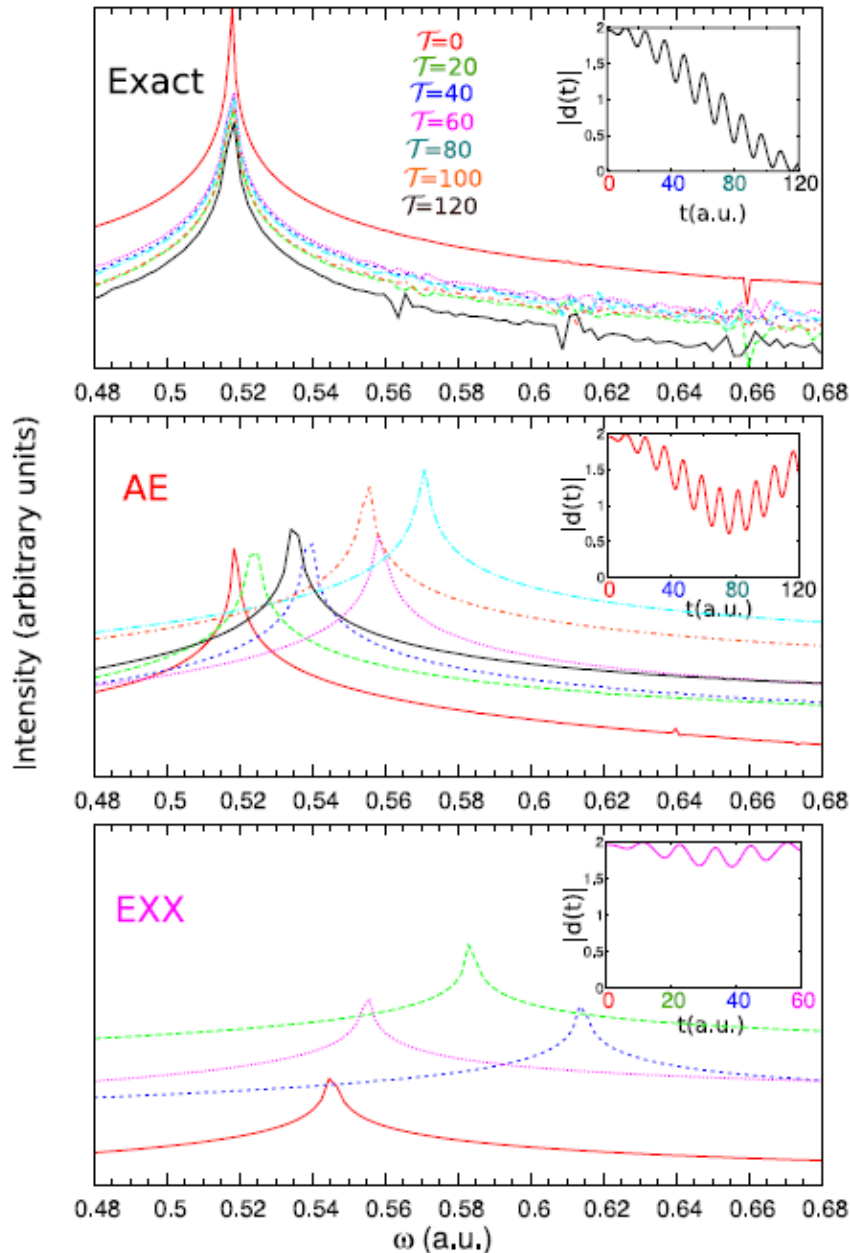
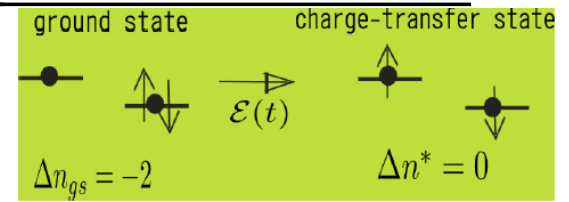
**Spectra taken at different times during the evolution with different functionals**

Peak *positions* shouldn't change -- but SIC-LSD ones do  $\rightarrow$  poor dynamics

J. I. Fuks, K. Luo, E. Sandoval, N. T. Maitra, Phys. Rev. Lett. **114**, 183002 (2015);

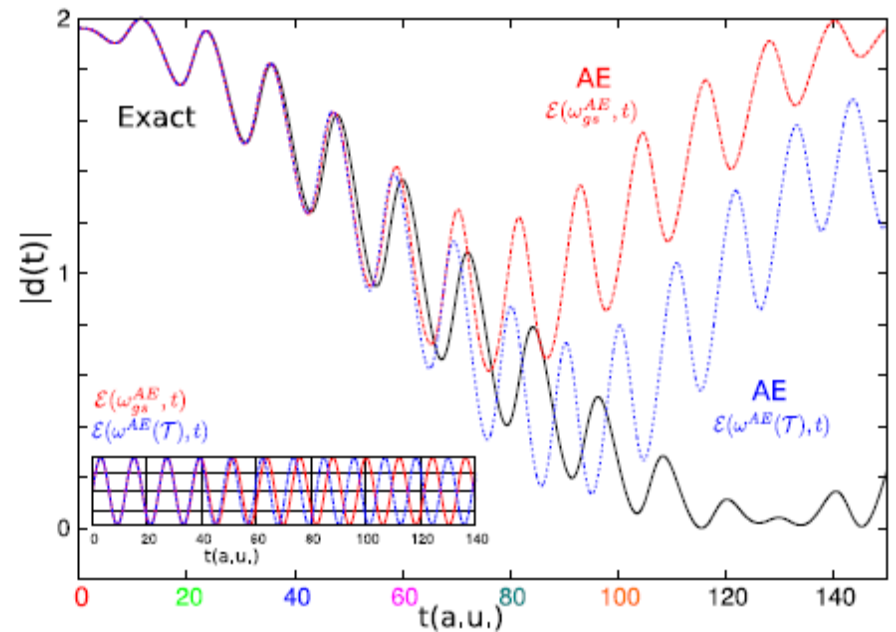
K. Luo, J. I. Fuks, N. T. Maitra, J. Chem. Phys. **145**, 044101 (2016).

# Revisiting charge-transfer from the ground-state ..recall Hubbard model

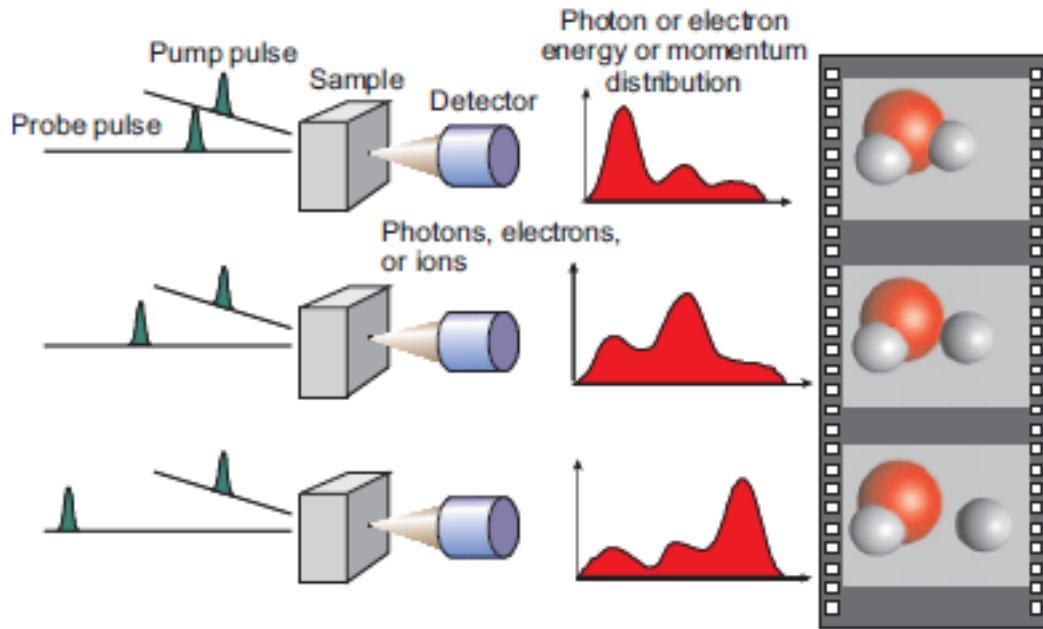


“Chirped laser” with frequency adjusted to be resonant with the instantaneous excitation gives more charge transfer:

$$\mathcal{E}[\omega^{AE}(\mathcal{T})](t) = 0.09 \sin(\omega^{AE}(\mathcal{T}) t)$$



# Implications for Time-Resolved Pump-Probe Spectroscopy



Taken from Krausz & Ivanov, Rev. Mod. Phys. **81**, 163 (2009)

- Spectrum depends on pump-probe delay, but *if the nuclei don't move, then the peak positions don't change.*
- Approximate TDDFT functionals violate this → muddled interpretation of spectra
- **Real Molecules:** Violation of exact condition explains erroneously “t-dep electronic structure” observed, e.g. de Giovannini et al. PCCP **14**, 1363 (2014); Raganathan & Nest JCTC **8**, 806 (2012); Habenicht et al. JCP **141**, 184112 (2014).

## A slew\* of related exact conditions...

We had, for a given transition between two states,  $\omega_i$ , pole of

$$\left( \tilde{\chi}_S^{-1}[n_{\mathcal{T}}^{(0)}, \Phi(\mathcal{T})] - \tilde{f}_{\text{HXC}}[n_{\mathcal{T}}^{(0)}; \Psi(\mathcal{T}), \Phi(\mathcal{T})] \right)^{-1} \quad \text{satisfies} \quad \frac{d\omega_i}{d\mathcal{T}} = 0$$

Relatedly, consider response of stationary states:

(1) Consider a given  $V_{\text{ext}}(0)$ , with a set of interacting eigenstates  $\{\Psi_1, \dots, \Psi_k, \dots\}$   
Frequency for given transition  $k \rightarrow k'$  must be independent of which of these states  $\Psi_k$  or  $\Psi_{k'}$  chosen to perturb around.  
And, “Consistency” for other transitions.

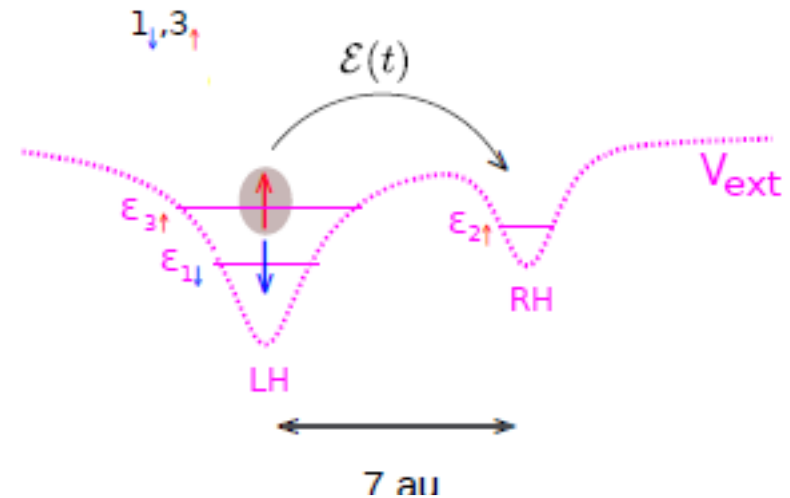
(2) Let  $\{\Phi_1, \Phi_2, \dots, \Phi_l, \dots\}$  be a set of stationary states of different KS potentials, all with the same density  $n_k$  of a particular stationary state of interacting potential  $V_{\text{ext}}(0)$ .

Frequency for a given transition must be independent of choice of  $\Phi_i$  in the response function

-- Can express these 2 conditions in Casida-like matrix equations

\*slew: noun, 1. multitude, 2. a violent or uncontrollable sliding movement

*How did EXX achieve full charge transfer? The resonant frequency remained about constant throughout the evolution.*



$$v_{\text{HXC}}^{\text{EXX},\uparrow}[n_{\uparrow}, n_{\downarrow}](t) = v_{\text{H}}[n_{\downarrow}(t)]$$

$$v_{\text{HXC}}^{\text{EXX},\downarrow}[n_{\uparrow}, n_{\downarrow}](t) = v_{\text{H}}[n_{\uparrow}(t)]$$

$v_{\text{HXC}}^{\text{EXX},\uparrow}[n_{\downarrow}](t)$  is basically static because  $n_{\downarrow}$  **remains basically unchanged during the evolution!**

in this sense, it mimics the exact potential...

# Summary

- ❖ The exact TDKS potential contains **steps and peaks** that have a spatially non-local & time non-local dependence on the density.
- ❖ Such non-adiabatic steps play important role in charge-transfer dynamics beginning in the ground-state.
- ❖ Charge-transfer dynamics from a photo-excited state may seem easier for approximate TDDFT...
- ❖ ...but then run into **spurious TD resonances**, a problem for general non-linear dynamics
- ❖ An **exact condition** can be formulated, the degree of violation of which indicates the functional's performance in dynamics

# Cutting the Apron Strings to the Adiabatic Approximation

1RDM, interacting, KS

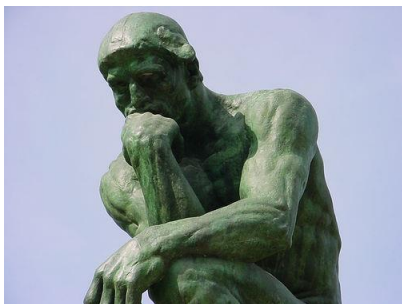
$$\nabla \cdot (n \nabla v_{xc}) = \nabla \cdot \left[ \frac{1}{4} (\nabla' - \nabla) (\nabla^2 - \nabla'^2) (\rho_1(\mathbf{r}', \mathbf{r}, t) - \rho_{1,s}(\mathbf{r}', \mathbf{r}, t)) \Big|_{\mathbf{r}'=\mathbf{r}} \right]$$

kinetic component  $\rightarrow v_c^T$

$$+ n(\mathbf{r}, t) \int n_{xc}(\mathbf{r}', \mathbf{r}, t) \nabla w(|\mathbf{r}' - \mathbf{r}|) d^3 r'$$

interaction component  $\rightarrow v_{xc}^W$

? What to do here?  
Not sure yet...



Approximate  $n_{xc}$  by  $n_{xc}^S$

- Gives an explicit orbital-functional
- reduces to EXX in the SSD case
- in the general case, includes correlation
- has time- and space-nonlocal density-dependence.

$$V_{xc} = V_{xc}^S + V_{xc}^{NS}$$

*J.I. Fuks, S.E.B. Nielsen, M. Ruggenthaler, N.T.Maitra, Phys. Chem. Chem. Phys.* **18**, 20976 (2016).

*N. T. Maitra, Perspective on Fundamental Aspects of TDDFT, J. Chem. Phys.* **144**, 220901 (2016).

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**Group at Hunter, Summer 2015**