Potentials that exactly capture correlated electron ~~and ion~~ dynamics in strong fields

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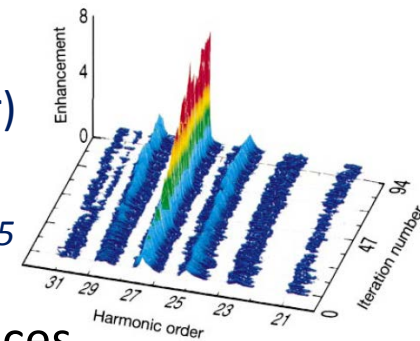
TDDFT is now applied in many exciting real-time calculations of fully non-linear dynamics (not just spectra…)

- solids in intense fields, e.g. dielectric breakdown, coherent phonon generation

- atoms and molecules in intense fields, e.g. HHG, CREI…
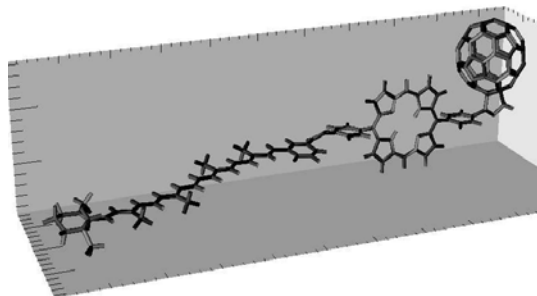
Optimizing a single harmonic (in Ar)

Murnane & Kapteyn et al, Nature 2000
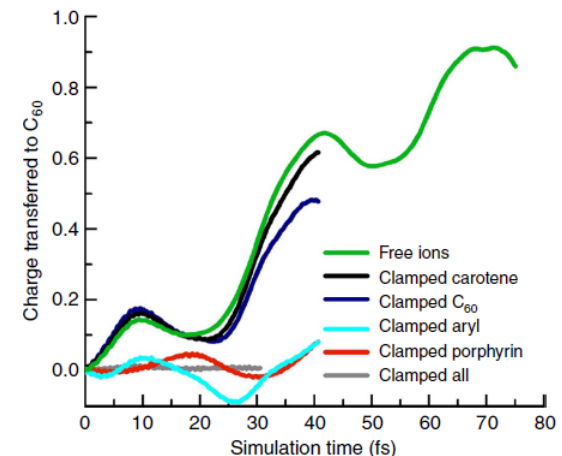
Castro, Rubio, &Gross, New J. Phys 2015

- photovoltaic design: charge migration across molecules, interfaces..
  …dynamics after photo-excitation, generally….

*Rozzi et al. Nature. Comm. **4**, 1602 (2013)*

Light-harvesting molecular triad:

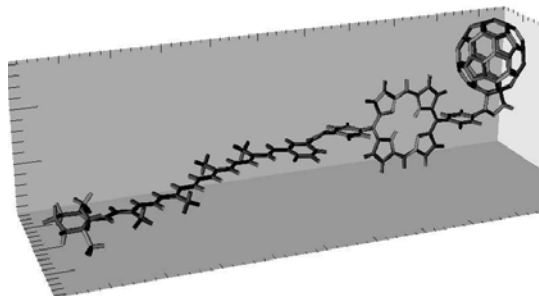Coherent correlated electron-ion dynamics in charge-transport needed.

TDDFT is now applied in many exciting real-time calculations of fully non-linear dynamics (not just spectra...)

- solids in intense fields, e.g. dielectric breakdown, coherent phonon generation

- *But how well do the TDDFT approximations really work ? What is missing?*
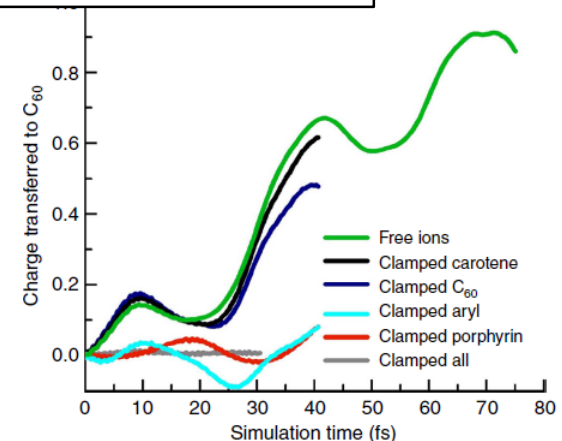
- **...Find some exactly-solvable model systems to look at the exact Vxc**

*Rozzi et al. Nature. Comm. **4**, 1602 (2013)*

Light-harvesting molecular triad:

Coherent correlated electron-ion dynamics in charge-transport needed.

Outline

❖**Exact TDDFT correlation potentials far from the ground-state**

-- a landscape of non-adiabatic steps and peaks

-- case study of charge-transfer

- beginning in the ground-state

- beginning in a photo-excited state

→ **new exact condition for general dynamics in TDDFT**

❖ **The potential acting on the electronic subsystem when coupled to ions and fields: Exact Factorization Approach**

-- potential acting on the electronic system in charge-resonance enhanced ionization

TDDFT

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

$$v_{\mathrm{S}}[n; \Phi_0](\mathbf{r}, t) = v_{\mathrm{ext}}(\mathbf{r}, t) + v_{\mathrm{H}}[n](\mathbf{r}, t) + v_{\mathrm{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$$

in practise approximated

Memory-dependence: $n(r, t' < t)$, Ψ_0, Φ_0

Adiabatic approximation

$$v_{\mathrm{xc}}^{\mathrm{A}}[n; \Psi_0, \Phi_0](\mathbf{r}t) = v_{\mathrm{xc}}^{\mathrm{gs}}[n(\mathbf{r}t)]$$

E.g. ALDA, AGGA…

e.g. $v_{\mathrm{xc}}^{\mathrm{ALDA}}(\mathbf{r}t) = v_{\mathrm{xc}}^{\mathrm{LDA}}[n(\mathbf{r}t)] = \dfrac{de_{\mathrm{xc}}^{\mathrm{unif}}(n(\mathbf{r}t))}{dn}$

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

What about the exact xc potential?

Finding the exact xc potential for a given known density-evolution

- In general, not easy
- But for 2 electrons spin-singlet, starting in a doubly-occupied orbital, it's easy -- in 1-dimension, very easy!

$$\Phi(x_1, x_2, t) = \phi(x_1, t)\phi(x_2, t)(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$$

Require orbital to reproduce exact *n(x,t)* and *j(x,t):*

$$\phi(x,t) = \sqrt{n(x,t)/2}\, e^{i\int^x dx'\, u(x',t)} \qquad u(x,t) = j(x,t)/n(x,t)$$

If insert $\phi(x,t)$ into TDKS equation, find:

$$v_S(x,t) = \frac{\partial_x^2 n(x,t)}{4n(x,t)} - \frac{(\partial_x n(x,t))^2}{8n^2(x,t)} - \frac{u^2(x,t)}{2} - \int^x \partial_t u(x',t)dx'$$
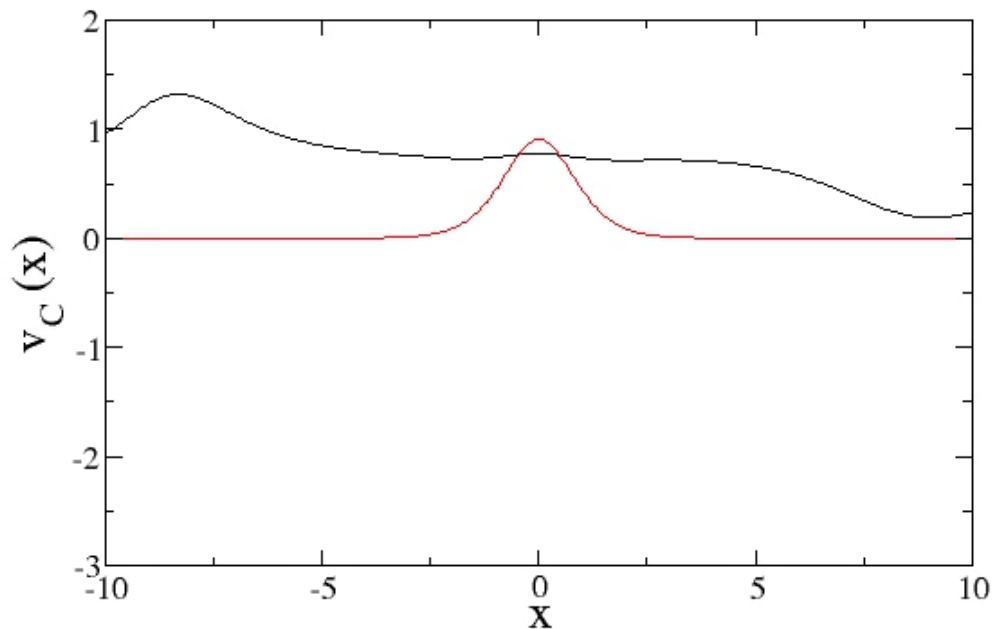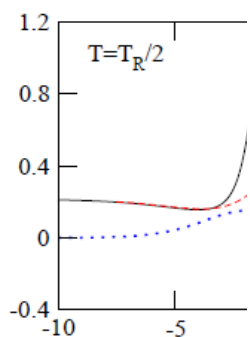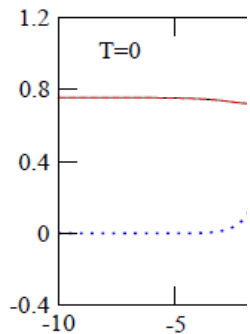
Further, we have $v_X(x,t) = -v_H(x,t)/2$

so we can extract $v_C(x,t) = v_S(x,t) - v_{ext}(x,t) - v_H(x,t)/2$

Preliminary example: Weak on-resonant driving of a "1D He atom"

2 soft-Coulomb interacting fermions living in $v_{ext} = -2/\sqrt{x^2 + 1}$
and subject to $\mathcal{E}(t) = A\cos(\omega t)$

^ = 0.00667 au
= 0.533 au (1st excn.)

exact"
[n(t)]

shots over a
cycle

Movie:

density
Vc

❖ The step structure has density-dependence that is ultra-non-local in space and non-local in time (i.e. non-adiabatic).

• Appear generically in nonlinear dynamics:
in applied fields, but also *field-free* evolution of *non-stationary* states

But they are missing in all approximations used today!

Ongoing <u>ground-state</u> functional development will not help!

Impact on reliability of TDDFT ?

P. Elliott, J. I. Fuks, A Rubio, N. T. Maitra, Phys. Rev. Lett. **109**, 266404 (2012)
J. D. Ramsden and R. W. Godby, Phys. Rev. Lett. **109**, 036402 (2012)
J. I. Fuks, P. Elliott, A Rubio, N. T. Maitra J. Phys. Chem. Lett. **4**, 735 (2013)
M. J. P. Hodgson, J.D. Ramsden, J.B.J. Chapman, P. Lillystone, R. Godby PRB **88**, 241102(R) (2013)
K. Luo, P. Elliott, N. T. Maitra, Phys. Rev. A. . **88**, 042508 (2013)
K. Luo, J. I. Fuks, E. Sandoval, P. Elliott, N. T. Maitra, J. Chem. Phys. **140**, 18A515 (2014)
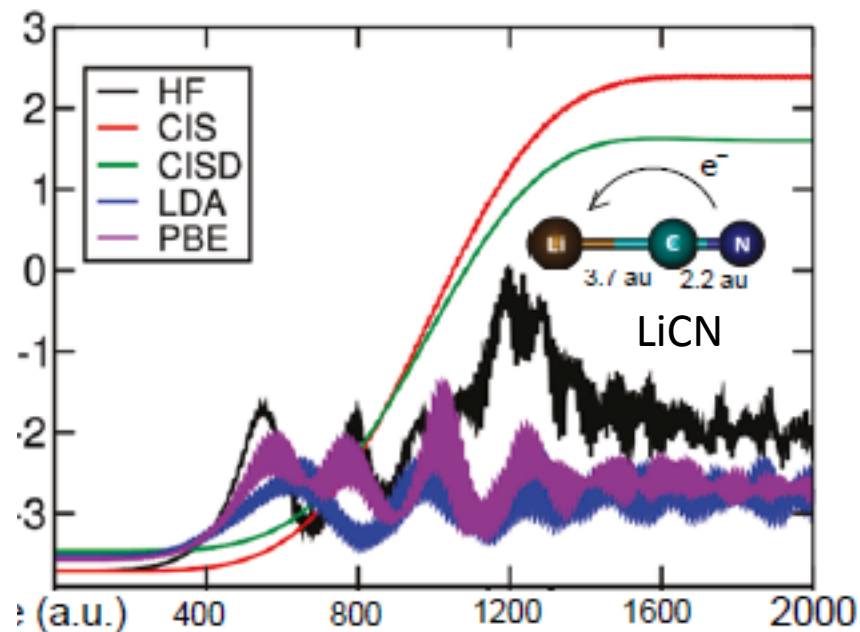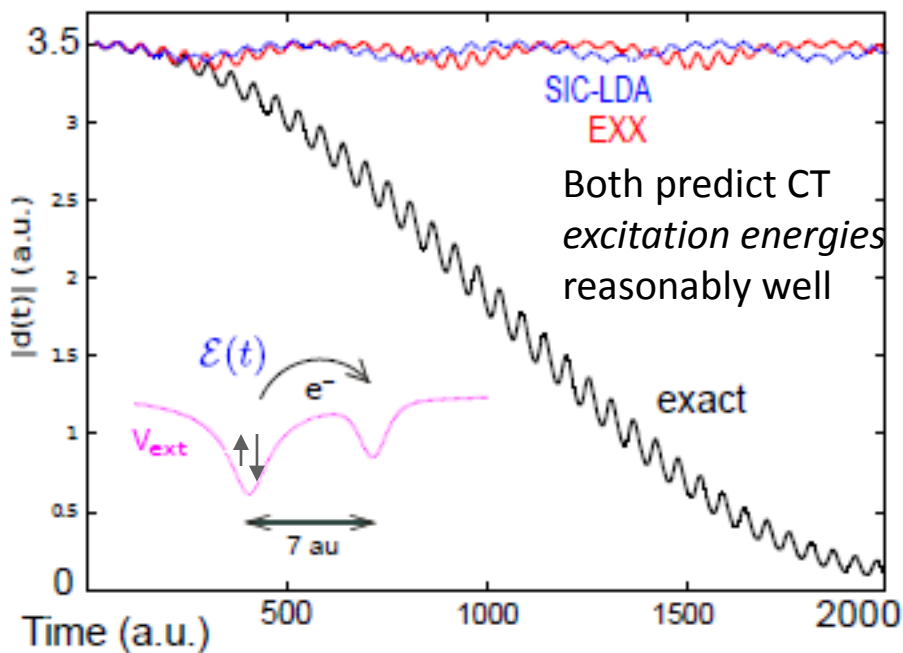
quasiparticle propagation in a wire

Time-Resolved Charge-Transfer 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

SIC-LDA
EXX

Both predict CT
excitation energies
reasonably well

$\mathcal{E}(t)$
e^-
V_{ext}
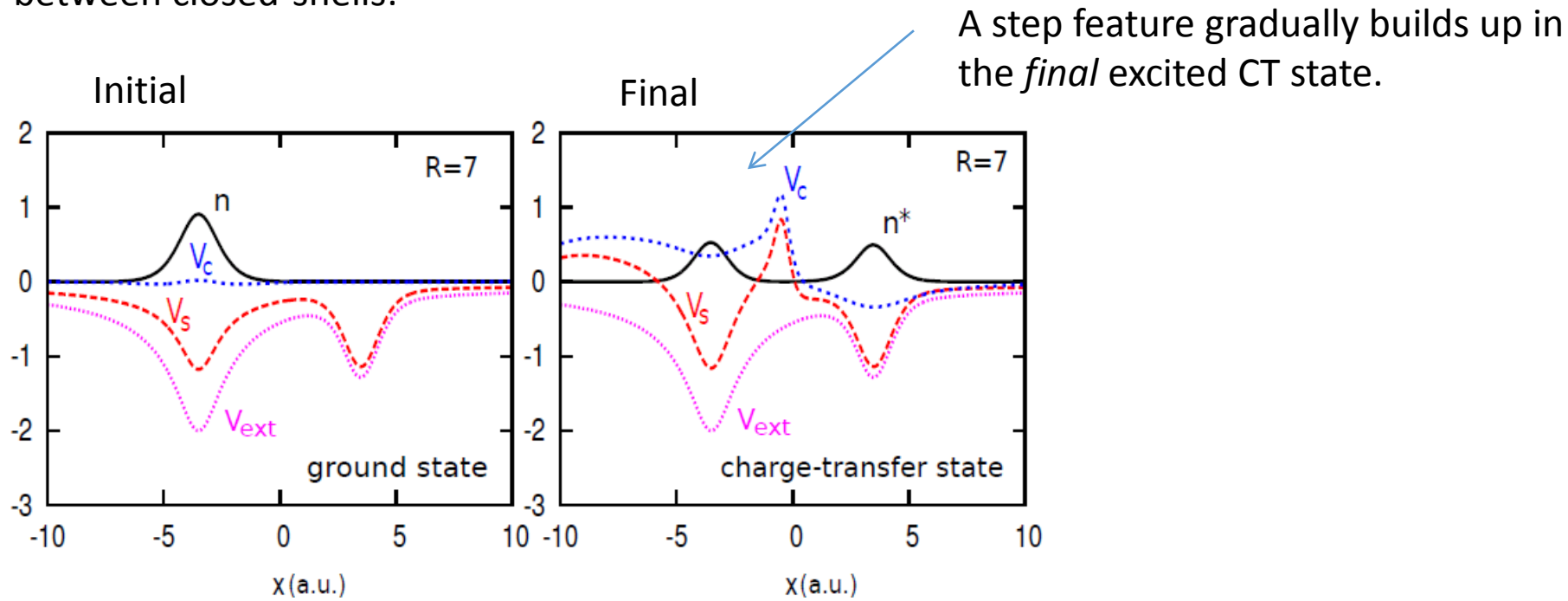7 au

exact

HF
CIS
CISD
LDA
PBE

e^-

3.7 au   2.2 au

LiCN

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

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

First ask, what is the final exact KS potential?

CT between closed-shells:

A step feature gradually builds up in the *final* excited CT state.
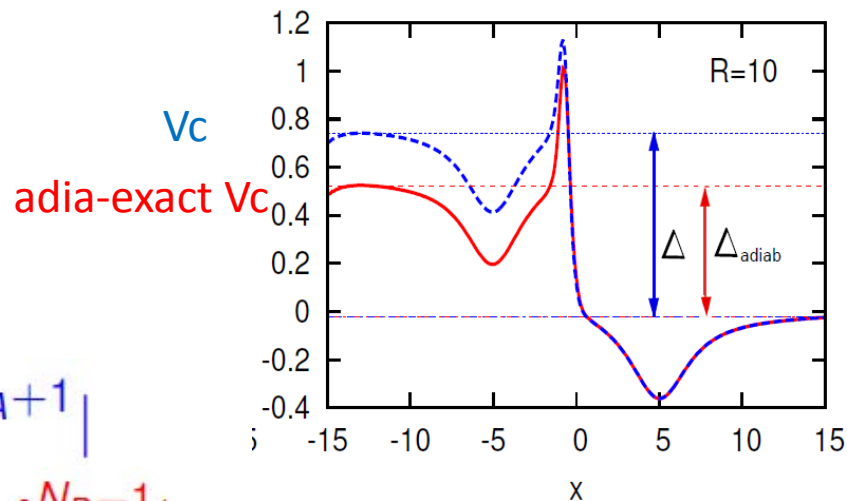

Certainly the step requires spatially non-local density-dependence, but can we get away with *time-local* density dependence, i.e. an adiabatic approx ?

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

Correlation potential in the final CT state, as R→ ∞

Vc

adia-exact Vc

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

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

R=10

- This CT step gradually builds up during the resonantly-driven CT, accompanied by a faster oscillating dynamical step.

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

But the <u>adiabatically-exact</u> approx does get a CT step, albeit with wrong size (& no dynamical step)...
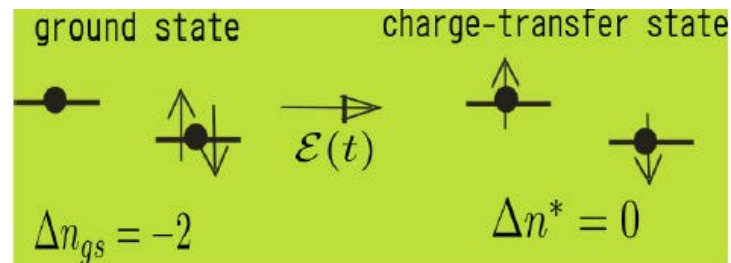
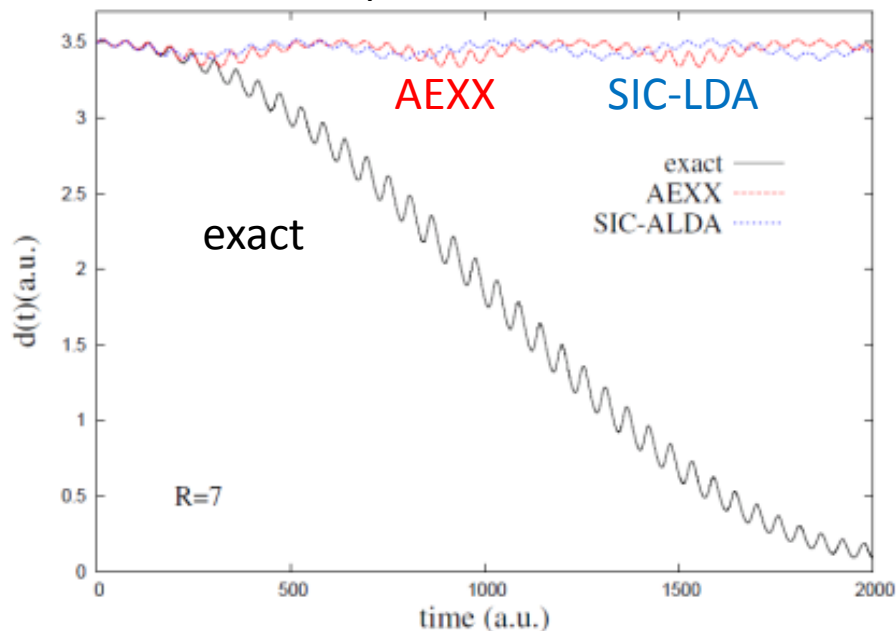If we propagate with it, is it enough to yield reasonable CT dynamics?

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

2-site asymmetric Hubbard model:

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

ground state   charge-transfer state

$\mathcal{E}(t)$

$\Delta n_{gs} = -2$ $\Delta n^* = 0$

CT in real-space molecule

AEXX   SIC-LDA

exact

R=7

CT in Hubbard molecule

AEXX

self-consistent adiabatically-exact

$\omega = \quad 0.5177$

$\omega_{cs-cs}^{AE} = 0.5187$

exact

Dipole Moments versus Time
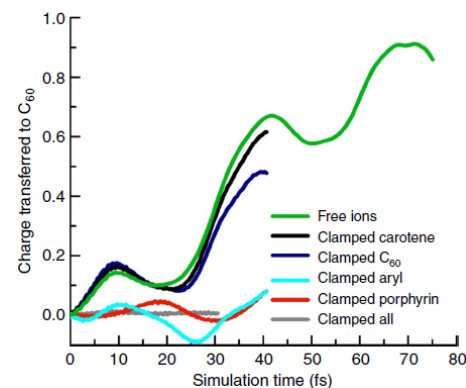
- **Despite extremely accurate CT excitation energies, CT is not achieved by the adiabatically-exact approximation.**

J.I. Fuks and Maitra, Phys. Rev. A. **89**, 062502 (2014); Phys. Chem. Chem. Phys. **16**, 14504 (2014)

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...

What about CT from an excited state?

Actually this is how CT dynamics is run in many calculations eg in photovoltaics...

- *Rozzi et al. Nature. Comm. **4**, 1602 (2013)*

What about charge-transfer from a local excitation?

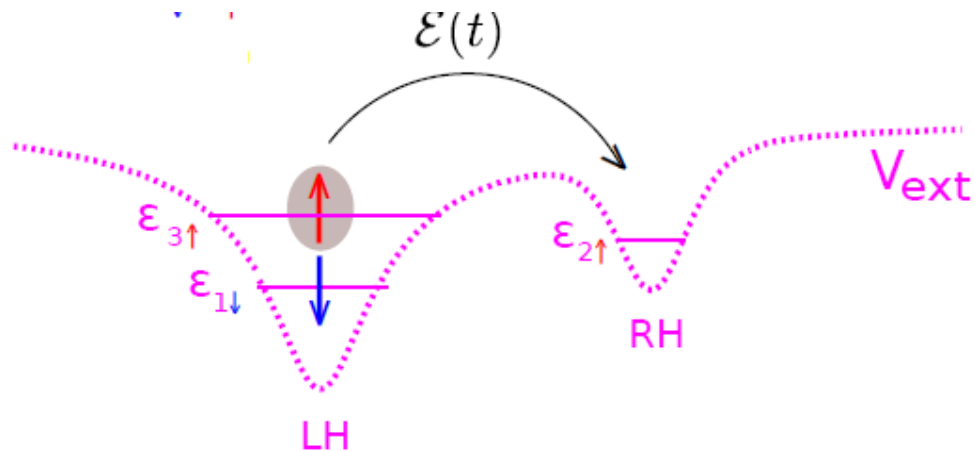Break the restriction of having a single orbital describing both the transferring electron and an electron that stays.

$$\mathcal{E}(t)$$

V_{ext}

$\varepsilon_{3\uparrow}$

$\varepsilon_{1\downarrow}$

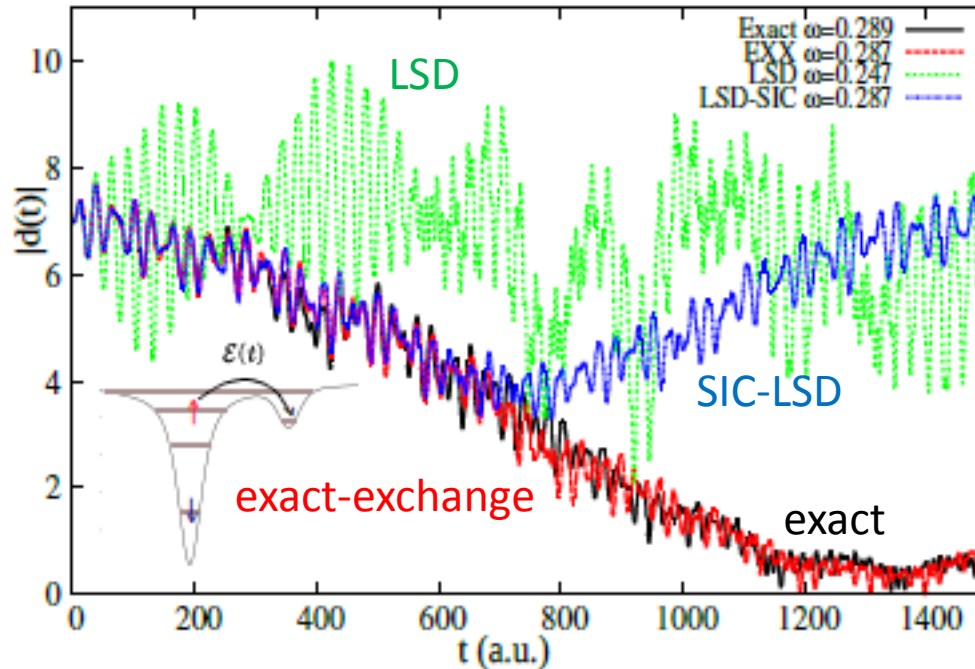$\varepsilon_{2\uparrow}$

RH

LH

Initial state is excited – so isn't ATDDFT wrong from the start?

Well, yes, but not so bad if the KS state is *also* excited, and similar character throughout…

*(Elliott and Maitra, PRA **85**, 052510 (2012))*

Adiabatic exact-exchange (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. $n(t)$ → $v_{xc}[n](t)$ time-dep.

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

These **two time-dependences** <u>cancel</u> with exact functional, but not with approximate functionals !   *Leads to a new exact condition…*

The ATDDFT frequencies typically change in time, unlike the exact.
Bare KS frequencies change in time & fxc correction also time-dependent

These two time-dependences <u>cancel</u> with exact functional, but not with approximate functionals!

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

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

and let ω_i be a pole of the Fourier transform w.r.t. (t-t') of

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

then

$$\boxed{\frac{d\omega_i}{d\mathcal{T}} = 0}$$
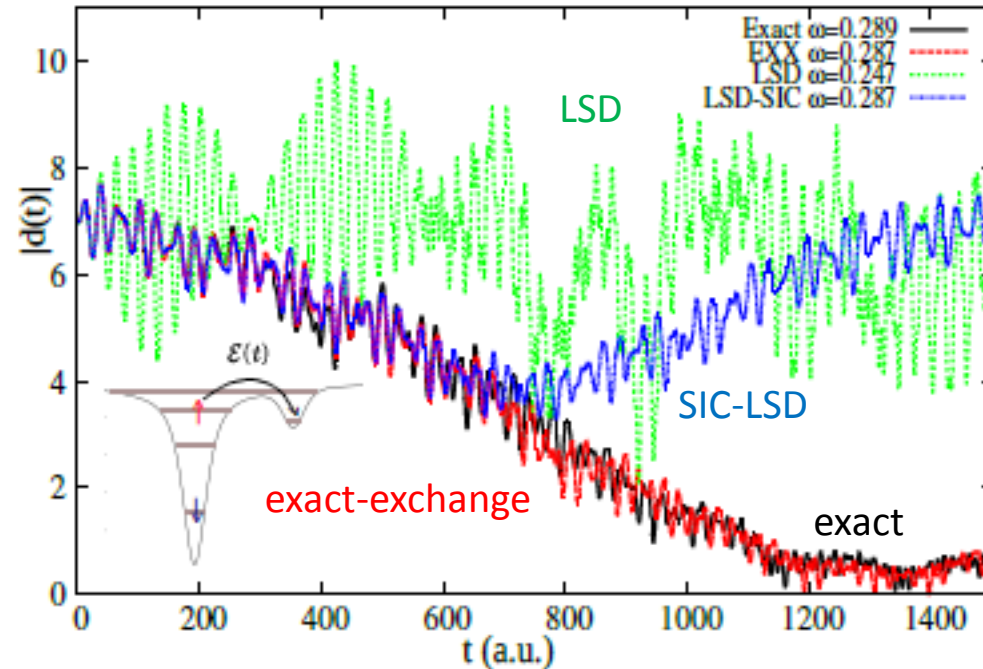
Adiabatic functionals with SCF excited states k, simpler SPA version:

$$\omega_i = \omega_{\mathrm{S},i}^k + 2 \int dr dr' \phi_i^k(\mathbf{r}) \phi_a^k(\mathbf{r}) \tilde{f}_{\mathrm{HXC}}^k(\mathbf{r}, \mathbf{r}') \phi_i^k(\mathbf{r}') \phi_a^k(\mathbf{r}')$$

independent of k

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

Adiabatic EXX fully charge-transfers the photo-excited electron,
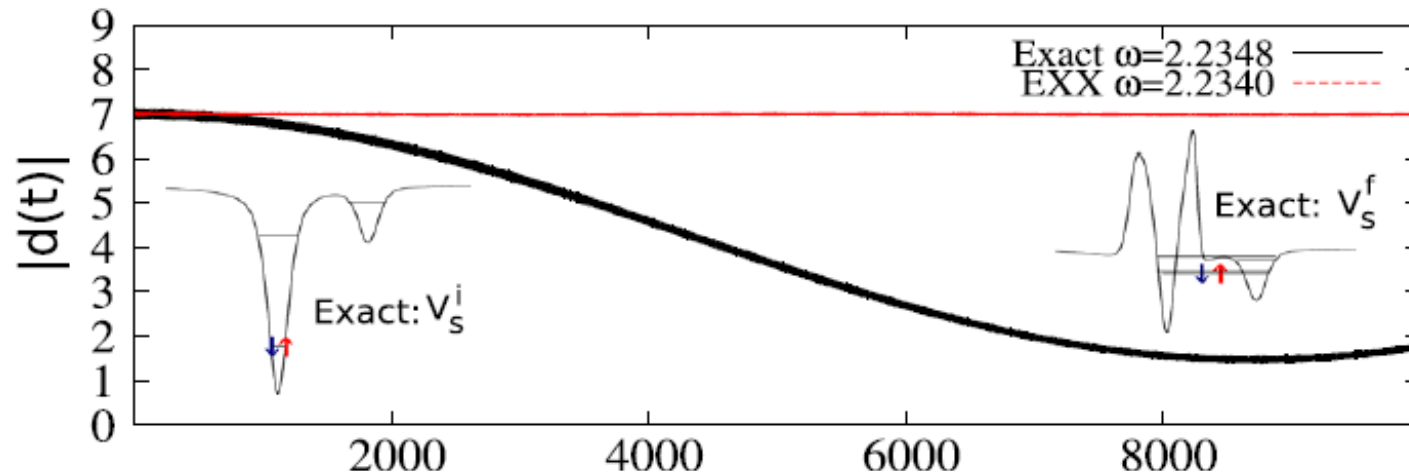### *But not other functionals? Why?*

	Bare KS …			TDDFT …	
	ω_S^i	ω_S^f	$\omega_S^{g.s.}$	TDDFT ω^i	TDDFT ω^f
EXX	0.286	0.286	0.288	0.287	0.287
LSD	0.247	0.094	0.482	–	0.091
SIC-LSD	0.287	0.236	0.267	0.287	0.237

… computed from scf at
i: initial photoex state
f: final CT state

The greater the difference in the frequencies computed in the initial and targeted-final state, the greater the violation of the exact condition, and the worse the dynamics.

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

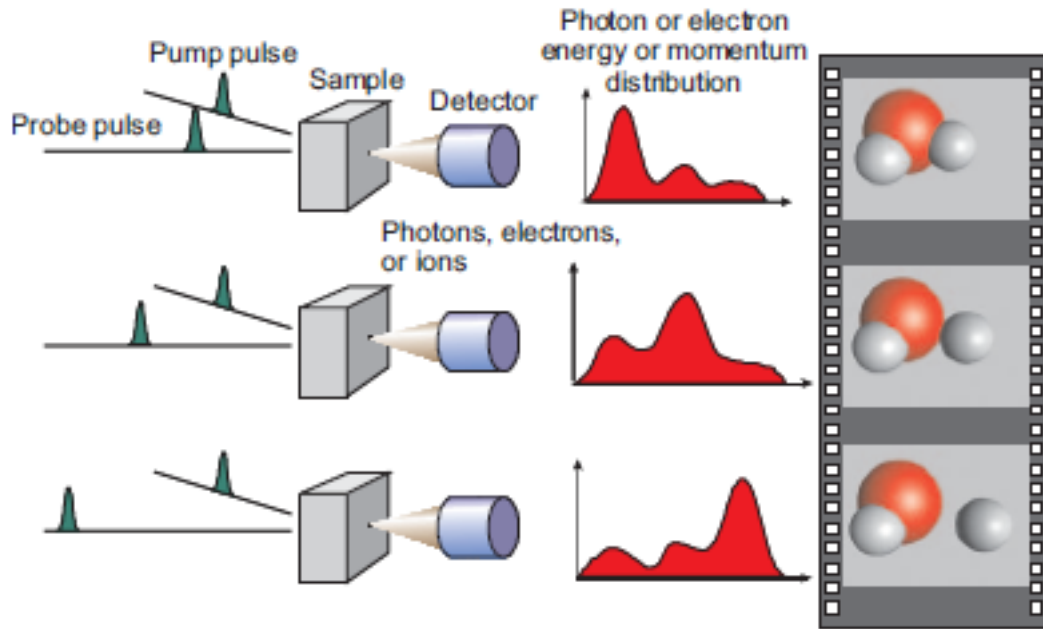And, returning to the disaster of charge transfer beginning in the GS:

Exact KS frequencies: $\omega_S^i = 2.2348$ a.u $\quad \omega_S^f = 0.0007$ a.u.

$\tilde{f}_{\mathrm{HXC}}$ plays increasingly important role during dynamics, maintaining

$$\omega^i = \omega^f = 2.2348 \text{ a.u.}$$

EXX: Again final KS frequency tiny but initial is finite, and f_{Hx} hardly makes any correction – huge violation of exact condition → failure of dynamics

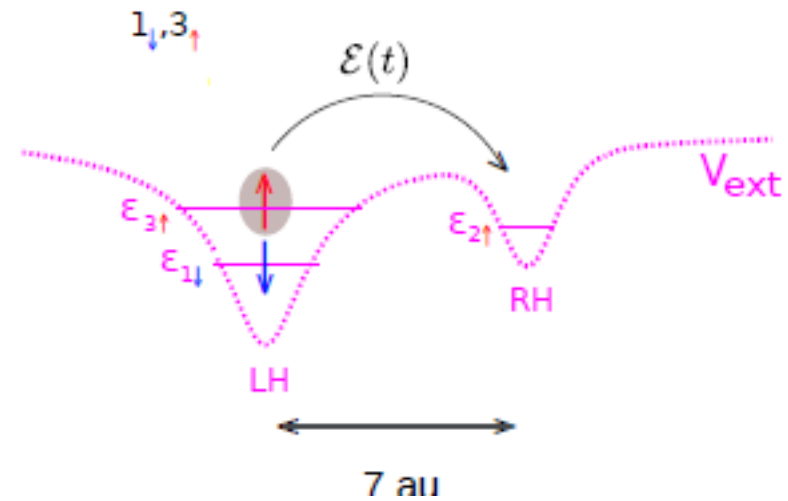# Implications for Time-Resolved Pump-Probe Spectroscopy

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 <u>positions</u> 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); Raganuthan & Nest JCTC **8**, 806 (2012); Habenicht et al. JCP **141**, 184112 (2014).

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

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

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

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

Correlated electron-ion dynamics

What about the exact potential acting on the electrons, accounting for coupling to dynamical quantum nuclei as well as external fields?
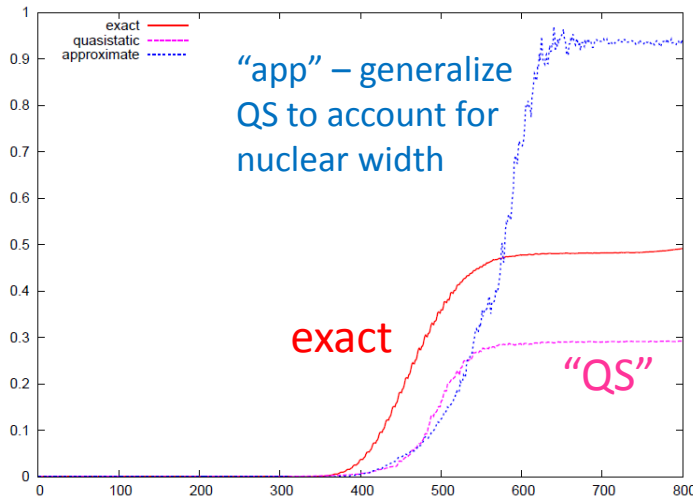
i.e. for the electronic subsystem, say for just one electron,

$$\left(-\frac{1}{2}\nabla^2 + \varepsilon(r,t)\right)\Phi(r,t) = i\partial_t\Phi(r,t)$$

Traditionally, use $\varepsilon^{QS} = \hat{W}_{en}(\underline{\mathbf{r}}, \underline{\mathbf{R}}(t)) + \hat{W}_{nn}(\underline{\mathbf{R}}(t)) + \hat{v}^e_{\text{ext}}(\underline{\mathbf{r}}, t)$

classical nuclear trajectory

Example: Charge-Resonance Enhanced Ionization (CREI) in 1D H$_2^+$

"app" – generalize QS to account for nuclear width

exact

"QS"

A. Abedi, N. T. Maitra, E.K.U. Gross, Phys. Rev. Lett. **105**, 123002 (2010);

Y. Suzuki, A. Abedi, N. T. Maitra, K. Yamashita, E. K. U. Gross, Phys. Rev. A **89**, 040501(R) (2014);

E. Khosravi, A. Abedi, N. T. Maitra, almost submitted (2015)

almost submitted (2015)

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