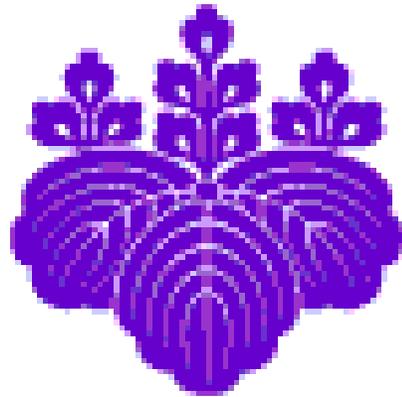


Application of real-time TDDFT simulation to nonlinear and nonequilibrium electron dynamics in matter

Shunsuke A. Sato

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2. Max Planck Institute for the Structure and Dynamics of Matter, Hamburg



<https://www.benasque.org/2022tddft/cgi-bin/talks/allprint.pl>



SCIENTIFIC ACTIVITY

PRESENT

2022

2023

2024

2025

PREVIOUS

OTHER ACTIVITIES

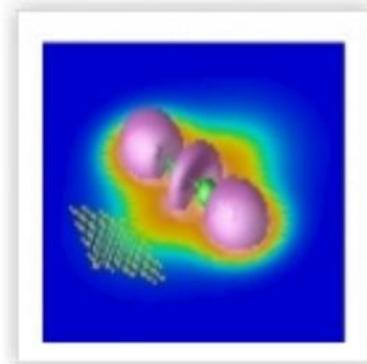
CULTURAL

VALLEY PROMOTION

MISC

OR

Y



9th Time-Dependent Density-Functional Theory: Prospects and Applications

2022, Oct 18 -- Oct 28

Organizers:

A. Castro (ARAID Foundation)

E. K. U. Gross (Hebrew University of Jerusalem)

N. Maitra (Rutgers University at Newark)

M. A. L. Marques (Halle Universitario, Germany)

A. Rubio (MPI for the Structure and Dynamics of Matter, Hamburg)

School Program

Wednesday, October 19

09:00-10:00 **DFT and TDDFT 1**

Hardy Gross

My slides are available here!!



11:30-12:30

Real-time TDDFT for extremely nonlinear and ultrafast phenomena

Shunsuke Sato

1. Analysis on partially/effectively interacting Kohn-Sham systems towards the combined theory of DFT and WFT
2. Conditional wavefunction theory for scattering problems beyond mean-field methods

Background: electronic systems

Schrödinger equation for many-electron systems

$$\hat{H}\Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = E_n \Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)$$

Ab-initio Hamiltonian (nuclei are treated as classical particles; Born-Oppenheimer approximation)

$$\hat{H} = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m_e} + \sum_{j=1}^N \sum_{a=1}^M \frac{-Z_a}{|\mathbf{r}_j - \mathbf{R}_a|} + \sum_{j>k}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \sum_{a>b}^M \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

Example 1. Hydrogen atom: 1 electron, 1 proton

$$\hat{H} = \frac{\mathbf{p}^2}{2m_e} - \frac{Z_p}{|\mathbf{r} - \mathbf{R}_p|} \quad \longrightarrow \quad \psi_{1s}(r) \sim e^{-Z_p|r-\mathbf{R}_p|}$$

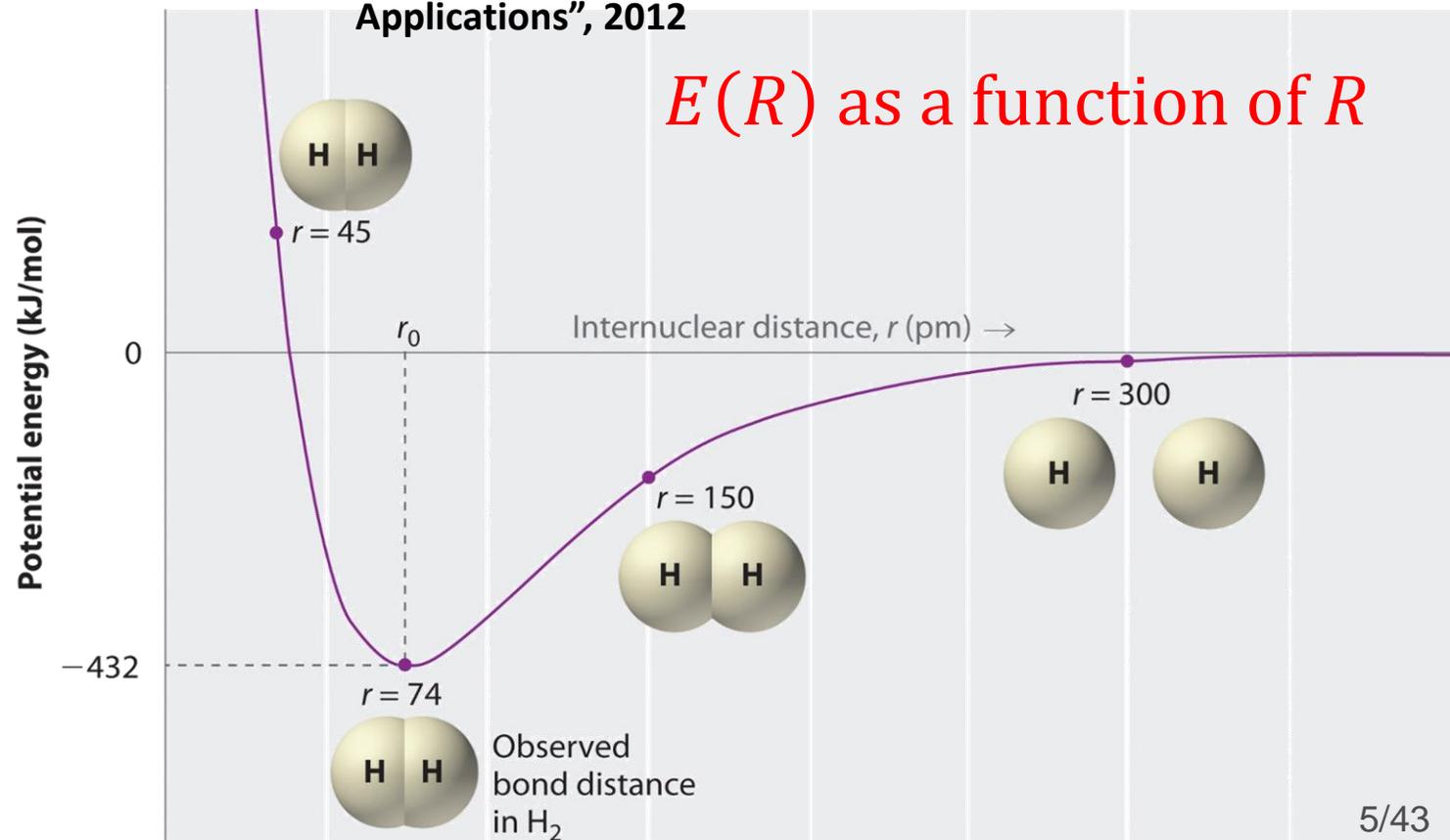
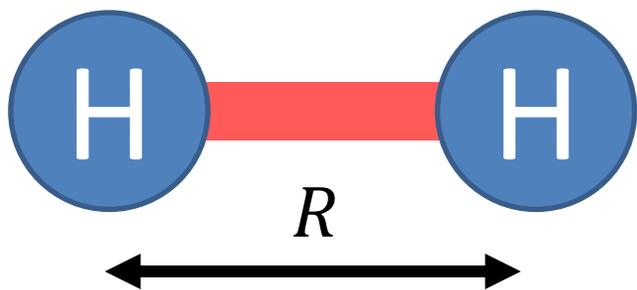
Background: electronic systems

Example 2. Hydrogen molecule: two electrons, two protons

$$\hat{H} = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|}$$

Andy Schmitz, "General Chemistry: Principles, Patterns, and Applications", 2012

Calculate the ground state energy by changing the proton-proton distance



Background: electronic systems

Many-electron Schrödinger equation

$$\hat{H}\Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = E_n \Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)$$

$$\hat{H} = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m_e} + \sum_{j=1}^N \sum_{a=1}^M \frac{-Z_a}{|\mathbf{r}_j - \mathbf{R}_a|} + \sum_{j>k}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \sum_{a>b}^M \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$



If this equation can be solved, various material properties can be understood.

Glass is transparent



Metals are conductivity



Background: difficulty in quantum many-body problems

Many-electron Schrödinger equation

$$\hat{H}\Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = E_n \Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)$$

$$\hat{H} = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m_e} + \sum_{j=1}^N \sum_{a=1}^M \frac{-Z_a}{|\mathbf{r}_j - \mathbf{R}_a|} + \sum_{j>k}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \sum_{a>b}^M \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$



- The increase in the number of electrons corresponds to the increase in the dimension of the wavefunction, resulting in the large dimensional problems (**exponential wall**)
- Many-body Schrodinger equations are often practically unsolvable.
- In practice, one needs approximated methods.

Wavefunction theory (WFT, quantum chemistry approach)

Hartree-Fock method:

Wavefunction is approximated by a single Slater determinant

$$\Psi^{HF}(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} |\phi_1(\mathbf{r}_1, \sigma_1), \phi_2(\mathbf{r}_2, \sigma_2), \dots, \phi_N(\mathbf{r}_N, \sigma_N)|$$

↓ Minimizing the energy (variational principle)

$$E = \frac{\langle \Psi^{HF} | H | \Psi^{HF} \rangle}{\langle \Psi^{HF} | \Psi^{HF} \rangle}$$

Hartree-Fock equation: Schrödinger-like equation for one-particle orbitals

$$\left[\frac{\mathbf{p}^2}{2m_e} + \sum_{a=1}^M \frac{-Z_a}{|\mathbf{r} - \mathbf{R}_a|} + v_H(\mathbf{r}) + \hat{v}_F \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r})$$

Hartree potential

Fock operator

Wavefunction theory (WFT, quantum chemistry approach)

Configuration interaction (CI) method:

Expand the variational space with a superposition of particle-hole states

$$|\psi^{CI}\rangle = \hat{T}|\Psi^{HF}\rangle$$

1-particle 1-hole 2-particle 2-hole

$$\hat{T} = c_0 + \sum_{A,J} c_{AJ} \hat{a}_A^\dagger \hat{a}_J + \sum_{A>B, J>K} c_{ABJK} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_J \hat{a}_K + \dots$$

Coupled Cluster (CC) method

$$|\psi^{CI}\rangle = e^{\hat{T}}|\Psi^{HF}\rangle$$

- ◆ Wavefunction-based approach offers **a systematic way of the accuracy improvement** by expanding the variational space.
- ◆ However, the computational costs tend to be larger, especially for larger systems.

Density functional theory (DFT)

(Trivial) Once the positions and charges of nuclei are given, the ground state electron density is determined by solving the Many-electron Schrödinger equation.

$$\hat{H}\Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = E_n \Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)$$

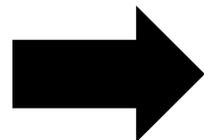
$$n(\mathbf{r}) = N \sum_{\sigma_1, \dots, \sigma_N} \int d\mathbf{r}_2 \cdots d\mathbf{r}_N |\Psi_n(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)|^2$$

(Question) If the ground electron density is known, can we know the position and charges of the nuclei?

Answer \Rightarrow Yes (Kato's theorem)

1s state of Hydrogen-like atom

$$\psi_{1s}(r) \sim e^{-Z_p|r-R_p|}$$



Sharp structure at nucleus (Cusp)

From cusp structure, one can find the positions and charges of nuclei

$$Z_a = - \left. \frac{1}{2n(\mathbf{r})} \frac{dn(\mathbf{r})}{dr} \right|_{r=R_a}$$

Density functional theory (DFT)

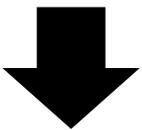
Hohenberg-Kohn theory (Runge-Gross theorem for time-dependent system)

For a general Hamiltonian with given particle-particle interaction $w(|\mathbf{r}_j - \mathbf{r}_k|)$,

$$\hat{H} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{ext}(\mathbf{r}_j) \right] + \sum_{j>k} w(|\mathbf{r}_j - \mathbf{r}_k|)$$

there **is one to one correspondence** between the one-body external potential $v_{ext}(\mathbf{r})$ and the ground state one-body density $n(\mathbf{r})$.

$$v_{ext}(\mathbf{r}) \longleftrightarrow n(\mathbf{r})$$



Kohn-Sham mapping

Based on the one-to-one correspondence, one can consider a mapping from **many-body interacting problems** to **many-body non-interacting problems**.

Density functional theory (DFT)

Kohn-Sham mapping

Fully interacting system

$$\hat{H} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{ext}(\mathbf{r}_j) \right] + \sum_{j>k} w(|\mathbf{r}_j - \mathbf{r}_k|)$$

1-to-1 correspondence
(HK theorem)

Ground state density
 $n(\mathbf{r})$



Kohn-Sham mapping

Non-interacting system
(Kohn-Sham system)

$$\hat{H}_{KS} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{KS}(\mathbf{r}_j) \right]$$

1-to-1 correspondence
(HK theorem for non-interacting system)

Kohn-Sham equation

$$\left[\frac{\mathbf{p}^2}{2m_e} + v_{KS}(\mathbf{r}) \right] \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r})$$

Kohn-Sham potential

$$v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$


Exchange-correlation potential:

- $v_{xc}(\mathbf{r})$ is defined so that the density of Kohn-Sham system reproduces the density of interacting system.
- Exact explicit expression is not known. So, it must be approximated in practical calculations.
- The accuracy of the KS-DFT calculation depends much on the accuracy of $v_{xc}(\mathbf{r})$. Currently, the accuracy of KS-DFT is limited.

WaveFunction Theory (WFT) and Density Functional Theory (DFT)

WaveFunction Theory (WFT)

- ❑ By expanding the variational space, the accuracy can be straightforwardly improved (**high accuracy**)
- ❑ In the large variational space, the computational costs becomes similar to the original many-body Schrödinger equation (**high cost**)

Density Functional Theory (DFT)

- ❑ Thanks to the Kohn–Sham mapping, the central equation becomes non-interacting problems in practical calculations (**low cost**)
- ❑ The exact expression of the exchange–correlation potential/functions is not known. The systematic improvement is not so straightforward (**low accuracy**)

 Can we combine the strong points of WFT and DFT to realize a **low-cost & high-accuracy** method?

Aim of this work

Examples of the combinations of WFT and DFT

- Including a part of the nonlocal Fock operator \hat{v}_F into the exchange-correlation potential $v_{xc}(\mathbf{r})$ (**Hybrid functional**): e.g. J. Chem. Phys. 105, 9982 (1996).
- Configuration interaction (multi-configuration) with Kohn-Sham orbitals from DFT: e.g. Chem. Phys. Lett. 259, 128 (1996)



- These combinations of WFT and DFT are very successful to recover some correlation effects beyond the simple DFT calculation!
 - However, (as far as I understood) the theoretical background is still under development towards more accurate extension with WFT.
-

Aim of this work

We explore **the properties of partially/effectively interacting Kohn–Sham systems** in order to develop **a combined WFH–DFT approach** towards low–cost & high–accuracy methods.

Effectively interacting Kohn-Sham systems

E. Fromager, J. Toulouse, H.J.A. Jensen, J. Chem. Phys. 126, 074111 (2007)

Kohn-Sham mapping

Fully interacting system

$$\hat{H} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{ext}(\mathbf{r}_j) \right] + \sum_{j>k} w(|\mathbf{r}_j - \mathbf{r}_k|)$$

1-to-1 correspondence
(HK theorem)

Ground state density
 $n(\mathbf{r})$



1. DFT is responsible for the modified Kohn-Sham mapping

Effectively-interacting Kohn-Sham system

$$\hat{H}_{KS} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{KS}(\mathbf{r}_j) \right] + \sum_{j>k} w_{eff}(|\mathbf{r}_j - \mathbf{r}_k|)$$



2. WFT is responsible for the Schrödinger equation

$$\hat{H}_{KS}|\Psi_{KS}\rangle = E|\Psi_{KS}\rangle$$

1-to-1
(HK theorem)

KS mapping to effectively interacting Kohn-Sham systems

Modified KS mapping

Fully interacting system

$$\hat{H} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{ext}(\mathbf{r}_j) \right] + \sum_{j>k} w(|\mathbf{r}_j - \mathbf{r}_k|)$$

↓ 1. DFT is responsible for the modified Kohn-Sham mapping

Effectively interacting Kohn-Sham system

$$\hat{H}_{KS} = \sum_{j=1}^N \left[\frac{\mathbf{p}_j^2}{2m} + v_{KS}(\mathbf{r}_j) \right] + \sum_{j>k} w_{eff}(|\mathbf{r}_j - \mathbf{r}_k|)$$

1. DFT takes care the residual interaction:

$$w_{res}(\mathbf{r}) = w(\mathbf{r}) - w_{eff}(\mathbf{r})$$

2. WFT takes care the effective interaction $w_{eff}(\mathbf{r})$.

By optimally choosing the effective interaction, one can rely on strong points of both WFT and DFT!!

2. WFT is responsible for the Schrödinger equation

→ $\hat{H}_{KS}|\Psi_{KS}\rangle = E|\Psi_{KS}\rangle$

Exact Kohn-Sham potentials for effectively interacting KS systems

1D Helium (1-dimensional 2-electron system)

$$\hat{H}\Psi(x_1, x_2) = E\Psi(x_1, x_2)$$

$$\hat{H} = \sum_{j=1}^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial x_j^2} + v_{ext}(x_j) \right] + w(|x_1 - x_2|)$$

Nuclear potential $v_{ext}(x) = -\frac{2}{\sqrt{x^2 + \sigma^2}}$

Interaction $w(x) = \frac{1}{\sqrt{x^2 + \sigma^2}}$

Softening parameter $\sigma = 0.5$ a.u.



Effectively interacting Kohn-Sham systems

$$\hat{H}_{KS} = \sum_{j=1}^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial x_j^2} + v_{KS}(x_j) \right] + w_{eff}(|x_1 - x_2|)$$

1. No-interacting system

$$w_{eff}(x) = 0$$

2. 1/4-interacting system

$$w_{eff}(x) = \frac{1}{4} w(x)$$

3. Long-range interacting system

$$w_{eff}(x) = \operatorname{erf}\left(\sqrt{x^2 + \sigma^2}\right) w(x)$$

How to obtain the exact Kohn-Sham potential (Iterative procedure)

1. Compute the target density by solving the many-body Schrödinger equation

$$\hat{H}\Psi(x_1, x_2) = E\Psi(x_1, x_2) \quad \longrightarrow \quad \rho^{target}(x) = 2 \int dx' |\Psi(x, x')|^2$$

2. Compute the density of the Kohn-Sham system under a trial potential $v_{KS}^{(i)}(x)$

$$\hat{H}_{KS}\Psi_{KS}(x_1, x_2) = E_{KS}\Psi_{KS}(x_1, x_2)$$

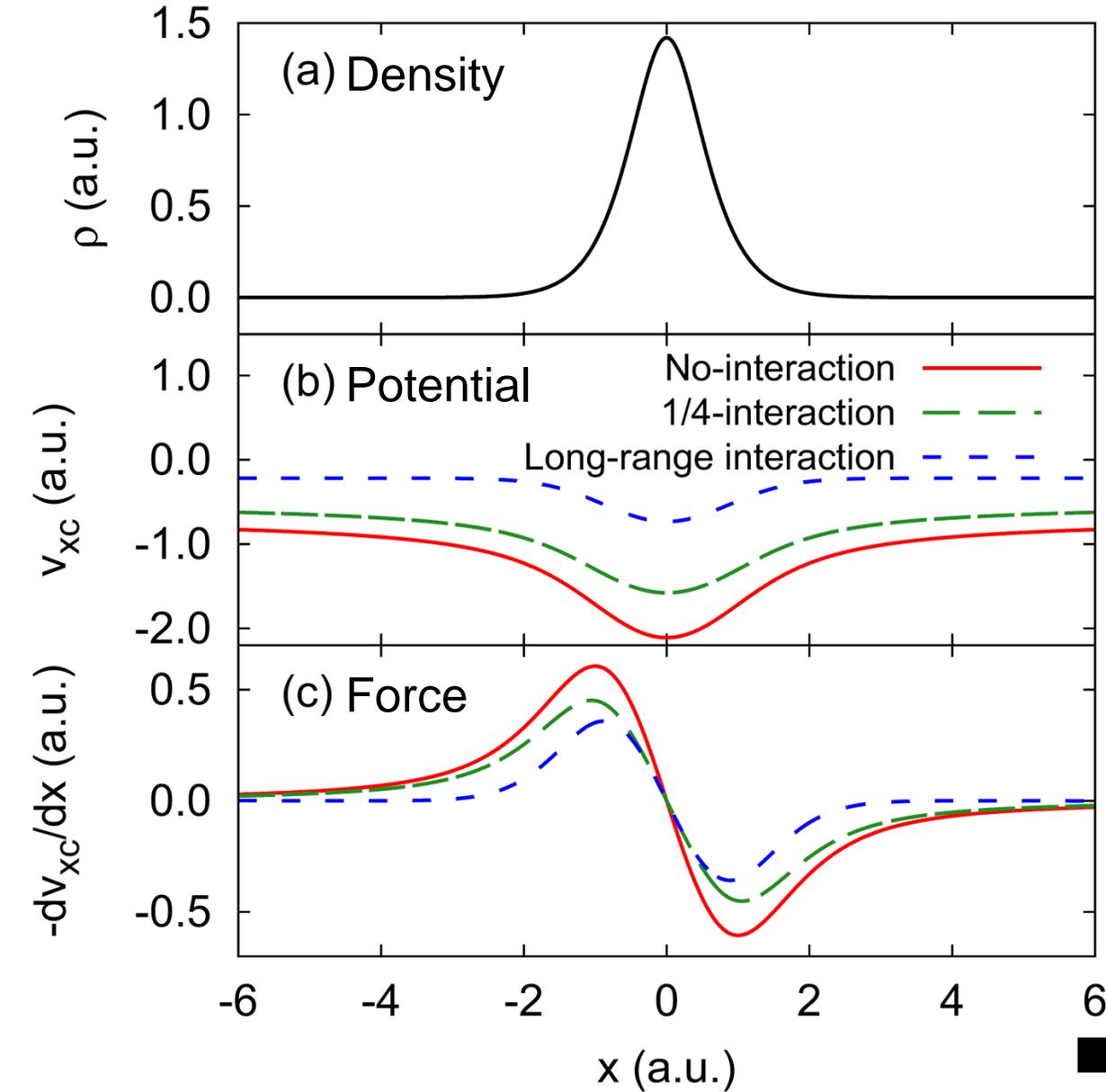
$$\hat{H}_{KS} = \sum_{j=1}^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial^2 x_j} + v_{KS}^{(i)}(x_j) \right] + w_{eff}(|x_1 - x_2|) \quad \longrightarrow \quad \rho^{(i)}(x) = 2 \int dx' |\Psi_{KS}(x, x')|^2$$

3. Update the Kohn-Sham potential and return to the procedure 2.

$$v_{KS}^{(i+1)}(x) = v_{KS}^{(i)}(x) + \alpha \frac{\rho^{(i)}(x) - \rho^{target}(x)}{\rho^{(i)}(x) + \rho^{target}(x) + \epsilon}$$

4. Repeat the procedures 2 and 3 until the residual error, $|\rho^{(i)}(x) - \rho^{target}(x)|$, becomes small enough

Exact exchange-correlation potential for 1D Helium atom



Exchange-correlation potential

$$v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H^{res}(\mathbf{r}) + v_{xc}(\mathbf{r})$$

$$v_H^{res}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w_{res}(\mathbf{r} - \mathbf{r}')$$

$$w_{res}(\mathbf{r}) \equiv w(\mathbf{r}) - w_{eff}(\mathbf{r})$$

1. No-interacting system

$$w_{eff}(x) = 0$$

2. 1/4-interacting system

$$w_{eff}(x) = \frac{1}{4} w(x)$$

3. Long-range interacting system

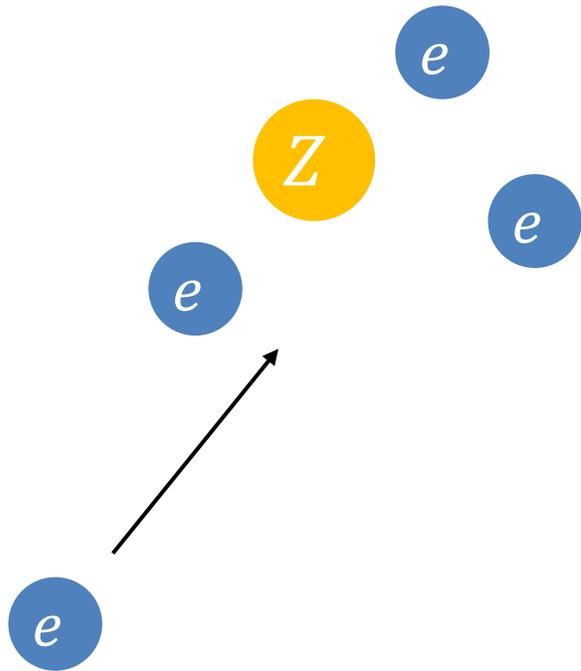
$$w_{eff}(x) = \text{erf}\left(\sqrt{x^2 + \sigma^2}\right) w(x)$$

Long-range interacting system has the weakest exchange-correlation force!

Asymptotic behavior of the exact exchange-correlation potential

R. van Leeuwen and E. J. Baerends, Phys. Rev. A 49, 2421 (1994).

For simplicity, here we consider an atom with nuclear charge Z surrounded by N electrons.



A far electron should see the charge of $Z - (N - 1)$.

$$V_{KS}(\mathbf{r}) = -\frac{Z}{r} + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

For large r (far from nucleus)

$$V_{KS}(\mathbf{r}) \approx -\frac{Z}{r} + \frac{N}{r} + v_{xc}(\mathbf{r})$$

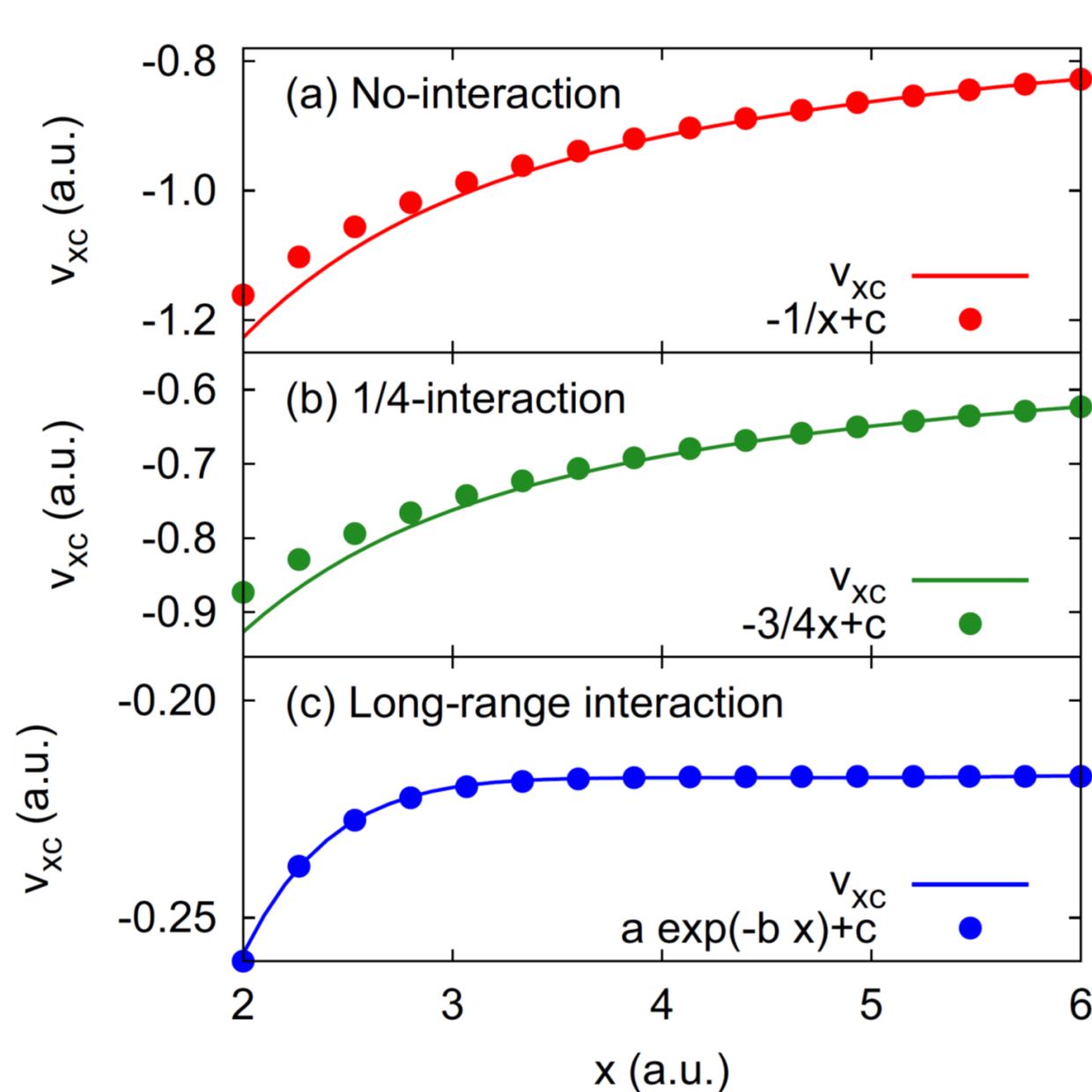
$$\approx -\frac{Z}{r} + \frac{N - 1}{r}$$



$v_{xc}(\mathbf{r})$ potential should have the following asymptotics:

$$v_{xc}(\mathbf{r}) \approx -\frac{1}{r} \quad \text{for large } r$$

Exact exchange-correlation potential for 1D Helium atom



Asymptotics of $v_{xc}(\mathbf{r})$

➔ Asymptotics of $-\frac{1}{x}$
(Typical Coulomb system)

➔ Asymptotics of $-\frac{3}{4} \frac{1}{x}$
(identical to the residual interaction)
 $w_{res}(\mathbf{r}) = w(\mathbf{r}) - w_{eff}(\mathbf{r})$

➔ Exponential decay
(identical to the decay of density)

➔ Local density approximation (LDA)
may work well?

Electronic correlation in the many-body wavefunction

Electronic correlation → Effects cannot be described by a single-Slater determinant

$$\hat{H}\Psi(x_1, x_2) = E\Psi(x_1, x_2)$$

Natural orbital analysis

$$\rho^{1RDM}(x, x') = 2 \int dx_2 \Psi(x, x_2) \Psi^*(x', x_2) = \sum_j n_j \phi_j^{NO}(x) \phi_j^{NO,*}(x)$$

$0 \leq n_j \leq 1$

If there is no electronic correlation (the case of the single Slater determinant):

$$n_j = 1 \text{ (for } 1 \leq j \leq N_{elec}\text{)}$$

$$n_j = 0 \text{ (otherwise)}$$

If many Slater determinants are required, many orbitals have non-zero occupation.

A set of natural orbitals provides a minimum number of configurations (multi-Slater determinants).

Electronic correlation in the many-body wavefunction

Electronic correlation  Effects cannot be described by a single-Slater determinant

$$\hat{H}\Psi(x_1, x_2) = E\Psi(x_1, x_2)$$

$$0 \leq n_j \leq 1$$

Natural orbital analysis

$$\rho^{1RDM}(x, x') = \sum_j n_j \phi_j^{NO}(x) \phi_j^{NO,*}(x)$$

$$\approx \sum_{j=1}^{N_{tra}} n_j \phi_j^{NO}(x) \phi_j^{NO,*}(x)$$

Assuming the decreasing order

$$n_1 \geq n_2 \geq n_j \geq \dots$$

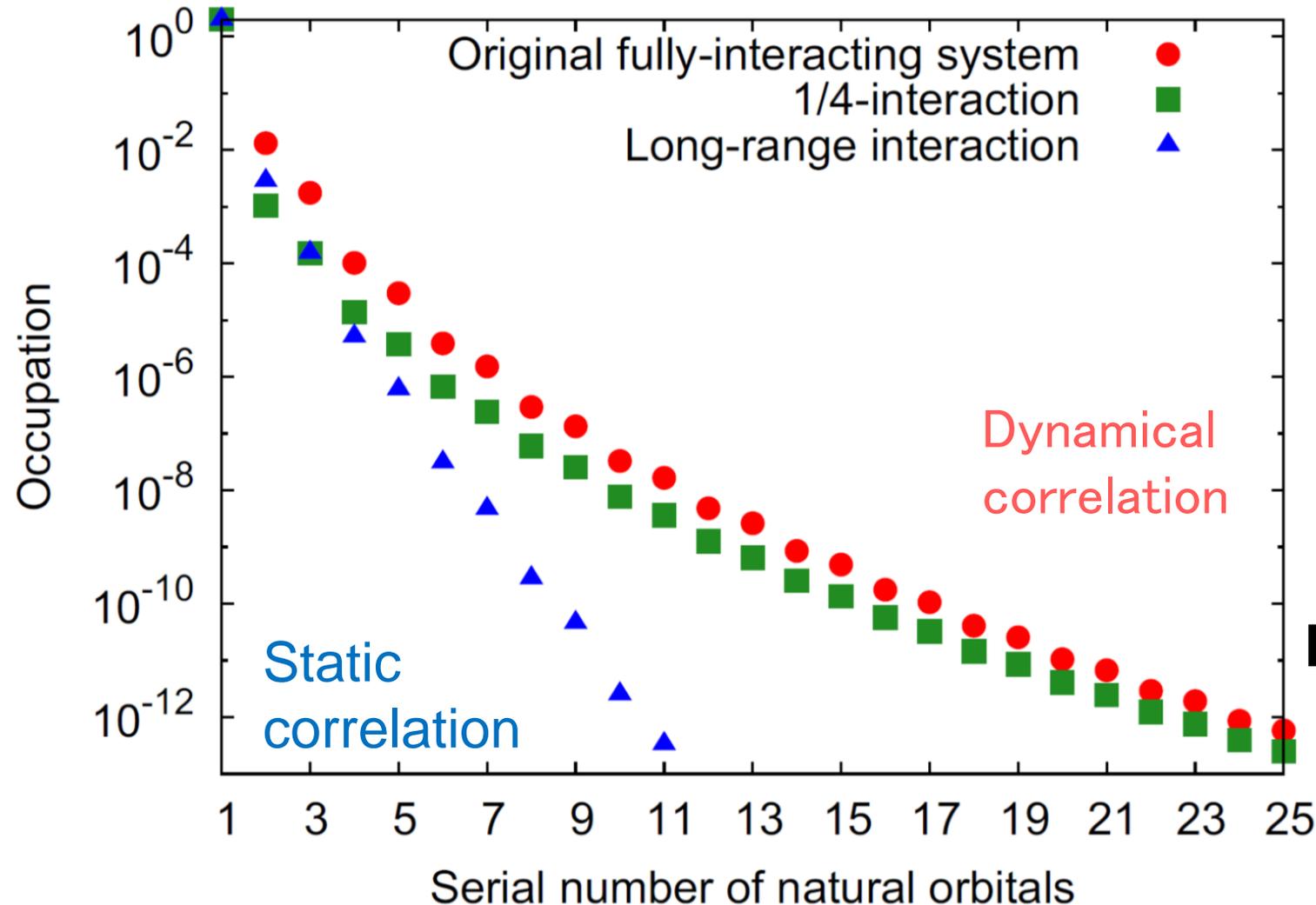
The natural orbitals give the best low rank approximation of the 1RDM.

Eckart–Young–Mirsky theorem for the low rank approximation and the singular value decomposition.

Electronic correlation in effectively-interacting KS systems

Test case for 1D Helium (2-electron system)

Occupation distribution of natural orbitals



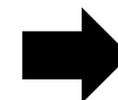
1. Fully-interacting system

2. $\frac{1}{4}$ -interacting system

$$w_{eff}(x) = \frac{1}{4} w(x)$$

3. Long-range interacting system

$$w_{eff}(x) = \text{erf}\left(\sqrt{x^2 + \sigma^2}\right) w(x)$$

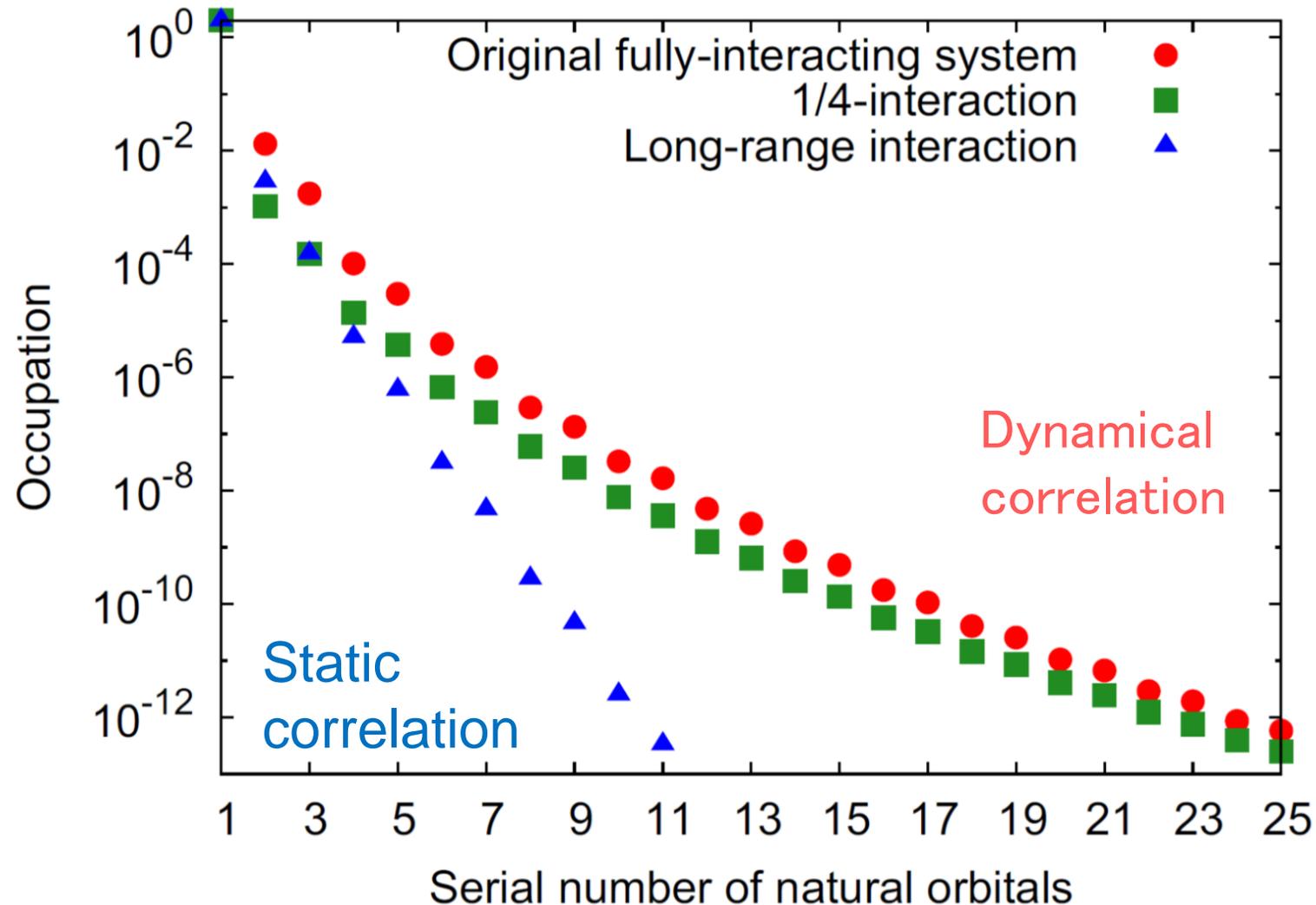


Long-range interacting system requires a smaller number of Slater determinants!

Electronic correlation in effectively-interacting KS systems

Test case for 1D Helium (2-electron system)

Occupation distribution of natural orbitals



Static correlation

The correlation can be well described by a **small number of Slater determinants**.

WFT tends to well describe it, while **DFT tends to fail to describe**.

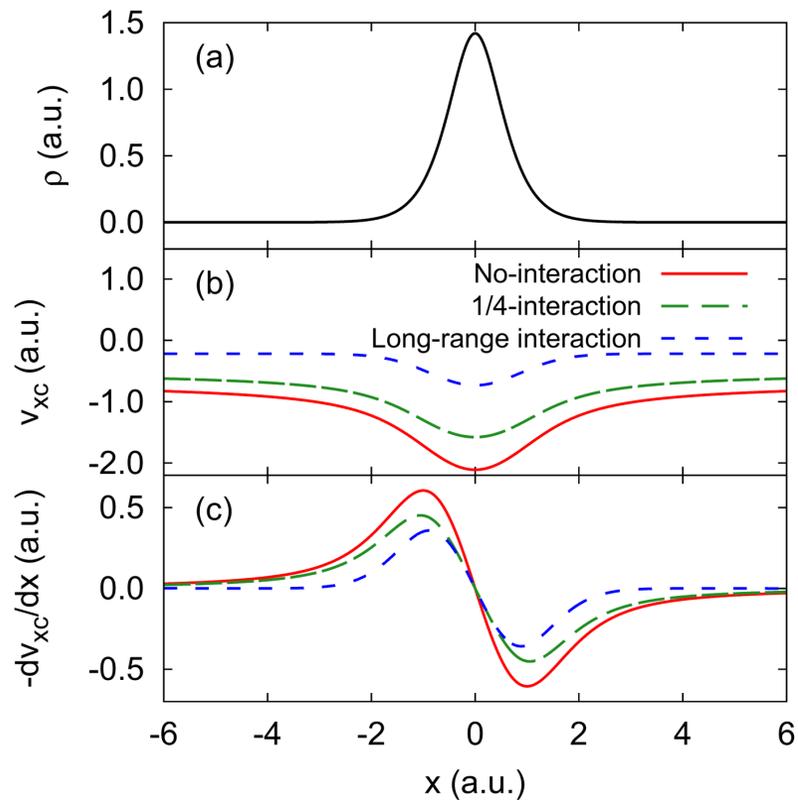
Dynamical correlation

The correlation can be well described by **many Slater determinants**.

WFT tends to fail to describe it, while **DFT tends to well describe**.

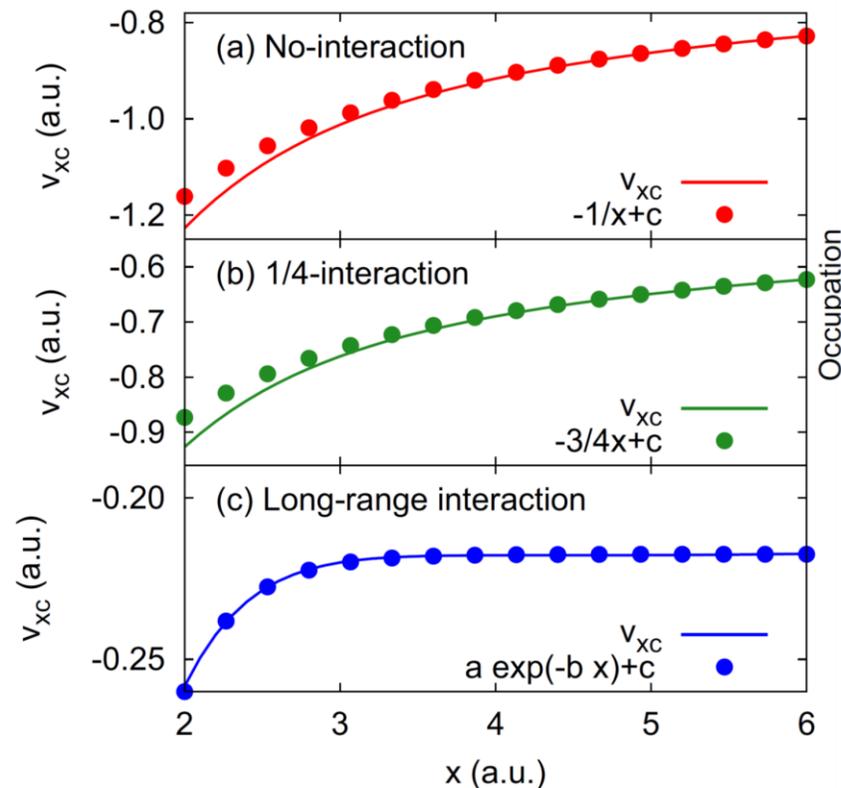
Properties of effectively-interacting Kohn-Sham systems

Exact exchange-correlation potential

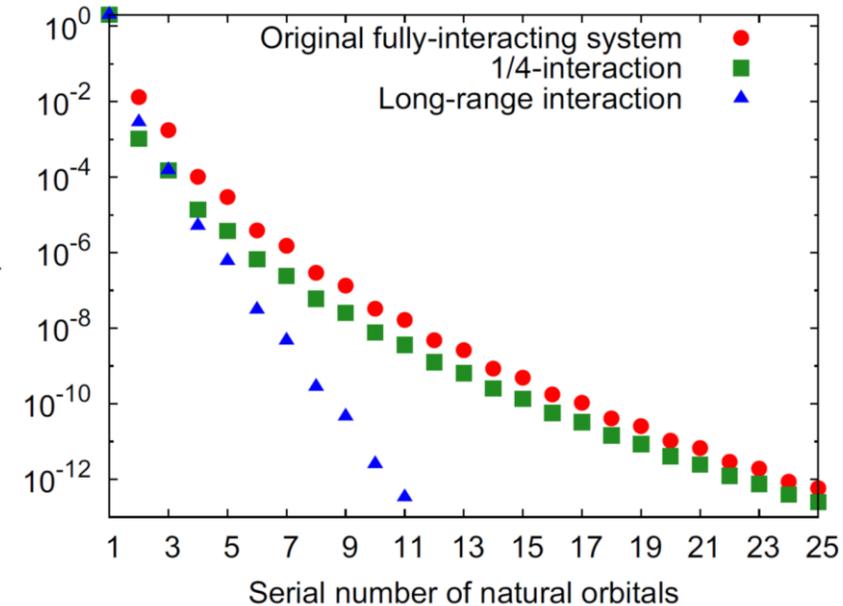


Asymptotics of $v_{xc}(r)$

SAS, A Rubio, PRA 101, 012510 (2020)



Correlation in the wavefunction



The long-range interacting KS system has the weakest exchange-correlation potential with a simpler asymptotics. Moreover, its wavefunction contains the weaker correlation.

With the range-separation, DFT can take care its preferred dynamical correlation, while the WFT can take care its preferred static correlation.

Background

- ❑ Wavefunction theory (WFT) tends to be accurate but high cost. On the other hand, DFT tends to be low cost but less accurate.

This work

- ❑ We want to develop a low-cost & high-accuracy method by combining WFT and DFT.
- ❑ For this, we studied the exact Kohn-Sham potential of effectively-interacting Kohn-Sham systems.
- ❑ The results indicate that the range-separation of Coulomb interaction with the effectively-interacting Kohn-Sham systems can offer a combination of DFT and WFT, where the static correlation can be treated in the WFT, while the dynamical correlation can be treated in the DFT (right theory in the right place!).

Outlook

- ❑ Developing the local density approximation for effectively-interacting KS system.
- ❑ Extension of the analysis to time-dependent Systems.

1. Analysis on partially/effectively interacting Kohn-Sham systems towards the combined theory of DFT and WFT
2. Conditional wavefunction theory for scattering problems beyond mean-field methods

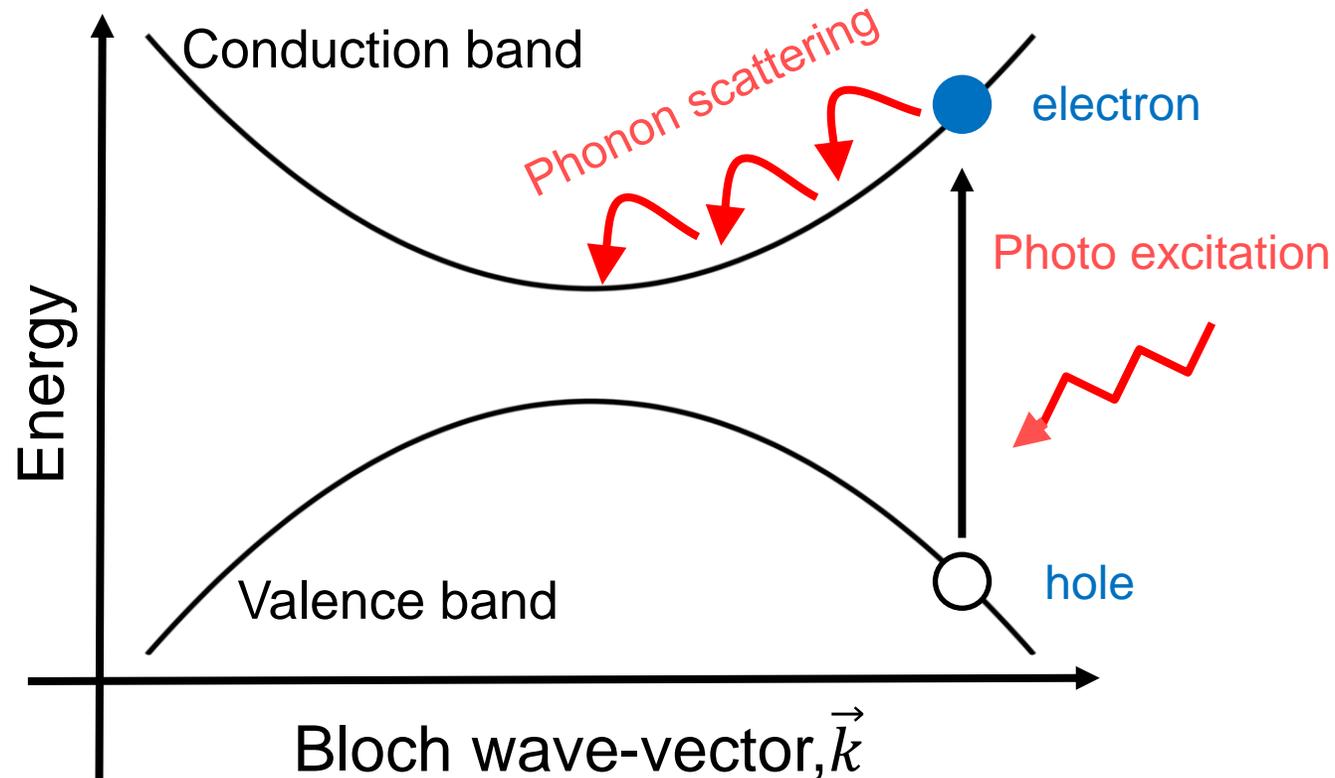
Introduction: Conditional wavefunction theory

- Aim of research

Accurate description of particle-particle scattering process

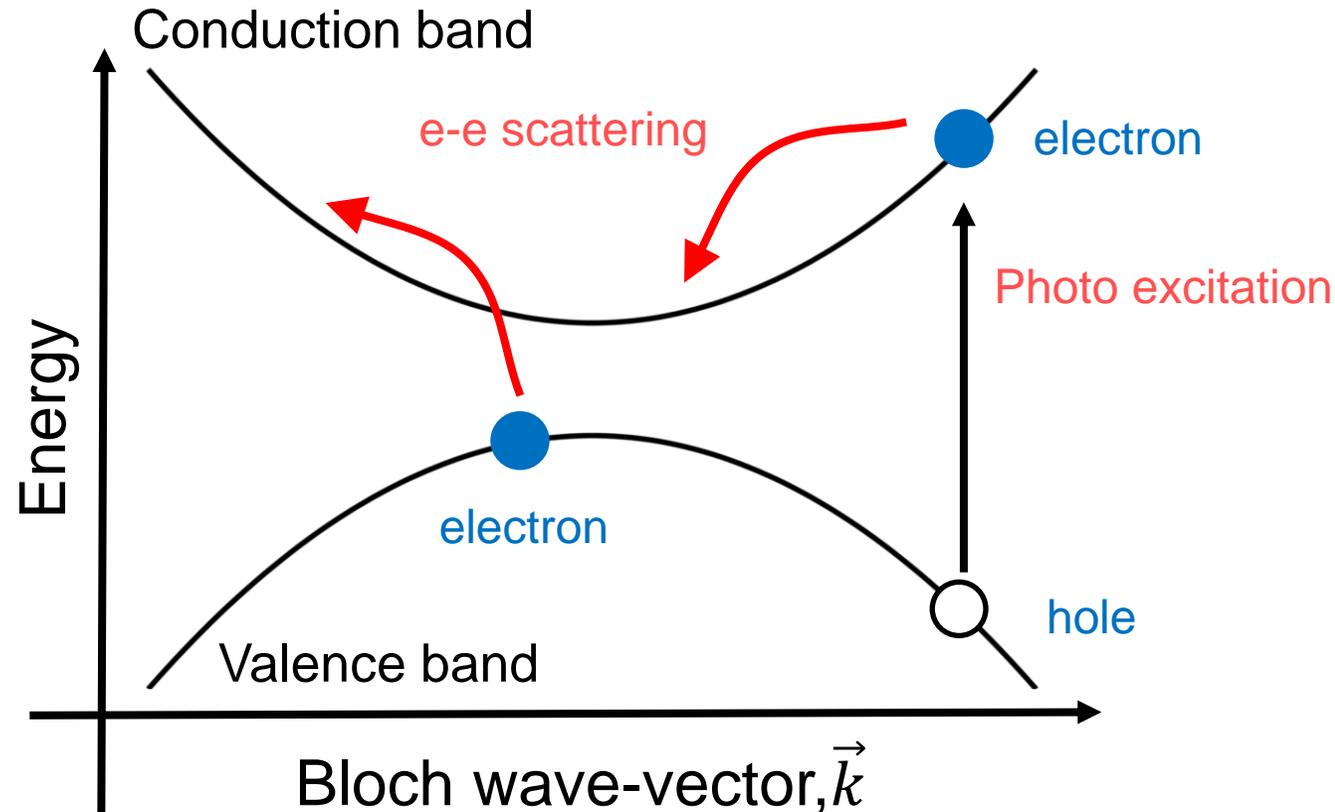
- Why scattering?

(i) Relaxation of photo-carrier (**electron-phonon scattering**)



Introduction: Conditional wavefunction theory

(ii) Relaxation of photo-carrier (**electron-electron scattering**)

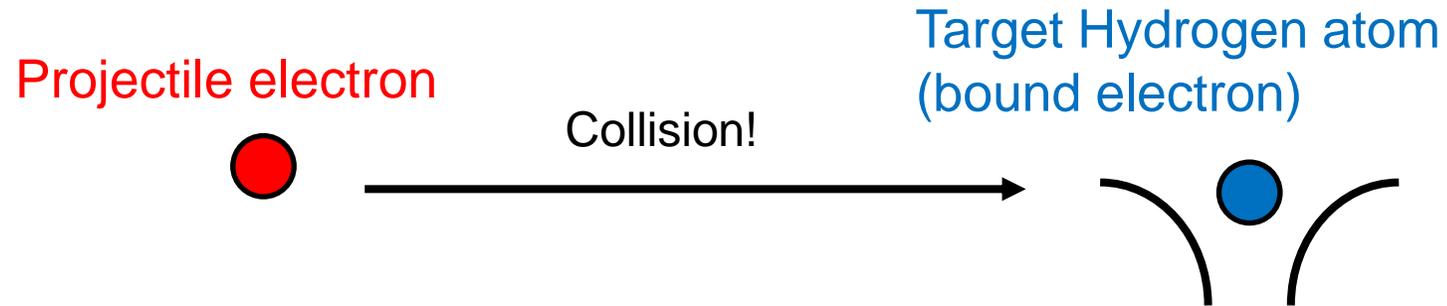


Particle-particle scattering process is important to describe photo-induced nonequilibrium dynamics (**excitation/relaxation**)!

However, it is difficult to describe by a mean-field theory...

Failure of mean-field theory for scattering

Example: Impact ionization (e-e scattering in 1D)



Projectile electron

- Gaussian wavepacket with the Kinetic energy of 0.6 a.u.

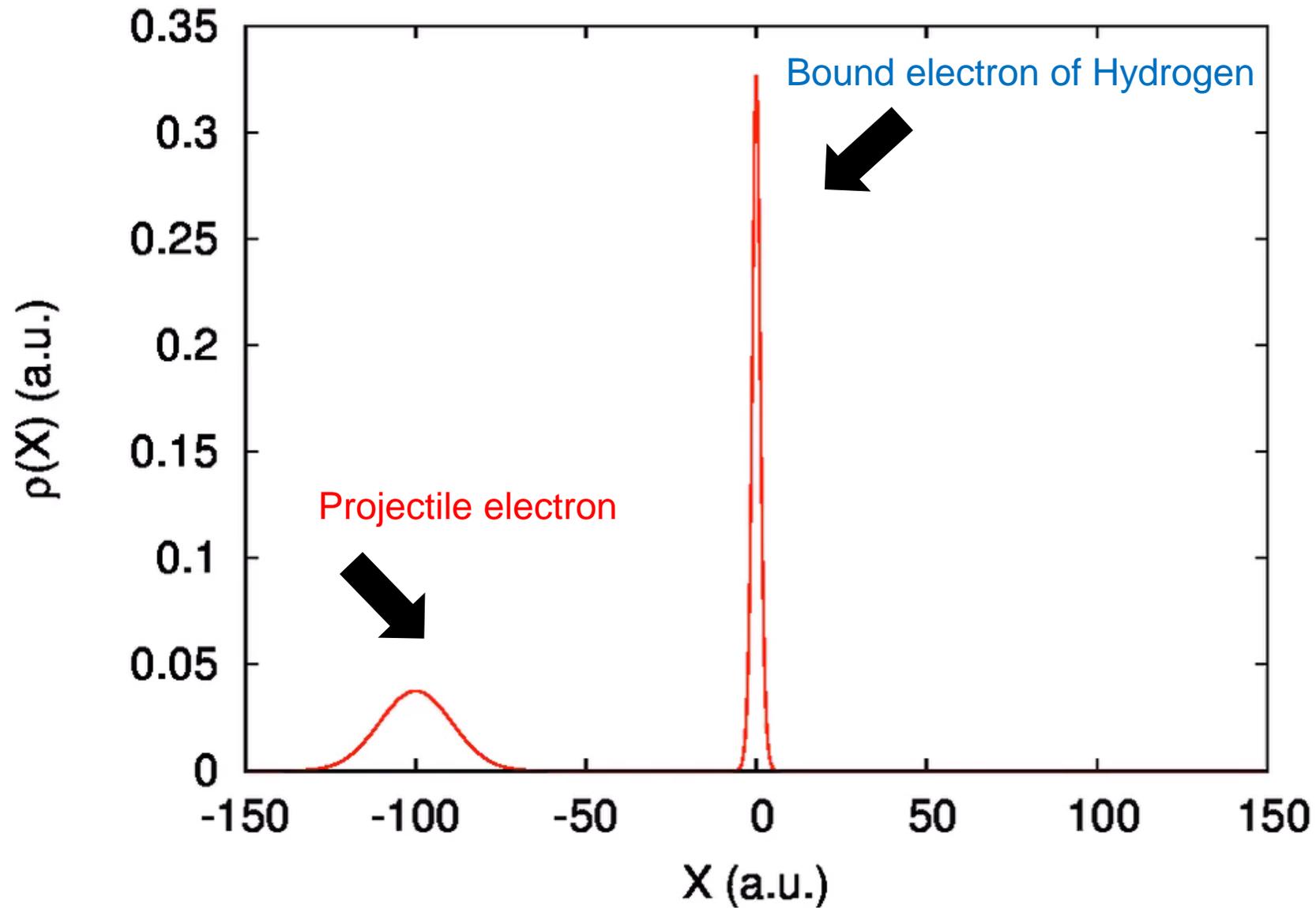
Target 1D Hydrogen

- One electron is bound by the soft Coulomb, $v_{proton}(x) = -1/\sqrt{2+x^2}$.
- The binding energy is 0.5 a.u.

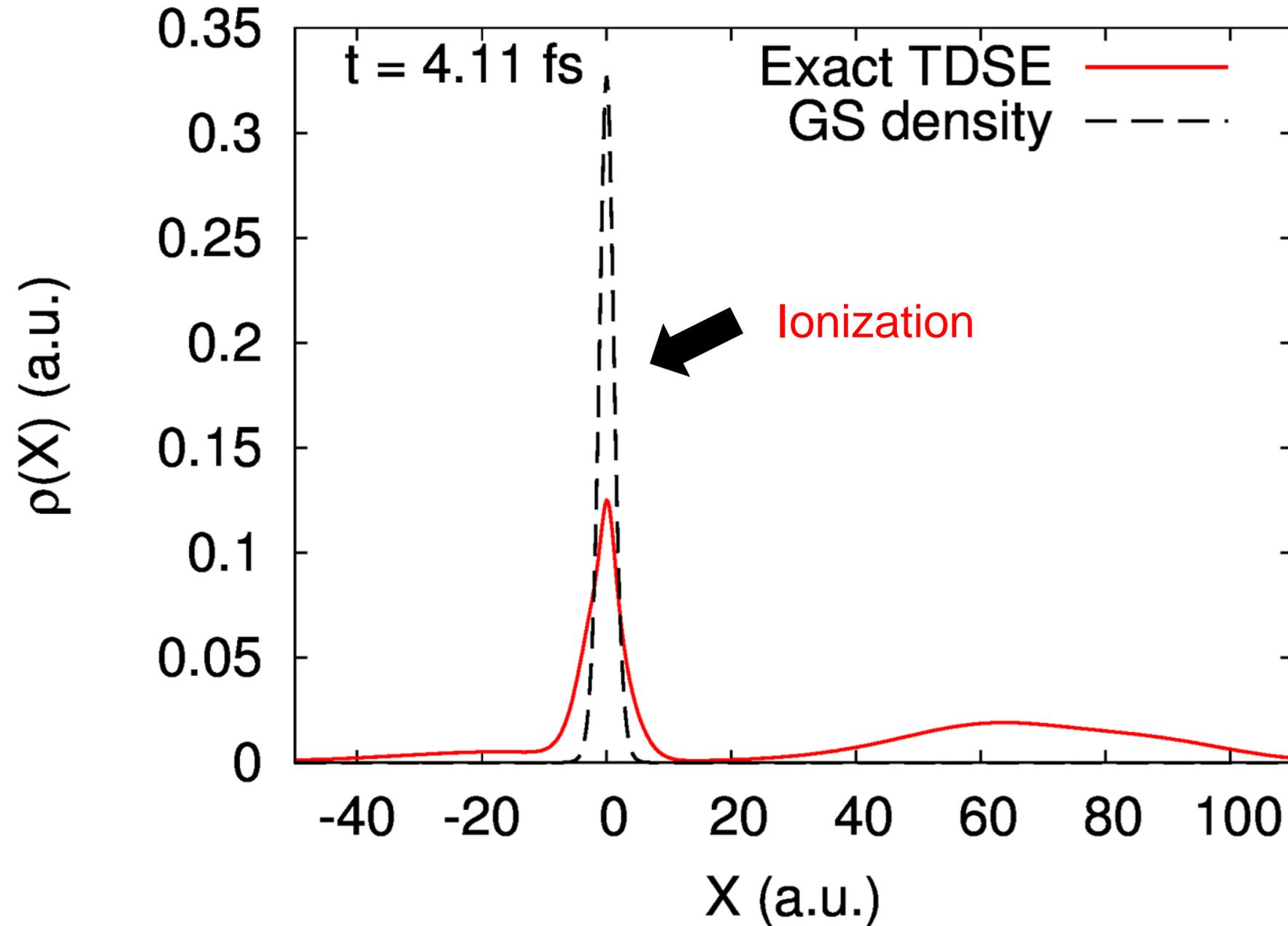
Kinetic energy is larger than the binding energy!

Impact ionization in 1D system

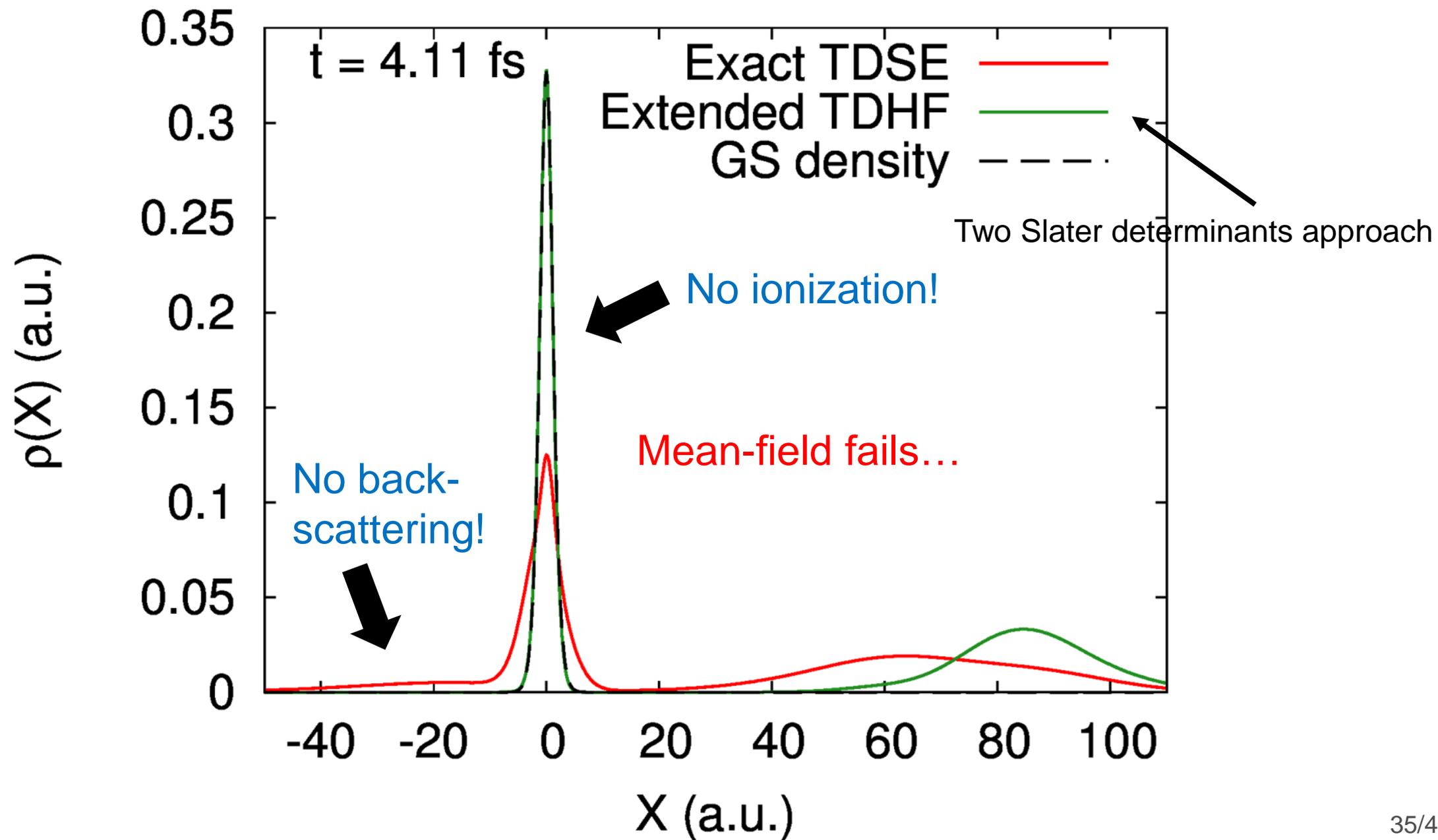
Result of Exact TDSE simulation



Failure of mean-field theory for scattering



Failure of mean-field theory for scattering



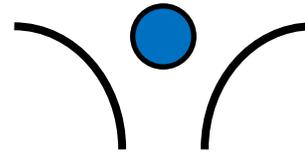
Failure of mean-field theory for scattering

Realistic scattering process (**classical description**)

Projectile electron



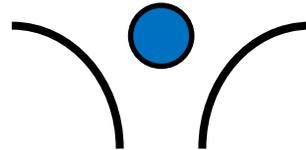
Target Hydrogen atom
(bound electron)



Mean-field description



Electron cloud



Does classical trajectory help to capture correlation?

Conditional wavefunction approach

G. Albareda, et al, PRL 113, 083003 (2014)

Schrodinger equation for 1D two-particle system

$$i \frac{\partial}{\partial t} \Psi(x_e, X_i, t) = \hat{H} \Psi(x_e, X_i, t)$$

$$H = T_e + T_i + v(x_e) + V(X_i) + w(x_e, X_i)$$

Conditional wavefunctions

Electronic part

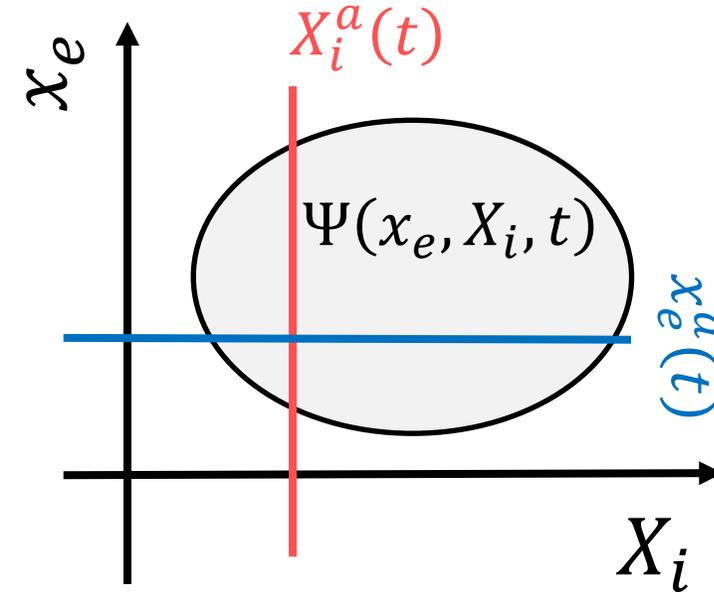
$$\phi_{elec}^a(x_e, t) := \Psi(x_e, X_i^a(t), t)$$

$$i \frac{\partial}{\partial t} \phi_{elec}^a(x_e, t) = [T_e + v(x_e) + w(x_e, X_i^a(t)) + \eta_{elec}^a(x_e)] \phi_{elec}^a(x_e, t)$$

Ionic part

$$\phi_{ion}^a(X_i, t) := \Psi(x_e^a(t), X_i, t)$$

$$i \frac{\partial}{\partial t} \phi_{ion}^a(X_i, t) = [T_i + V(X_i) + w(x_e^a(t), X_i) + \eta_{ion}^a(X_i)] \phi_{ion}^a(X_i, t)$$



Conditional wavefunction approach

G. Albareda, et al, PRL 113, 083003 (2014)

Schrodinger equation for 1D two-particle system

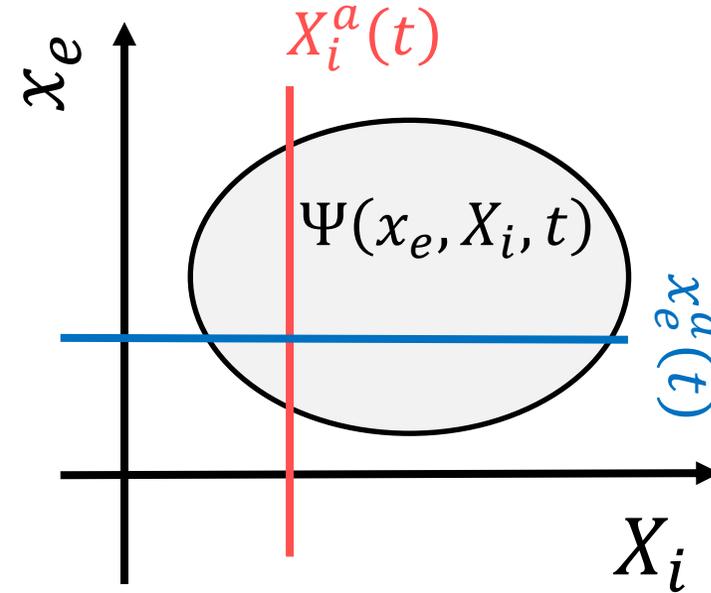
$$i \frac{\partial}{\partial t} \Psi(x_e, X_i, t) = \hat{H} \Psi(x_e, X_i, t)$$

$$H = T_e + T_i + v(x_e) + V(X_i) + w(x_e, X_i)$$

Conditional wavefunctions

$$\phi_{elec}^a(x_e, t) := \Psi(x_e, X_i^a(t), t)$$

$$\phi_{ion}^a(X_i, t) := \Psi(x_e^a(t), X_i, t)$$



Bohmian trajectory

$$\frac{d}{dt} x_e^a(t) = \frac{j_{elec}(x_e^a(t))}{\rho_{elec}(x_e^a(t))} = \frac{\text{Re} \left[\phi_{elec}^{a,*}(x_e, t) \frac{1}{i} \frac{\partial}{\partial x_e} \phi_{elec}^a(x_e, t) \right]_{x_e=x_e^a(t)}}{|\phi_{elec}^a(x_e^a(t), t)|^2}$$

$$\frac{d}{dt} X_i^a(t) = \frac{j_{ion}(X_i^a(t))}{\rho_{ion}(X_i^a(t))}$$

Conditional wavefunction approach

Conditional wavefunction scheme with Hermitian approximation

$$i \frac{\partial}{\partial t} \phi_{elec}^a(x_e, t) = [T_e + v(x_e) + w[x_e, X_i^a(t)] + \cancel{\eta_{elec}^a(x_e)}] \phi_{elec}^a(x_e, t)$$

$$i \frac{\partial}{\partial t} \phi_{ion}^a(X_i, t) = [T_i + V(X_i) + w[x_e^a(t), X_i] + \cancel{\eta_{ion}^a(X_i)}] \phi_{ion}^a(X_i, t)$$

Bohmian trajectory

$$\frac{d}{dt} x_e^a(t) = \frac{j_{elec}(x_e^a(t))}{\rho_{elec}(x_e^a(t))} = \frac{\text{Re} \left[\phi_{elec}^{a,*}(x_e, t) \frac{1}{i} \frac{\partial}{\partial x_e} \phi_{elec}^a(x_e, t) \right]_{x_e=x_e^a(t)}}{|\phi_{elec}^a(x_e^a(t), t)|^2}$$

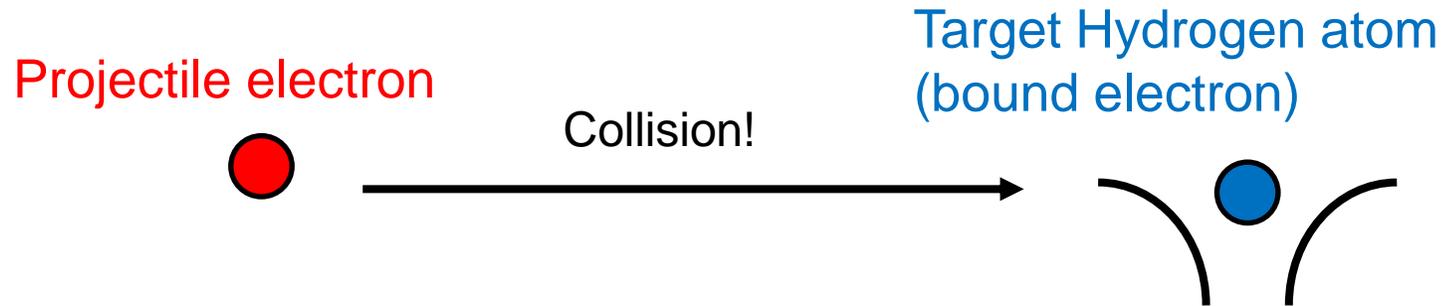
$$\frac{d}{dt} X_i^a(t) = \frac{j_{ion}(X_i^a(t))}{\rho_{ion}(X_i^a(t))}$$

Observable

$$\langle A \rangle = \sum_a \frac{\langle \phi_{elec}^a | A | \phi_{elec}^a \rangle}{\langle \phi_{elec}^a | \phi_{elec}^a \rangle} = \sum_a \frac{\langle \phi_{ion}^a | A | \phi_{ion}^a \rangle}{\langle \phi_{ion}^a | \phi_{ion}^a \rangle}$$

Impact ionization in 1D hydrogen

Example: Impact ionization (e-e scattering in 1D)



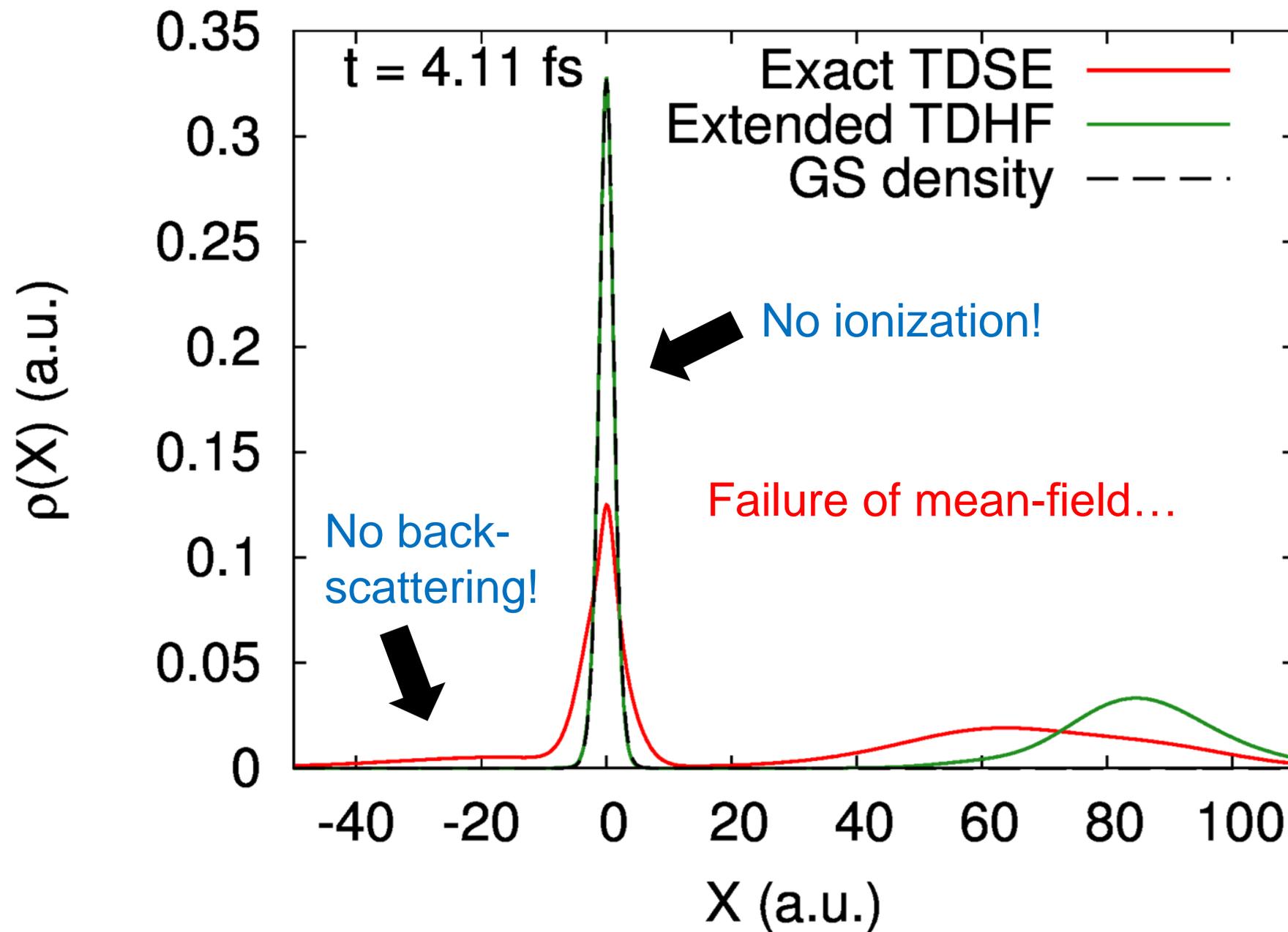
Projectile electron

- Gaussian wavepacket with the Kinetic energy of 0.6 a.u.

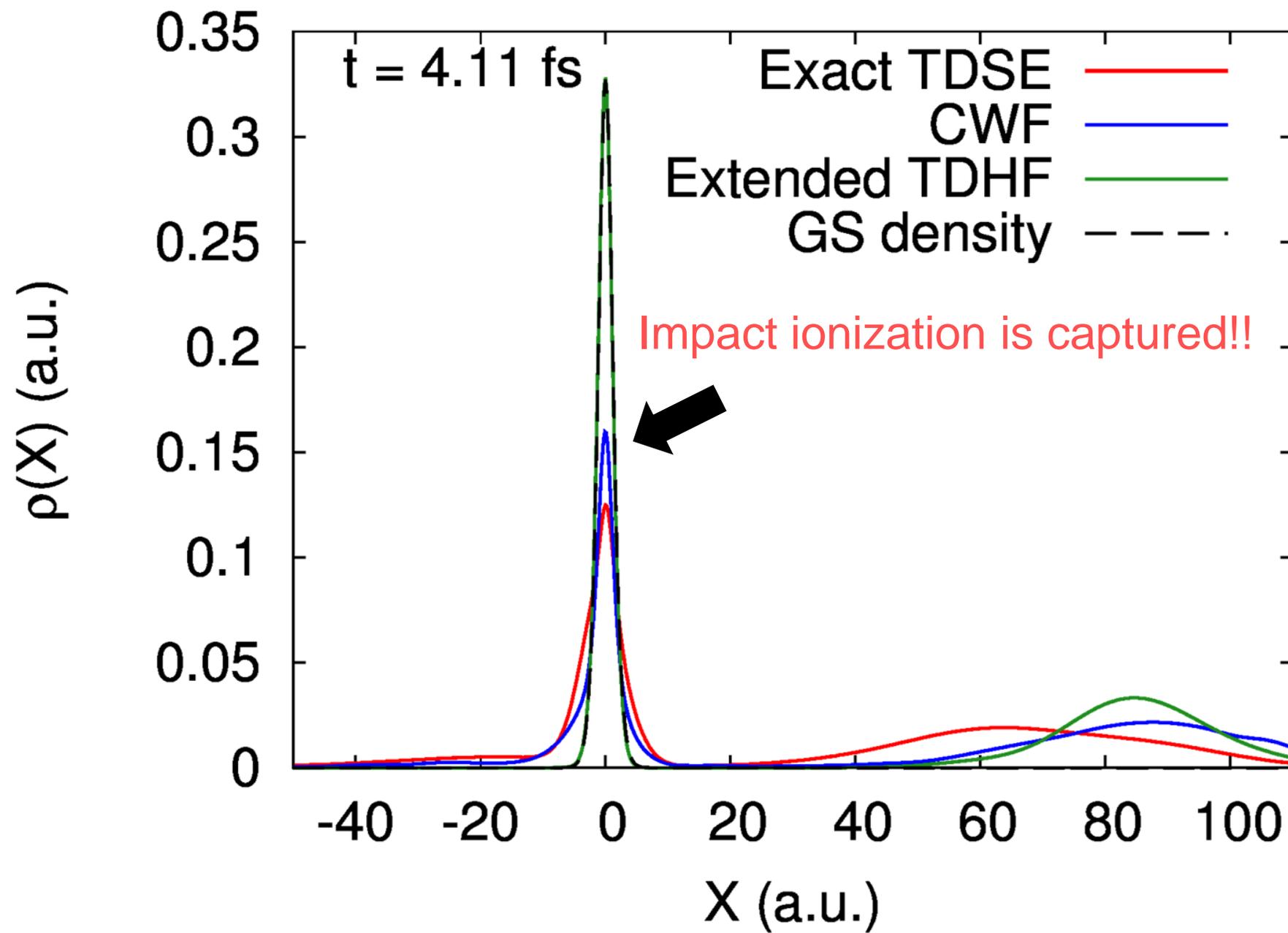
Target 1D Hydrogen

- One electron is bound by the soft Coulomb, $v_{proton}(x) = -1/\sqrt{2 + x^2}$.
- The binding energy is 0.5 a.u.

Impact ionization in 1D hydrogen



Impact ionization in 1D hydrogen



Summary

- We are investigating many-body phenomena (e-e, electron-ion, and so on) based on **the conditional wavefunction approach**.
G. Albareda, K. Lively, SAS, A. Kelly, A. Rubio, J. Chem. Theory Comput. 17, 7321 (2021)
- The conditional wavefunction approach considers **semi-classical (Bohmian) trajectories** in addition to **wavefunction**.
- The semi-classical trajectories help to capture **important correlation effect** for scattering problems.

Out look

- Develop more accurate description beyond the Hermitian approximation.
G. Albareda, K. Lively, SAS, A. Kelly, A. Rubio, J. Chem. Theory Comput. 17, 7321 (2021)
- Develop more realistic description combining ab-initio scheme (e.g. TDDFT)
- More applications.

Thank you for your attention!