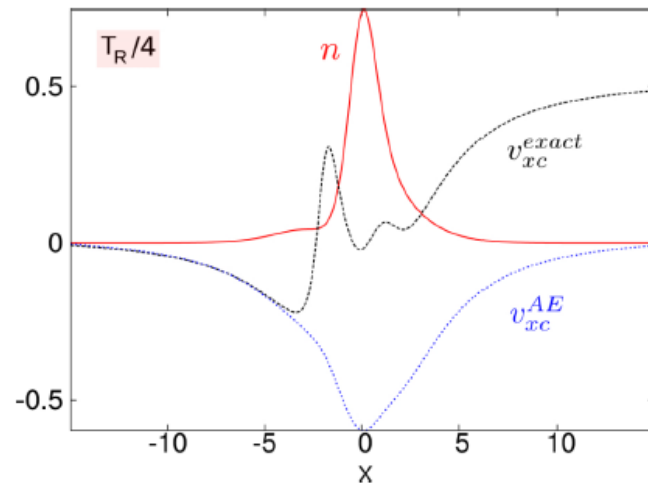# Memory in TDDFT I: Real-Time TDDFT

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Plan

❖ Introduction to what is memory in TDDFT

-- the adiabatic approximation

❖ Approximations that include memory, and some exact conditions

❖ Some examples

-- field-free superposition state dynamics

-- charge-transfer dynamics

-- electron-atom scattering

How did memory come in?

Runge-Gross:

$$n \xleftrightarrow[\text{1-1}]{\Psi_0} v_{ext}$$

true system

$$n \xleftrightarrow[\text{1-1}]{\Phi_0} v_s$$

KS system

Hartree is naturally *adiabatic* – depends only on instantaneous density

$$v_s[n; \Phi_0](\mathbf{r}t) = v_{ext}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$

Actually, $v_{ext}[n, \Psi_0](rt)$
but $v_{ext}(rt)$ is prescribed by problem at hand, so functional dependence not explicit

History: $n(r \ t' < t)$ and **initial states** Ψ_0 and Φ_0 of true and KS systems

Ψ_0: true initial state

Φ_0: initial state to start the KS calculation -- any state with same $n(r,0)$ and $\dot{n}(r,0)$ as Ψ_0

usually choose Slater determinant but not necessary

Memory

$$v_{\mathrm{xc}}[n; \Psi_0, \Phi_0](rt)$$

Functional depends on history, $n(r\,t' < t)$, and initial states Ψ_0 and Φ_0 of true and KS systems

• Also, for a general observable: A[n; Φ_0]

• Special, and common, case:
$$\Psi_0 = \Psi_{GS}$$
$$\Phi_0 = \Phi_{GS}$$

Then, by the Hohenberg-Kohn theorem, $\Psi_0 = \Psi_0[n(0)]$ and $\Phi_0 = \Phi_0[n(0)]$

-- no explicit initial-state-dependence → $v_{xc}[n](r,t)$ (but still history-dependent)

e.g. linear response regime.

The Adiabatic Approximation

• Almost all calculations today ignore memory, and use an
adiabatic approximation:
input instantaneous density into a ground-state approximation

$$v_{\mathrm{XC}}^{\mathrm{A}}[n; \Psi_0, \Phi_0](\mathbf{r}, t) = v_{\mathrm{XC}}^{\mathrm{g.s.}}[n(t)](\mathbf{r}) = \left.\frac{\delta E_{\mathrm{XC}}[n]}{\delta n(\mathbf{r})}\right|_{n=n(\mathbf{r},t)}$$

$$f_{\mathrm{XC}}^{\mathrm{A}}[n_0](\mathbf{r}, \mathbf{r}', t-t') = \left.\frac{\delta^2 E_{\mathrm{XC}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n_0(\mathbf{r})} \delta(t-t')$$

$$f_{\mathrm{XC}}^{\mathrm{A}}[n_0](\mathbf{r}, \mathbf{r}', \omega) = \left.\frac{\delta^2 E_{\mathrm{XC}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n_0(\mathbf{r})}$$

Example: $$v_{\mathrm{XC}}^{\mathrm{ALDA}}(\mathbf{r}, t) = v_{\mathrm{XC}}^{\mathrm{LDA}}[n(\mathbf{r}, t)] = \left.\frac{d\left(n\mathcal{E}_{\mathrm{XC}}^{unif}(n)\right)}{dn}\right|_{n=n(\mathbf{r},t)}$$

$$f_{\mathrm{XC}}^{\mathrm{ALDA}}[n_0](\mathbf{r}, \mathbf{r}', t-t') = \left.\frac{d^2\left(n\mathcal{E}_{\mathrm{XC}}^{unif}(n)\right)}{dn^2}\right|_{n=n_0(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

The Adiabatic Approximation

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

• Two sources of error:
(i) Adiabatic approximation itself
(ii) Ground-state functional approximation

• To disentangle, study "adiabatically-exact" potential *(see examples soon!)*

$$v_{\text{XC}}^{\text{adia}-\text{ex}}[n; \Psi_0, \Phi_0](\mathbf{r}, t) = v_{\text{XC}}^{\text{exact}-\text{g.s.}}[n(t)](\mathbf{r})$$

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Development of Memory-Dependent Functionals…

➢ Gross-Kohn (1985)

*Phys. Rev. Lett. **55**, 2850 (1985)*

linear-response kernel of the uniform electron gas at finite frequency

$$f_{\text{XC}}^{\text{GK}}[n_0](\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') f_{\text{XC}}^{unif}[n_0(\mathbf{r})](q = 0, \omega)$$

$$v_{\text{XC}}^{(1)\text{GK}}[n](\mathbf{r}, t) = \int f_{\text{XC}}^{unif}[n_0(\mathbf{r})](t - t')\delta n(\mathbf{r}, t')dt'$$

✓ Non-adiabatic -- time-non-local although spatially local; "finite-frequency LDA"

⚠ Violates exact conditions: harmonic potential theorem, zero-force theorem

A couple of exact conditions in TDDFT:

(i) Harmonic Potential Theorem (Dobson (*PRL **73**, 2244, (1994)*); Vignale *PRL **74**, 3233, (1995)*))

N electrons in a harmonic well subject to a TD uniform electric field, E(t)
→ density rigidly sloshes back and forth following classical center of mass

$$n(\textbf{\textit{r}},t) = n_{GS}(\textbf{\textit{r}} - \textbf{\textit{r}}_{CM}(t))$$

$$\rightarrow v_{\text{xc}}(\textbf{\textit{r}},t) = v_{\text{xc}}{}^{GS}(\textbf{\textit{r}} - \textbf{\textit{r}}_{CM}(t))$$

- Instead, GK finds an n-dependent shift in the frequency of the CM motion, and a damping of the oscillations.

    One way to think about why is that when you only look locally at the density at r, you can't tell difference between sloshing motion and local compression/rarefaction *…sketch.*

A couple of exact conditions in TDDFT:

(ii) Zero Force Theorem (Vignale *PRL* **74**, *3233, (1995)*; *Phys. Lett. A,* **209**, *206 (1995)*)

xc field cannot exert a net force on itself $\int n(\mathbf{r},t)\nabla v_{\text{XC}}(\mathbf{r},t)d^3r = 0$

Can prove by: evaluate $\frac{d^2}{dt^2}$<r> using Ψ(t) and then Φ(t); then subtract...)

(exercise! Prove this !)

Linear response regime: $\int d^3r' f_{\text{XC}}[n^{\text{GS}}](\mathbf{r},\mathbf{r}',\omega)\nabla n^{\text{GS}}(\mathbf{r}') = \nabla v_{\text{XC}}^{\text{GS}}[n^{\text{GS}}](\mathbf{r})$

- Using GK:

$\nabla n_{GS}(r) f_{\text{xc}}^{unif}[n_{GS}(r)](q=0,\omega)$
ω-dependent

ω-independent

❖ The exact conditions imply *time-non-locality* → *spatially non-local n-dependence,* i.e. a local density approximation with memory does not exist.

even in limit of slowly-varying densities → "ultra-non-locality"

$$v_{\mathrm{xc}}[n; \Psi(0), \Phi(0)](\boldsymbol{r},t)$$
$$f_{\mathrm{xc}}[n](\boldsymbol{r}, \boldsymbol{r}',\omega)$$

… Development of Memory-Dependent Functionals

➤ Vignale-Kohn (VK) (1996) – spatially local approx in terms of the *current-density, j(r,t)* → TD-current-density-FT

Phys. Rev. Lett. **77**, 2037 (1996); Vignale, Ullrich, Conti, , PRL **79**, 4878 (1997)

Based on map: $\qquad \boldsymbol{j} \xleftarrow[\text{1-1}]{\Psi_0} \boldsymbol{A}_{\text{ext}}$

VK constructed from dynamical longitudinal and transverse responses to slowly-varying perturbations of uniform electron liquid; involves Navier-Stokes-like eqn with complex viscosity coefficients.

✓ Non-adiabatic, and satisfies harmonic potential theorem, zero-force theorems…

Similar concept was proposed by Dobson-Bünner-Gross (1997)
*Phys. Rev. Lett. **79**, 1905 (1997)*

Apply Gross-Kohn in frame that moves along with local velocity of electron fluid: memory resides with the fluid element.

$R',t' \quad\longrightarrow\quad r,t$

Spatially-local relative to where a fluid element at (r,t) was at earlier times t', $R'(t'\,|\,r,t)$.

Agrees with VK in 1D.

… A little more about Vignale-Kohn and TDCDFT…

- Note that RG's 1st step was $j \longleftrightarrow v_{ext}$

Using **A** instead of v makes it easier to satisfy *non-interacting representability*: many currents of interacting systems in *scalar* potentials can only be reproduced by a non-interacting systems in *vector* potentials

- Note that spatially local current **j** dependence → spatially ultra-nonlocal dependence on density *n*

$$\text{E.g.} \quad j_{\mathrm{L}}(r, t) = \int \mathrm{d}^3 r' \frac{\partial n(r', t)}{\partial t} \nabla_r \frac{1}{4\pi |r - r'|}$$

So even for static response (no memory), VK can help when spatial-non-locality important.

- Some success for: correcting overestimate of LDA polarizabilities in long-chain polymers, dissipation in extended systems, spin-Coulomb drag, stopping power in metals….*BUT* problems for finite systems due to spurious damping

… Other Memory-Dependent Functionals

➤ **Lagrangian frame action functional**

Y. Kurzweil & R. Baer (J. Chem. Phys. **121** 8731 (2004).

➤ **Time-dependent deformation functional theory**

I. V. Tokatly (Phys. Rev. B **71 (**2005), Phys. Rev. B **75**, 125105 (2007); Chap. 25 in Fundamentals of TDDFT (Springer, 2012)

➤ **Bootstrapping many-body perturbation theory**

R. Van Leeuwen, Phys. Rev. Lett. **51**, 1888 (1983); von Barth et al. Phys. Rev. B **72** 235109 (2005)

➤ **Orbital functionals** $v_{xc}[\{\phi_i(t)\}]$

H. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008)

Finite systems

Initial-state dependent

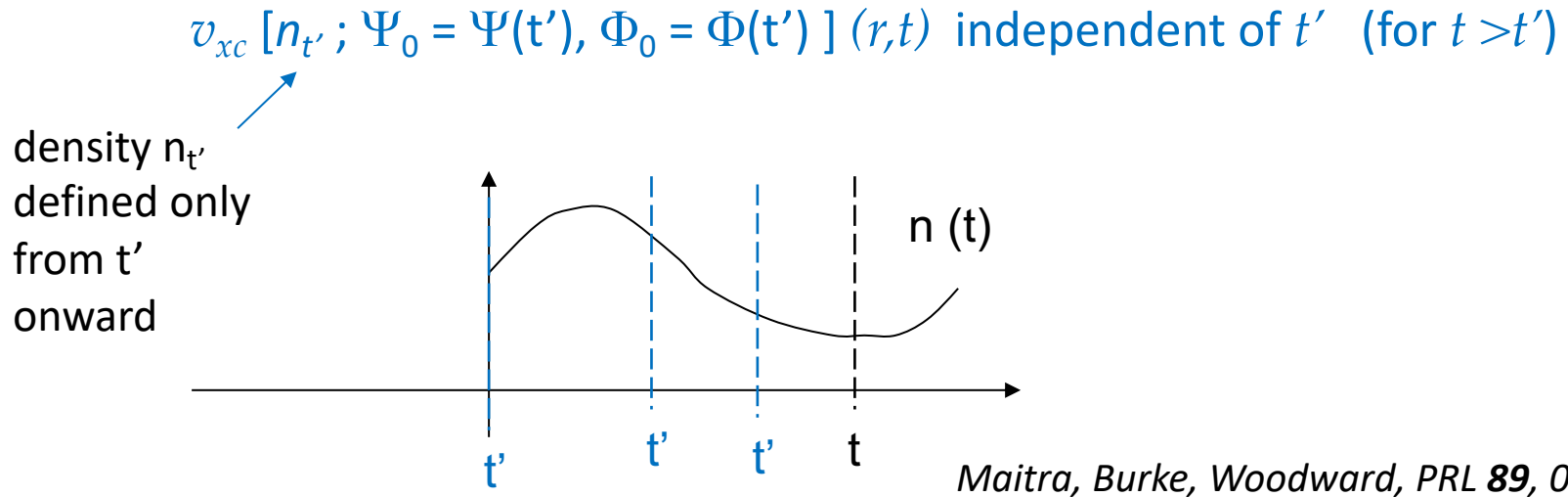➤ **Approximations based on an exact decomposition of the xc potential**
L. Lacombe and N. T. Maitra, J. Chem. Theory and Comput. **15**, 1672 (2019).
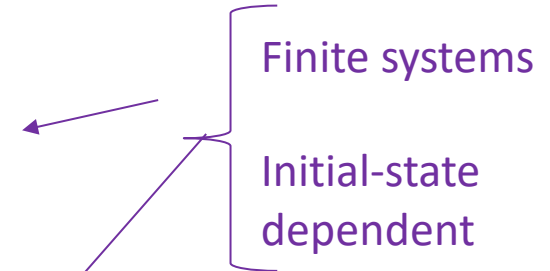
• **Recent Review of Memory-Dependent Approximations :** L. Lacombe and N. T. Maitra, *Nonadiabatic approximations in TDDFT: Progress and prospects* NPJ Comput. Mat, to appear (2023); arXiv:2302.11366

Another exact condition: **"Memory" condition**

❖ History and initial-state dependence are entangled

v_{xc} $[n_{t'}$; $\Psi_0 = \Psi(t')$, $\Phi_0 = \Phi(t')$ $]$ (r,t) independent of t' (for $t > t'$)

density $n_{t'}$
defined only
from t'
onward

n (t)

t'   t'   t'   t

*Maitra, Burke, Woodward, PRL **89**, 023002 (2002*

❖ This is a very hard condition to satisfy for non-adiabatic functionals.

❖ When finding exact xc potentials for a given model dynamics, this condition is useful
to generalize your results! It says for *any* dynamics that reaches the instantaneous
interacting and KS states $\Psi(t)$, $\Phi(t)$, at some time *t*, the exact xc potential you might
find in a given dynamics applies to all.

We will next look at some systems where we can find the exact TD xc potential, and compare with the adiabatic approximation.

To do this, we need a system for which we can find the exact interacting wavefunction from which we obtain the time-dependent density.

Then the question is what is the Kohn-Sham potential that reproduces this density evolution?

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

- Generally, not so easy.
- One can show:

$$\phi_i(\mathbf{r},t) = \sqrt{n_i(\mathbf{r},t)}e^{i\alpha_i(\mathbf{r},t)}$$

into TDKS

$$v_{\rm S}(\mathbf{r},t) = \frac{\nabla^2\sqrt{n_i(\mathbf{r},t)}}{2\sqrt{n_i(\mathbf{r},t)}} - \frac{(\nabla\alpha_i(\mathbf{r},t))^2}{2} - \partial_t\alpha_i(\mathbf{r},t)$$

orbital-density and orbital-phase of *any one* of the occupied orbitals

where $\quad \nabla\cdot(n_i\nabla\alpha_i(\mathbf{r},t)) = -\partial_t(n_i(\mathbf{r},t))$

Exercise: show this!

- In 1D, can express in terms of orbital-density and orbital-"velocity", $u_i = j_i/n_i$

$$v_{\rm S}(x,t) = \frac{\nabla^2\sqrt{n_i(x,t)}}{2\sqrt{n_i(x,t)}} - \frac{1}{2}u_i(x,t)^2 - \int^x \partial_t u_i(x',t)dx'$$

- So, problem becomes finding the exact KS orbitals -- generally difficult, but possible,   *Nielsen, Ruggenthaler, van Leeuwen, Europhys. Lett. 101, 33001 (2013)*

- One easy case: 2 electrons spin-singlet in 1D, in a doubly-occupied KS orbital

$n_i(x,t) \rightarrow$ ½ $n(x,t)$, the exact density, and $u_i(x,t) \rightarrow j(x,t)/n(x,t)$, where j is the exact current-density

Expression directly for the exact exchange-correlation potential …

Those expressions are directly for v_s; to find v_{xc} we must subtract Hartree and v_{ext}

But there is also an expression directly for v_{xc}:

Equate equation of motion for $\partial^2 n(r,t)/\partial t^2$ coming from interacting system,

$$\ddot{n}(\mathbf{r}, t) = -\nabla \cdot (n \nabla v_{\text{ext}}) + i \nabla \cdot \langle \Psi(t) | [\hat{j}(\mathbf{r}), \hat{T} + \hat{W}] | \Psi(t) \rangle$$
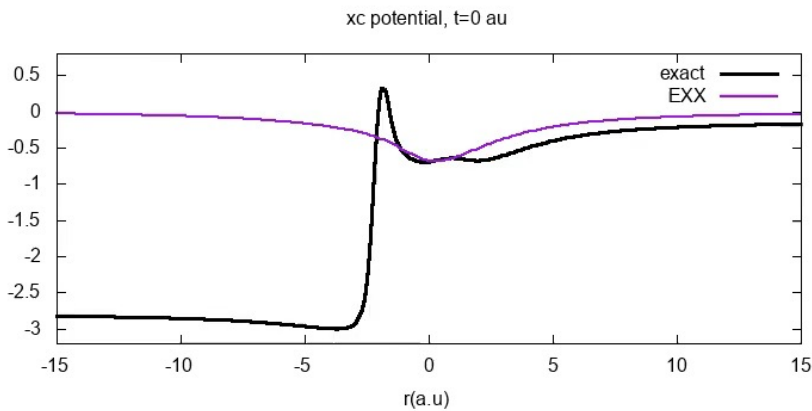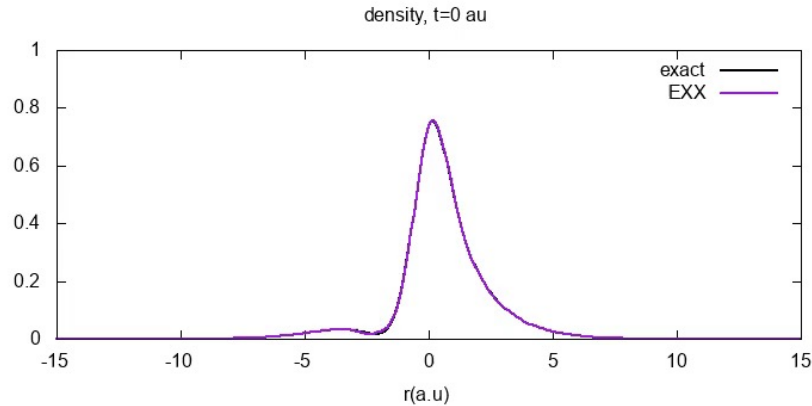
with that of the KS system, and then subtract →

Exact expression for the TD exchange-correlation potential

TD one-body density-matrix: interacting,   KS

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

TD exchange-correlation hole

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

A simple example of memory-dependence:
Field-Free Evolution of Superposition State in 1D He

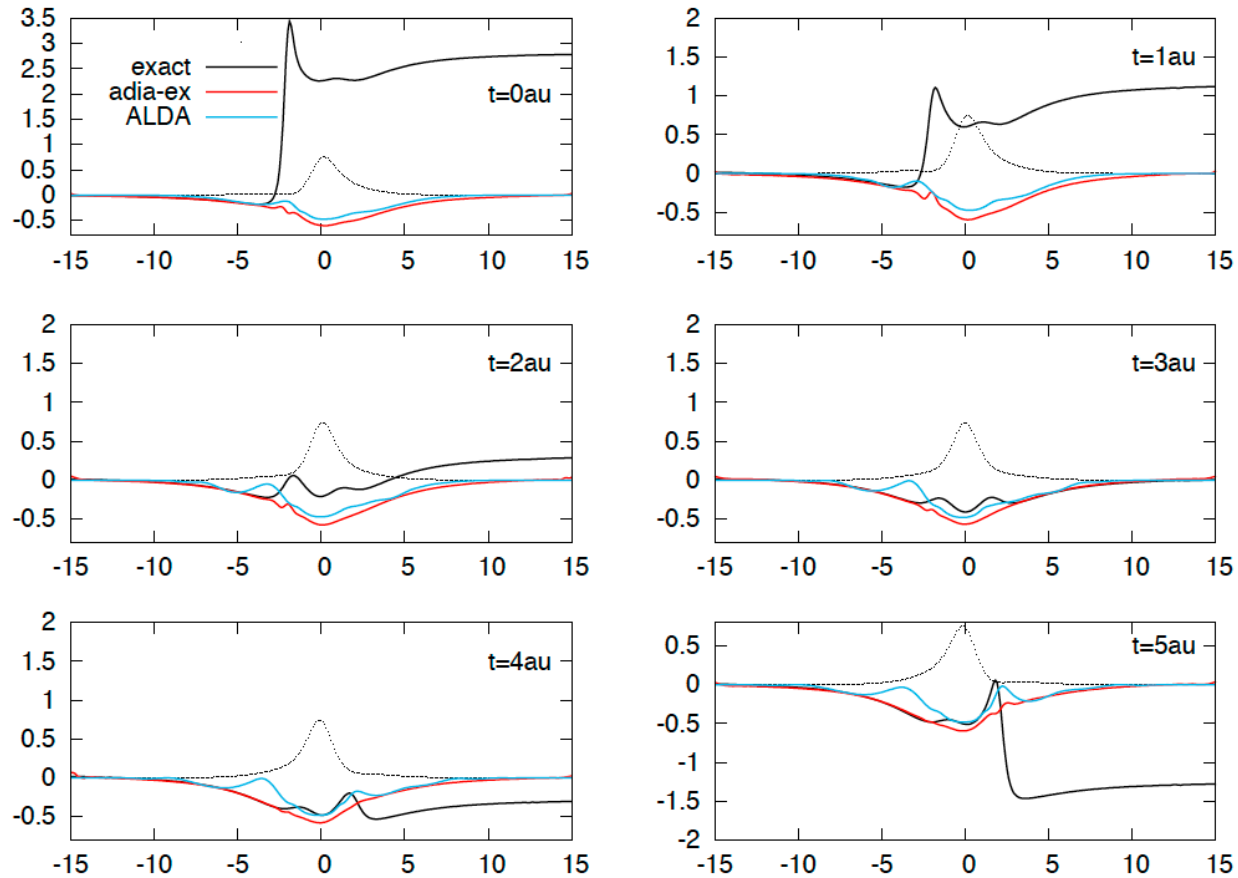density, t=0 au

xc potential, t=0 au

$$\Psi(0) = \frac{1}{\sqrt{2}} \left(\Psi_0 + \Psi_1 \right)$$

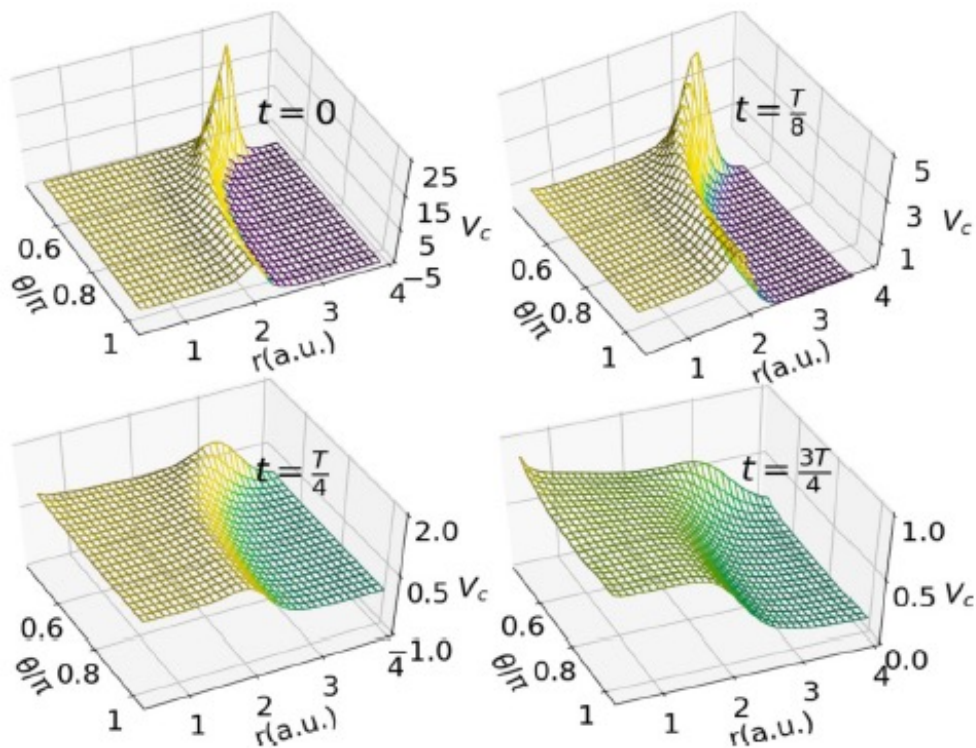These large step and peak features cannot be captured by even the best adiabatic approximation, $v_{xc}^{A\text{-}ex}$ ...

υ_xc

Adiabatic approximations, even adiabatically-exact, lack the dynamical step and look really different

The large non-adiabatic features are not a consequence of 1D – they are equally present in real 3D systems,

e.g. 50:50 superposition state $1^1S_0 : 2^1P_1$ in the He atom

$$\varphi(\mathbf{r},t) = \sqrt{n(\mathbf{r},t)/2}\,e^{i\alpha(\mathbf{r},t)} \qquad \nabla \cdot [n(\mathbf{r},t)\nabla\alpha(\mathbf{r},t)] = -\frac{\partial}{\partial t}n(\mathbf{r},t) \qquad v_s(\mathbf{r},t) = \frac{\nabla^2\sqrt{n(\mathbf{r},t)}}{2\sqrt{n(\mathbf{r},t)}} - \frac{|\nabla\alpha(\mathbf{r},t)|^2}{2} - \frac{\partial\alpha(\mathbf{r},t)}{\partial t}$$

- Non-adiabatic features in v_c appear generically in non-perturbative dynamics: resonantly-driven processes, charge-transfer dynamics, field-free evolution of non-stationary states, quasiparticle propagation in wires…
  …but missing in all adiabatic approximations

E.g.
Elliott, Fuks, Rubio, Maitra, *PRL* **109***, 266404 (2012)*
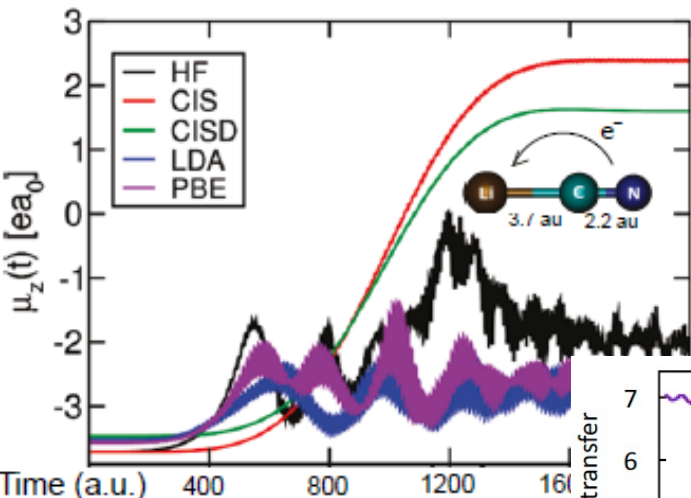Ramsden, Godby, *PRL* **109***, 036402 (2012)*
…
N. T. Maitra, *Perspective* in J. Chem. Phys. **144**, 220901 (2016)
D. Dar, L. Lacombe, N. T. Maitra, Chem. Phys. Rev. **3**, 031307 (2022)

- What is the impact on dynamics?? Propagate with adiabatically-exact approximation to compare…

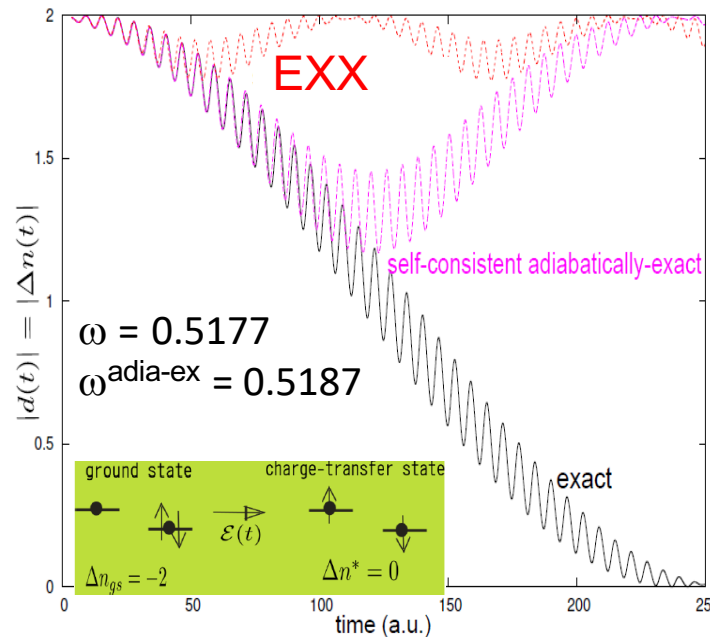# Another Example: Charge-transfer dynamics out of the ground-state

LiCN molecule

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

J. I. Fuks, P. Elliott, A Rubio, N. T. Maitra J. Phys. Chem. Lett. **4**, 735 (2013)
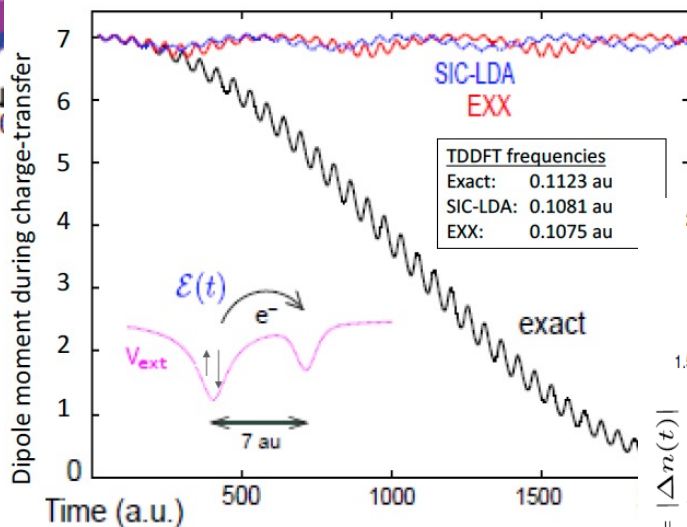
J.I. Fuks and Maitra, Phys. Rev. A. **89**, 062502 (2014); Phys. Chem. Chem. Phys. **16**, 14504 (2014)


TDDFT frequencies
Exact: 0.1123 au
SIC-LDA: 0.1081 au
EXX: 0.1075 au

EXX

self-consistent adiabatically-exact

$\omega = 0.5177$

$\omega^{adia-ex} = 0.5187$

exact

ground state   charge-transfer state

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

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

But charge-transfer out of the ground-state is challenging for KS, since *a single KS orbital must always describe both the transferring electron and one that stays...*

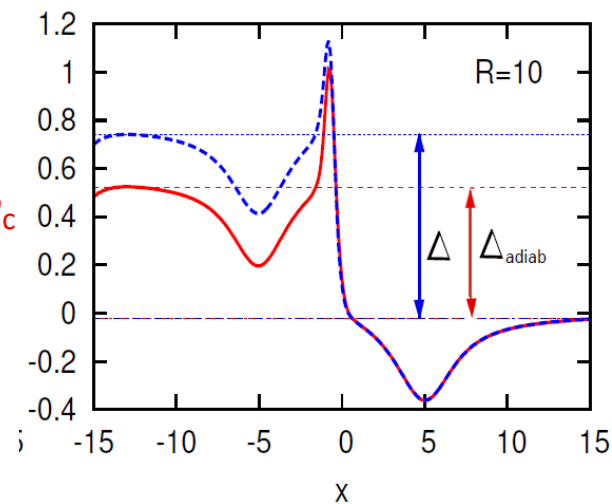Step features build up in time – even $v_c{}^{adia-ex}$ fails to correctly capture
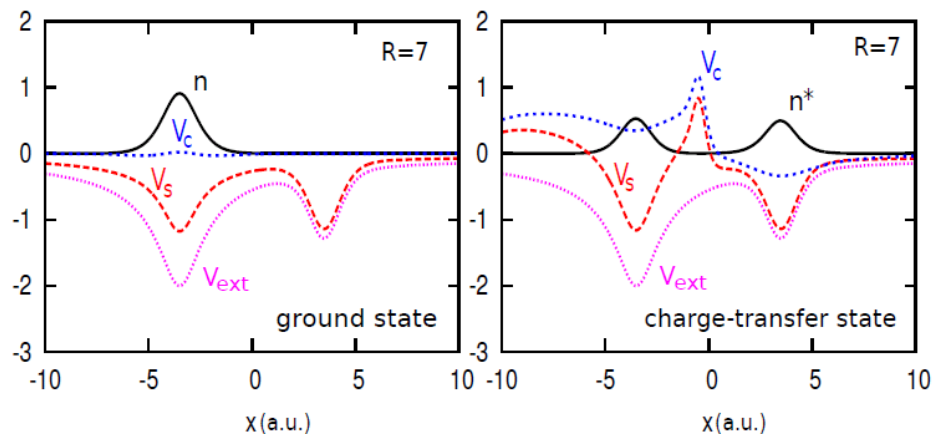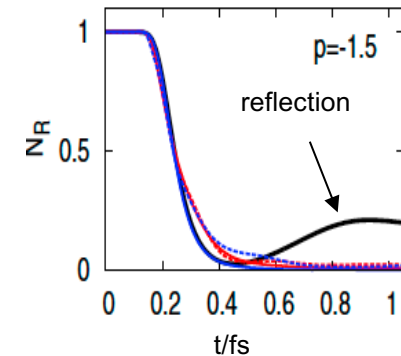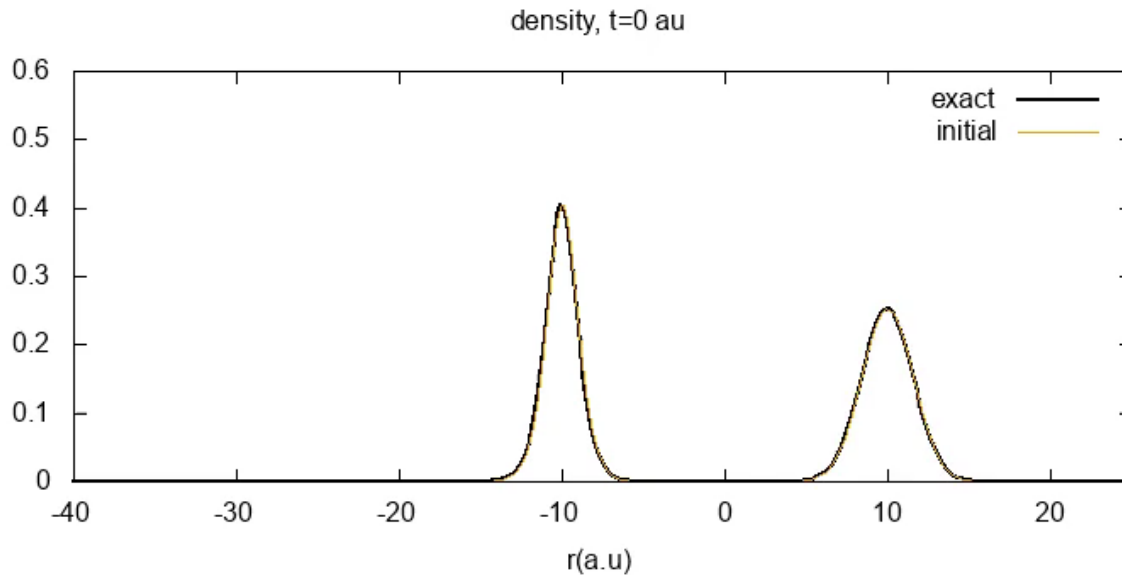

Correlation potential in the final
CT state, as R→ ∞

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

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

v_c

adia-exact v_c

A final example: Time-Resolved e-H scattering

density, t=0 au

How do the TDDFT approximations do?

Choice of **initial spin-singlet KS wavefunction**: $v_{xc}[n; \Psi_0, \Phi_0](rt)$

(1) Slater determinant (one orbital, doubly-occupied)
(2) Two-orbital state: one for the electron in the atom, one for the incoming
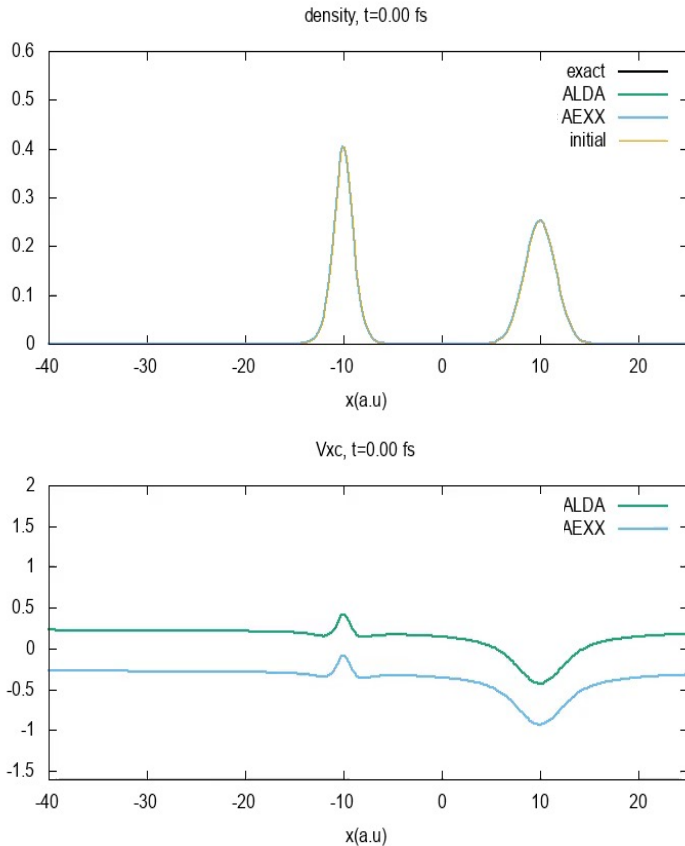
Y. Suzuki, L. Lacombe, K. Watanabe, N. T. Maitra, PRL **119**, 263401 (2017)
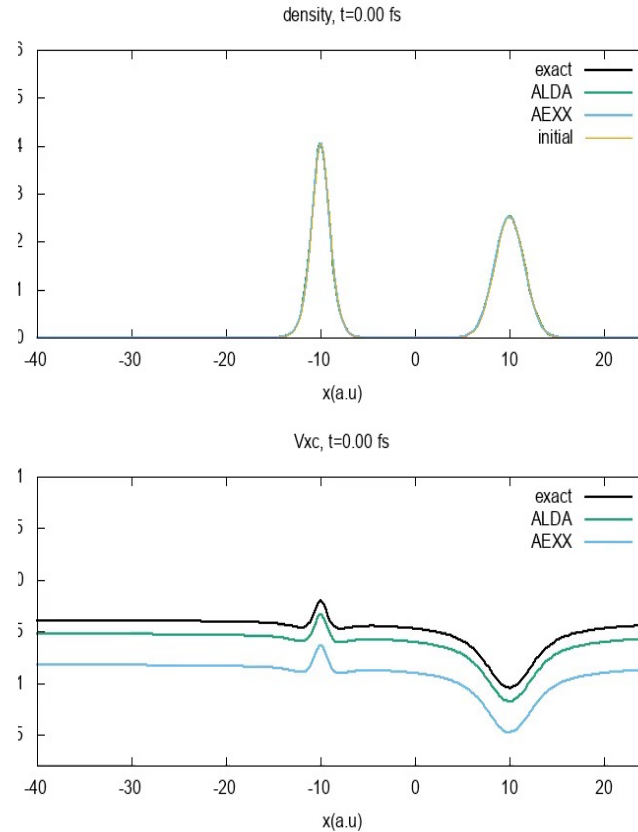L. Lacombe, Y. Suzuki, K. Watanabe, N. T. Maitra, Eur. Phys. J. B. **91,** 96 (2018)

Time-Resolved e-H scattering

Choice (1) Slater determinant

density, t=0.00 fs

Vxc, t=0.00 fs

Choice (2) Two-orbital

density, t=0.00 fs

Vxc, t=0.00 fs

❖ Although ALDA and AEXX densities don't show unphysical oscillations for choice (2), they overspread and ultimately fail to scatter – v_{xc} lacks crucial peak and valley structures.

❖ Same trend for elastic case – here scattering coeffs extracted from linear response using AEXX are good but time-resolved calculation fails!
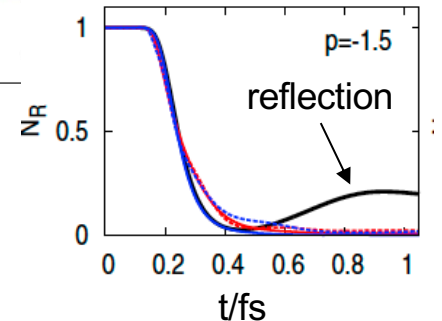
p=-1.5

reflection

N_R

t/fs

Y. Suzuki, L. Lacombe, K. Watanabe, N. T. Maitra, PRL **119**, 263401 (2017)
L. Lacombe, Y. Suzuki, K. Watanabe, N. T. Maitra, Eur. Phys. J. B. **91,** 96 (2018)

Short summary so far: memory in non-perturbative dynamics

❖ The exact functional depends on the history of the density, the initial state, and choice of KS initial state. Neglect of this memory-dependence responsible for some failures

-- Resonantly driven dynamics (another exact cond, not discussed here, is violated)
-- Charge-transfer dynamics out of the ground-state
-- Lack of relaxation/dissipation in extended systems

❖ Generically, dynamical steps and peaks appear in v_c that require non-adiabatic density-dependence

-- impact on ensuing dynamics can be large, but not always

❖ Approximations giving good response can give bad non-perturbative dynamics

-- probing the functional in a very different domain.

❖ With a judicious choice of Φ_0 the adiabatic approx can better approximate v_{xc}

❖ But the adiabatic approximation has provided useful results and interpretation in many applications, especially for integrated observables…and two-electrons may be the worst case… a better understanding of non-adiabatic effects is still needed