

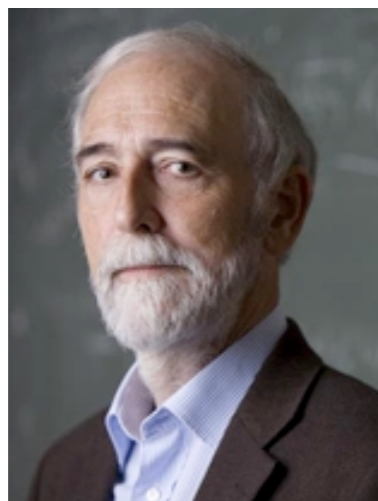
# Density Functional Theory for Strongly- Correlated Systems

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# my background...

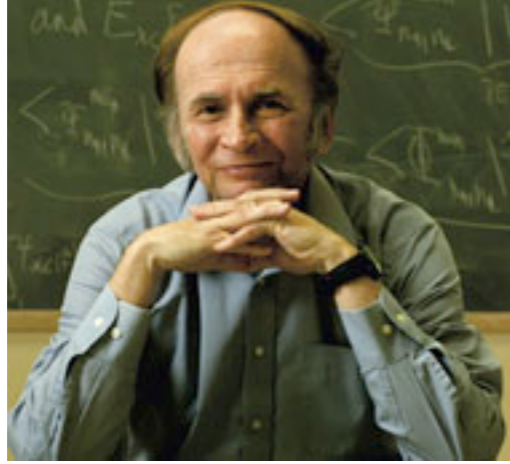
Postdoc in New Orleans, US

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# My DFT teachers



John Perdew

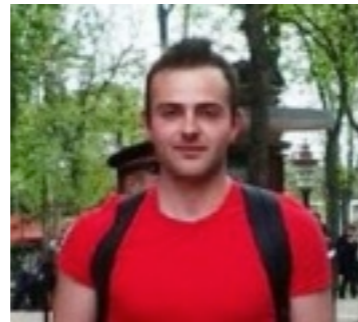


Andreas Savin

# Research group



André Mirtschink



Stefan Vuckovic

## PhD students



Francesc Malet



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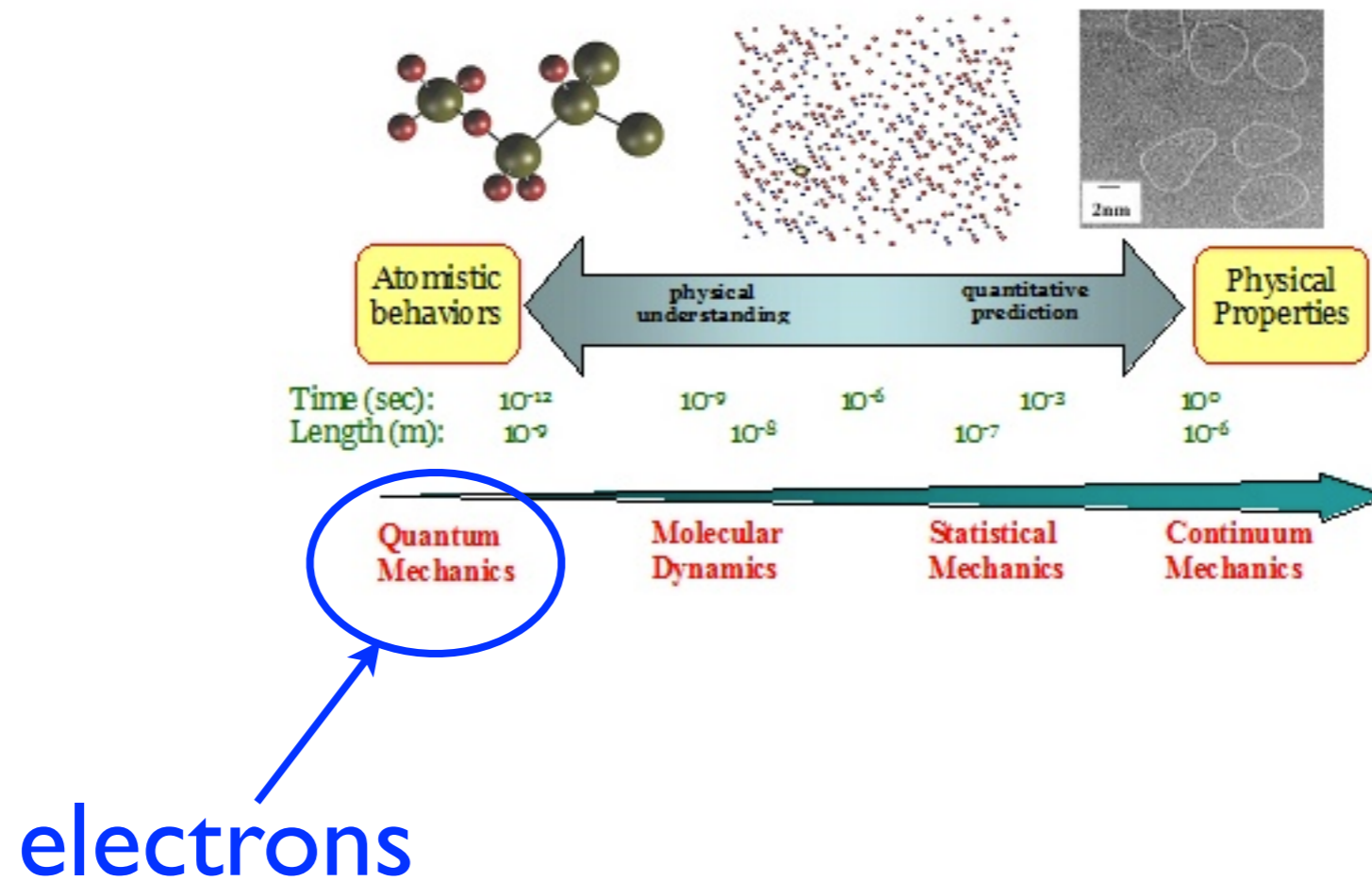


Giovanna Lani  
(starting May 2014)

## postdocs



# Different scales need different treatments



# Many-electron hamiltonian (Born-Oppenheimer)

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

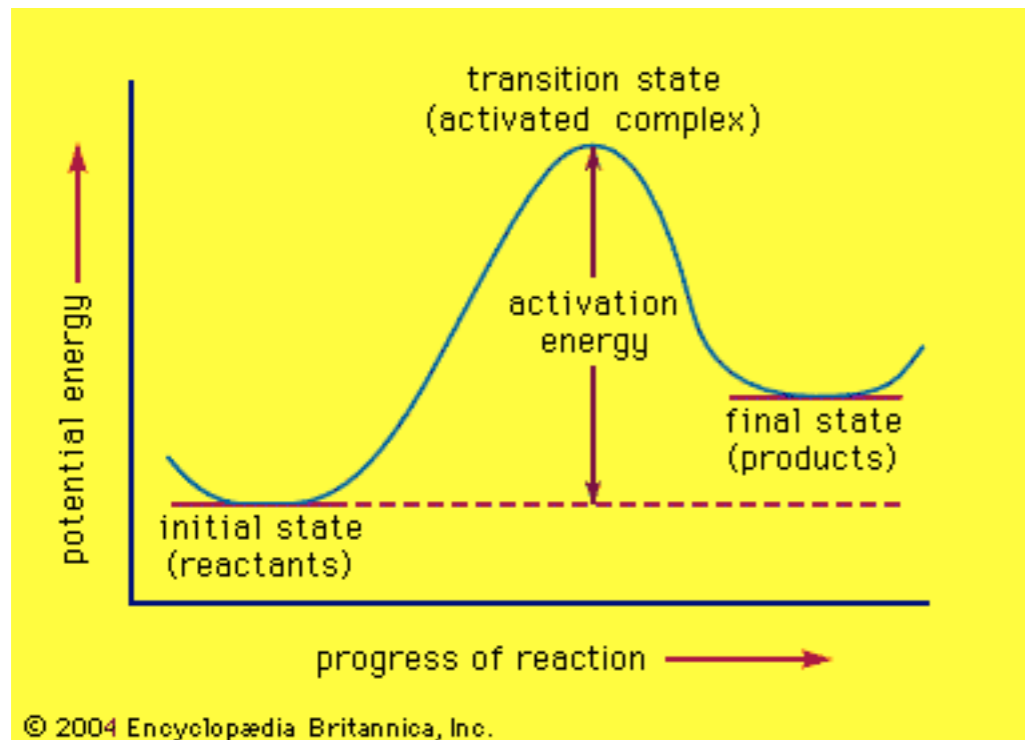
$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$$

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|}$$

$$\hat{H}\Psi = E_0\Psi$$

$$E_0 = E_0(\mathbf{R}_{\alpha})$$

nuclei move in the  
electronic potential  
energy



# Electrons are fermions...

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

with fermionic (spin 1/2) antisymmetry

Mathematically, we don't look for the ground-state of the hamiltonian operator  $H$   
(the lowest energy state is always the bosonic one).

We look for the lowest state with the fermionic antisymmetry



## Wave-function methods, e.g:

CI, CC expand the wavefunction as sum of Slater determinants  
(antisymmetry automatically fulfilled)

QMC project the ground state with stochastic techniques  
(antisymmetry needs to be imposed - e.g. fix the nodes)

## Methods based on reduced quantities

(Hamiltonian has only 2- and 1-body operators)

2<sup>nd</sup>-order reduced density matrix

1<sup>st</sup>-order reduced density matrix

pair density

density (DFT)

# Energy and reduced density matrices

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad \hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$$

we don't need the whole wavefunction to compute the energy

## 2<sup>nd</sup>-order reduced density matrix

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\sigma_i} \sum_{\sigma'_i} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

enough to compute the energy

## 2<sup>nd</sup>-order reduced density matrix

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\sigma_i} \sum_{\sigma'_i} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

## 1<sup>st</sup>-order reduced density matrix

$$\gamma_1(\mathbf{r}, \mathbf{r}') = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

## pair density

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

## density

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$$

which minimal reduced quantity is needed for which expectation value?

## 2<sup>nd</sup>-order reduced density matrix

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\sigma_i} \sum_{\sigma'_i} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

## 1<sup>st</sup>-order reduced density matrix

$$\gamma_1(\mathbf{r}, \mathbf{r}') = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

## pair density

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

## density

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$$

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{1}{2} \int \nabla_{\mathbf{r}'}^2 \gamma_1(\mathbf{r}, \mathbf{r}') |_{\mathbf{r}=\mathbf{r}'} d\mathbf{r}$$

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int \frac{P_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

## 2<sup>nd</sup>-order reduced density matrix (2-RDM)

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\sigma_i} \sum_{\sigma'_i} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

## 1<sup>st</sup>-order reduced density matrix (1-RDM)

$$\gamma_1(\mathbf{r}, \mathbf{r}') = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

### pair density

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

### density

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{1}{2} \int \nabla_{\mathbf{r}'}^2 \gamma_1(\mathbf{r}, \mathbf{r}') |_{\mathbf{r}=\mathbf{r}'} d\mathbf{r}$$

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int \frac{P_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

we need these 3

However, there is no way to get the 1-RDM from the pair density or viceversa (exception: single Slater determinant). For a general wavefunction only the 2-RDM generates both.

# The energy is a simple functional of the 2-RDM

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2)$$

$$\gamma_1(\mathbf{r}, \mathbf{r}'_1) = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{1}{2} \int \nabla_{\mathbf{r}'}^2 \gamma_1(\mathbf{r}, \mathbf{r}') |_{\mathbf{r}=\mathbf{r}'} d\mathbf{r}$$

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int \frac{P_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

$$E[\gamma_2]$$

then it's easy: just solve, for any number of electrons

$$\min_{\gamma_2} E[\gamma_2]$$

*where is the catch?*

if we try to minimize the exact 2-RDM energy functional

$$\min_{\gamma_2} E[\gamma_2]$$

we get an energy way too low

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

with fermionic (spin 1/2) antisymmetry

The variational principle holds only for 2-RDM's  
obtained from a fermionic wavefunction

The right formulation of the problem is then

$$\min_{\gamma_2 \in \mathcal{N}} E[\gamma_2]$$

$\mathcal{N}$ -representable: it comes from an  $N$ -electron fermionic wavefunction

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\sigma_i} \sum_{\sigma'_i} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

One often reads that the  $N$ -representability conditions for the 2-RDM are not known.

*Actually they are known, but in a form that is useless (way more expensive than CI)*

Nonetheless: work has been done by imposing only some conditions.  
Promising or dead end?

THE UNIVERSITY OF  
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D. Mazziotti

 Ghent Quantum  
Chemistry  
Group

H. van  
Aggelen





$$\gamma_1(\mathbf{r}, \mathbf{r}'_1) = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{1}{2} \int \nabla_{\mathbf{r}'}^2 \gamma_1(\mathbf{r}, \mathbf{r}') |_{\mathbf{r}=\mathbf{r}'} d\mathbf{r}$$

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int \frac{P_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

to reduce further (1-RDM, density...) we need to approximate parts of the energy functional

e.g.  $E[\gamma_1]$  then  $V_{ee}[\gamma_1]??$

## I-RDM functional theory

$$\gamma_1(\mathbf{r}, \mathbf{r}') = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

*N*-representability conditions are known

$V_{ee}[\gamma_1]??$  *needs approximate functionals for the e-e repulsion*

## pair-density functional theory

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

*N*-representability conditions are not known  
(or known but useless)

$T[P_2]??$  *needs approximate functionals for the kinetic energy*

## density functional theory (DFT)

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

*N*-representability conditions are known  
(and very simple to impose)

$T[\rho]??$   $V_{ee}[\rho]??$  *needs approximate functionals for the kinetic energy  
and e-e repulsion*

# I-RDM functional theory

$$\gamma_1(\mathbf{r}, \mathbf{r}'_1) = \frac{1}{N-1} \int \gamma_2(\mathbf{r}, \mathbf{r}_2, \mathbf{r}', \mathbf{r}_2) d\mathbf{r}_2$$

*N*-representability conditions are known

$V_{ee}[\gamma_1]??$  *needs approximate functionals for the e-e repulsion*

## Developing field

TC-VU Amsterdam (Baerends & coworkers)

Max Planck Halle (Gross & coworkers)

San Sebastian (Piris & coworkers)

Lodz (Pernal & coworkers)

# pair-density functional theory

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$$

*N*-representability conditions are not known  
(or known but useless)

$T[P_2]??$  *needs approximate functionals for the kinetic energy*

## Still recent work on it...

McMaster - Canada (Ayers & coworkers)

Japan (Higuchi & Higuchi)

## density functional theory (DFT)

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

*N*-representability conditions are known

$T[\rho]??$   $V_{ee}[\rho]??$  *needs approximate functionals for the kinetic energy and e-e repulsion*

Most widely used method by far in  
electronic structure calculations

*so... it probably works reasonably well!*

# Density Functional Theory

rigorous (Hohenberg-Kohn theorem)

practical, rigorous, formulation: Kohn-Sham equations

Nobel prize in Chemistry 1998  
(shared with John Pople)



Walter Kohn

## density functional theory (DFT)

$$\rho(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r}) = \frac{1}{N-1} \int P_2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2$$

*N*-representability conditions are known

$T[\rho]??$   $V_{ee}[\rho]??$  *needs approximate functionals for the kinetic energy and e-e repulsion*

$$E[\rho] = \boxed{T[\rho] + V_{ee}[\rho]} + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

$F[\rho]$

# Hohenberg-Kohn functional $F$

$$\rho(\mathbf{r}) = \langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$E[\rho] = \boxed{T[\rho] + V_{ee}[\rho]} + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

$F[\rho]$

$$E = \min_{\rho} \left\{ F[\rho] + \int \rho v_{\text{ext}} \right\}$$

$F[\rho]$  is “universal”... why?



# Hohenberg-Kohn DFT

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad \hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$$

are the same for all many-electron systems,  
we just need to know  $N$

$$N = \int \rho(\mathbf{r}) d\mathbf{r}$$

# Many people don't get it....

In an article (I will not mention the authors...) it is argued that the HK functional  $F$  cannot be universal.

As a proof, the authors say that the functional  $F$  is exactly known for the H atom

$$E[\rho] = F[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

$$F[\rho] = -\frac{1}{2} \int \sqrt{\rho(\mathbf{r})} \nabla^2 \sqrt{\rho(\mathbf{r})} d\mathbf{r} \quad \text{H atom}$$

However, if you apply this functional to other systems it does not yield the exact ground-state energies.

So, the functional cannot be universal.

*Why this argument does not make any sense?*

# Hohenberg-Kohn DFT

$$\rho(\mathbf{r}) = \langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$$

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

only a mathematical  
definition: not useful in  
practice!

$$E = \min_{\rho} \left\{ F[\rho] + \int \rho v_{\text{ext}} \right\}$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

## Hohenberg-Kohn Theorem

$$\rho(\mathbf{r}) \Leftrightarrow v_{\text{ext}}(\mathbf{r})$$

Legendre conjugated variables

$$E = \min_{\rho} \left\{ F[\rho] + \int \rho v_{\text{ext}} \right\}$$

$$F[\rho] = \max_v \left\{ E_v - \int \rho v \right\}$$

$$F[\rho] = \max_v \left\{ \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle - \int \rho v \right\}$$

# The exact Hohenberg-Kohn density functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

or, in an operational form:

$$F[\rho] = \max_v \left\{ \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle - \int \rho v \right\}$$

this has been implemented for small systems  
(to show that you can, and to investigate some properties)

You often read that the exact HK functional is unknown

*It is known, but in a form that is useless (way more expensive than CI)*

# Electrons are fermions...

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

with fermionic (spin 1/2) antisymmetry

$E_0[\rho]$  ← how to include the fermionic character ?

**Kohn-Sham DFT**

# Kohn-Sham DFT

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

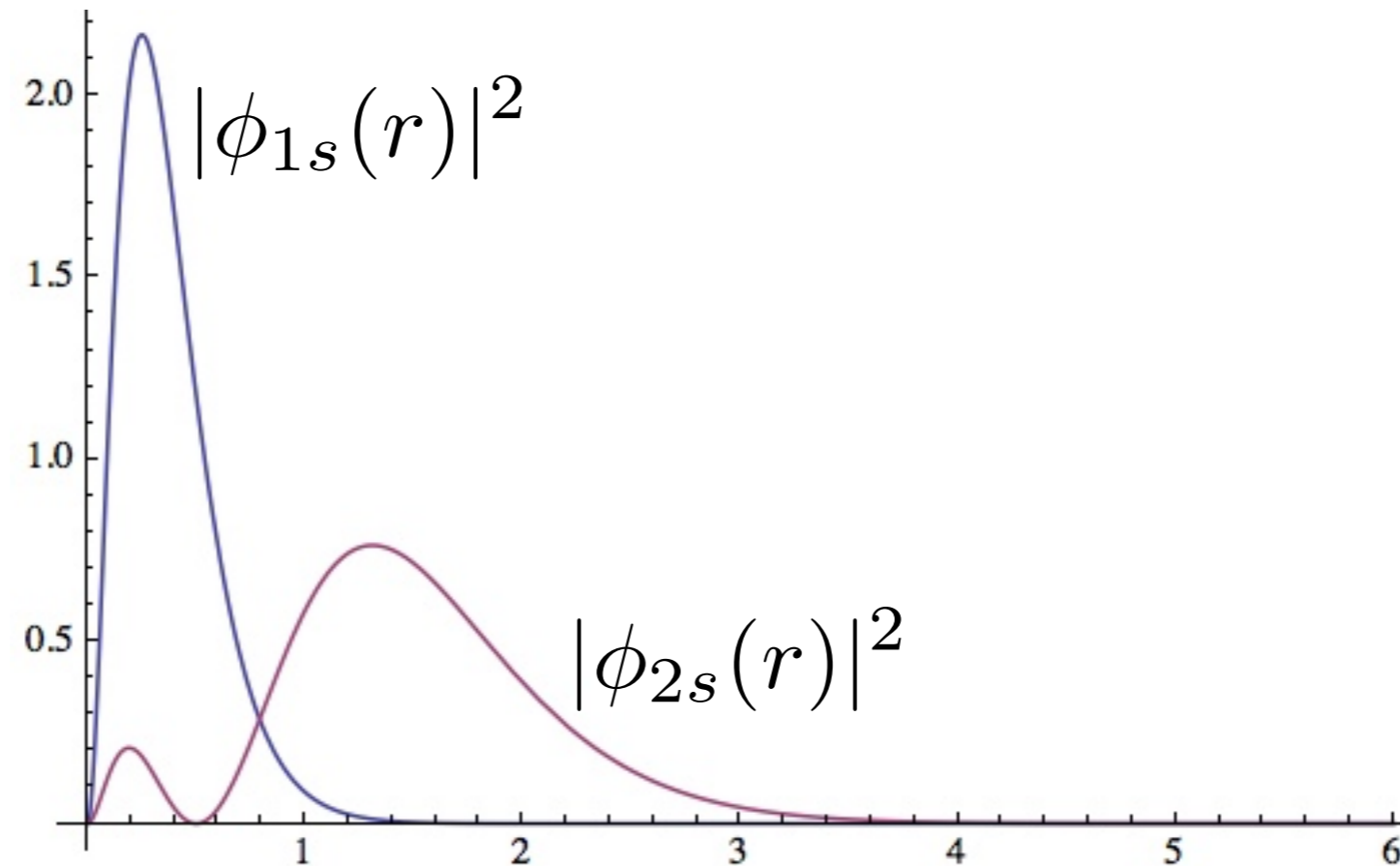
define  $T_s[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle$

decompose the HK functional as

$$F[\rho] = T_s[\rho] + E_{\text{Hxc}}[\rho]$$

$T_s$  capture shell structure, Friedel oscillations,... (Fermionic character!)

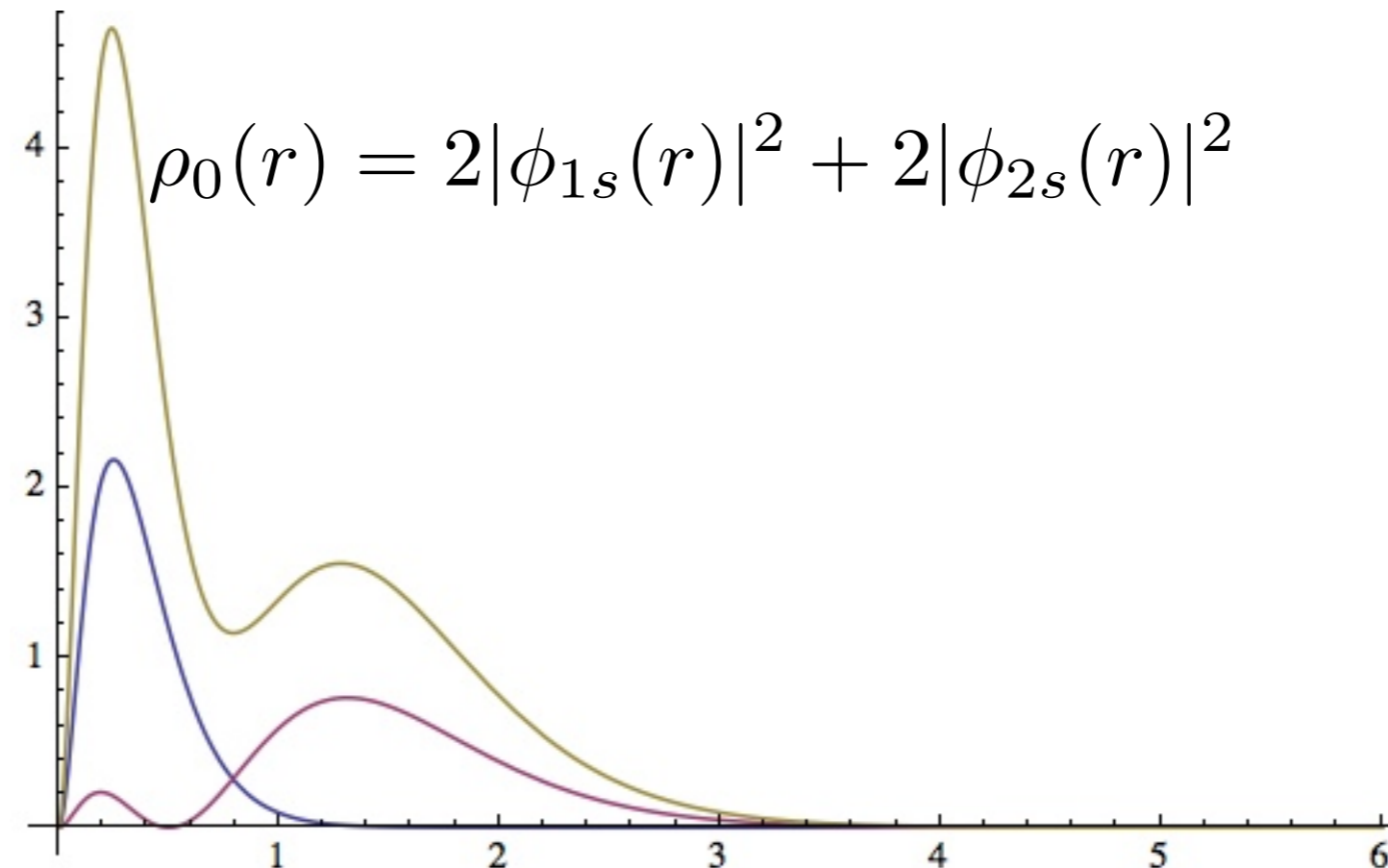
# Example: non-interacting Be atom



(solve the Be atom problem removing e-e interaction)



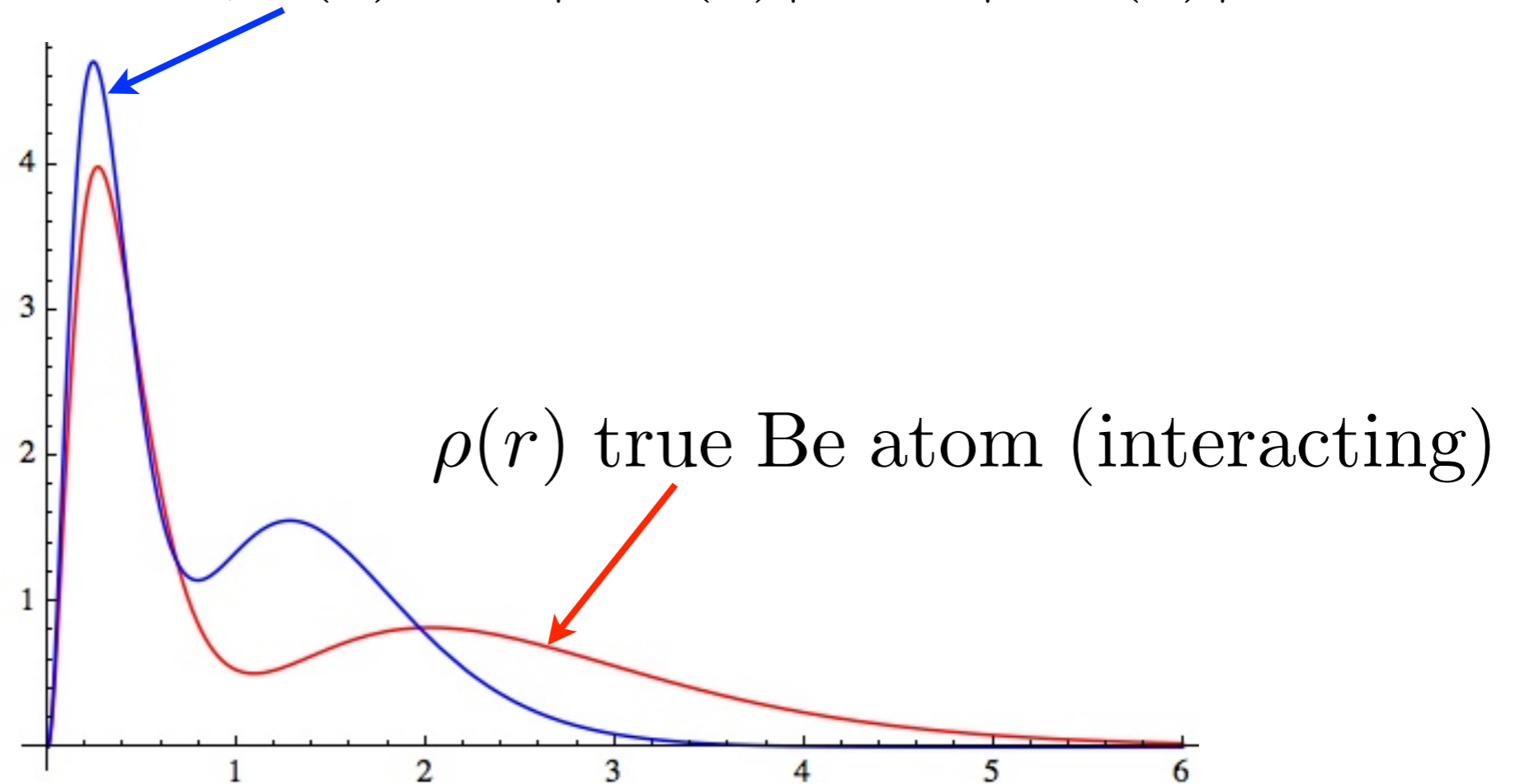
# Example: non-interacting Be atom



(solve the Be atom problem removing e-e interaction)

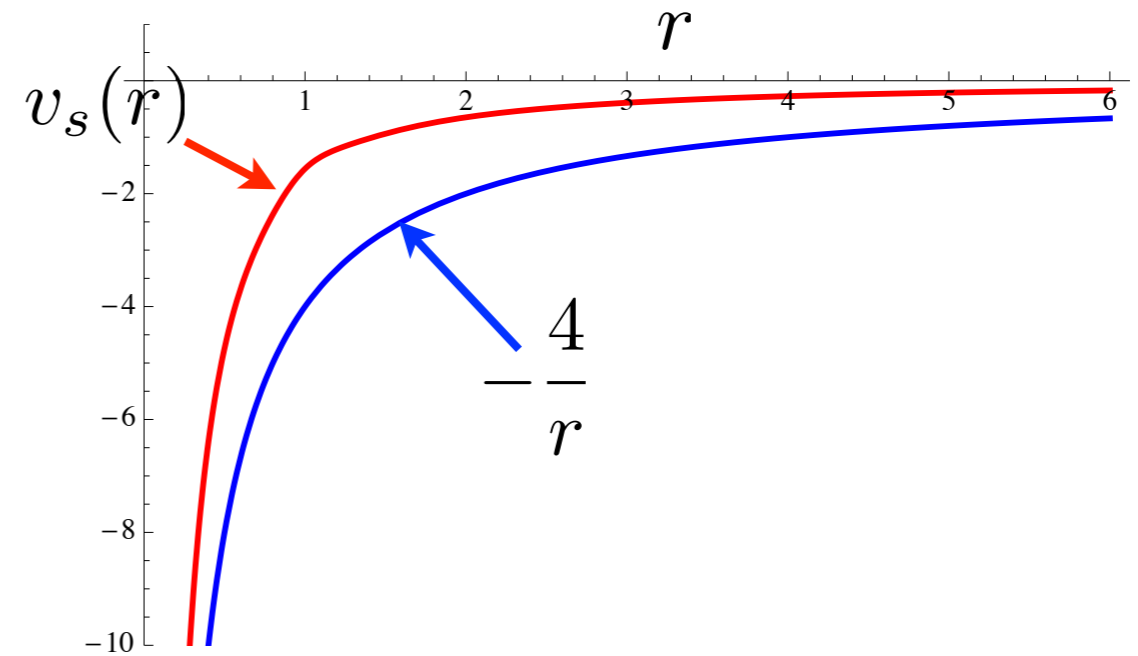
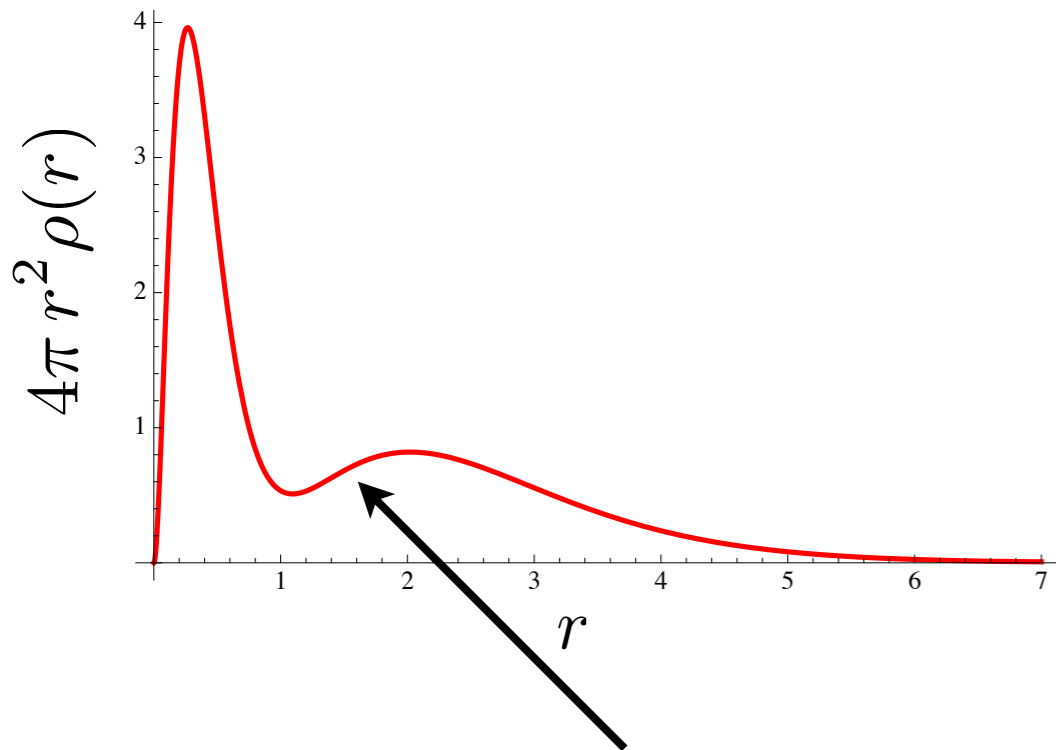
# non-interacting Be atom vs true Be atom

$$\rho_0(r) = 2|\phi_{1s}(r)|^2 + 2|\phi_{2s}(r)|^2$$



e-e interaction changes the density but, for many systems, does not wash away the fermionic (Pauli) shells

# Example: Be atom



shell structure: easy to reproduce  
with  $1s^2 2s^2$  non-int. electrons

impossible (so far) with a functional  
of the density alone

# Kohn-Sham DFT

$$E[\rho] = \overbrace{T_s[\rho] + U_H[\rho] + E_{xc}[\rho]}^{F[\rho]} + \int \rho v_{\text{ext}}$$

$$T_s[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle = \sum_i f_i \langle \phi_i(\mathbf{r}) | -\frac{1}{2} \nabla^2 | \phi_i(\mathbf{r}) \rangle$$

$$\sum_i f_i |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r}) \quad f_i = \theta(\epsilon_F - \epsilon_i)$$

$$U_H[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{xc}[\rho] = \langle \hat{T} \rangle - T_s[\rho] + \langle \hat{V}_{ee} \rangle - U_H[\rho] \quad \text{approximated}$$

# Kohn-Sham DFT

$$E[\rho] = T_s[\rho] + U_H[\rho] + E_{xc}[\rho] + \int \rho v_{\text{ext}}$$

$$\sum_i f_i |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r})$$

**solve self-consistently**

$$\frac{\delta E[\rho]}{\delta \phi_i^*(\mathbf{r})} = \left( -\frac{1}{2} \nabla^2 + \overbrace{v_H(\mathbf{r}; [\rho]) + v_{xc}(\mathbf{r}; [\rho]) + v_{\text{ext}}(\mathbf{r})}^{v_s(r; [\rho])} - \epsilon_i \right) \phi_i(\mathbf{r}) = 0$$

$$v_H(\mathbf{r}; [\rho]) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$v_{xc}(\mathbf{r}; [\rho]) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

$$v_H(\mathbf{r}; [\rho]) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$v_{xc}(\mathbf{r}; [\rho]) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

The Hartree and xc potentials are *local* operators  
(in the sense of multiplicative)

$$\hat{V}_{xc}\phi(\mathbf{r}) = v_{xc}(\mathbf{r})\phi(\mathbf{r})$$

non-local in this sense is:  $\hat{K}\phi(\mathbf{r}) = \int k(\mathbf{r}, \mathbf{r}')\phi(\mathbf{r}')d\mathbf{r}'$

(e.g. the HF exchange operator)

But they are *non-local functionals* of the density  
(in the sense that they also depend on the density in points  
different than  $\mathbf{r}$ )

# First approximations for xc functional: local or semi-local density dependence

$$E_{xc}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}))$$

xc energy of uniform electron gas  
(parametrized QMC data)

$$E_{xc}^{\text{GGA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \tilde{\epsilon}_{xc}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \dots)$$

not uniquely defined: many GGA's

also mix with a fraction of Hartree-Fock (functional “zoology”)

## Hartree-Fock is:

$$E_{\text{HF}} = \min_{\Phi} \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} | \Phi \rangle \quad \Phi = \text{Det}[\varphi_i]$$

# Hartree-Fock

$$E_{\text{HF}} = \min_{\Phi} \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} | \Phi \rangle \quad \Phi = \text{Det}[\varphi_i]$$

*can never be exact*

# KS DFT

$$E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ext}} | \Phi \rangle + E_{\text{Hxc}}[\rho_{\Phi}] \right\}$$

*can give exact energy and density*

*if “only” we had the exact functional*

# KS DFT with hybrid functionals

$$E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ext}} + a\hat{V}_{ee} | \Phi \rangle + E_{\text{Hxc}}^{(a)}[\rho_{\Phi}] \right\}$$

*can give exact energy and density*

*if “only” we had the exact functional*



## KS DFT

$$E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ext}} | \Phi \rangle + E_{\text{Hxc}}[\rho_{\Phi}] \right\} \quad \Phi = \text{Det}[\varphi_i]$$

*can give exact energy and density*

*if “only” we had the exact functional*

If we had the exact xc functional...

$$\epsilon_{\text{HOMO}} = -I$$

$$I = E_{N-1} - E_N$$

exact ionization energy of the physical system

Why this is exact? (not in HF sense, but really EXACT)

## Example of DFT accuracy (solids)

	LDA	GGA (new)
Lattice constants	1-2 %	0.5-1 %
Bulk moduli	10-15 %	5-8 %

Csonka et al., Phys. Rev. B 79, 155107 (2009)

For Chemistry LDA is useless (GGA's, hybrides,...)

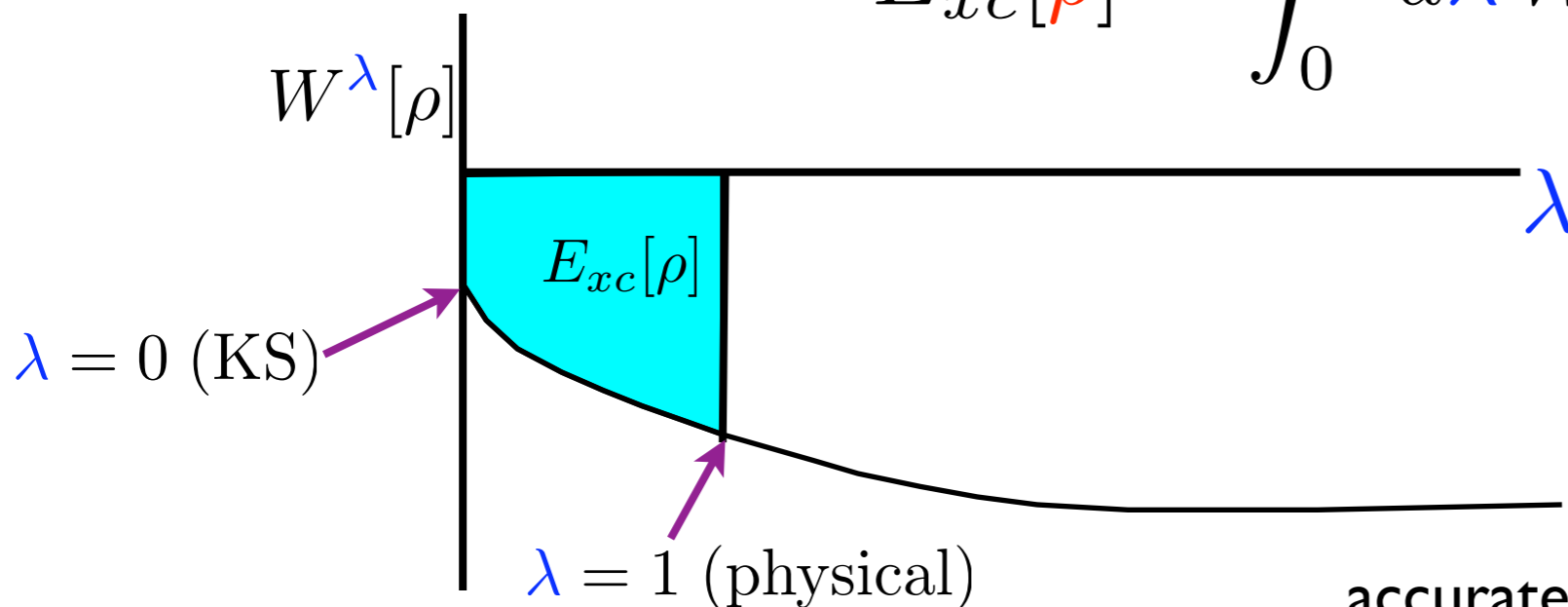
# “Adiabatic connection”

$$\hat{H}^\lambda[\rho] = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^\lambda[\rho]$$

$$\hat{V}^\lambda[\rho] = \sum_{i=1}^N v^\lambda(\mathbf{r}_i, [\rho]) \quad v^\lambda(\mathbf{r}, [\rho]) \Leftrightarrow \rho^\lambda(\mathbf{r}) = \rho(\mathbf{r}) \quad \forall \lambda$$

$$W^\lambda[\rho] = \langle \Psi^\lambda[\rho] | \hat{V}_{ee} | \Psi^\lambda[\rho] \rangle - U_H[\rho]$$

$$E_{xc}[\rho] = \int_0^1 d\lambda W^\lambda[\rho]$$



accurate calculations possible:

Teale, Coriani, Helgaker, *J. Chem. Phys.* 132, 164115 (2010)

# Spin DFT and Unrestricted KS

$$T_s[\rho_\uparrow, \rho_\downarrow] = \min_{\Phi \rightarrow \rho_\uparrow, \rho_\downarrow} \langle \Phi | \hat{T} | \Phi \rangle$$

define a non-interacting system with the **same spin densities** of the interacting system

two sets of KS equations  
(up and down spins)  $v_{s,\uparrow}, v_{s,\downarrow}$

notice that  $T_s[\rho_\uparrow, \rho_\downarrow] + E_{xc}[\rho_\uparrow, \rho_\downarrow] = T_s[\rho] + E_{xc}[\rho]$

# Functional zoology

	functional	year	cites	like	neutral	hate	empty	points
<i>Primera Divisió</i>								
1	PBE	1996	24231	75	45	7	44	263
2	PBE0	1996	3754	70	40	11	50	239
3	B3LYP	1994	25488	66	36	32	37	202
4	PW91	1992	9582	45	43	11	72	167
5	BP86	1988	909	38	45	10	78	149
6	B97-D	2006	85	28	50	11	82	123
7	B3LYP-D	2006	56	29	50	21	71	116
8	M06-2X	2008	389	41	25	33	72	115
9	BLYP	1988	1347	28	48	18	77	114
10	revPBE	1998	561	25	44	11	91	108
11	CAM-B3LYP	2004	1033	23	45	11	92	103
12	B2PLYP	2006	428	21	44	12	94	95
13	B3PW91	1993	1218	21	45	14	91	94
14	SSB-D	2009	39	15	43	11	102	77
15	TPSSH	2003	62	12	48	12	99	72
16	M06-L	2006	121	22	36	33	80	69
17	B3LYP*	2001	397	17	41	29	84	63
18	PWPB95-D <sub>3</sub>	2011	3	11	41	11	108	63
19	revTPSS-D	2009	66	10	44	12	105	62
20	revTPSS	2009	66	9	45	14	103	58
<i>Segona Divisió</i>								
1	LDA	1980	11795	42	34	24	71	136
2	$\omega$ B97X-D	2008	402	41	26	13	91	136
3	HSE	2003	875	31	28	10	102	111
4	M06	2008	636	24	33	28	86	77
5	OLYP	2001	101	16	34	14	107	68
6	LC-wPBE	2006	312	15	34	14	108	65
7	LC-PBE	2007	95	11	34	14	112	53
8	SAOP	2000	77	9	33	8	121	52
9	PW6B95	2005	19	11	33	15	112	51
10	LB94	1994	35	9	32	10	120	49
11	RPBE	1999	1796	9	38	16	108	49
12	mPW1K	2000	774	7	38	16	110	43
13	M05-2X	2006	945	15	32	35	89	42
14	optB88-vdW	2010	75	11	11	5	144	39
15	APBE	2011	13	4	36	9	122	39
16	BHandH	1993	57	8	35	22	106	37
17	DSD-BLYP	2010	25	7	29	13	122	37
18	M05	2005	243	10	36	33	92	33
19	VSXC	1998	43	3	34	18	116	25
20	$\tau$ -HCTH	2002	158	3	30	17	121	22
21	X3LYP	2004	79	5	31	25	110	21
22	XLYP	2004	4	0	29	25	117	4

## Density functionals poll

Organized by M. Swart, F.M. Bickelhaupt and M. Duran



# Approximate xc functionals (a whole zoology)

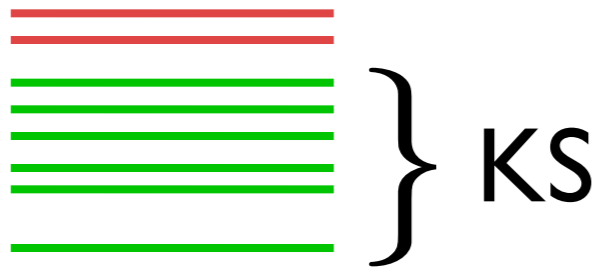
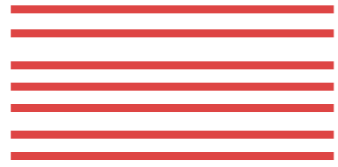
- Some are built from exact properties/ constraints
- Some are built by fitting very many parameters
- Successful in very many cases; but often one needs different approximations for different systems
- Problems when e-e interaction plays an important role (system radically different from non-interacting)  
broken-symmetry/wrong solutions

*focus of my research*

Defining strong/weak (static/  
dynamical) correlation is a  
research field by itself.

Different communities/people  
mean different things.

near-degeneracy  
(static correlation;  
sometimes called also strong)



few more important  
states to capture  
the right physics

$$\text{some } n_i \sim 1/2$$

strong correlation  
(non-trivial static correlation)



many more  
important states to  
capture the right  
physics

$$\text{all } n_i \ll 1$$



# Broken symmetry & strong correlation...

- Broken symmetry solutions can **mimic** strong correlation (not always!)
- Often better energies, but **wrong characterizations of several properties**
- Potential energy surfaces with **kinks/discontinuous**
- Huge literature: controversial, wrong interpretation, etc...
- Crucial for: **transition metals, Mott insulators, bond breaking, nanostructures,...**

Approximations from  
the exact strong-  
interaction limit of the  
HK functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

HK functional

$$T_s[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle$$

KS kinetic energy

$$V_{ee}^{\text{SCE}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

SCE functional  
“*strictly correlated electrons*”

# SCE: Equivalent to the strong-interaction limit of the standard adiabatic connection

$$F_\lambda[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle$$

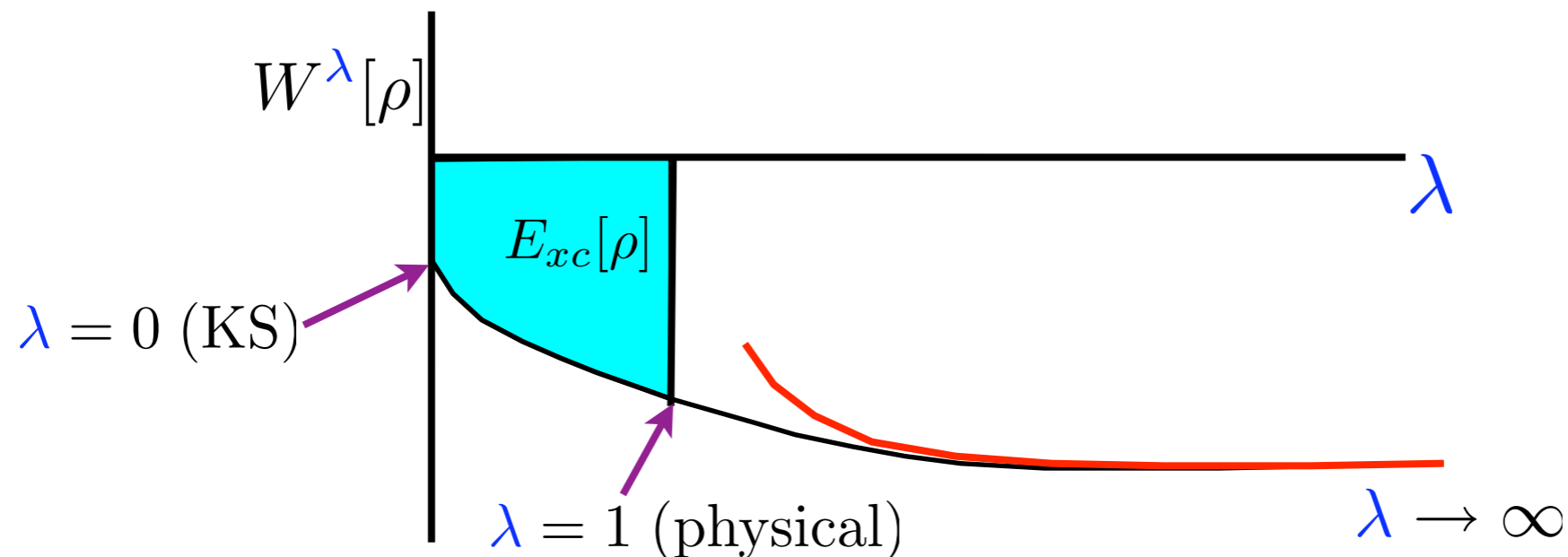
$$W^\lambda[\rho] = \langle \Psi^\lambda[\rho] | \hat{V}_{ee} | \Psi^\lambda[\rho] \rangle - U_H[\rho]$$

M. Seidl, J.P. Perdew, and M. Levy, *PRA* **59**, 51 (1999)

M. Seidl, *PRA* **60**, 4387 (1999)

M. Seidl, J.P. Perdew, and S. Kurth, *PRL* **84**, 5070 (2000)

M. Seidl, J.P. Perdew, and S. Kurth, *PRA* **62**, 012502 (2000)



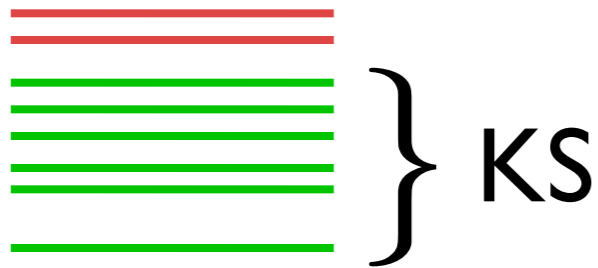
$$W^{\lambda \rightarrow \infty}[\rho] = V_{ee}^{\text{SCE}}[\rho] - U_H[\rho] + O\left(\frac{1}{\sqrt{\lambda}}\right)$$

Seidl, Gori-Giorgi & Savin, *PRA* **75**, 042511 (2007)

Gori-Giorgi, Vignale & Seidl, *JCTC* **5**, 743 (2009)

*exact treatment*

near-degeneracy  
(static correlation;  
sometimes called also strong)



few more important  
states to capture  
the right physics

$$\text{some } n_i \sim 1/2$$

strong correlation  
(non-trivial static correlation)



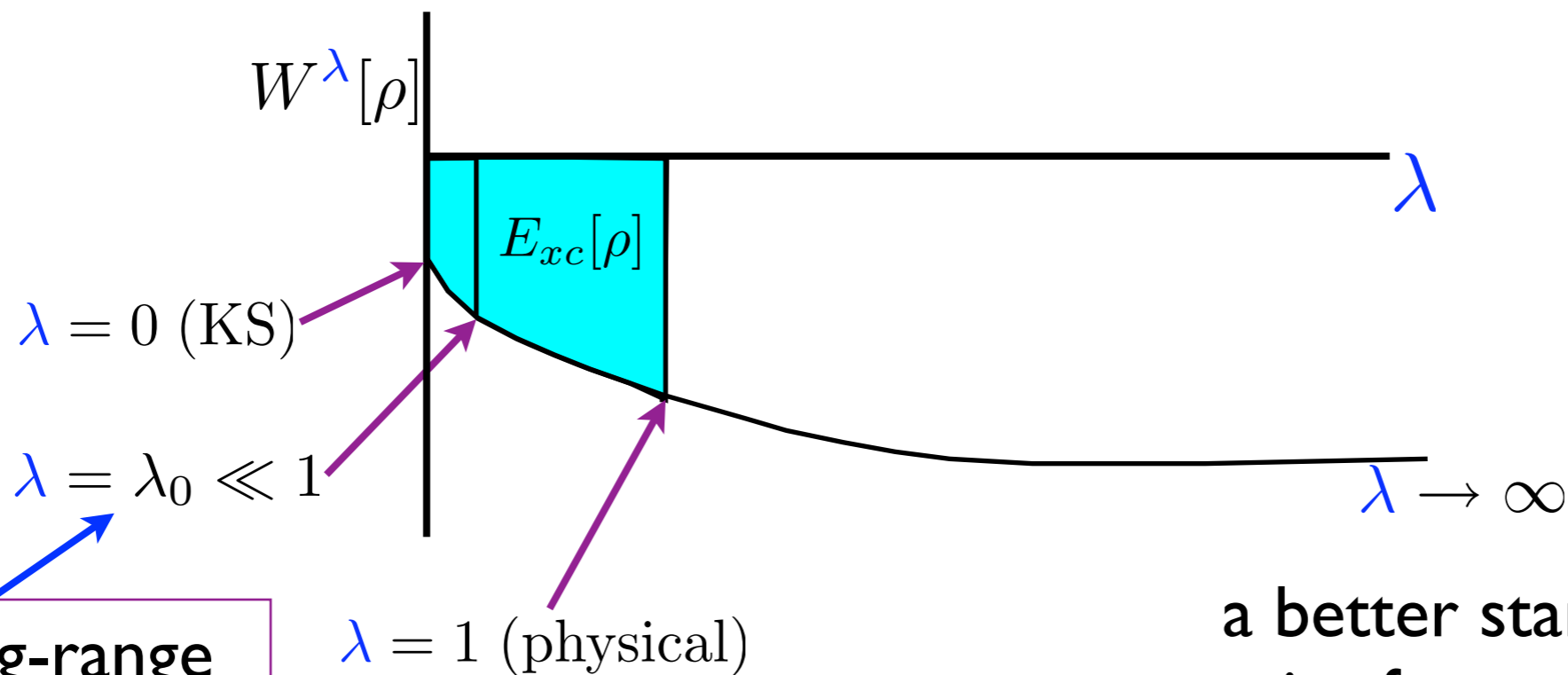
many more  
important states to  
capture the right  
physics

$$\text{all } n_i \ll 1$$

# DFT: what is the best reference hamiltonian?

$$\hat{H}^\lambda[\rho] = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^\lambda[\rho]$$

$$W^\lambda[\rho] = \langle \Psi^\lambda[\rho] | \hat{V}_{ee} | \Psi^\lambda[\rho] \rangle - U_H[\rho]$$



e.g., long-range  
weak interaction  
+ appropriate  
functional

long-range, e.g., with MP2, CI, MCSCF, RPA...  
(Savin, Stoll, Scuseria,...)

a better starting  
point for systems  
dominated by  $V_{ee}$ ?

(our original motivation)

here: use SCE for KS

# How to build the SCE functional?

$$V_{ee}^{\text{SCE}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

one-body potential needed  
to impose this constraint

# What is the “wave function” for a classical problem?

$$\hat{H} = \hat{V}_{ee} + \hat{V}$$

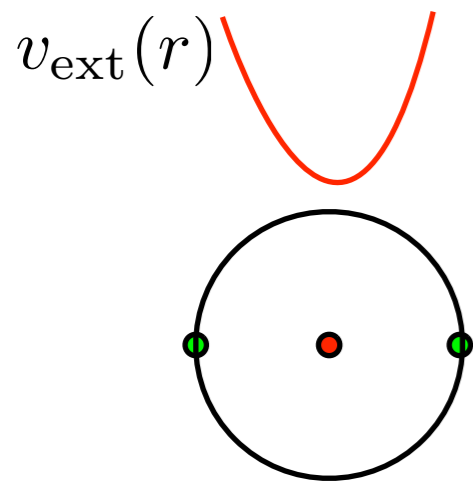
$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{ee} + \hat{V} \equiv E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N)$$

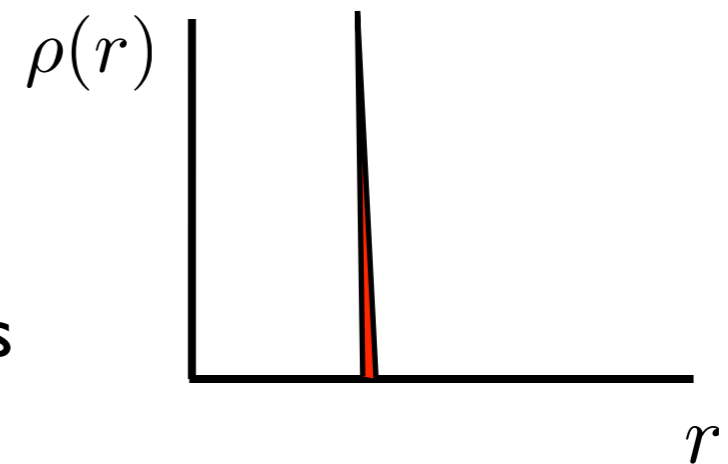
$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i)$$

$$\min_{\psi} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 E_{\text{pot}}([v]; \mathbf{r}_1, \dots, \mathbf{r}_N)$$

probability of finding the  $N$  electrons  
at positions  $\mathbf{r}_1, \dots, \mathbf{r}_N$



$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$  zero everywhere  
except at classical equilibrium positions



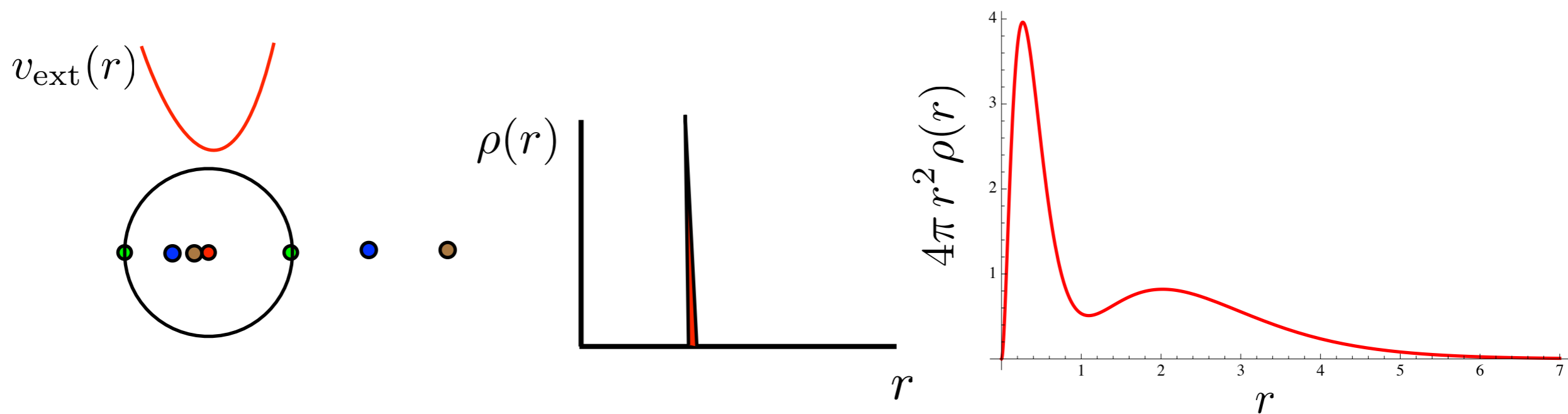


$$\hat{H} = \sum_{i=1}^N \sum_{j>1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{SCE}}(\mathbf{r}_i) = \hat{V}_{ee} + \hat{V}_{\text{SCE}}$$

adjusted to reproduce  $\rho(\mathbf{r})$

## Classical problem with a given smooth density

usually for a classical problem  $\rho(\mathbf{r}) \propto \sum_k \delta(\mathbf{r} - \mathbf{r}_k)$



To have a smooth density, the minimum must be degenerate over a 3d subspace of the  $3N$  space

$$M = \{\mathbf{r}_1 = \mathbf{f}_1(\mathbf{r}), \mathbf{r}_2 = \mathbf{f}_2(\mathbf{r}), \dots, \mathbf{r}_N = \mathbf{f}_N(\mathbf{r})\}, \quad \mathbf{f}_1(\mathbf{r}) \equiv \mathbf{r}$$

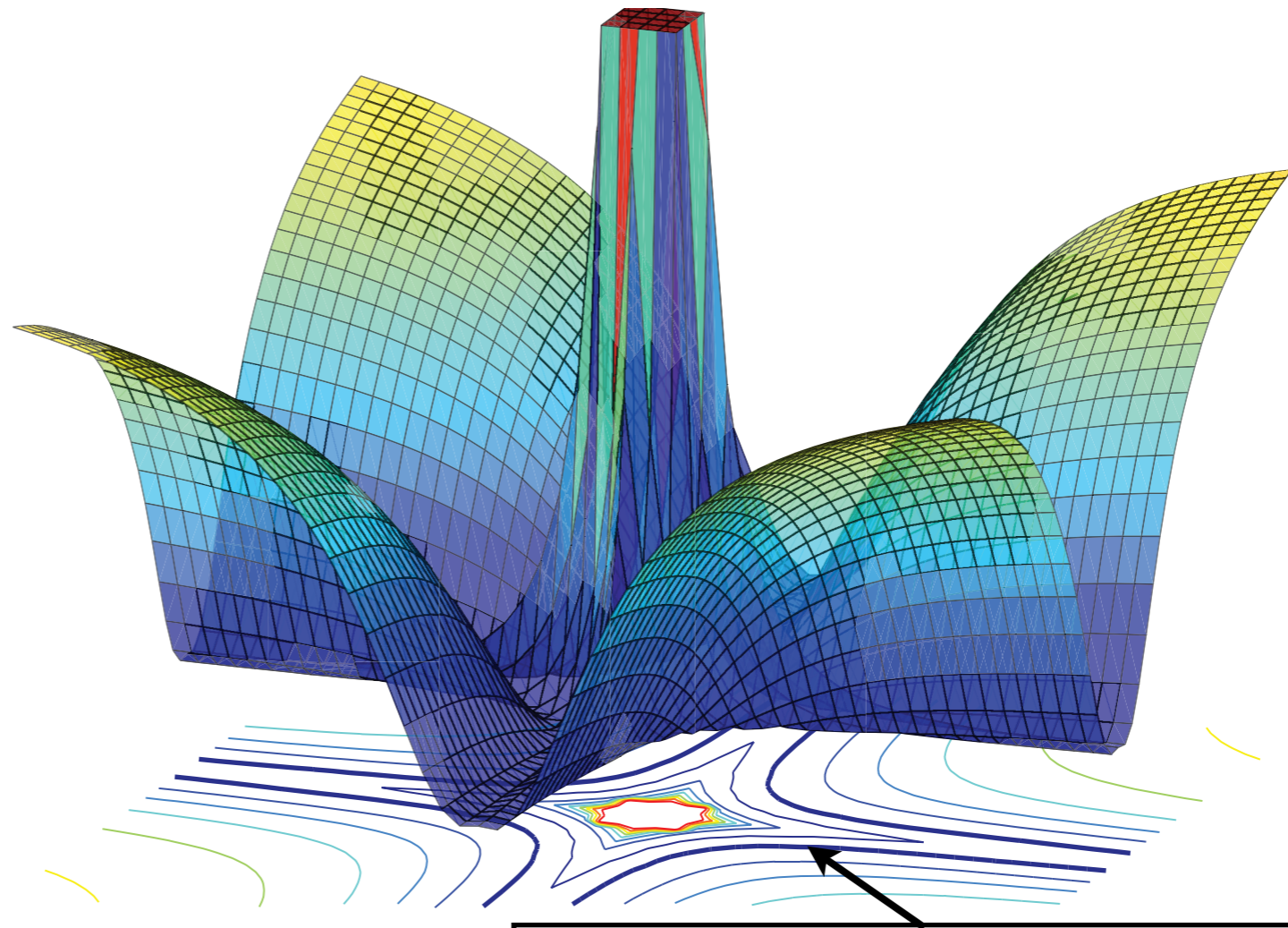
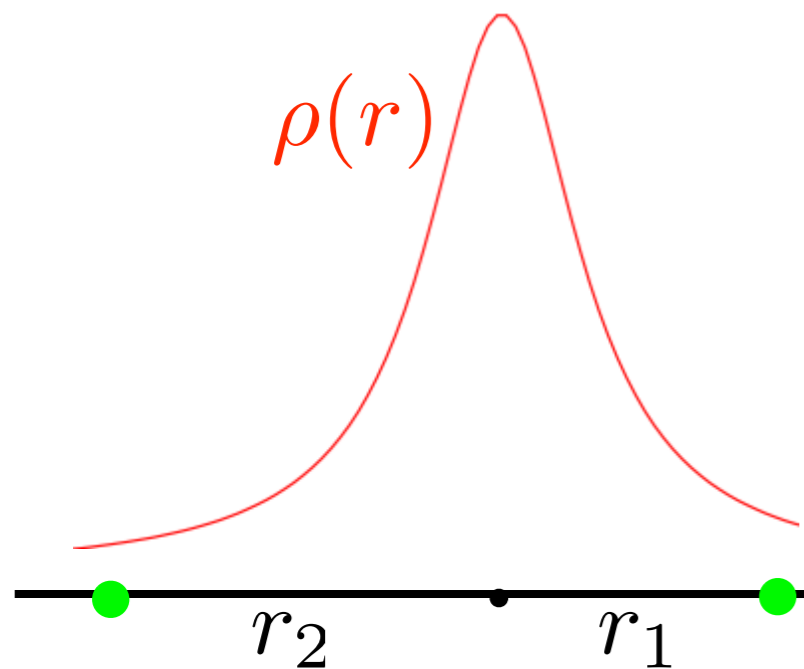
Physically, the position of one electron fixes all the other  $N-1$  electronic positions

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

The external potential is given by  $\nabla v(\mathbf{r}) = \sum_{i \neq 1}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$

The functions  $\mathbf{f}_i(\mathbf{r})$  must satisfy group properties

# Get the picture: 1D system with N=2



$$\begin{aligned} r_1 &= r, \quad r_2 = f(r) \\ \rho(r)dr &= \rho(f(r))f'(r)dr \end{aligned}$$

$$E_{\text{pot}}(r_1, r_2) = \frac{1}{r_1 + r_2} + v(r_1) + v(r_2)$$

The equation  $\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$   
 can also be proven by constructing

$$|\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 = \frac{1}{N!} \sum_P \int d\mathbf{s} \frac{\rho(\mathbf{s})}{N} \delta(\mathbf{r}_1 - \mathbf{f}_{P(1)}(\mathbf{s})) \dots \delta(\mathbf{r}_N - \mathbf{f}_{P(N)}(\mathbf{s}))$$

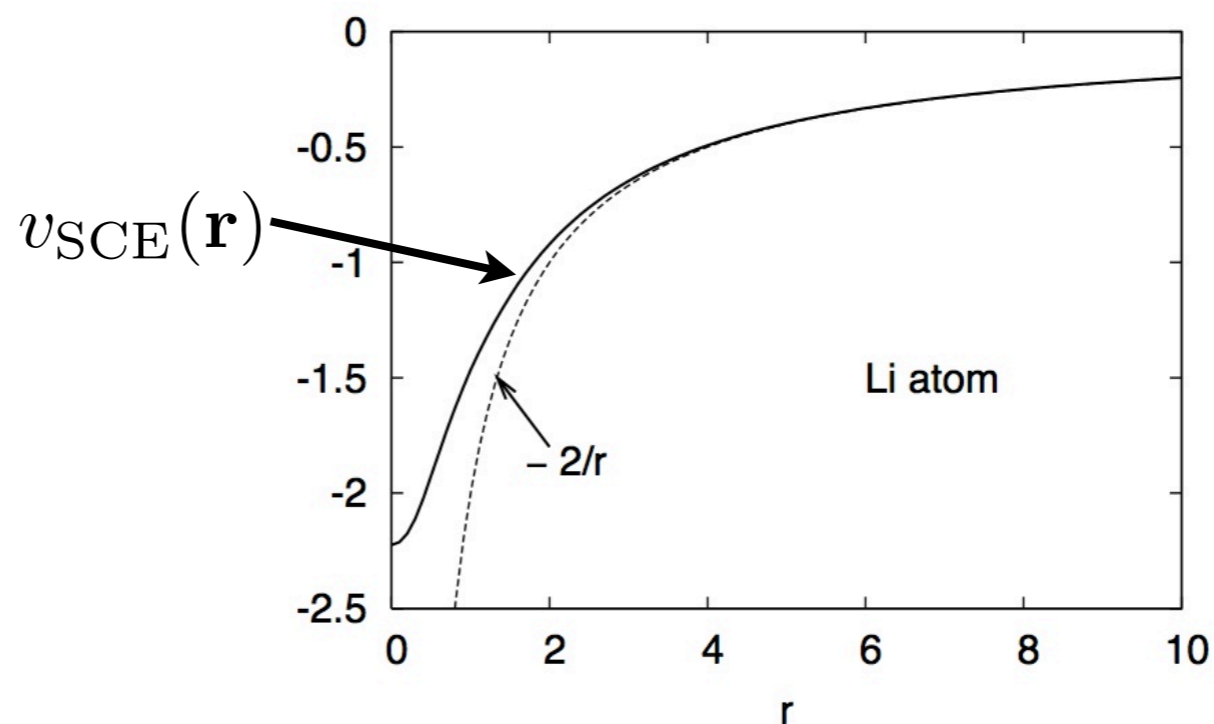
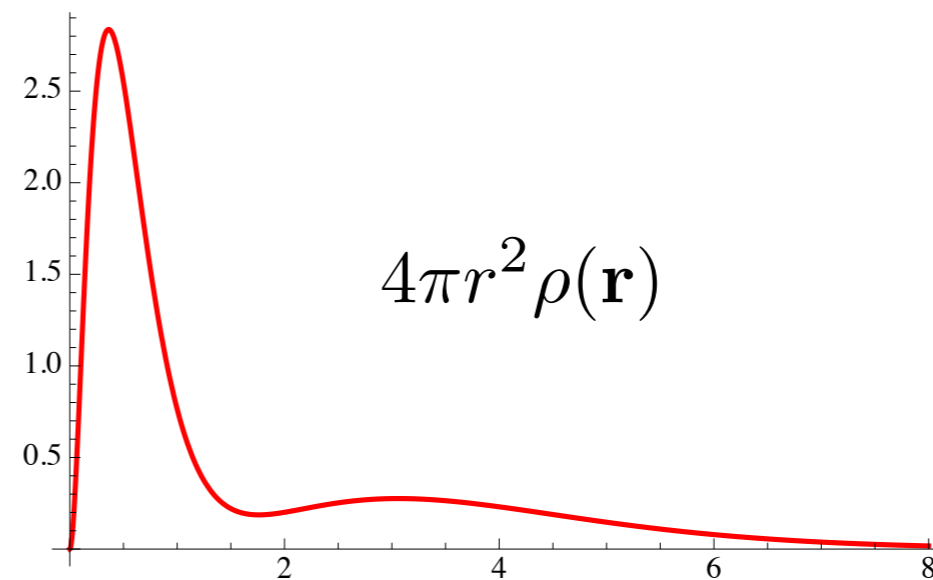
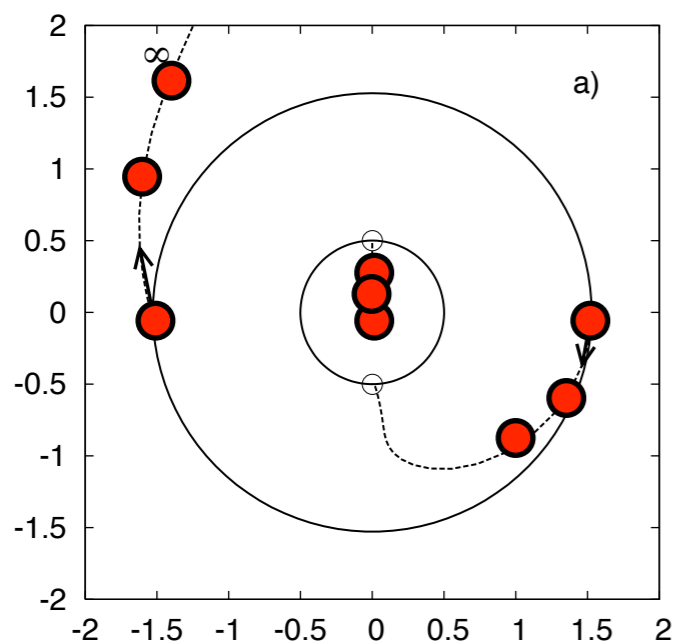
and imposing the constraint of the density expectation

$$V_{ee}^{\text{SCE}}[\rho] = \int d\mathbf{r} \frac{\rho(\mathbf{r})}{N} \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|}$$

$$\frac{\delta V_{ee}^{\text{SCE}}[\rho]}{\delta \rho(\mathbf{r})} = -v(\mathbf{r})$$

$$\nabla v(\mathbf{r}) = \sum_{i \neq 1}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

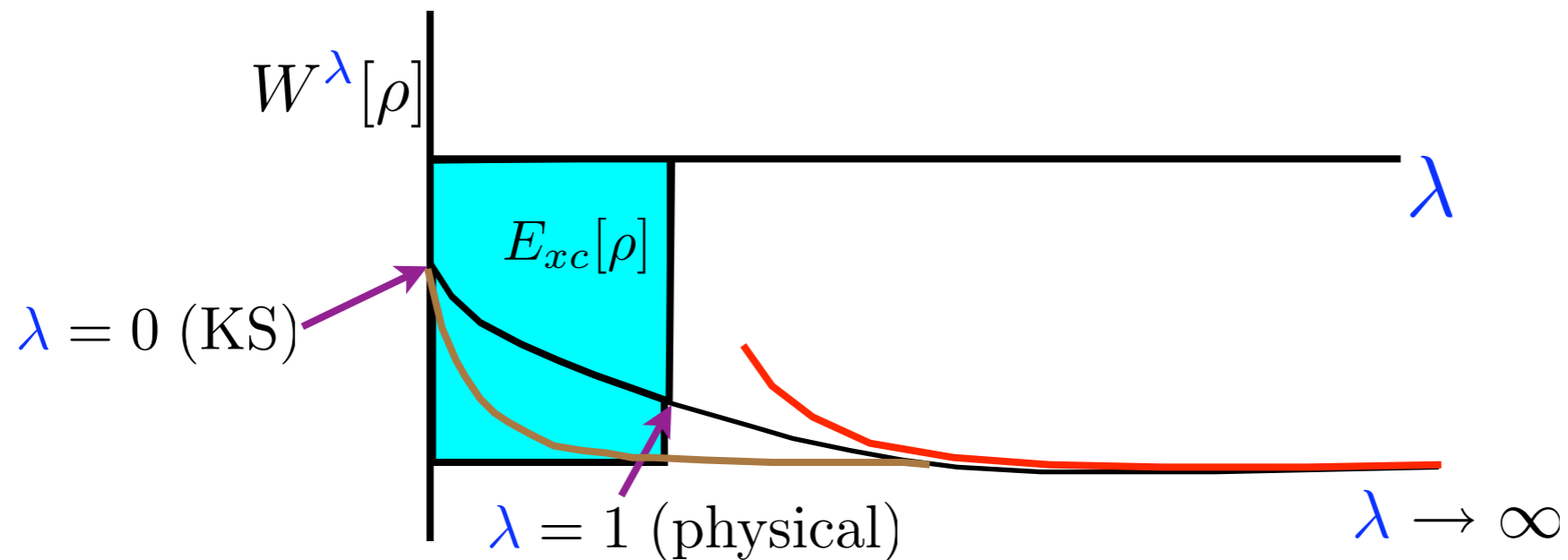
# Example: the degenerate minimum for the Li atom density



# Use the SCE functional in KS DFT: a first step

$$F_\lambda[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle$$

$$W^\lambda[\rho] = \langle \Psi^\lambda[\rho] | \hat{V}_{ee} | \Psi^\lambda[\rho] \rangle - U_H[\rho]$$



$$F[\rho] = T_s[\rho] + V_{ee}^{\text{SCE}}[\rho] + \cancel{\Delta}[\rho]$$

# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle}_{\mathbf{T}_s[\rho]} + \underbrace{E_{\text{Hartree}}[\rho]}_{\mathbf{(known)}} + \underbrace{E_{\text{xc}}[\rho]}_{\mathbf{(unknown)}}$$

$\mathbf{(known)}$



# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

## Kohn-Sham equations:

$$\left( -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$v_{\text{KS}}[\rho] = v_{\text{ext}}[\rho] + v_{\text{Hartree}}[\rho] + v_{\text{xc}}[\rho]$$

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

$$v_{\text{Hartree}}[\rho] = \frac{\delta E_{\text{Hartree}}[\rho]}{\delta \rho}$$
$$v_{\text{xc}}[\rho] = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}$$

# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

## Our approach:

$$\approx \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

## Our approach:

$$\approx \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle}_{\mathbf{T}_s[\rho]} + \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle}_{\mathbf{V}_{ee}^{\text{SCE}}[\rho]}$$

## *Strictly-correlated-electrons (SCE) DFT:*

- M. Seidl, PRA **60**, 4387 (1999)
- M. Seidl, P. Gori-Giorgi and A. Savin, PRA **75**, 042511 (2007)
- P. Gori-Giorgi, G. Vignale and M. Seidl, JCTC **5**, 743 (2009)
- P. Gori-Giorgi, M. Seidl, and G. Vignale, PRL **103**, 166402 (2009).

e-e interaction energy of system with zero kinetic energy and density  $\rho$  (SCE reference system)

# KS DFT with SCE functional

## Kohn-Sham DFT:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

## Our approach:

$$\approx \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle}_{V_{ee}^{\text{SCE}}[\rho]}$$

$$V_{ee}^{\text{SCE}}[\rho]$$



$$v_{\text{SCE}}[\rho] \simeq v_{\text{Hartree}}[\rho] + v_{\text{xc}}[\rho]$$

$$\left( -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

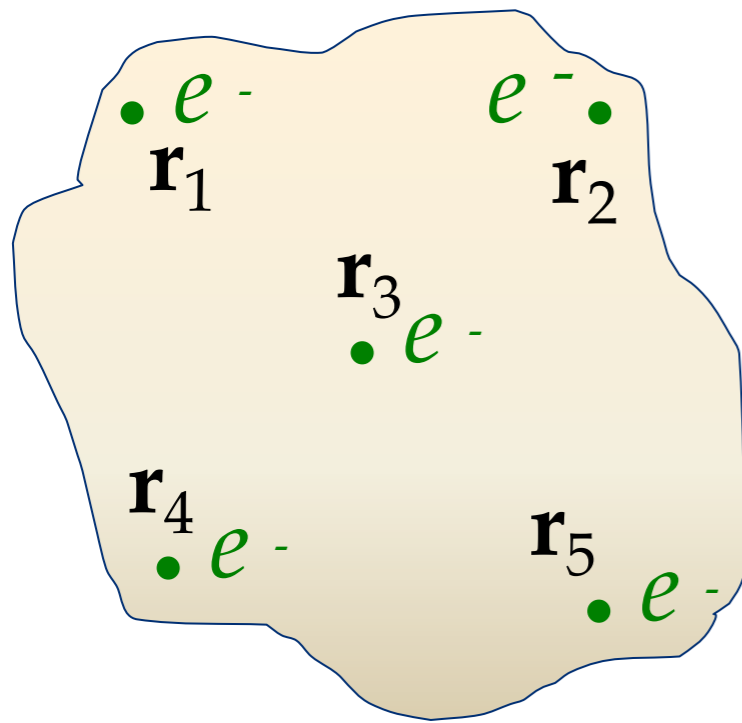
$$v_{\text{KS}}[\rho] = v_{\text{ext}}[\rho] + v_{\text{SCE}}[\rho]$$

$$v_{\text{SCE}}[\rho] = \frac{\delta V_{ee}^{\text{SCE}}[\rho]}{\delta \rho}$$

# Strictly-interacting-electrons (SCE) DFT

## The SCE reference system

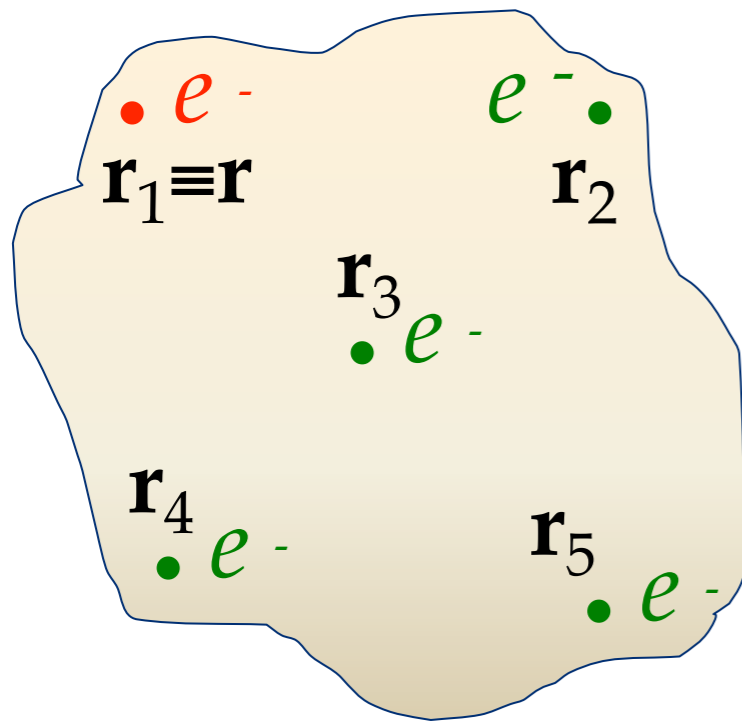
- $N$  classical charges, equilibrium positions  $\mathbf{r}_i$



# Strictly-interacting-electrons (SCE) DFT

## The SCE reference system:

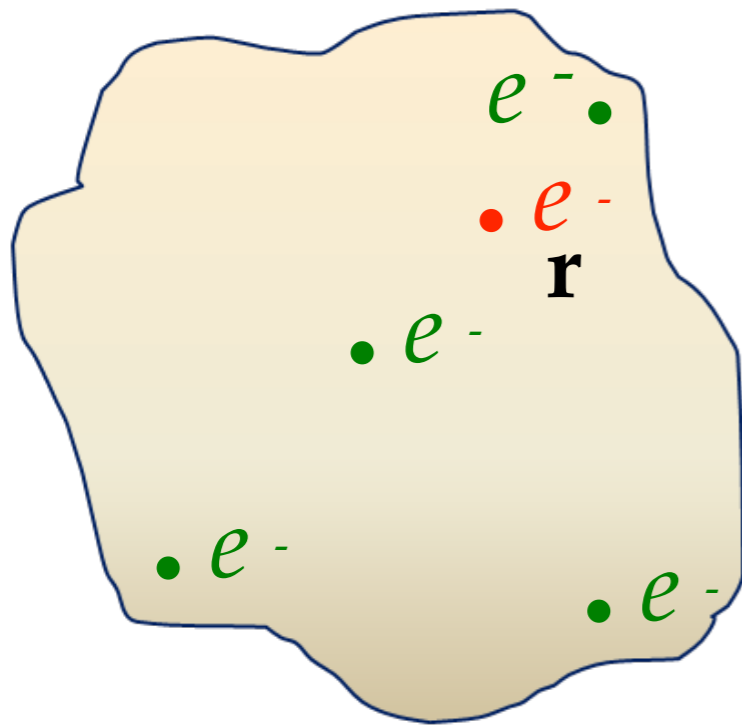
- $N$  classical charges, equilibrium positions  $\mathbf{r}_i$
- Take one (e.g. #1) as reference



# Strictly-interacting-electrons (SCE) DFT

## The SCE reference system:

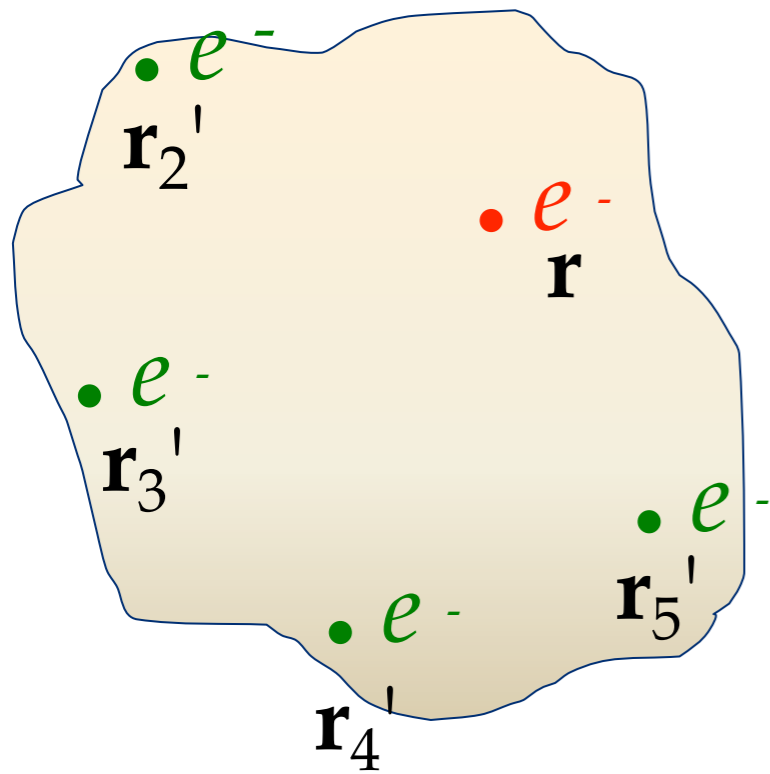
- $N$  classical charges, equilibrium positions  $\mathbf{r}_i$
- Take one (e.g. #1) as reference



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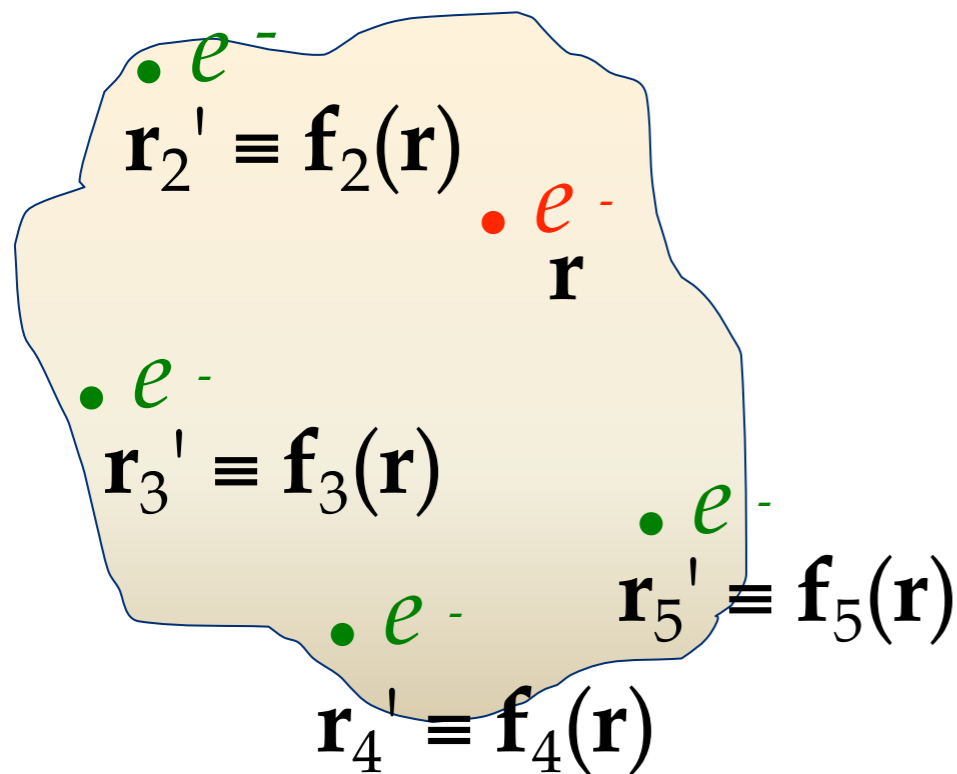




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## The SCE reference system:

- $N$  classical charges, equilibrium positions  $\mathbf{r}_i$
- Take one (e.g. #1) as reference
- The position of the other  $N-1$  charges become a function of  $\mathbf{r}$ :  $\mathbf{r}_i \equiv \mathbf{f}_i(\mathbf{r})$



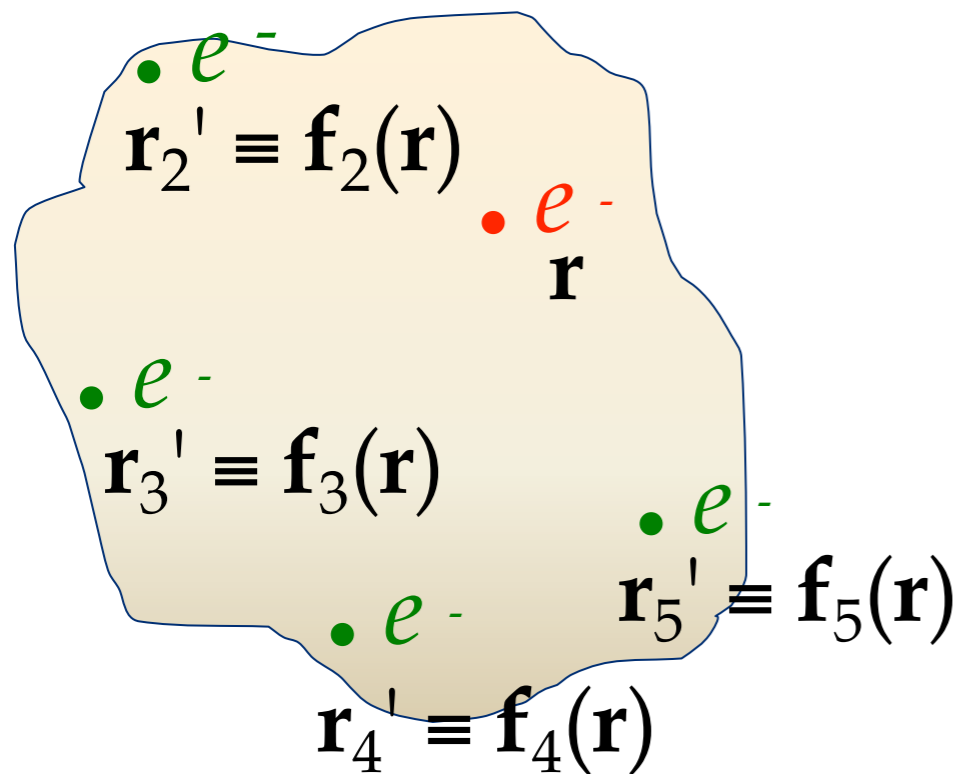
$\mathbf{f}_i(\mathbf{r})$  : co-motion functions

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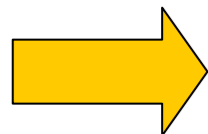
## The SCE reference system:

- For a given smooth density  $\rho(\mathbf{r})$ :

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$



$\mathbf{f}_i(\mathbf{r})$  : co-motion functions



$$\text{Prob} \left( \begin{array}{l} \text{find electron } \mathbf{1} \\ \text{at position } \mathbf{r} \end{array} \right) = \text{Prob} \left( \begin{array}{l} \text{find electron } i \\ \text{at position } \mathbf{f}_i(\mathbf{r}) \end{array} \right)$$

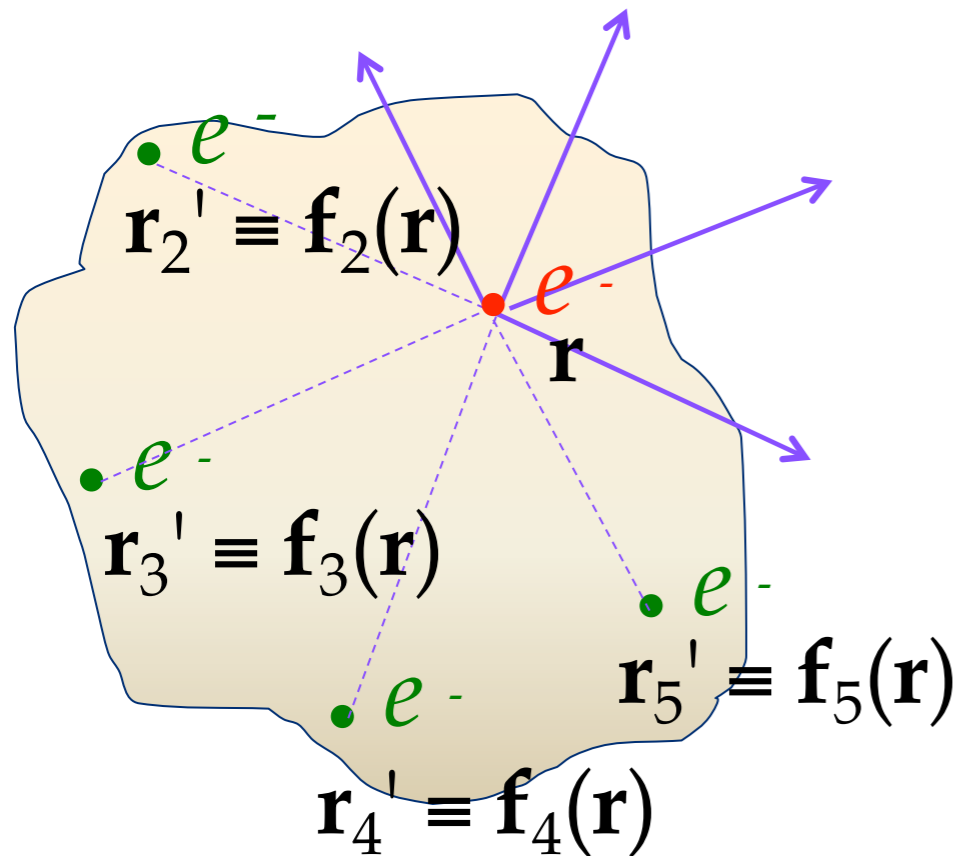
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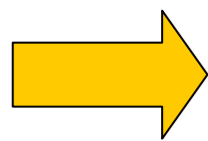
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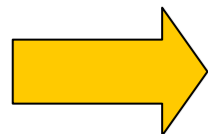
$$\mathbf{F}_{\text{Coul}}(\mathbf{r}) = \sum_{i=2}^N \frac{\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})|^3}$$



$\mathbf{f}_i(\mathbf{r})$  : co-motion functions



The total Coulomb force acting on the electron at position  $\mathbf{r}$  becomes a function of only  $\mathbf{r}$  itself



Prob  $\left( \begin{array}{l} \text{find electron 1} \\ \text{at position } \mathbf{r} \end{array} \right) = \text{Prob} \left( \begin{array}{l} \text{find electron } i \\ \text{at position } \mathbf{f}_i(\mathbf{r}) \end{array} \right)$

# Strictly-interacting-electrons (SCE) DFT

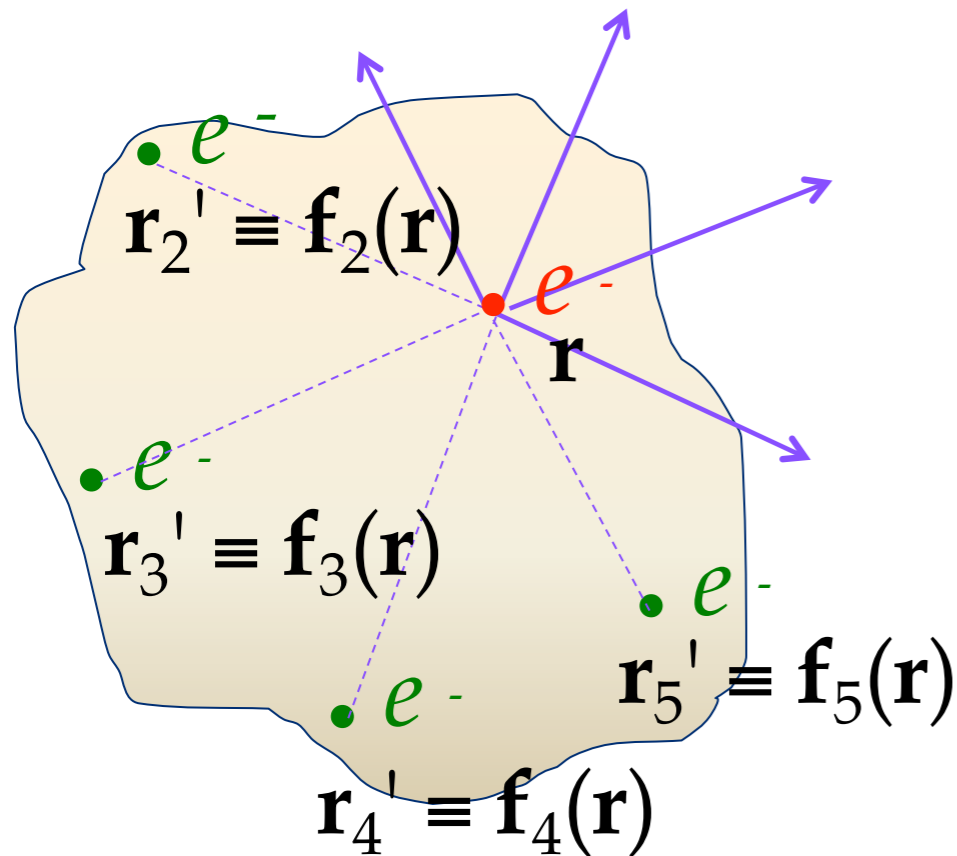
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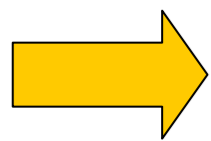
$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

- A local one-body potential can be defined:

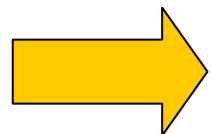
$$-\nabla v_{\text{SCE}}[\rho](\mathbf{r}) = \mathbf{F}_{\text{Coul}}(\mathbf{r}) = \sum_{i=2}^N \frac{\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})|^3}$$



$\mathbf{f}_i(\mathbf{r})$  : co-motion functions



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$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r} \quad (1)$$

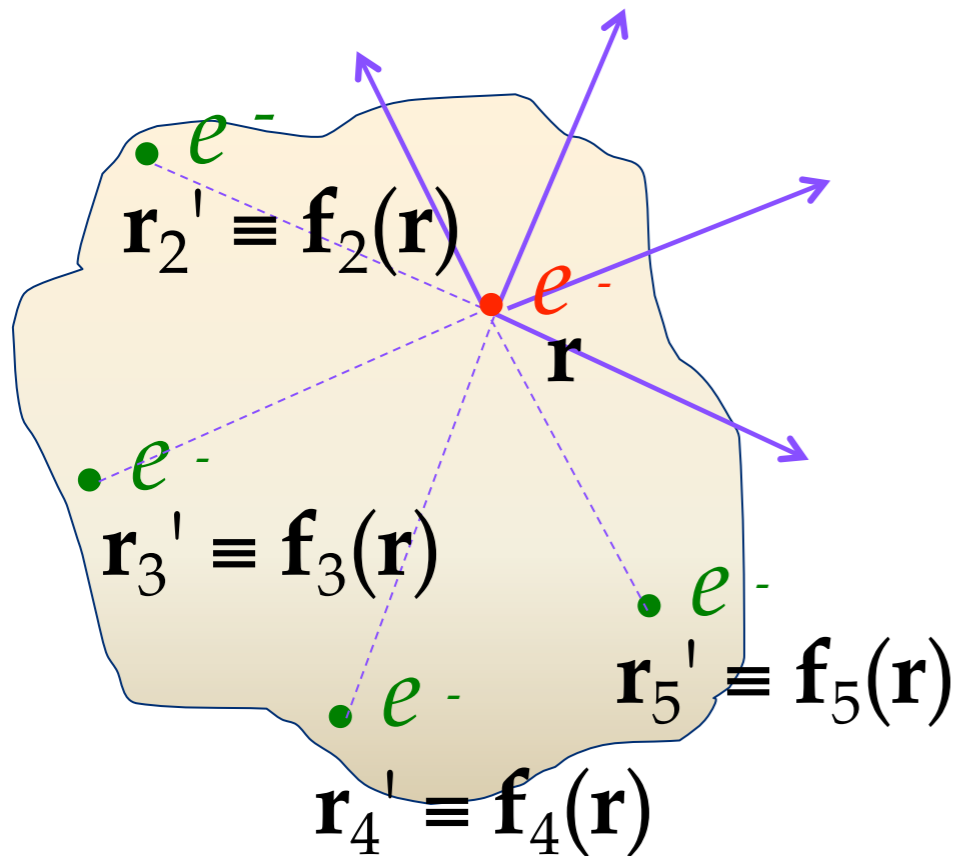
- A local one-body potential can be defined:

$$-\nabla v_{\text{SCE}}[\rho](\mathbf{r}) = \mathbf{F}_{\text{Coul}}(\mathbf{r}) = \sum_{i=2}^N \frac{\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i[\rho](\mathbf{r})|^3} \quad (2)$$

## KS-SCE approach:

- 1-Integrate (1) to obtain the co-motion functions  $\mathbf{f}_i(\mathbf{r})$
- 2-Integrate (2) to obtain the potential  $v_{\text{SCE}}(\mathbf{r})$
- 3-Approximate the **Hxc** potential of KS DFT with  $v_{\text{SCE}}(\mathbf{r})$

$$v_{\text{SCE}}[\rho] \simeq v_{\text{Hartree}}[\rho] + v_{\text{xc}}[\rho]$$



$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

$\mathbf{f}_1(\mathbf{r}) \equiv \mathbf{r}$ ,  $\mathbf{f}_2(\mathbf{r}) \equiv \mathbf{f}(\mathbf{r})$ ,  $\mathbf{f}_3(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{r}))$ ,  $\mathbf{f}_4(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{f}(\mathbf{r})))$ , ... with  $\underbrace{\mathbf{f}(\mathbf{f}(\dots\mathbf{f}(\mathbf{r})))}_{N \text{ times}} = \mathbf{r}$

$$V_{ee}^{\text{SCE}}[\rho] = \int d\mathbf{r} \frac{\rho(\mathbf{r})}{N} \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|}$$

$$\frac{\delta V_{ee}^{\text{SCE}}[\rho]}{\delta \rho(\mathbf{r})} = v_{\text{SCE}}(\mathbf{r}) \quad \nabla v_{\text{SCE}}(\mathbf{r}) = \sum_{i=2}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

shortcut to the functional derivative

**The self-consistent KS SCE total energy is a rigorous lower bound to the exact energy**

**The proof is trivial  
(minimum of a sum is always larger than the sum of the minima; self-consistency lowers the energy)**

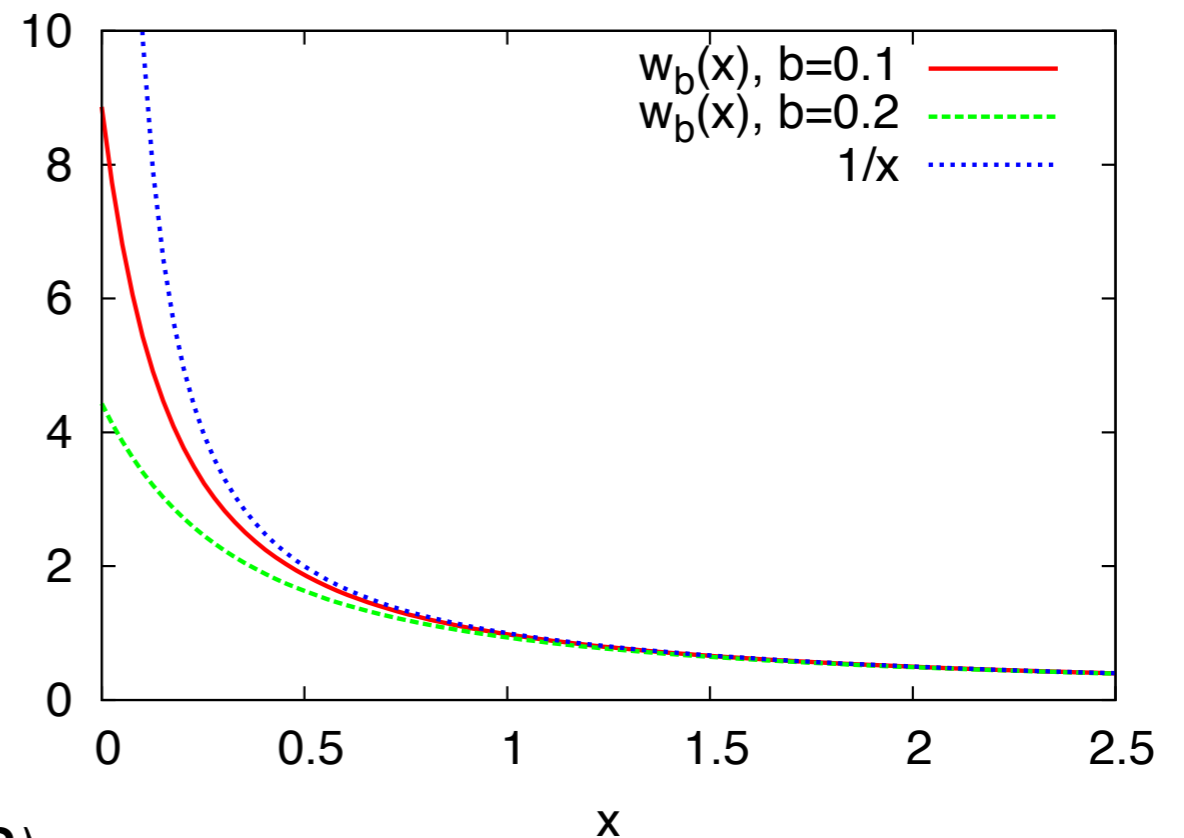
# First tests: quasi 1D systems

$$V_{\perp}(y, z) = \frac{1}{2} m \omega_{\perp}^2 (y^2 + z^2)$$

$$b^2 = \frac{\hbar}{2m\omega_{\perp}}$$

$$H_{1D} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \frac{\partial^2}{\partial x_i^2} + \sum_{i=1}^N \sum_{j>i}^N w_b(|x_i - x_j|) + \sum_{i=1}^N v_{\text{ext}}(x_i)$$

$$w_b(x) = \frac{\sqrt{\pi}}{2} \frac{e_*^2}{b} e^{x^2/4b^2} \text{erfc}\left(\frac{x}{2b}\right)$$



Bednarek et al. PRB 68, 045328 (2003)

LDA: Casula, Sorella & Senatore PRB 74, 245427 (2006)



# Electrons confined in (quasi) 1D

## Co-motion functions:

$$f_i(x) = \begin{cases} N_e^{-1} [N_e(x) + i - 1] & x \leq a_{N+1-i} \\ N_e^{-1} [N_e(x) + i - 1 - N] & x > a_{N+1-i}, \end{cases}$$

$$N_e(x) = \int_{-\infty}^x \rho(x') dx' \quad a_k = N_e^{-1}(k)$$

$$v'_{\text{SCE}}[\rho](x) = - \sum_{i=2}^N w'_b(|x - f_i(x)|) \text{sgn}(x - f_i(x))$$

Seidl, *Phys. Rev. A* 60, 4387 (1999)

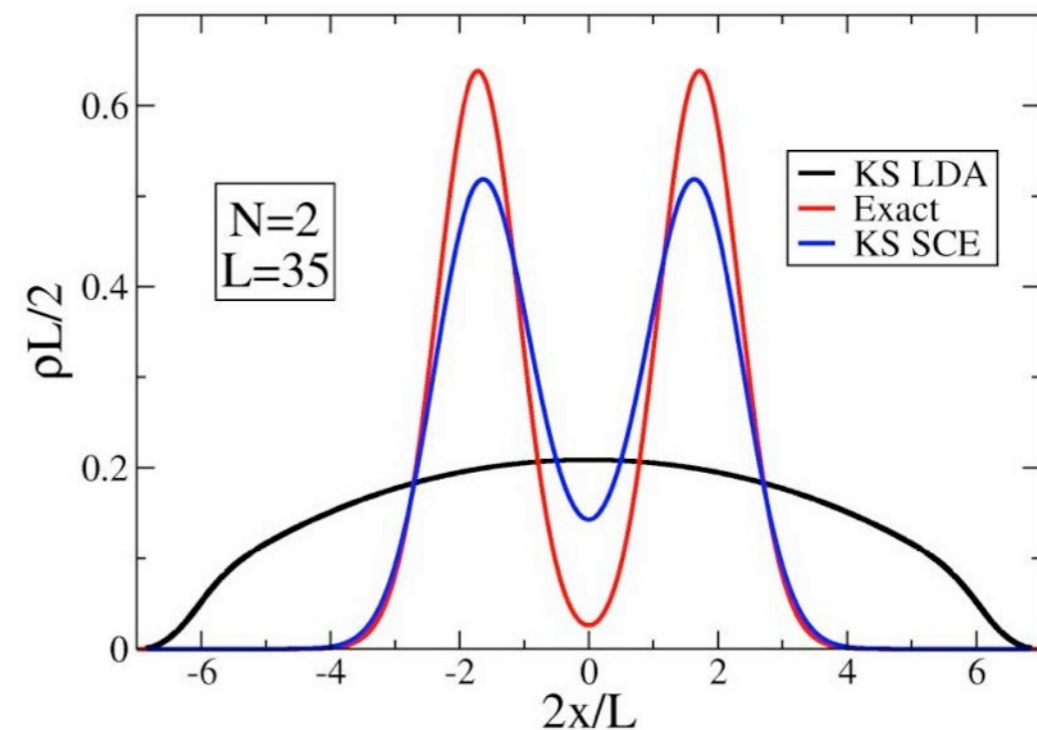
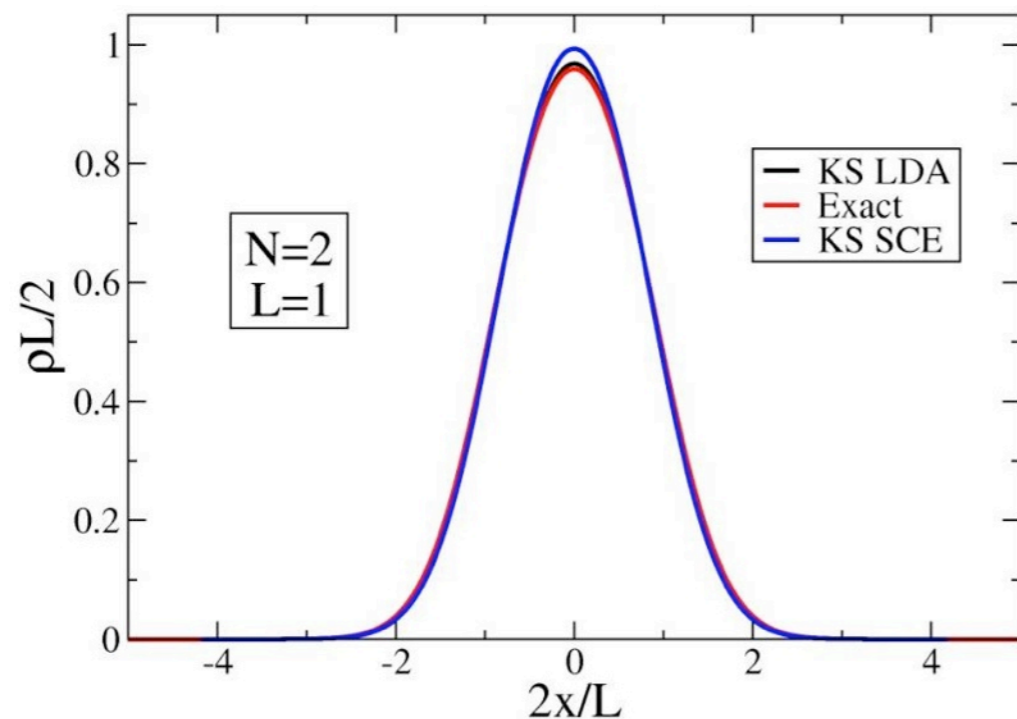
Buttazzo, De Pascale, & Gori-Giorgi, *Phys. Rev. A* 85, 062502 (2012)

Malet & Gori-Giorgi, *Phys. Rev. Lett.*, 109, 246402 (2012)

# Applications to 1D systems

**1D harmonic confinement:**  $v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2$     $\omega = \frac{4}{L^2}$     $L$ : effective length

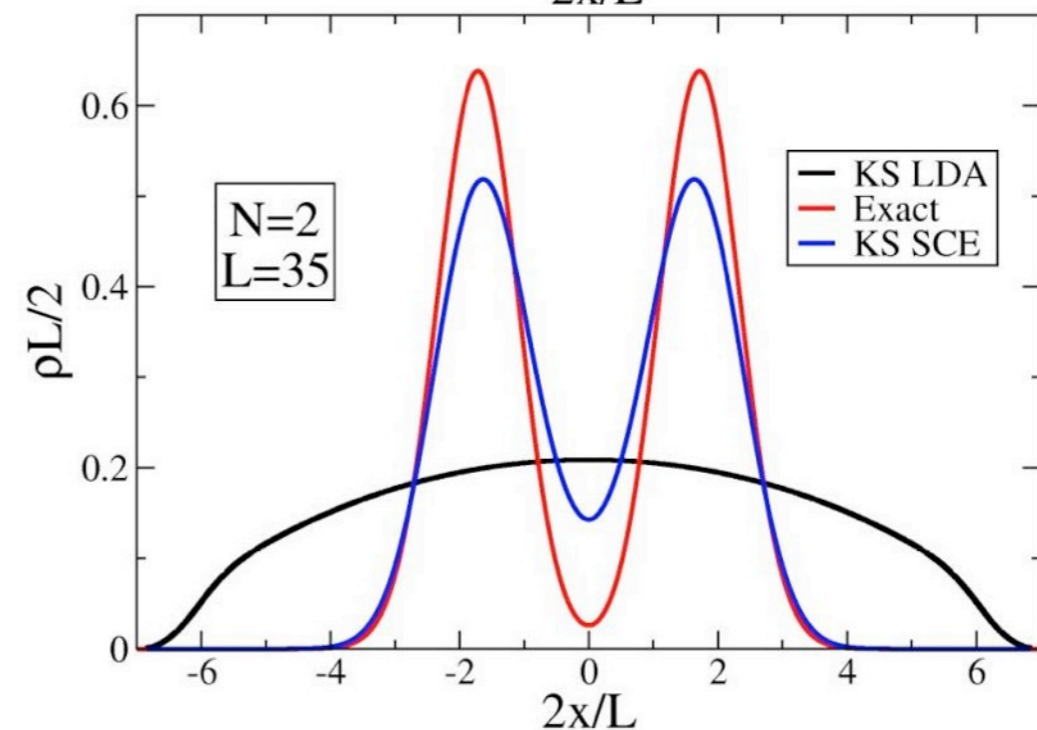
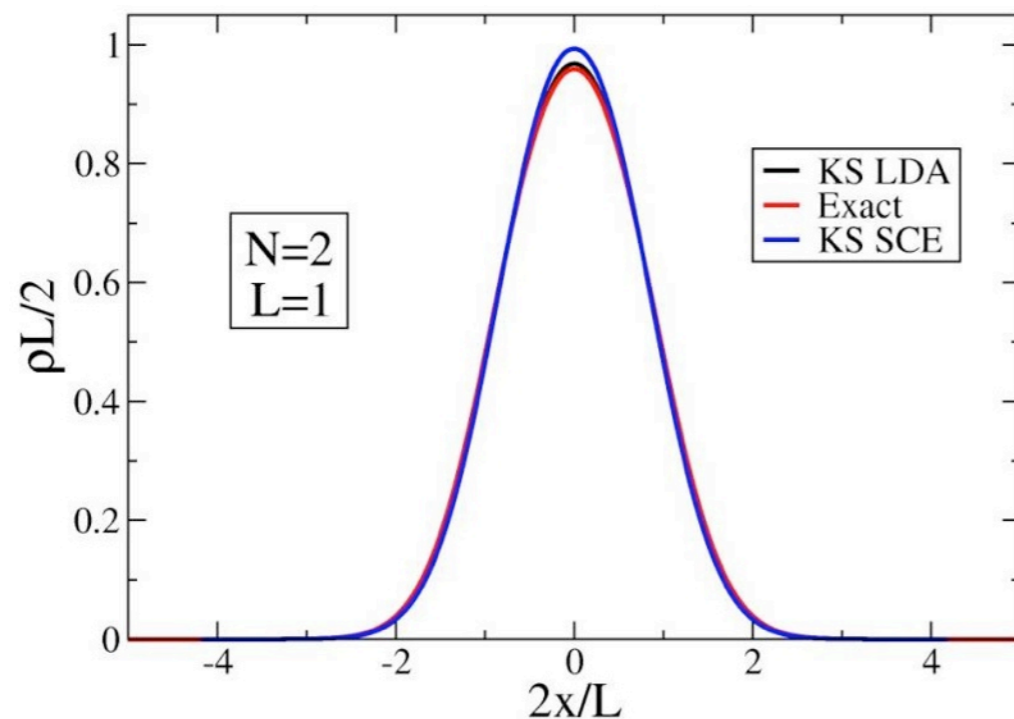
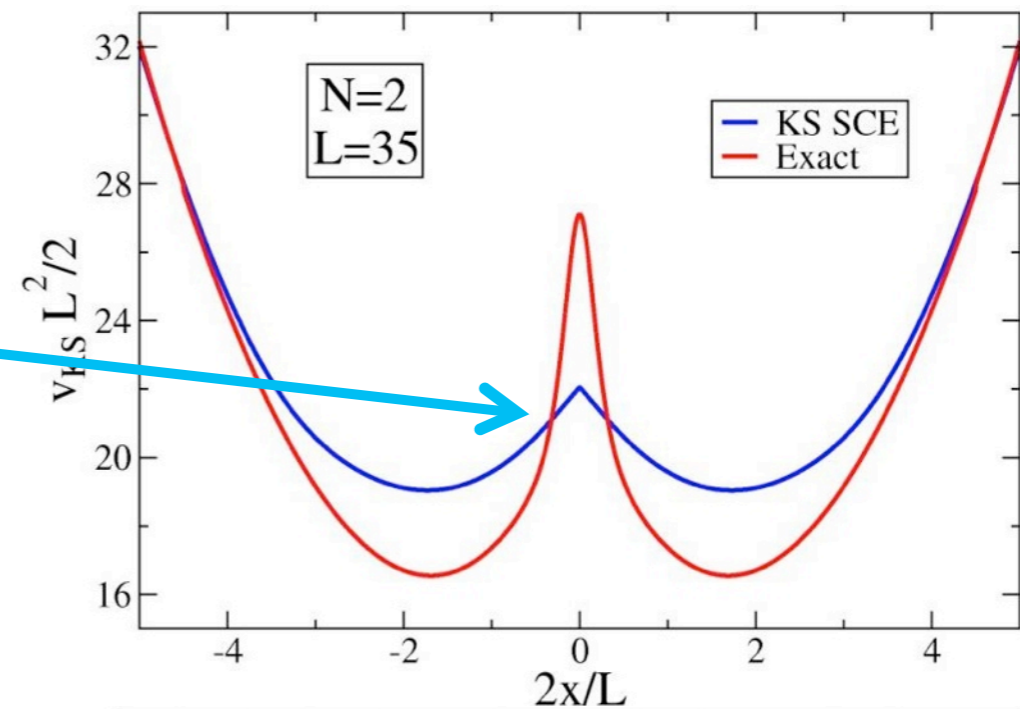
- Qualitatively good results in both the weak and strong correlation regimes



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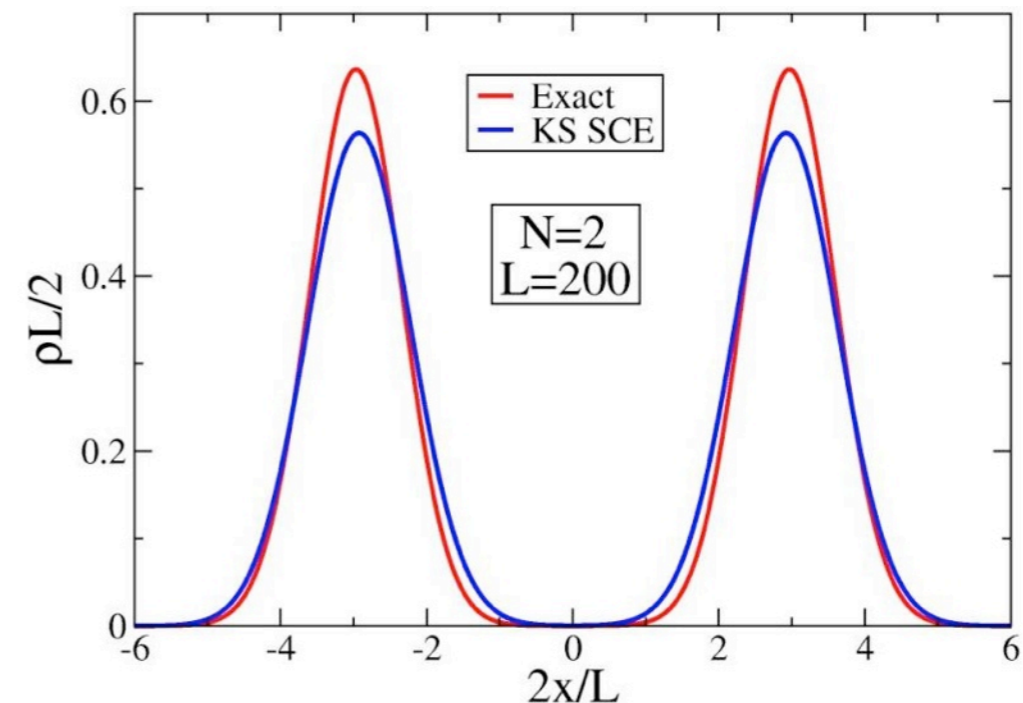
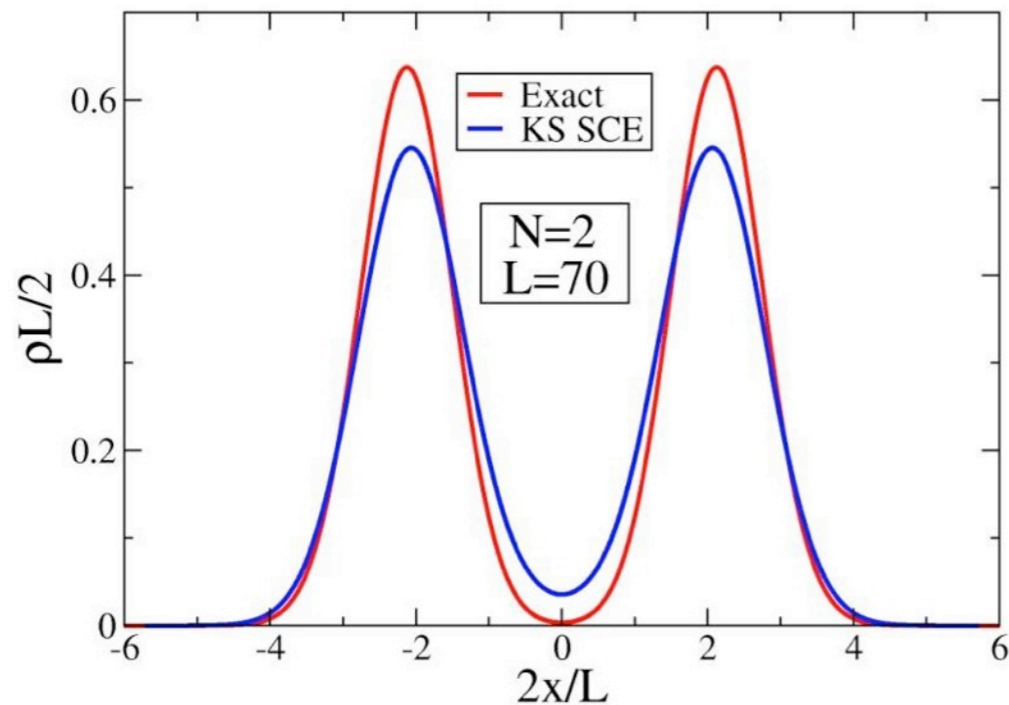
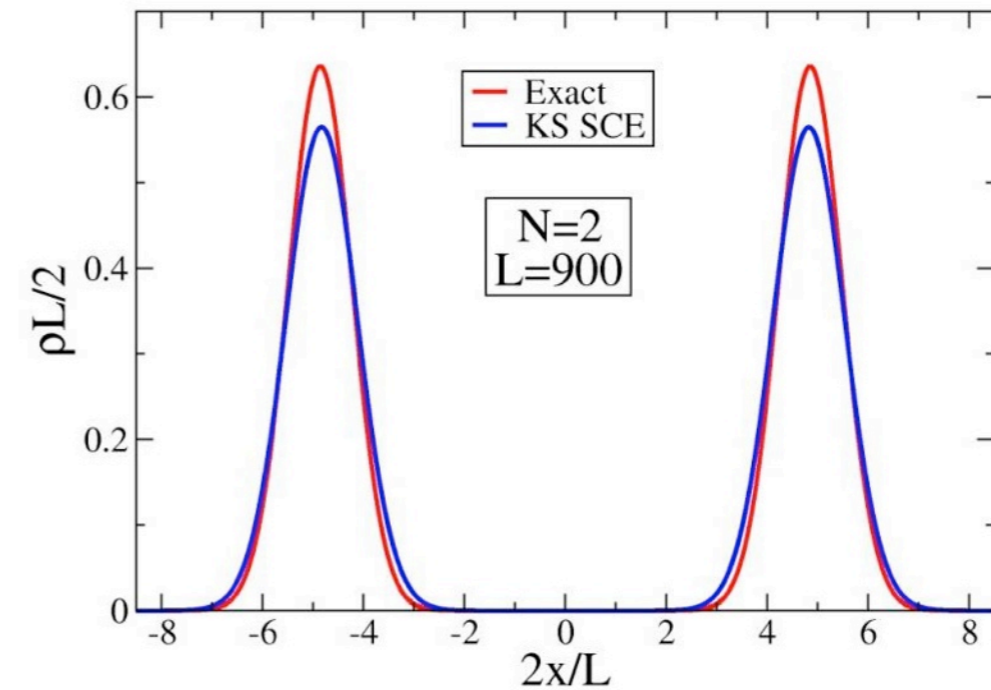
- Qualitatively good results in both the weak and strong correlation regimes
- “Bump” in the KS-SCE potential



# Applications to 1D systems

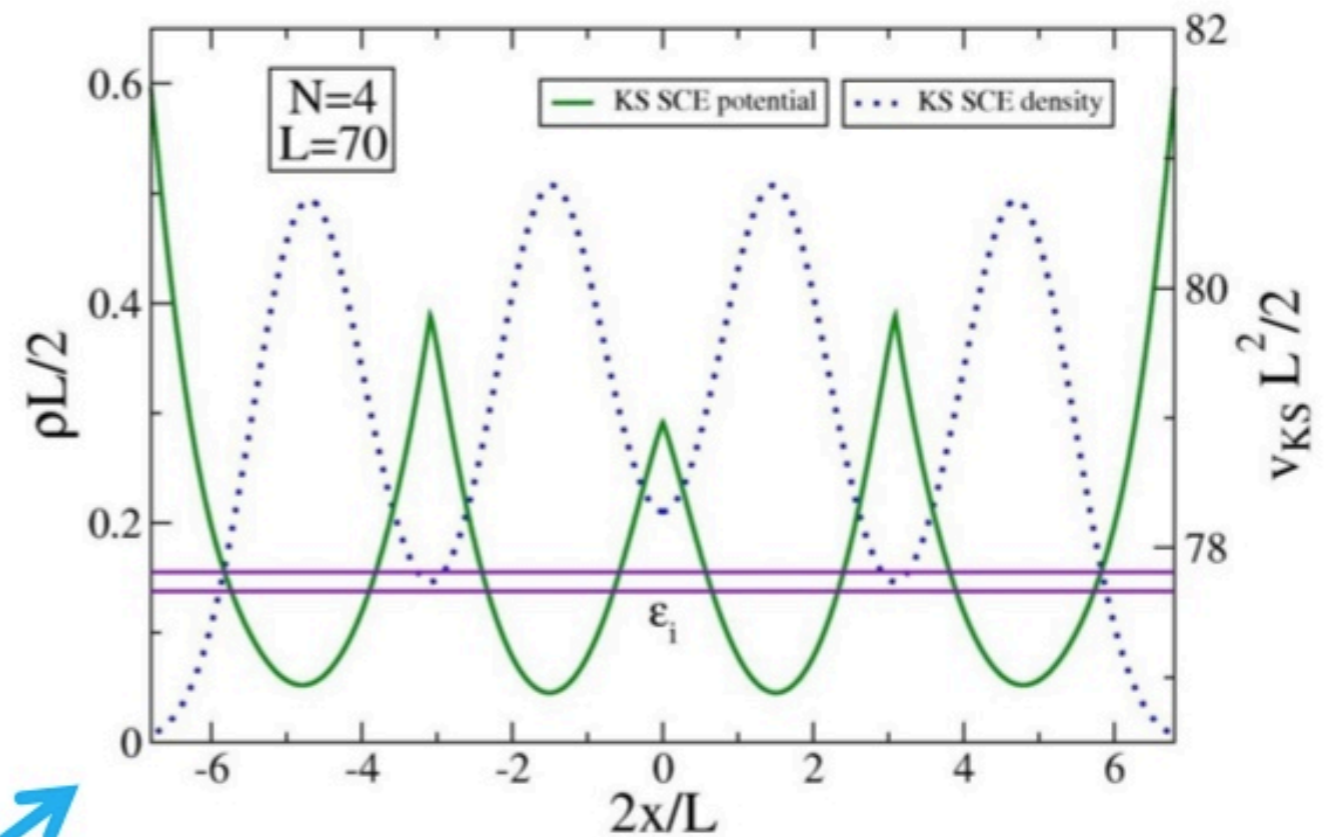
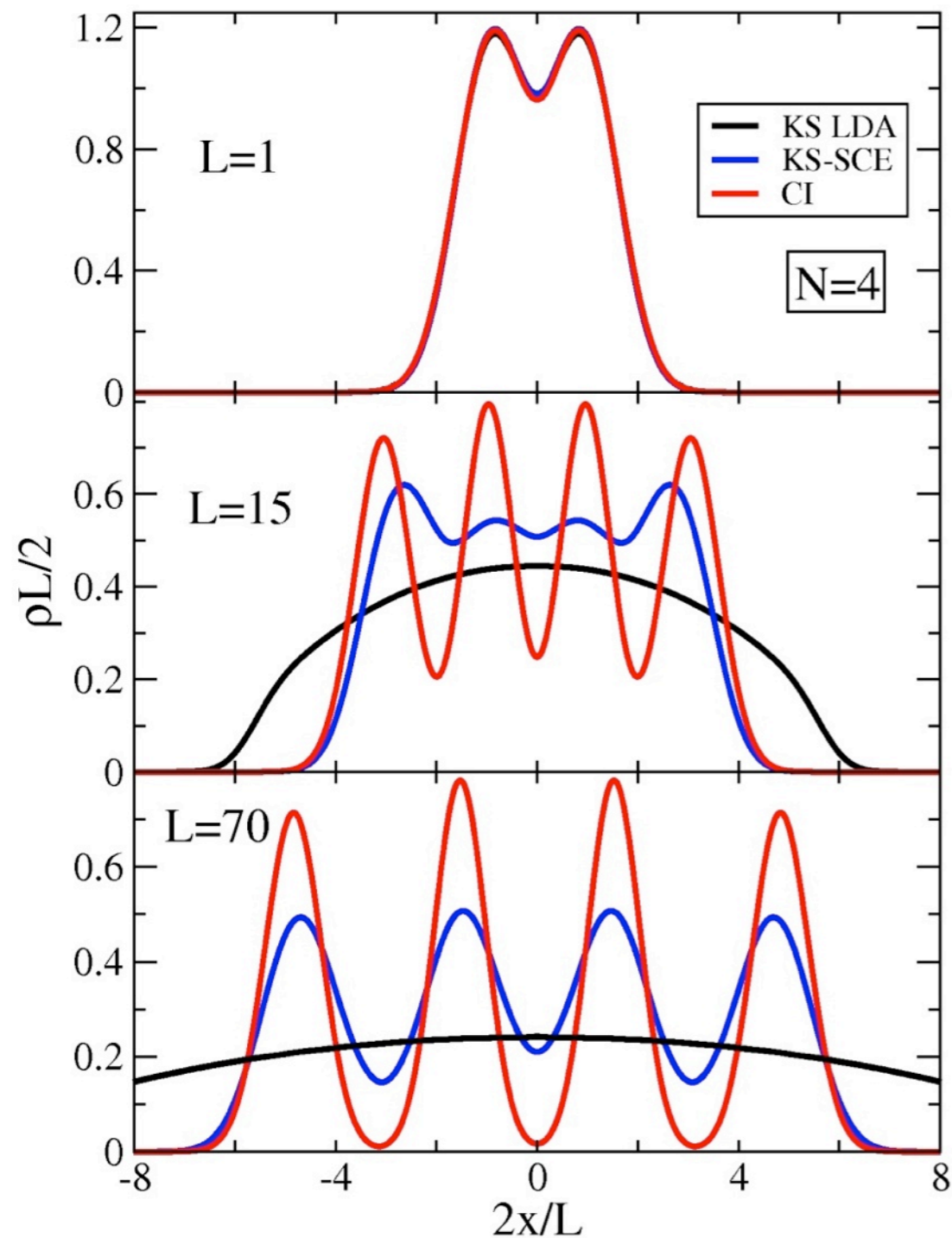
**1D harmonic confinement:**  $v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2$   $\omega = \frac{4}{L^2}$   $L$ : effective length

- Qualitatively good results in both the weak and strong correlation regimes
- “Bump” in the KS-SCE potential
- Tends to the exact result in the very strongly-interacting limit



# Applications to 1D systems

**1D harmonic confinement:**  $v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2$     $\omega = \frac{4}{L^2}$     $L$ : effective length



KS SCE is the first KS DFT approach able to capture the density peak splitting in quasi 1D without introducing magnetic order

Previous attempts include self-interaction corrections (SIC) and GGA:

S. H. Abedinpour, M. Polini, G. Xianlong, and M. P. Tosi, *Eur. Phys. J. B* 56, 127 (2007)

D. Vieira and K. Capelle, *J. Chem. Theory Comput.* 6, 3319 (2010)

D. Vieira, *Phys. Rev. B* 86, 075132 (2012)

# Total Energies

$N$	$L$	KS SCE	CI	KS LDA
2	2	1.81	2.49	2.59
2	15	0.0942	0.106	0.130
2	70	0.0112	0.0115	0.0182
4	1	25.08	28.42	28.57
4	2	8.46	10.60	10.68
4	15	0.491	0.541	0.580
4	70	0.0602	0.0629	0.0771
5	15	0.787	0.871	0.915
5	70	0.099	0.102	0.121

CI matrix  $10^5 - 10^6$

KS SCE is a rigorous lower bound to the exact ground-state energy

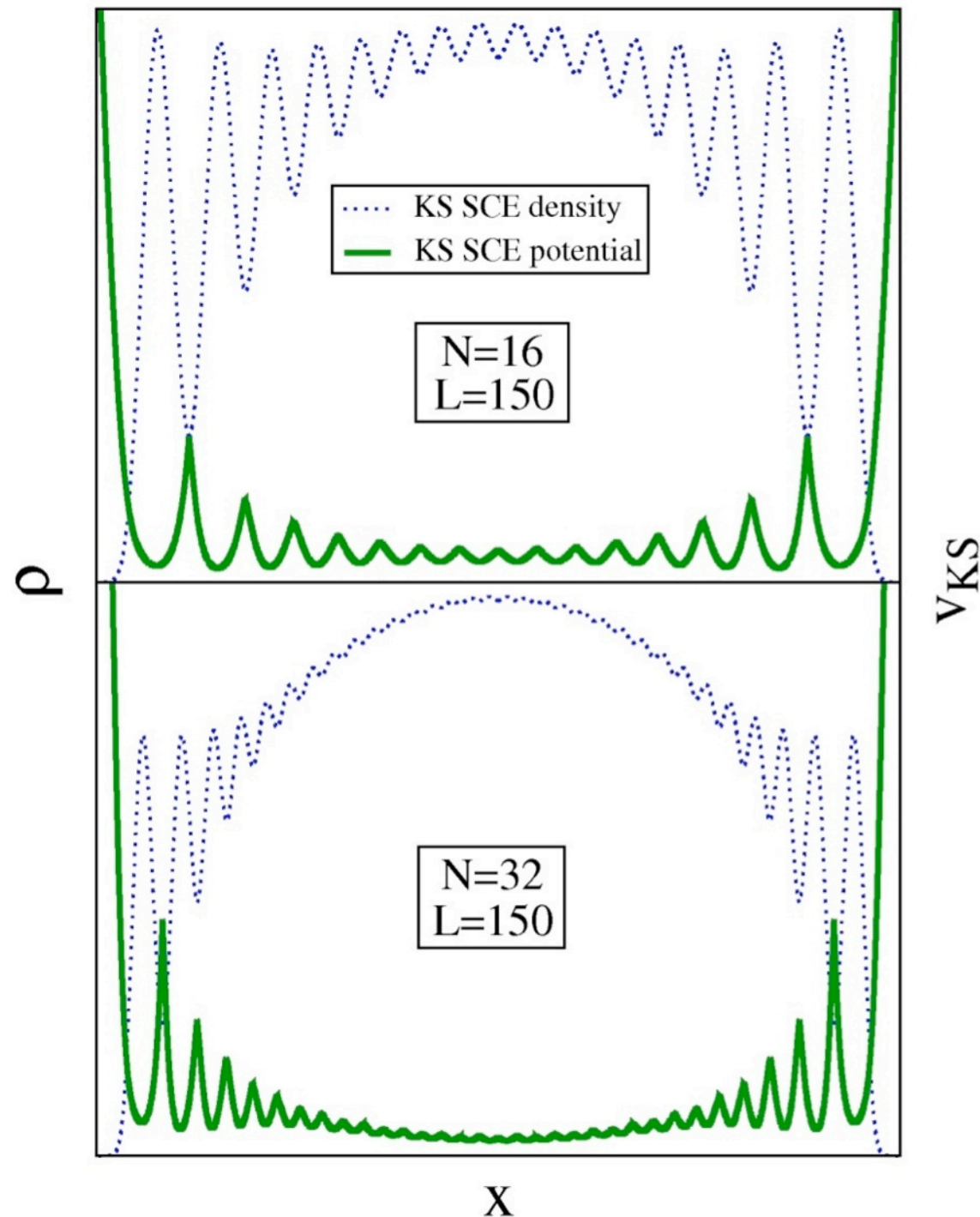
# Ionization potentials from minus HOMO

$N$	$L$	KS SCE	CI	KS LDA
2	2	1.65	1.99	2.56
2	15	0.104	0.097	0.263
2	70	0.0126	0.0111	0.040 87
4	1	11.26	11.86	12.56
4	2	4.08	4.65	5.02
4	15	0.248	0.256	0.453
4	70	0.0318	0.0304	0.069 09
5	15	0.325	0.330	0.539
5	70	0.0408	0.0391	0.081 72



# Applications to 1D systems

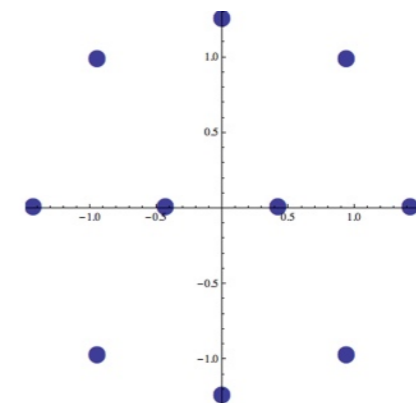
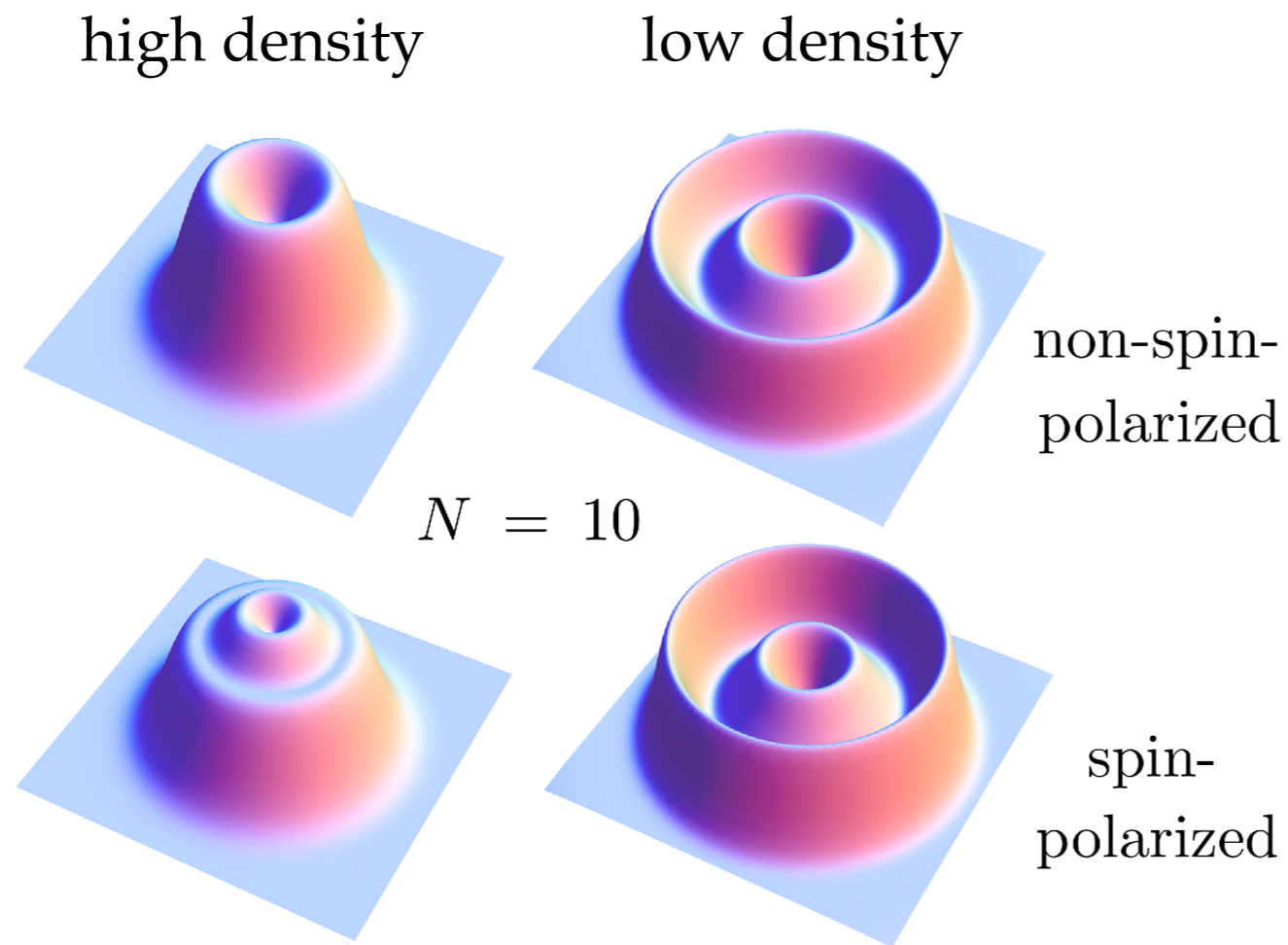
**1D harmonic confinement:**  $v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2$     $\omega = \frac{4}{L^2}$     $L$ : effective length



- **KS-SCE allows to treat large strongly-correlated quasi 1D systems (vs CI, limited to 6-8 particles, QMC and DMRG ~ 100 electrons).**
- **Computational time similar to KS LDA calculations**
- **Applications in Physics (model semiconductor quantum wires); nanotransport, quantum computation, ...**

# Model Quantum Dots

Example: Electrons confined in semiconductor heterostructures  
Self-consistent KS densities with the SCE functional



# 1D as a test lab for 3D chemistry

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 8581–8590

www.rsc.org/pccp

PAPER

## Reference electronic structure calculations in one dimension†

Lucas O. Wagner,<sup>\*a</sup> E. M. Stoudenmire,<sup>a</sup> Kieron Burke<sup>ab</sup> and Steven R. White<sup>a</sup>

Received 24th December 2011, Accepted 1st May 2012

DOI: 10.1039/c2cp24118h

THE JOURNAL OF CHEMICAL PHYSICS **131**, 224105 (2009)

## Exact Kohn–Sham potential of strongly correlated finite systems

N. Helbig,<sup>1,a)</sup> I. V. Tokatly,<sup>1,2</sup> and A. Rubio<sup>1,3</sup>

<sup>1</sup>Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPIC, Av. Tolosa 72, San Sebastián E-20018, Spain

<sup>2</sup>IKERBASQUE. Basque Foundation for Science. Bilbao E-48011. Spain

PHYSICAL REVIEW A **83**, 032503 (2011)

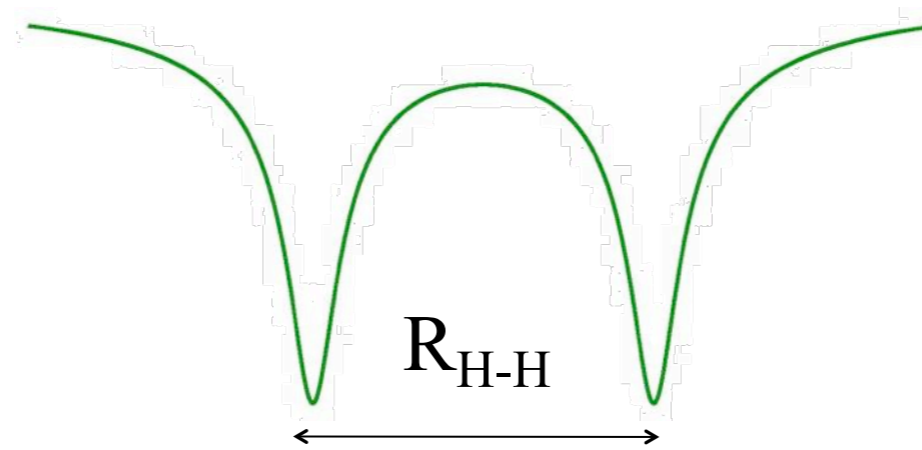
## Density functional theory beyond the linear regime: Validating an adiabatic local density approximation

N. Helbig,<sup>1</sup> J. I. Fuks,<sup>1</sup> M. Casula,<sup>2</sup> M. J. Verstraete,<sup>3,4</sup> M. A. L. Marques,<sup>5,4</sup> I. V. Tokatly,<sup>1,6</sup> and A. Rubio<sup>1,7</sup>

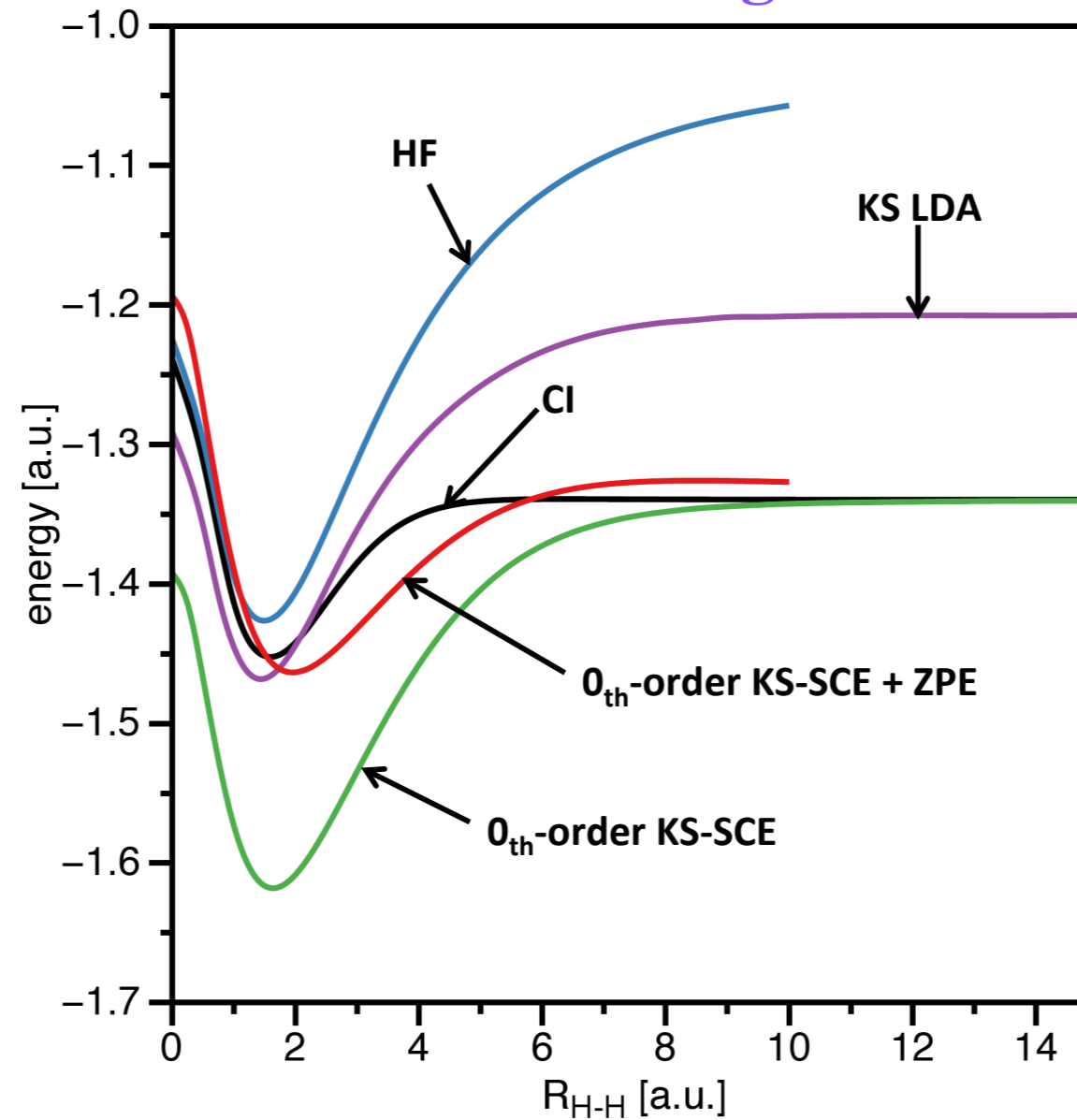
$$w_s(x) = \frac{1}{\sqrt{x^2 + a^2}}$$

# Model Chemistry

1D model for  $H_2$  :



Total energies

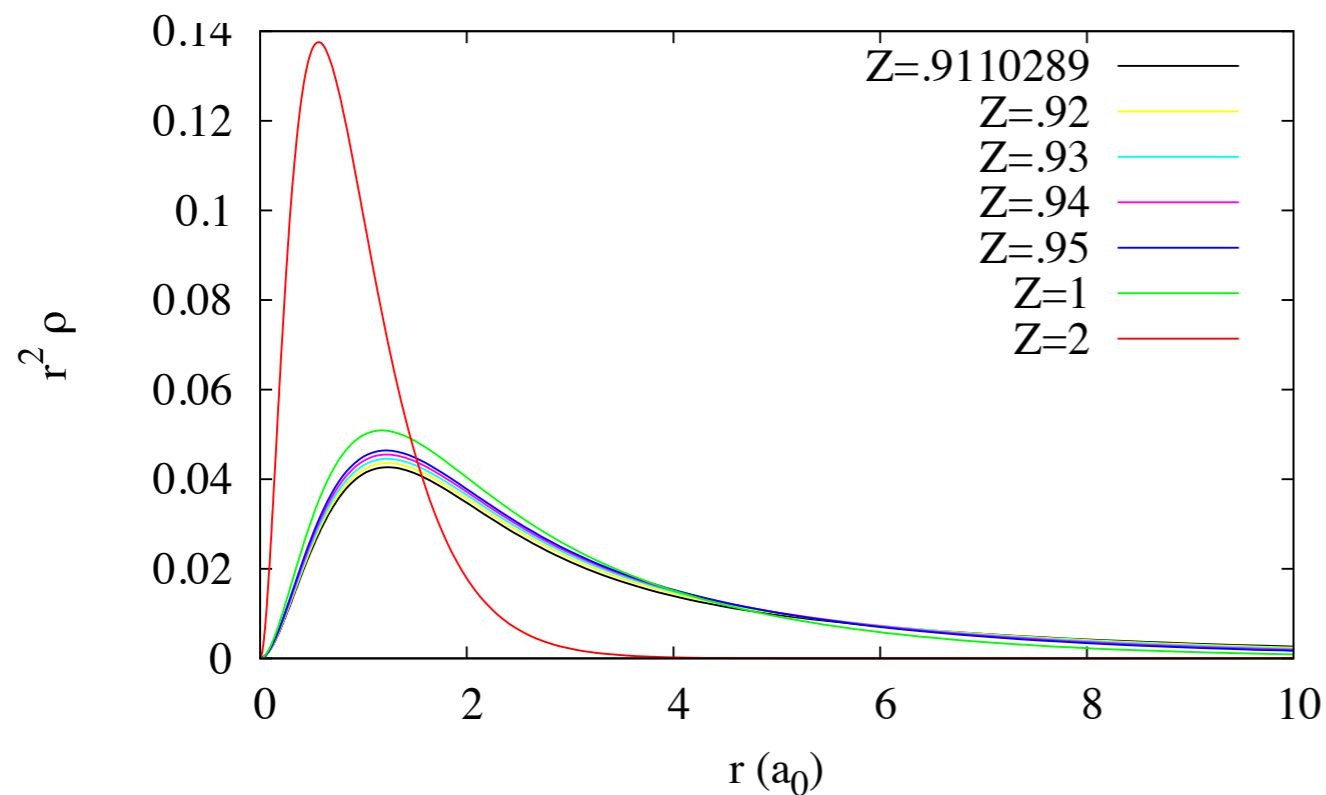


# Negative ions (3D)

$$N = 2 \quad v_{\text{ext}}(\mathbf{r}) = -\frac{Z}{r}$$

$$Z \rightarrow Z_{\text{crit}} \approx 0.9110289$$

the system loses 1 electron



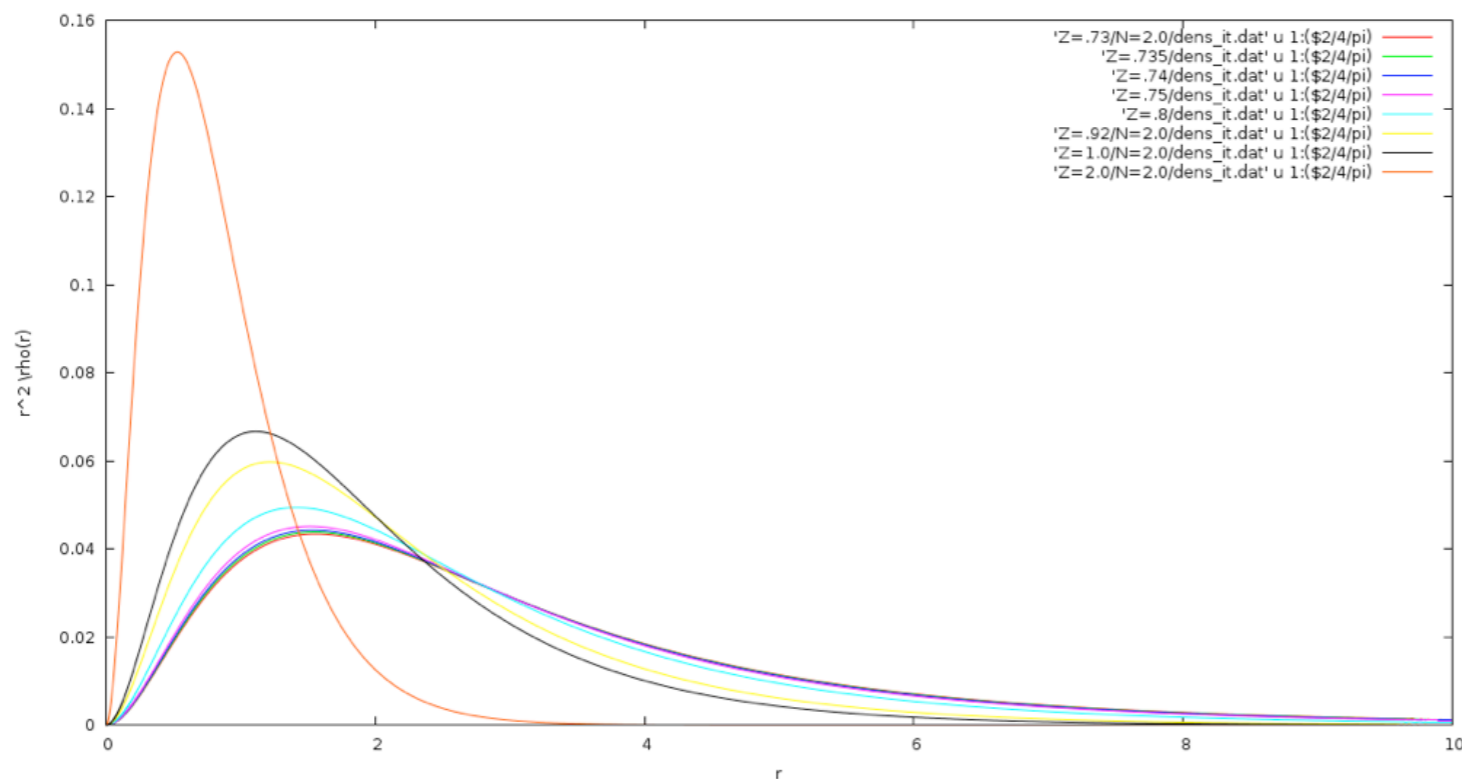
accurate results  
(C. Umrigar & J. Morgan)

# Negative ions (3D)

$$N = 2 \quad v_{\text{ext}}(\mathbf{r}) = -\frac{Z}{r}$$

$Z \rightarrow Z_{\text{crit}} \approx 0.9110289$  the system loses 1 electron

KS SCE self-consistent:  $Z_{\text{crit}} \approx 0.73$



A. Mirtschink

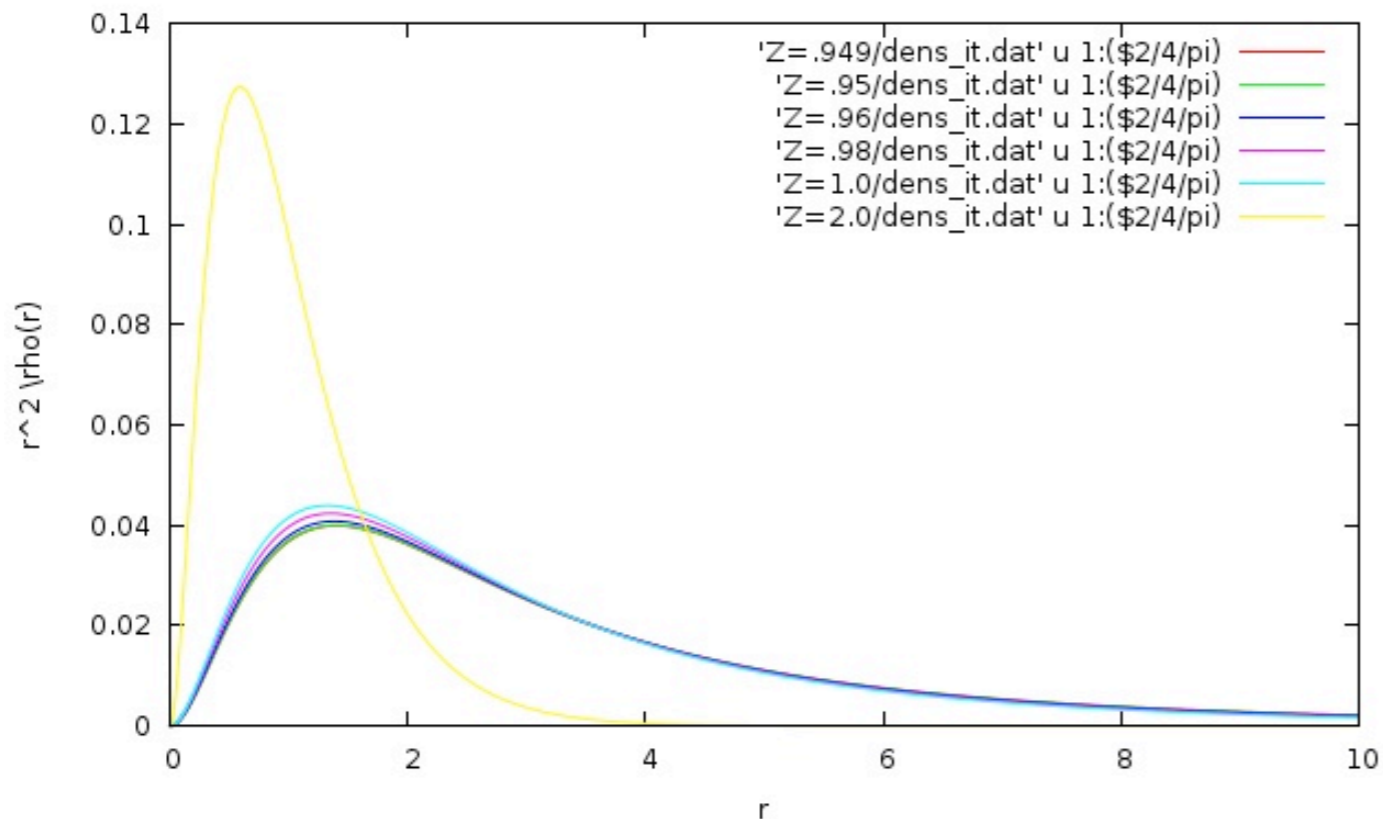
# Negative ions (3D)

$$N = 2 \quad v_{\text{ext}}(\mathbf{r}) = -\frac{Z}{r}$$

$Z \rightarrow Z_{\text{crit}} \approx 0.9110289$  the system loses 1 electron

KS SCE +local correction (self-consistent):

$$Z_{\text{crit}} \approx 0.94$$



A. Mirtschink

# How to treat general 3D systems?

## Monge-Kantorovich formulation

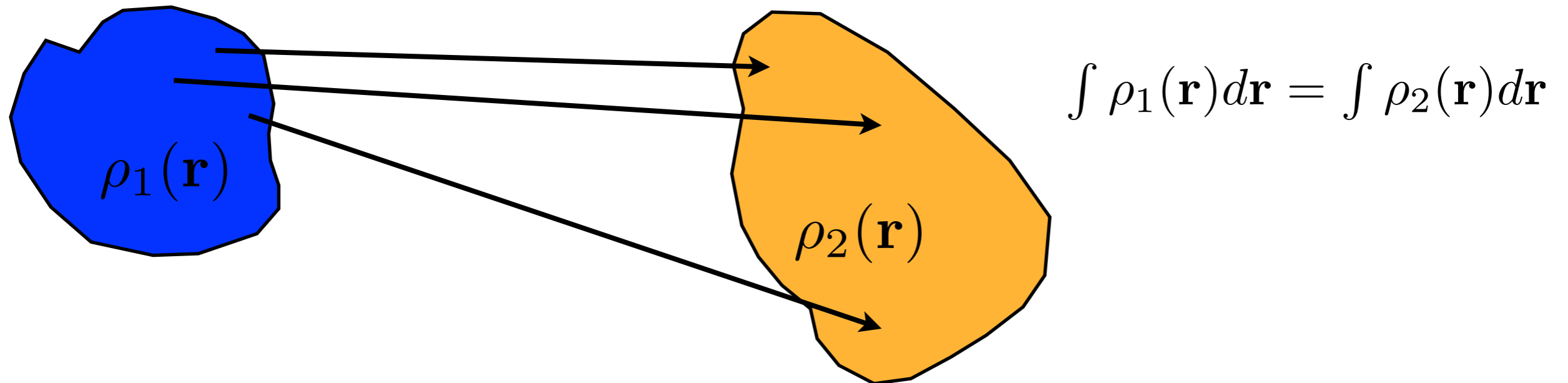
Buttazzo, De Pascale, and Gori-Giorgi, *Phys. Rev. A*. **85**, 062502 (2012)

Cotar, Friesecke, and Kluppelberg, *Comm. Pure Appl. Math.* **66**, 548 (2013)



# Optimal transport formulation

(Monge-Kantorovich)



**cost function** (work necessary to move a unit mass)

$$c(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_2 - \mathbf{r}_1|$$

minimize total cost  $\Rightarrow \min_{\mathbf{f}} \int c(\mathbf{r}, \mathbf{f}(\mathbf{r})) \rho_1(\mathbf{r}) d\mathbf{r}$

*optimal map*

Difficult to prove in general the existence of  
the optimal map...

## Relaxed Kantorovich formulation

search  $P(\mathbf{r}_1, \mathbf{r}_2)$  that minimizes the cost

$$\min_P \int P(\mathbf{r}_1, \mathbf{r}_2) c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad \text{with} \quad \begin{cases} \int P(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \rho_1(\mathbf{r}_1) \\ \int P(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = \rho_2(\mathbf{r}_2) \end{cases}$$

# with more than 2 masses

$$\min_P \int P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \sum_{i>j}^N c(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$$

$$\int P(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N = \rho_1(\mathbf{r})$$

$$\int P(\mathbf{r}_1, \mathbf{r}, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_3 \dots d\mathbf{r}_N = \rho_2(\mathbf{r})$$

⋮

**SCE problem**  $\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$

Giuseppe Buttazzo  
Luigi De Pascale

$$P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$$

$$c(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

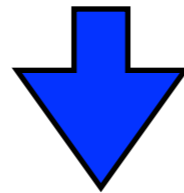
$$\rho_1(\mathbf{r}) = \rho_2(\mathbf{r}) = \dots = \rho_N(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N}$$

# Things you can prove from Optimal Transport

- Existence of  $P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) (= |\Psi_{\text{SCE}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2)$
- $v_{\text{SCE}}(\mathbf{r})$  exists and it is bounded (Kantorovich potential)
- Not possible (so far) to prove general existence of  $\mathbf{f}_i(\mathbf{r})$
- Dual Kantorovich problem

# Dual Kantorovich problem

$$V_{\text{SCE}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$



$$V_{\text{SCE}}[\rho] = \max_u \left\{ \int \rho(\mathbf{r}) u(\mathbf{r}) d\mathbf{r} : \sum_{i=1}^N u(\mathbf{r}_i) \leq \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\}$$

$$v_{\text{SCE}}(\mathbf{r}) = u(\mathbf{r}) + C$$

Kantorovich potential

# Kantorovich formulation: key to treat the 3D case?

PHYSICAL REVIEW B **87**, 125106 (2013)

## **Kantorovich dual solution for strictly correlated electrons in atoms and molecules**

Christian B. Mendl<sup>1</sup> and Lin Lin<sup>2</sup>

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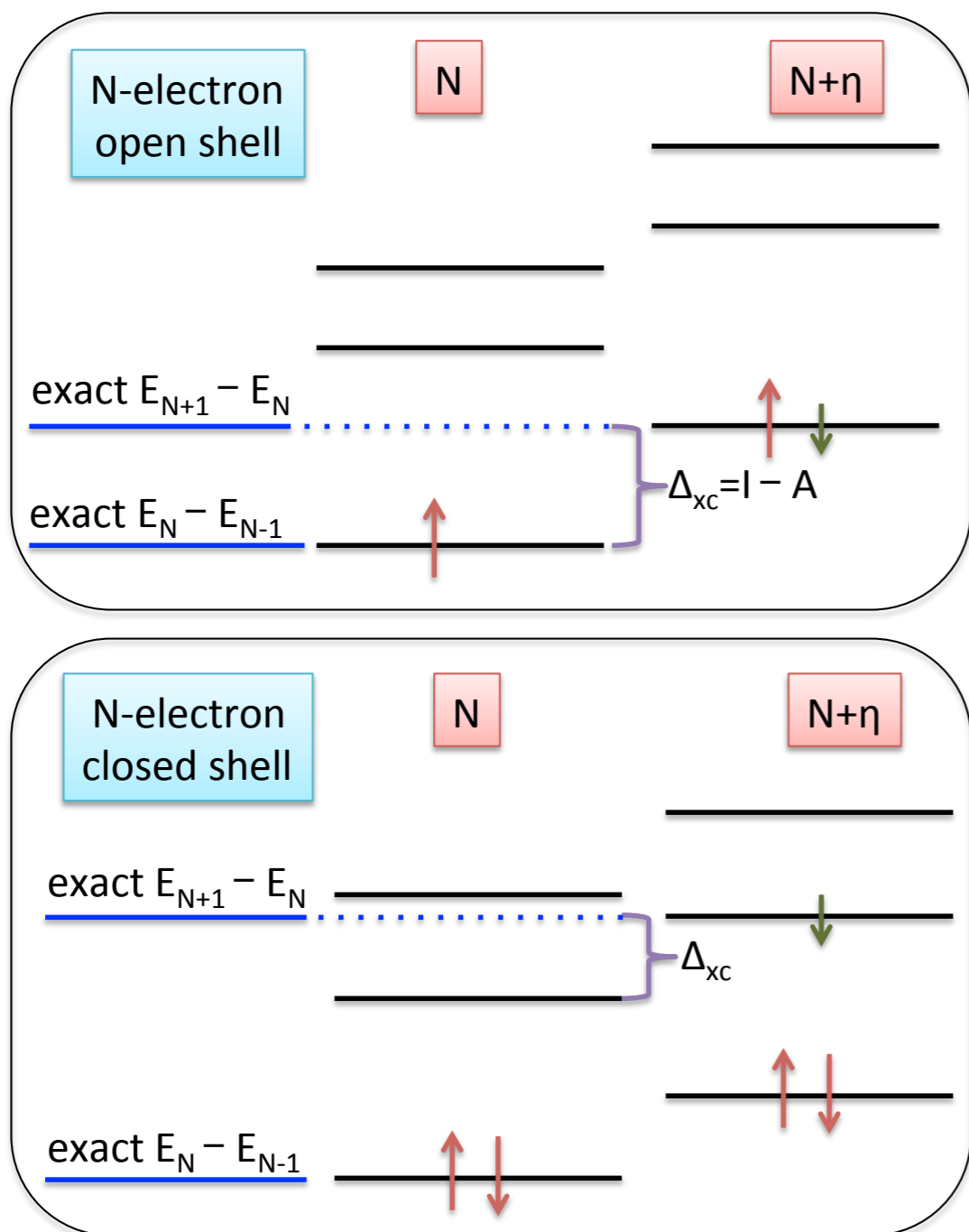
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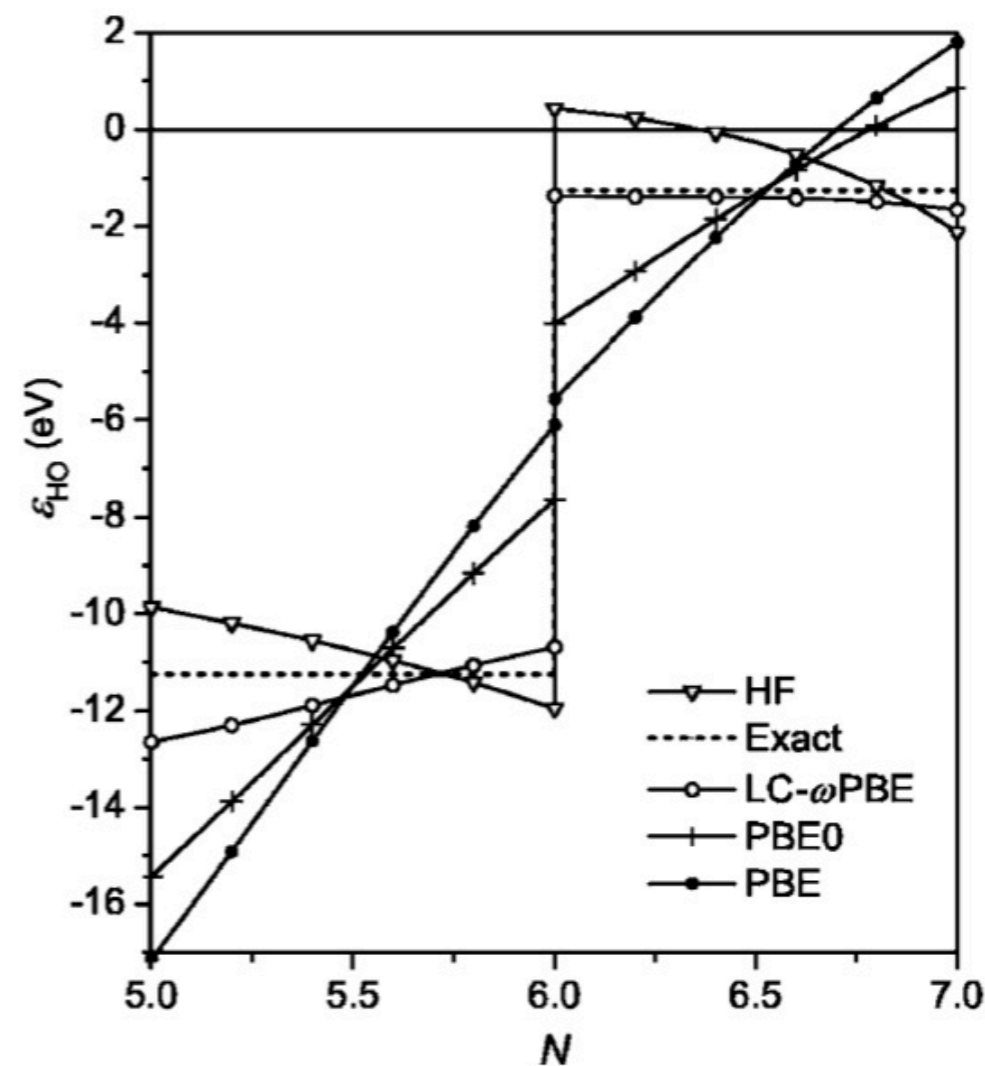
The many-body Coulomb repulsive energy of strictly correlated electrons provides direct information on the exact Hohenberg-Kohn exchange-correlation functional in the strong interaction limit. Until now the treatment of strictly correlated electrons has been based on the calculation of comotion functions with the help of semianalytic formulations. This procedure is system-specific and has been limited to spherically symmetric atoms and strictly one-dimensional systems. We develop a nested optimization method which solves the Kantorovich dual problem directly, and thus facilitates a general treatment of strictly correlated electrons for systems including atoms and small molecules.

Generalization to open systems:  
The Derivative Discontinuity at  
integer particle numbers

# What exact spin-restricted KS should do



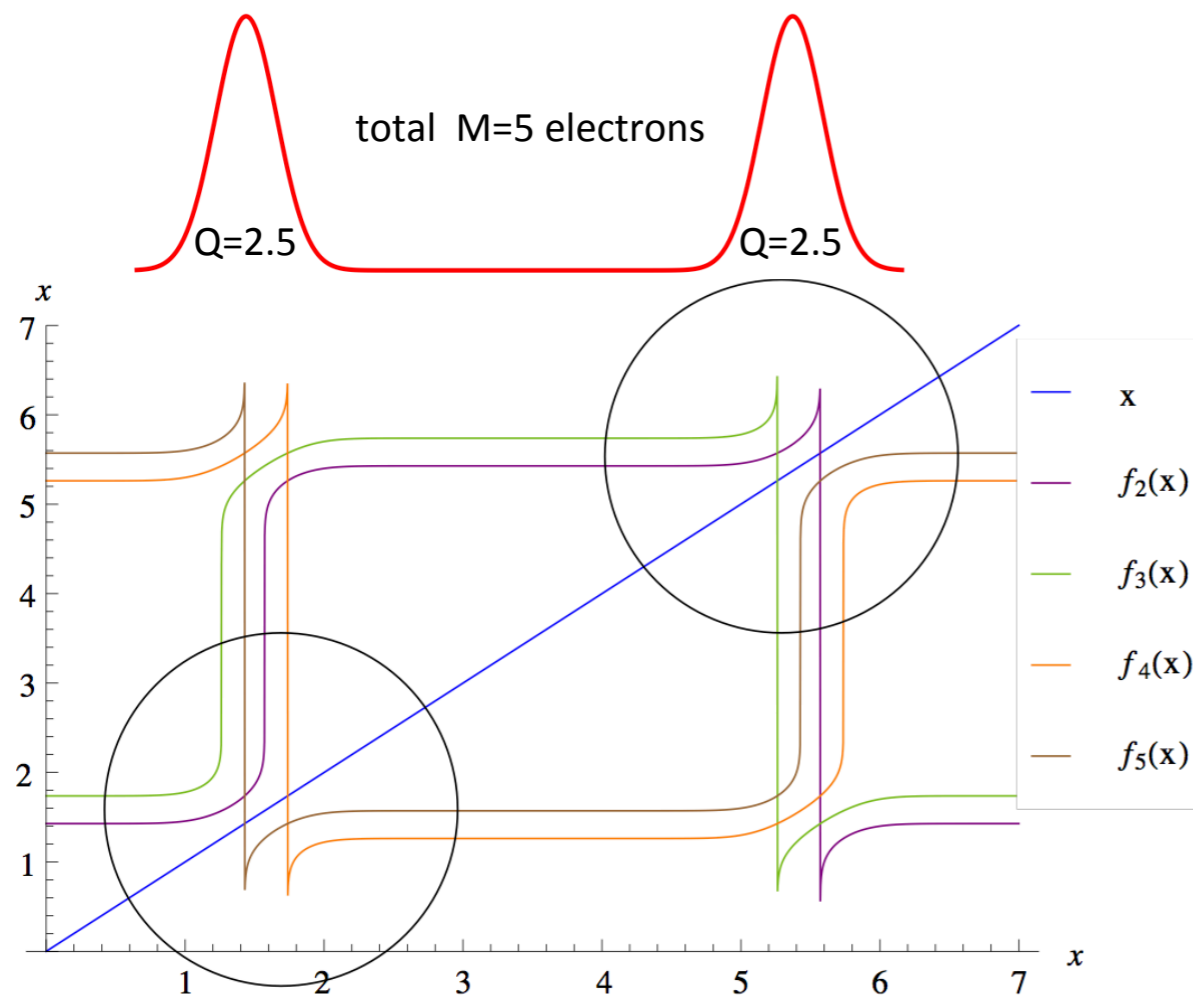
What approximate functionals do (UKS)



Vydrov, Scuseria & Perdew, JCP 126, 154109 (2007)

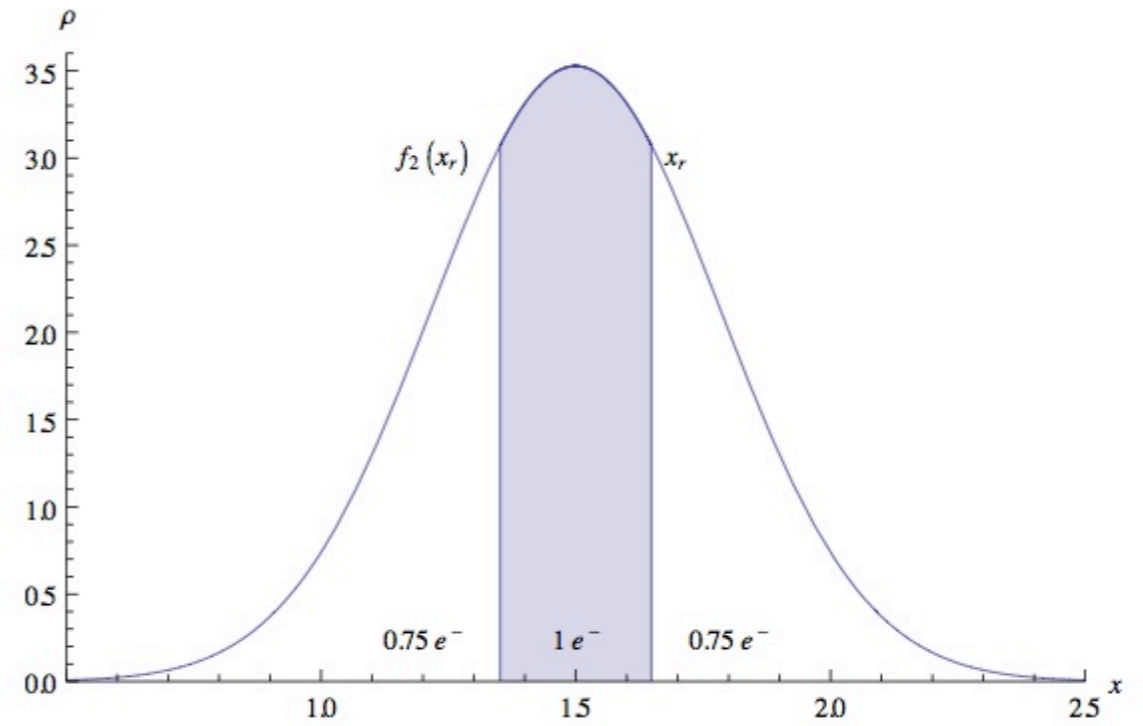
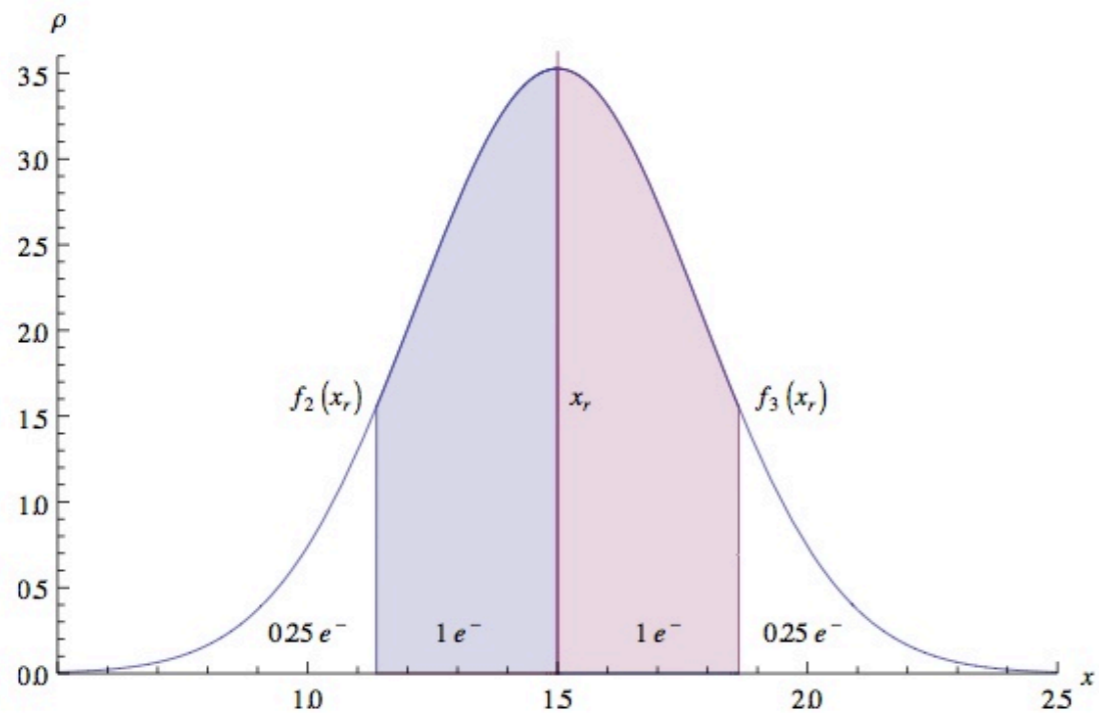


# SCE for fractional particle numbers

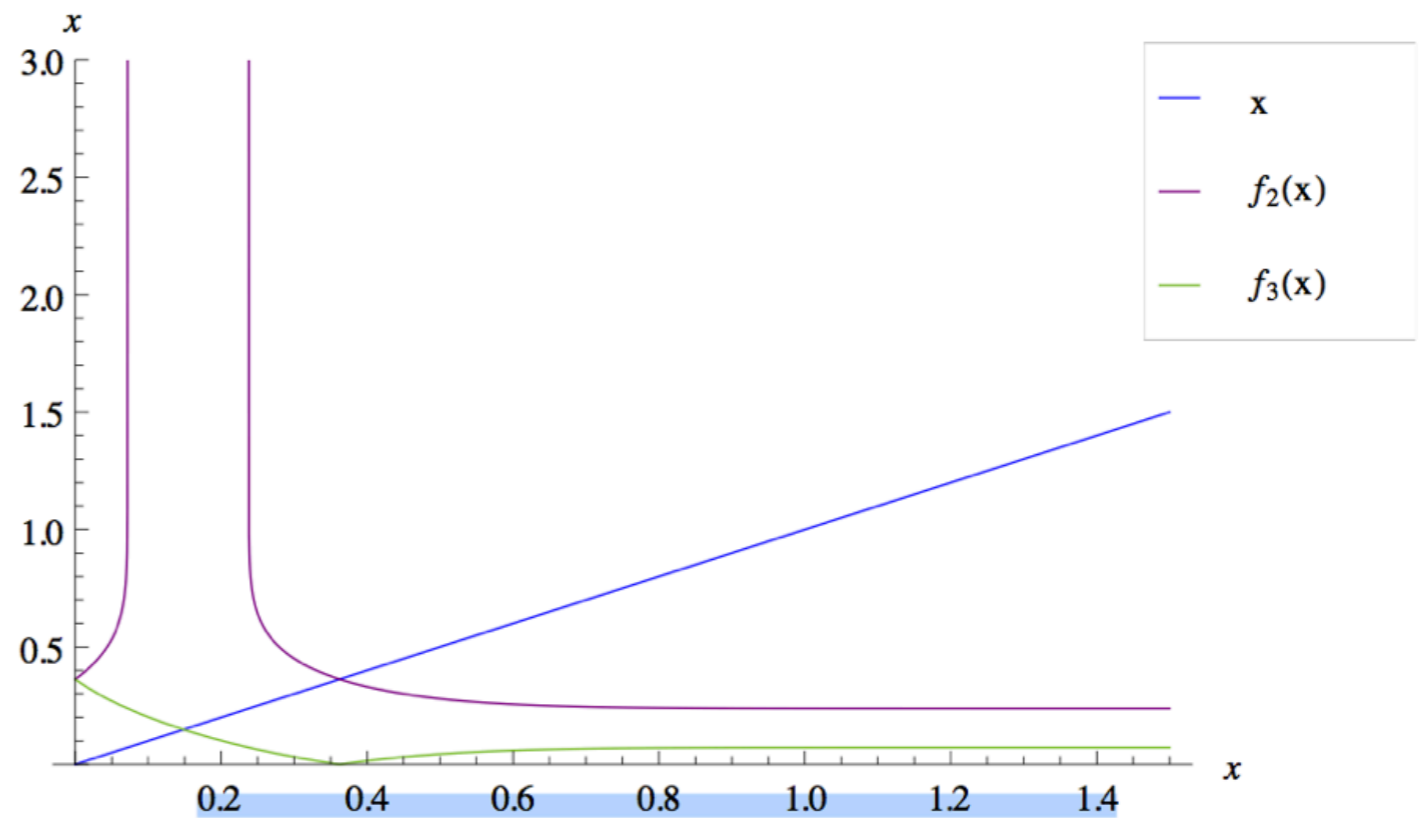


$$\int_{f_i(x)}^{f_{i+1}(x)} \rho(y) dy = 1$$

## example: $N=2.5$



$$\int_{f_i(x)}^{f_{i+1}(x)} \rho(y) dy = 1$$



co-motion functions for  $N + \eta$  electrons

$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + 2i] & x < a_{N-2i+\eta} \\ N_e^{-1}[|N_e(x) - 2(N + 1 - i)|] & x > a_{N+2-2i-\eta} \\ \infty & \text{otherwise,} \end{cases}$$

get the SCE potential by integrating

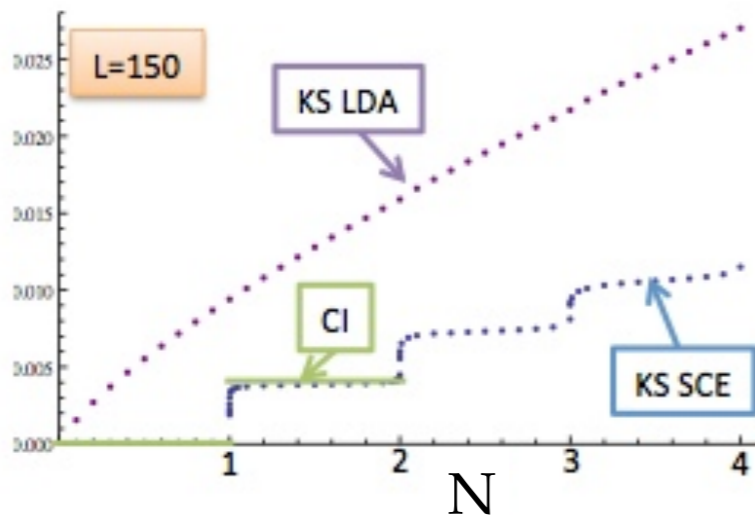
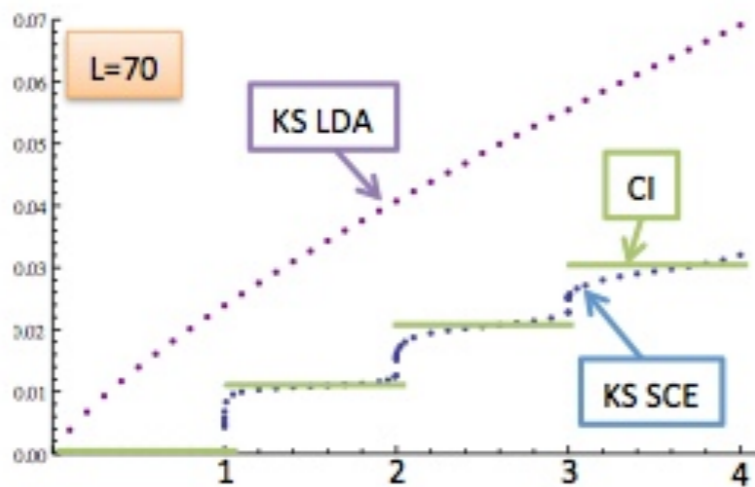
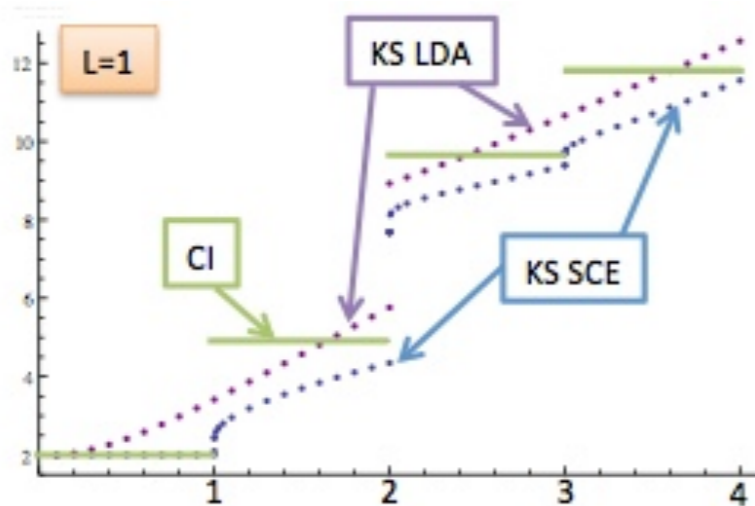
$$v'_{\text{SCE}}[\rho](x) = - \sum_{i=2}^N w'_b(|x - f_i(x)|) \text{sgn}(x - f_i(x))$$

with boundary condition

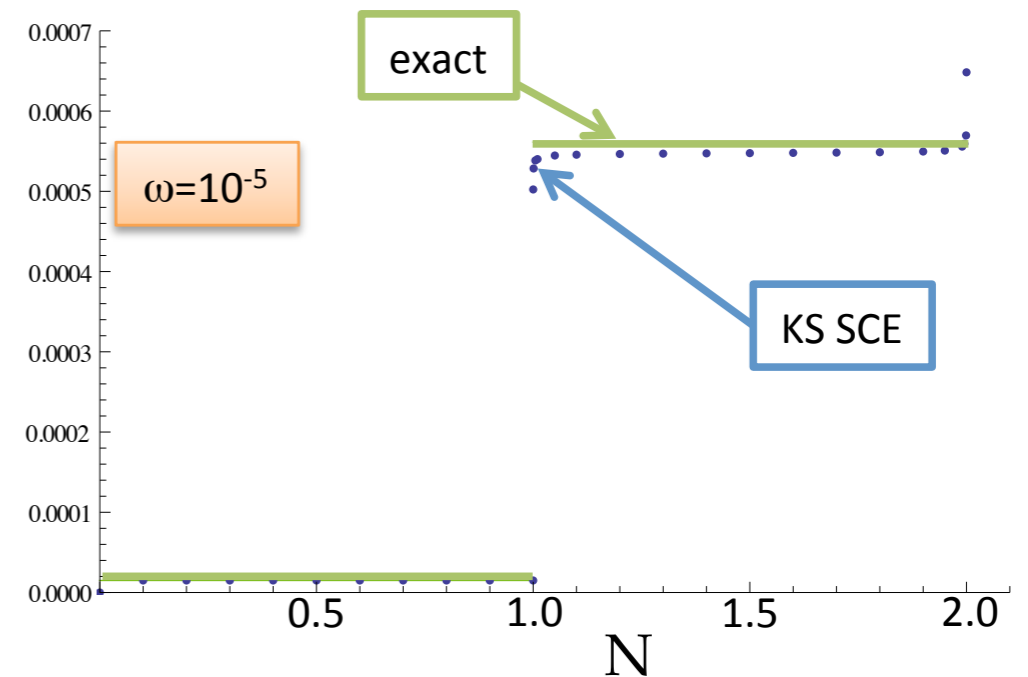
$$v_{\text{SCE}}[\rho](x \rightarrow \infty) = 0$$

# Self-consistent KS HOMO eigenvalue

quasi 1D



3D (Hooke's atom)



# Conclusions and outlook

- **Strongly-interacting limit of DFT: approximations for the xc functional able to describe strong correlation within the restricted KS scheme (no artificial symmetry breaking)**
- **One can treat strongly-correlated quasi 1D systems with large electron numbers**

## Perspectives:

- **Improve the algorithms for 2D and 3D systems**
- **Corrections to the KS SCE functional:**

$$F[\rho] = T_s[\rho] + V_{ee}^{\text{SCE}}[\rho] + T_c[\rho] + V_{ee}^d[\rho]$$

- **Inclusion of spin states**
- **Approximate SCE forms for new non-local functionals**
- **Nanotransport**

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*Thank you for your  
attention!*