

# Outline

- The many-electron problem (ground state)
- Kohn-Sham DFT
- A bird-eye's view of density functional approximations
- Levy-Lieb DFT and Generalized KS (in brief)

# **THE MANY-ELECTRON PROBLEM**

# State of electrons = solution of Schrödinger equation

$$\hat{H}\Psi_E = E\Psi_E$$

Electronic wavefunction (BOA)

$$\Psi_{\underline{\mathbf{R}}}(\underline{\mathbf{x}})$$

$$\underline{\mathbf{R}} = \{\mathbf{R}_A\}_{A=1}^{M=3}$$

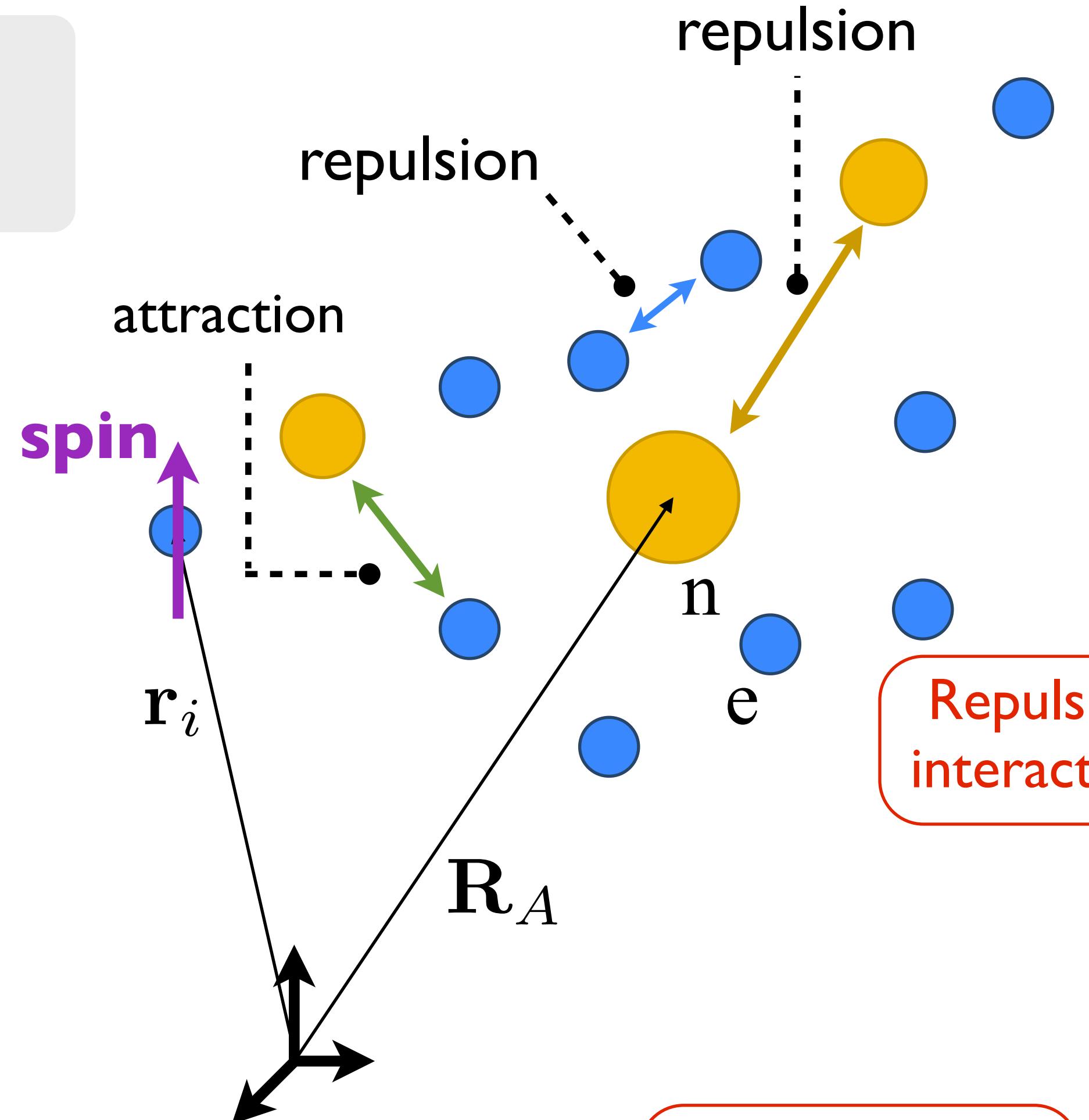
$$\underline{\mathbf{x}} = \{\mathbf{x}_i\}_{i=1}^{N=10}$$

$$\mathbf{x}_i = (\mathbf{r}_i, s_i)$$

**within the Born-Oppenheimer approximation**

# Electronic Hamiltonian

e = electron  
n = nucleus



Atomic units:  $e = m = \hbar = 1$

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}$$

$$\hat{T}_e = - \sum_i \frac{\nabla_i^2}{2}$$

Kinetic operator

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{ne} = \sum_i \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

External potential

$$\hat{V}_{nn} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

A constant  
(for fixed nuclei)

# State of electrons = solution of Schrödinger equation

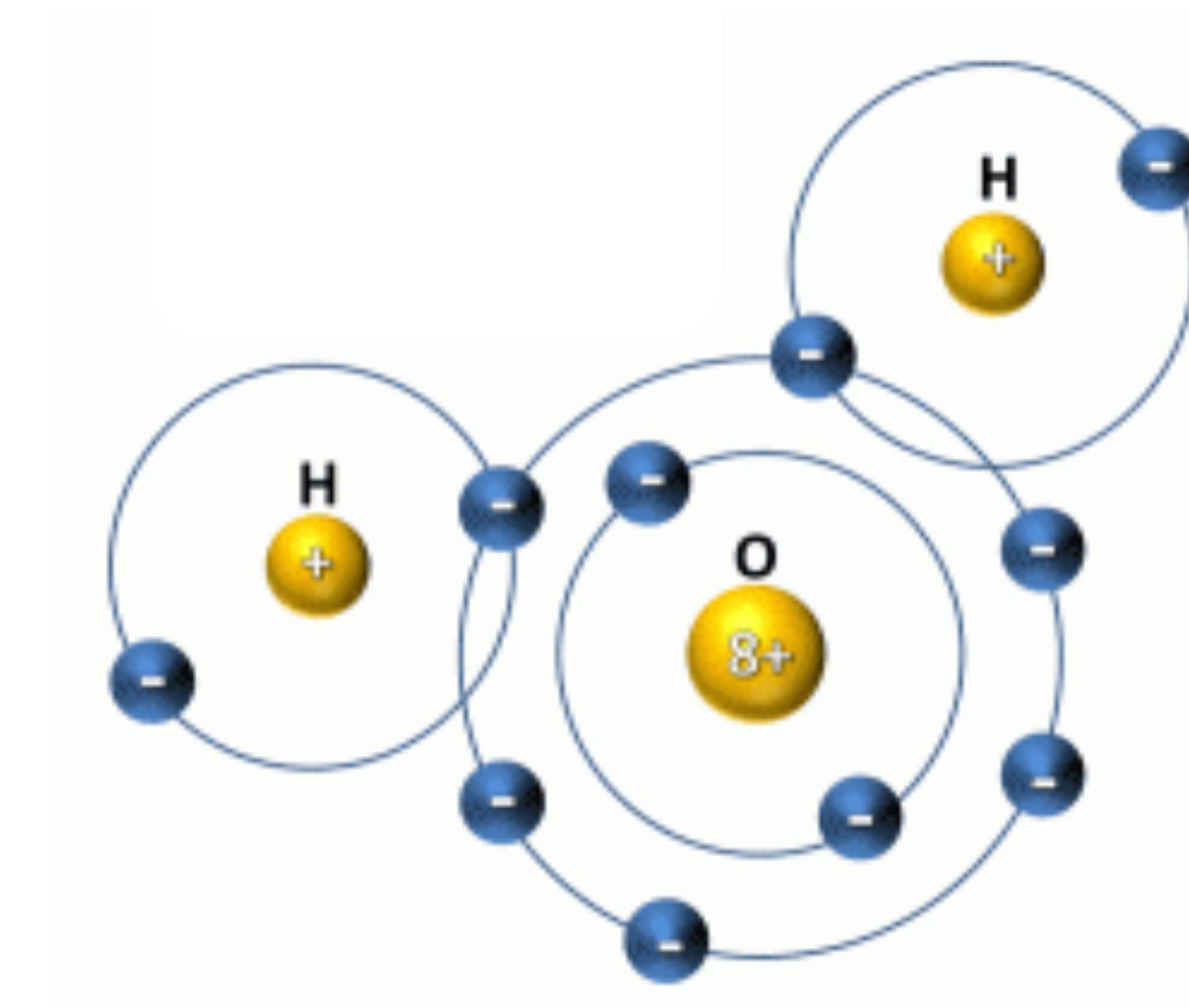
$$\hat{H} \Psi_F = \Psi_E$$

wavefunction (BOA)

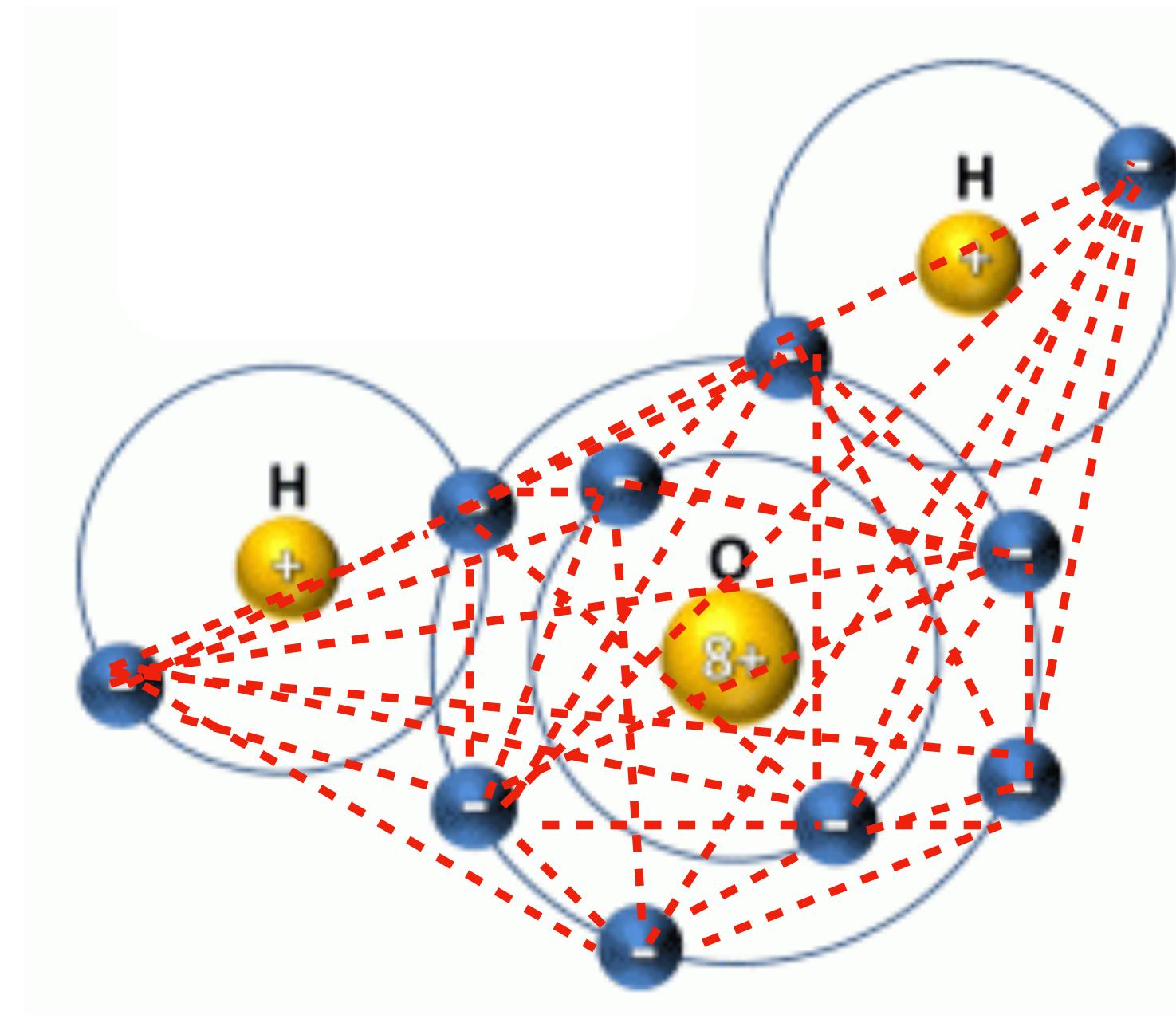
$$\Psi_{\underline{R}}(\underline{x})$$
$$\underline{R} = \{\underline{R}_A\}_{A=1}^M$$
$$\underline{x} = (x_1, \dots, s_i)$$

But we cannot solve it exactly...  
not even for a few electrons!

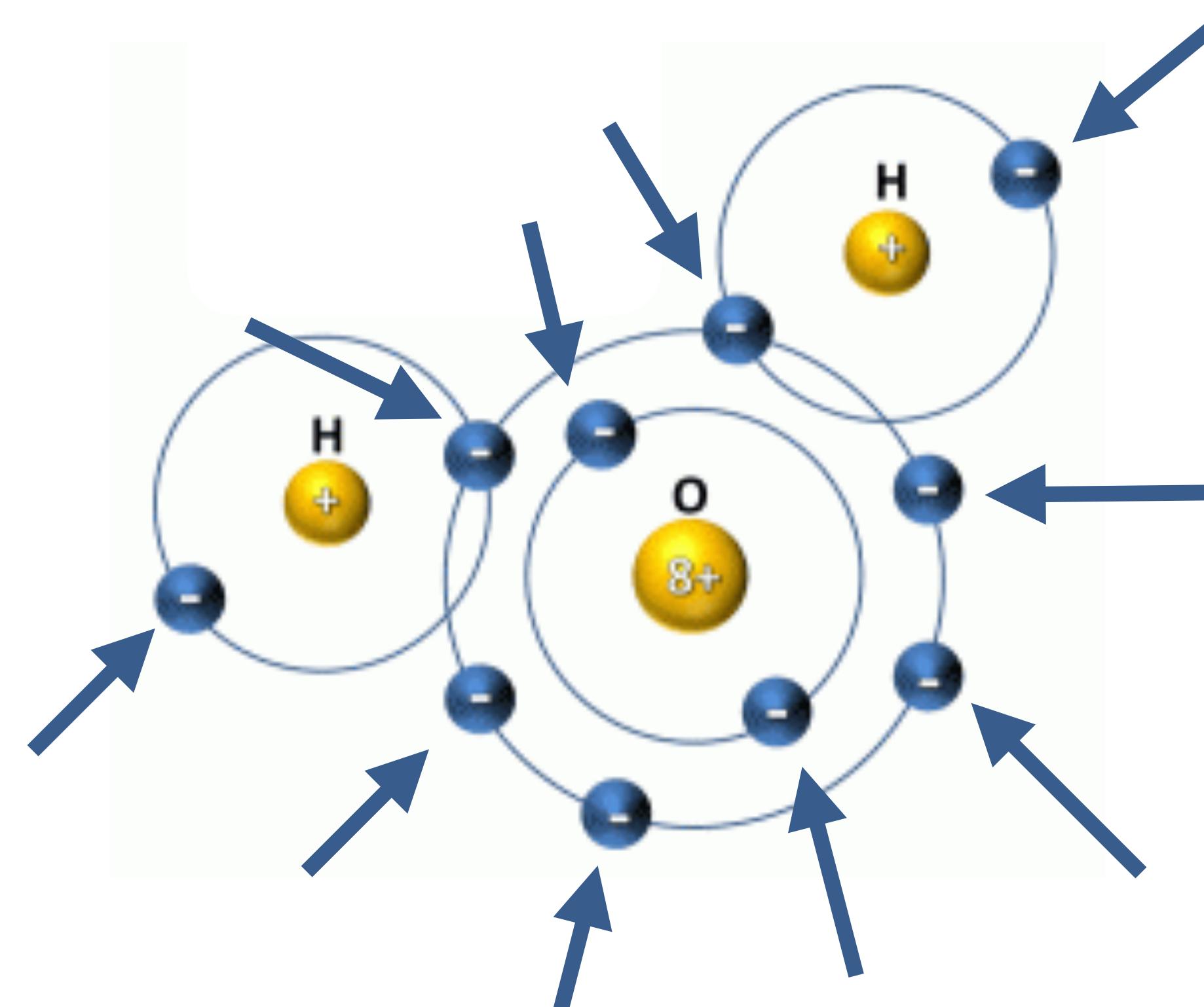
# Need models and approximations



# Difficulty 1: electron-electron interaction



# Difficulty 2: many electrons



# As an alternative to solving a diff. eq.

**Ground state energy** can be obtained from the minimization of a functional

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$
$$= \min_{\Psi} E[\Psi]$$

Anti-symmetric wavefunction  
for  $N$  electrons satisfying:

- proper boundary conditions
- normalization

$$\langle \Psi | \Psi \rangle = 1$$

Our first functional!

# As an alternative to solving a diff. eq.

**Ground state energy** can be obtained from the minimization of the functional

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

Let's reformulate it in terms of simpler quantities

- Anti-symmetry for exchange:
- Boundary conditions
- Normalization

$$\langle \Psi | \Psi \rangle = 1$$

Our first functional!

# **Kohn-Sham DFT**

# Particle density

$$n(\mathbf{r}) = N \sum_{\sigma} \int d\mathbf{x}_2 \dots d\mathbf{x}_N |\Psi(\mathbf{r}\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2$$

Given  $n(\mathbf{r})$  we can obtain the energy due to the external potential

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int d^3r \ v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

$$\hat{V}_{\text{en}} = \sum_i \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

$$n(\mathbf{r}) \rightarrow \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle$$

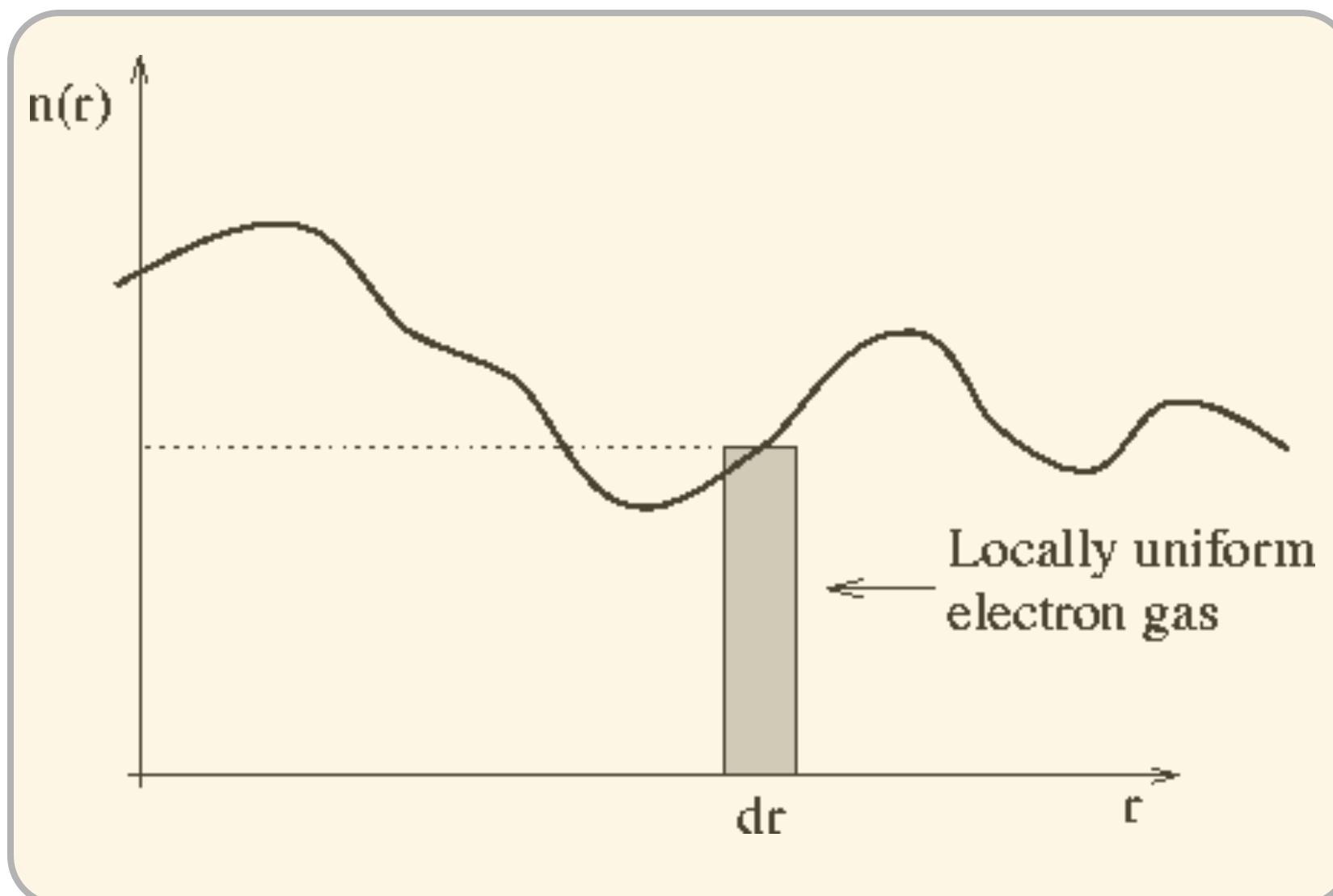
# Thomas-Fermi approximation

interaction energy borrowed  
from classical electrostatics

$$E_{\text{TF}}[n] = \frac{3}{5}C \int d^3r \ n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r \ n(\mathbf{r})v_{ext}(\mathbf{r})$$

kinetic energy density  
borrowed from  
Fermi gas

proper form for the energy  
due to external couplings



- *Semiclassical approximation*
- *pairs distributed independently*
- *wrong density, no quantum shells,  
no molecular binding*

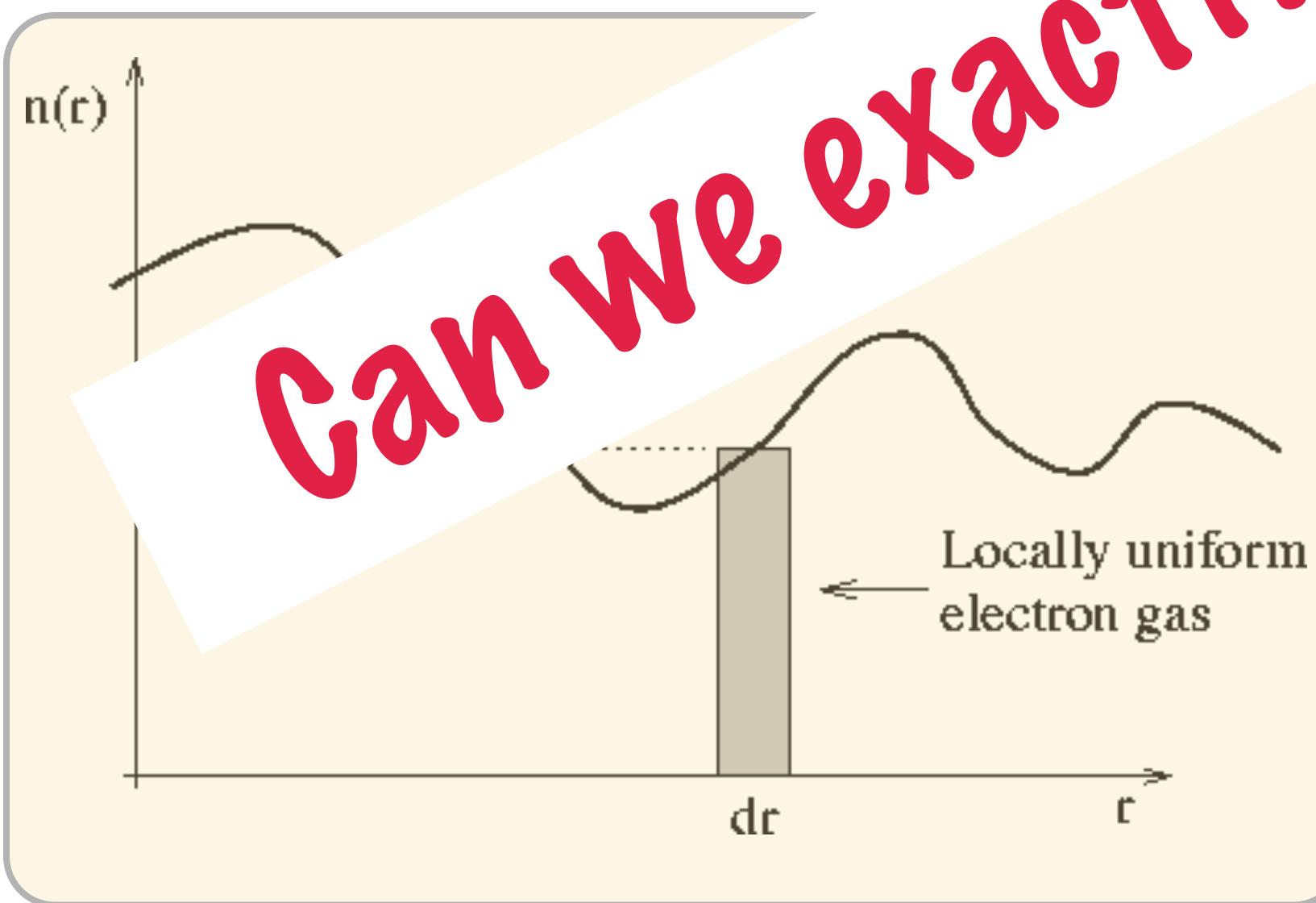
# Thomas-Fermi approximation

interaction energy borrowed  
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$$E_{TF}[n] = \frac{3}{5}C \int d^3r \ n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} v_{ext}(\mathbf{r})$$

kinetic energy density  
borrowed from  
Fermi gas

proper form for the energy  
due to external couplings



Can we exactify it? (in some sense)

Semiclassical approximation

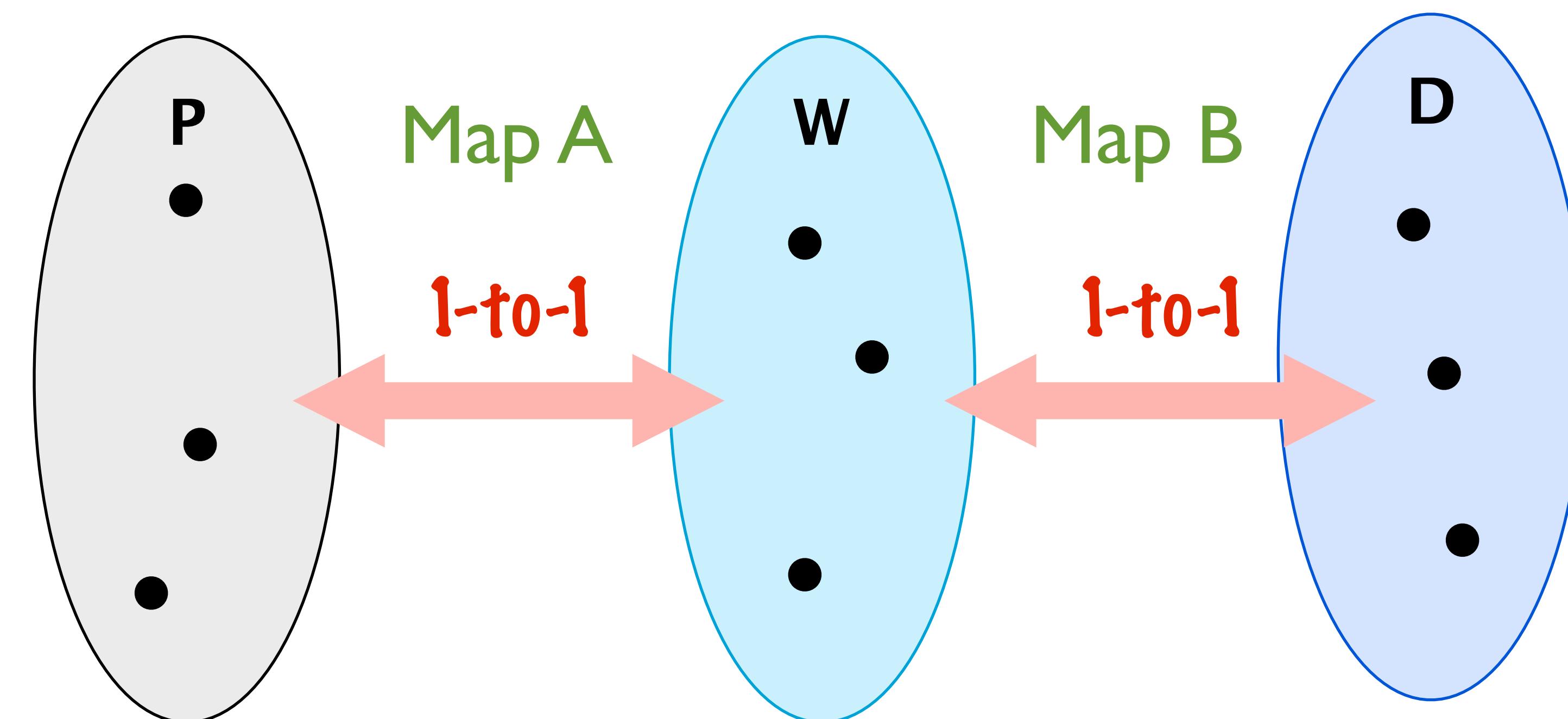
pairs distributed independently

wrong density, no quantum shells,  
no molecular binding

# Hohenberg-Kohn Theorem

P: Set of external (local) potentials with non-deg. gs  
(It can be extended to degenerate gs)

D: Set of gs particle density



W: Set of gs wavefunctions

Note: 'gs' stands for ground state



# Observables as density functionals

All ground state observables are functional of  $n(\mathbf{r})$

$$O[n] := \langle \Psi[n] | \hat{O} | \Psi[n] \rangle$$

An important example

$$E[n] := \langle \Psi[n] | \hat{H} | \Psi[n] \rangle = F[n] + \int d^3r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

$$F[n] := \langle \Psi[n] | \hat{T} + \hat{V}_{\text{ee}} | \Psi[n] \rangle$$

# Variational principle — reformulated!

From wavefunctions

$$E_{v_{\text{ext}}} := \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} | \Psi \rangle$$

To particle densities

$$E_{v_{\text{ext}}} := \min_n \left\{ F[n] + \int d^3r \ v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

# Variational principle — reformulated!

From wavefunctions

$$E_{v_{\text{ext}}} := \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} | \Psi \rangle$$

To particle densities

$$E_{v_{\text{ext}}} := \min_n \left\{ F[n] + \int d^3r \ v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

In principle... but in practice...?



# Single Slater determinant

## Single-particle states

### Spin-orbitals

$$\varphi_j(\mathbf{r}, \sigma) = \varphi_\alpha(\mathbf{r})\chi_s(\sigma)$$

### Spin-eigenfunction

$$\chi_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \chi_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

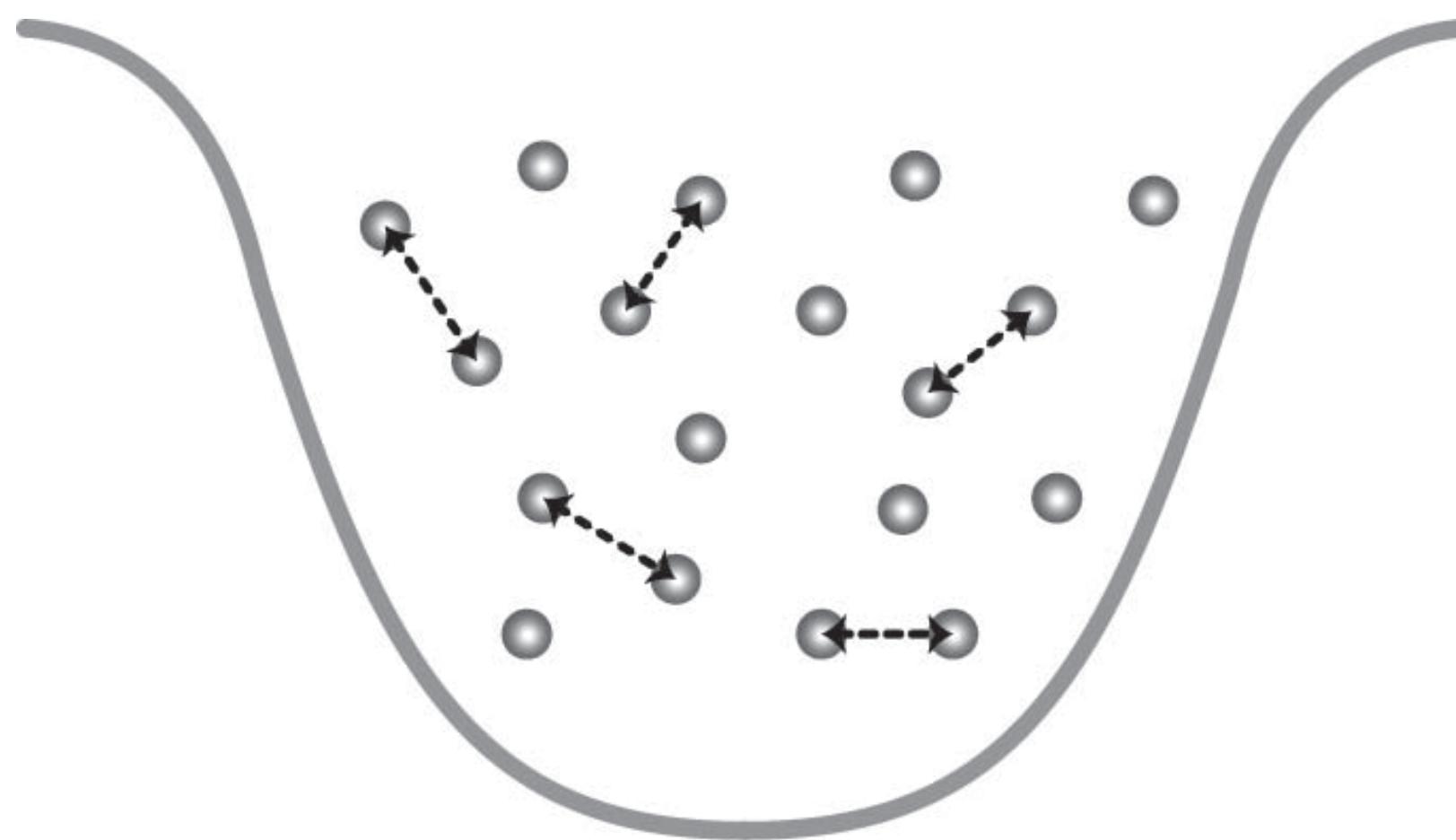
## Anti-symmetric $N$ -particle state

$$\Phi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \varphi_1(\mathbf{r}_1\sigma_1) & \dots & \varphi_N(\mathbf{r}_1\sigma_1) \\ \dots & & \dots \\ \varphi_1(\mathbf{r}_N\sigma_N) & \dots & \varphi_N(\mathbf{r}_N\sigma_N) \end{bmatrix}$$

from orthonormal orbitals

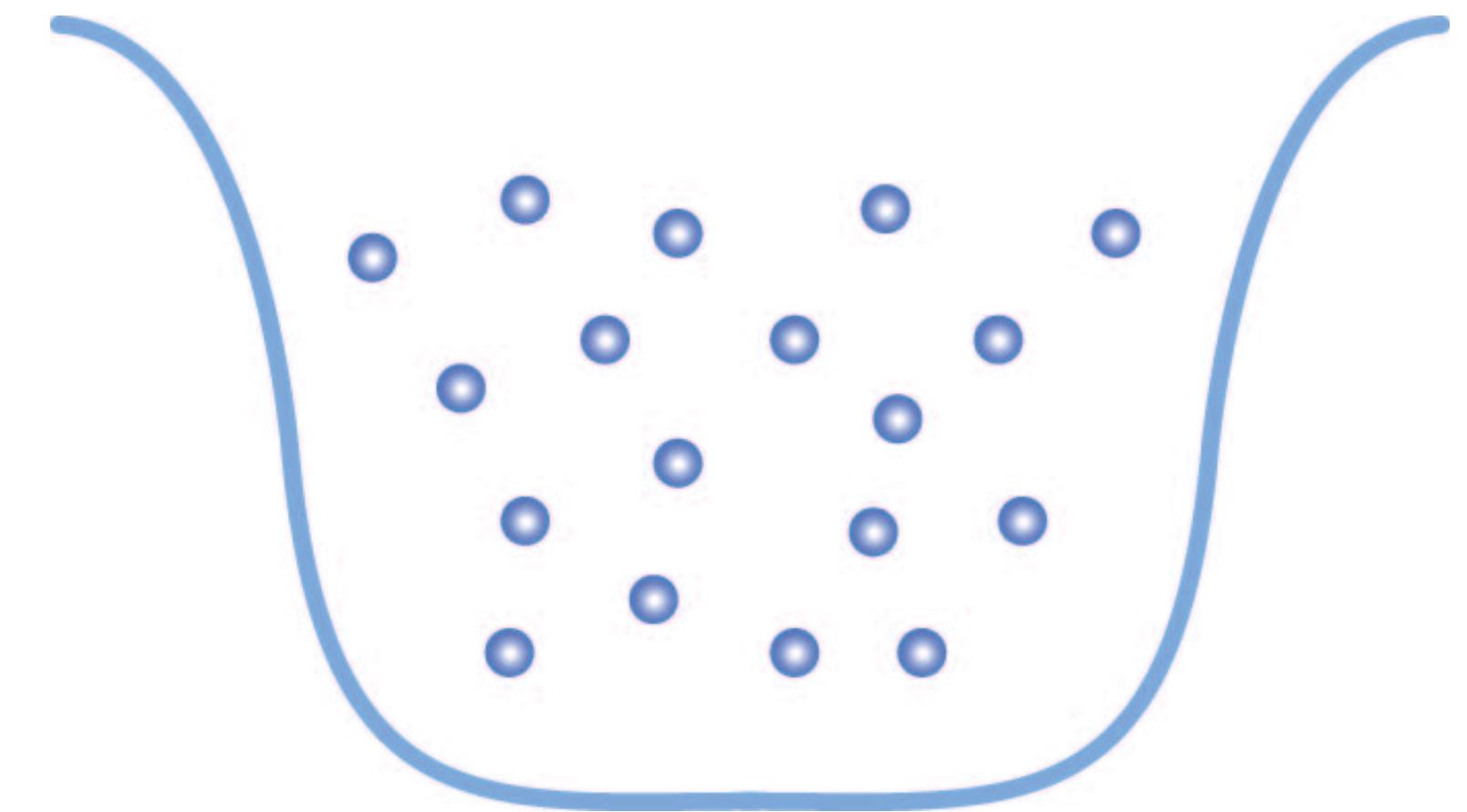
# Kohn-Sham systems

Real system



**Interacting** electrons  
in a given  
external potential

Kohn-Sham system



**Non-interacting** electrons  
in a **different** potential  
but with **same** ground-state density  
as the *interacting* electrons.

$$\hat{H}\Psi_{\text{gs}} = E_{\text{gs}} \Psi_{\text{gs}}$$

Let us restrict to  
systems with **non-degenerate** gs

$$\left\{ -\frac{\nabla^2}{2} + v_s(\mathbf{r}) \right\} \varphi_j = \varepsilon_j \varphi_j$$

The KS state is a single Slater determinant

# Kohn-Sham formulation of DFT

Exact (ground-state) energy density functional

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d^3r v_{\text{ext}}(\mathbf{r})n(\mathbf{r})$$

By definition

$$T_s[n] = - \sum_j^{\text{occ}} \frac{\varphi_j^* \nabla^2 \varphi_j}{2}$$

$$\varphi_j \equiv \varphi_j[n]$$

Kinetic energy of the KS system

$$E_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

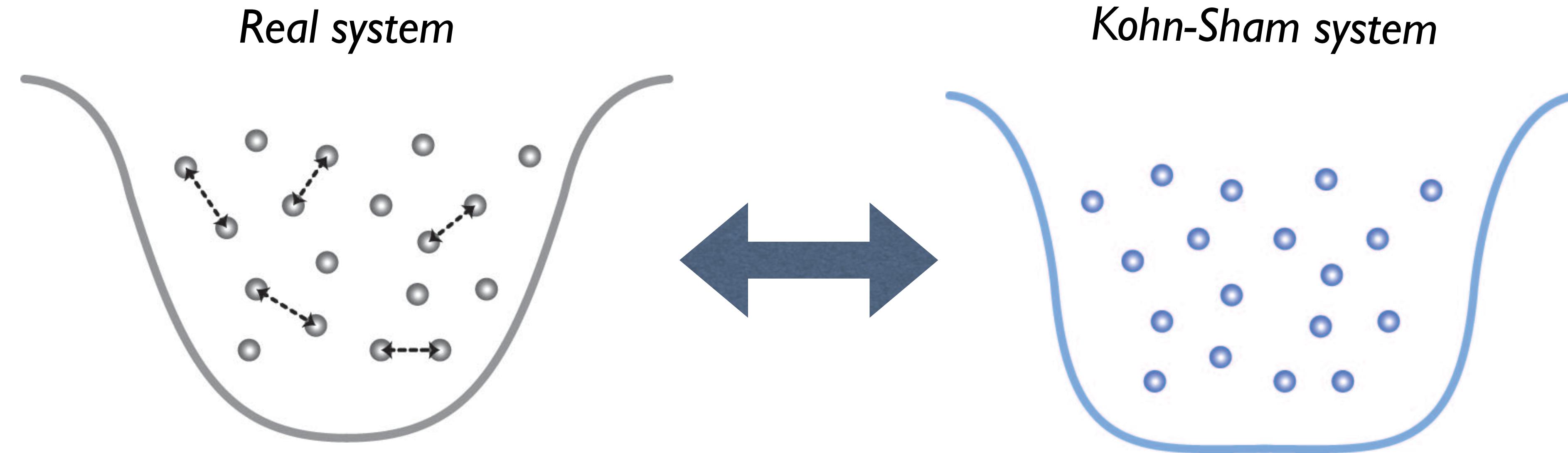
Hartree energy

$$E_{xc}[n] := F[n] - (T_s[n] + E_H[n])$$

Exchange-correlation energy  
(must be approximated!)

Implicitly, functionals  
of the density

# Kohn-Sham systems



**Interacting** electrons  
in a given  
external potential

$$\hat{H} \Psi_{\text{gs}} = E_{\text{gs}} \Psi_{\text{gs}}$$

**Let us restrict to**  
**systems with non-degenerate gs**

**Non-interacting** electrons  
in a **different** potential  
but with **same** ground-state density  
as the interacting electrons.

$$\left\{ -\frac{\nabla^2}{2} + v_s(\mathbf{r}) \right\} \varphi_j = \varepsilon_j \varphi_j$$

**The KS state is a single Slater determinant**

# Kohn-Sham formulation of DFT

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})$$

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \Big|_{n=n_0}$$

**NEED APPROX.s !**

$$n_0(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

# **A bird-eye's view of density functional approximations**

# xc-energy approximations



**MBP-diagrams:** unoccupied orbitals /eigenvalues

**Hybrids:**

**Meta-GGAs:**

**GGAs:**

**LDA**

$$E_{\text{xc}} \approx \alpha E_{\text{x}}^{\text{Fock}} + (1 - \alpha) E_{\text{x}}^{\text{DFA}} + E_{\text{c}}^{\text{DFA}}$$

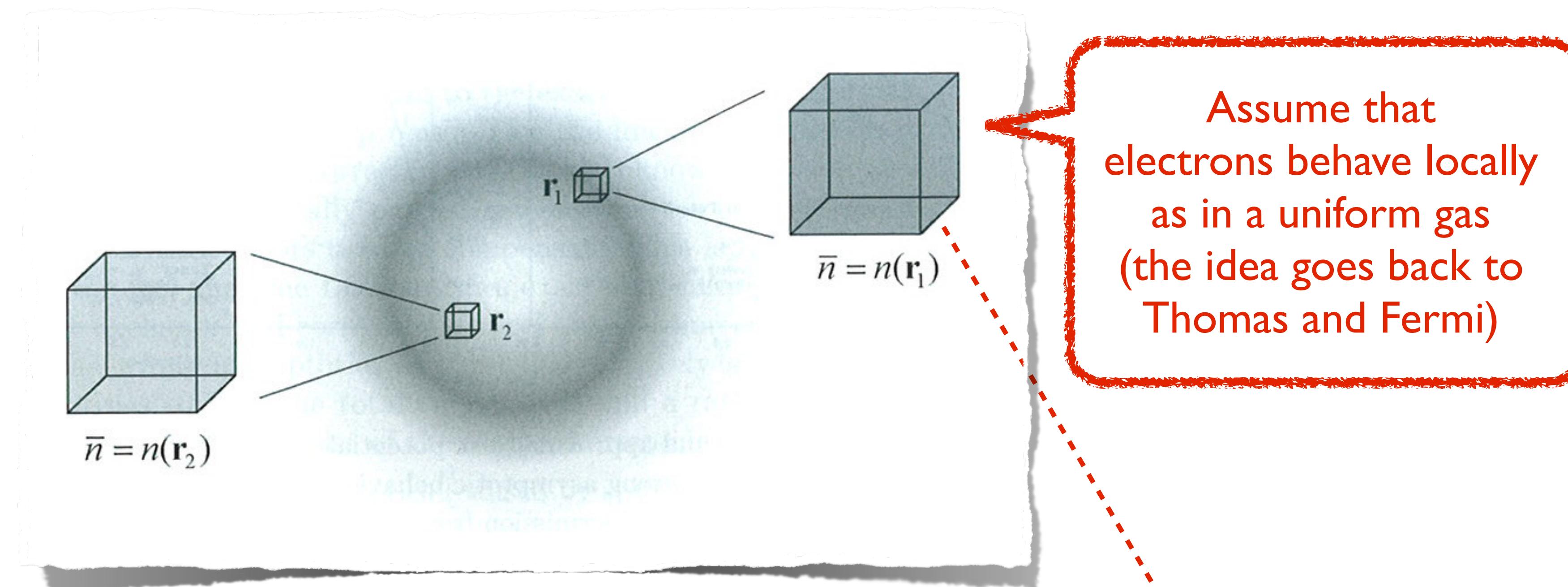
$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

$$\tau = \frac{1}{2} \sum_j^{\text{occ}} |\nabla \varphi_j|^2$$

$$E_{\text{x}}^{\text{Fock}} = - \sum_{\sigma} \int \int \frac{d^3r d^3r'}{2} \ \frac{|\sum_i \varphi_{i,\sigma}^*(\mathbf{r}) \varphi_{i,\sigma}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

# Local Density Approximation 1/2



$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r \ n(\mathbf{r}) \epsilon_{\text{xc}}^{\text{unif}}(n(\mathbf{r}))$$

Picture from: C.A. Ullrich “Time-Dependent Density-Functional Theory Concepts and Applications”, Oxford University Press, 2012.

# Local Density Approximation 2/2

- **Uniform Electron Gas (UEG):** constant electron density that fills the entire universe; the negative charge of the electrons is neutralized by a rigid uniform positive background; periodic boundary condition (for a cube of volume growing to infinity);
- **Many Body Perturbation Theory** and **Quantum Monte Carlo** provide us with accurate, if not exact, detailed information.

# xc-energy approximations



**MBP-diagrams:** unoccupied orbitals /eigenvalues

**Hybrids:**

**Meta-GGAs:**

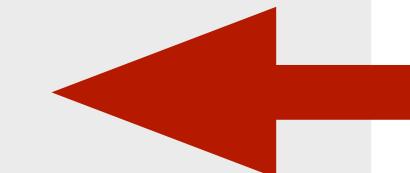
**GGAs:**

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$$E_{\text{xc}} \approx \alpha E_{\text{x}}^{\text{Fock}} + (1 - \alpha) E_{\text{x}}^{\text{DFA}} + E_{\text{c}}^{\text{DFA}}$$

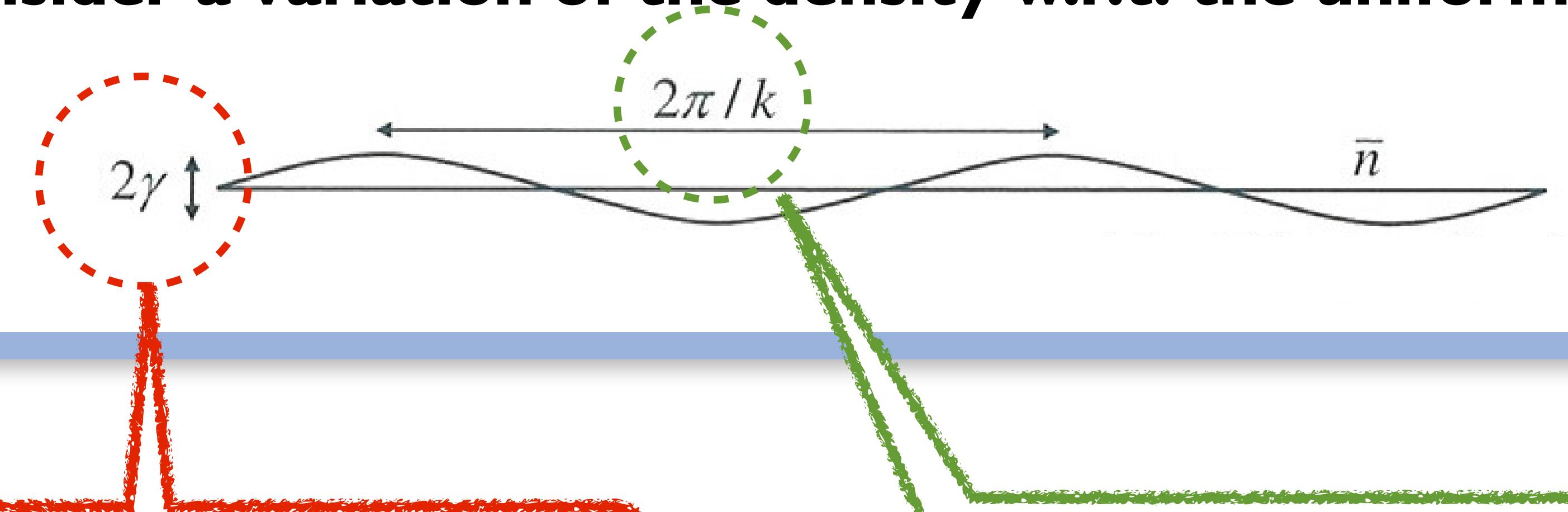
$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}))$$



# Gradient Expansion Approximation 1/2

**Consider a variation of the density w.r.t. the uniform state**



Variation is small if  $\frac{|\delta n|}{n_0} \ll 1$

Fermi wave number

$$k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$$

TF screening wave number

$$k_s(\mathbf{r}) = \sqrt{4k_F(\mathbf{r})}$$

# Gradient Expansion Approximation 2/2

For slow density variations, we get

$$E_x[n] = A_x \int d^3r \ n^{4/3} [1 + \mu s^2 + \dots]$$

$$s(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2k_F(\mathbf{r})n(\mathbf{r})}$$

It applies for  $s \ll 1$

*It can be determined  
from linear response*

$$E_c[n] = \int d^3r \ [e_c^{\text{unif}}(n) + \beta(n)t^2 + \dots]$$

$$t(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2k_s(\mathbf{r})n(\mathbf{r})}$$

It applies for  $t \ll 1$

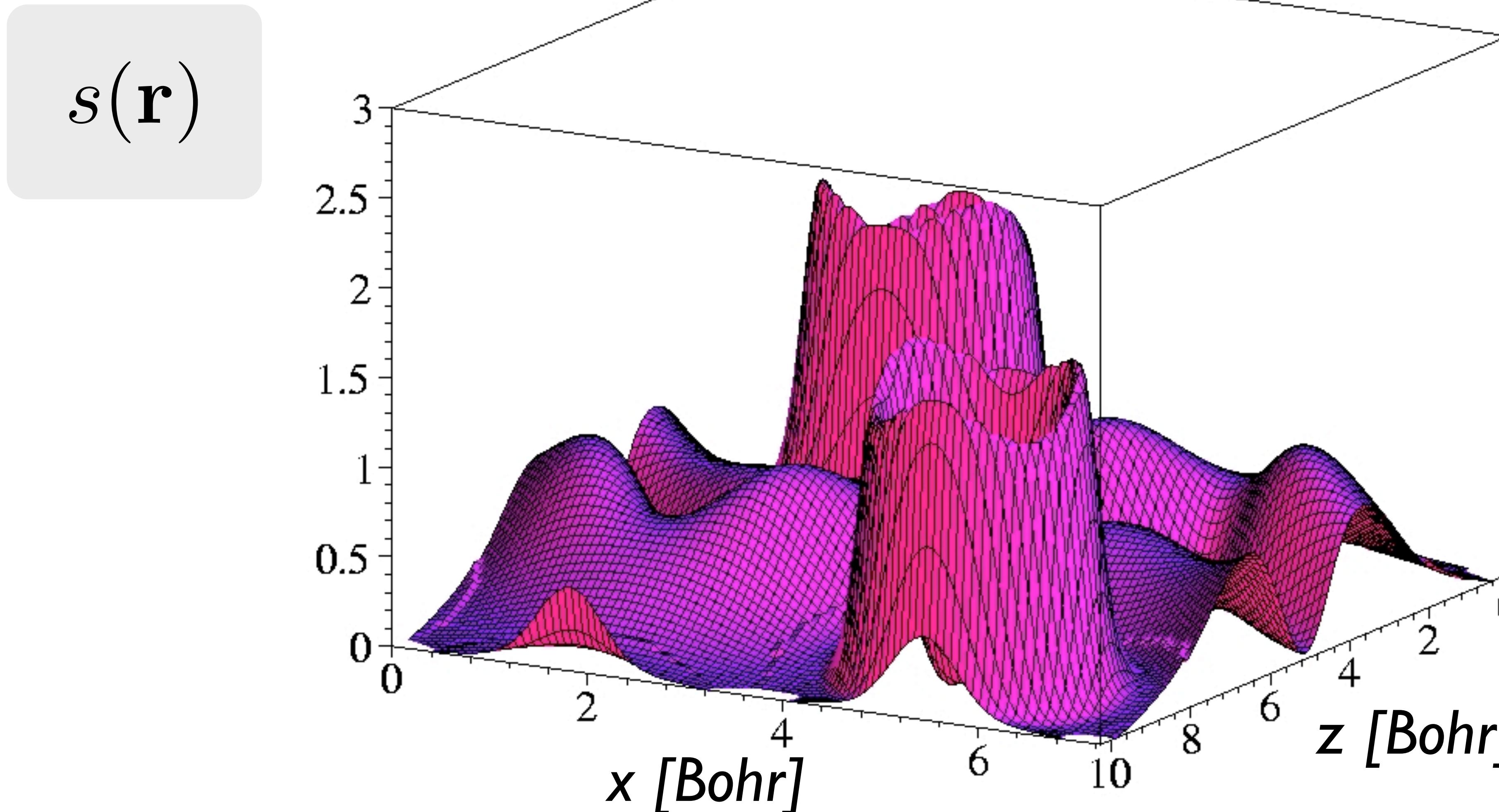
*It can be determined  
from linear resp. +  
high-density limit*

GEAs do **not** improve over LDA...

Both  $x$  and  $c$  are INADEQUATE

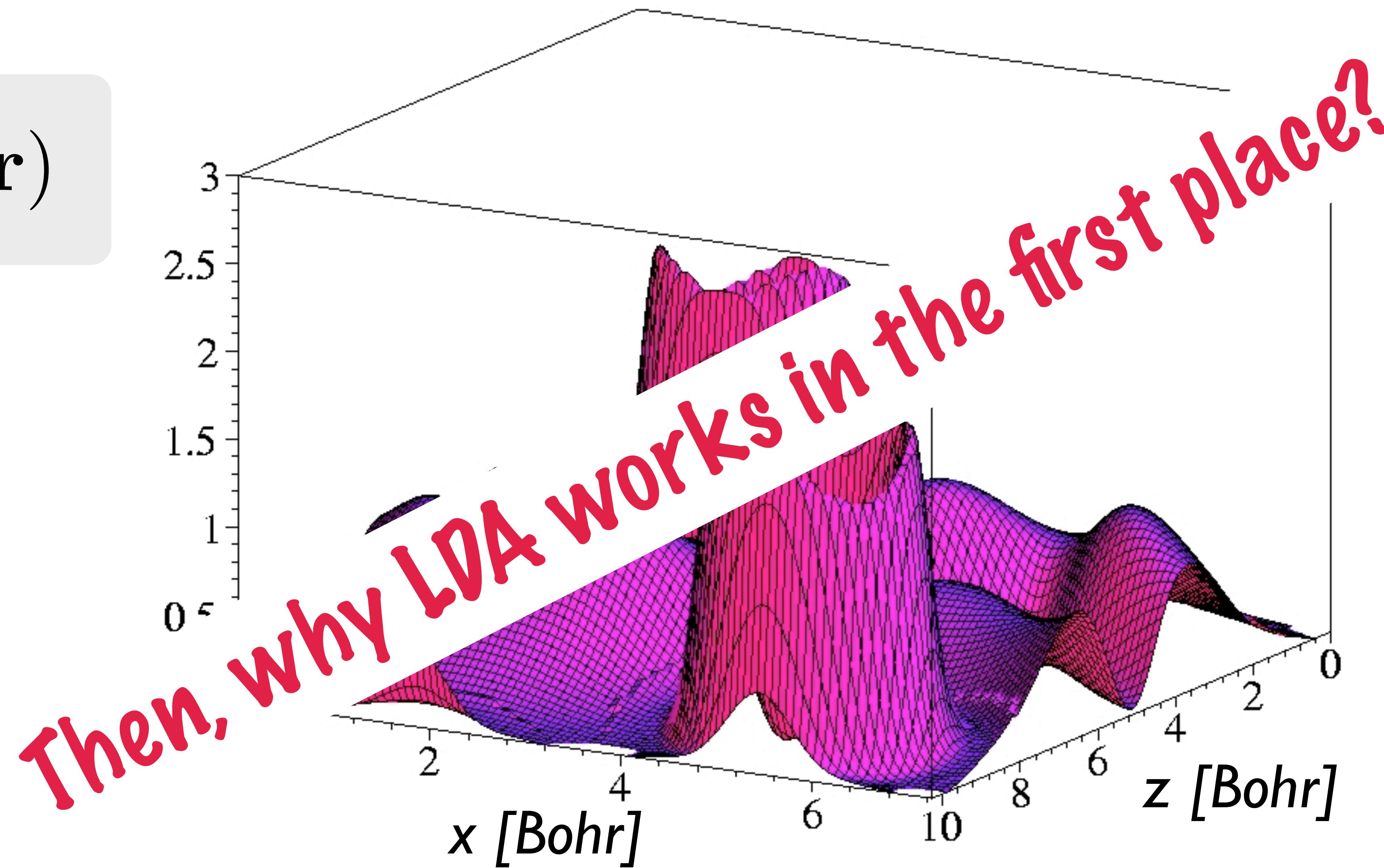
$E_c > 0$  — wrong sign!

# Bulk Silicon (diamond structure)



# Bulk Silicon (diamond structure)

$s(\mathbf{r})$

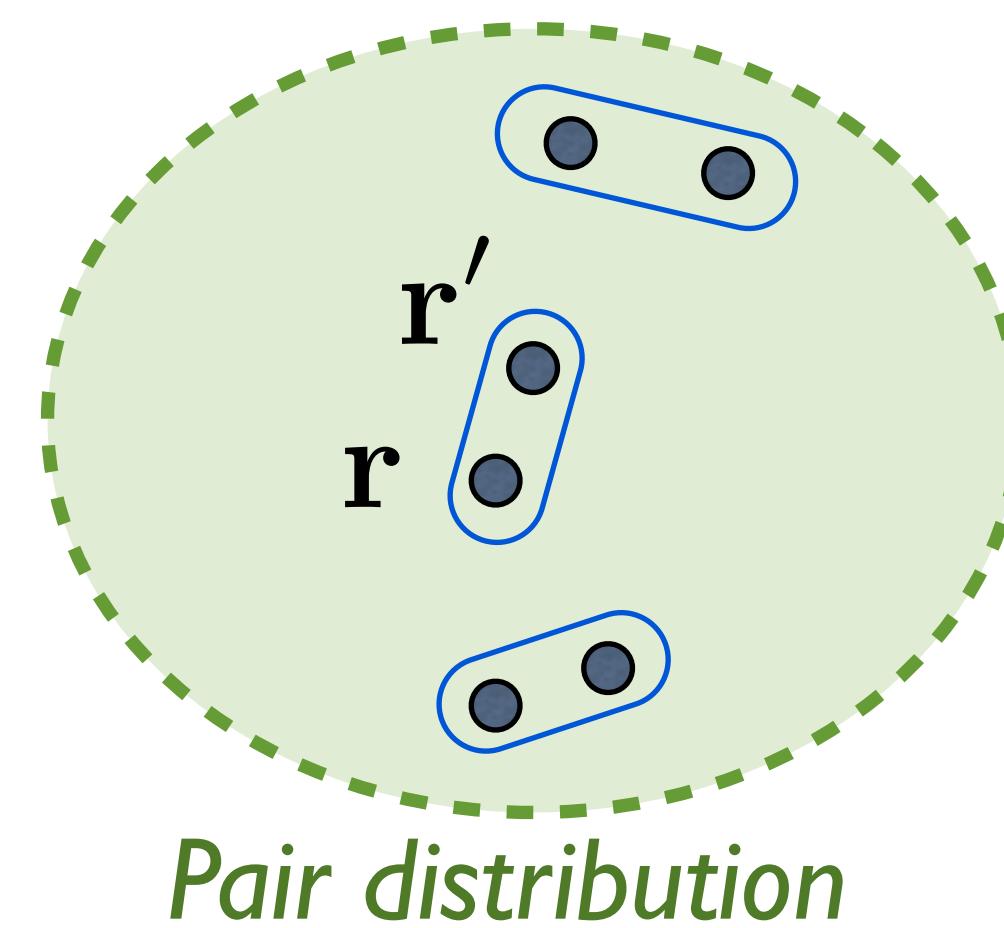


**DFT was stuck in a hole!**

**So, let's give a look at the hole function...**

# Interaction energy and pairs

Electron-electron interaction



$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int d^3 r \int d^3 r' \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Exact electronic wavefunction

$$n_2(\mathbf{r}, \mathbf{r}') = N(N-1) \sum_{\sigma, \sigma'} \int dx_3 \dots dx_N |\Psi(\mathbf{r}\sigma, \mathbf{r}'\sigma', \mathbf{x}_3, \dots, \mathbf{x}_N)|^2$$

# Hole function

Pair distribution in terms of the particle density and hole function

$$n_2(\mathbf{r}, \mathbf{r}') \equiv n(\mathbf{r}) [n(\mathbf{r}') + h(\mathbf{r}, \mathbf{r}')] \quad \text{[Equation 1]}$$

The hole function accounts for -1 electron

$$\int d^3 r' h(\mathbf{r}, \mathbf{r}') = -1$$

*Electrons avoid each others*

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \frac{1}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad \text{Hartree energy}$$

$$+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})h(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

# x- and c-hole functions in KS-DFT

$$E_x[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} < 0$$

$$E_c[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n_c(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \leq 0$$

The **exchange hole** is defined by:

$$n_x(\mathbf{r}, \mathbf{r}') = - \sum_{\sigma} \frac{\left| \sum_{i=1}^{N_{\sigma}} \varphi_{i\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}) \right|^2}{n(\mathbf{r})} < 0$$

it **satisfies**:

$$\int d^3r' n_x(\mathbf{r}, \mathbf{r}') = -1$$

The **correlation hole** is ( see, for example, \* )

$$n_c(\mathbf{r}, \mathbf{r}') = \int_0^1 h^{\lambda}(\mathbf{r}, \mathbf{r}') d\lambda - n_x(\mathbf{r}, \mathbf{r}')$$

↑  
(interaction strength)

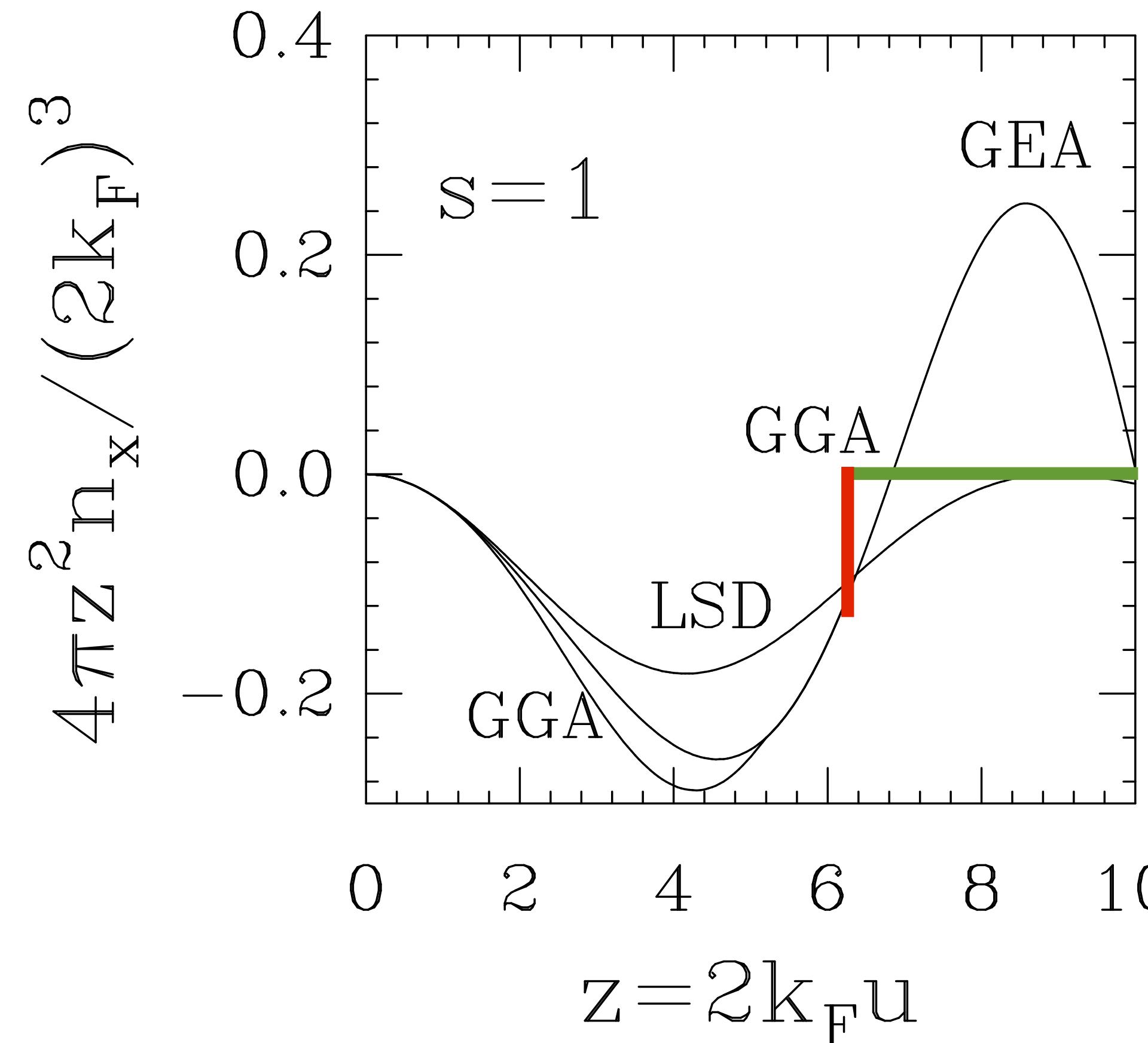
it **satisfies**:

$$\int d^3r' n_c(\mathbf{r}, \mathbf{r}') = 0$$

\* Koch and Holthausen "A Chemist's Guide to Density Functional Theory", Second Edition, Wiley-VCH Verlag GmbH

\* Becke J. Phys. Chem. 88, 1053 (1988)

# From GEA to GGA: exchange

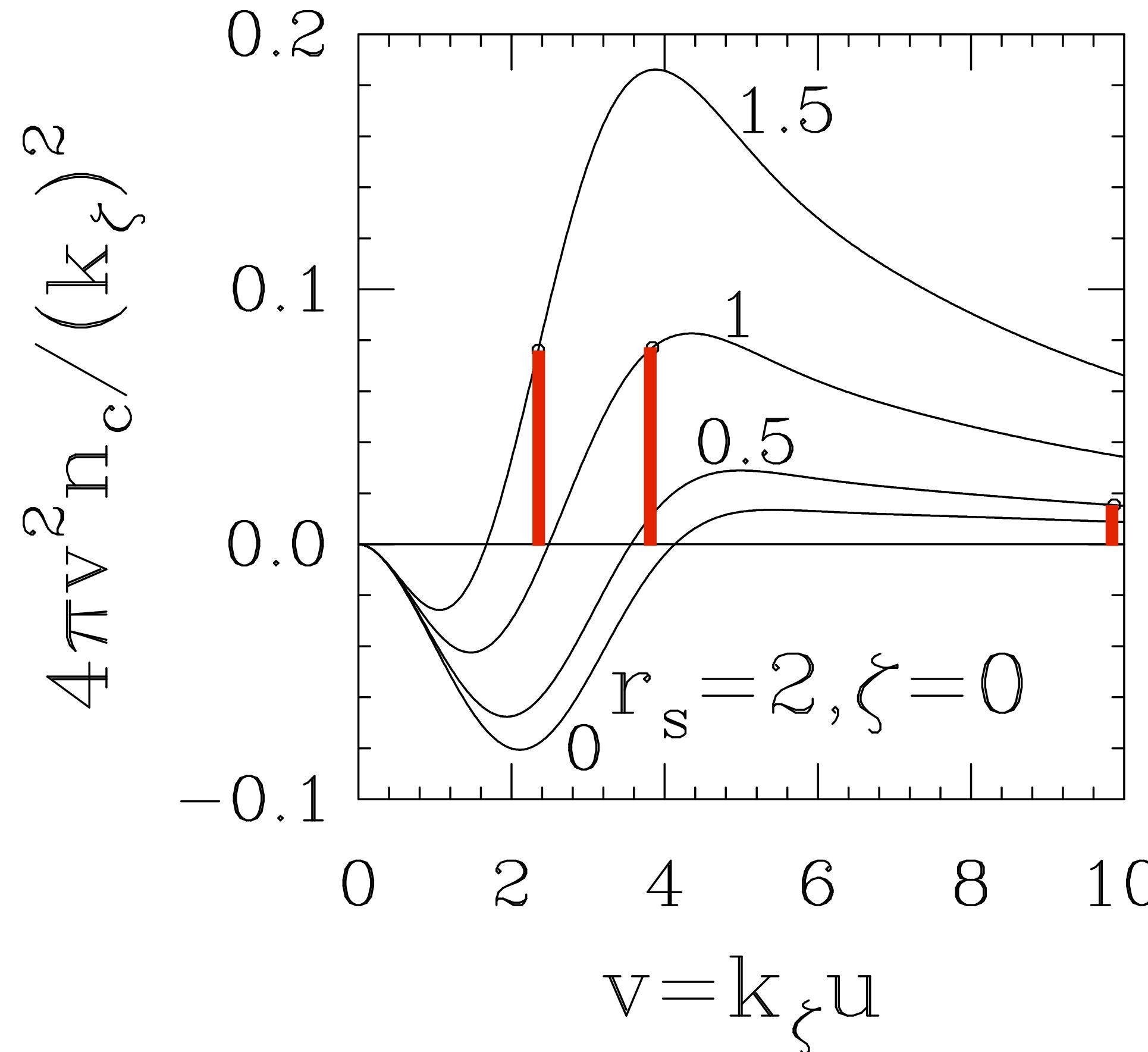


**GGA:**  
makes the GEA x-hole non-positive  
and  
enforces x-normalization

$$\int d^3r' n_x(\mathbf{r}, \mathbf{r}') = -1$$

**Figure 1.** Spherically-averaged exchange hole density  $n_x$  for  $s = 1$ .

# From GEA to GGA: correlation



**GGA:**  
enforces c-normalization  
(correlation hole may be positive, too)

$$\int d^3r' n_c(\mathbf{r}, \mathbf{r}') = 0$$

**Figure 4.** Spherically-averaged correlation hole density  $\tilde{n}_c$  for  $r_s = 2$  and  $\zeta = 0$ . GEA holes are shown for four values of the reduced density gradient,  $t = |\nabla n|/(2k_\zeta n)$ . The vertical lines indicate where the numerical GGA cuts off the GEA hole to make  $\int_0^{v_c} dv 4\pi v^2 \tilde{n}_c(v) = 0$ .

# Importance of fulfilling exact conditions

VOLUME 77, NUMBER 18

PHYSICAL REVIEW LETTERS

28 OCTOBER 1996

## Generalized Gradient Approximation Made Simple

John P. Perdew, Kieron Burke,\* Matthias Ernzerhof

*Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118*

(Received 21 May 1996)

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential.

# xc-energy approximations



**MBP-diagrams:** unoccupied orbitals /eigenvalues

**Hybrids:**

**Meta-GGAs:**

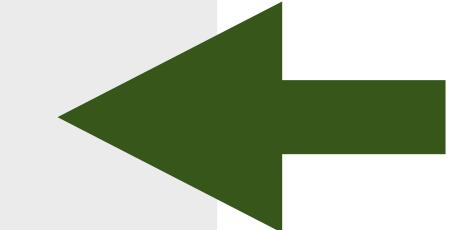
**GGAs:**

**LDA**

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$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}))$$



# XC-hole also helps to understand “Meta-GGAs”

Exact short-range behavior of the x-hole

$$n_x^\sigma(\mathbf{r}, u) = -n_\sigma - \frac{1}{6} \left[ \nabla^2 n_\sigma - 2\tau_\sigma + \frac{1}{2} \frac{(\nabla n_\sigma)^2}{n_\sigma} \right] u^2 + \dots$$

Spherically  
averaged

Laplacian

inter-particle  
distance

kinetic energy density

$$\tau_\sigma = \sum_i |\nabla \varphi_{i\sigma}|^2$$

# Importance of fulfilling exact conditions

PRL 115, 036402 (2015)

PHYSICAL REVIEW LETTERS

week ending  
17 JULY 2015

## Strongly Constrained and Appropriately Normed Semilocal Density Functional

Jianwei Sun,<sup>1,\*</sup> Adrienn Ruzsinszky,<sup>1</sup> and John P. Perdew<sup>1,2</sup>

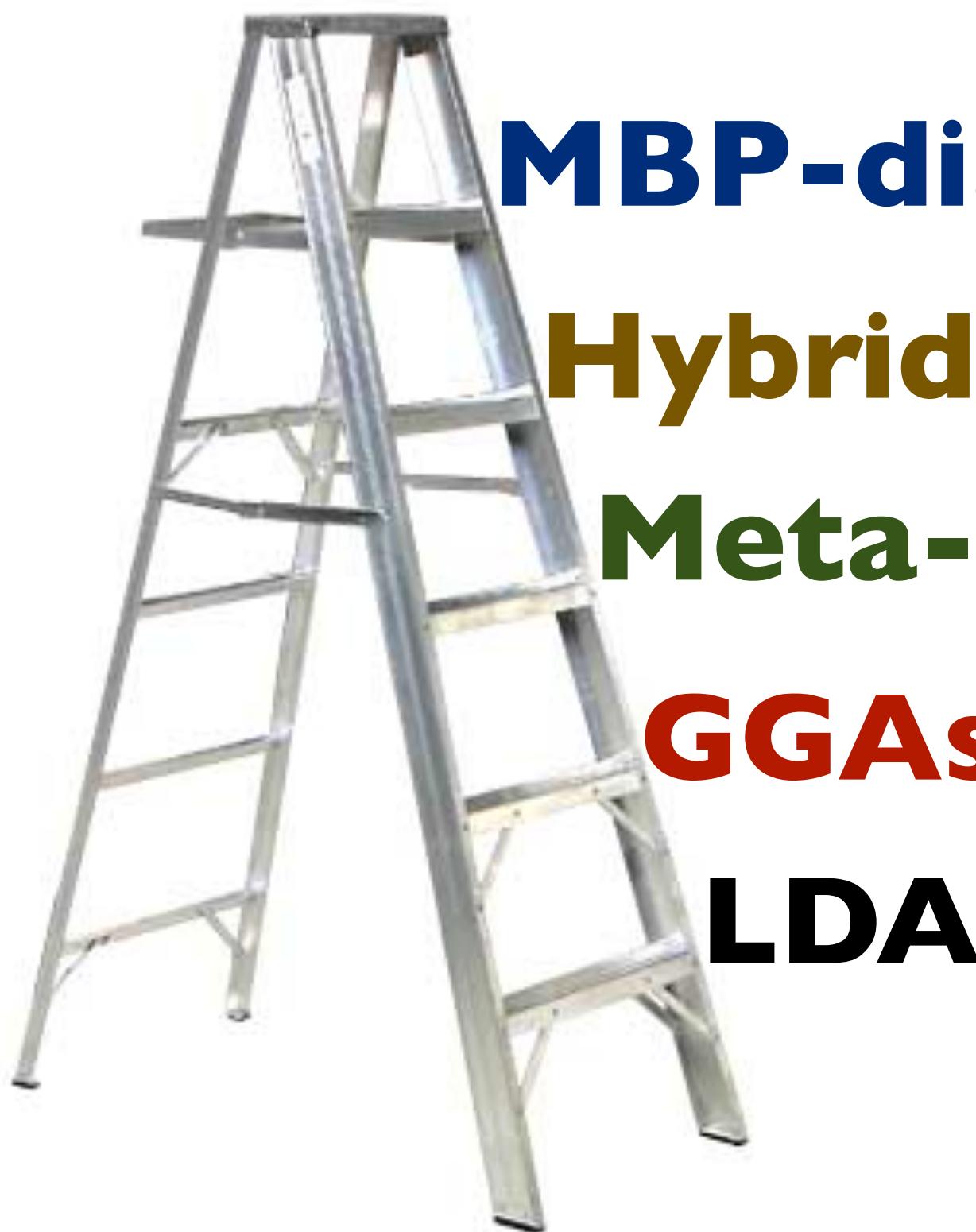
<sup>1</sup>*Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA*

<sup>2</sup>*Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, USA*

(Received 12 April 2015; published 14 July 2015)

The ground-state energy, electron density, and related properties of ordinary matter can be computed efficiently when the exchange-correlation energy as a functional of the density is approximated semilocally. We propose the first meta-generalized-gradient approximation (meta-GGA) that is fully constrained, obeying all 17 known exact constraints that a meta-GGA can. It is also exact or nearly exact for a set of “appropriate norms,” including rare-gas atoms and nonbonded interactions. This strongly constrained and appropriately normed meta-GGA achieves remarkable accuracy for systems where the exact exchange-correlation hole is localized near its electron, and especially for lattice constants and weak interactions.

# xc-energy approximations



**MBP-diagrams:** unoccupied orbitals /eigenvalues

**Hybrids:**

**Meta-GGAs:**

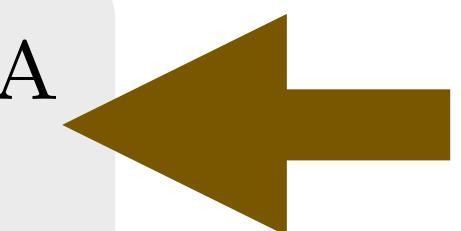
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$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

$$E_{\text{xc}}[n] \approx \int d^3r \ \epsilon(n(\mathbf{r}), \nabla n(\mathbf{r}))$$



$$E_{\text{x}}^{\text{Fock}} = - \sum_{\sigma} \int \int \frac{d^3r d^3r'}{2} \ \frac{|\sum_i \varphi_{i,\sigma}^*(\mathbf{r}) \varphi_{i,\sigma}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

# Density-functional thermochemistry. III. The role of exact exchange

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Despite the remarkable thermochemical accuracy of Kohn–Sham density-functional theories with gradient corrections for exchange-correlation [see, for example, A. D. Becke, *J. Chem. Phys.* **96**, 2155 (1992)], we believe that further improvements are unlikely unless *exact-exchange* information is considered. Arguments to support this view are presented, and a semiempirical exchange-correlation functional containing local-spin-density, gradient, and exact-exchange terms is tested on 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 total atomic energies of first- and second-row systems. This functional performs significantly better than previous functionals with gradient corrections only, and fits experimental atomization energies with an impressively small average absolute deviation of 2.4 kcal/mol.

# **Levy-Lieb DFT and Generalized KS (in brief)**

# Plus a forth crucial step!

$$\begin{aligned} E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle \\ &= \min_n \left\{ F[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}) \right\} \\ &= \min_n \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3r n(\mathbf{r})v(\mathbf{r}) \right\} \\ &= \min_n \left\{ \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle + E_c[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}) \right\} \\ &= \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle + E_c[n[\Phi]] + \int d^3r n[\Phi](\mathbf{r})v(\mathbf{r}) \right\} \end{aligned}$$

Orthonormal orbitals

Generalized-KS DFT

DFT

KS DFT



# Understanding band gaps of solids in generalized Kohn–Sham theory

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Most of the (standard) KS “discontinuity” is then adsorbed into the G-KS gap.

**Have fun with DFT**