Nonperturbative quantum dynamics

I. Laser interactions with atoms/molecules

II. Model systems and TDDFT

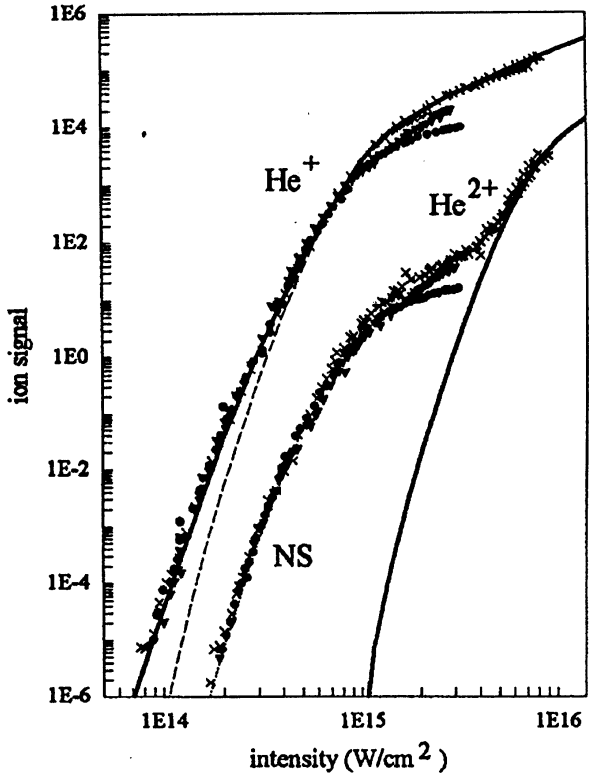
Manfred Lein, TDDFT school Benasque 2014

Outline

Model systems and TDDFT

- Double ionization of Helium
- Relevance of the derivative discontinuity
- Adiabatic approximations

Nonsequential double ionization of Helium



Walker et al., PRL **73**, 1227 (1994)

Experimental observations:

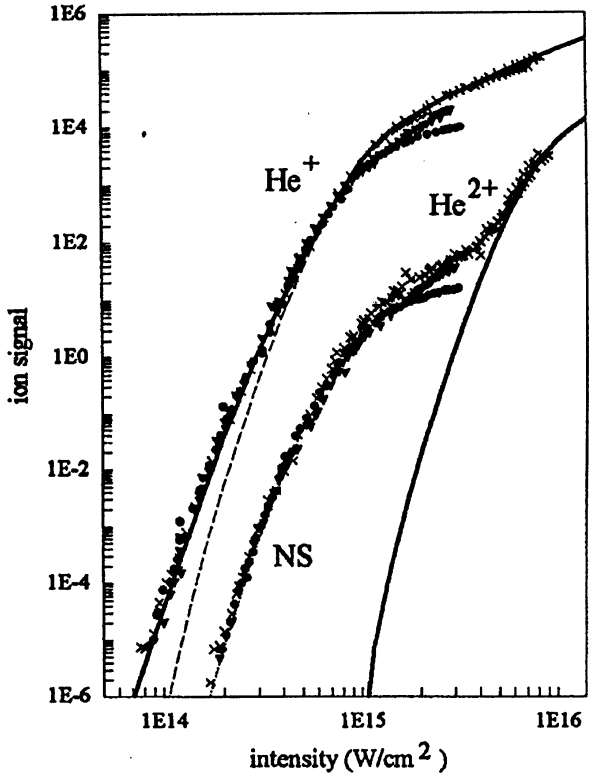
- double ionization orders of magnitude larger than expected from sequential ionization

  "sequential" ionization probability means:

  $p_{\mathrm{seq}} = p(\mathrm{He} \to \mathrm{He}^{+})\; p(\mathrm{He}^{+} \to \mathrm{He}^{++})$

- He^{2+} knee at He^{+} saturation intensity

Nonsequential double ionization of Helium



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- He^{2+} knee at He^{+} saturation intensity

Theory: Knee is reproduced by

- exact solution of the two-body TDSE
- S-matrix theory (Becker and Faisal)
- **TDDFT with derivative discontinuity**

Time-dependent density functional theory

- **Runge-Gross theorem:**

The density $n(\mathbf{r},t)$ determines the external potential uniquely (up to a time dependent constant).

- **Time-dependent Kohn-Sham (KS) scheme:**

Ficticious system of non-interacting particles described by orbitals φ_k

$$n(\mathbf{r},t) = \sum_{k=1}^{N} |\varphi_k(\mathbf{r},t)|^2$$
$$i\frac{\partial}{\partial t}\varphi_k(\mathbf{r},t) = \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\mathbf{r},t)\right)\varphi_k(\mathbf{r},t)$$
$$v_{\mathrm{KS}}[n]\mathbf{r}(,t) = v_{\mathrm{ext}}(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{xc}}[n](\mathbf{r},t)$$

- **Physical observables** are calculated as functionals of the density.

TDDFT for two electrons

For Helium (two electrons in a singlet state), there is only one KS orbital

$$\varphi_\uparrow(\mathbf{r},t) = \varphi_\downarrow(\mathbf{r},t) = \varphi(\mathbf{r},t)$$

and

$$n(\mathbf{r},t) = 2|\varphi(\mathbf{r},t)|^2.$$

The exact exchange potential is

$$v_{\rm x}(\mathbf{r},t) = -\tfrac{1}{2} v_{\rm H}(\mathbf{r},t),$$

and furthermore

x-only TDDFT = TD Hartree-Fock.

Conventional TDDFT for He double ionization

- Simple expressions for the xc potential: adiabatic LDA, LDA-SIC, TDKLI, ...

- Mean-field approach for ionization probabilities:
  Assume $\Psi(\mathbf{r_1}, \mathbf{r_2}, t) \approx$ Kohn-Sham state

$$\Rightarrow p(\mathrm{He}) = \left(\int_A d^3r |\varphi(\mathbf{r}, t)|^2\right)^2, \qquad p(\mathrm{He}^{++}) = \left(1 - \int_A d^3r |\varphi(\mathbf{r}, t)|^2\right)^2$$

$\rightarrow$ No success to reproduce the knee
Underestimation of single ionization

Conventional TDDFT for He double ionization

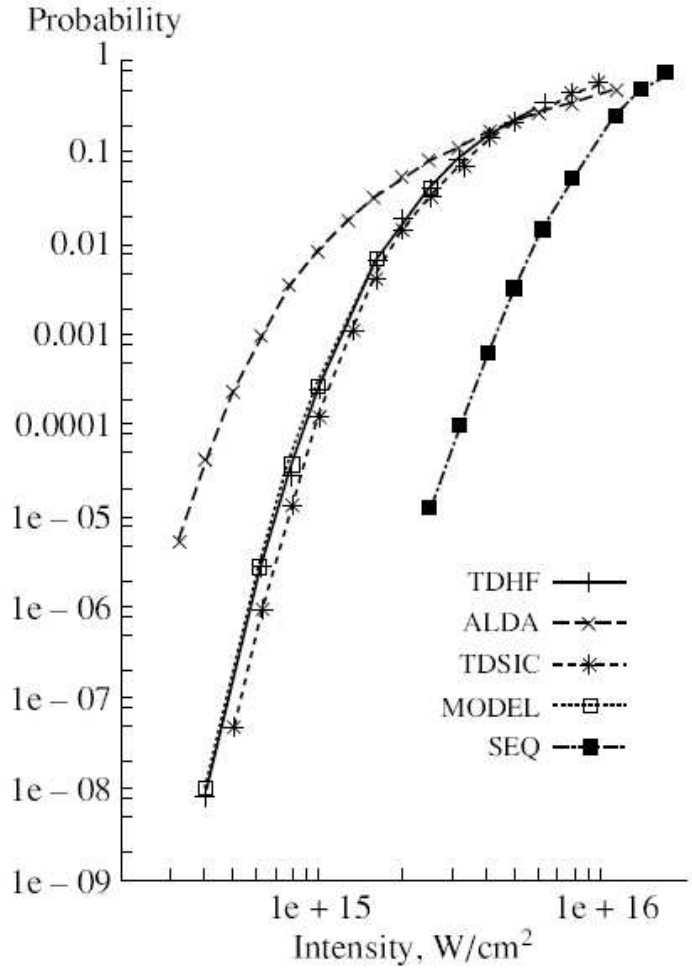


Fig. 2. Calculated double-ionization probabilities from the ground state of the Helium atom irradiated by a 6-cycle (16 fs), 780-nm laser pulse, using equation (14) and for different exchange-correlation potentials (see text).

Petersilka and Gross, Laser Phys. **9**, 105 (1999)

A one-dimensional two-electron model atom

Two electrons along a line parallel to the laser polarization axis:

$$H(t) = -\tfrac{1}{2}\frac{\partial^2}{\partial z_1^2} - \tfrac{1}{2}\frac{\partial^2}{\partial z_2^2} - \frac{2}{\sqrt{z_1^2+1}} - \frac{2}{\sqrt{z_2^2+1}} + \frac{1}{\sqrt{(z_1-z_2)^2+1}} + E(t)(z_1+z_2)$$

[Grobe and Eberly, PRA **48**, 4664 (1993)]

All particle-particle interactions are soft-core potentials with Coulomb tail (gives Rydberg series).

The TDSE can be solved numerically exactly, so the model is useful to obtain

- qualitative insight into ionization mechanisms,
- exact results for comparison with DFT approaches.

Calculation of ionization probabilities

Box integration: consider electron as free when it is farther from the nucleus than some given distance, e.g. $a = 5$ a.u.:

$$p(\mathrm{He}) = \int_{-a}^{a} dz_1 \int_{-a}^{a} dz_2 |\ \Psi(z_1, z_2)|^2$$

$$p(\mathrm{He}^{+}) = 2 \int_{-a}^{a} dz_1 \int_{|z_2|>a} dz_2\ |\Psi(z_1, z_2)|^2$$

$$p(\mathrm{He}^{++}) = \int_{|z_1|>a} dz_1 \int_{|z_2|>a} dz_2 |\ \Psi(z_1, z_2)|^2$$

Only approximate, but useful for comparison with DFT results.

Origin of the knee structure

Both the exact 1D He simulation as well as using the **exact densities** in the mean-field functional for ionization probabilities reproduces a knee:

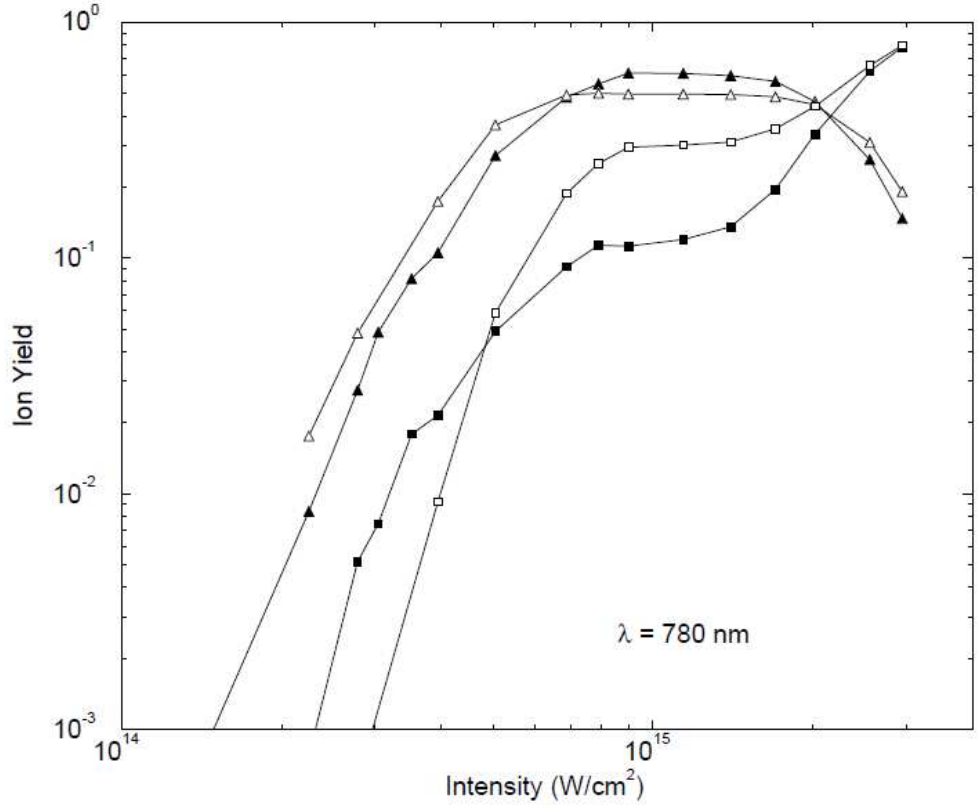


Figure 2. Single- and double-ionization yields of He from the fully correlated exact model (full triangles and squares), and the estimate based on equations (8) and (9) in the text with the same 'exact' electron densities (open triangles and squares).

Lappas and v. Leeuwen, J. Phys. B **31**, L249 (1998)

Calculation of exact xc potential

- One-dimensional model system
  $H(t) = -\frac{1}{2}\frac{\partial^2}{\partial z_1^2} - \frac{1}{2}\frac{\partial^2}{\partial z_2^2} - \frac{2}{\sqrt{z_1^2+1}} - \frac{2}{\sqrt{z_2^2+1}} + \frac{1}{\sqrt{(z_1-z_2)^2+1}} + E(t)(z_1+z_2)$

- Solve time-dependent Schrödinger equation and calculate exact time-dependent density $n(z,t)$ and current $j(z,t)$

- Calculate exact KS orbital $\varphi(z,t) = \sqrt{n(z,t)/2}\,\exp\left(i\alpha(z,t)\right)$ with phase α from current density $j = \frac{1}{i}(\varphi^*\partial_z\varphi - c.c.) = n\partial_z\alpha$

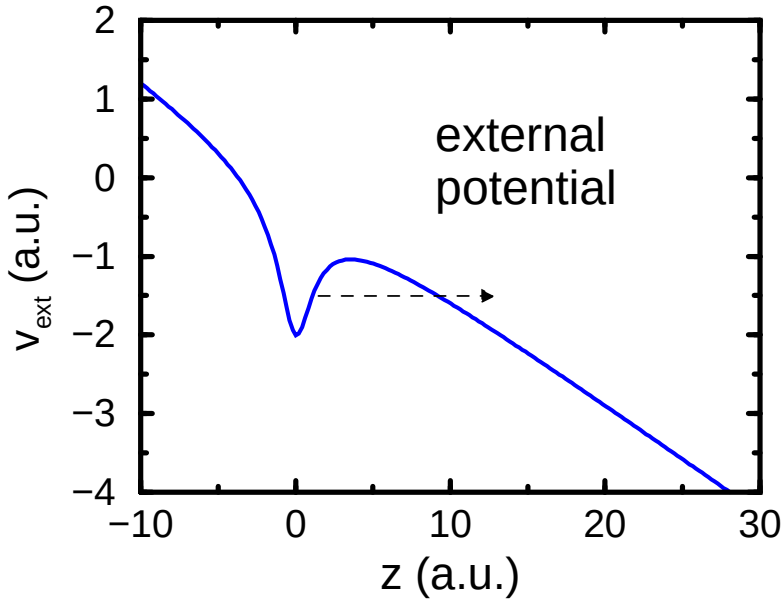
- Calculate "exact" KS potential by inversion of the split-operator propagator: $\varphi(z,t+\delta t) = e^{-iT_\mathrm{s}\delta t}e^{-2iv_\mathrm{KS}\delta t}e^{-iT_\mathrm{s}\delta t}\varphi(z,t-\delta t)$

  $\rightarrow$ $\boxed{v_\mathrm{KS}(z,t) = -\frac{\hbar}{2\delta t}\arcsin\Im\frac{e^{+iT_\mathrm{s}\delta t/\hbar}\varphi(z,t+\delta t)}{e^{-iT_\mathrm{s}\delta t/\hbar}\varphi(z,t-\delta t)} + \mathrm{const}}$

Exact xc potential for a model system

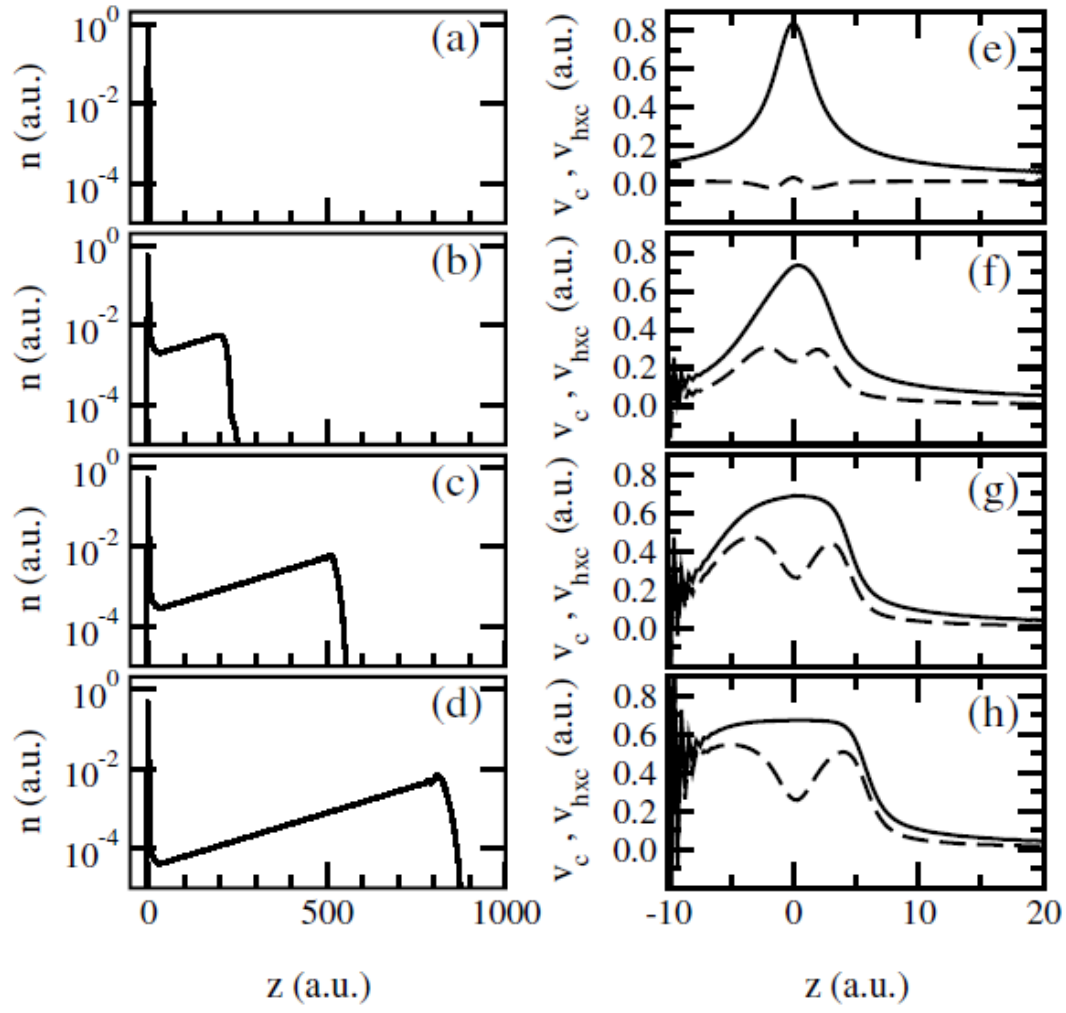
To avoid numerical difficulties: choose (ramped up) static field

$$E = 0.14 \text{ a.u.}$$



Exact xc potential for a model system

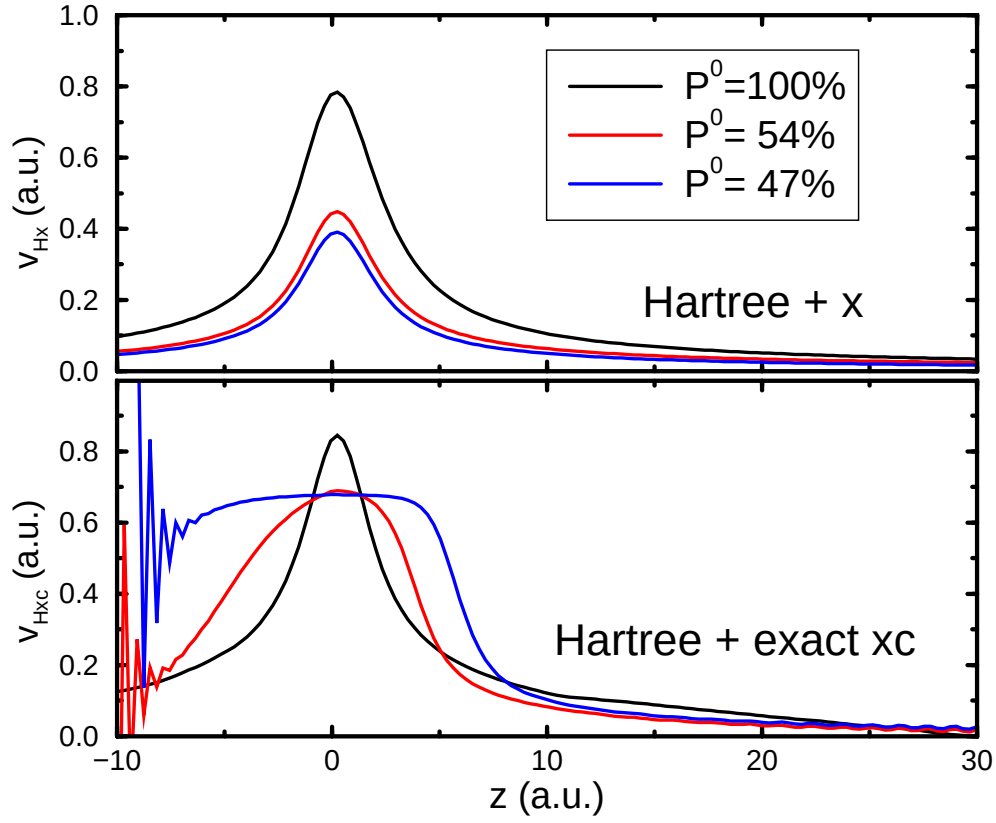
Densities/potentials at different times ($t=0$, $t=108$au, $t=215$au, $t=323$au)



M.L., S. Kümmel, PRL **94**, 143003 (2005)

Exact xc potential for a model system

Comparison of TD Hartree-Fock and exact potentials



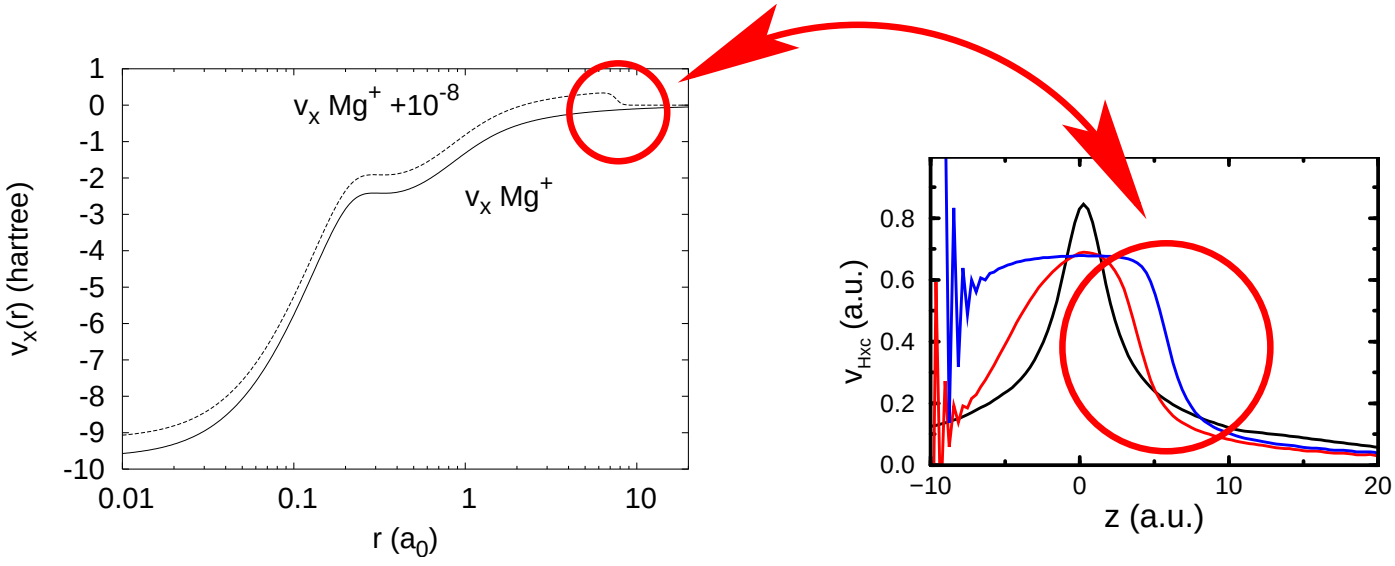
M.L., S. Kümmel, PRL **94**, 143003 (2005)

→ x-only DFT gives

- good description of initial state
- wrong time-evolution

Exact xc potential for a model system

Relation to derivative discontinuities in static DFT



Static DFT with fractional occupation

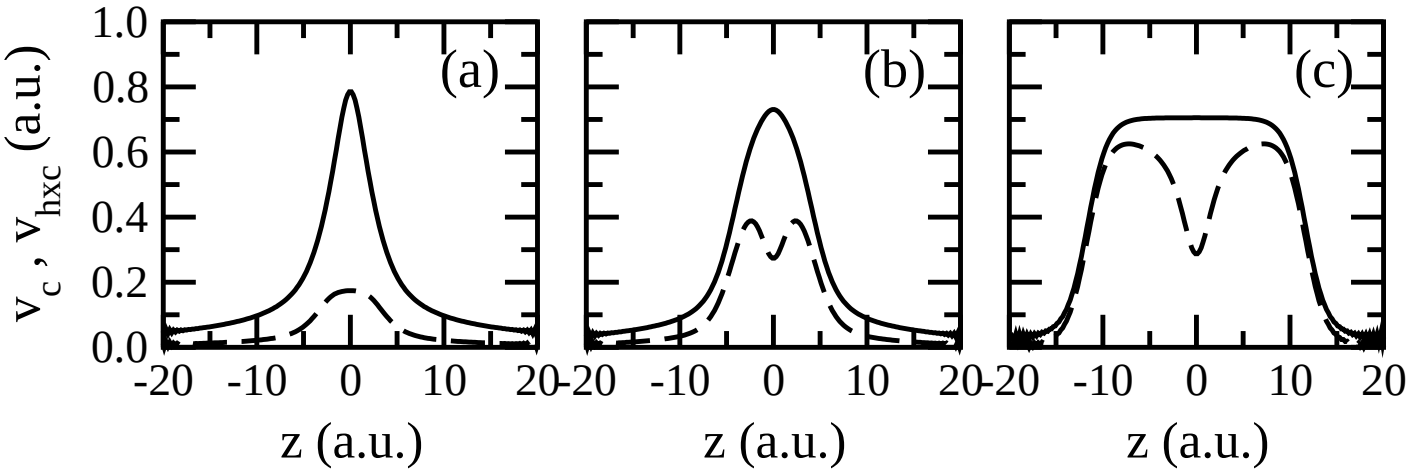
Time−dependent DFT

Exact xc potential for a model system

Exact static potentials for various fractional particle numbers

$$N = 1 + \epsilon,$$

using the ground-state density $n(z) = (1-\epsilon)n_1(z) + \epsilon\, n_2(z)$



(a) N=1.5 (b) N=1.1 (c) N=1.0001

solid: v_{Hxc},
dashed: v_{c}

Derivative discontinuity

Fractional particle numbers in static DFT:

xc potential jumps by $\Delta_{\rm xc}$ when the particle number passes through an integer.

Interpretation of time-dependent results:

In ionization a small fraction of an electron is ejected; if the process is adiabatic, a ground-state with fractional number of bound electrons is left.

Difficulty: the discontinuity around $N = 1$ is not in the exchange but in the correlation potential.

Derivative discontinuity

Suitable quantity for comparison of DFT and exact calculations:

the number of bound electrons $N_{\mathrm{bound}} = \int_V n(\mathbf{r})\, d^3r$ with an appropriate region V around the nucleus.

Advantage compared to ionization probabilities: no problems with expressing the functional.

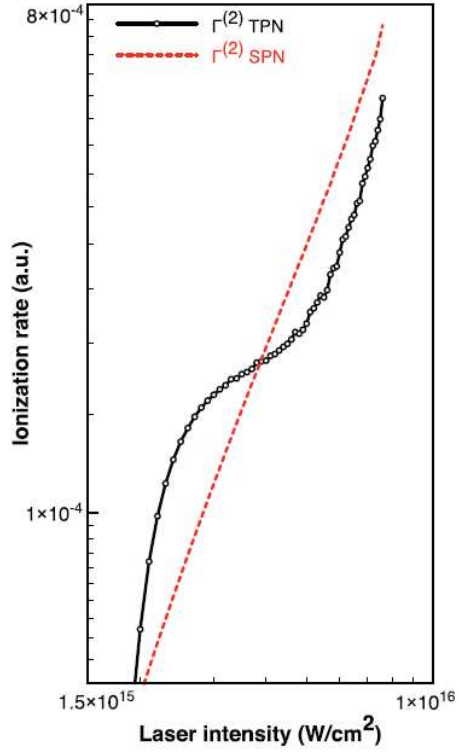
3D TDDFT calculations with derivative discontinuity

TDDFT using LDA-SIC-KLI

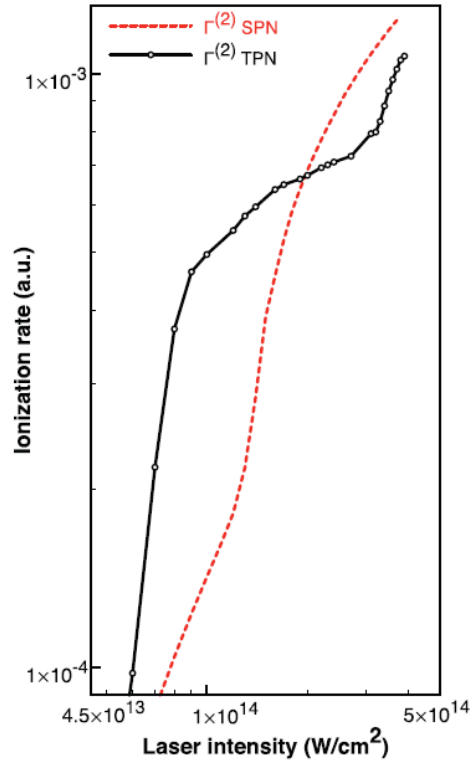
- usual form: discontinuity only at integer spin-particle number (SPN)
- modification: discontinuity at total particle number (TPN) by "reassigning" spin

Results:

He double ionization



Be double ionization



Heslar et al., PRA 87, 052513 (2013)

N-Adiabatic approximation

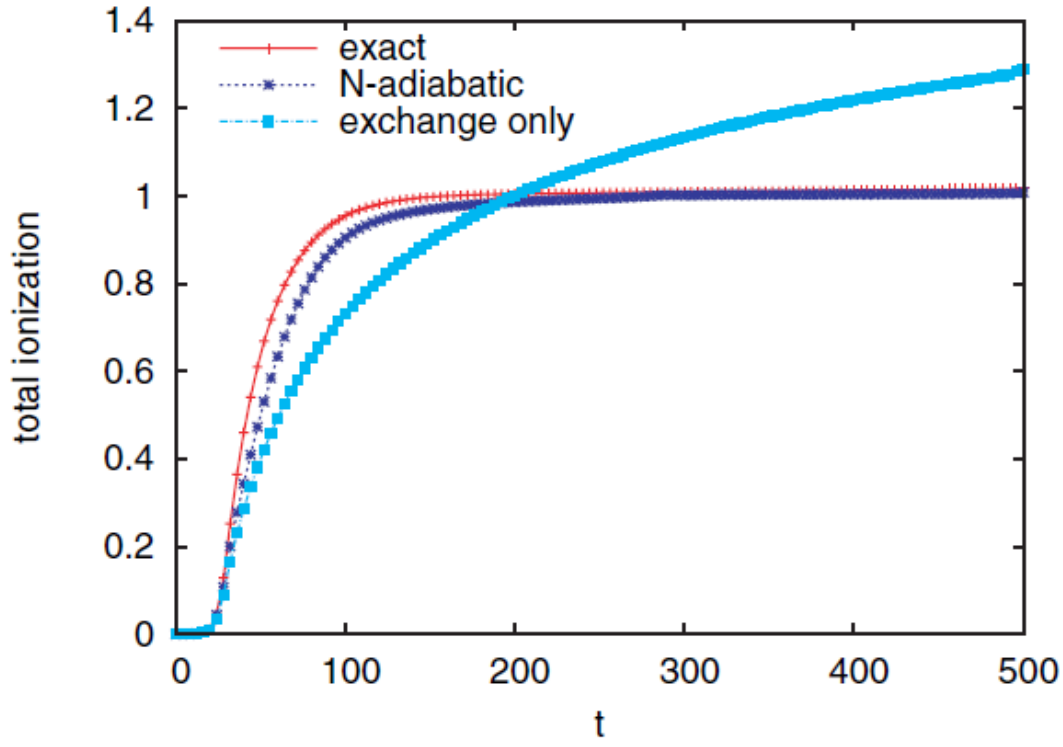
Goal: avoid suddenly switching potential shape at integer particle number

TDKS scheme with the following additions:

- Determine at every time the (fractional) number $N_{\mathrm{bound}} = N - 1 + \epsilon$ of bound electrons.
- Construct ground-state density for this fractional particle number: $\boxed{n_0(\mathbf{r}) = [1-\epsilon(t)]\, n_{0,N-1}(\mathbf{r}) + \epsilon(t)\, n_{0,N}(\mathbf{r})}$.
- Determine exact static KS potential for this ground-state density.
- Use correlation part of the static KS potential in the TDKS scheme.

N-Adiabatic approximation

Good results for “total ionization” = number of lost electrons:



A. de Wijn, M.L., S. Kümmel, Europhys. Lett. 84, 43001 (2008)

Exact adiabatic potential

- For given density n, construct the external potential $v_{\rm ext}^{\rm adia}$ that yields n as ground state density of an interacting system.

  (Use an iterative scheme based on repeated solution of the static many-body Schrödinger equation)

- Construct the potential $v_{\rm KS}^{\rm adia}$ that yields n as ground state densitites of a noninteracting system.

  For two electrons: $v_{\rm KS}^0(z) = \frac{1}{2\phi(z)} \frac{d^2\phi(z)}{dz^2} + \text{const}$ with $\phi(z) = \sqrt{n(z)/2}$

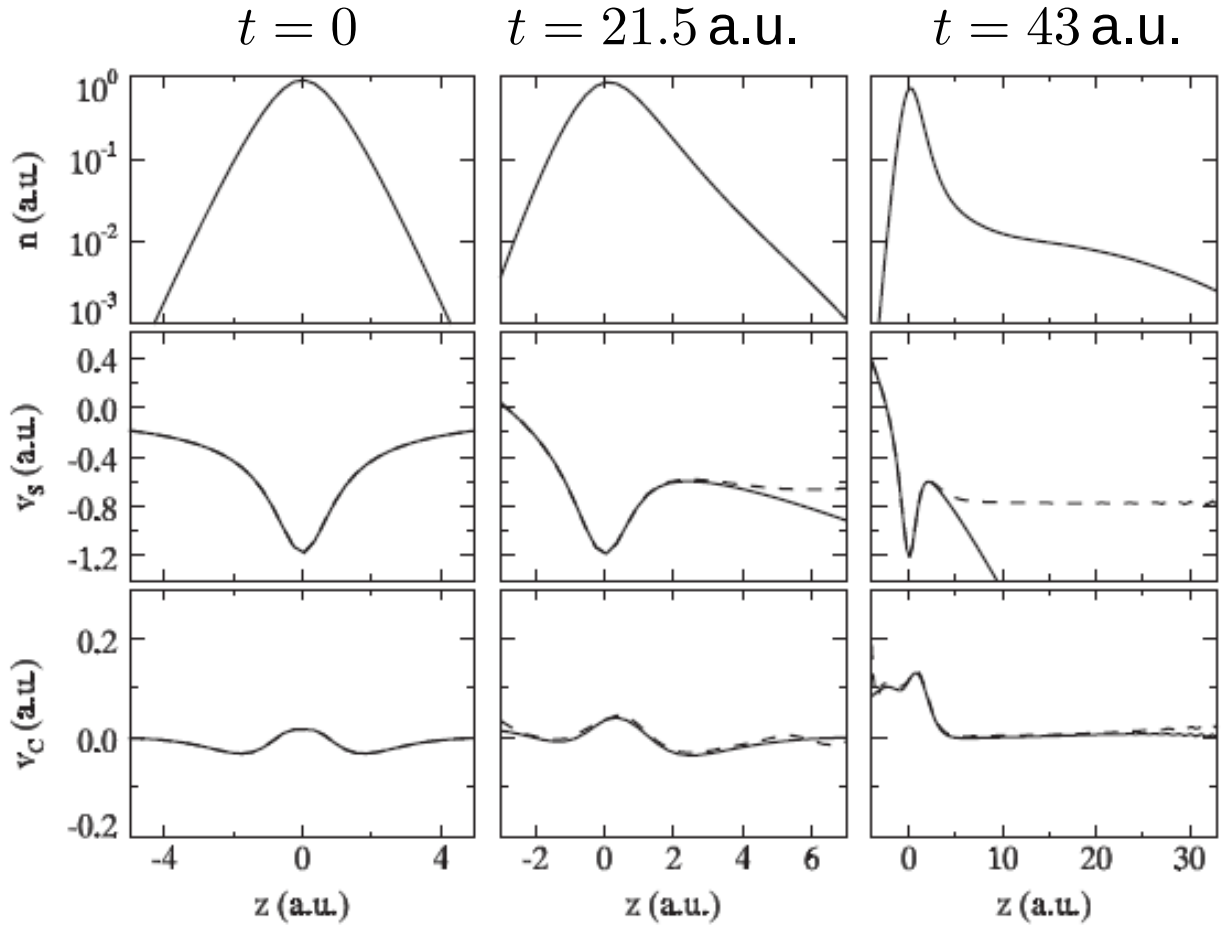
- Obtain adiabatic exchange correlation potential as

$$v_{\rm xc}^{\rm adia} = v_{\rm KS}^{\rm adia} - v_{\rm ext}^{\rm adia} - v_{\rm H}.$$

Exact adiabatic potential

Excellent agreement with exact xc potential

(calculation for 1D He in a ramped up static field):



M. Thiele, E.K.U. Gross, S. Kümmel, Phys. Rev. Lett. **100**, 153004 (2008)

Exact adiabatic potential in a TDKS calculation

1D He in a 780 nm field: **results undistinguishable from exact results**

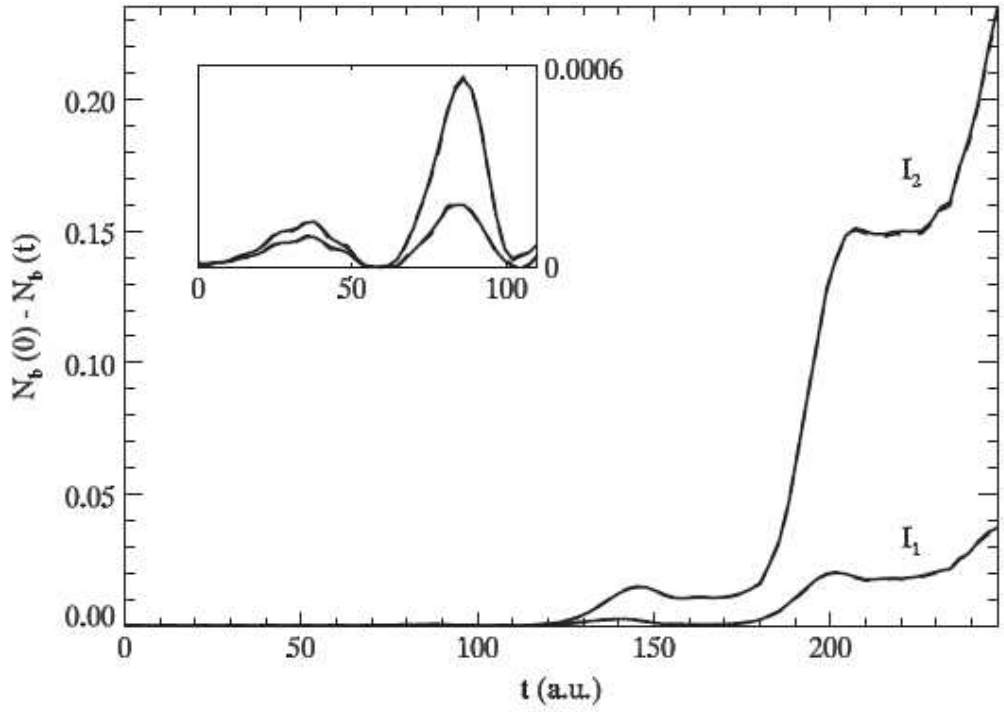


FIG. 3. Total ionization during the interaction of the two-electron atom with a laser pulse of maximum intensity $I_1 = 4 \times 10^{14}$ W/cm^2 (lower two curves) and $I_2 = 7 \times 10^{14}$ W/cm^2 (upper two curves). Solid curves: exact TDSE calculation; dashed curves: adiabatically exact TDKS scheme. The inset shows a magnification of the first part of the curve.

M. Thiele, E.K.U. Gross, S. Kümmel, Phys. Rev. Lett. **100**, 153004 (2008)

Adiabatic approximation based on ground-state spin DFT

Thiele et al. have used the exact adiabatic potential in a time-dependent KS calculation $\rightarrow$ computationally very demanding

Alternative: solve ground-state problem for $n \rightarrow v$ mapping with an approximate method, which nevertheless mimics static correlation

$\rightarrow$ Ground-state spin DFT

Still use $v_{\rm xc}^{\rm adia} = v_{\rm KS}^{\rm adia} - v_{\rm ext}^{\rm adia} - v_{\rm H}$ but now with $v_{\rm ext}^{\rm adia}$ chosen such that it reproduces then given density n within ground-state spin DFT:

$$-\frac{1}{2}\frac{d^2\phi_\sigma(z)}{dz^2} + v_{{\rm KS},\sigma}[n_\uparrow, n_\downarrow](z)\phi_\sigma(z) = \epsilon_\sigma\,\phi_\sigma(z)$$

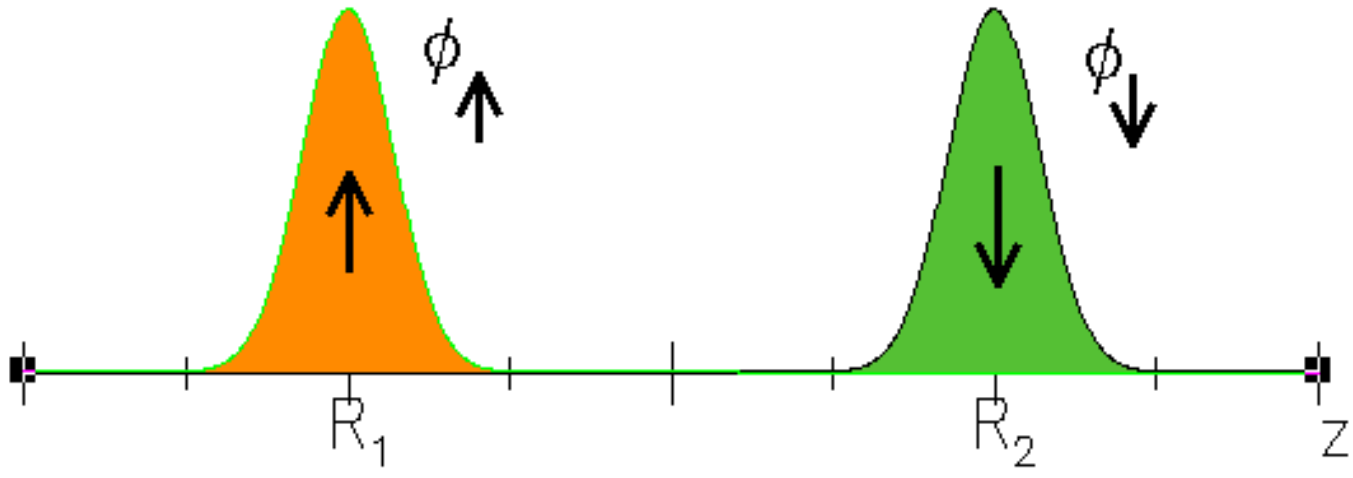
$$v_{{\rm KS},\sigma}[n_\uparrow, n_\downarrow](z) = v_{\rm ext}^{\rm adia} + v_{{\rm hx},\sigma}[n_\uparrow, n_\downarrow](z) + v_{{\rm c},\sigma}(z)$$

$$v_{{\rm hx},\uparrow}(z) = \int dz'\, n_\downarrow(z')w(z-z'), \quad v_{{\rm hx},\downarrow}(z) = \int dz'\, n_\uparrow(z')w(z-z')$$

Spin-symmetry breaking in spin DFT

Molecule at large internuclear distance R beyond a critical distance:

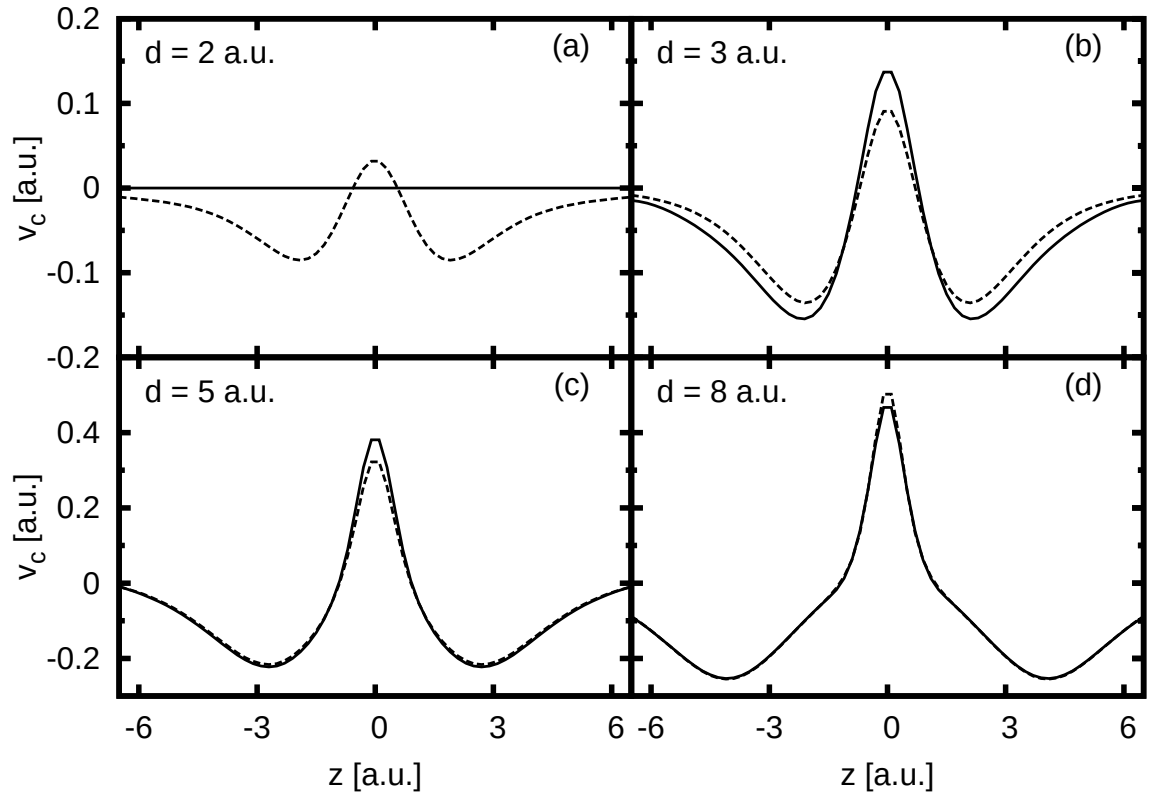
"spontaneous" localization of the spin densities



Results for 1D H_2

Input density: exact density for $v_{\rm ext}(z) = \frac{-1}{\sqrt{(z-R_1)^2+1}} + \frac{-1}{\sqrt{(z-R_2)^2+1}}$.

$\rightarrow$ Good agreement with exact correlation potential (dashed), especially above critical distance for spin-symmetry breaking:

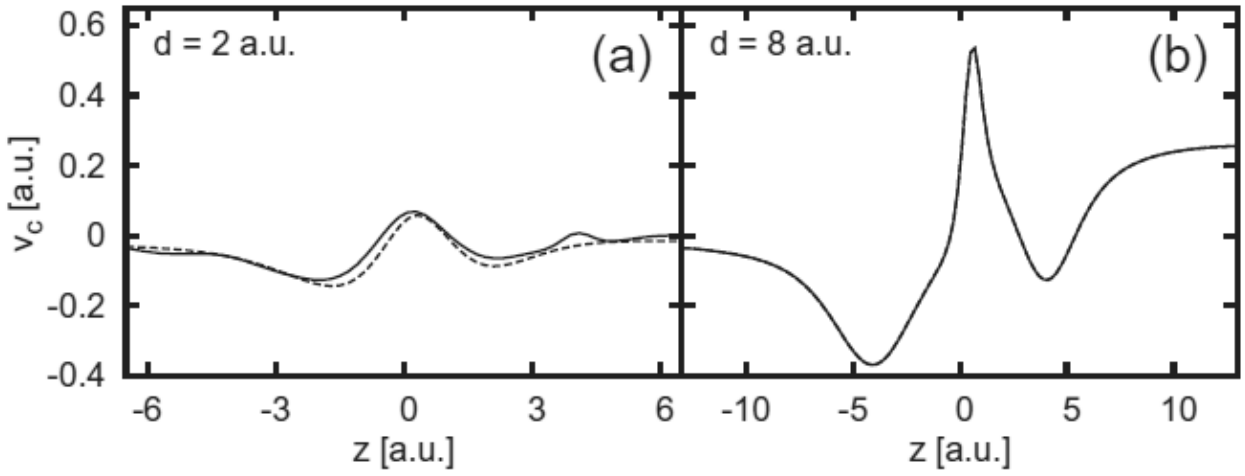


I. Dreissigacker and M.L., Chem. Phys. **391**, 143 (2011)

Results for 1D LiH

Input density: exact density for $v_{\rm ext}(z) = \frac{-1}{\sqrt{(z-R_1)^2+0.7}} + \frac{-1}{\sqrt{(z-R_2)^2+2.25}}$.

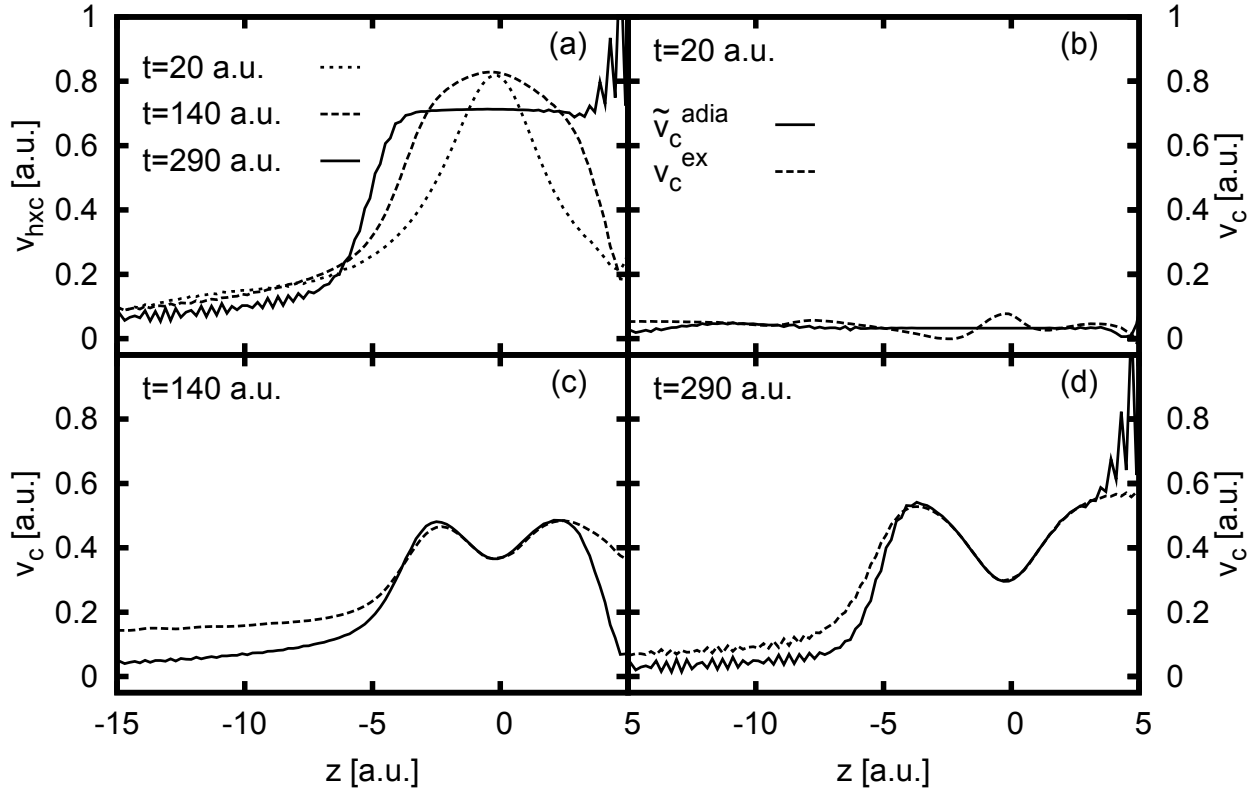
Reproduces step and peak of the exact correlation potential (dashed):



I. Dreissigacker and M.L., Chem. Phys. **391**, 143 (2011)

Results for 1D He in ramped-up static field

Good agreement with the exact potential (dashed):

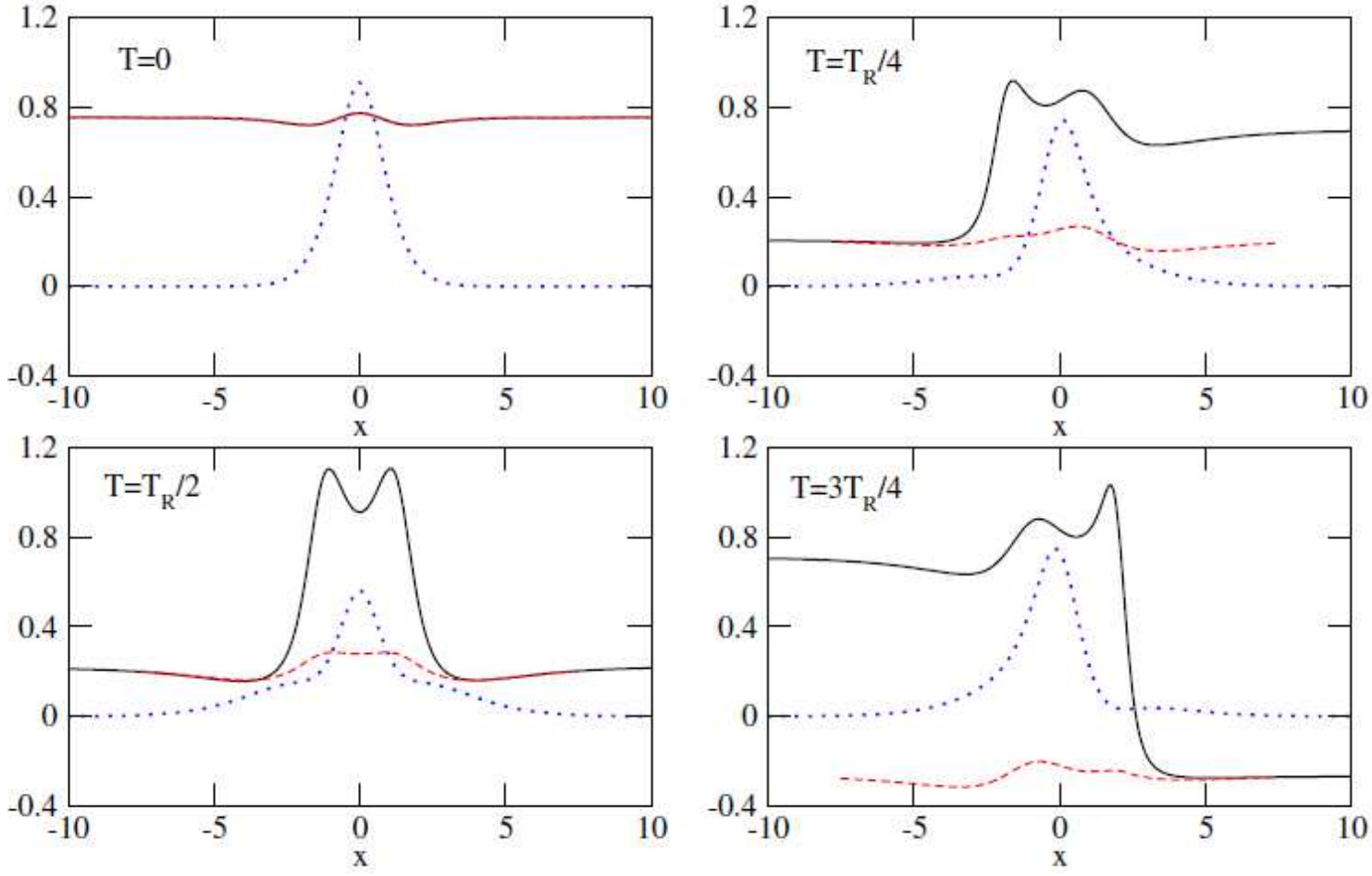


I. Dreissigacker and M.L., Chem. Phys. **391**, 143 (2011)

Failures of adiabatic correlation potential

Example: Rabi cycling between ground and excited state in 1D He

Comparison of exact (black) and adiabatic (red) potentials:



Elliot et al., PRL 109, 266404 (2012)

Conclusions

- Derivative discontinuity plays a key role in ionization processes.
- Nonlocal adiabatic approximations are a promising tool for ionization processes in realistic laser fields.
- Adiabatic correlation fails when excited bound states are strongly populated.
- Spin DFT can mimic static correlation.