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

We will next look at some systems where we can find the exact time-dependent exchange-correlation potential, and compare with the adiabatic approximation.

To do this, we find a system where 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?

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

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

into TDKS

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

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

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

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", $u_i = j_i/n_i$

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

- 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

$n_i(x,t)$ → ½ $n(x,t)$, the exact density, and $u_i(x,t)$ → $j(x,t)/n(x,t)$, 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

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

TD exchange-correlation hole

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

An example of history dependence

Weak on-resonant driving of 1D He atom:

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

$A = 0.00667$ au
$\omega = 0.533$ au (1st excn.)
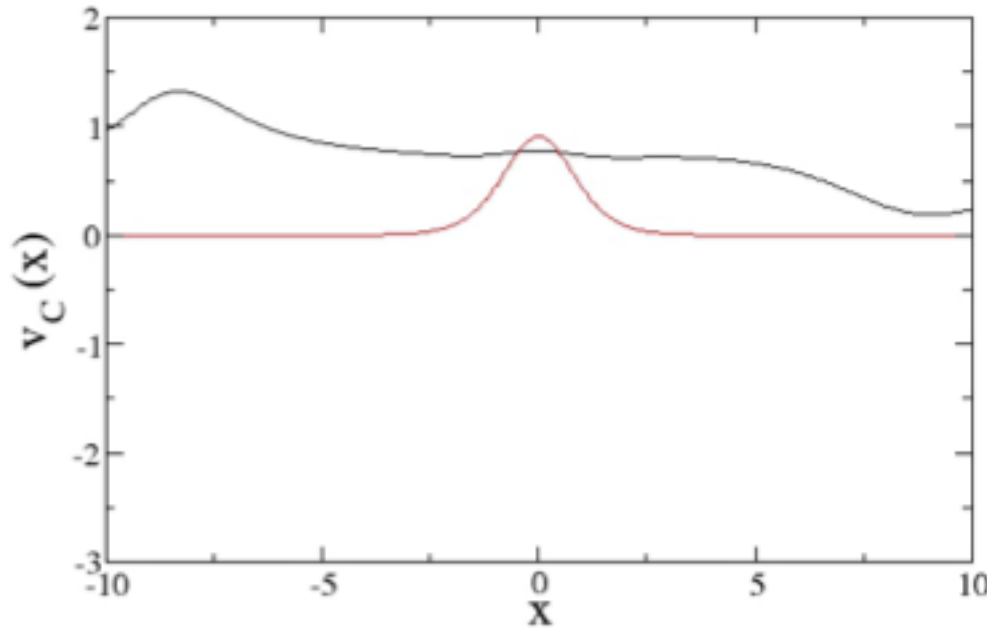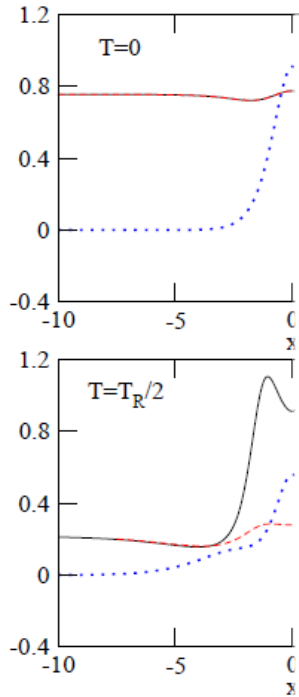
density
Vc

- 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.
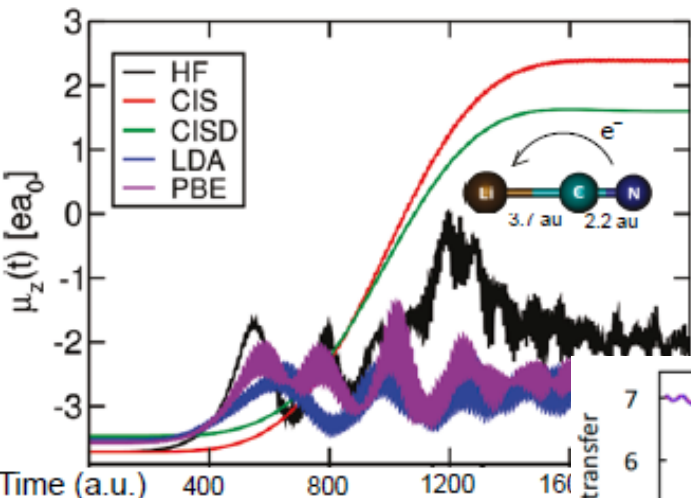Elliott, Fuks, Rubio, Maitra, *PRL **109**, 266404 (2012)*
Ramsden, Godby, *PRL **109**, 036402 (2012)*
….

- What is the impact on dynamics?? Propagate with adiabatically-exact approximation to compare…
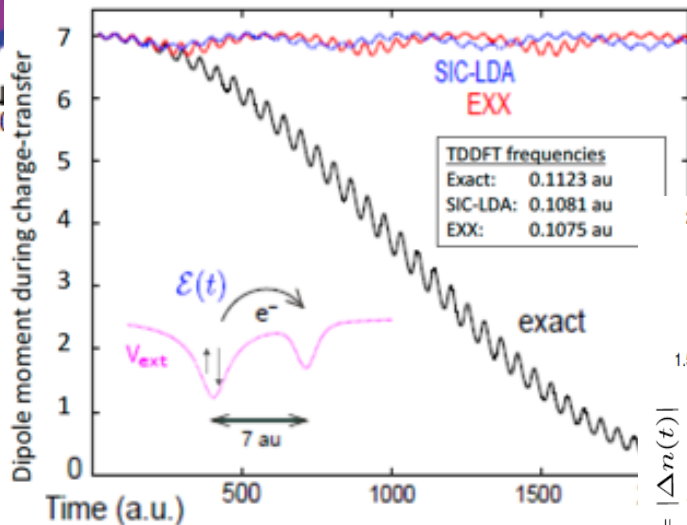
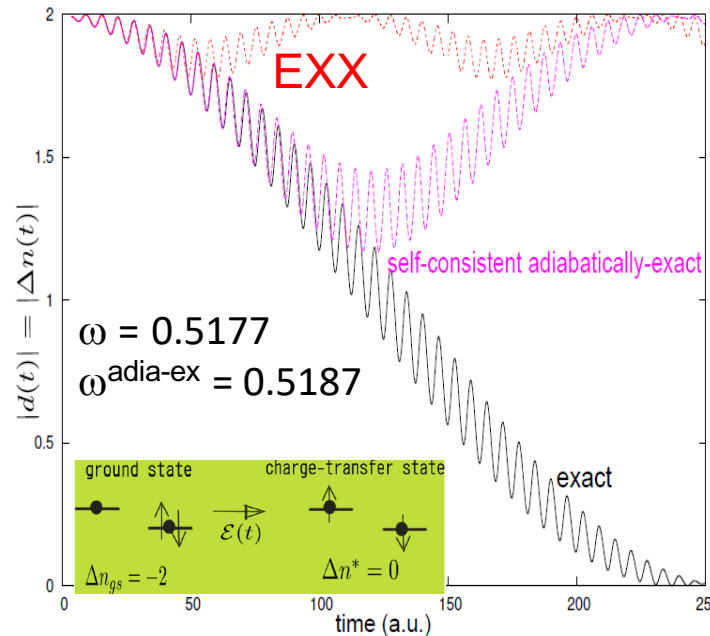# Example: Charge-transfer dynamics out of the ground-state

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)

ω = 0.5177
$\omega^{adia-ex}$ = 0.5187

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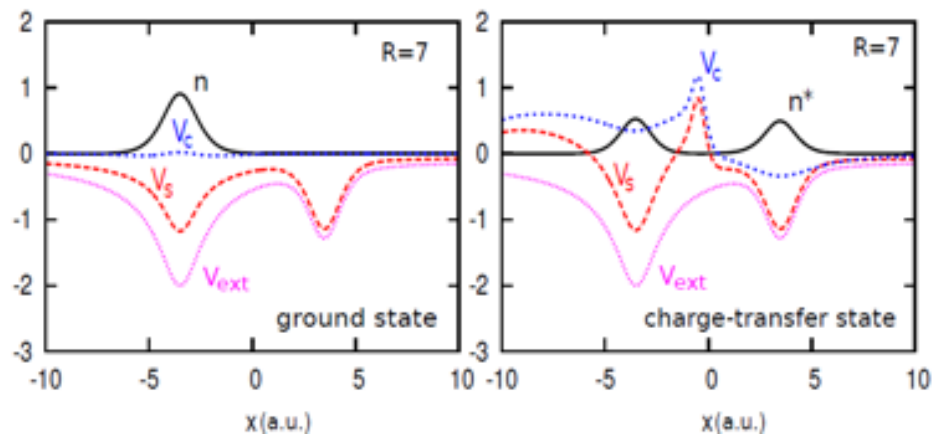
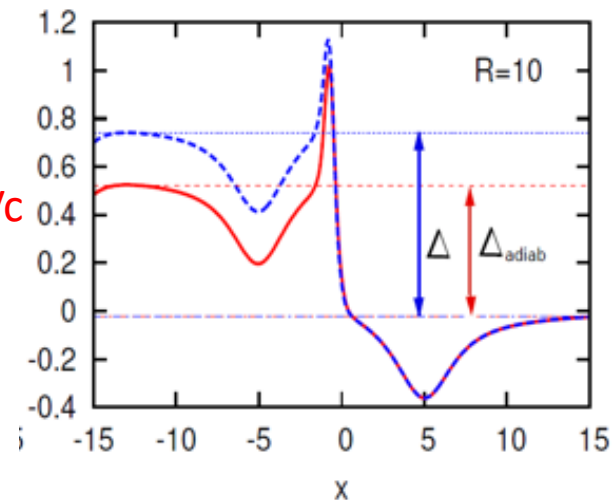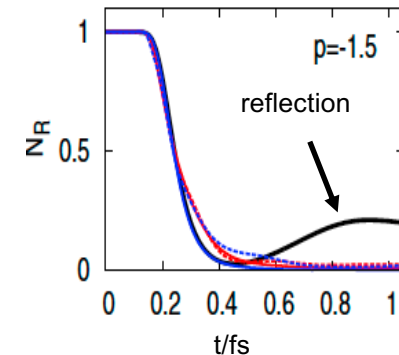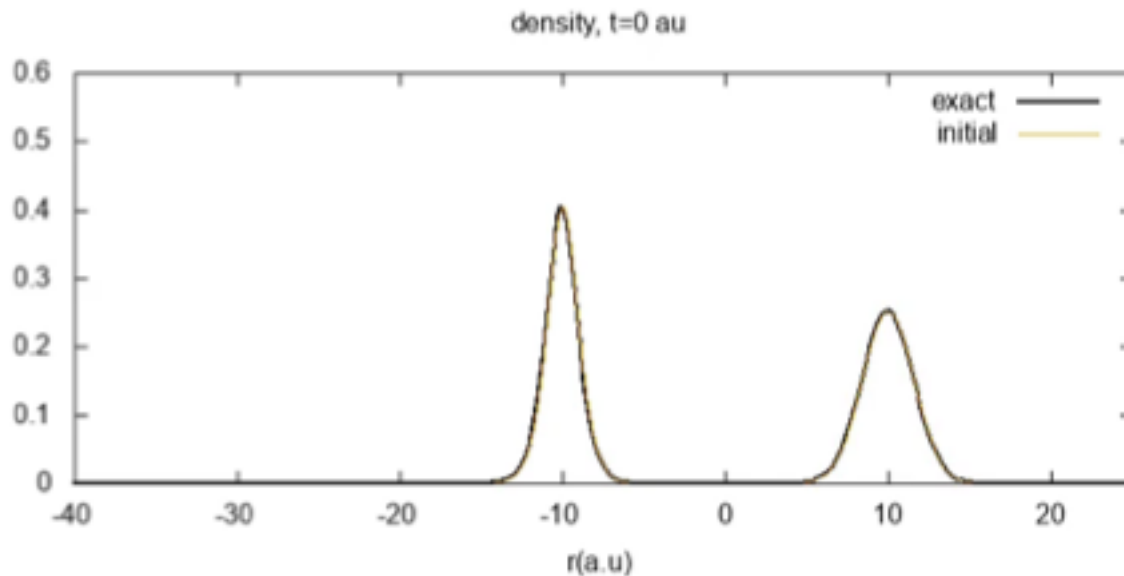Correlation potential in the final CT state, as R→ ∞

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

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

Vc

adia-exact Vc

A final example: Time-Resolved e-H

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)
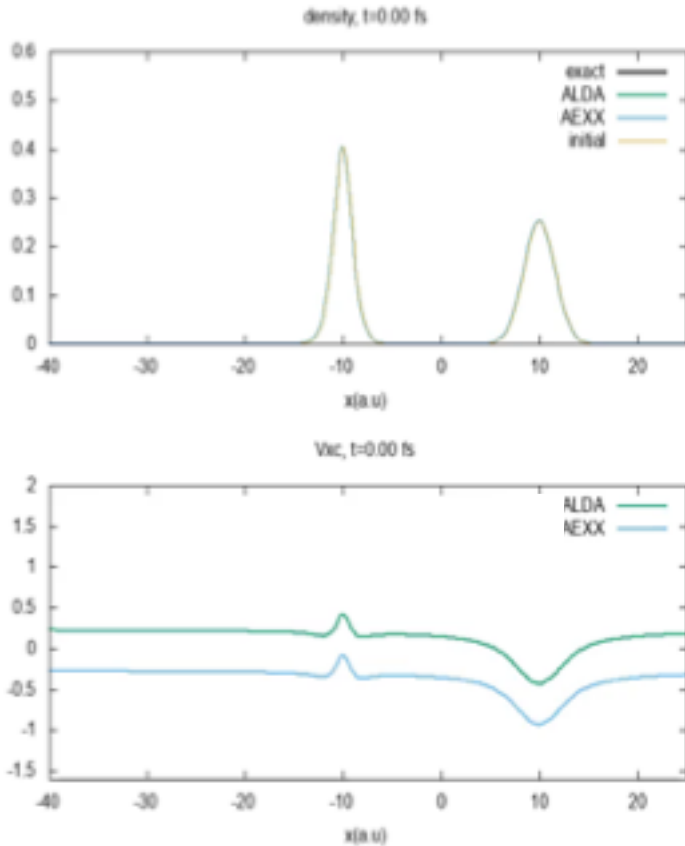(2) Two-orbital state: one for the electron in the atom, one for the incoming

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) (Hardy Gross special issue)

Time-Resolved e-H scattering

Choice (1) Slater determinant

Choice (2) Two-orbital

❖ 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!

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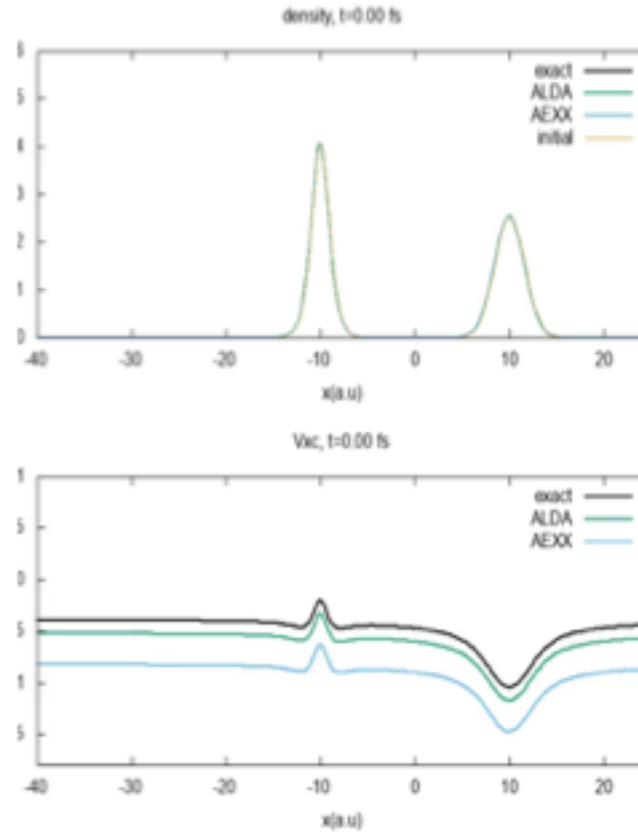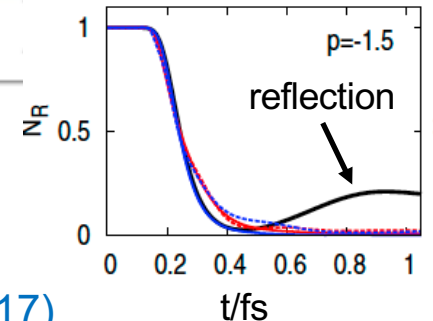L. Lacombe, Y. Suzuki, K. Watanabe, N. T. Maitra, Eur. Phys. J. B. **91,** 96 (2018) (Hardy Gross special issue)

Short summary: memory in non-perturbative dynamics

❖ Neglect of memory-dependence responsible for failures
  -- Resonantly driven dynamics (I didn't discuss here, another exact cond violated)
  -- (Pump/probe spectroscopy)
  -- Charge-transfer dynamics out of the ground-state

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

❖ Approximations giving good response can give bad non-perturbative dynamics
  -- probing the functional in a very different domain.

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

• But the adiabatic approximation has provided useful results and interpretation in many applications -- two-electrons is probably worst case...
  -- a better understanding of these non-adiabatic effects is still needed