
Models for Time-Dependent Phenomena

- I. Phenomena in laser-matter interaction: atoms*
- II. Phenomena in laser-matter interaction: molecules*
- III. Model systems and TDDFT*

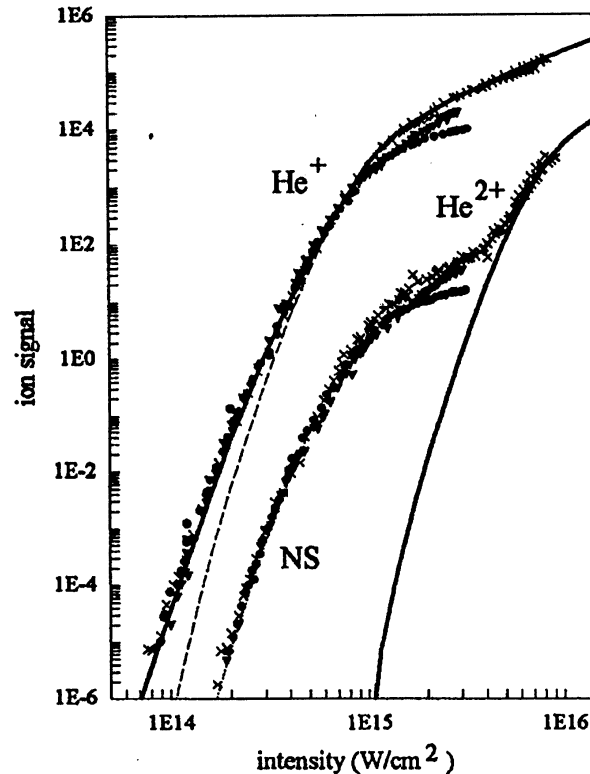
Manfred Lein



Model systems and TDDFT

- Double ionization of Helium
- Adiabatic approximations
- Multicomponent TDDFT
- The dissociation problem revisited
- Numerical issues

Nonsequential double ionization of Helium



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

Experimental observations:

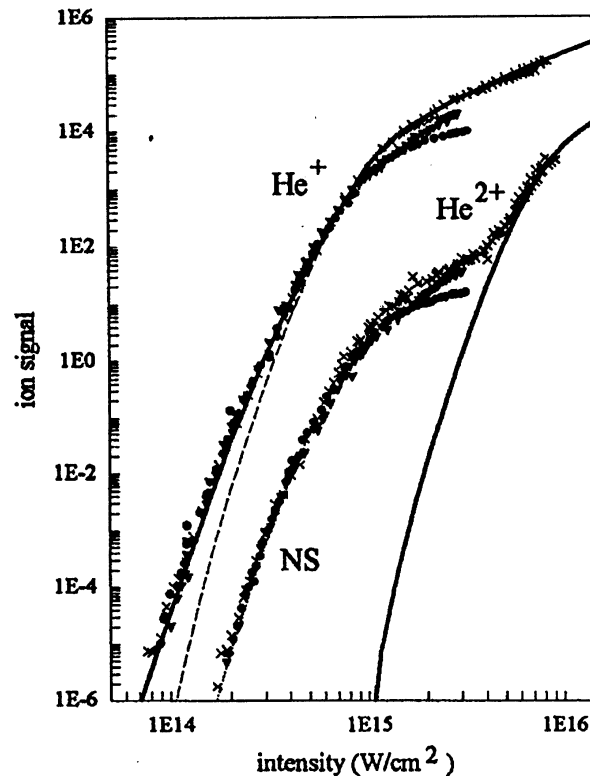
- double ionization orders of magnitude larger than expected from sequential ionization

“sequential” ionization probability means:

$$p_{\text{seq}} = p(\text{He} \rightarrow \text{He}^+) p(\text{He}^+ \rightarrow \text{He}^{++})$$

- He²⁺ knee at He⁺ saturation intensity

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

Experimental observations:

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

“sequential” ionization probability means:

$$p_{\text{seq}} = p(\text{He} \rightarrow \text{He}^+) p(\text{He}^+ \rightarrow \text{He}^{2+})$$

- He²⁺ knee at He⁺ saturation intensity

Theory: Knee is only reproduced by

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

A one-dimensional two-electron model atom

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

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

[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.:

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

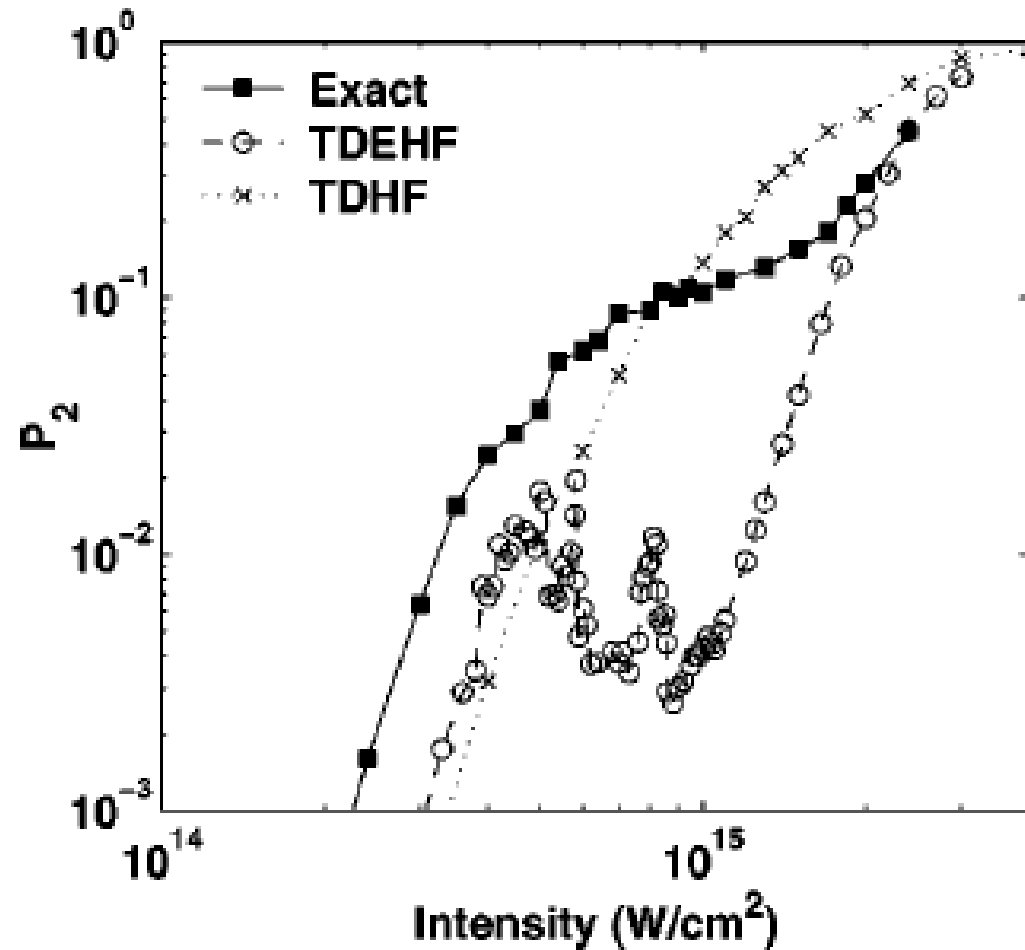
$$p(\text{He}^+) = 2 \int_{-a}^a dz_1 \int_{|z_2|>a} dz_2 |\Psi(z_1, z_2)|^2$$

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

Only approximate, but useful for comparison with DFT results.

Calculation of ionization probability

1D Model yields knee structure for double ionization.



[Dahlen and van Leeuwen, PRA **64**, 023405 (2001)]

Mechanism of nonsequential double ionization

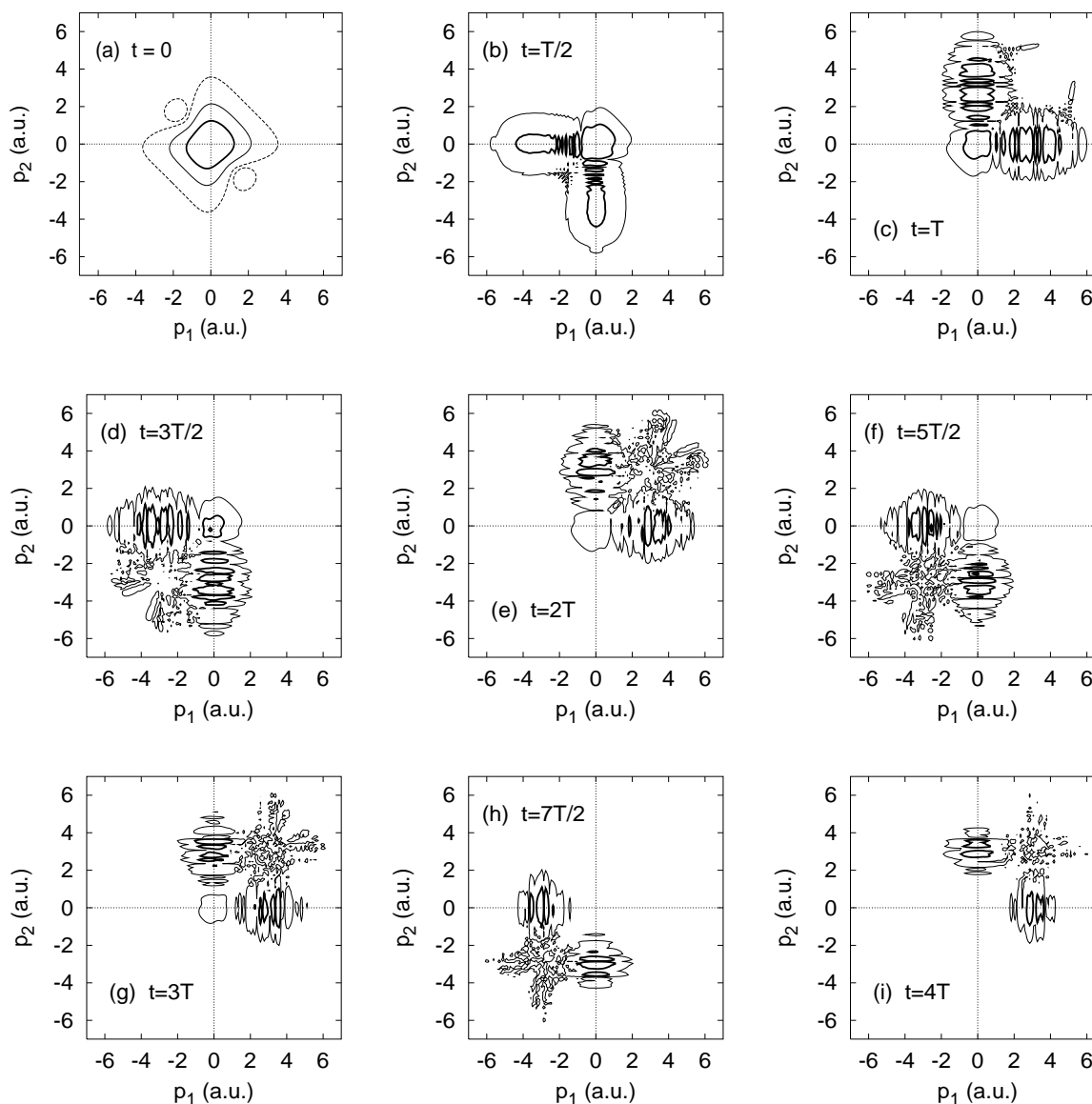
Mechanisms under discussion were

- rescattering
- shake-off (relevant mechanism for high photon energies)
- collective tunneling

TDSE contains all information, but difficult to extract.

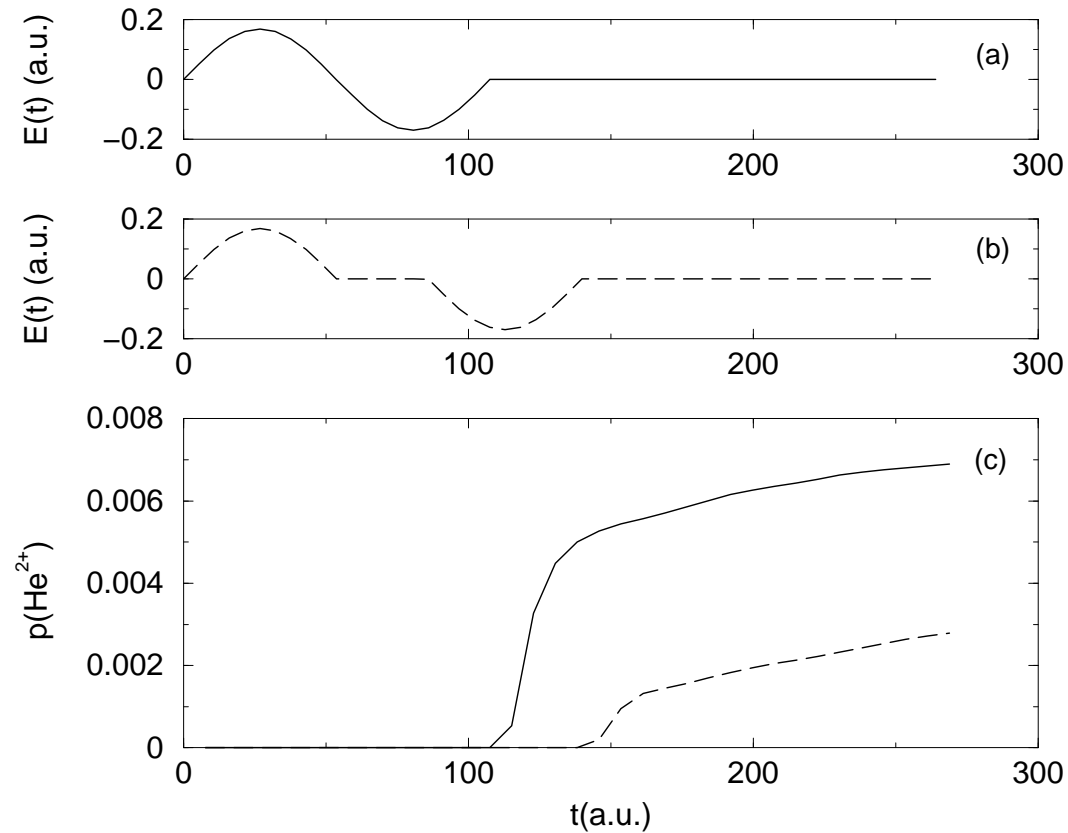
Mechanism of nonsequential double ionization

Evolution in two-electron momentum space ($\lambda = 780$ nm, $I = 10^{15}$ W/cm²)



Mechanism of nonsequential double ionization

Numerical experiment to test ionization mechanism

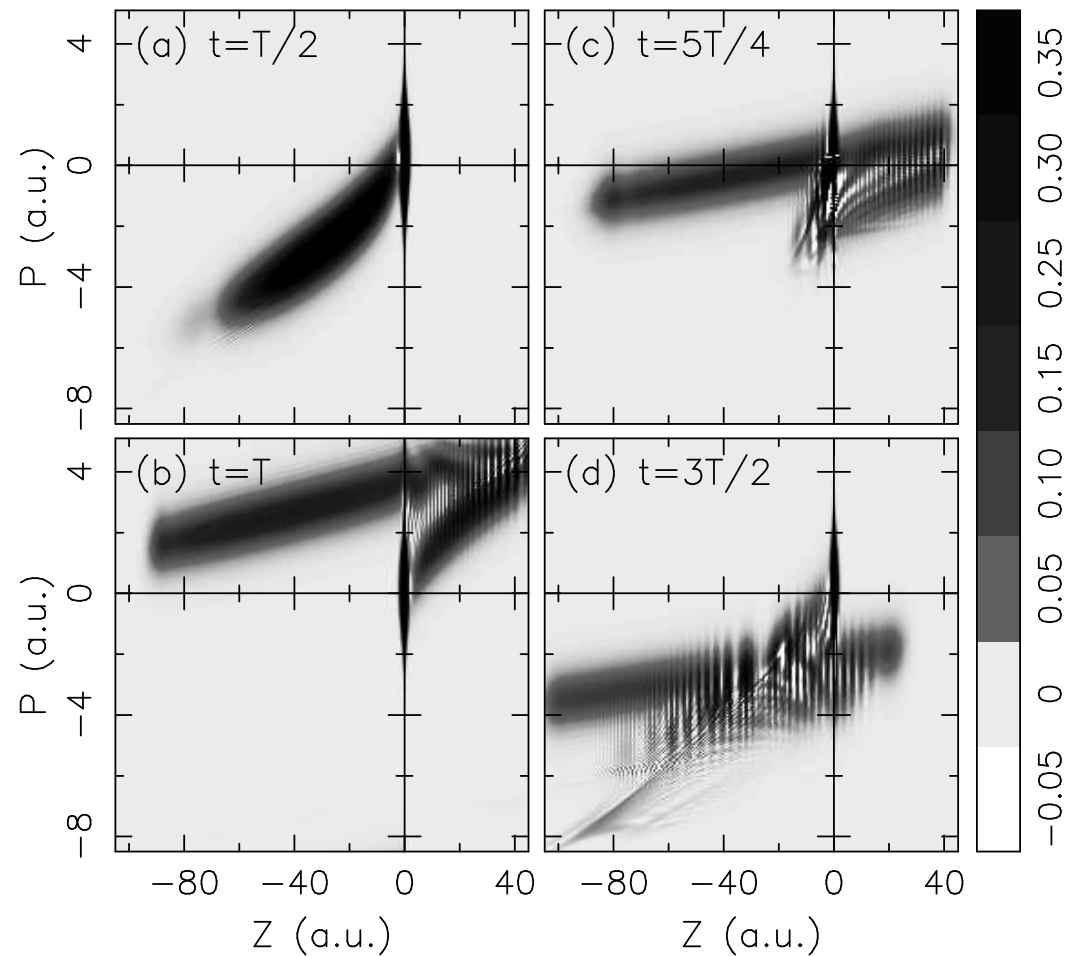


[M.L., E.K.U. Gross, V. Engel, J. Phys. B **33**, 433 (2000)]

→ excludes shake-off or collective tunneling.

Mechanism of nonsequential double ionization

Wigner function evolution for el. center of mass provides classical picture:



[M.L., E.K.U. Gross, V. Engel, PRL **85**, 4707 (2000)]

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:**

Fictitious system of non-interacting particles described by orbitals φ_k

$$n(\mathbf{r}, t) = \sum_{k=1}^N |\varphi_k(\mathbf{r}, t)|^2$$

$$i \frac{\partial}{\partial t} \varphi_k(\mathbf{r}, t) = \left(-\frac{1}{2} \nabla^2 + v_{\text{KS}}(\mathbf{r}, t) \right) \varphi_k(\mathbf{r}, t)$$

$$v_{\text{KS}}[n](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r}, t)$$

- **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

$$v_x(\mathbf{r}, t) = -\frac{1}{2}v_H(\mathbf{r}, t),$$

and furthermore

x-only TDDFT = TD Hartree-Fock.

Usual approximations

- 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

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

→ No success to reproduce the knee

Underestimation of single ionization

However, inserting the exact density into mean-field functional reproduces a knee.

[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 $\varphi(z, t) = \sqrt{n(z, t)/2} \exp(i\alpha(z, t))$ 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: $\varphi(z, t + \delta t) = e^{-iT_s \delta t} e^{-2iv_{\text{KS}} \delta t} e^{-iT_s \delta t} \varphi(z, t - \delta t)$

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

The Kohn-Sham current density

Question:

Is KS current density = current density in the interacting system?

The Kohn-Sham current density

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Continuity equation must hold in both systems:

$$\dot{n} + \nabla \mathbf{j} = 0$$

$$\dot{n}_{\text{KS}} + \nabla \mathbf{j}_{\text{KS}} = 0$$

Because densities n, n_{KS} are equal, we have $\nabla \mathbf{j} = \nabla \mathbf{j}_{\text{KS}}$.

In general, it is unclear whether $\mathbf{j} = \mathbf{j}_{\text{KS}}$, but in 1D, we have

$$\partial_z j = \partial_z j_{\text{KS}},$$

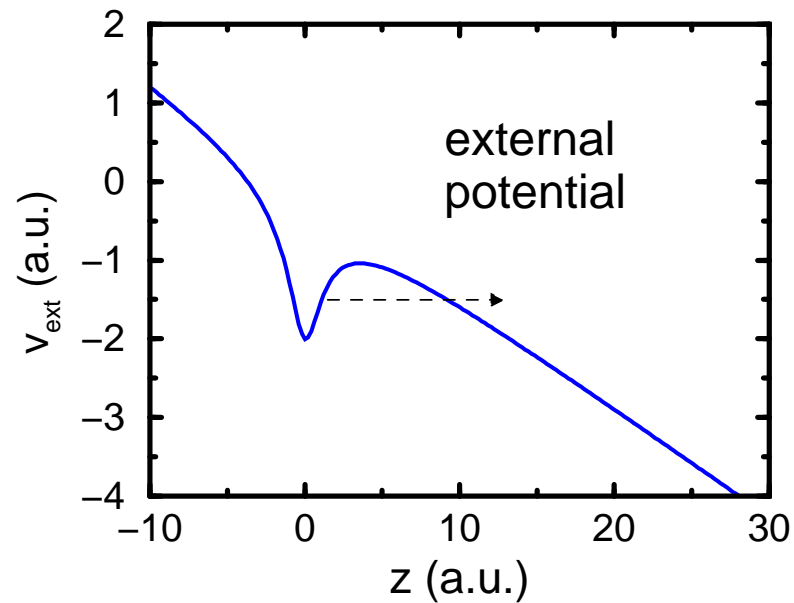
and for finite systems, we have $j \rightarrow 0$ for $|z| \rightarrow \infty$.

Therefore $j = j_{\text{KS}}$ in 1D finite systems.

Exact xc potential for a model system

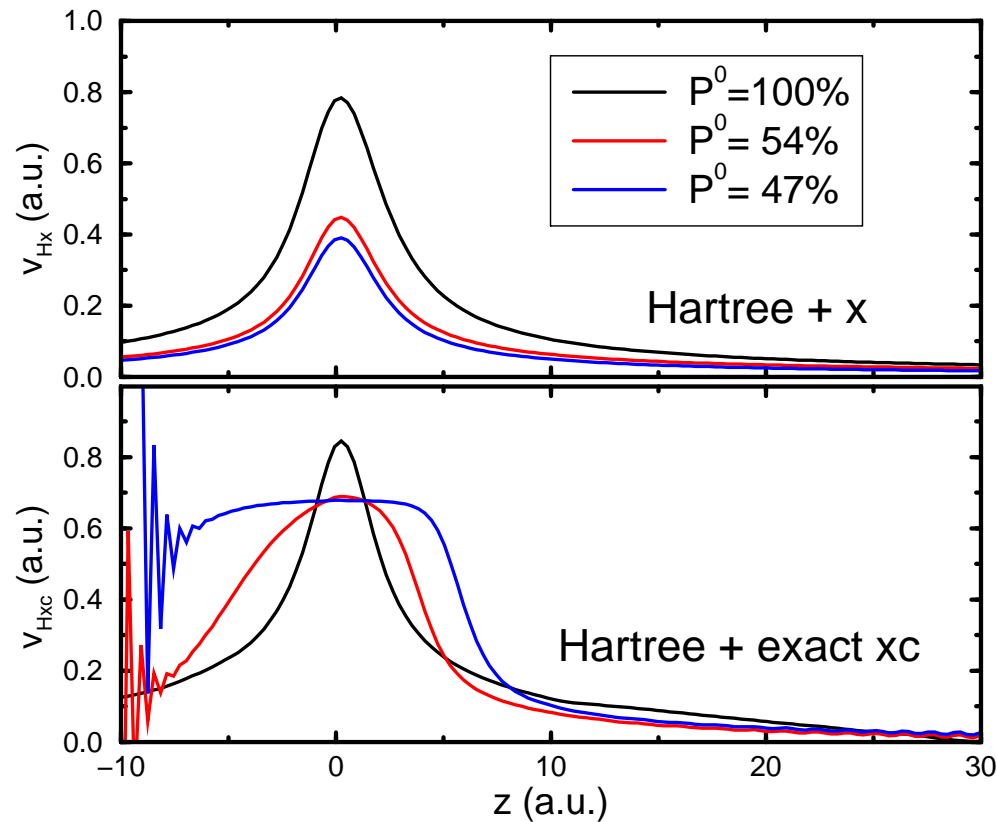
To avoid numerical difficulties: choose static field

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



Exact xc potential for a model system

Numerical results

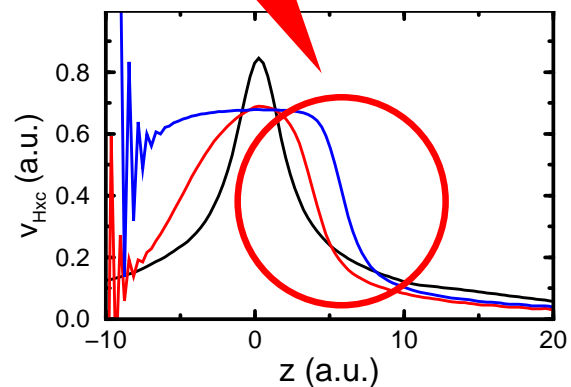
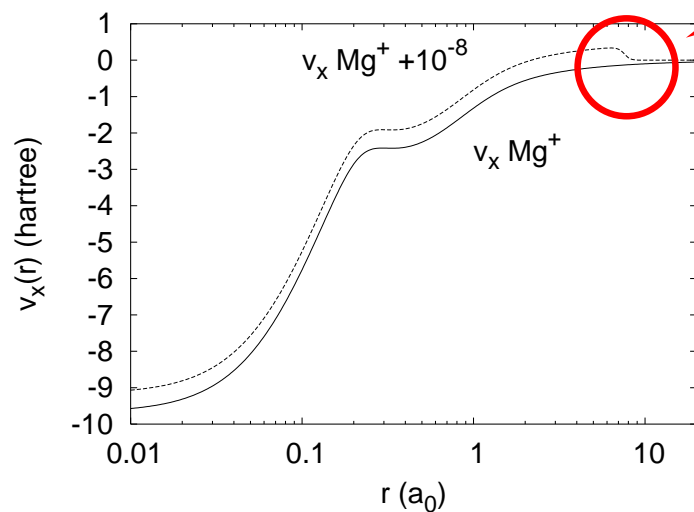


M.L., S. Kümmel, PRL **94**, 143003 (2005)

- 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

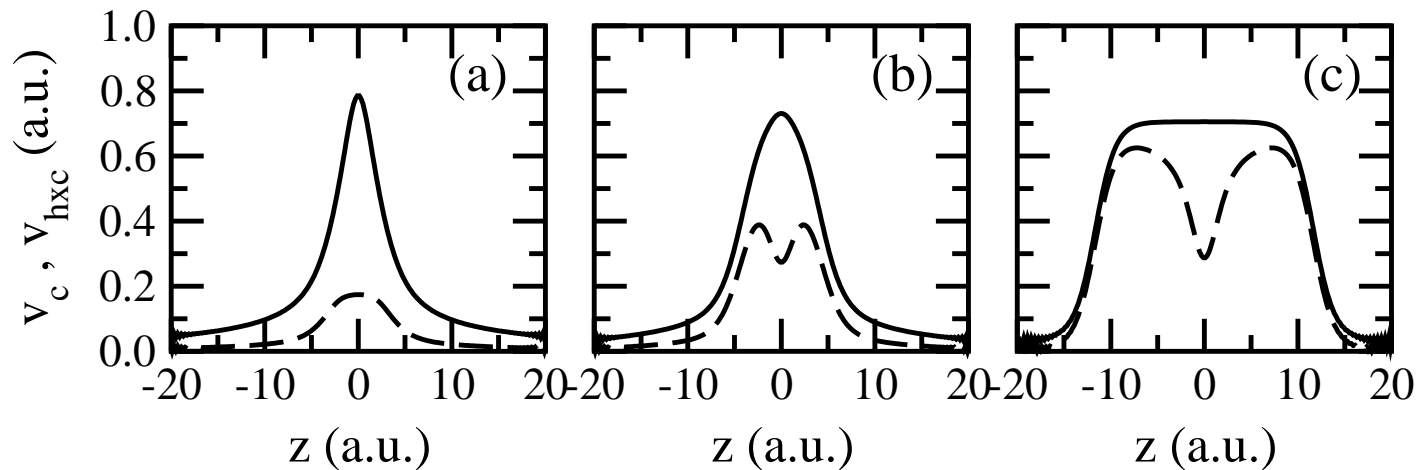
Time-dependent DFT

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 Δ_{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 $N_{\text{bound}} = \int_V n(\mathbf{r}) d^3r$
with an appropriate region V around the nucleus.

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

Simple guess for a functional

KS potential should retain its initial repulsive character.

→ Introduce weighting factor to compensate for loss of electron density:

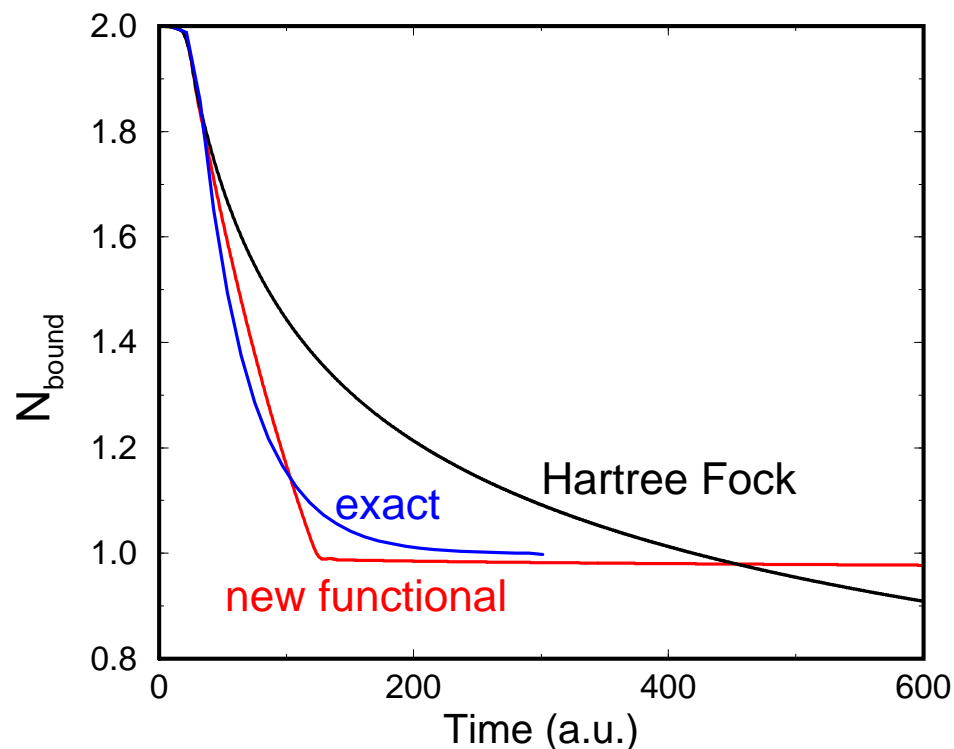
$$\begin{aligned} v_{\text{Hxc}}(\mathbf{r}, t) &= \frac{2}{N_{\text{bound}}} v_{\text{Hx}}(\mathbf{r}, t), & N_{\text{bound}} > 1 \\ v_{\text{Hxc}}(\mathbf{r}, t) &= 0, & N_{\text{bound}} \leq 1 \end{aligned}$$

Simple guess for a functional

KS potential should retain its initial repulsive character.

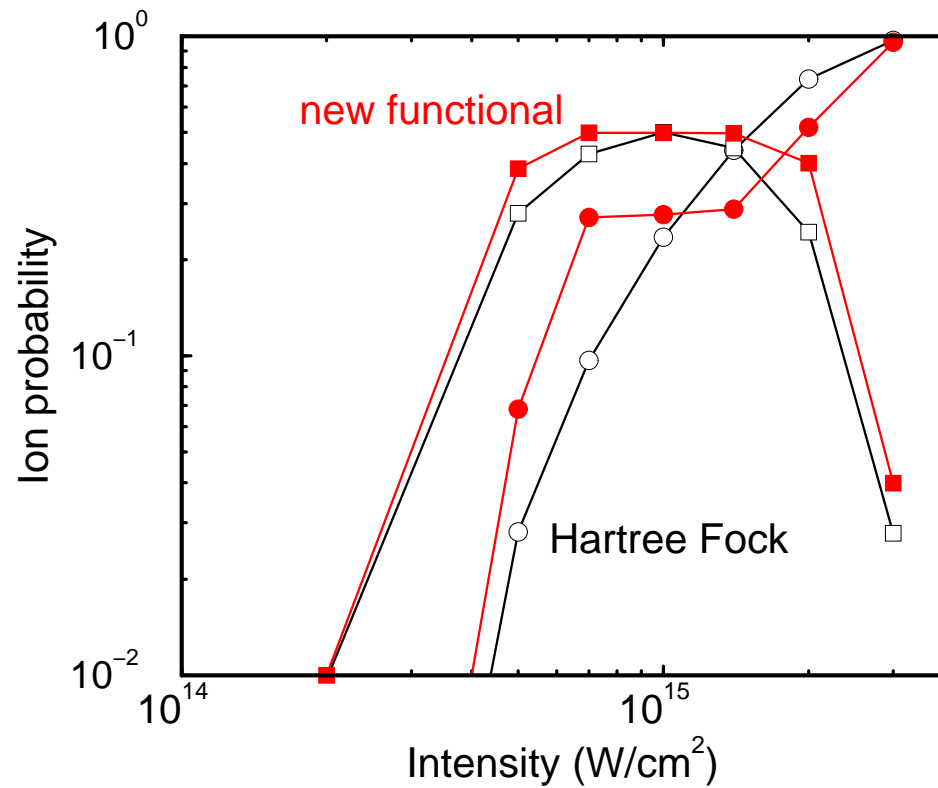
→ Introduce weighting factor to compensate for loss of electron density:

$$v_{\text{Hxc}}(\mathbf{r}, t) = \frac{2}{N_{\text{bound}}} v_{\text{Hx}}(\mathbf{r}, t), \quad N_{\text{bound}} > 1$$
$$v_{\text{Hxc}}(\mathbf{r}, t) = 0, \quad N_{\text{bound}} \leq 1$$



Ionization in a laser pulse

$\lambda = 780 \text{ nm}, 8 \text{ cycles}$



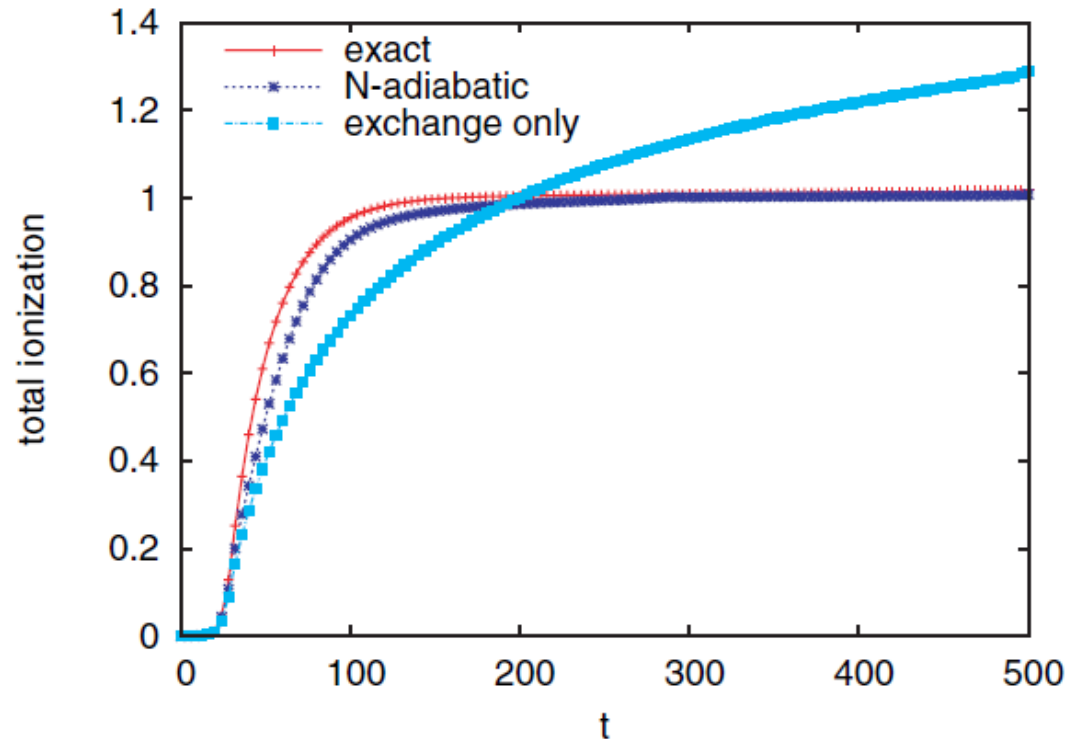
N-Adiabatic approximation

TDKS scheme with the following additions:

- Determine at every time the (fractional) number $N_{\text{bound}} = N - 1 + \epsilon$ of bound electrons.
- Construct ground-state density for this fractional particle number:
$$n_0(\mathbf{r}) = [1 - \epsilon(t)] n_{0,N-1}(\mathbf{r}) + \epsilon(t) n_{0,N}(\mathbf{r}).$$
- 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)]

Adiabatic approximation for pair correlation function

For further improvement of ionization probabilities, better functionals are needed for these observables:

$$p(\text{He}^+) = 2p(t)[1 - p(t)] - I_c$$

$$p(\text{He}^{++}) = [1 - p(t)]^2 + \frac{1}{2}I_c$$

with

$$p(t) = \int_A d^3r |\varphi(\mathbf{r}, t)|^2$$

and the correlation integral

$$I_c = \int_A d^3r_1 \int_A d^3r_2 n(\mathbf{r}_1, t)n(\mathbf{r}_2, t)g_c(\mathbf{r}_1, \mathbf{r}_2, t),$$

where

$$g_c(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{2|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2}{n(\mathbf{r}_1, t)n(\mathbf{r}_2, t)} - \frac{1}{2}$$

is the correlation part of the pair correlation function.

Adiabatic approximation for pair correlation function

Adiabatic approximation for pair correlation function

[F. Wilken and D. Bauer, PRL **97**, 203001 (2006)]:

$$g_c^A(\mathbf{r}_1, \mathbf{r}_2, t) = -\frac{1}{2}, \quad N_{\text{bound}} < 1$$
$$g_c^A(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{\rho^A(\mathbf{r}_1, \mathbf{r}_2, t)}{n^A(\mathbf{r}_1, t)n^A(\mathbf{r}_2, t)} - \frac{1}{2}, \quad 1 \leq N_{\text{bound}} \leq 2$$

with

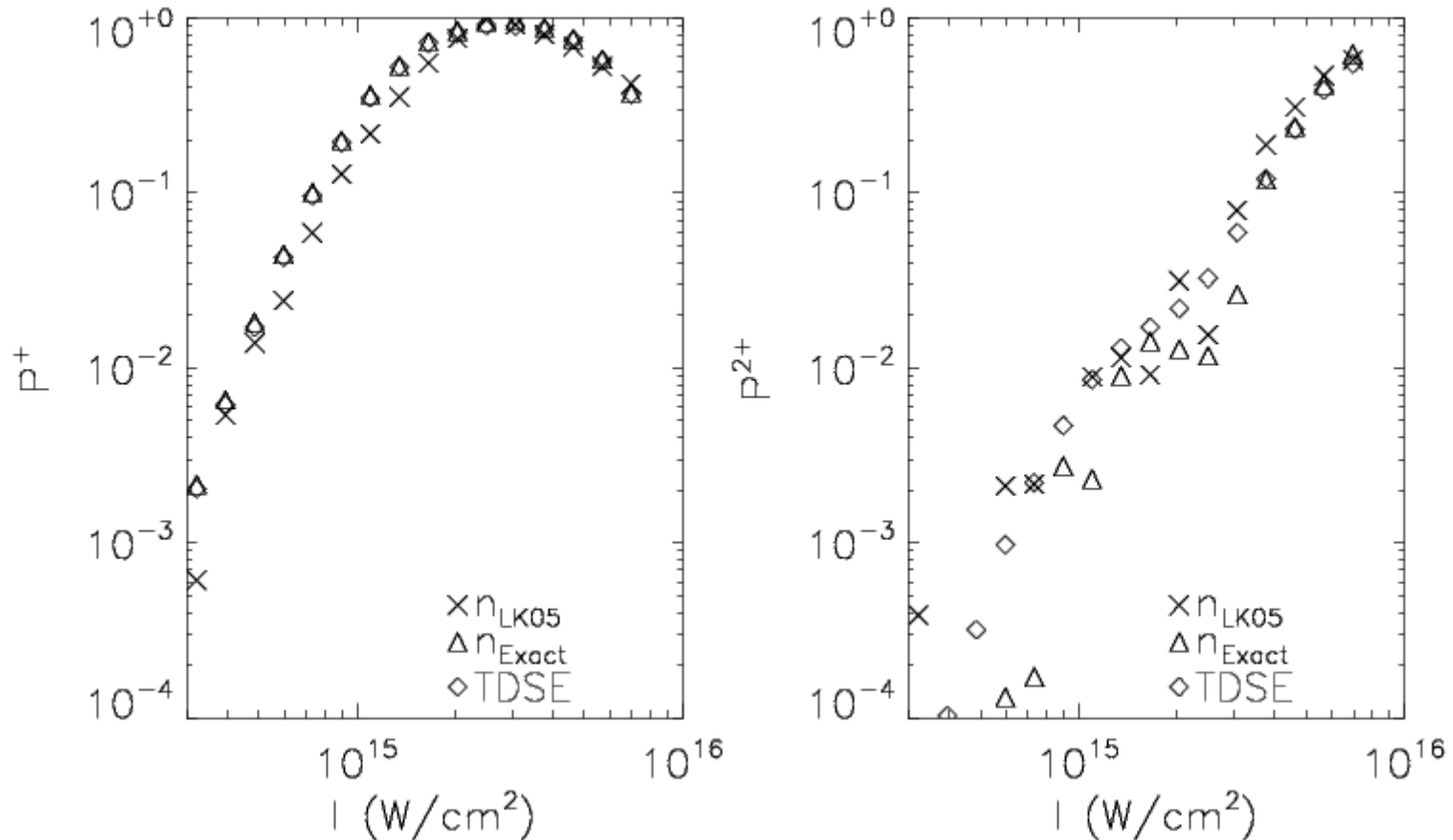
$$n^A(\mathbf{r}, t) = (1 - \epsilon)n_1(\mathbf{r}) + \epsilon n_2(\mathbf{r}_2), \quad 1 \leq N_{\text{bound}} \leq 2$$
$$\rho^A(\mathbf{r}_1, \mathbf{r}_2, t) = 2(1 - \epsilon)|\Psi_1(\mathbf{r}_1, \mathbf{r}_2)|^2 + 2\epsilon|\Psi_2(\mathbf{r}_1, \mathbf{r}_2)|^2, \quad 1 \leq N_{\text{bound}} \leq 2$$

Ψ_j = ground state of j-particle system,
 n_j = ground-state density of j-particle system

$$N_{\text{bound}} = 1 + \epsilon$$

Adiabatic approximation for pair correlation function

Good results for single and double ionization



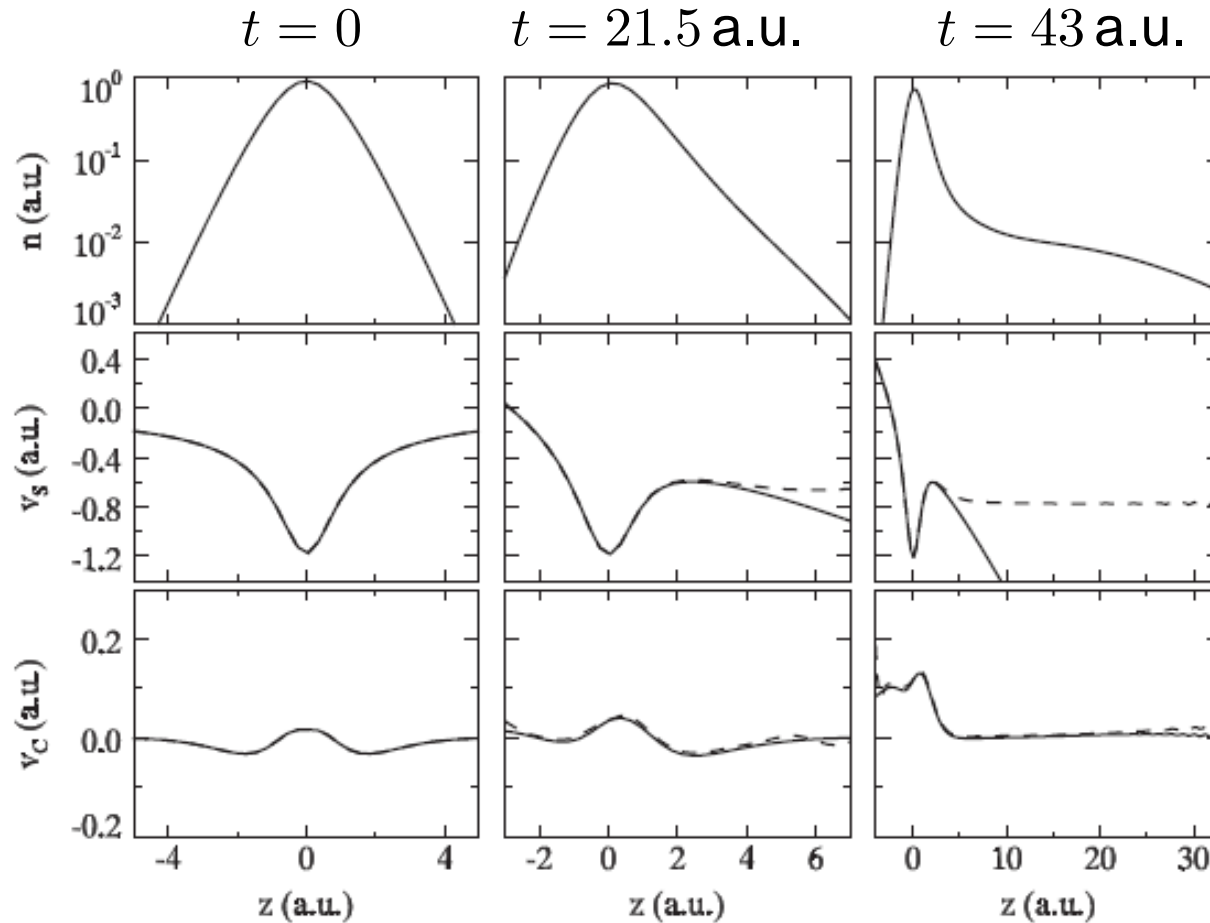
Exact adiabatic potential

- For given density n , construct the external potential v_{ext}^0 that yields n as ground state density of an interacting system.
- Construct the potential v_{KS}^0 that yields n as ground state densities of a noninteracting system.
- Obtain adiabatic exchange correlation potential as

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

Exact adiabatic potential

Excellent agreement with exact xc potential:



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

Multicomponent problems

Multicomponent TDDFT describes quantum mechanical motion of nuclei and electrons with nuclear and electronic KS potentials:

$$i \frac{\partial}{\partial t} \varphi_k(\mathbf{r}, t) = \left(-\frac{1}{2} \nabla^2 + v_{\text{KS}}^{\text{el}}(\mathbf{r}, t) \right) \varphi_k(\mathbf{r}, t) \quad \text{for electrons}$$

$$i \frac{\partial}{\partial t} \chi(\underline{\mathbf{R}}, t) = \left(-\sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + v_{\text{KS}}^{\text{nuc}}(\underline{\mathbf{R}}, t) \right) \chi(\underline{\mathbf{R}}, t) \quad \text{for nuclei}$$

with electron density

$$n(\mathbf{r}, t) = \sum_k |\varphi_k(\mathbf{r}, t)|^2$$

and nuclear probability distribution $\Gamma(\underline{\mathbf{R}}, t) = |\chi(\underline{\mathbf{R}}, t)|^2$.

Advantages: nonperturbative, non-Born-Oppenheimer theory

Disadvantage: so far no practical functional

Idea: calculate exact KS potentials for a model system

A 1D model H_2^+ molecular ion

One electron moving along the molecular axis, parallel to the external field:

$$H(t) = -\frac{1}{2} \frac{\partial^2}{\partial z^2} - \frac{\partial^2}{M \partial R^2} - \frac{1}{\sqrt{(z-R/2)^2+1}} - \frac{1}{\sqrt{(z+R/2)^2+1}} + \frac{1}{R} + E(t)z$$

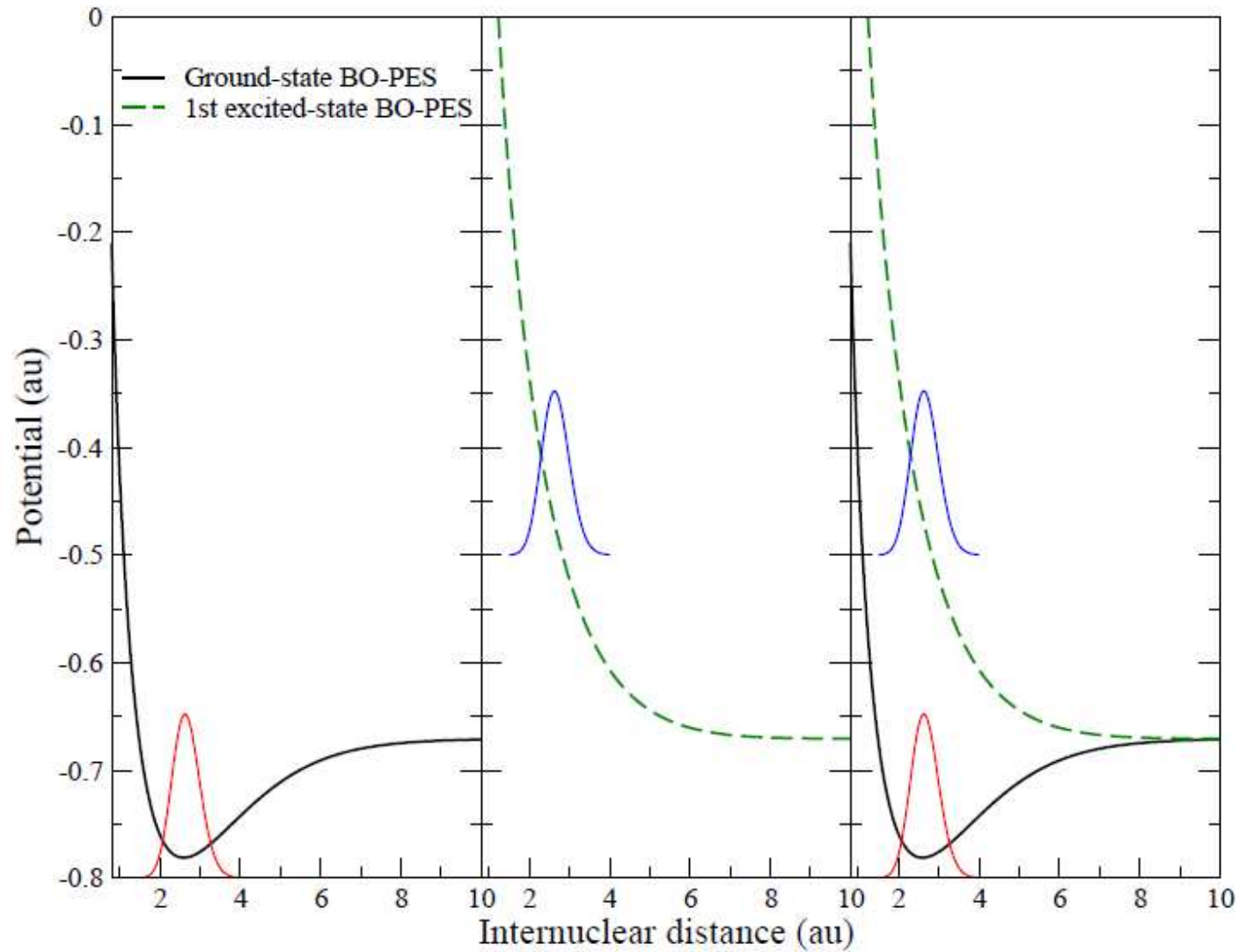
[Kulander, Mies, and Schafer, PRA **53**, 2562 (1996)]

with z = electron coordinate, R = internuclear distance.

Calculation of KS potentials for electron and internuclear coordinate for various types of dynamics:

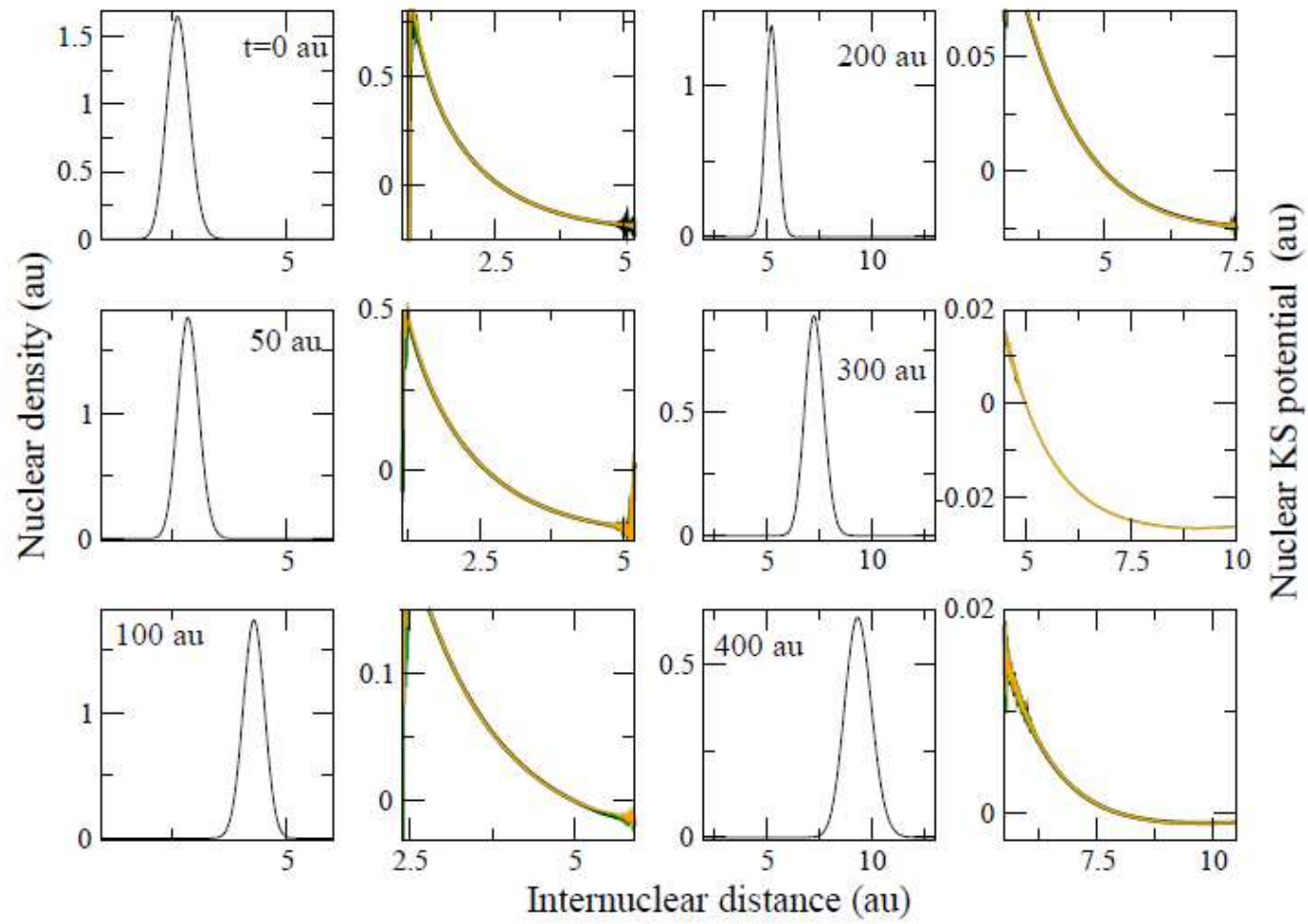
- Wave-packet motion on one Born-Oppenheimer surface
- Superposition of electronic states
- System in the presence of a static electric field

A 1D model H_2^+ molecular ion



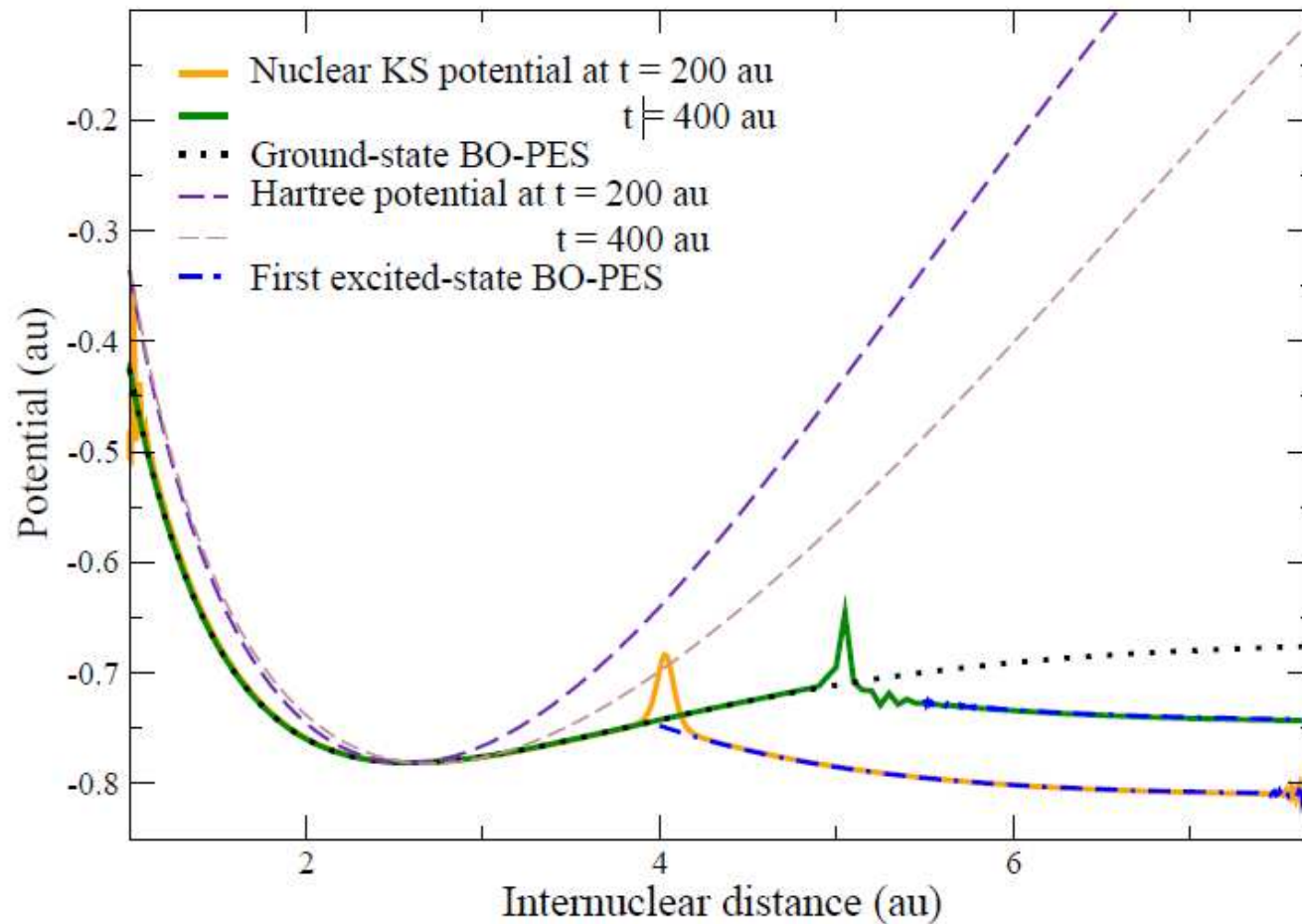
A 1D model H_2^+ molecular ion

Nuclear KS potential for wave-packet dynamics on one BO potential



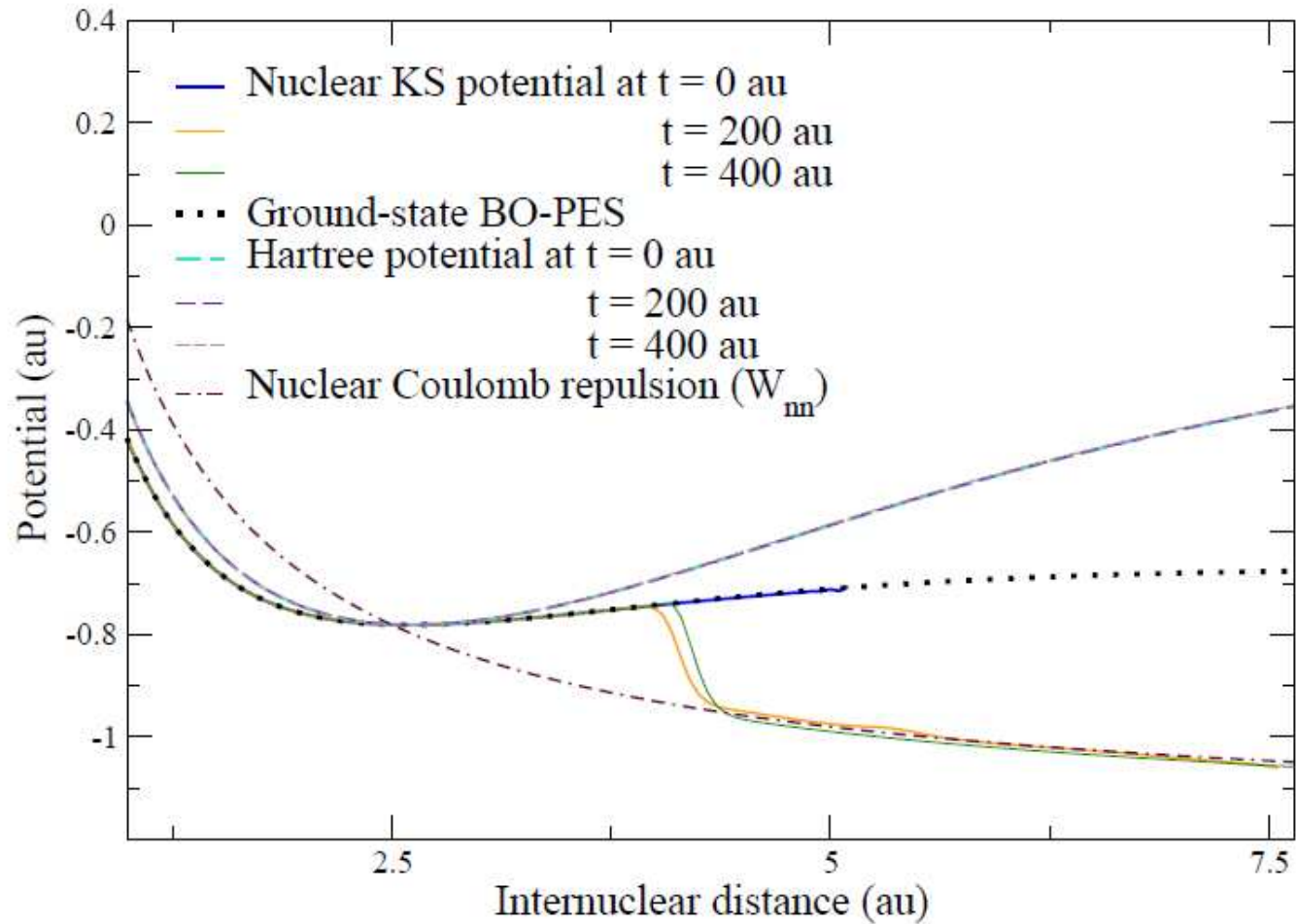
A 1D model H_2^+ molecular ion

Nuclear KS potential for superposition of two electronic states



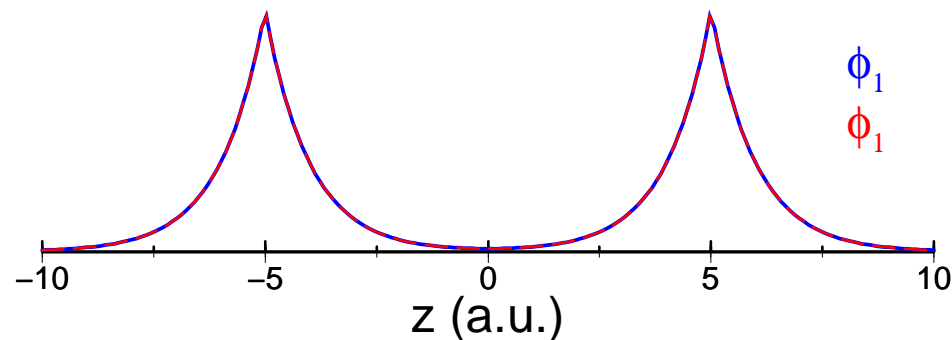
A 1D model H_2^+ molecular ion

Nuclear KS potential for system in static electric field



Molecules - the dissociation problem

H₂ in Hartree-Fock or in conventional DFT implementations: two identical delocalized orbitals at large distances.

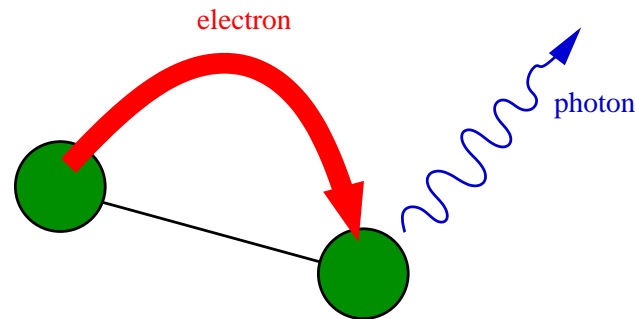


→ wrong prediction of ground-state energy due to spurious Hartree energy, hard to correct in DFT.

[see Baerends PRL **87**, 133004 (2001) for solution in orbital-DFT]

The dissociation problem in high-harmonic generation

Consider high-harmonic generation in molecules at large internuclear distances. Then a transfer mechanism is possible:



Ionization and recombination at different atomic sites

[P. Moreno et al., PRA **55**, R1593 (1997), R. Kopold et al., PRA **58**, 4022 (1998)]

predicted cutoff: up to $8U_p$

... but only possible if the initial state consists of two coherent pieces at the two centers, as in H_2^+ .

The dissociation problem in high-harmonic generation

To show the difference between localized and delocalized states, we study 1D H_2^+ described by

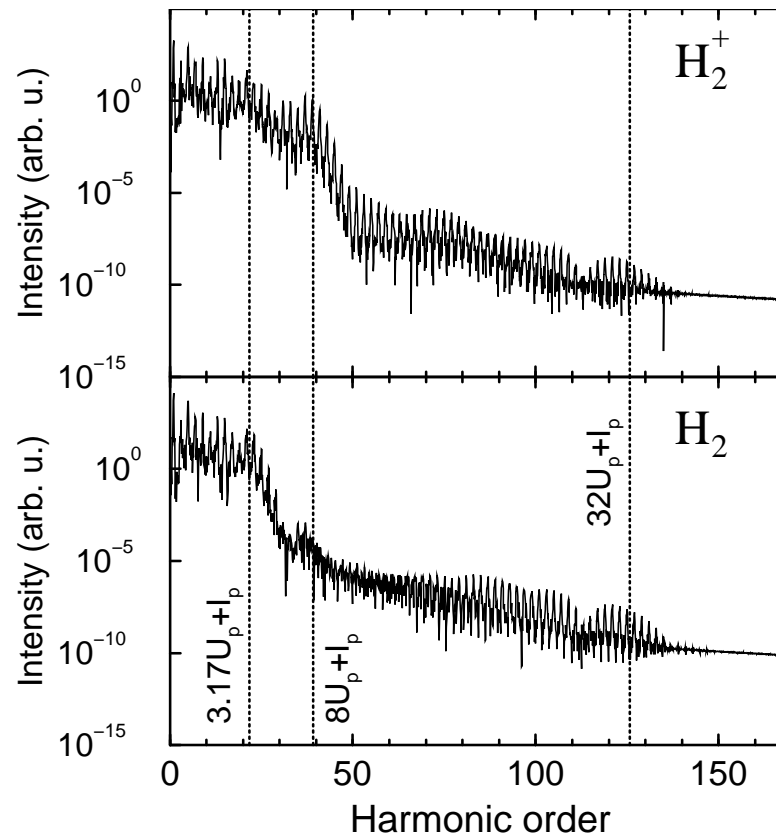
$$H(t) = -\frac{1}{2} \frac{\partial^2}{\partial z^2} - \frac{1}{\sqrt{(z-R/2)^2+2}} - \frac{1}{\sqrt{(z+R/2)^2+2}} + E(t)z$$

and 1D H_2 described by

$$H(t) = -\frac{1}{2} \frac{\partial^2}{\partial z_1^2} - \frac{1}{2} \frac{\partial^2}{\partial z_2^2} - \frac{1}{\sqrt{(z_1 - R/2)^2 + 2}} - \frac{1}{\sqrt{(z_1 + R/2)^2 + 2}} \\ - \frac{1}{\sqrt{(z_2 - R/2)^2 + 2}} - \frac{1}{\sqrt{(z_2 + R/2)^2 + 2}} \\ + \frac{1}{\sqrt{(z_2 - z_1)^2 + 1.621}} + E(t)z.$$

The dissociation problem in high-harmonic generation

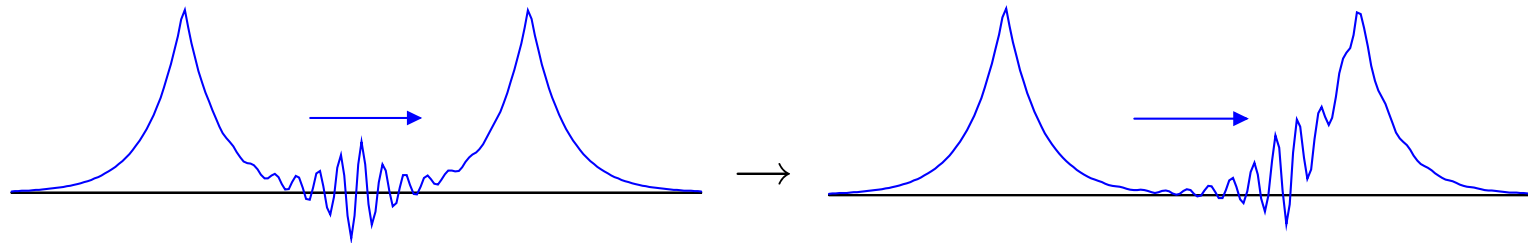
Comparison of harmonics in H_2^+ and H_2
($R=150$ a.u., 800 nm, 9.35×10^{13} W/cm 2)



Vertical lines indicate the cutoffs expected from classical modeling.

The dissociation problem in high-harmonic generation

Conventional TDDFT for H_2 will produce situations like this:



The (unphysical) oscillations are similar to those taking place in H_2^+ and give rise to an unphysical $8 U_p$ cutoff.

Numerical issues with TDKS and TDSE for strong fields

Main problem: large electron excursions - hundreds of a.u.

→ need for large grids

Alternatively, small grid with absorbing boundary, i.e.

- repeated multiplication with an absorbing mask function
- or addition of negative imaginary potential,
because $\exp(-iV_{\text{opt}}dt) = \exp(-|V_{\text{opt}}|dt)$.

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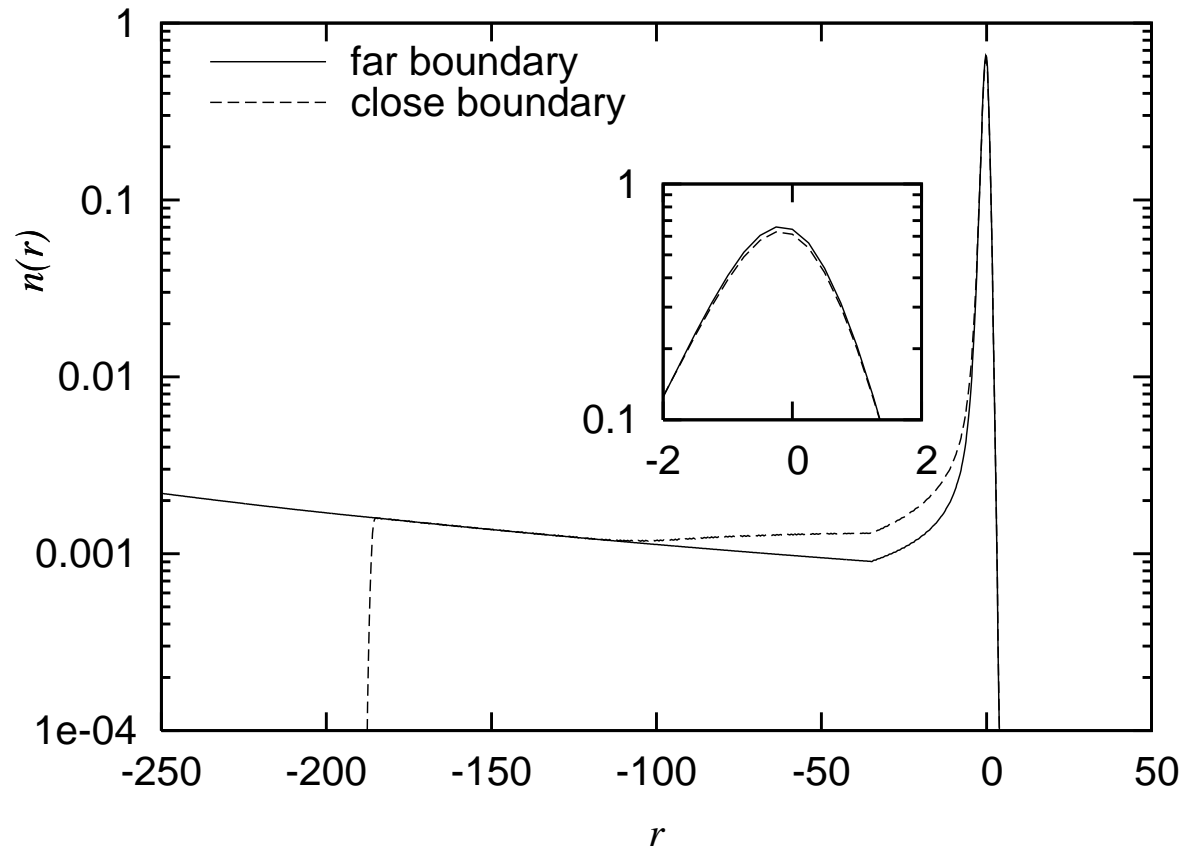
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because $\exp(-iV_{\text{opt}}dt) = \exp(-|V_{\text{opt}}|dt)$.

Problems with absorbing boundaries:

- in TDKS scheme: distortion of the KS potential due to nonlocal Hartree functional,
- in many-body TDSE: absorption of particle density not only near the boundary but also in the middle, due to correlation

Absorbing boundaries

Absorption in Hartree-Fock calculation (1D He, dc field)



[A. de Wijn, S. Kümmel, M.L., J. Comput. Phys. **226**, 89 (2007)]

Missing repulsion leads to faster ionization!

Absorbing boundaries

In many-body TDSE: mask absorbs not individual particles, but parts of the many-body wave function

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

when

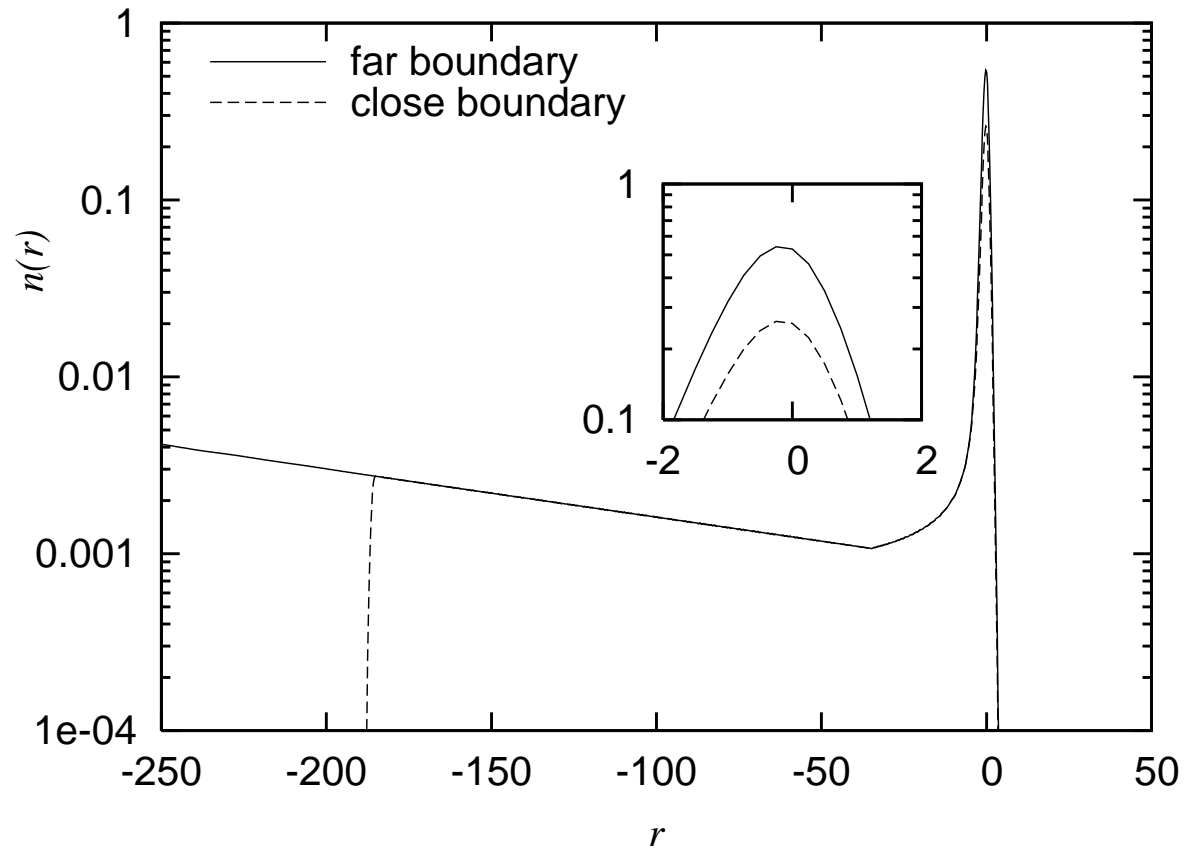
$$|\mathbf{r}_j| > R_{\text{mask}}$$

for *one of* the \mathbf{r}_j . Other \mathbf{r}_k , $k \neq j$, are usually small.

→ Density is absorbed not only at the boundary.

Absorbing boundaries

Absorption in exact calculation (1D He, dc field)



Density around the origin is absorbed!

Conclusions

- **Derivative discontinuity** plays a key role in ionization processes.
- (Nonlocal) **adiabatic approximations** open up new perspectives.
- The dissociation problem remains to be solved in TDDFT.
- Absorbing boundaries should be used with care in TDDFT.