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Towards a Density Functional Theory Exchange-Correlation Functional for f-electron elements and compounds

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Quantum Mechanics

Dirac (1929)

" The general theory of quantum mechanics is now almost complete… The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. "

P.A.M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).

Note: For *f*-electron materials we probably need to solve the Dirac Equation.

How do we learn from the Quantum Mechanical equations?

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Exact Hamiltonian with exact solution.

Exact Hamiltonian with approximate solution.

Approximate Hamiltonians with exact solutions.

Approximate Hamiltonians with approximate solutions.

Ideally we would like to solve for example the non-relativistic limit of the Dirac Equation, the Schrödinger Equation, exactly. Only feasible for one-electron systems such as the Hydrogen atom. Already for the two-electron system of the He atom we need to start doing (at least numerical) approximations. For Condensed Matter systems we cannot expect to solve the Dirac or SE directly, even with the largest and fastest computers in the world.

Walter Kohn awarded the Nobel Prize in Chemistry 1998 for Density Functional Theory

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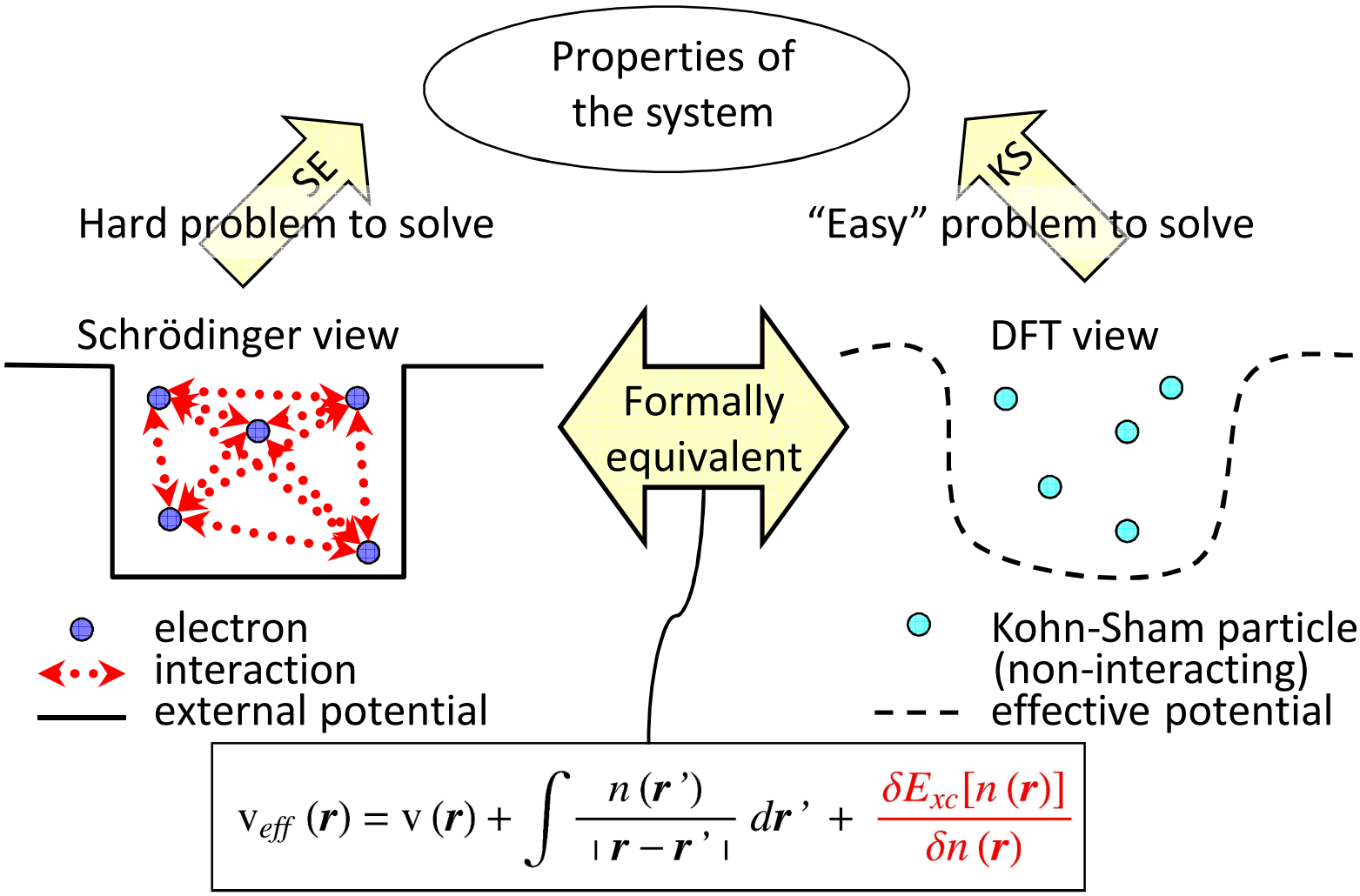
Hohenberg-Kohn theorem:
Phys. Rev. 136, B864 (1964).
The electron density contains all information needed to determine ground state properties of a system.

Kohn-Sham equations:
Phys. Rev. 140, 1133 (1965).
Practical scheme for solving the quantum mechanical problem based on the HK theorem.

DFT versus the Schrödinger Equation



$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(\boldsymbol{r})]$.

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Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu \psi_\nu(\boldsymbol{r}) \quad \nu = 1, 2, \ldots, N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\boldsymbol{r})|^2$$

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

If we had the divine exchange-correlation functional, self-consistently solving these equations would give exactly the same density as the Schrödinger Equation, and thus via the HK theorem, we should be able to extract all information about the system.

We do not need the many-body wave functions.

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Approximations for the exchange-correlation functional

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$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu \psi_\nu(\boldsymbol{r}) \quad \nu = 1, 2, \ldots, N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\boldsymbol{r})|^2$$

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

AM05, LDA, GGA, Meta-GGA, Hybrids

The form of the divine exchange-correlation functional is unknown.
We need to find good approximations.
There is nothing like a free lunch.

DFT versus Mean Field Theory

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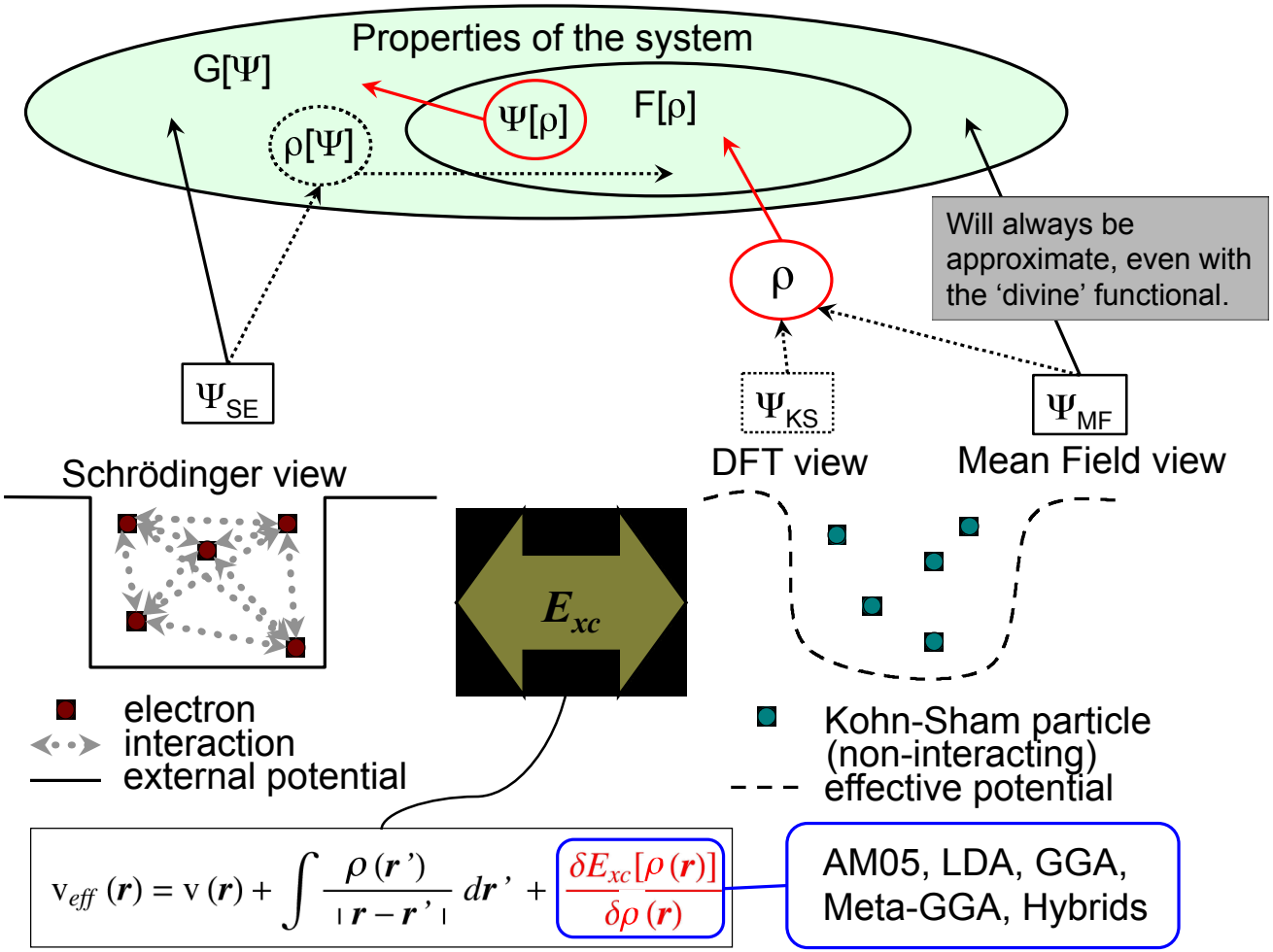
Density = ρ in chemistry
n in physics

From "Metallic Systems: A Quantum Chemist's Perspective", the chapter "Some practical considerations for density functional theory studies of chemistry at metal surfaces" to be published by Taylor and Francis in 2011.



Copenhagen interpretation of Quantum Mechanics (quotes from Wikipedia)

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Bohr emphasized that science is concerned with predictions of the outcomes of experiments, and that any additional propositions offered are not scientific but meta-physical

The Copenhagen Interpretation denies that the wave function is anything more than a theoretical concept

… the wave function is merely a mathematical tool for calculating the probabilities in a specific experiment

Carl Friedrich von Weizsäcker suggested instead that the Copenhagen interpretation follows the principle "What is observed certainly exists; about what is not observed we are still free to make suitable assumptions

DFT versus the Schrödinger Equation

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We have moved our problem from here ...

Properties of the system

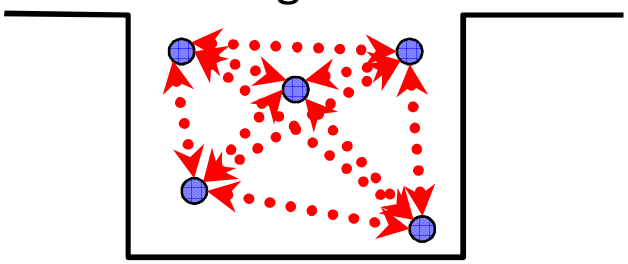
SE

Hard problem to solve

KS

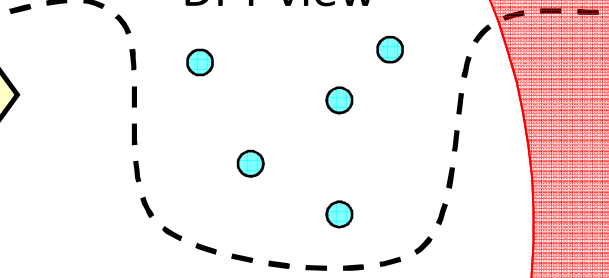
"Easy" problem to solve

Schrödinger view



Formally equivalent

DFT view



electron

interaction

external potential

Kohn-Sham particle (non-interacting)

effective potential

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

... to here

All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(\boldsymbol{r})]$.

DFT versus Mean Field Theory

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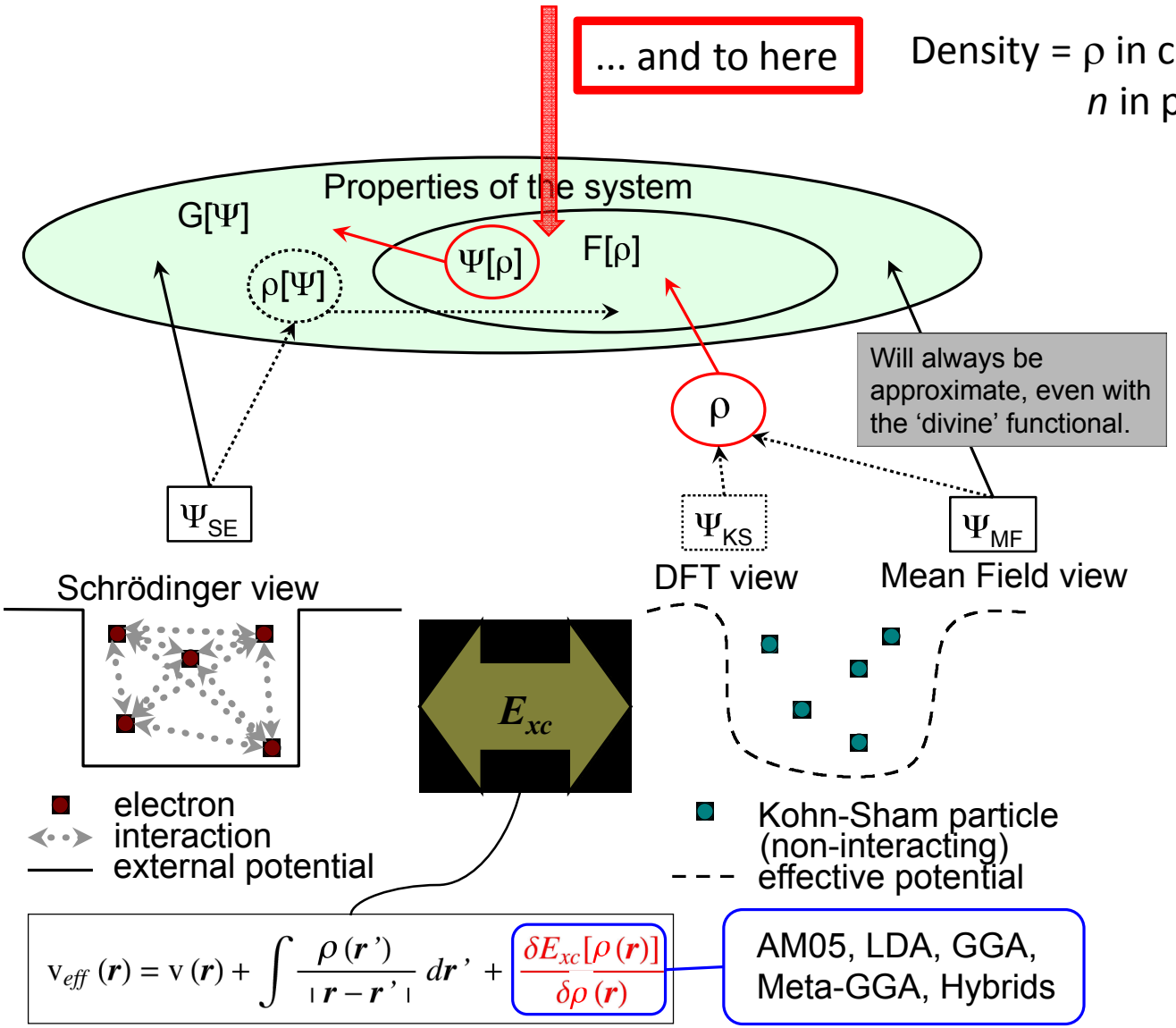
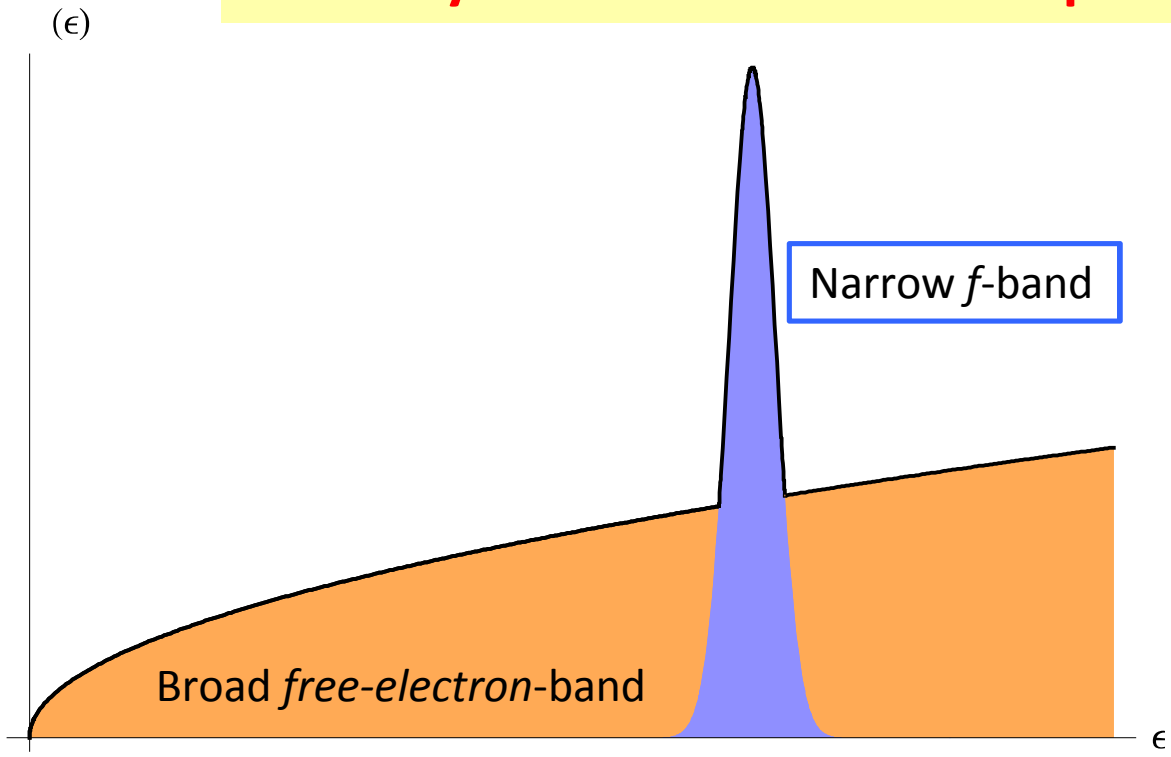
From "Metallic Systems: A Quantum Chemist's Perspective", the chapter "Some practical considerations for density functional theory studies of chemistry at metal surfaces" to be published by Taylor and Francis in 2011.



f-electron Physics: Electrons are fermions

Electrons are fermions,
they each need their own quantum state.



f-band: 14 *f*-electron states at an ion all have their own quantum number. Even with interaction between ions, the *f*-electrons do not need to use the kinetic energy to differentiate between themselves. Compared to the broad free-electron band, the *f*-band is a collection of discrete levels.

Free-electron band: The paradigm system describing this situation is the uniform electron gas. No potential energy difference gives that they need to differentiate by different kinetic energies.

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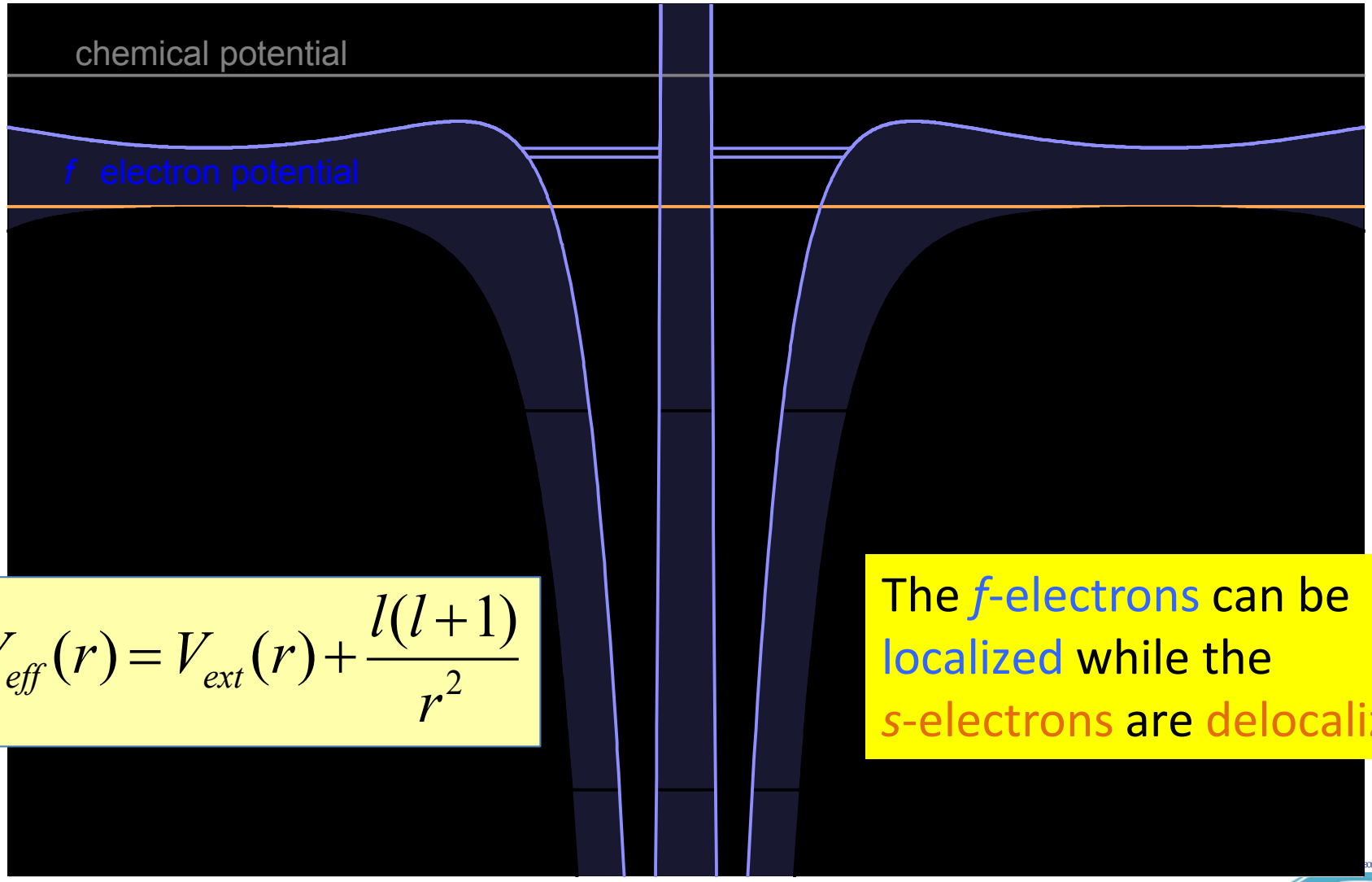
f-electron Physics: Competition between localization and delocalization



$$V_{eff}(r) = V_{ext}(r) + \frac{l(l+1)}{r^2}$$

The *f*-electrons can be localized while the *s*-electrons are delocalized.

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f-electron Physics: Competition between localization and delocalization

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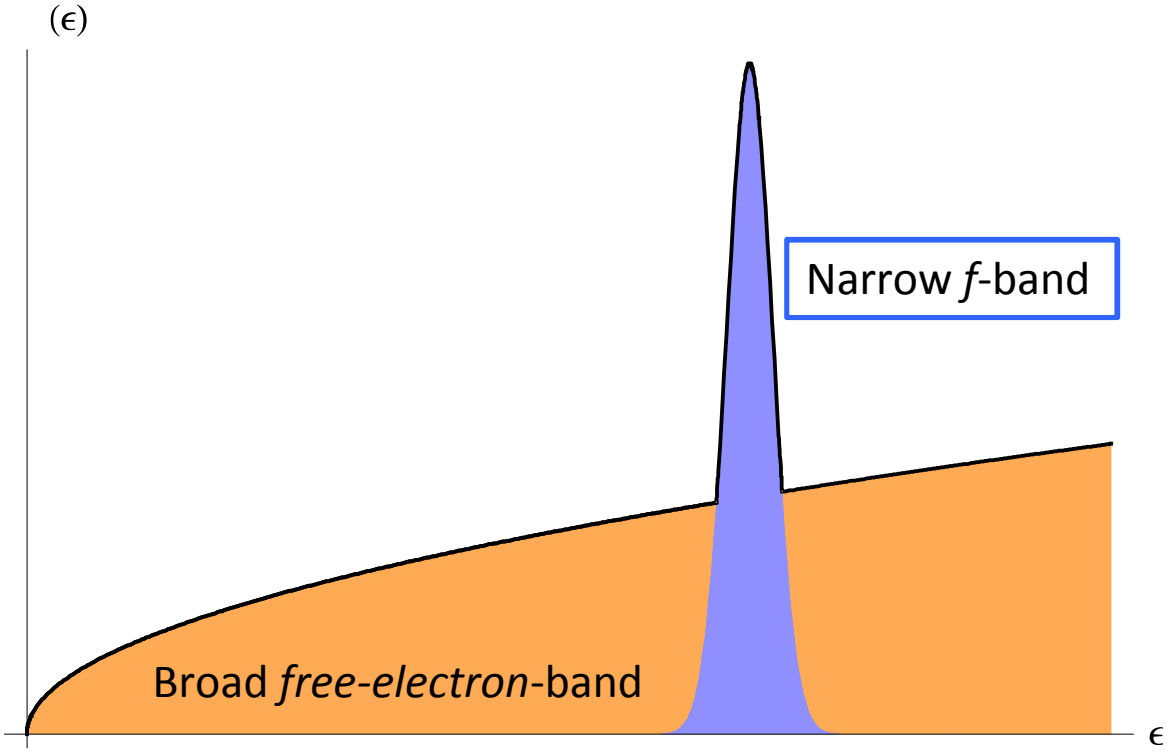

The delocalized electrons in the broad *free-electron* band and the localized electrons in the narrow *f*-electron band are behaving very differently. The interesting physics and chemistry of *f*-electron materials are governed by a competition between these two different pictures.

f-electron Physics: Density Functional Theory

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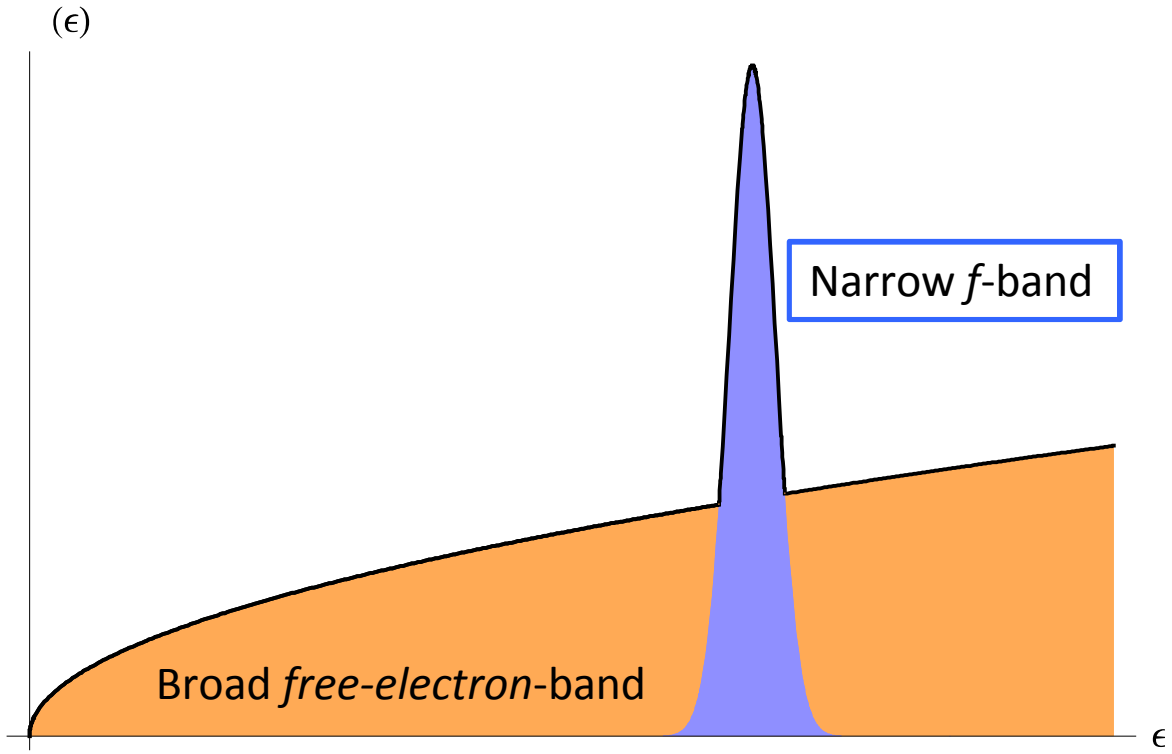

LDA and other functionals based on the uniform electron gas can be expected to work on the broad free-electron band.

The Pauli exclusion principle embedded in the exchange energy is the main source for describing the fermionic nature of electrons. Hybrids and exact exchange are considered needed for discrete levels.

Since the physics of *f*-electron materials is due to the competition between these two types of states, a functional needs to be able to describe the two situations equally well.

Functionals are applied in real space. How do we take the discrete level/uniform electron gas picture to real space?.

Electron localization function (ELF)

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A.D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990)

Interpretation in terms of fermion character: B. Silvi and A. Savin, Nature **371**, 683 (1994)
Note: Kohn-Sham particles are fermions! Despite the name, not only valid for electrons.

$$ELF = \frac{1}{1+(D/D_h)^2}$$

$$D = \tau - \frac{1}{8}\frac{|\nabla n|^2}{n}$$

$$D_h = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3}$$

τ: kinetic energy density
n: electron density

D: kinetic energy excess with respect to a boson gas.
D_h: kinetic energy of a uniform electron gas.

D = 0: kinetic energy is equivalent to that in a boson gas *with the same density*. Fermions do not need to adjust their kinetic energy because of other fermions nearby.

D = 1/2: Uniform electron gas by construction. All fermions have same potential energy and need to adjust their kinetic energy to stay different.

D -> ∞: Very high kinetic energy needed for fermions in classically forbidden region.

ELF ≈ 1: strong localization, discrete levels.
ELF ≈ 1/2: uniform electron gas like
ELF ≈ 0: Classically forbidden region.

Subsystem functionals

Constructing a general purpose functionals from specialized functionals

$$E_{xc} = \int_V n(\boldsymbol{r})\, \epsilon_{xc}(\boldsymbol{r};[n])\, dV$$

Use specialized functionals in the different subsystems

Divide integration over V into integrations over subsystems

Note: The integration over subsystems is done automatically by the use of an interpolation function

For the subsystem functional scheme we need:

1) One specialized functional for each subsystem we want to describe.

2) An interpolation index that can tell us the character of the system in each point so that we can apply the different specialized functionals accordingly.

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A specialized functional: The LDA functional

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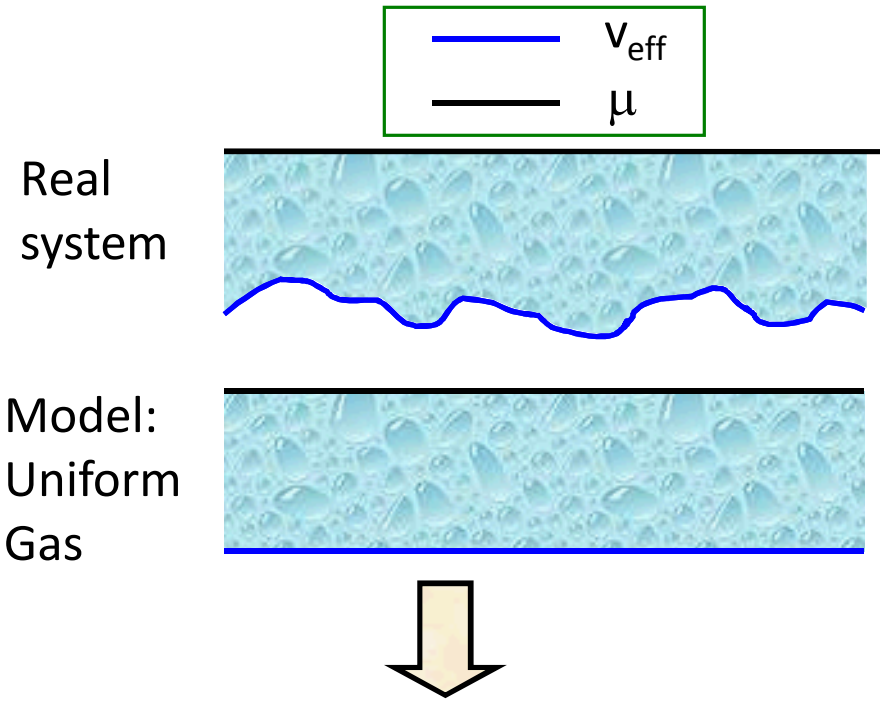

Assume each point in the real system contribute the amount of exchange-correlation energy as would a uniform electron gas with the same density.

Obviously exact for the uniform electron gas.

Basic concept and first explicit LDA published in 1965 (Kohn and Sham).

A general functional from specialized functionals: AM05, PRB 72, 085108 (2005)

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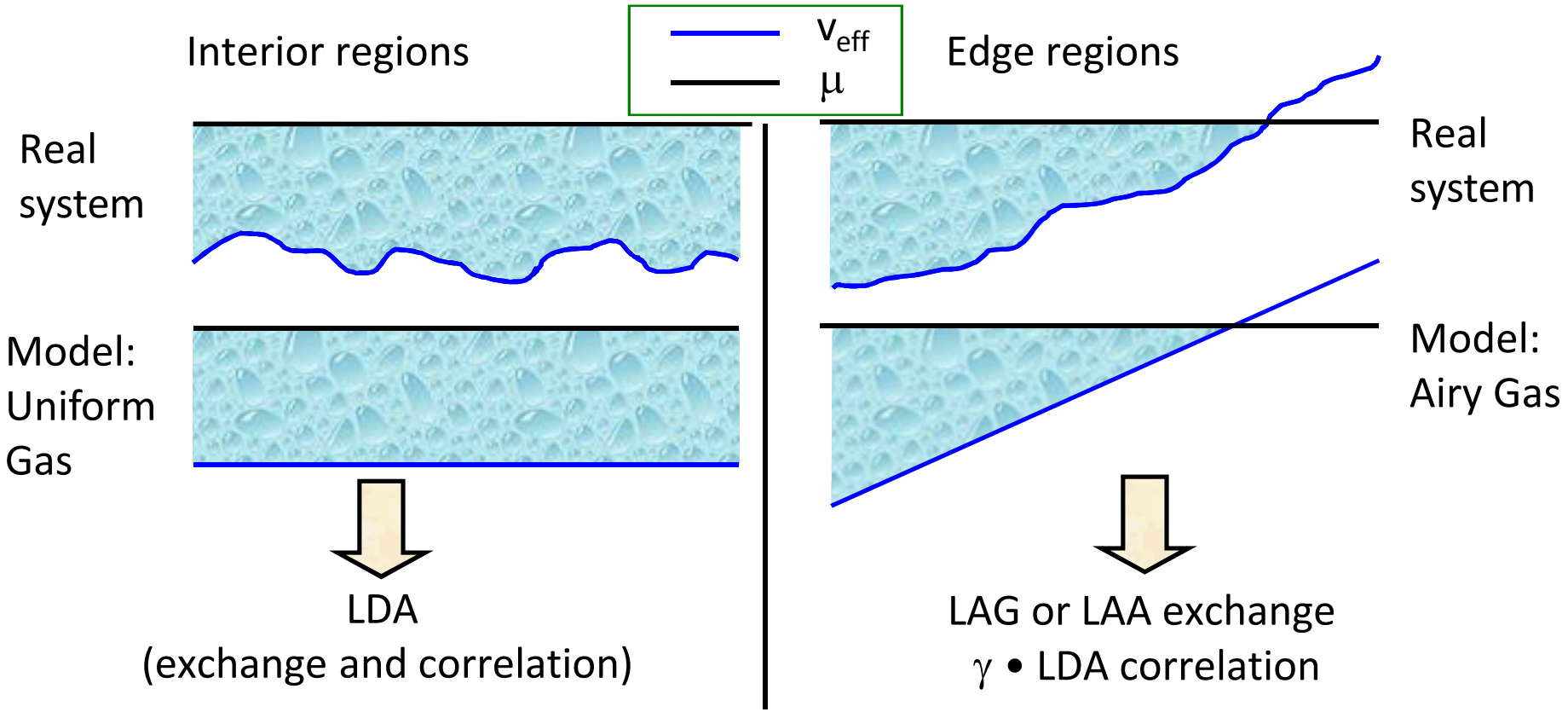


Interpolation
with an index based on the gradient of the density

Two constants (one is γ above, one is in interpolation index) are determined by fitting to yield correct jellium surface energies.

Subsystem Functional Scheme:

$$E_{xc} = \int_V n(\vec{r})\, \varepsilon_{xc}(\vec{r};[n])\, dV$$

Dividing V into sub-regions where different subsystem functionals apply: Interpolation index.

Specialized functionals in different subsystems

?

ELF ≈ 1

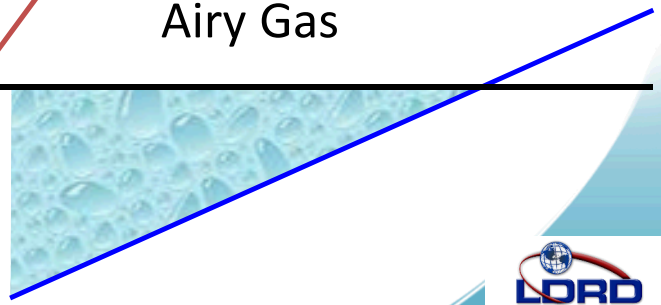
ELF ≈ 1/2

ELF ≈ 0

Interpolation Index: **ELF**

Interior physics:
Uniform electron gas

Surface physics:
Airy Gas



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Harmonic Oscillator model (HO)

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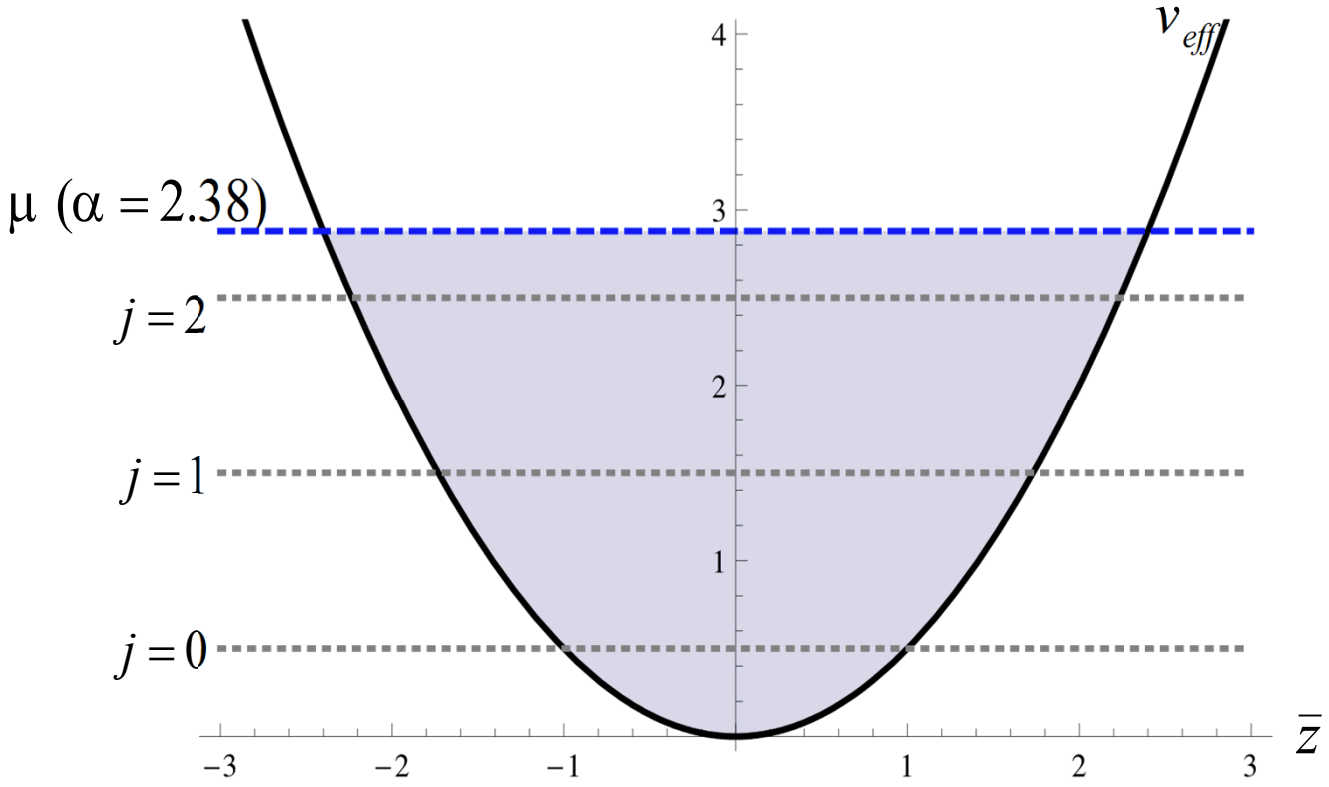
Hao, Armiento and Mattsson Phys, Rev. B **82**, 115103 (2010).

HO model: Localized electron levels in a continuum.

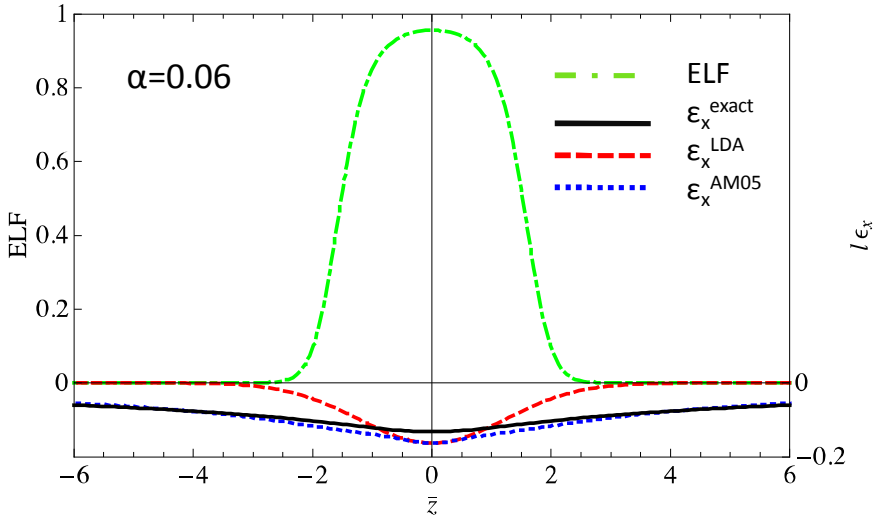


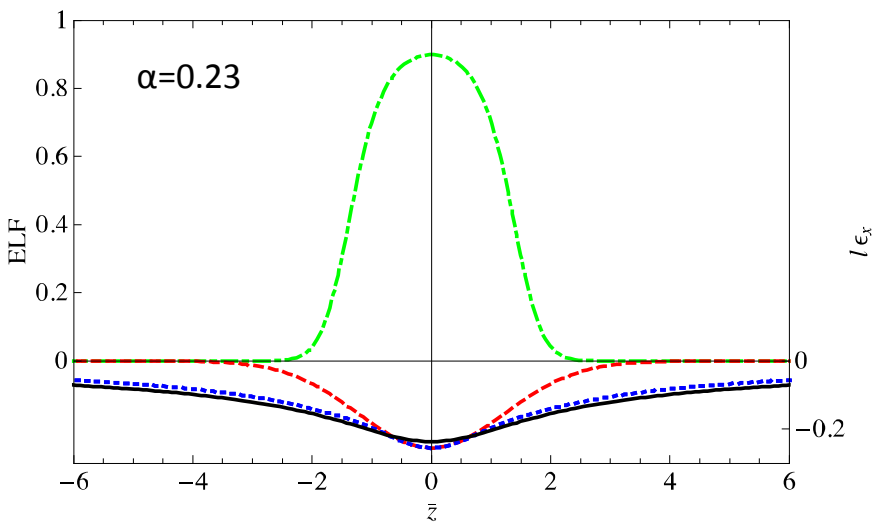
Energy of subbands $\varepsilon_j = (j + \frac{1}{2})\frac{1}{l^2}$

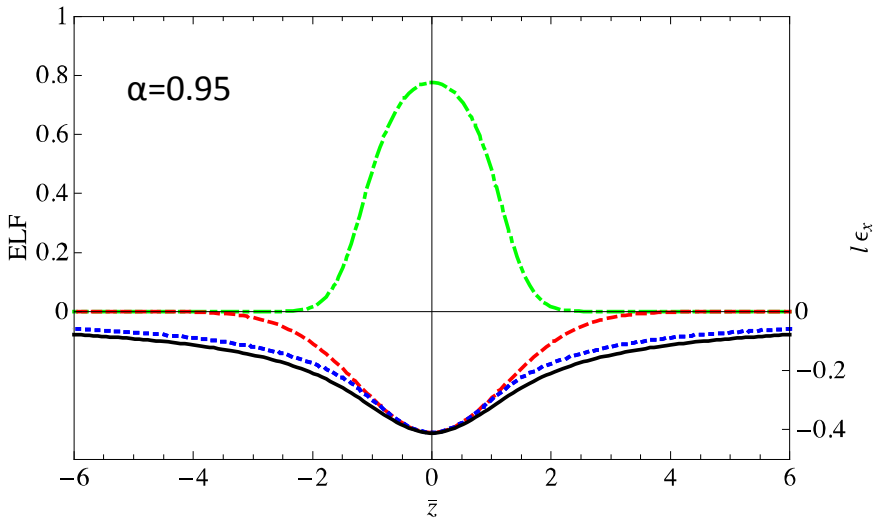
Chemical potential $\mu = (\alpha + \frac{1}{2})\frac{1}{l^2}$

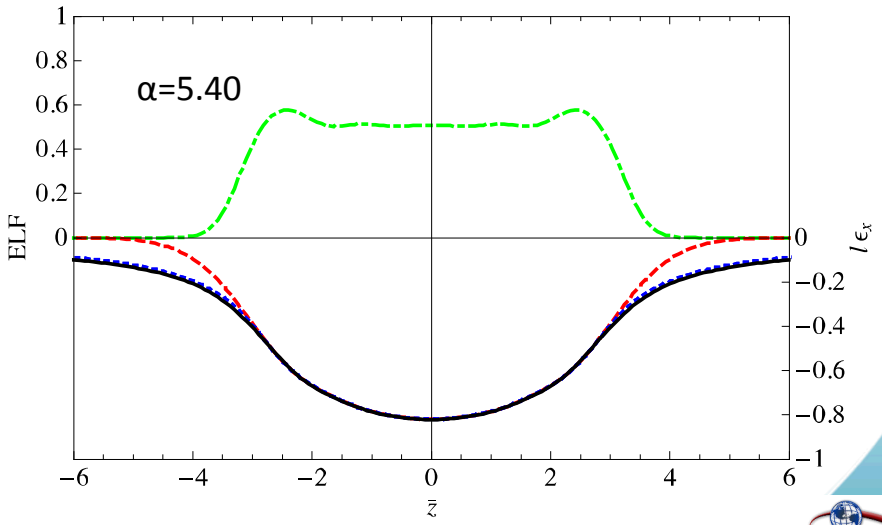
α characterizes how many subbands have been occupied, and determines the level of confinement.

ELF in HO systems versus Exchange Energy









ELF is correlated with the exchange energy errors!

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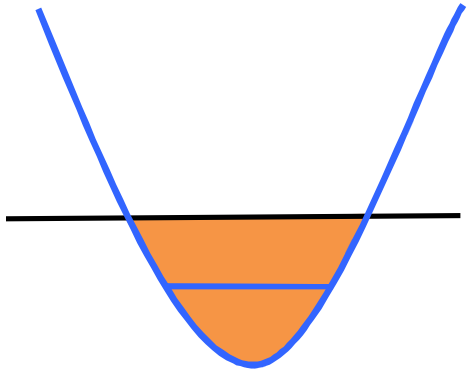
Subsystem Functional Scheme:

$$E_{xc} = \int_V n(\vec{r})\, \varepsilon_{xc}(\vec{r};[n])\, dV$$

Dividing V into sub-regions where different subsystem functionals apply

Specialized functionals in different subsystems

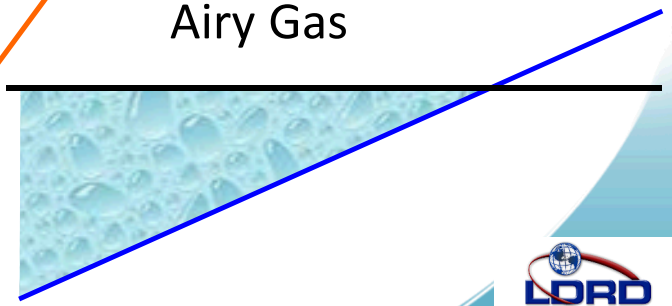
Confinement physics:
Harmonic oscillator gas



Interpolation Index:
ELF

Interior physics:
Uniform electron gas

Surface physics:
Airy Gas



Feng Hao, Rickard Armiento, and Ann E. Mattsson
Journal of Chemical Physics **140**, 18A536 (2014).

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ELF in a ‘real’ system: CuO, transition metal oxide

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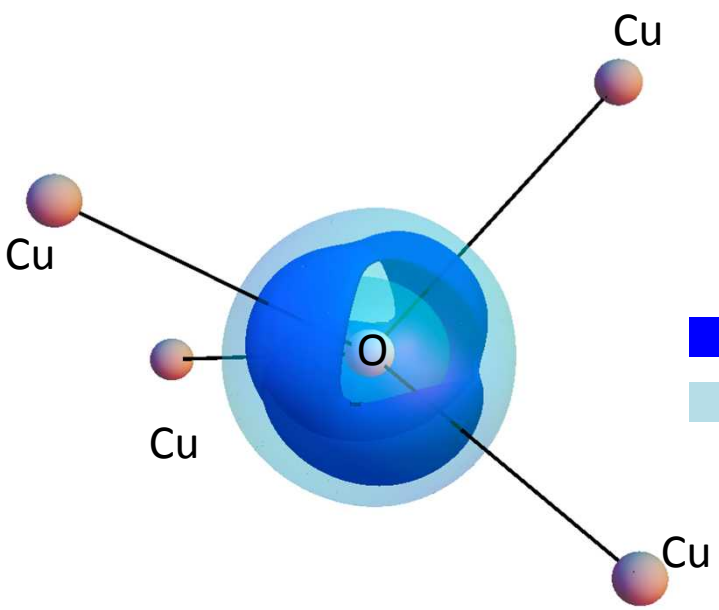

ELF ≈ 1/2: uniform electron gas like

ELF ≈ 1: strong localization, discrete levels

ELF > 0.83

ELF > 0.77

CuO: Monoclinic structure obtained when starting from the experimental structure with each dimension scaled by 3%

Feng Hao, Rickard Armiento, and Ann E. Mattsson
Journal of Chemical Physics **140**, 18A536 (2014).

The high ELF regions are around the oxygen atoms. We identify these as the regions where hybridization in solid materials occur.

Summary

- The interesting properties of *f*-electron systems comes from a simultaneous existence of free and discrete level electrons.
- The challenge we have is to describe free electrons and discrete level electrons equally well in a unified picture.
- The ELF index can be used to find regions in real space where discrete level physics needs to be taken into account.
- We have identified the HO gas as a model system that can be used to gain insight about this kind of physics.
- We will use the HO gas model system for creating a functional suitable for these systems via the subsystem functional scheme.

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Heavy Materials: The problematic $p_{1/2}$ states

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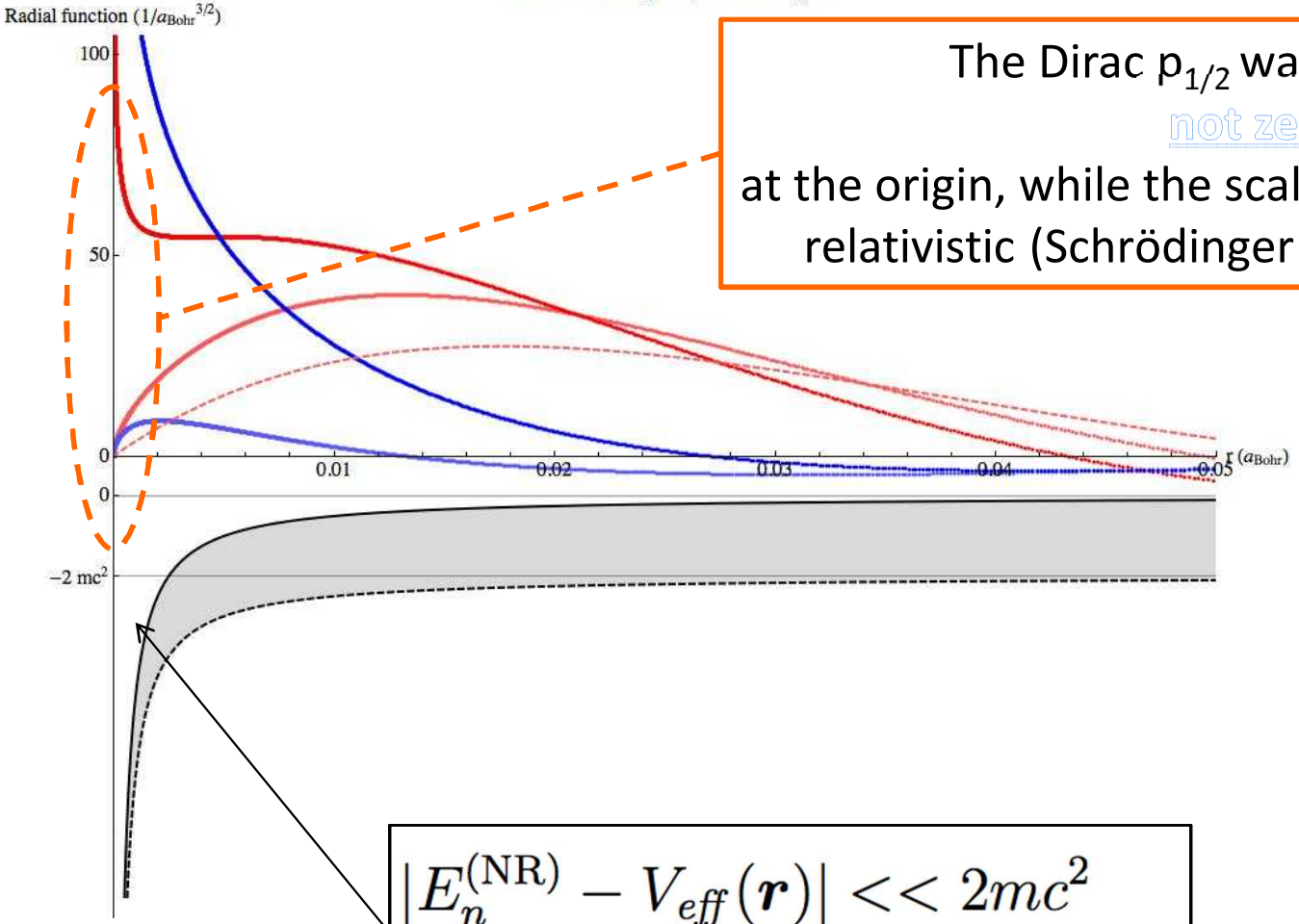
The radial function for the upper components (red) and the lower components (blue) of the $6p_{1/2}$ state, calculated with the Harmon and Koelling scalar relativistic equation (lighter), the Dirac equation (darker), and the Schrödinger equation (dashed). Note the discrepancy at the origin.



The Dirac $p_{1/2}$ wavefunction is

not zero

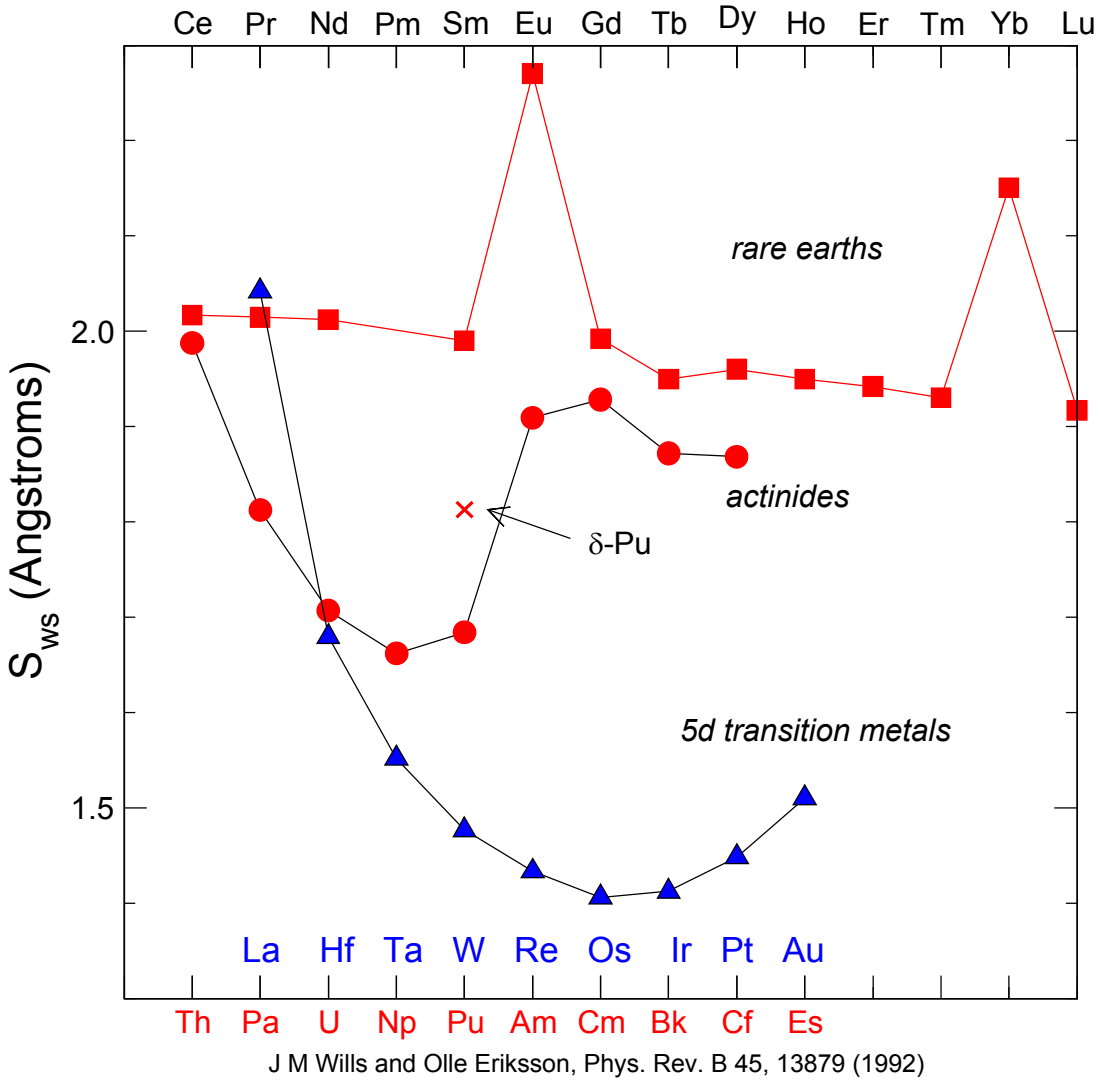
at the origin, while the scalar-relativistic and non-relativistic (Schrödinger Equation) ones are.

We need to use a DFT method based on the Dirac Equation.

$$|E_n^{(\mathrm{NR})} - V_{eff}(\boldsymbol{r})| << 2mc^2$$

violated

Confinement physics



J M Wills and Olle Eriksson, Phys. Rev. B 45, 13879 (1992)

Experimental equilibrium volumes.

- LDA/AM05/PBE work reasonably well for 5d transition metals (-2%/0 %/+2 %), but, contrary to experiments, give the same parabolic trend for rare earths and actinides.
- Dirac treatment not likely to change this dramatically.

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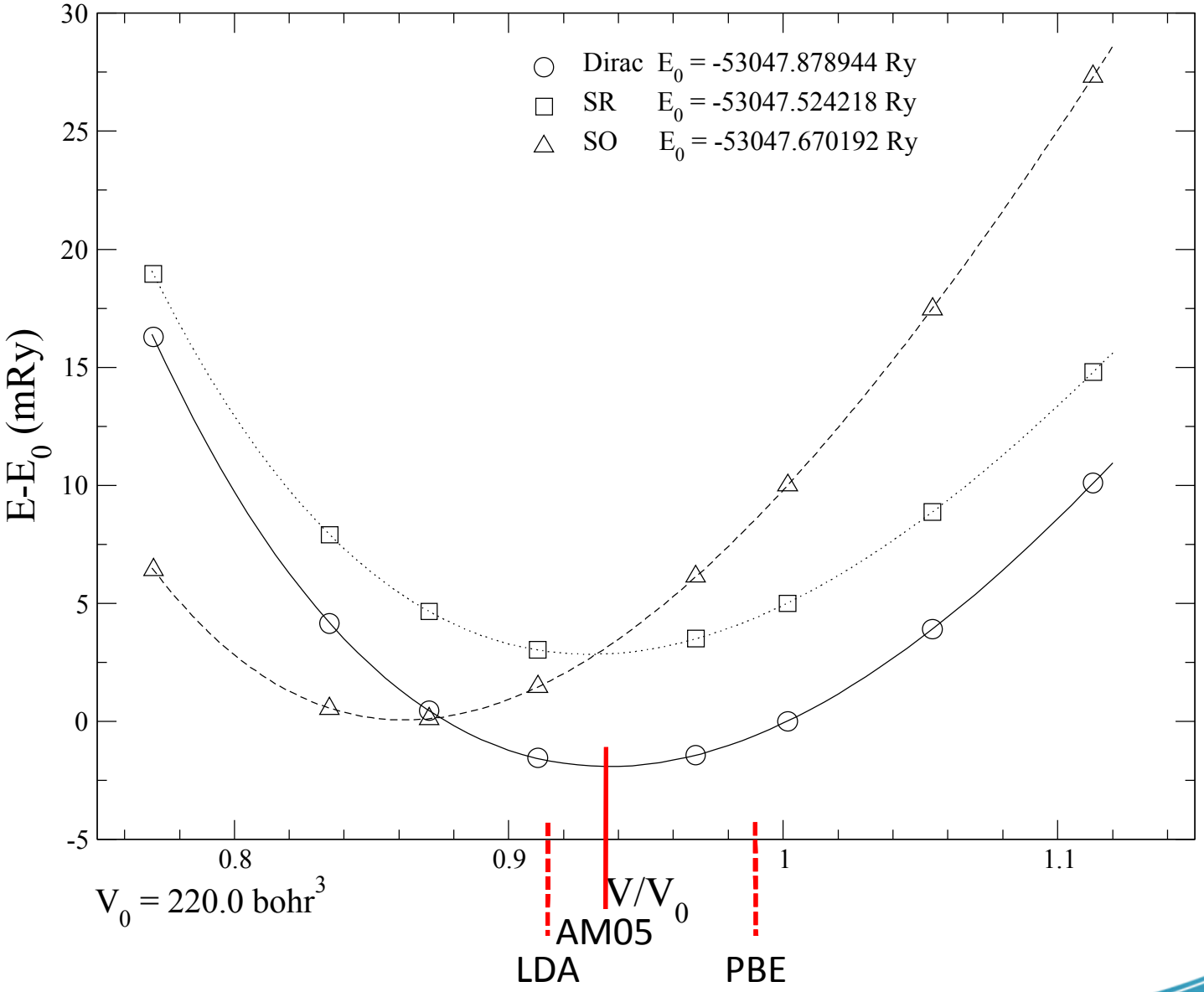
Thorium AM05 results



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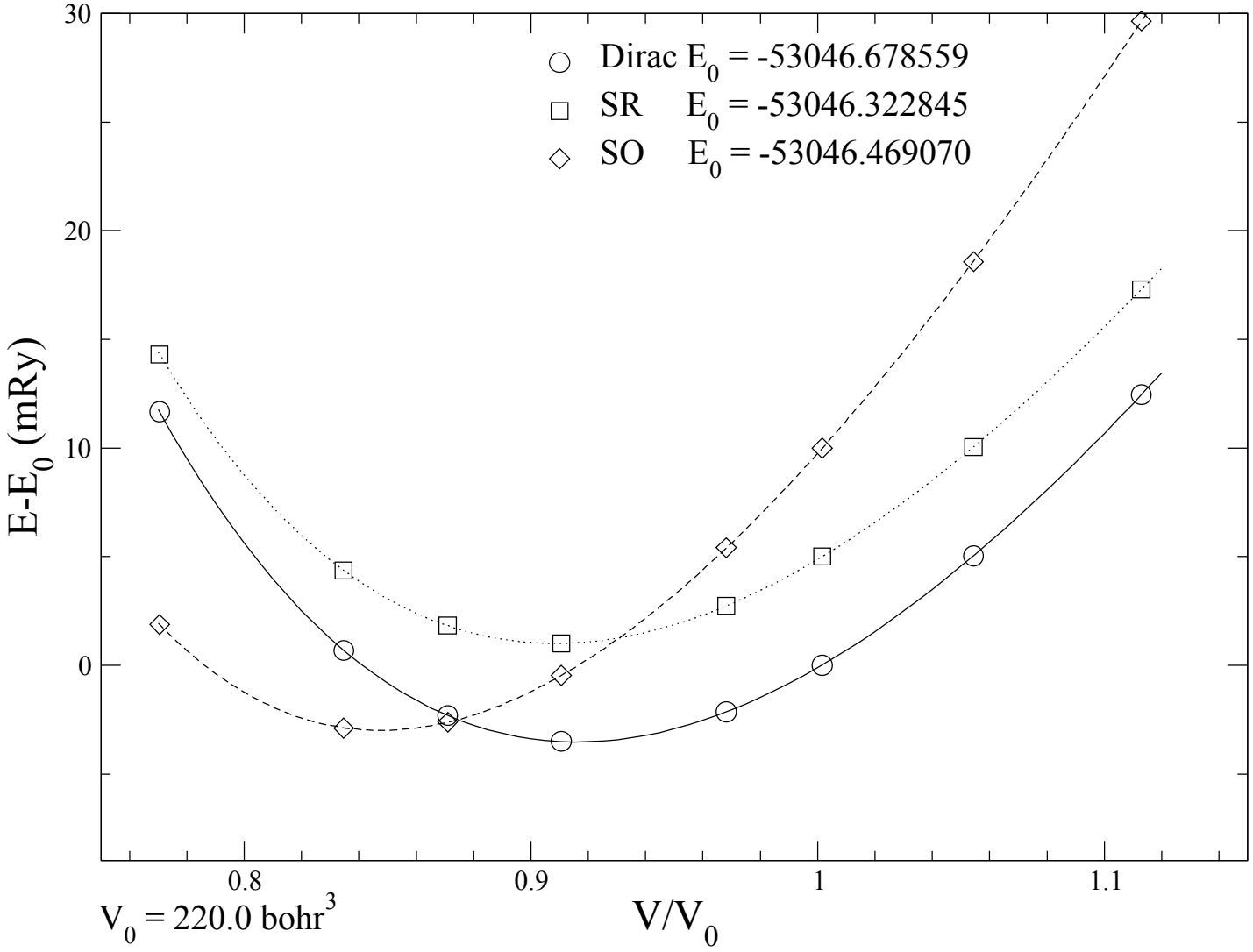
Thorium LDA-PW results



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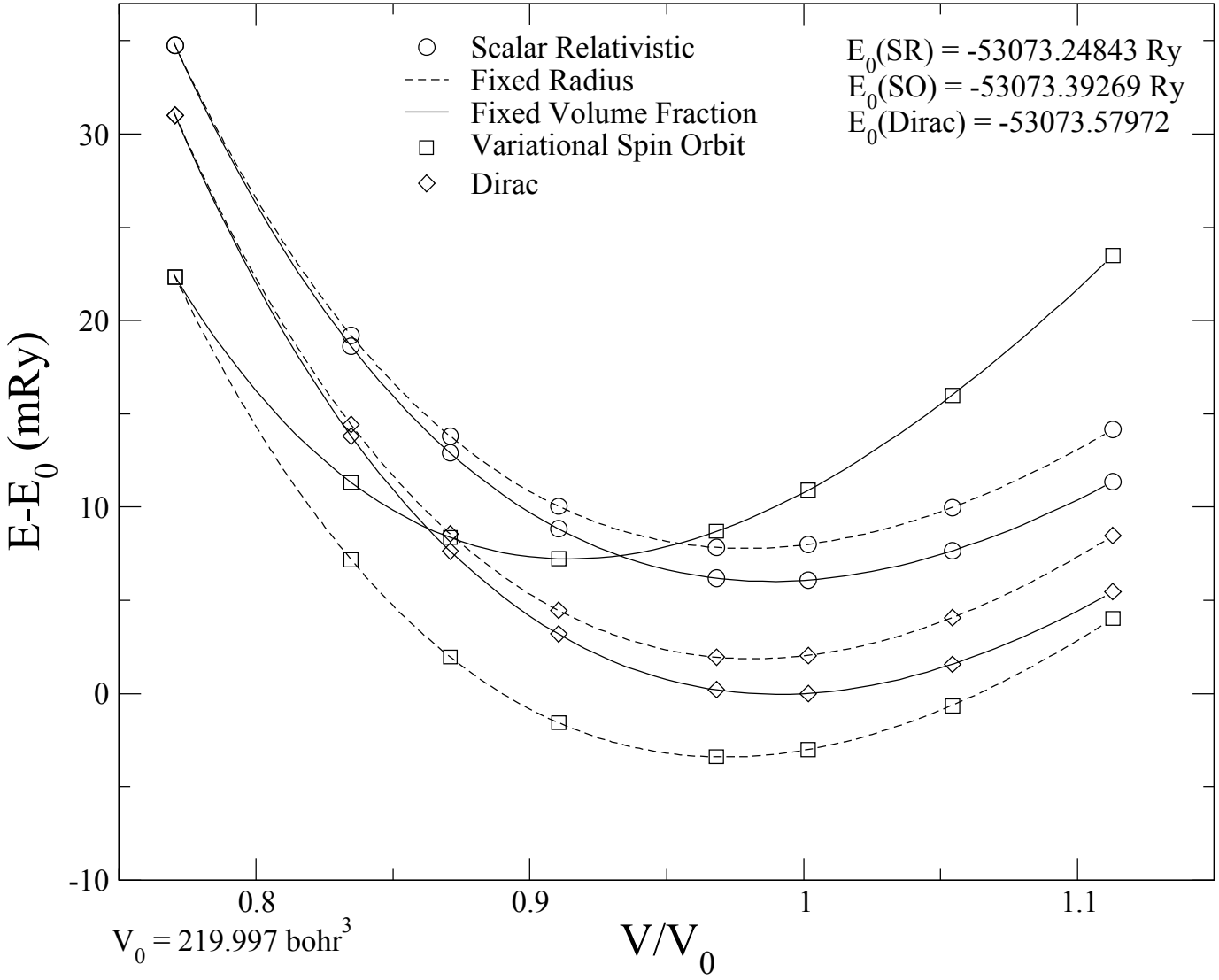
Thorium PBE results



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Summary Thorium

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TABLE I: Thorium equilibrium volumes in cubic bohrs and bulk moduli in GPa calculated with scalar relativistic, scalar relativistic with variational spin-orbit, and full Dirac methodologies, using AM05[17], PBE[2], and PW[18] functionals as described in the text. The zero temperature experimental volume, with zero point motion subtracted, is 220.00 bohr^3[13]. Reference 13 gives 205.14 for AM05. 218.02 for PBE, and 200.89 for PW.

	V/a_0^3			B (GPa)		
	AM05	PBE	PW	AM05	PBE	PW
Scalar Relativistic	204.55	217.36	199.89	58.9	54.5	65.5
Scalar Relativistic+Spin Orbit	189.62	201.21	186.45	74.1	68.6	80.4
Full Dirac	205.98	217.98	201.54	62.4	58.3	68.0

Note: PBE is giving 7% too large volume for gold. Generally underbinding.
"When PBE gets the right equilibrium volume, you should get suspicious".
Seen like an indication that a hybrid functional or exact exchange is needed.
Confinement physics…

Confinement error and Harmonic Oscillator model (HO)

Hao, Armiento and Mattsson Phys, Rev. B **82**, 115103 (2010).

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HO model: Localized electron levels in a continuum.

Energy of subbands $\varepsilon_j = (j + \frac{1}{2})\frac{1}{l^2}$

Chemical potential $\mu = (\alpha + \frac{1}{2})\frac{1}{l^2}$

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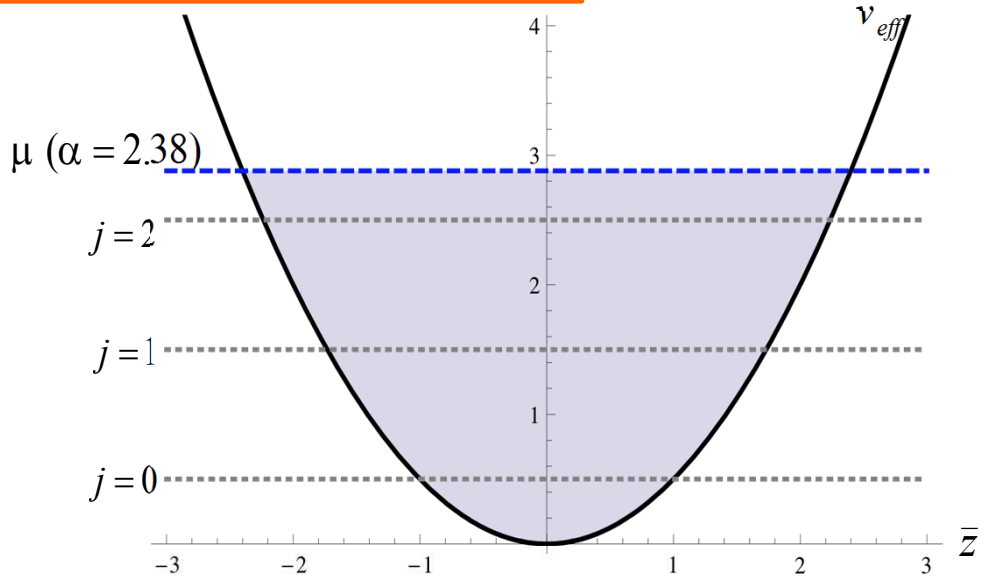
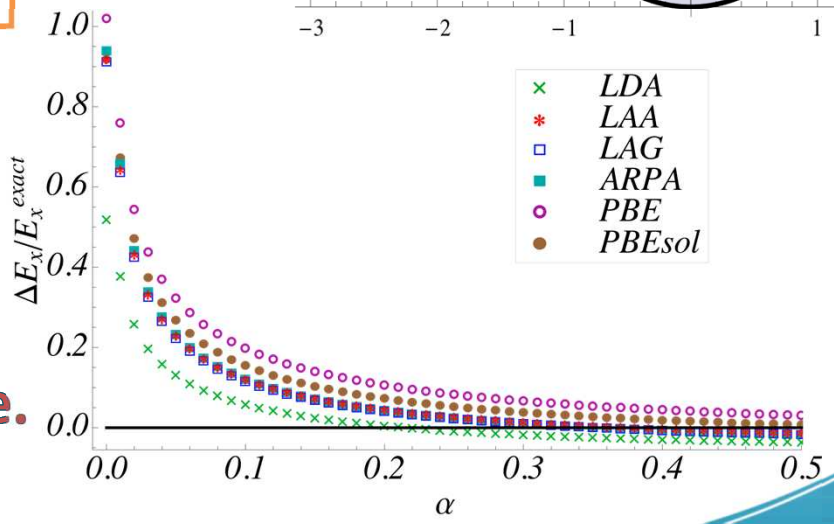
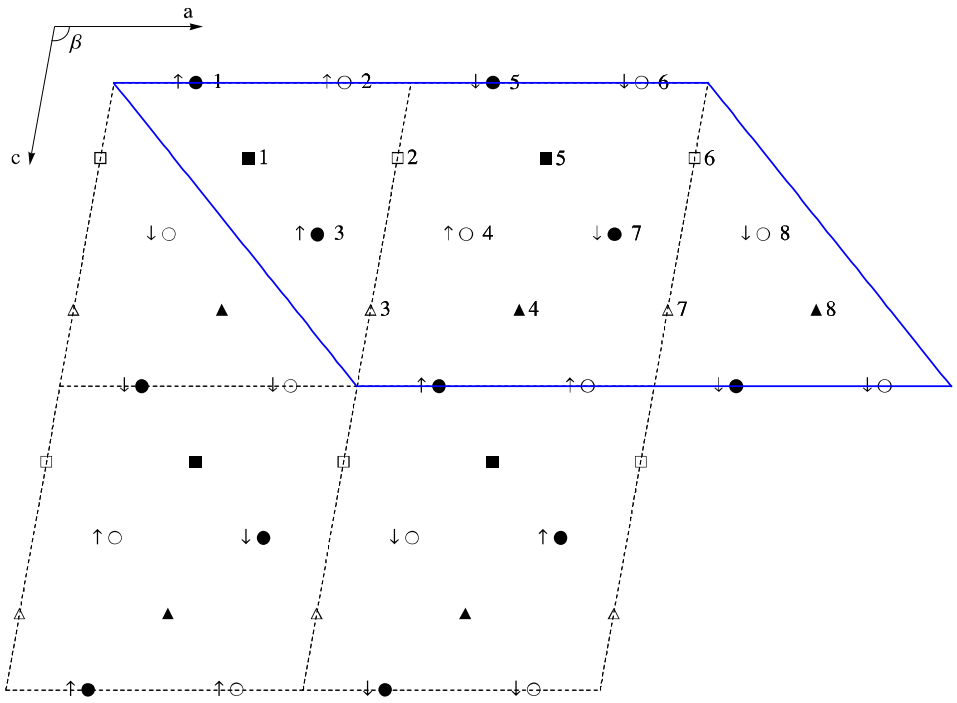


Relative errors of E_x of the HO gas introduced by different functionals.



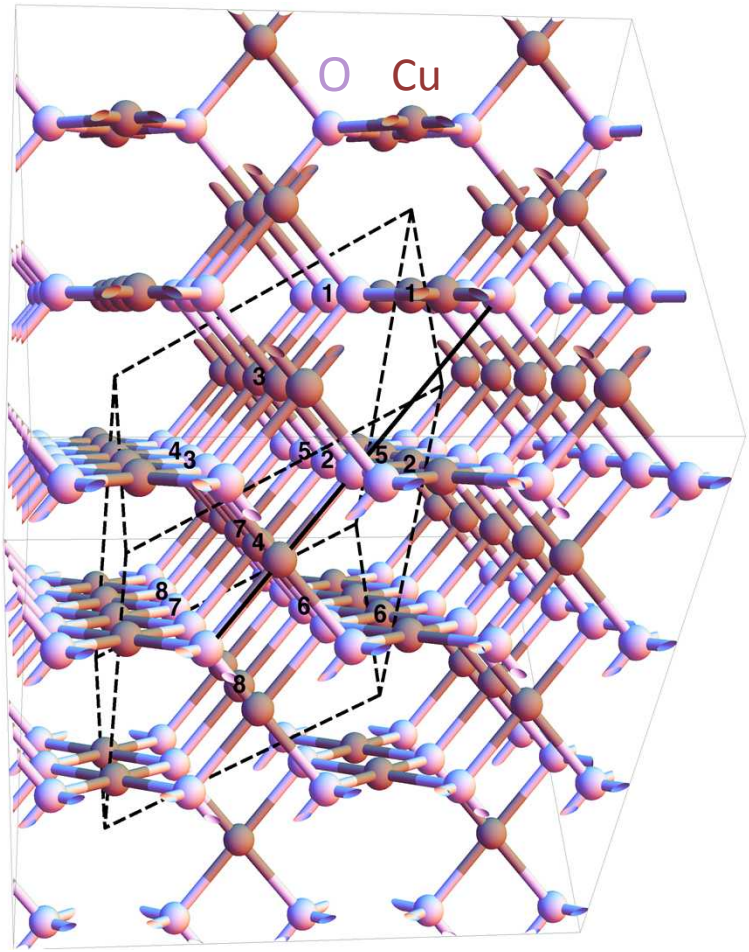
As α decreases, the confinement errors increase.

Experimental structure of CuO



● Cu y = 1/4
○ Cu y = 3/4
■ O y = 1/2+u
□ O y = u
▲ O y = 1/2−u
△ O y = 1−u
↑↓ spins

Experimental lattice parameters:
a = 4.6837Å, b = 3.4266 Å, c=5.1288 Å ,β = 99.54°, u=0.4184



Rectangular shape obtained from DFT calculation.
a = 4.0396Å, c/a=1.23, b/a=1.0, β = 90°, u=0.5

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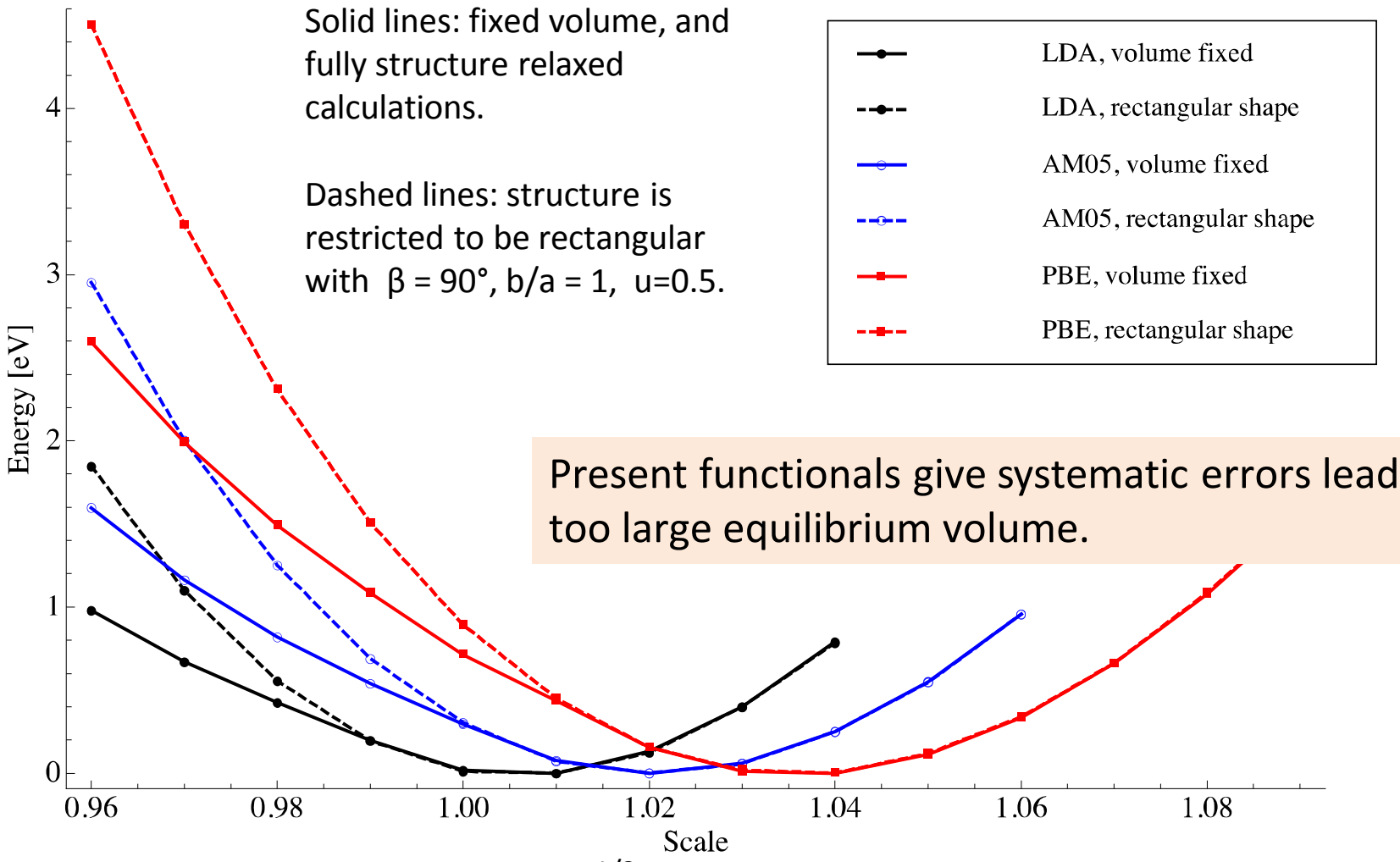
DFT calculations of CuO structure

Ann E. Mattsson

Solid lines: fixed volume, and fully structure relaxed calculations.

Dashed lines: structure is restricted to be rectangular with β = 90°, b/a = 1, u=0.5.



Present functionals give systematic errors leading to too large equilibrium volume.

Scale $=(V/V_0)^{1/3}$

V_0 is the lattice volume of the experimental structure

DFT calculations of CuO structure

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Solid lines: fixed volume, and fully structure relaxed calculations.

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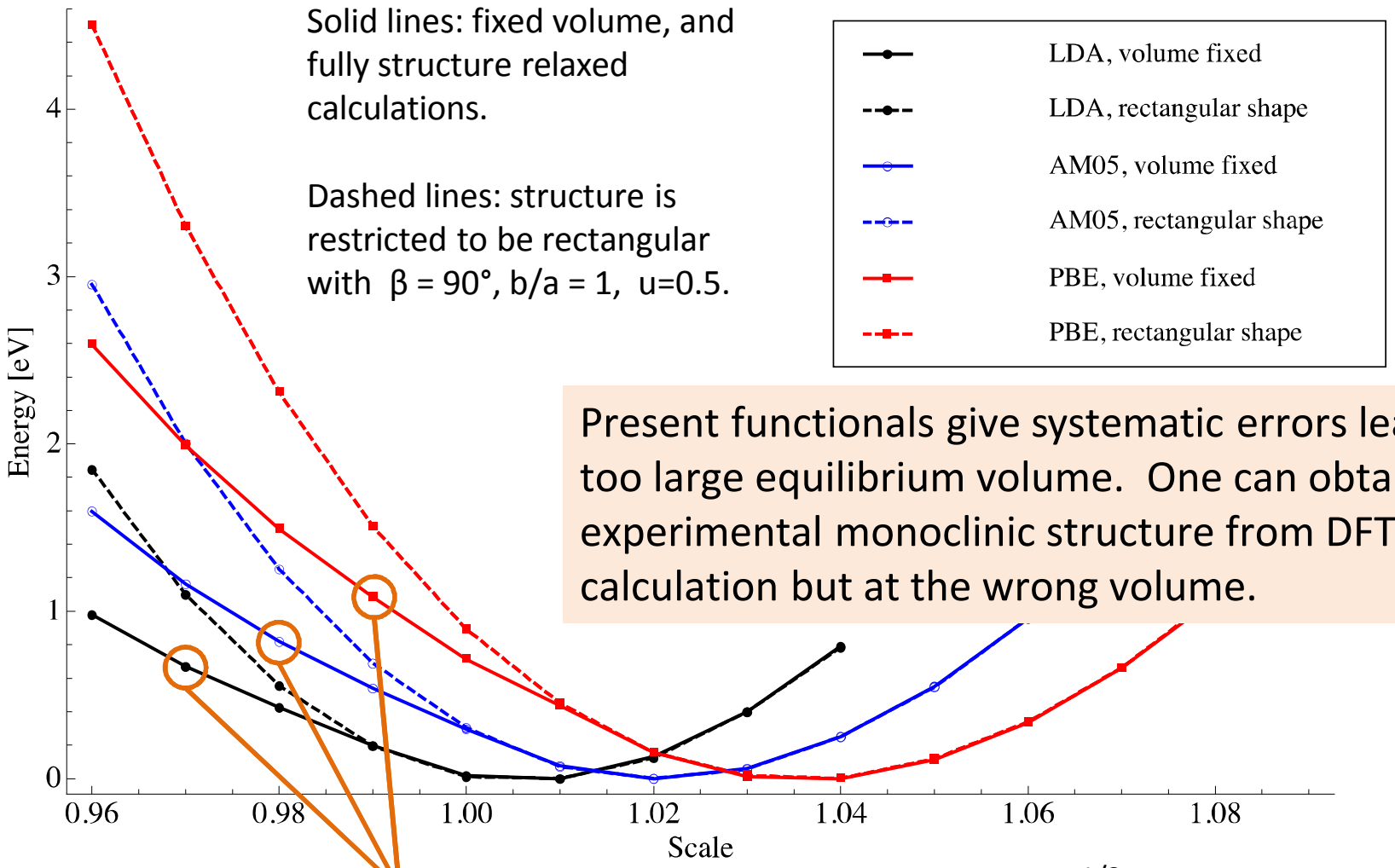

Present functionals give systematic errors leading to too large equilibrium volume. One can obtain the experimental monoclinic structure from DFT calculation but at the wrong volume.

Structures with relative dimensions close to the experimental structure are obtained in these points.

Scale $=(V/V_0)^{1/3}$

V_0 is the lattice volume of the experimental structure

Possible mechanism for correction

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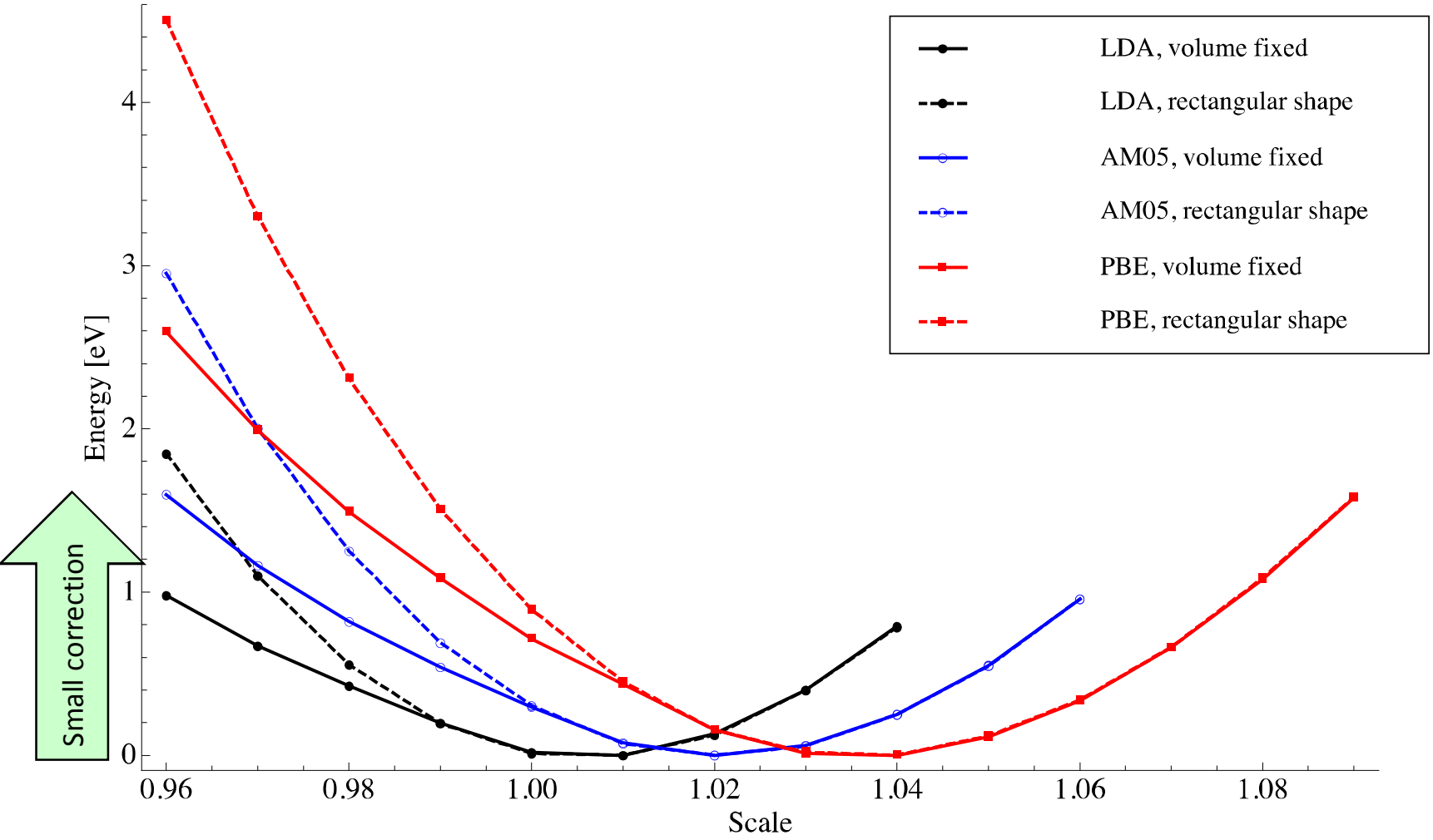

The minimum moves to smaller volumes.

Confinement error correction scheme:
Presented by Feng Hao, a few talks ago

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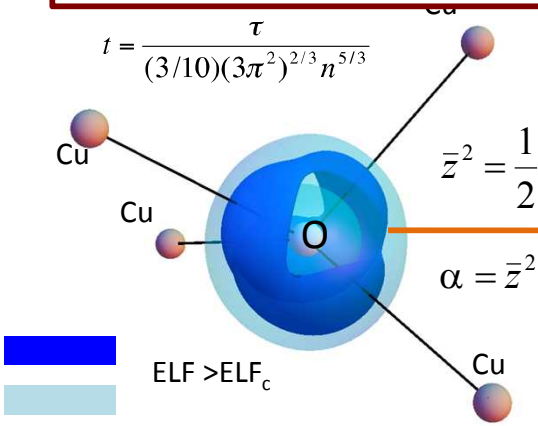
Electron localization function (ELF).

Harmonic oscillator (HO) model system.

$$t = \frac{\tau}{(3/10)(3\pi^2)^{2/3} n^{5/3}}$$

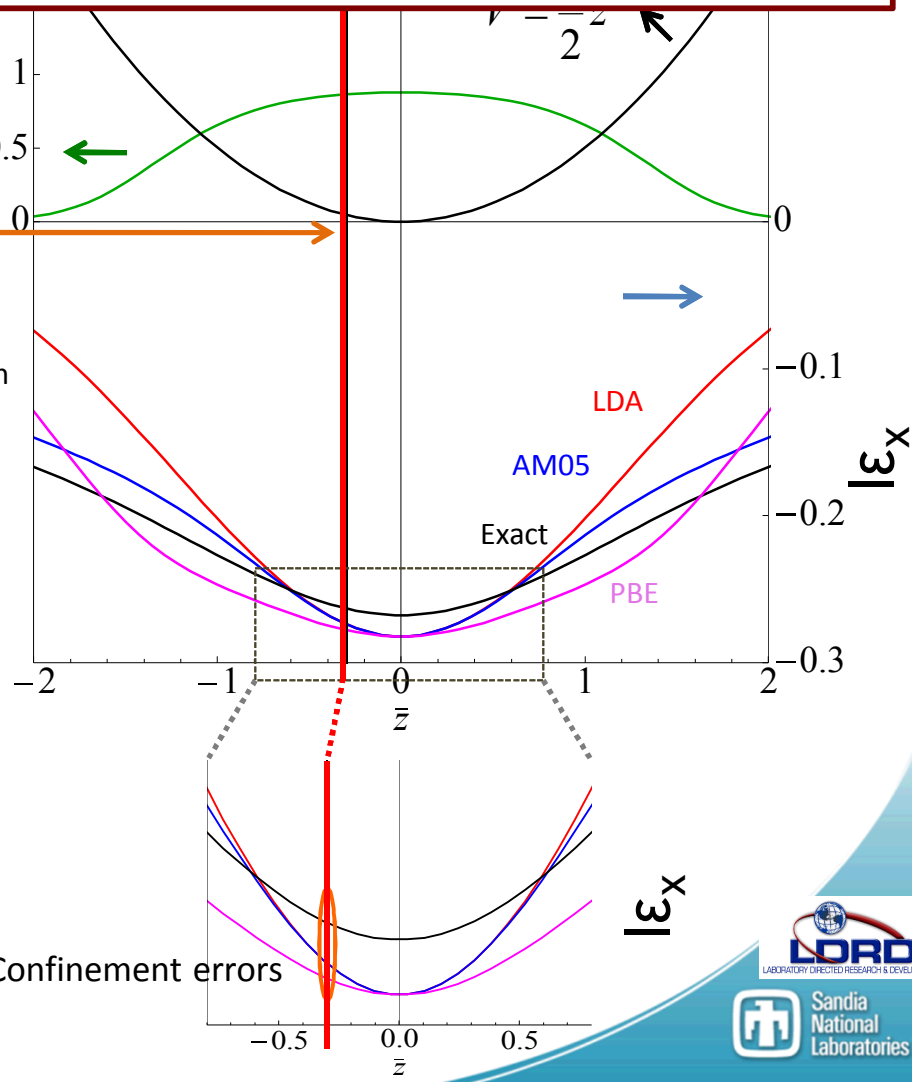
$$\bar{z}^2 = \frac{1}{2} W\left[18\pi\left(\frac{3}{5}t - s^2\right)^2 s^2\right]$$

$$\alpha = \bar{z}^2\left(\frac{3}{5}\frac{t}{s^2} - 1\right)^2$$



W(x) is the Lambert W function

Harmonic Oscillator (HO) model α=0.31



Confinement errors

Total confinement error correction in exchange energy:

$$\Delta E_x^{conf} = \int_{V(ELF>ELF_c)} d\vec{r}\, n(\vec{r})\varepsilon_x^{DFA}(\vec{r})\Delta\varepsilon_x(\vec{r})$$

Relative errors from density functional approximation (DFA) **in the HO model**:

$$\Delta\varepsilon_x = [l\varepsilon_x^{exact}(\alpha,\bar{z})]/[l\varepsilon_x^{DFA}(\alpha,\bar{z})] - 1$$

Confinement error correction for CuO

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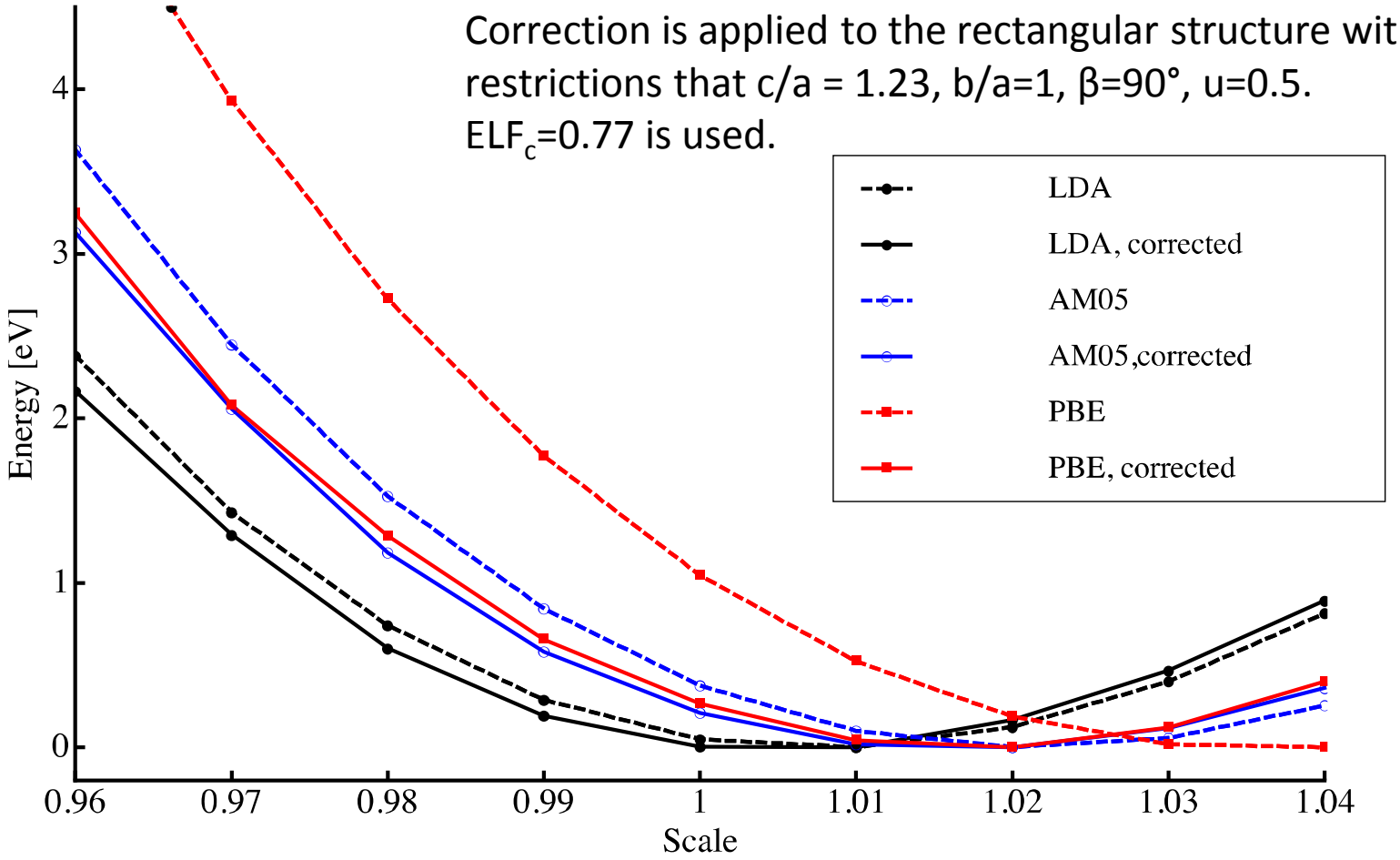
Correction is applied to the rectangular structure with restrictions that c/a = 1.23, b/a=1, β=90°, u=0.5. ELF_c=0.77 is used.



Equilibrium structure has been shifted to have smaller volume after correcting the confinement errors. AM05 and PBE have approximate same line shape after the correction.

ELF Contribution from core electrons

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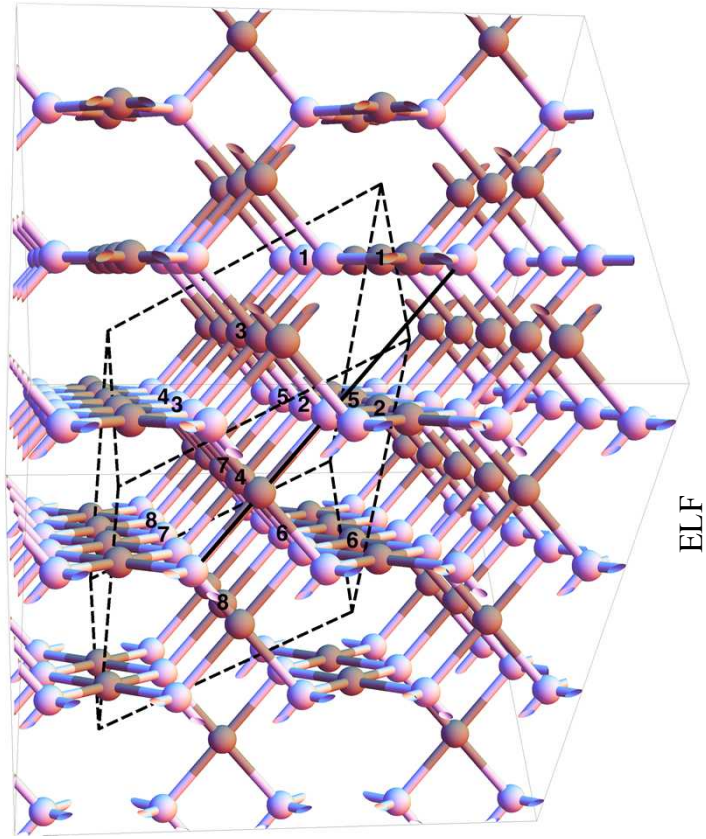

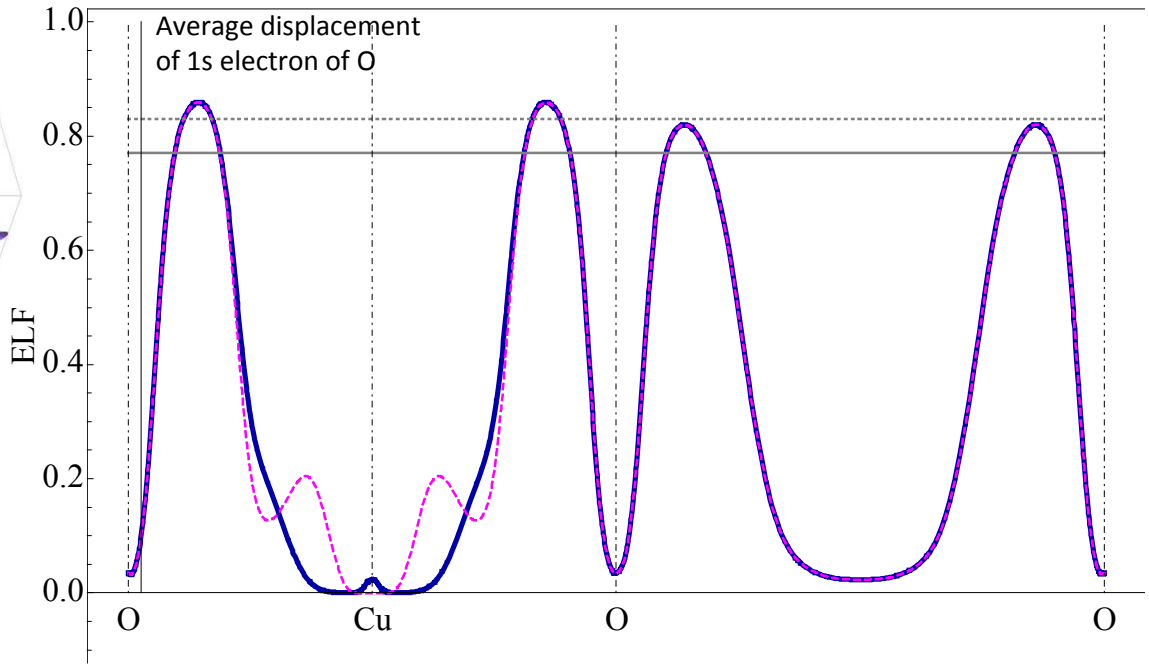

Core electrons will not affect the confinement correction results using current scheme.

Confinement error correction for Si

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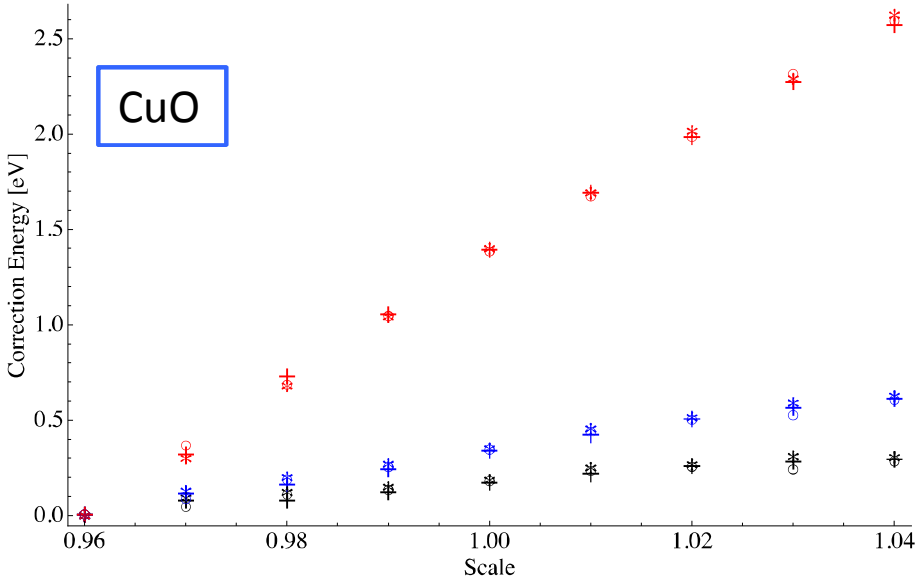
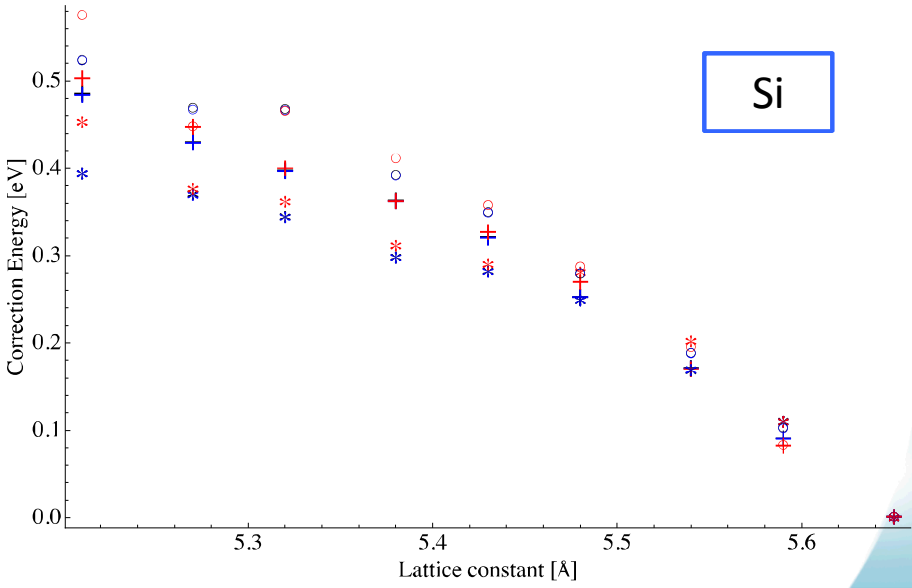
Lattice constant of Si

	LDA	AM05	PBE	Experimental
Before correction	5.38 Å	5.43 Å	5.47 Å	5.43 Å
After correction	5.43 Å	5.48 Å	5.52 Å	

Confinement correction energy





Color: correction energy for different functionals

Black: LDA, Blue: AM05, Red: PBE

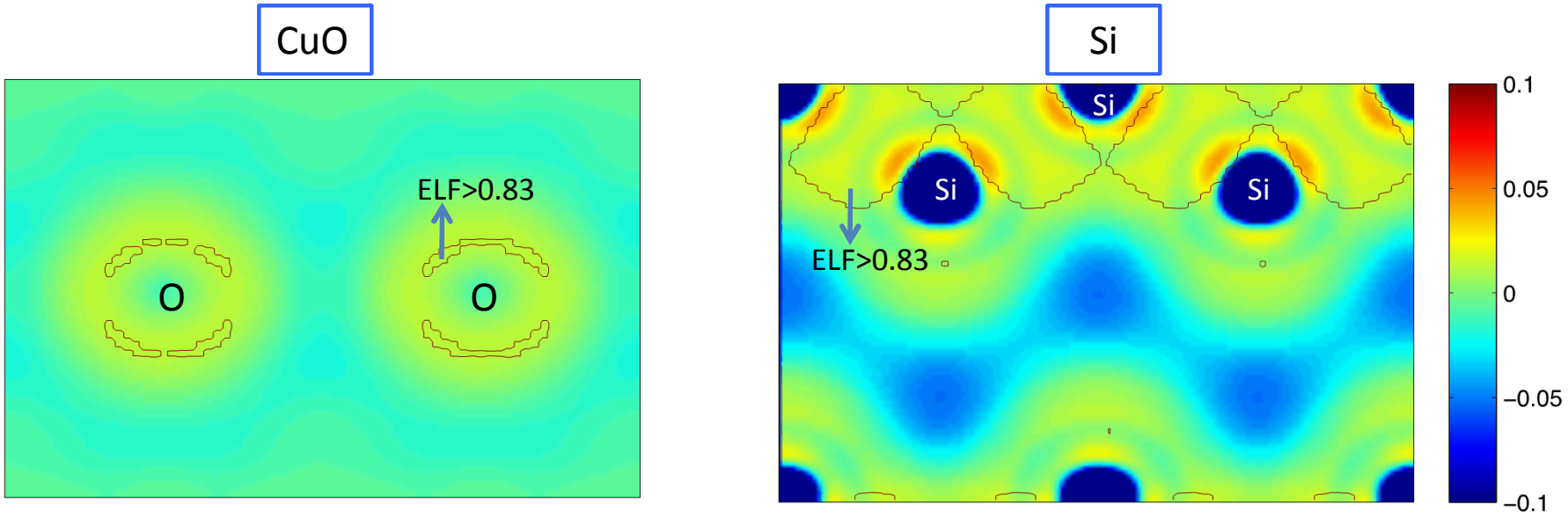
Symbols: densities obtained from different functionals

* : LDA, + : AM05, ° : PBE

Self consistency needed for, for example, Si

Relative density difference between PBE and LDA calculation:

$(n^{PBE}-n^{LDA})/n^{LDA}$



Density difference obtained from different functionals are larger in Si than in CuO.

The confinement errors have to be treated self-consistently for Si.

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Si from QMC

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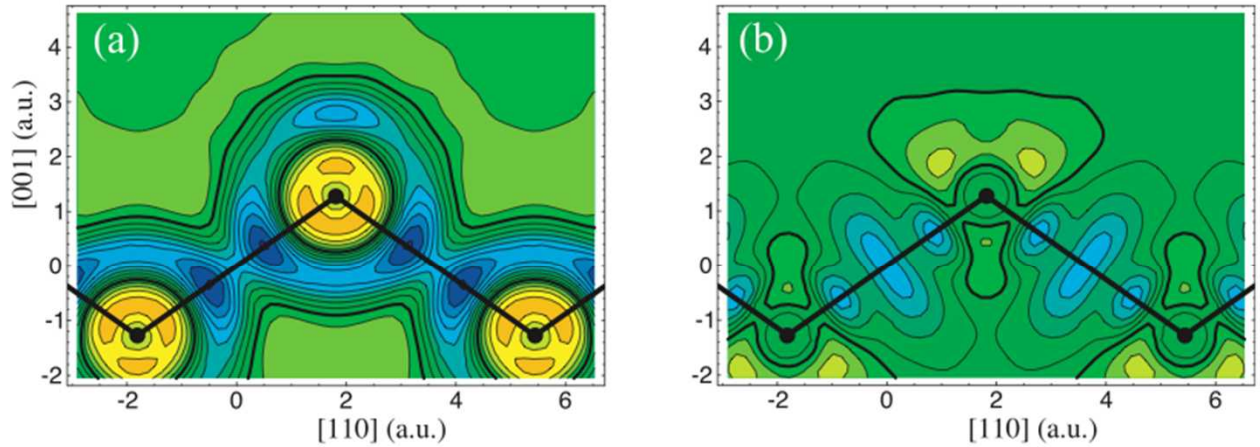
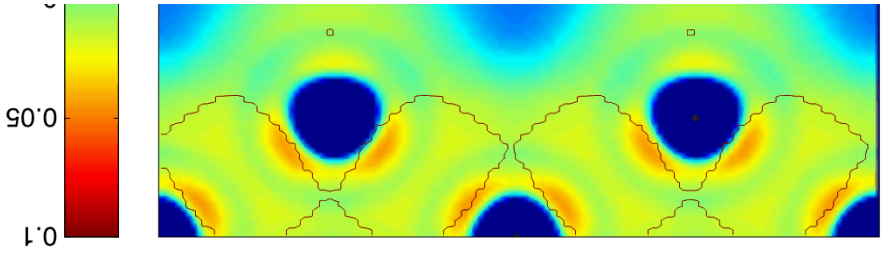


FIG. 1. (Color) Comparison of DFT and VMC e_{xc}'s on the (110) plane of the Si crystal. (a) Difference between the LDA e_{xc} and that of VMC data (Ref. 10). Difference between that of the GGA^{++} model described in the text and the VMC result. Contours in increments of 0.2×10^{-3} a.u., with thicker contour that for zero difference. Bluer (darker) regions show negative difference and redder (lighter) regions, positive.



Si from QMC

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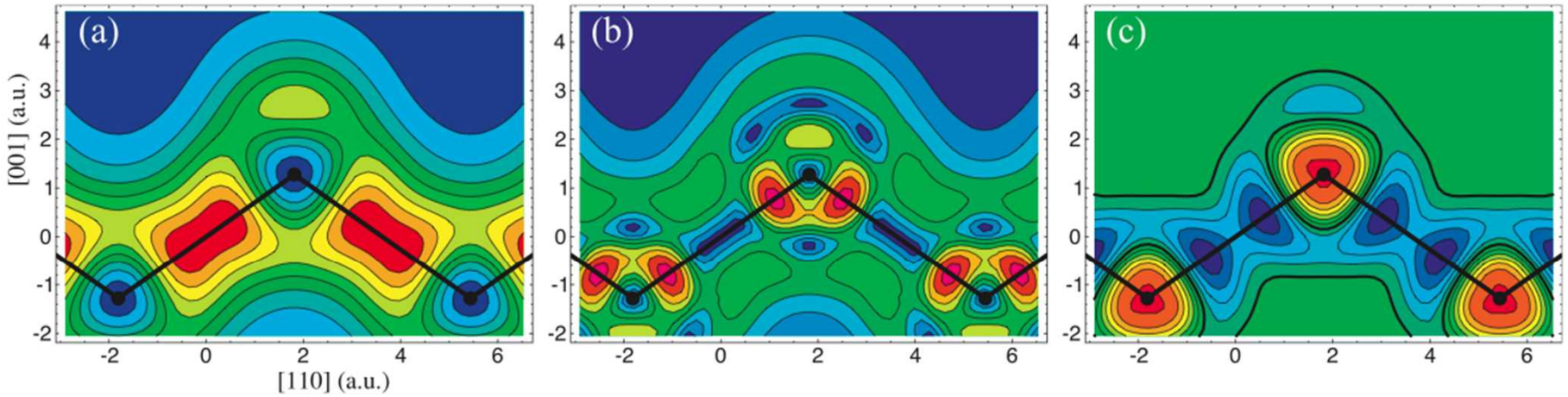

FIG. 2. (Color) Gradient analysis of the density of crystalline Si. The density n (a), $|\nabla n|$ (b), and $\nabla^2 n$ (c) on the (110) plane of the Si crystal. Atoms and bonds outlined in black. Shading varies from blue (dark gray) (low) to red (light gray) (high) and contours are in increments of 0.01 (a), 0.01 (b), and 0.05 a.u. (c). In (c) the zero contour is the thicker black line.