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Improving the Predictive Power of Calculations for the Warm Dense Matter Region

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IPAM, University of California, Los Angeles, CA, 24 May 2012

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).

How do we learn from the Quantum Mechanical equations?

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 SE directly, even with the largest and fastest computers in the world.

My personal view of the field

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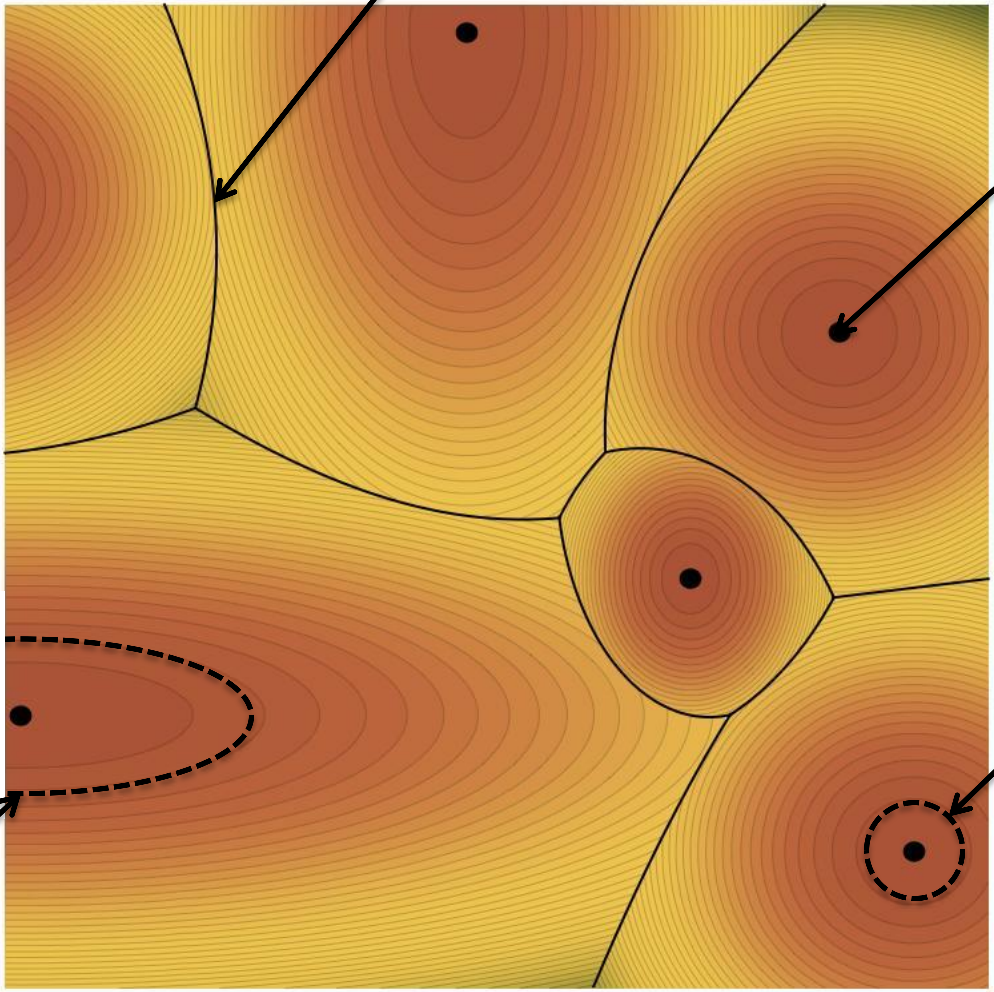
But using different theories for different types of systems is not truly predictive and also is not helping us to calculate properties at a macroscopic/engineering scale.



Marginal Physics is quite exciting.

"Attractor" Physics: The dominant physical behavior in a specific type of systems

Perturbation Theory can take small influences from other types of physics into account.

Quasi Particle Theory can take small influences from other types of physics into account.

How do we learn from the Quantum Mechanical equations?

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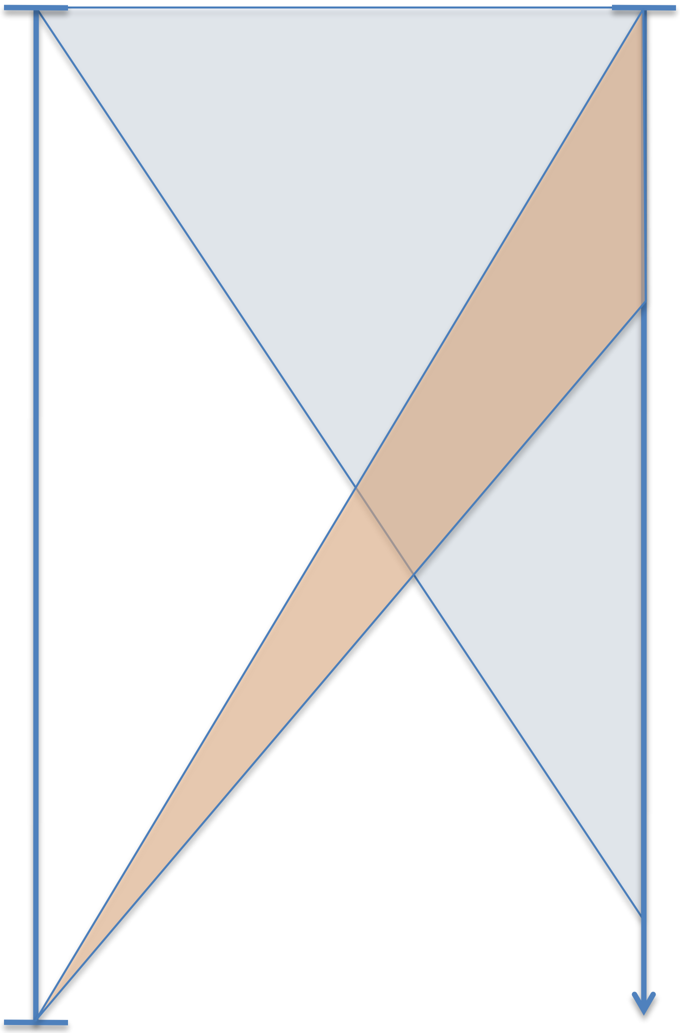


Exact Solution

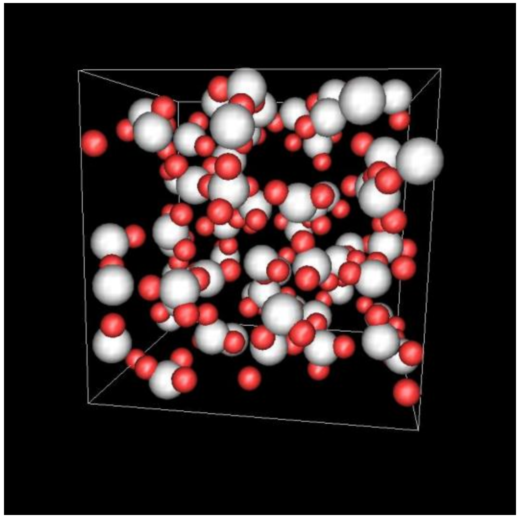
Exact Hamiltonian

Approximate Hamiltonian
("Attractor" Hamiltonian)

Approximate Solution

Speed is also very important

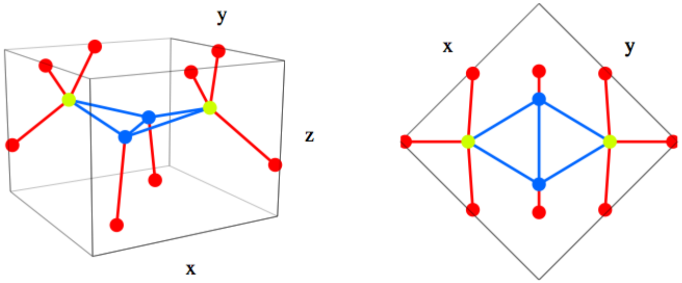
DFT-MD (also called QMD)



Snap shot of water simulation (64 molecules) done with AM05. Thomas Mattsson.

DFT is increasingly employed in quantum MD simulations of hundreds of atoms for tens of ps. This application demands functionals that are both accurate and fast. Every calculation with a temperature needs to be done with MD. Examples: Critical points and melting curves for EOS construction; Realistic calculations with water present.

Large cells and diffusion:



The Si ‹110› - split interstitial

Since all solid state DFT calculations uses periodic boundary conditions, large supercells are required for defect simulations in order to avoid uncontrolled interactions between defects. Calculating diffusion coefficients also require nudge elastic band type calculations where several copies of the same systems are needed.

Molecular Dynamics

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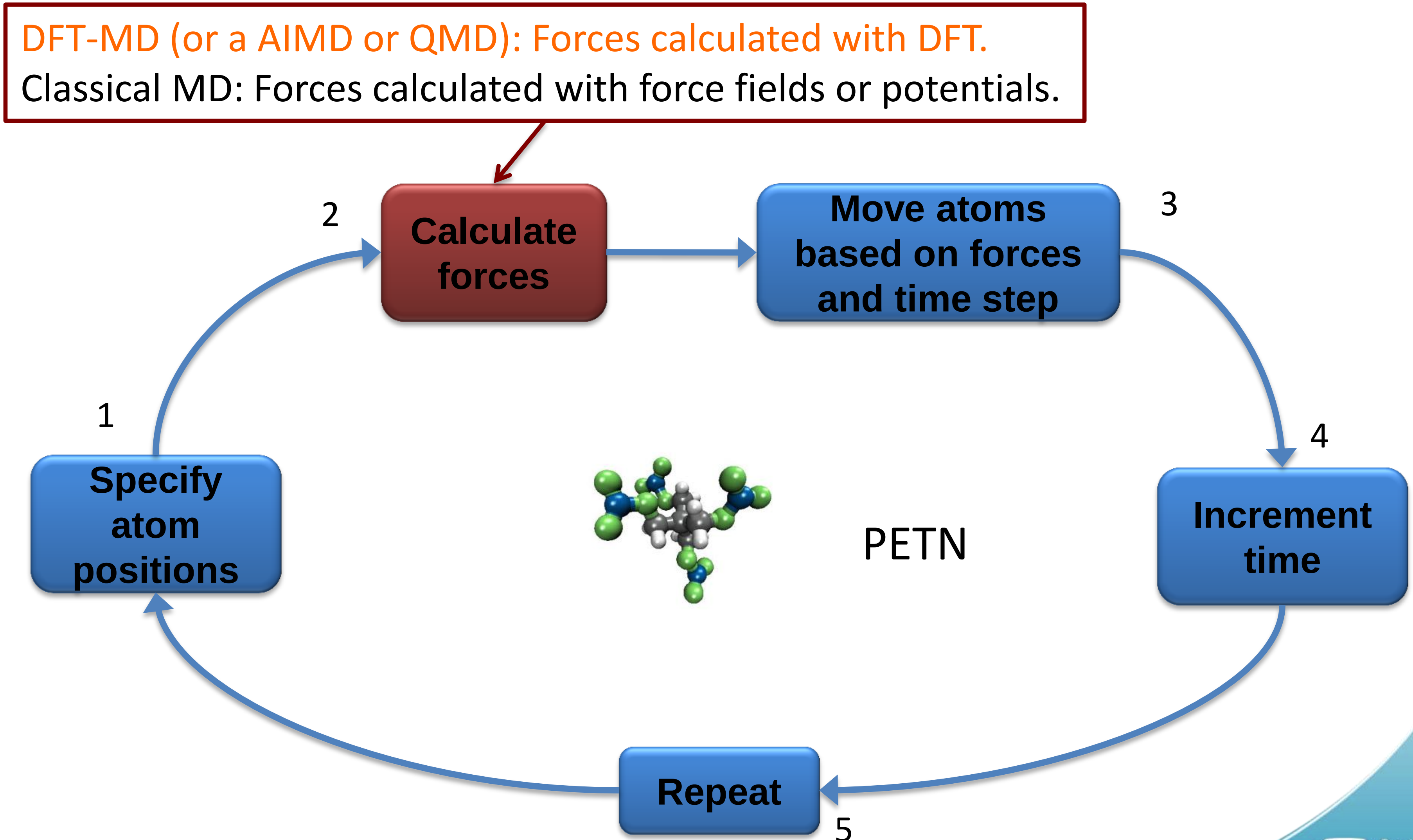

DFT-MD (or a AIMD or QMD): Forces calculated with DFT.
Classical MD: Forces calculated with force fields or potentials.

1 **Specify atom positions**

2 **Calculate forces**

3 **Move atoms based on forces and time step**

4 **Increment time**

5 **Repeat**

PETN

Adapted from slides by Ryan Wixom, SNL.

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

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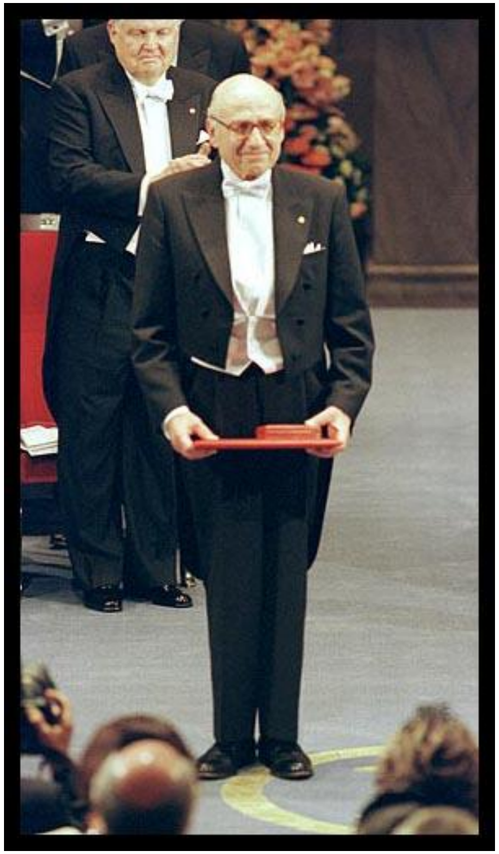
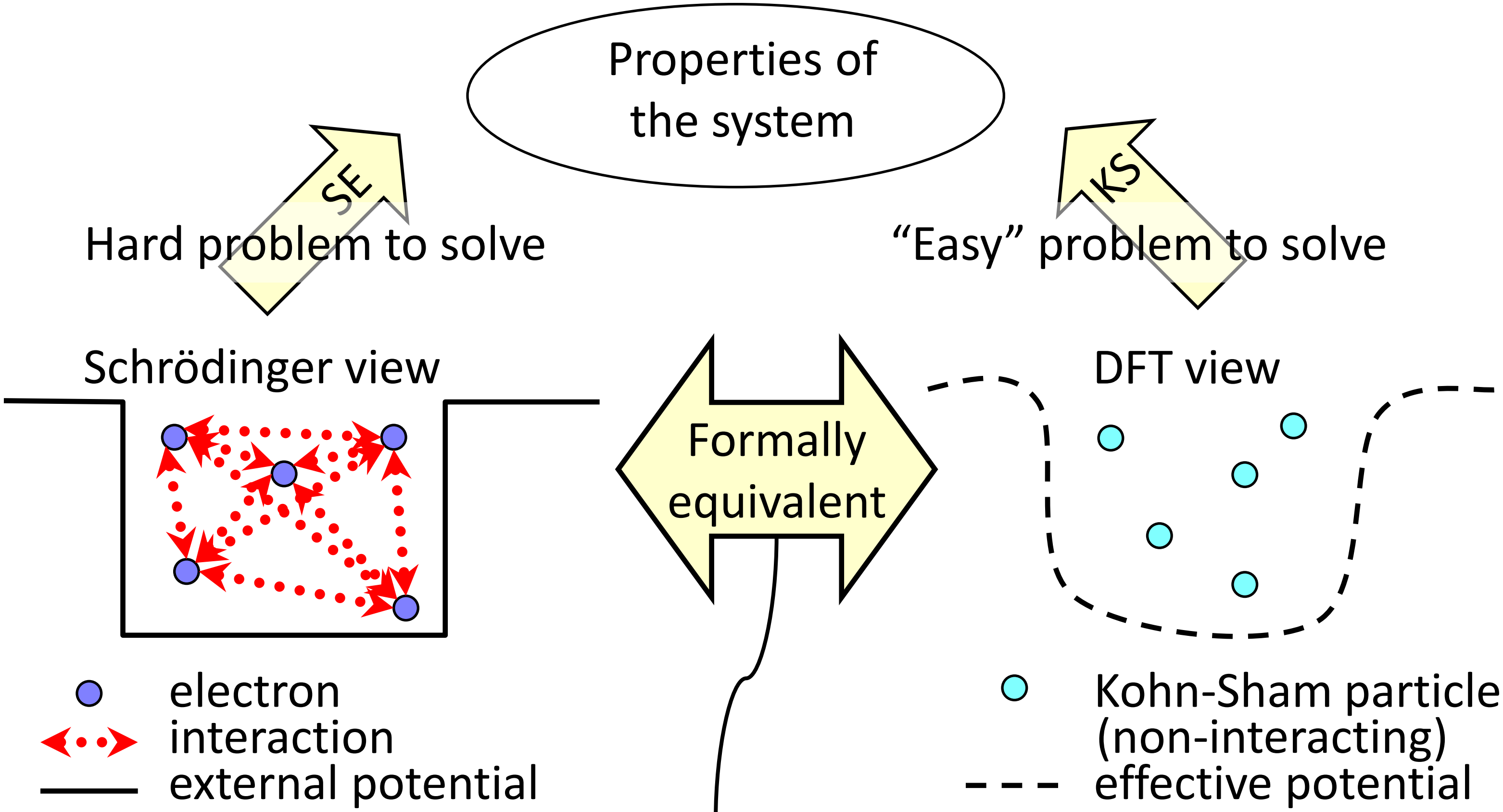


Hohenberg-Kohn theorem:
Phys. Rev. **136**, B864 (1964).
The electron density contains all information needed to determine ground state properties of a system.

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



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

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

Kohn-Sham equations:

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

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

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

If we had the divine exchange-correlation functional, 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.

Approximations for the exchange-correlation functional

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$$\left(-\frac{\hbar^2}{2\,m}\nabla^2 + \mathrm{v}_{eff}(\mathbf{r})\right)\psi_\nu(\mathbf{r}) = \epsilon_\nu\,\psi_\nu(\mathbf{r}) \quad \nu = 1,\ 2,\ \ldots.,\ N$$

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

$$\mathrm{v}_{eff}(\mathbf{r}) = \mathrm{v}(\mathbf{r}) + \int \frac{n(\mathbf{r}\,')}{|\,\mathbf{r}-\mathbf{r}\,'\,|}\,d\mathbf{r}\,' + \boxed{\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}}$$

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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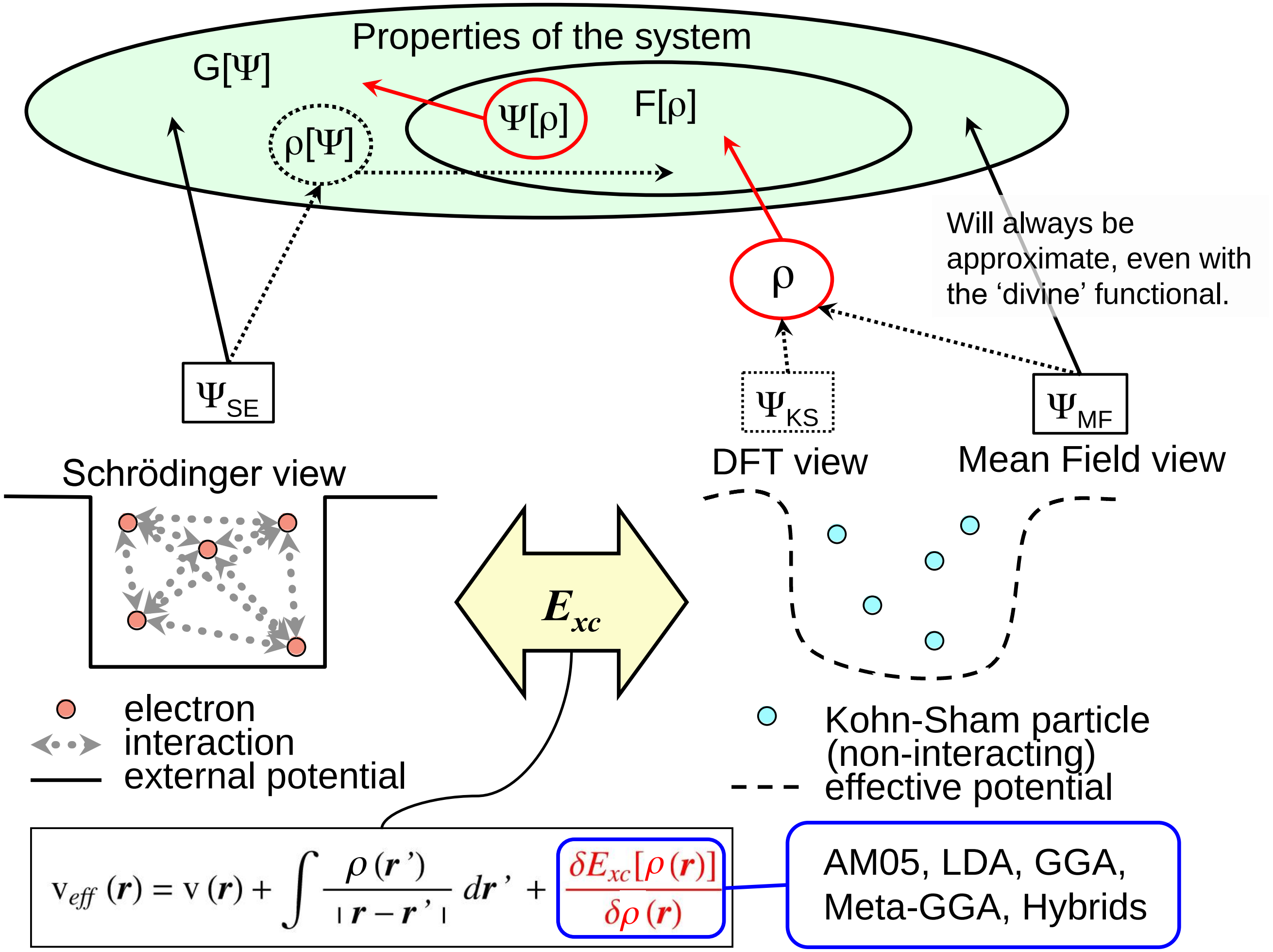
Density = ρ in chemistry

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” published by Taylor and Francis in 2011.



Will always be approximate, even with the ‘divine’ functional.

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

AM05, LDA, GGA, Meta-GGA, Hybrids

Bridges between Fundamental Law of Nature and Engineering

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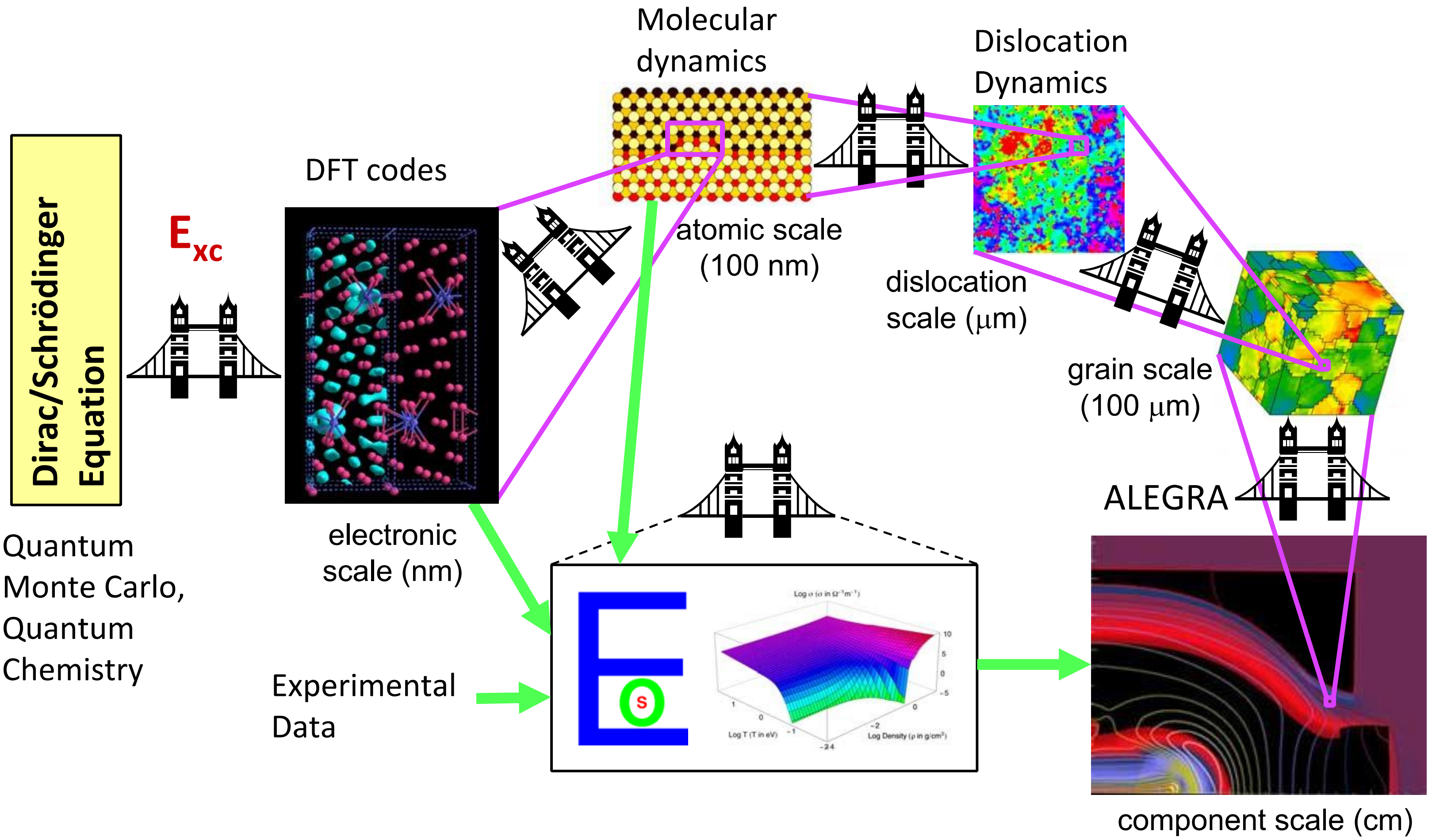


Dirac/Schrödinger Equation

E_{xc}

DFT codes

electronic scale (nm)

Molecular dynamics

atomic scale (100 nm)

Dislocation Dynamics

dislocation scale (μm)

grain scale (100 μm)

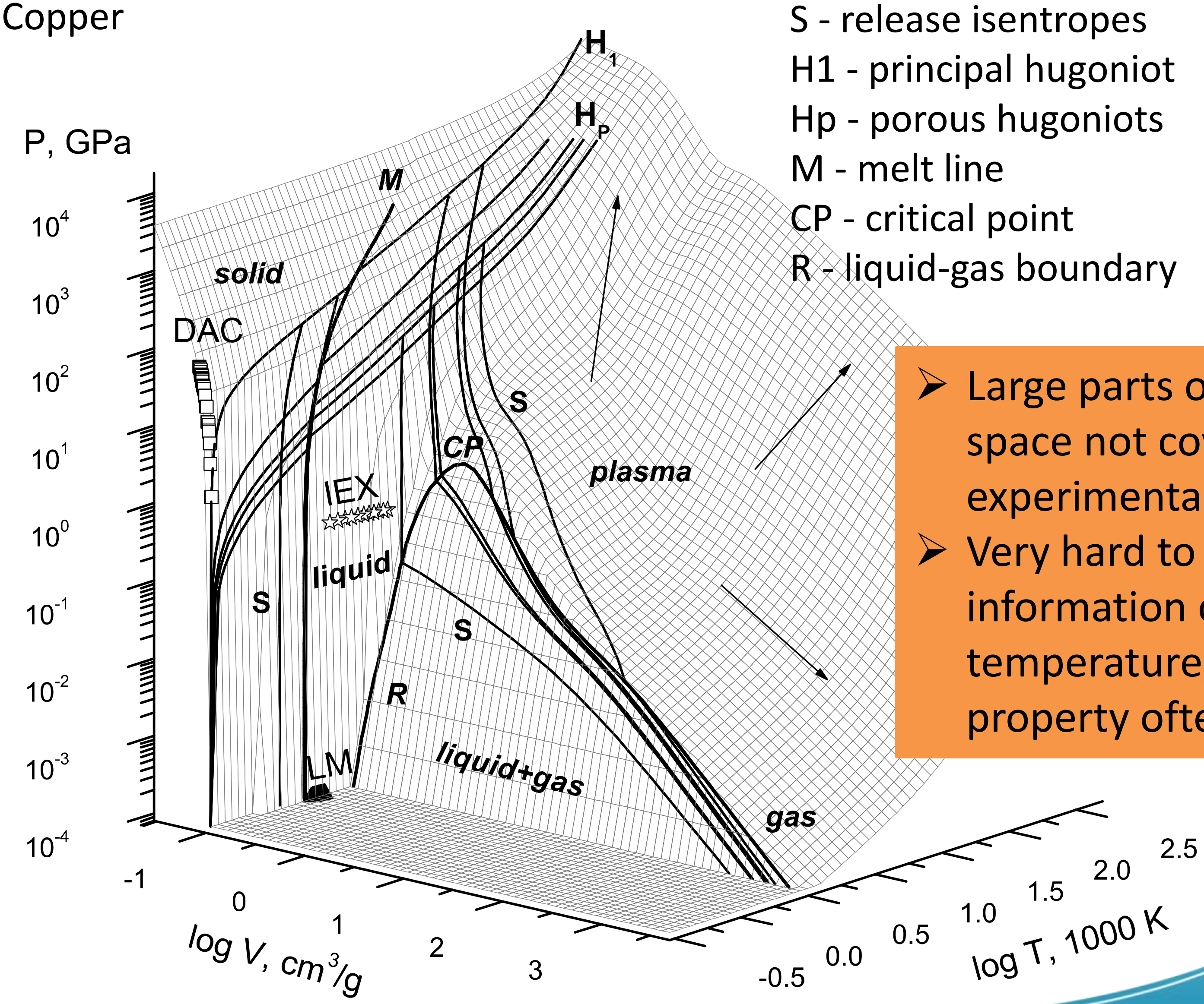
ALEGRA

component scale (cm)

Quantum Monte Carlo, Quantum Chemistry

Experimental Data

Equation of State: Example of Material input



DAC - diamond anvil cell measurements
IEX - isobaric expansion experiments
S - release isentropes
H1 - principal hugoniot
Hp - porous hugoniots
M - melt line
CP - critical point
R - liquid-gas boundary

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- Large parts of parameter space not covered by any experimental technique.
- Very hard to get information on temperature, this property often inferred.

Predictive DFT calculations for EOS construction: Example of Xe

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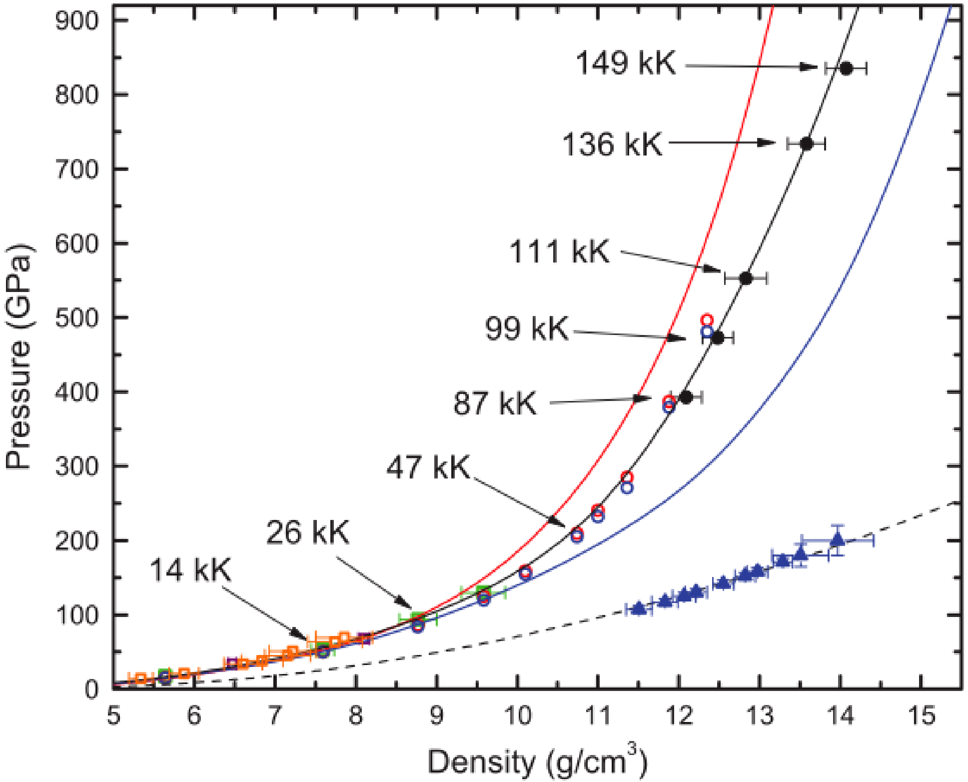

FIG. 3 (color). P-ρ Hugoniot plot. Lines and symbols as in Fig. 2. Black dashed line, 5191 298 K isotherm; blue triangles, solid xenon compression data [17]. Also indicated are Hugoniot temperatures calculated using 5191. Our DFT calculated isotherm [37] agrees with the experimental data [17].

Seth et al. PRL 105, 085501 (2010)

Red circle: LDA
Blue circle: AM05
Black circles: Z data
Black line: New EOS 5191
Blue line: SESAME 5190
Red line: LEOS 540

Note: DFT calculations published *before* Z data was available. Shown is the Hugoniot. DFT data is added also in other parts of phase space (e.g., cold curve and melt line).

Bridges between Fundamental Law of Nature and Engineering

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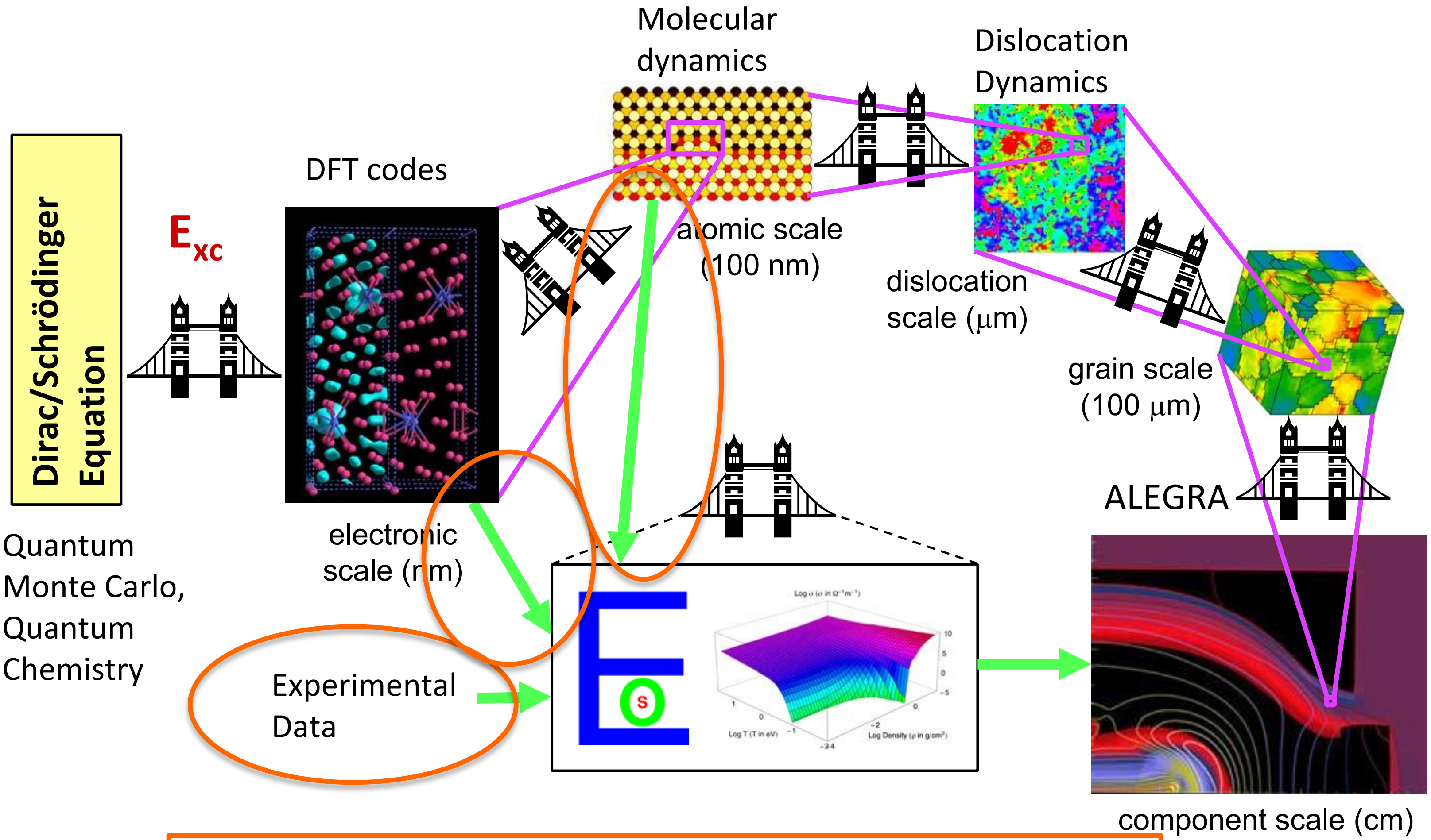

Dirac/Schrödinger Equation

E_{xc}

DFT codes

electronic scale (nm)

Quantum Monte Carlo, Quantum Chemistry

Experimental Data

Molecular dynamics

atomic scale (100 nm)

Dislocation Dynamics

dislocation scale (µm)

grain scale (100 µm)

ALEGRA

component scale (cm)

The ability to perform high-fidelity calculations is most important for cases where experiments are impossible, dangerous, and/or prohibitively expensive to perform.

Better ab initio methods for f-electron systems identified as a Basic Research Need

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Basic Research Needs for Advanced Nuclear Energy Systems

Report of the Basic Energy Sciences Workshop on Basic Research Needs for Advanced Nuclear Energy Systems

July 31– August 3, 2006

Scientific grand challenges:

- Resolving the f-electron challenge to master the chemistry and physics of actinides and actinide-bearing materials.
- Developing a first-principles, multiscale description of materials properties in complex materials under extreme conditions.
- Understanding and designing new molecular systems to gain unprecedented control of chemical selectivity during processing.

We want to be able to do DFT based calculations for all materials

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While DFT is very successful for many materials and many properties, not all materials and properties are equally well treated with DFT. This is the case with, for example, actinides.

We have two problems:

- High atomic numbers means relativistic effects.

- Localized *f*-electrons means DFT exchange-correlation functionals (including AM05) are not accurate enough.

Schrödinger based Kohn-Sham Equations

First: The Dirac/Schrödinger equation is <u>not a model</u>, but a fundamental law of nature.

$$\left[\frac{1}{2m}\left(\boldsymbol{p}-\frac{e\boldsymbol{A}_{\text{eff}}}{c}\right)^2-\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B}+V_{\text{eff}}(\boldsymbol{r})\right]\psi_{A,n}=E_n^{(\text{NR})}\psi_{A,n}$$

This is the non-relativistic limit of the Dirac equation. Spin-orbit coupling can be put in as a perturbation. Scalar relativistic treatment is also routinely included in DFT codes.

But for some properties of some materials, in particular actinides, this is not enough.

Note, however: Even if the use of non- or scalar-relativistic DFT for actinides is not as straightforward as for lower Z materials, useful results can still be obtained for some properties if insight from calculations is carefully paired with insights from other sources, such as experiments. BUT it is not PREDICTIVE.

Relativistic Kohn-Sham equations: Functionals

$$\left(c\,\boldsymbol{\alpha}\cdot\left(\boldsymbol{p}-\boxed{\frac{e\boldsymbol{A}_{\mathit{eff}}}{c}}\right)+\begin{pmatrix}I & 0\\ 0 & I\end{pmatrix}V_{\mathit{eff}}(\boldsymbol{r})+\beta\,mc^2\right)\psi_n(\boldsymbol{r})=E_n\,\psi_n(\boldsymbol{r})$$

$$\begin{aligned}
V_{\mathit{eff}}(\boldsymbol{r}) &= -e\left(A^0_{\mathit{ext}}(\boldsymbol{r})+\int d^3r'\,\frac{J^0(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+\frac{\delta E_{xc}[J^\mu]}{\delta J^0(\boldsymbol{r})}\right)\\
\boxed{e\boldsymbol{A}_{\mathit{eff}}(\boldsymbol{r})} &= -e\left(\boldsymbol{A}_{\mathit{ext}}(\boldsymbol{r})+\int d^3r'\,\frac{\boldsymbol{J}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+\frac{\delta E_{xc}[J^\mu]}{\delta \boldsymbol{J}(\boldsymbol{r})}\right)
\end{aligned}$$

$$J^\mu=(J^0,\boldsymbol{J})=-e\sum_{-mc^2<E_n<E_F}\left(\psi_n^\dagger\psi_n,\boxed{\psi_n^\dagger\boldsymbol{\alpha}\,\psi_n}\right)$$

But functionals available from non-relativistic Kohn-Sham theory use spin densities, not currents. The vector potential term is the tricky one, coupling upper and lower components.

From currents to spin densities

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Spin density:

$$\boldsymbol{S} = -\sum_{-mc^2<E_n<E_F} \psi_n^\dagger \beta \boldsymbol{\Sigma} \psi_n \qquad \Sigma_k = \begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix}$$

Gordon decomposition

$$\boldsymbol{J} = \boldsymbol{I} + \mu_B \nabla \times \boldsymbol{S}$$

$$\boldsymbol{I} = \frac{e}{2mc} \sum_{-mc^2<E_n<E_F} \left\{ \psi_n^\dagger \beta \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\mathit{eff}}}{c} \right) \psi_n \right] + \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\mathit{eff}}}{c} \right) \psi_n \right]^\dagger \beta \psi_n \right\}$$

Orbital current: Neglecting this gives…

Approximate Dirac for spin density functionals

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$$\left(c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \mu_B\,\beta\,\boldsymbol{\Sigma}\cdot\boldsymbol{B}_{\mathit{eff}} + \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} V_{\mathit{eff}}(\boldsymbol{r}) + \beta\,mc^2 \right) \psi_n(\boldsymbol{r}) = E_n\,\psi_n(\boldsymbol{r})$$

$$\begin{aligned} V_{\mathit{eff}}(\boldsymbol{r}) &= -e\left(A^0_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{J^0(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^\mu]}{\delta J^0(\boldsymbol{r})} \right) \\ \mu_B\boldsymbol{B}_{\mathit{eff}}(\boldsymbol{r}) &= \left(\mu_B\boldsymbol{B}_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{\boldsymbol{M}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^0,\boldsymbol{M}]}{\delta \boldsymbol{M}(\boldsymbol{r})} \right) \end{aligned}$$

$$\boldsymbol{M} = \mu_B\boldsymbol{S}$$

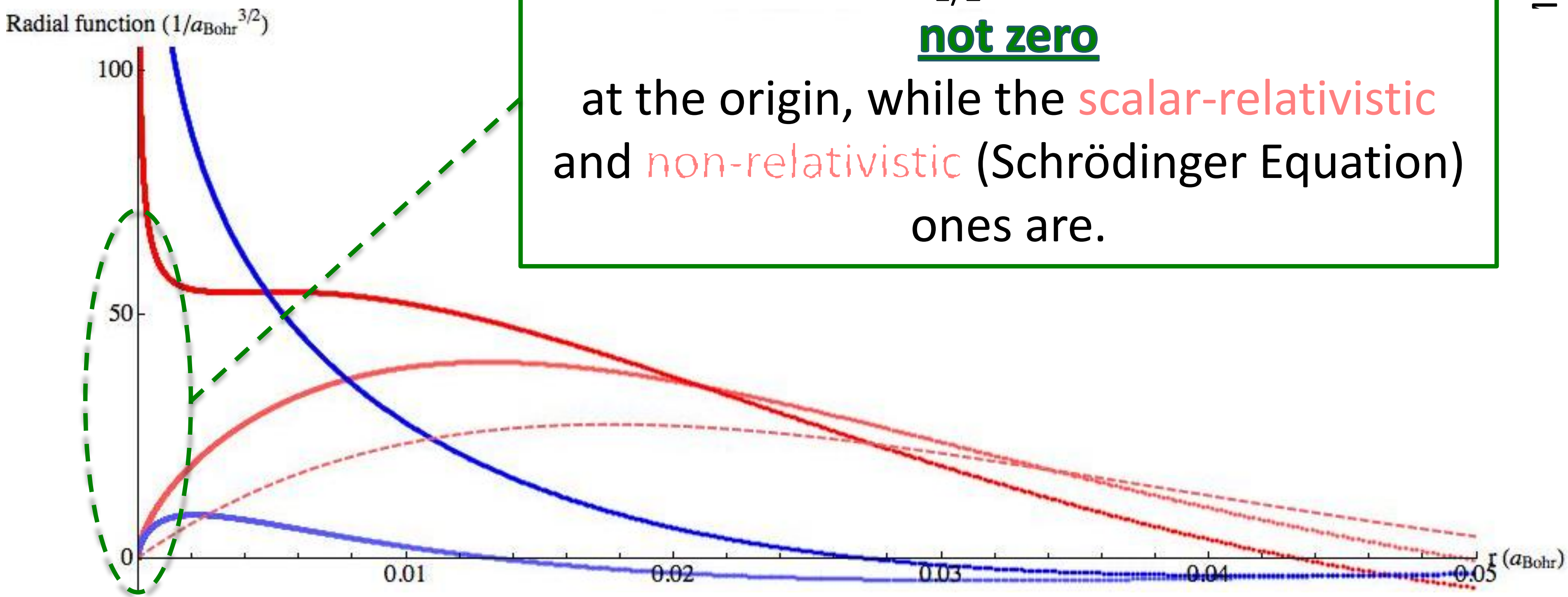
Now ordinary DFT spin functionals can be used.

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

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

not zero

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



Conclusion: We need to use a DFT method based on the Dirac Equation. This has been implemented into the RSPt code and we are just now testing what this gives as results.

Probing different relativistic treatments in Au: Setting the stage

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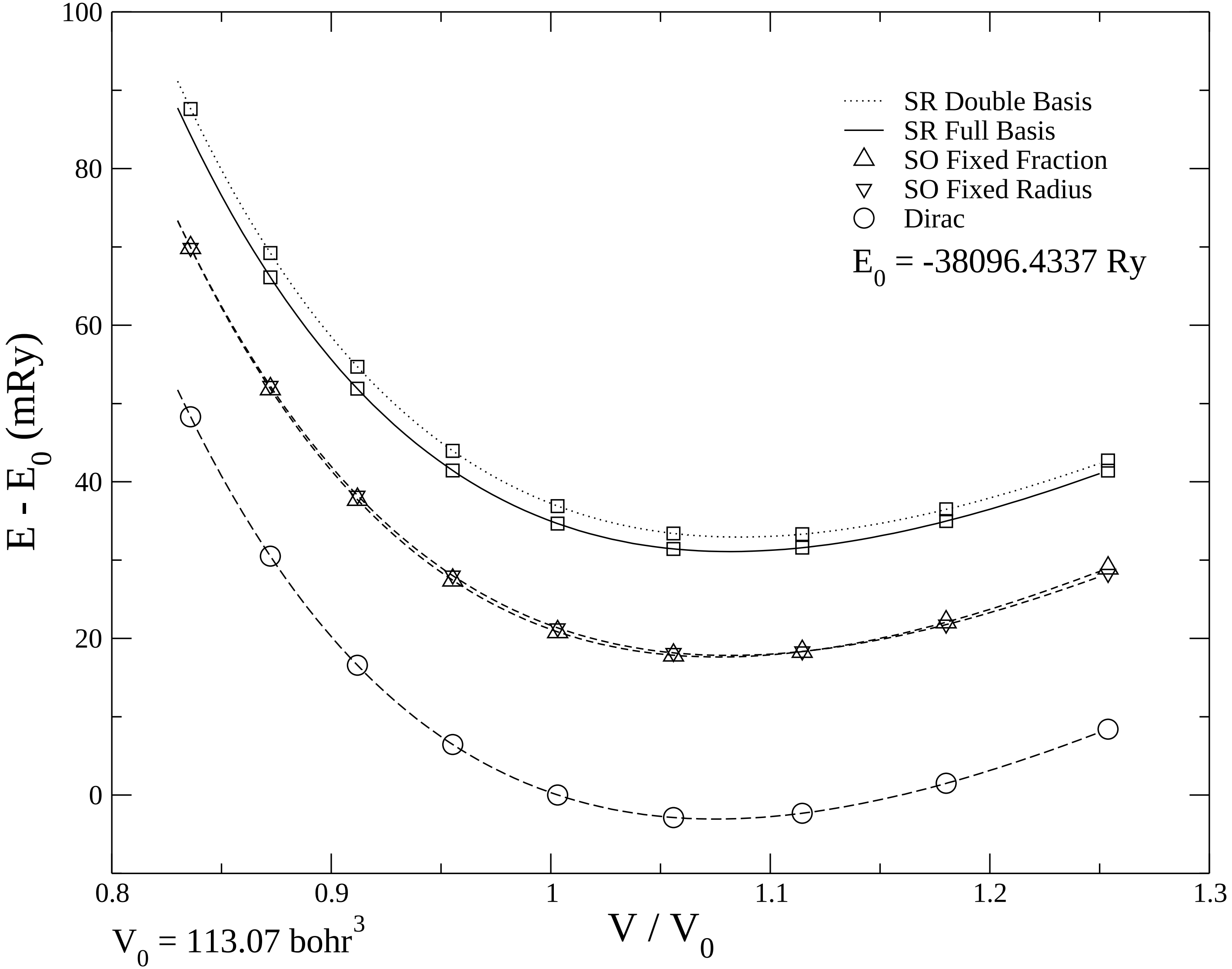
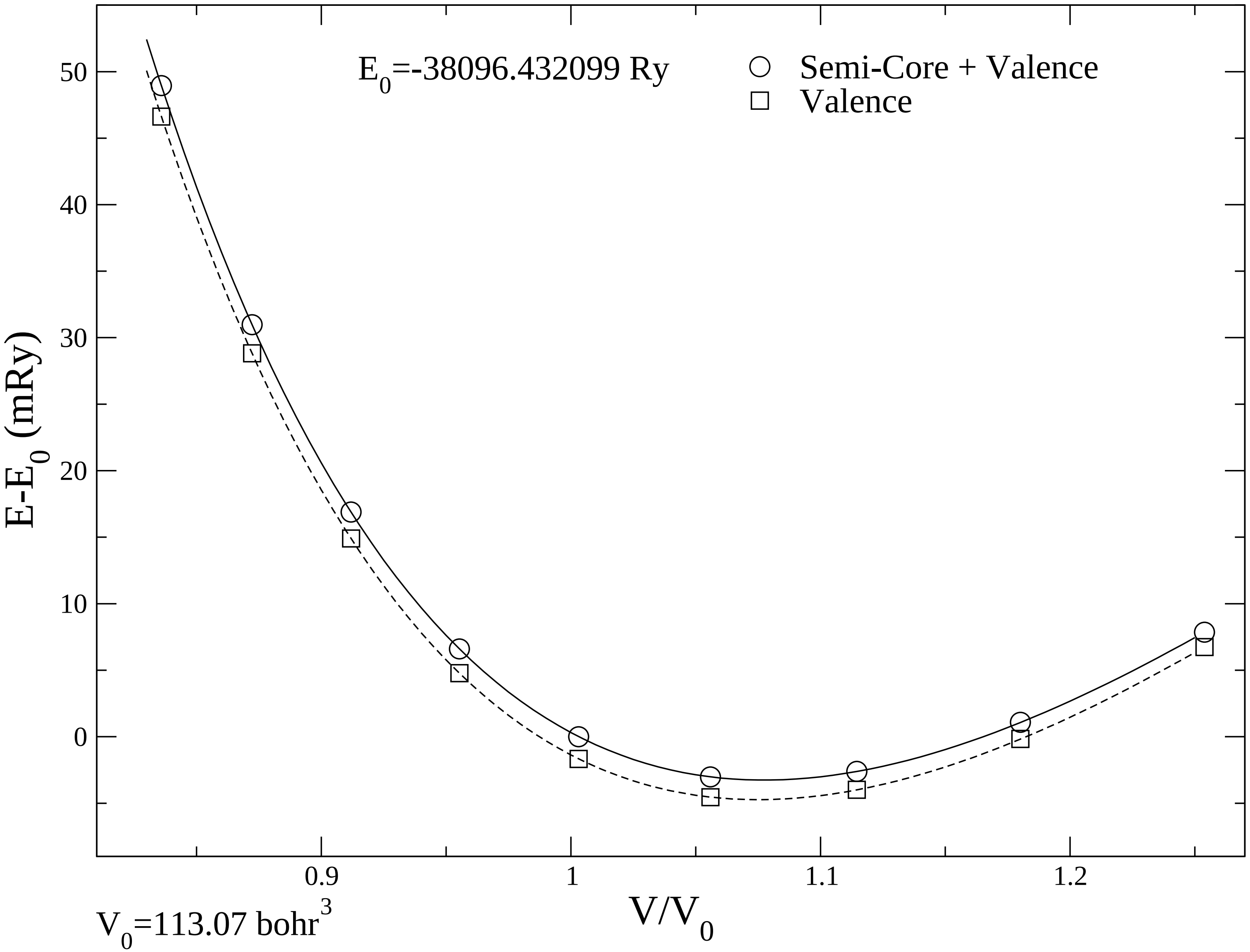


The spin-orbit coupling among the bonding valence electrons (10 5d and 1 6s) is small, but not insignificant.

All Au electrons treated with the Dirac equation: Semi-Core (5p) and Valence



V_0=113.07 bohr^3

The 5p electrons are well separated from the rest of the valence and can be treated in the core (with no interaction with the rest of the valence).

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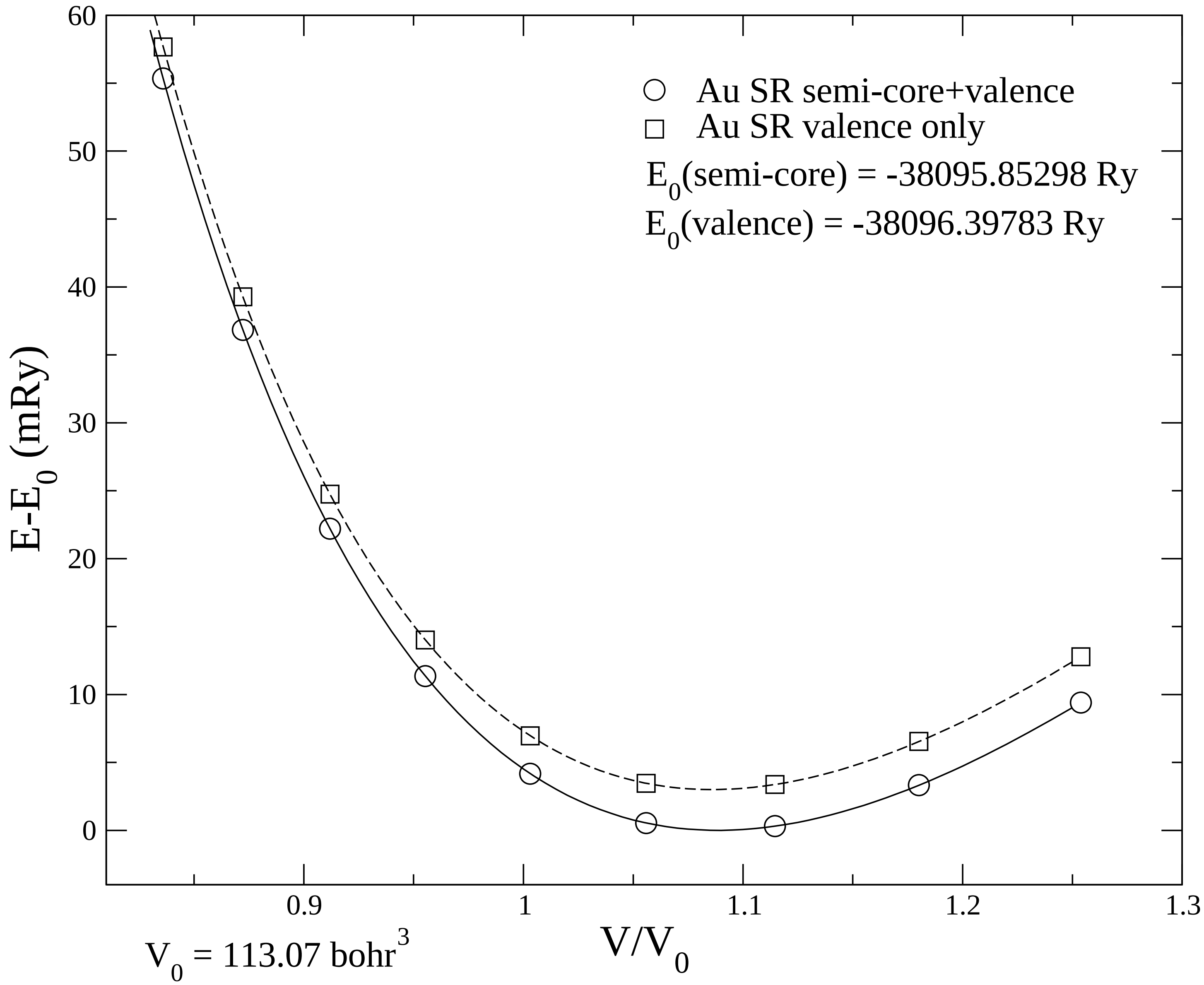
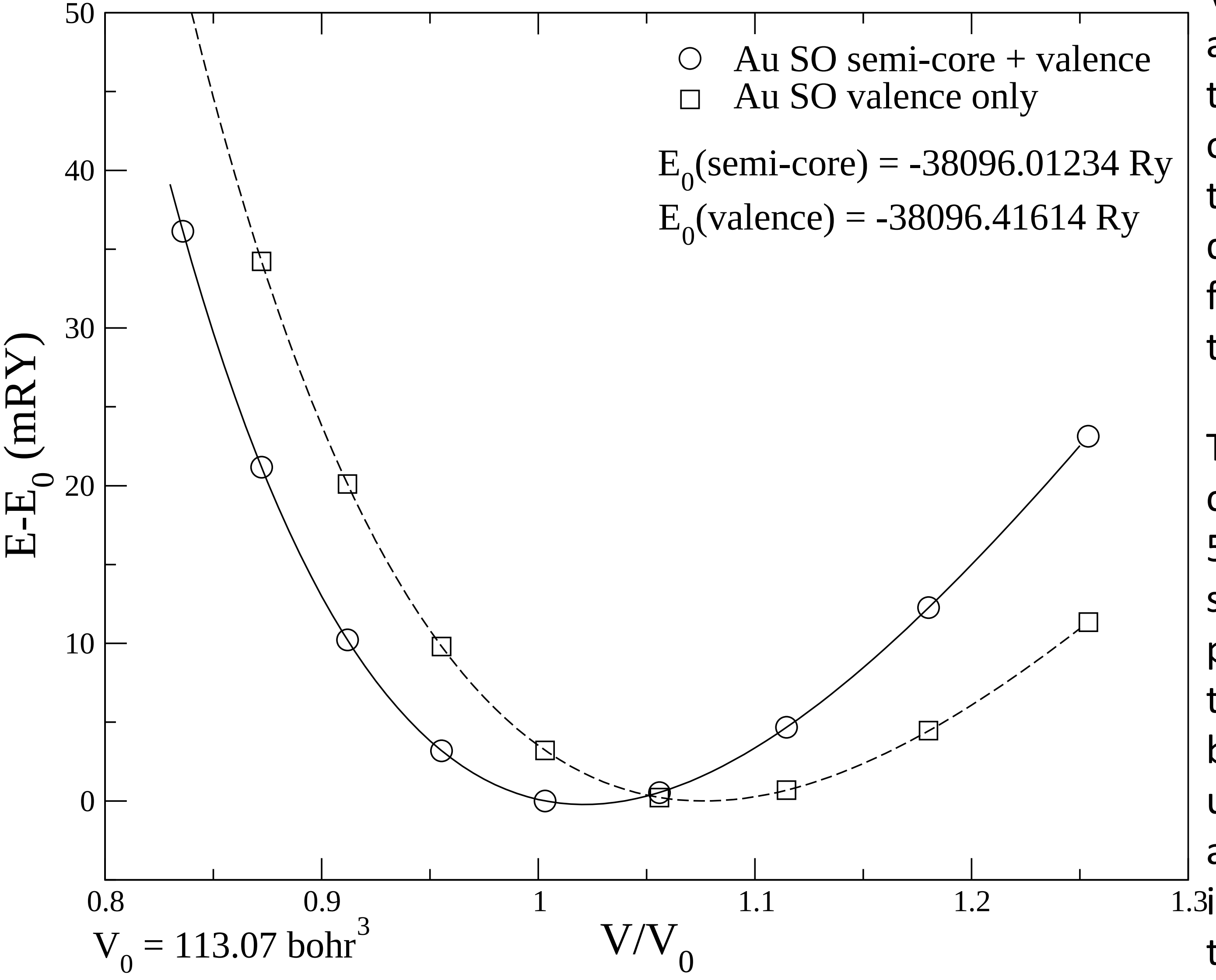
Au 5p treated with Dirac vs Scalar relativistic



Since the non-bonding 5p semi-core electrons do not participate in the binding as the rest of the valence, treating them scalar relativistically gives the same error for all volumes.

Au 5p: Dirac vs variational spin-orbit coupling



Variationally adding a relativistic treatment (spin-orbit coupling) to the 5p electrons does not mimic the full Dirac treatment.

The spin-orbit coupling among the 5p electrons is strong, not a small perturbation, and the erroneous behavior of the unperturbed basis at the nuclei results in an invalid treatment.

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Consequences for heavy elements

Relativistic effects need to be incorporated via the Dirac equation.

When relativistic semi-core electrons are participating in the bonding, and thus need to be treated in the valence, there is no way around using the Dirac equation.

Adding Dirac p local orbitals to a scalar relativistic calculation, as done in some codes, might work but needs to be validated.

Simply removing the spin-orbit coupling on the 5p’s, as is done in some other codes, is risky.

We can validate different treatments against Dirac results with the RSPt code.

Note: A cancellation of error in the variational spin-orbit coupling calculation makes the PBE functional give ‘the right result’.

Which leads us into the next topic:

Confinement physics

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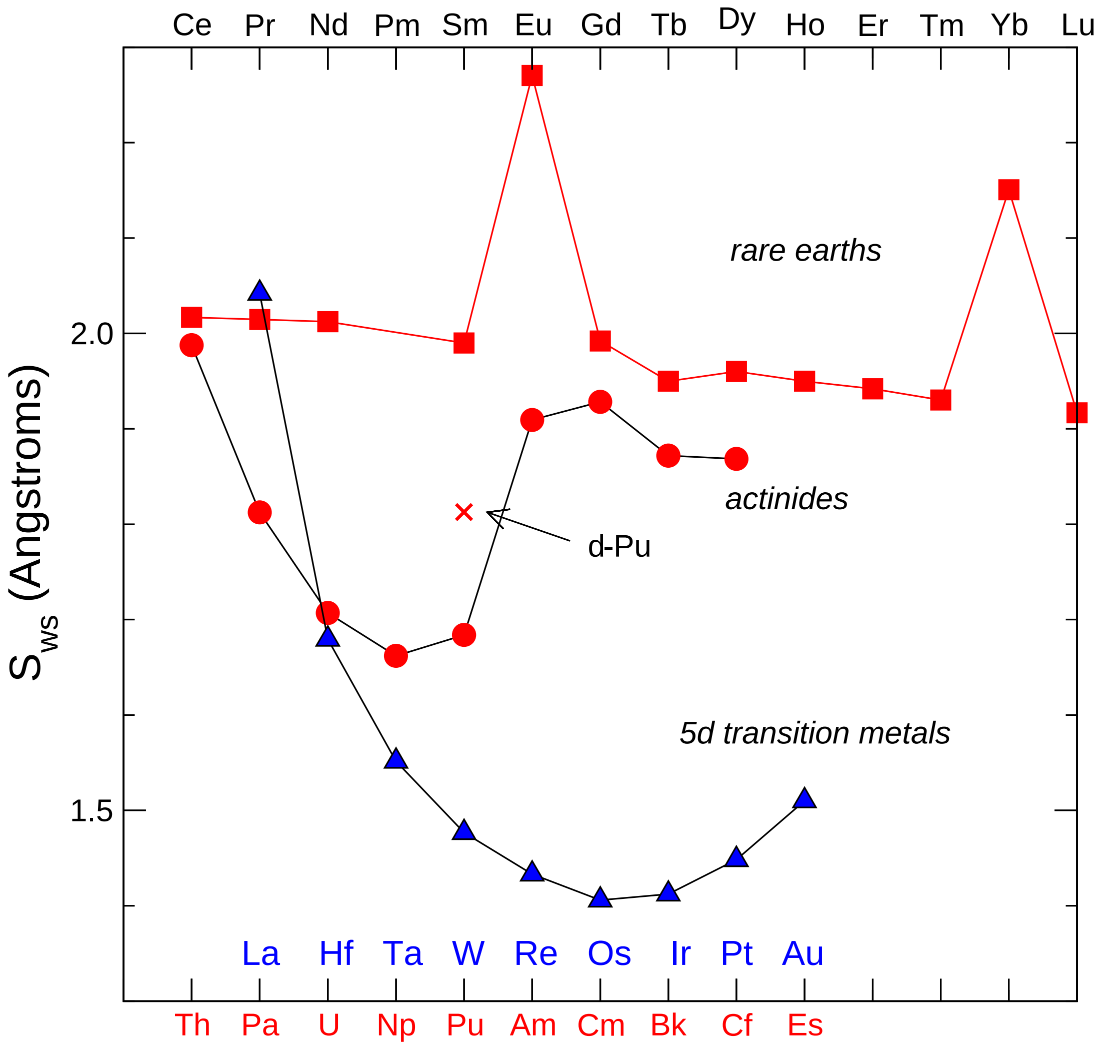
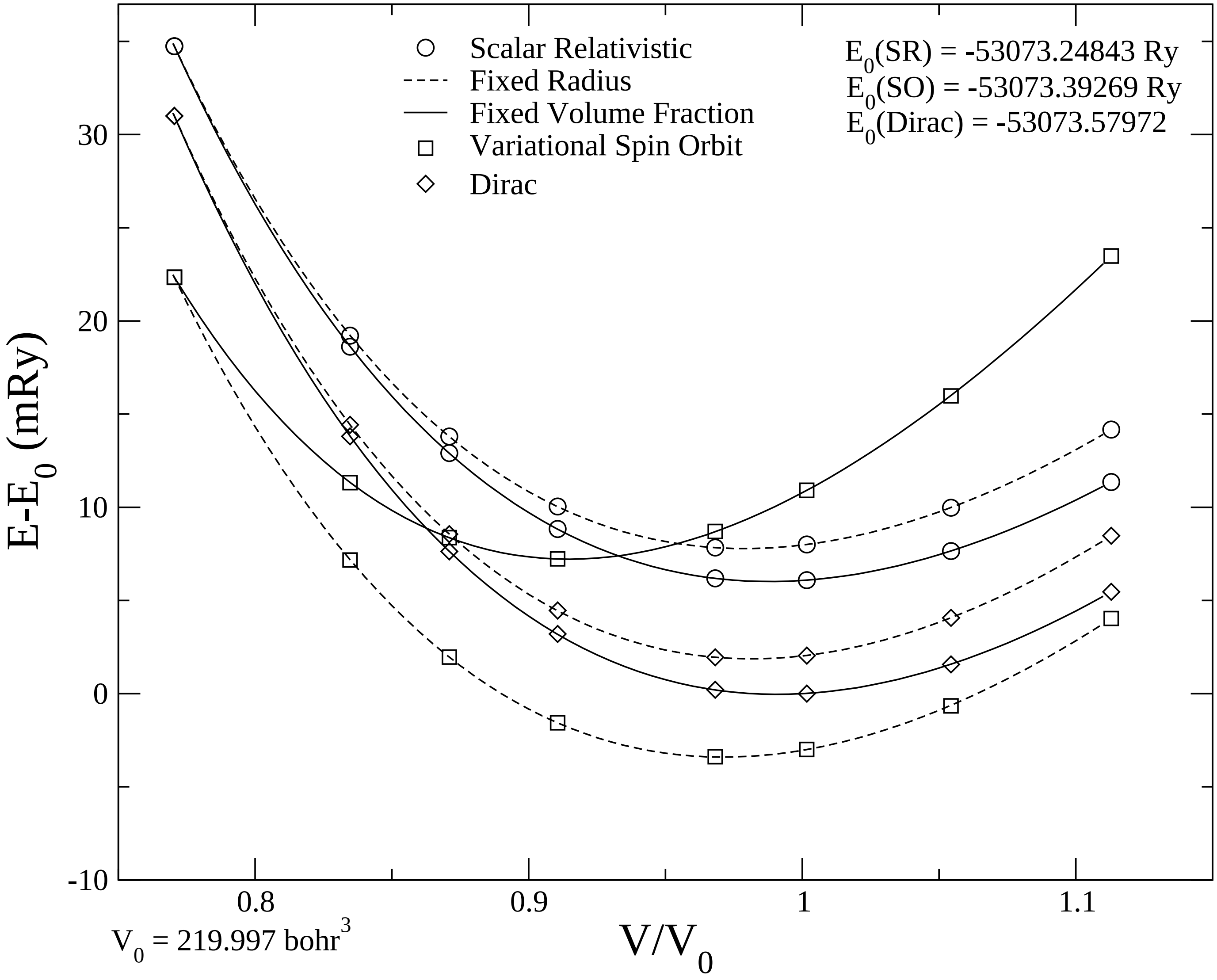


J M Wills and Olle Eriksson, Phys. Rev. B 45, 13879 (1992)

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.

Thorium PBE results



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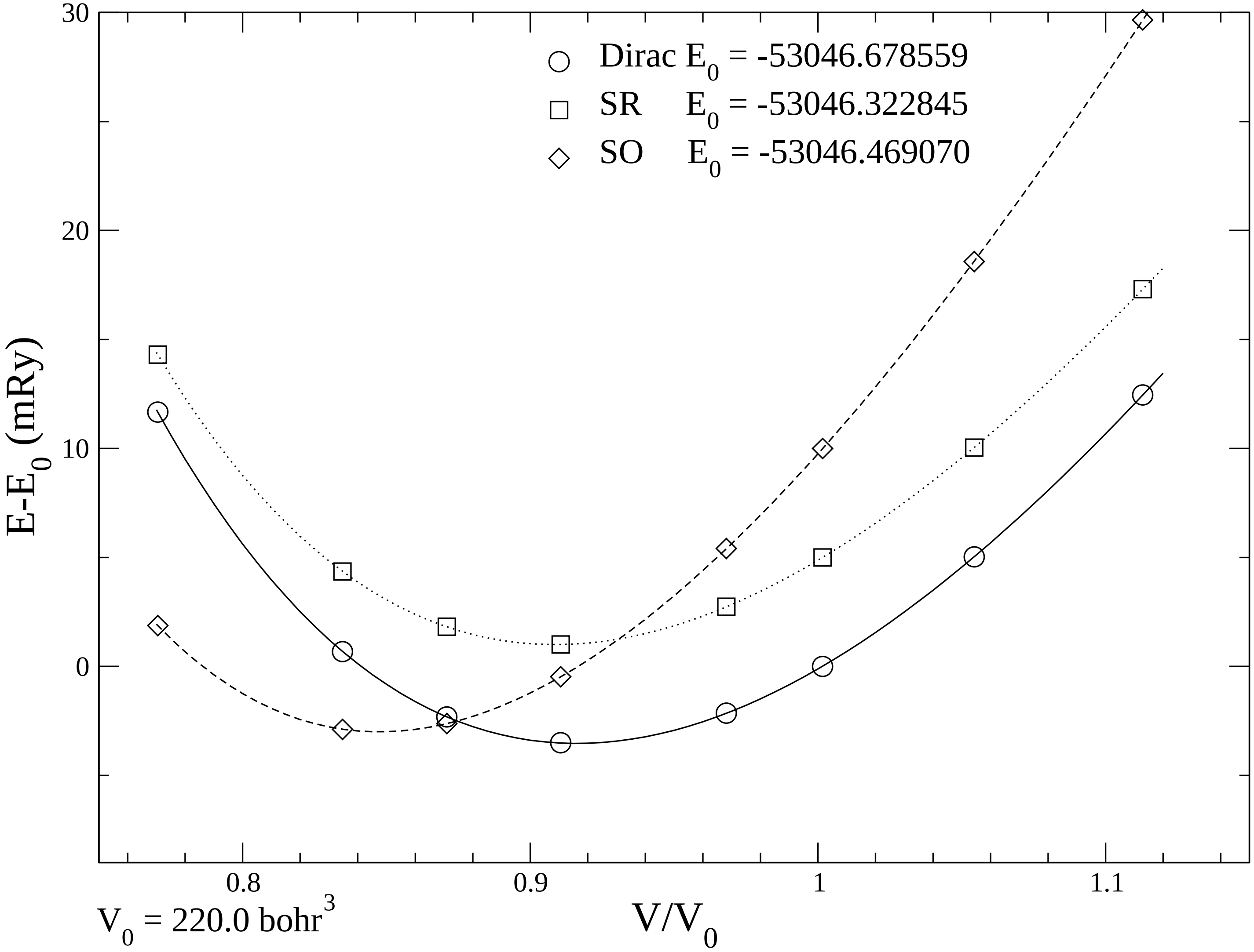
Thorium LDA-PW results



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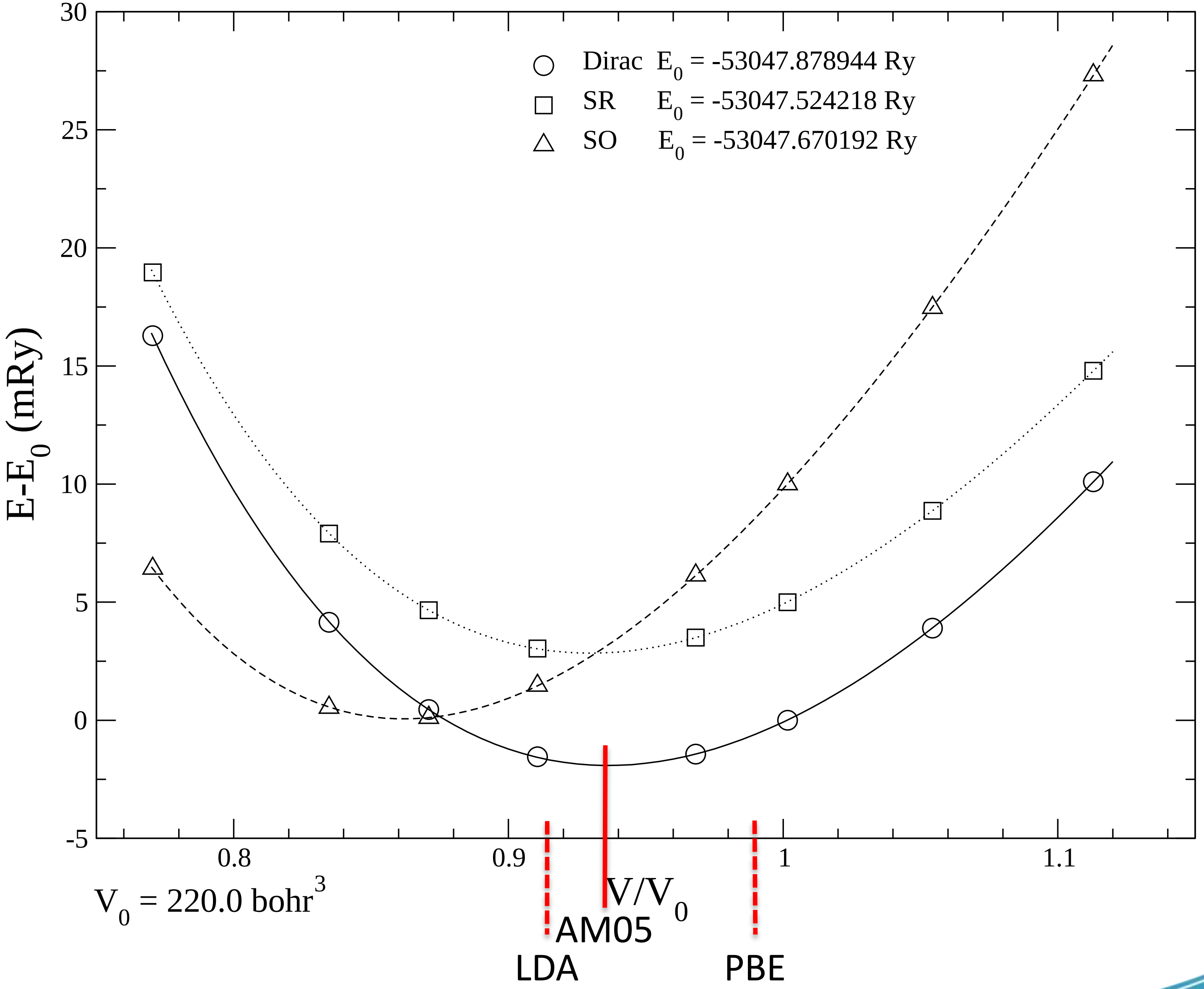
Thorium AM05 results



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Summary Thorium

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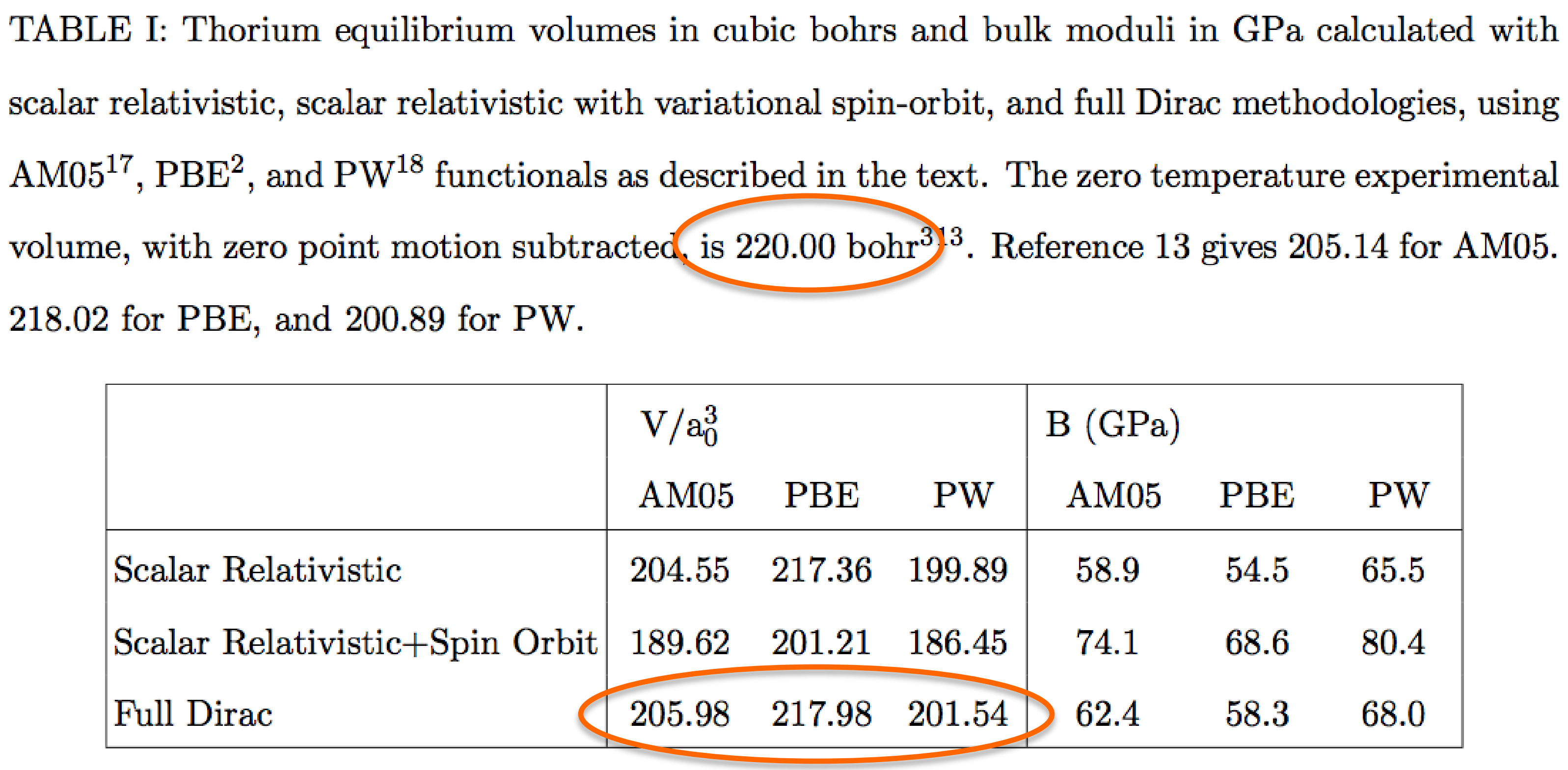


TABLE I: Thorium equilibrium volumes in cubic bohrs and bulk moduli in GPa calculated with scalar relativistic, scalar relativistic with variational spin-orbit, and full Dirac methodologies, using AM05^{17}, PBE^{2}, and PW^{18} functionals as described in the text. The zero temperature experimental 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).

HO model: Localized electron levels in a continuum.

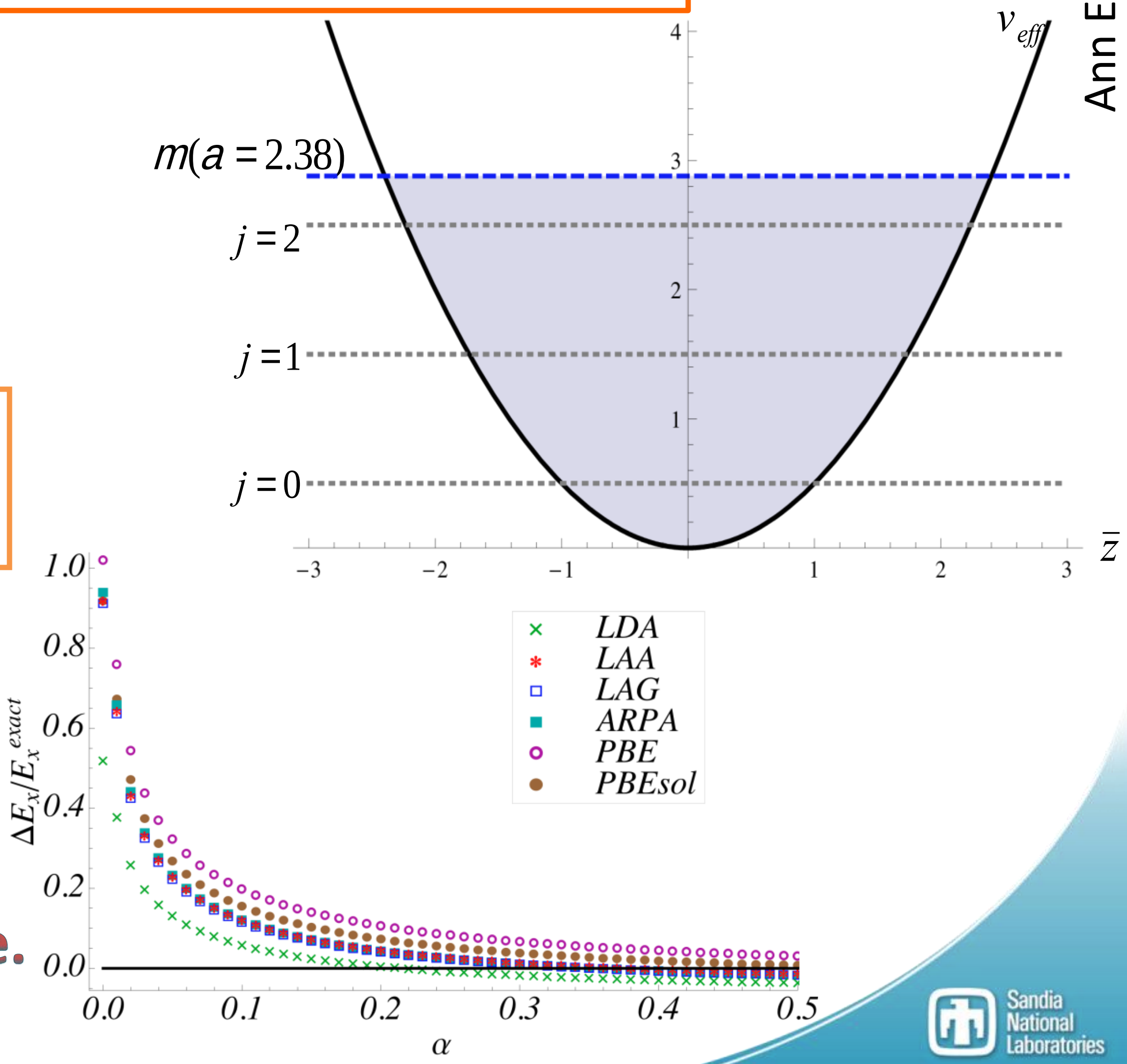
Energy of subbands $e_j = (j + \frac{1}{2})\frac{1}{l^2}$

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.

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

As α decreases, the confinement errors increase.



Electron localization function (ELF)

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

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

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

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

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.

ELF ≈ 1/2: uniform electron gas like
ELF ≈ 1: strong localization

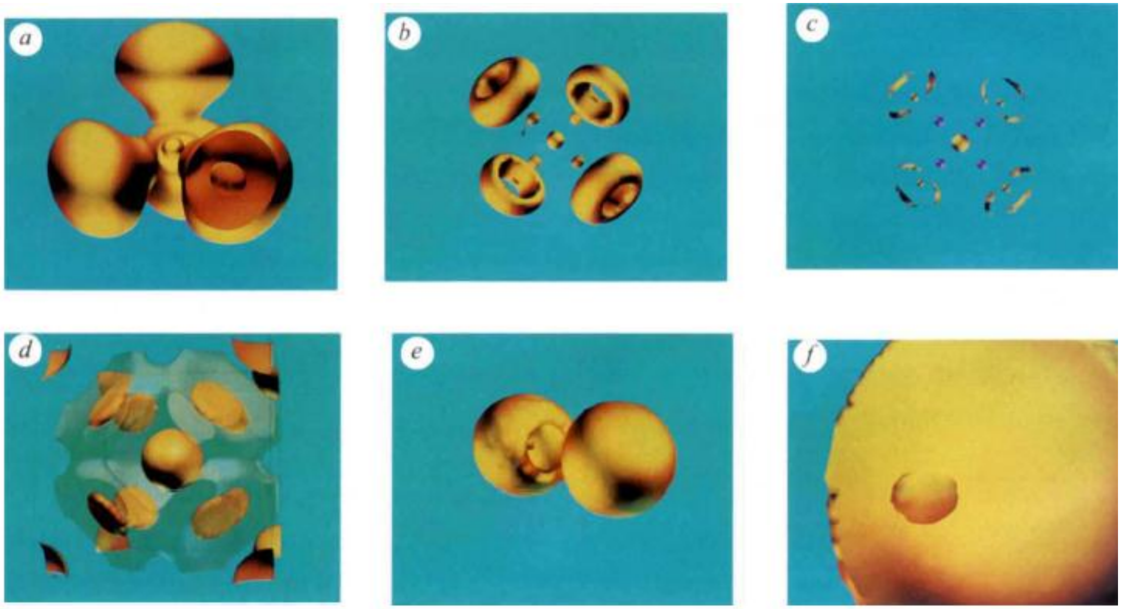


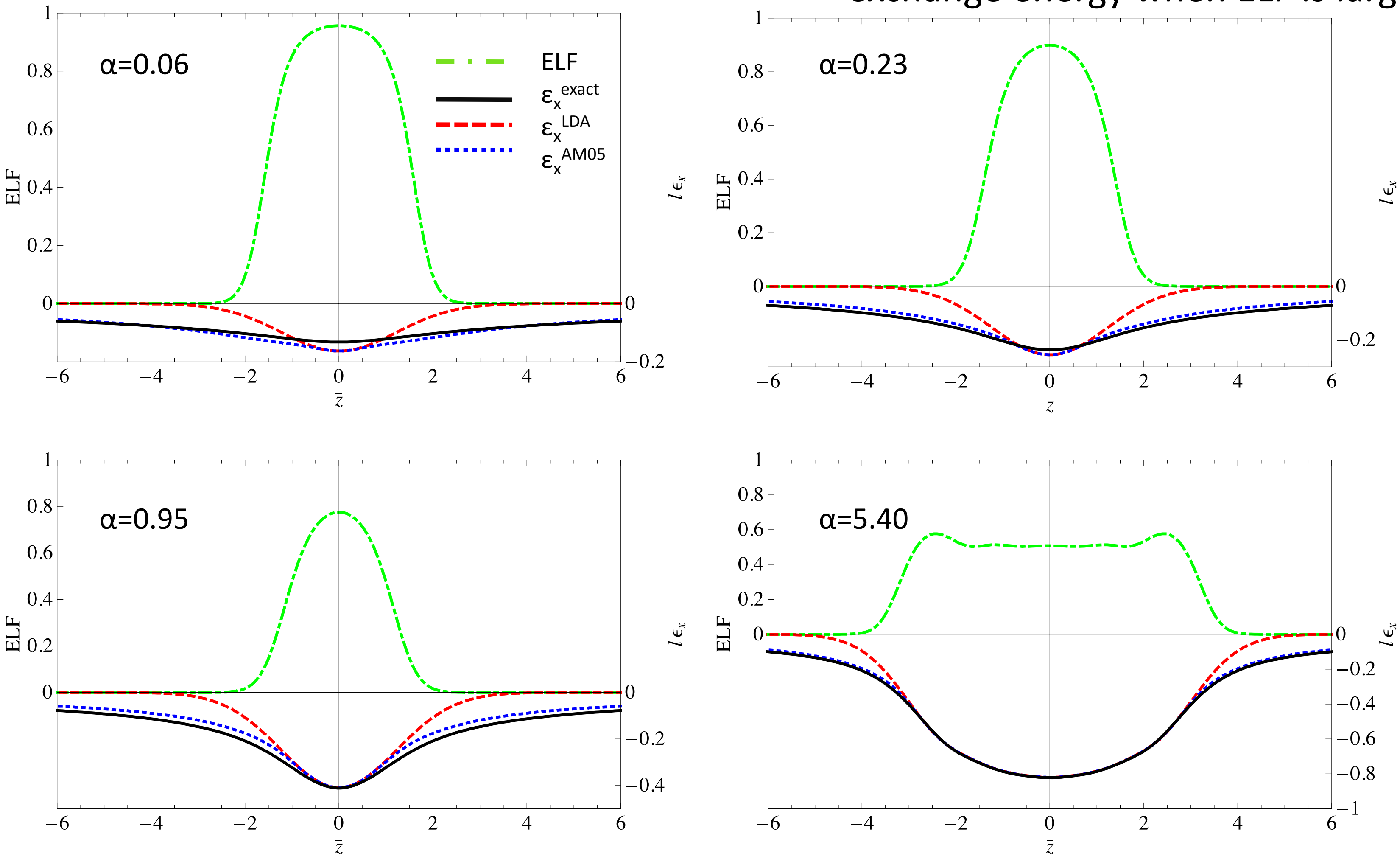
FIG. 1 Localization domains of CF_4 (*a*–*c*), Li (*d*), LiF (*e*) and LiH (*f*). *a*–*c*, Reduction of the localization domains of CF_4. Below ELF = 0.37 (where ELF is the localization function; see text) there are six localization domains: five core and one valence. The bifurcation at ELF = 0.37 splits the common valence domain into four atomic ones. The ELF = 0.75 map (*a*) shows the carbon core surrounded by the four fluorine valence domains; the front cutting plane has been chosen so that a fluorine core domain can be seen. The bonding attractors are responsible for the bulges towards the carbon centre. A further bifurcation occurs at ELF = 0.78, giving rise to bonding point attractors and non-bonding ring attractor domains as shown in *b* (ELF = 0.85). Each ring is itself resolved into three non-bonding point attractors for ELF > 0.883. In *c*, the bonding attractors at which ELF = 0.879 are represented by purple spheres because the bounding isosurface 0.885 only encapsulates the core and non-bonding attractors. b.c.c. lithium: the core and bonding attractors are located at the 8*a* (centre and vertices of the cubic lattice) and 8*c* (midpoints between the centre and the vertices) positions respectively. Their domains are bounded by the ELF = 0.625 isosurfaces, and the ELF = 0.575 isosurface forms a network of channels connecting the bonding attractors. These bonding attractors are unsaturated because there are eight per cell sharing two valence electrons. For LiF *e*, the localization domains shown are bounded by the ELF = 0.84 isosurface. The fluorine valence domain (which is almost spherical at lower ELF values) shows a hole in front of the lithium core; increasing the threshold leads to a single attractor lying on the internuclear axis on the side of the fluorine core that is away from the lithium. The ELF = 0.999 isosurfaces of LiH (*f*) encapsulate, on the one hand, the lithium core and, on the other hand, a very large area which extends, in principle, to infinity. The calculation of the grid points has been limited to a box of dimensions 7 × 7 × a.u., therefore only one face of the largest domain can be seen. The roughness of the surface is due to interpolation limitations and a density cutoff.

B. Silvi and A. Savin, Nature **371**, 683 (1994)

Confinement error and ELF

HO systems:

Note, all functionals give too negative exchange energy when ELF is large.



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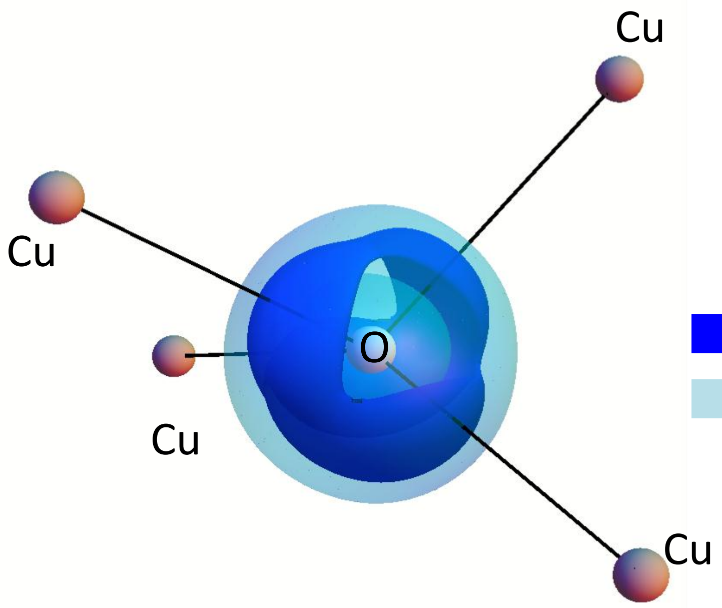
ELF is correlated with the confinement errors!

ELF in a ‘real’ system: CuO

ELF ≈ 1/2: uniform electron gas like
ELF ≈ 1: strong localization



🟦 ELF > 0.83
▭ ELF > 0.77

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

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

Experimental structure of CuO

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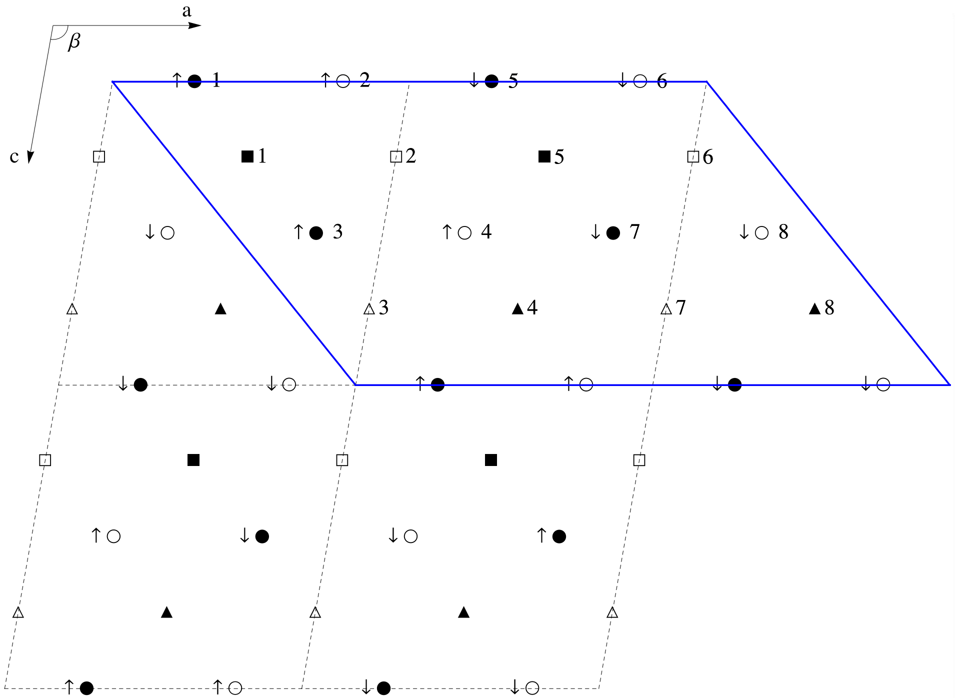
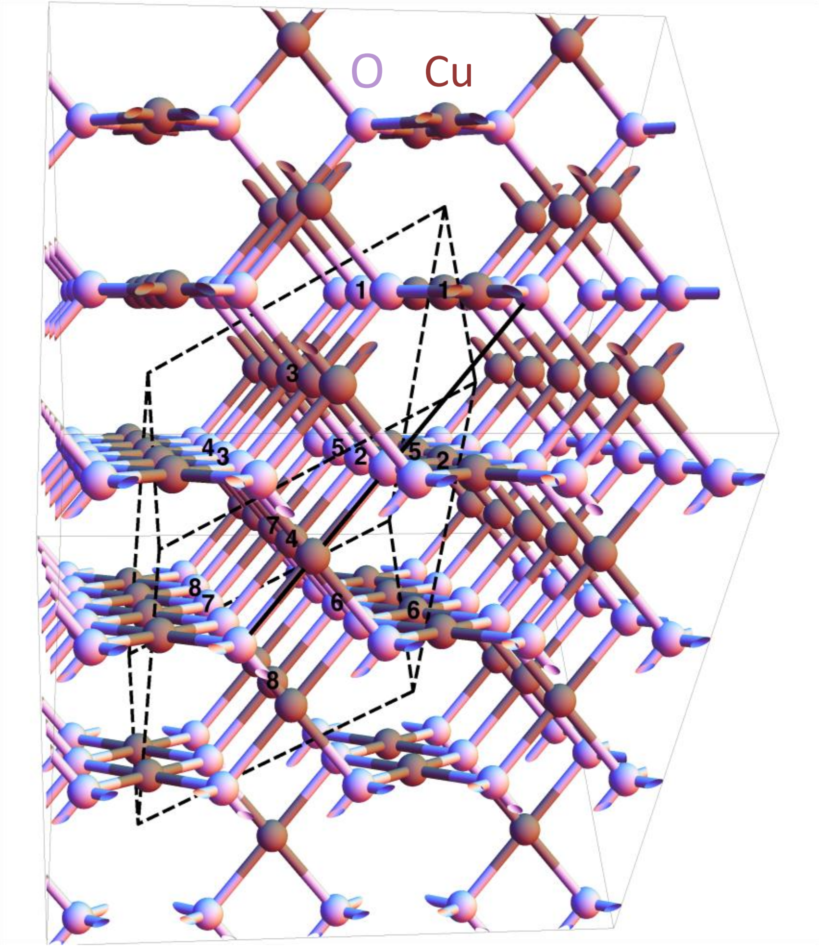


● Cu y = 1/4
○ Cu y = 3/4
■ O y = 1/2+u
□ O y = u
▲ O y = 1/2−u
△ O y = 1−u
↑↓ spins

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

DFT calculations of CuO structure

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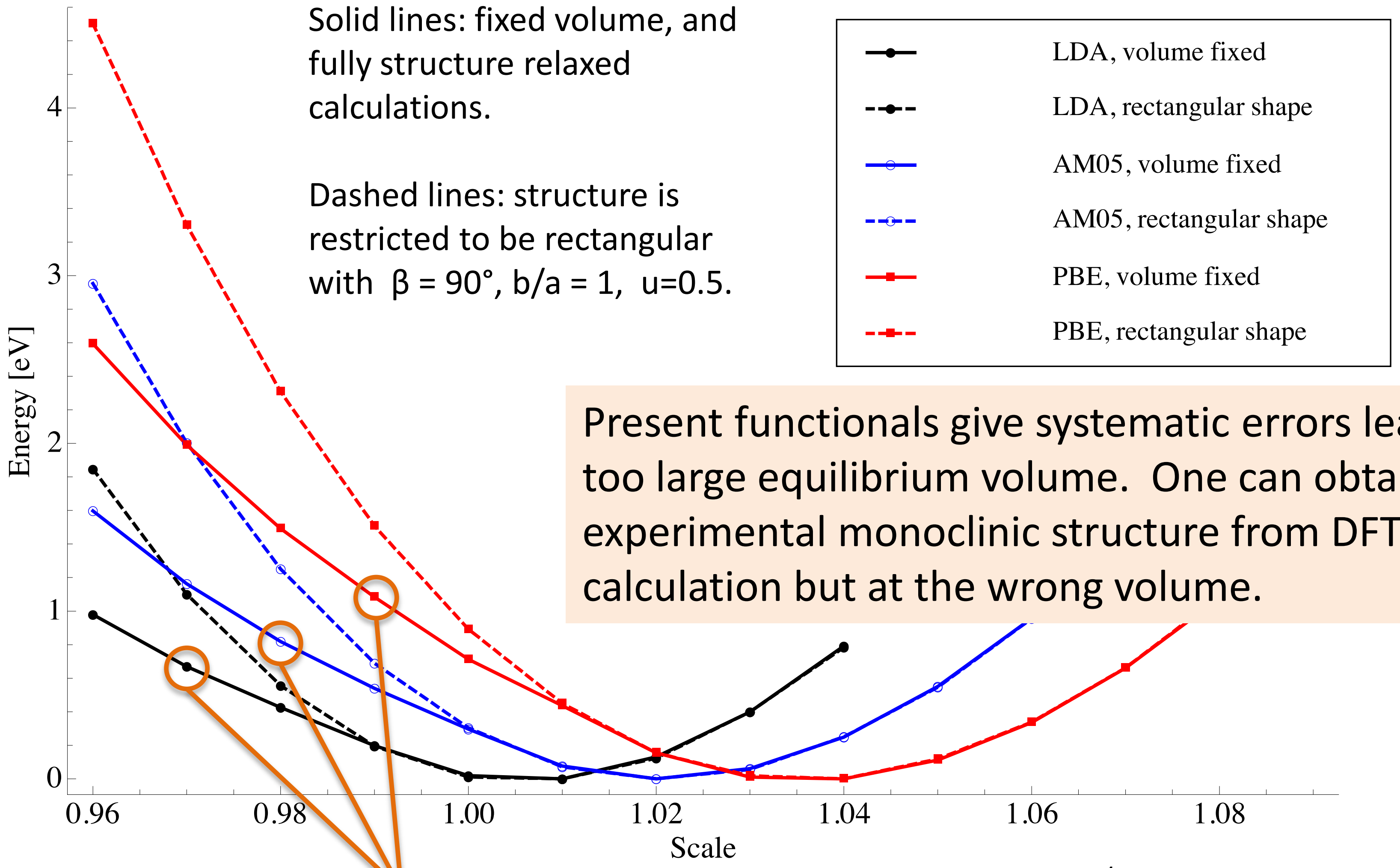

Solid lines: fixed volume, and fully structure relaxed calculations.

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. 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

Confinement error correction scheme

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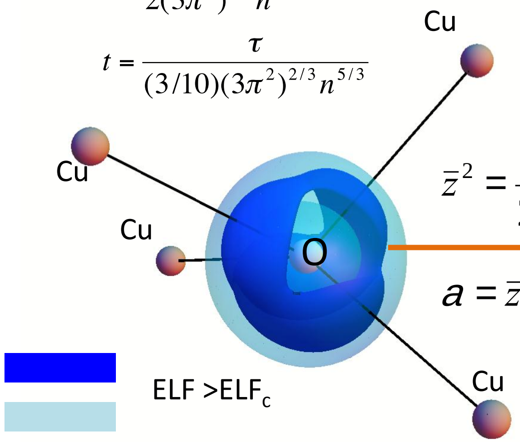
$$s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$$

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

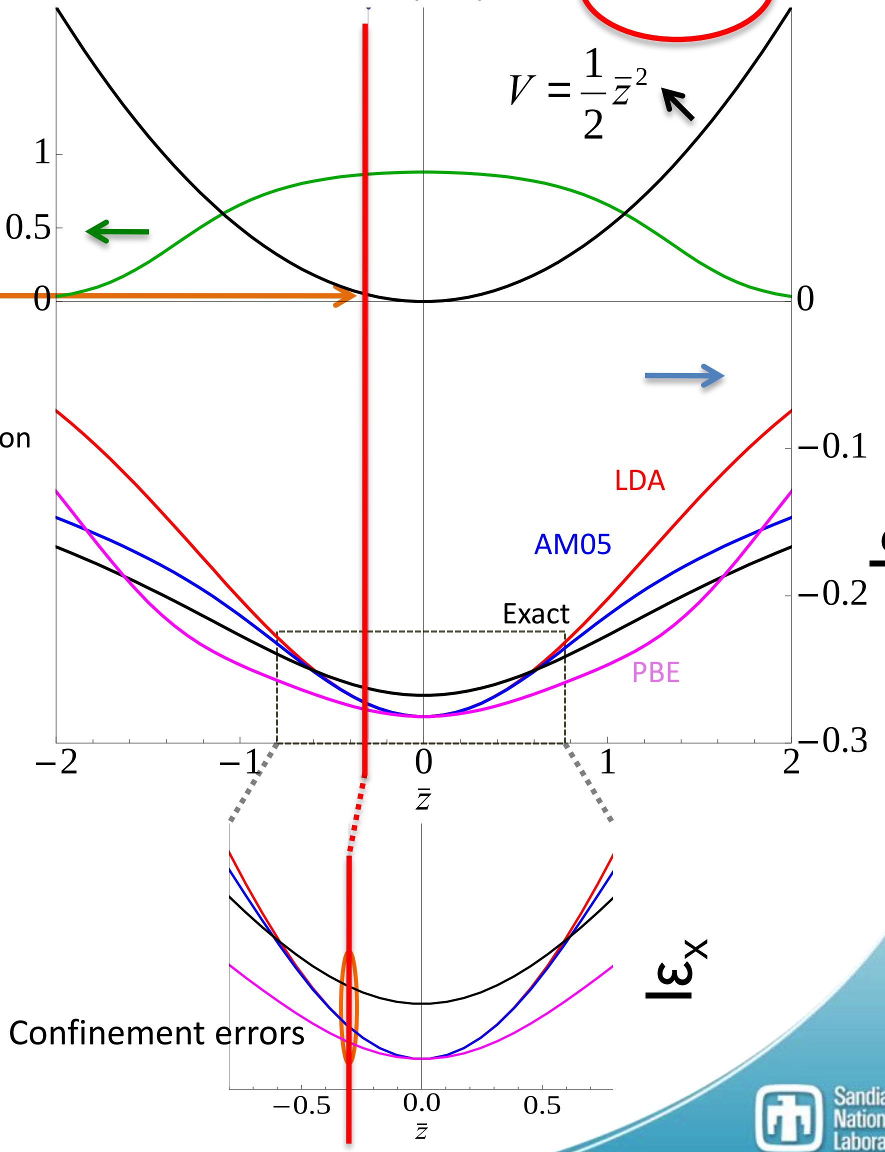


$$\bar z^2 = \frac{1}{2} W\left[18\pi\left(\frac{3}{5}t - s^2\right)^2 s^2\right]$$

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

W(x) is the Lambert W function

Harmonic Oscillator (HO) model α=0.31



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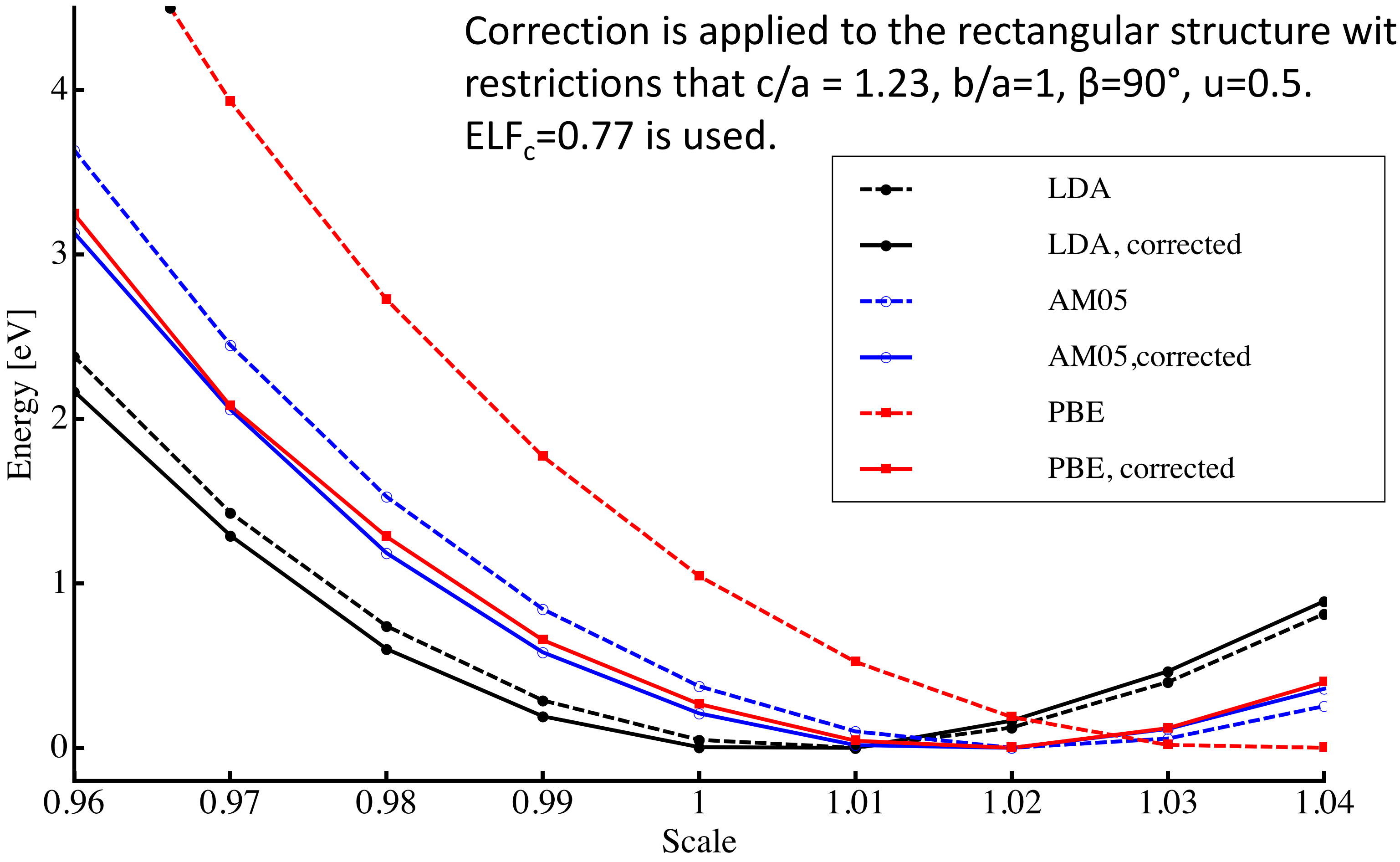
Correction is applied to the rectangular structure with restrictions that c/a = 1.23, b/a=1, β=90°, u=0.5. ELF_c=0.77 is used.



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.

Self consistency needed for, for example, Si

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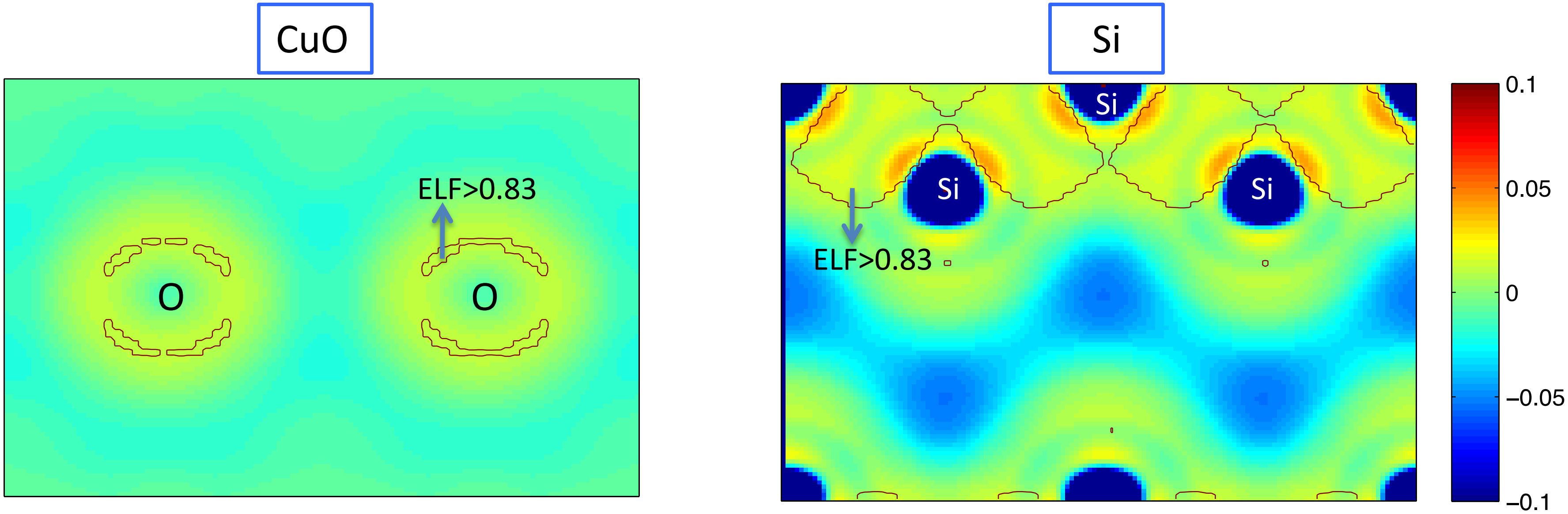
Relative density difference between PBE and LDA calculation:

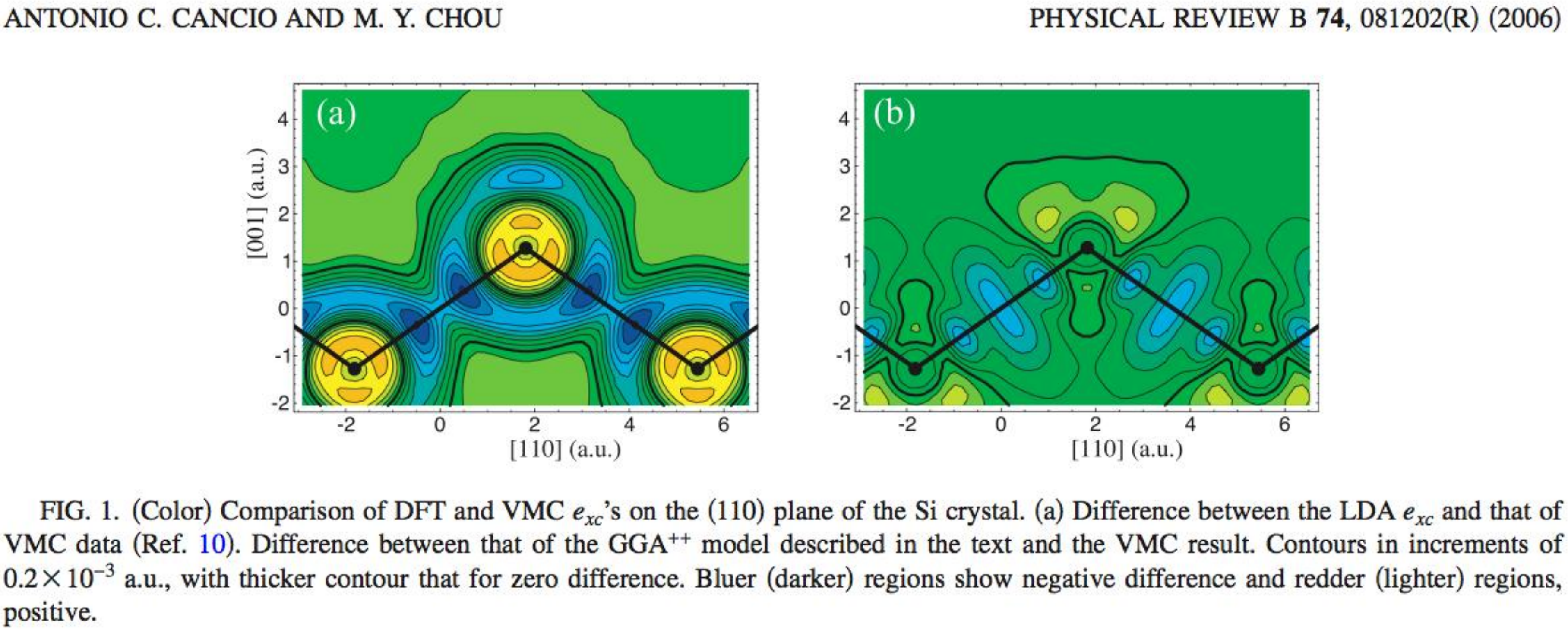
$(n^{PBE}-n^{LDA})/n^{LDA}$



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

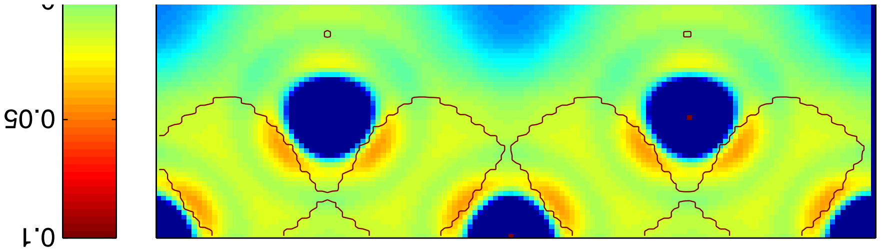
The confinement errors have to be treated <u>self-consistently</u> for Si.

Si from QMC



ANTONIO C. CANCIO AND M. Y. CHOU PHYSICAL REVIEW B **74**, 081202(R) (2006)

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

lattsson

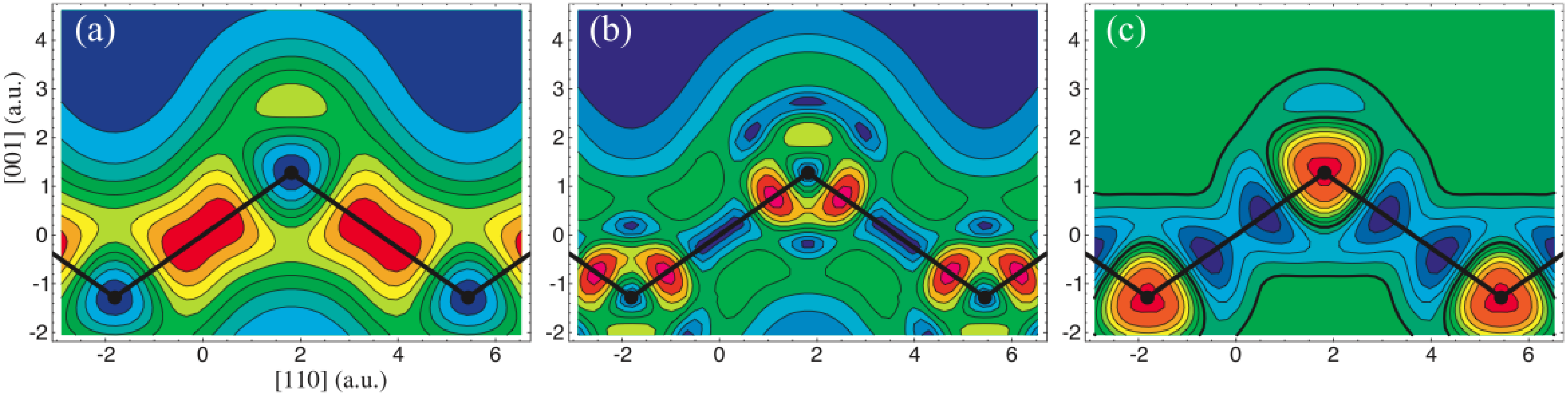
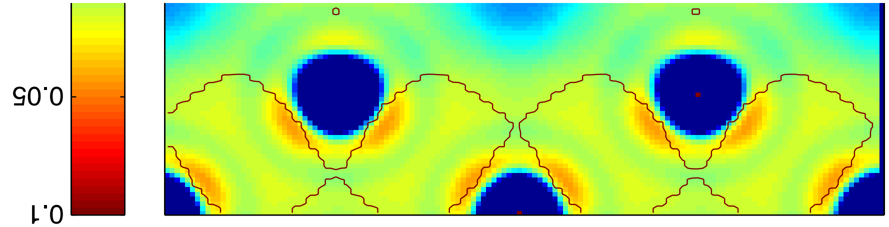
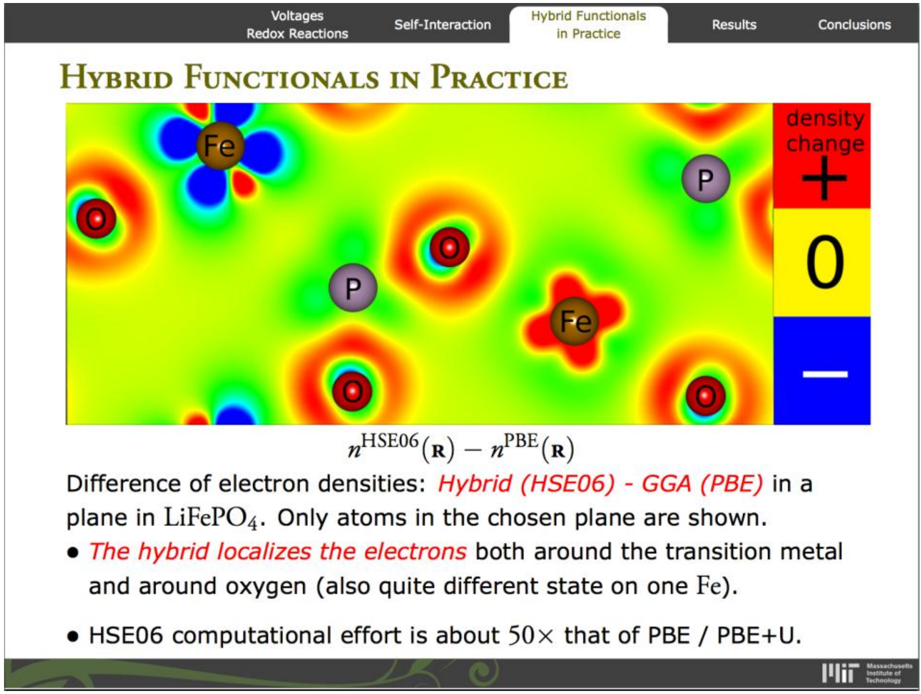


FIG. 2. (Color) Gradient analysis of the density of crystalline Si. The density n (a), $|\nabla n|$ (b), and $\nabla^2 n$ (c) on the (110) plane of the Si crystal. Atoms and bonds outlined in black. Shading varies from blue (dark gray) (low) to red (light gray) (high) and contours are in increments of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



We need to understand the physics in terms of the electron charge density

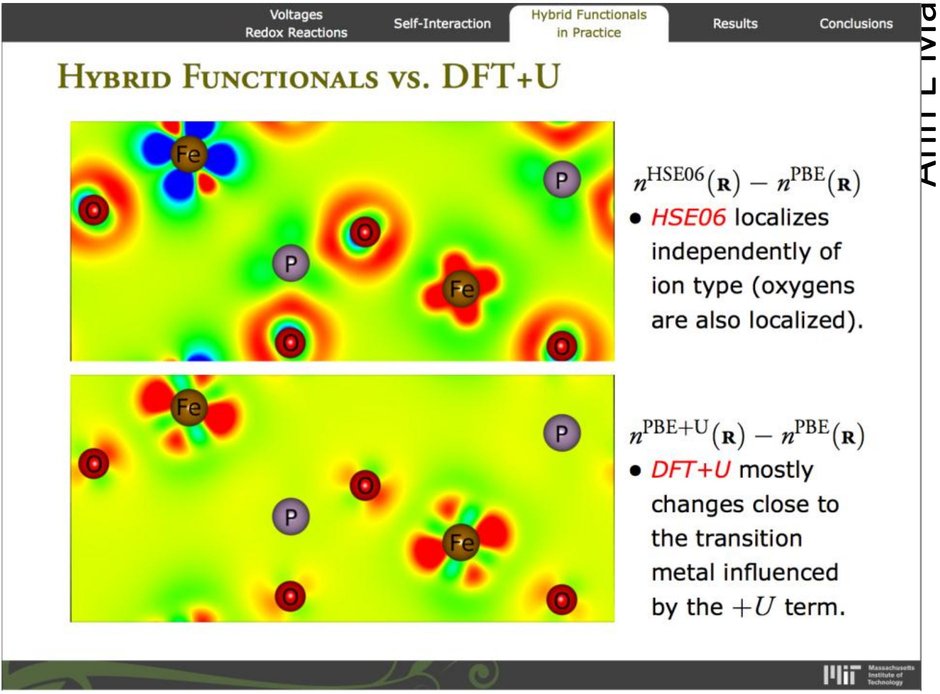


HYBRID FUNCTIONALS IN PRACTICE

$n^{\mathrm{HSE06}}(\mathbf{R}) - n^{\mathrm{PBE}}(\mathbf{R})$

Difference of electron densities: *Hybrid (HSE06) - GGA (PBE)* in a plane in $\mathrm{LiFePO_4}$. Only atoms in the chosen plane are shown.

- *The hybrid localizes the electrons* both around the transition metal and around oxygen (also quite different state on one Fe).
- HSE06 computational effort is about $50\times$ that of PBE / PBE+U.



HYBRID FUNCTIONALS VS. DFT+U

$n^{\mathrm{HSE06}}(\mathbf{R}) - n^{\mathrm{PBE}}(\mathbf{R})$

- *HSE06* localizes independently of ion type (oxygens are also localized).

$n^{\mathrm{PBE+U}}(\mathbf{R}) - n^{\mathrm{PBE}}(\mathbf{R})$

- *DFT+U* mostly changes close to the transition metal influenced by the $+U$ term.

Two slides from the 2010 APS March meeting talk by my collaborator Rickard Armiento.

This also shows the trend towards more and more computationally expensive methods for increasing the accuracy.
And the trend to mix DFT and SE theory.

Subsystem functionals

From
general purpose functionals
to
specialized functionals

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

Use specialized functionals
in the different subsystems

Divide integration over V
into integrations over subsystems

Subsystem functionals

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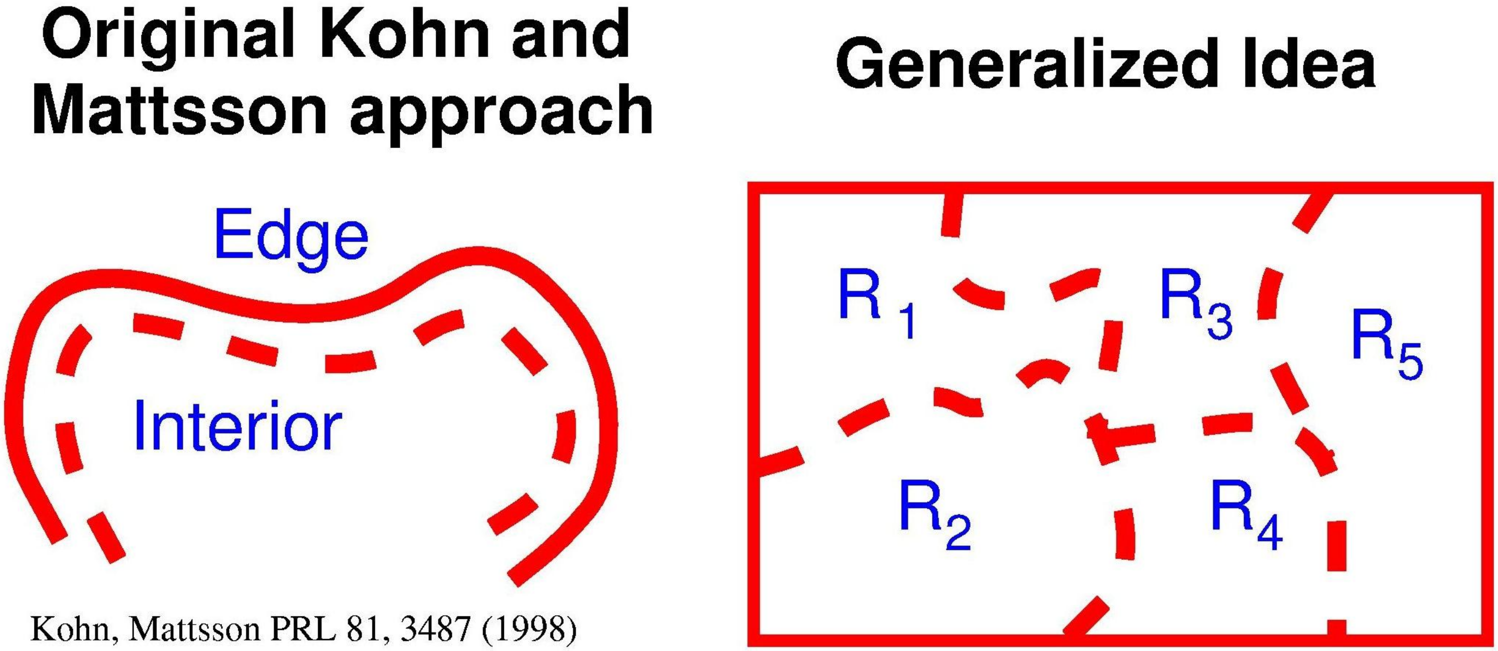


Original Kohn and Mattsson approach

Kohn, Mattsson PRL 81, 3487 (1998)

Generalized Idea

Every subsystem functional is designed to capture a specific type of physics, appropriate for a particular subsystem.

LDA and Ceperly-Alder

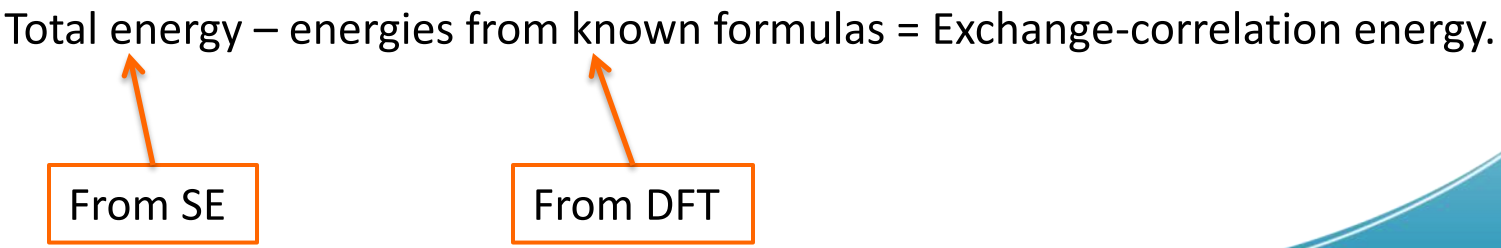
Ceperly and Alder, PRL 45, 566 (1980).

Quantum Monte Carlo calculations of the ground-state energy of uniform electron gases (model systems) of different densities.

Most correlation functionals in use today are based on their data.

ALL LDA correlation functionals in common use are based on (fitted to) their data.

(Before 1980, for example, Wigner correlation was used)



Total energy – energies from known formulas = Exchange-correlation energy.

From SE

From DFT

The LDA functional

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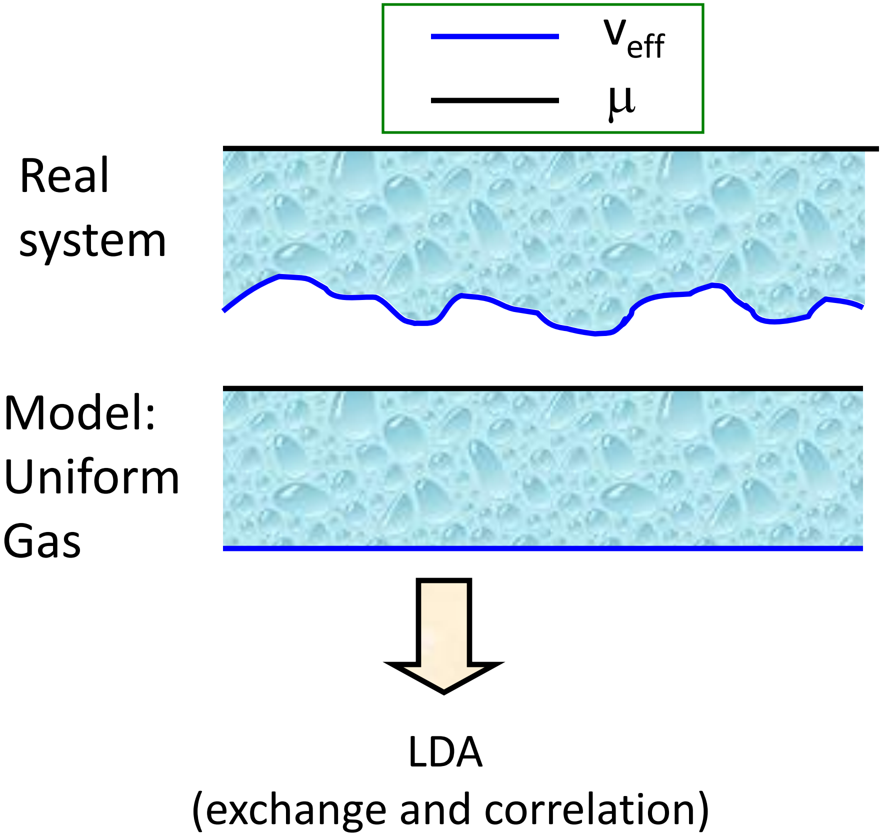

v_{eff}

μ

Real system

Model: Uniform Gas

LDA
(exchange and correlation)

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).

General functional from subsystem functionals: AM05, PRB 72, 085108 (2005)

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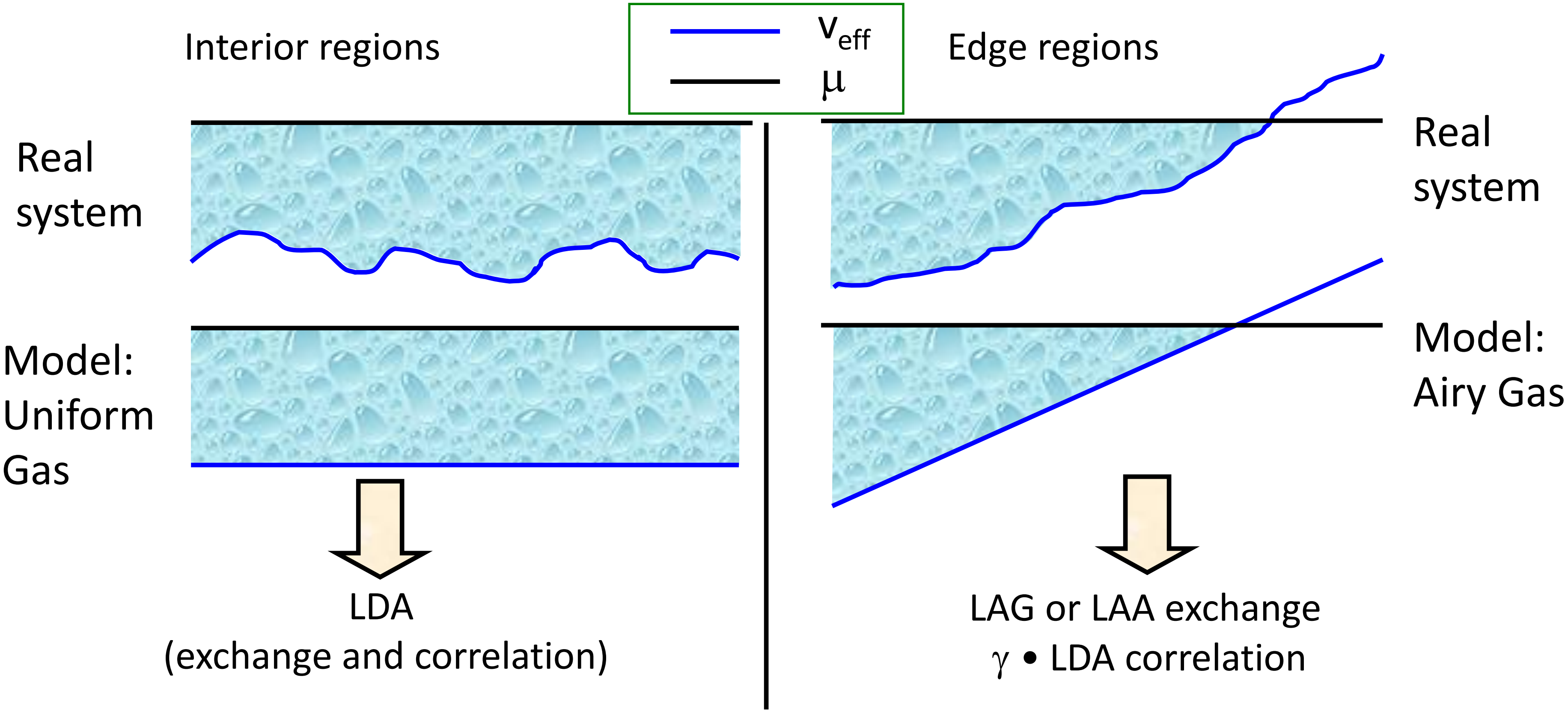

Interior regions

v_{eff}

μ

Edge regions

Real system

Model: Uniform Gas

Real system

Model: Airy Gas

LDA
(exchange and correlation)

LAG or LAA exchange
γ • LDA correlation

Interpolation

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

AM05 is as accurate as a hybrid, but much faster

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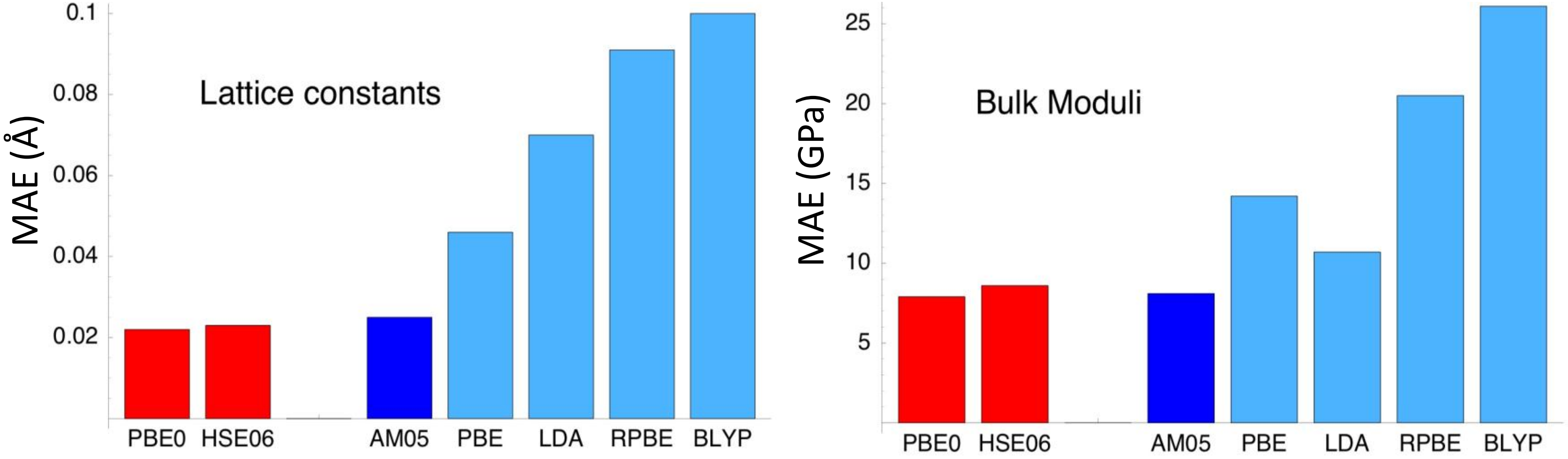
JCP 128, 084714 (2008)

Comparison of mean absolute errors (MAE) for properties of 20 solids calculated with seven different functionals.



GGA type functionals (blue) are one to three order of magnitudes faster to use than hybrids (red). AM05 has the same accuracy as hybrids for solids and thus enable accurate and fast DFT calculations of, for example, defects in semi-conductors. It also allows for the use of DFT-MD as an accurate tool in EOS construction.

AM05 also proves that fast AND accurate is possible.

What is next?

The construction of AM05 shows that the subsystem functional scheme can be a fruitful way of constructing exchange-correlation functionals.

We want to use this scheme for developing a general functional that can also give good results for some systems that presently available functionals have problems with:

- Systems with ‘localized’ electrons, such as transition metal oxides and actinides.

- Systems where van der Waals’ forces dominate the physics.

Subsystem Functional Scheme:

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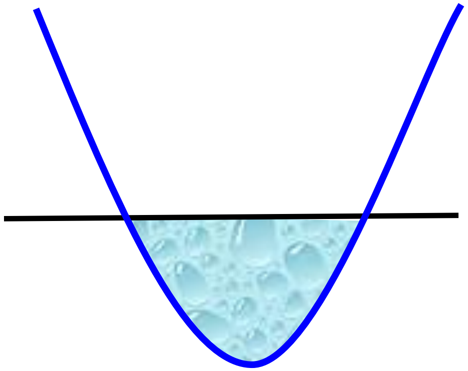
$$E_{xc} = \int_V n(\vec{r})\, e_{xc}(\vec{r};[n])\; dV$$

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

We want to be able to do DFT based calculations for all materials

While DFT is very successful for many materials and many properties, not all materials and properties are equally well treated with DFT. This is the case with, for example, equilibrium properties of explosives.

We have one problem:

- The van der Waals' forces

The Future: Hydrocode simulations with explicit microstructure

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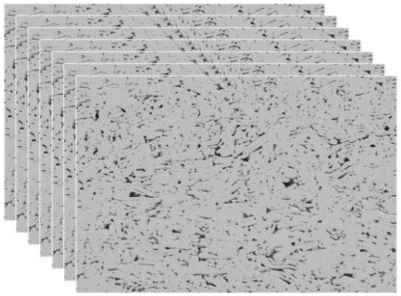
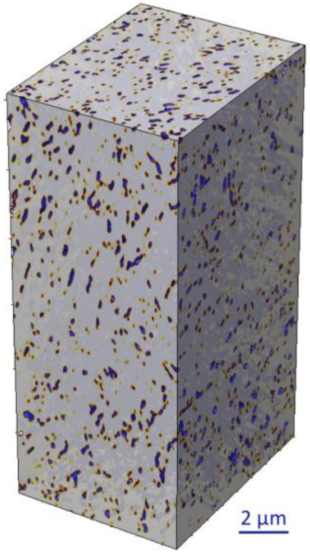
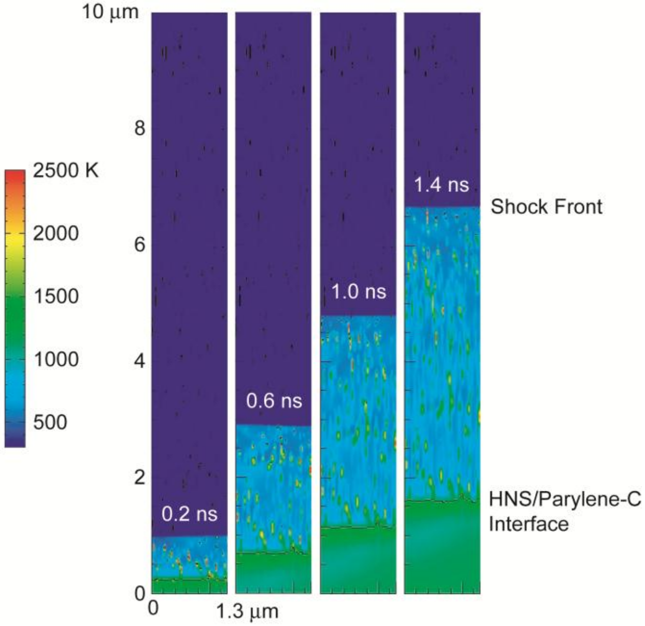
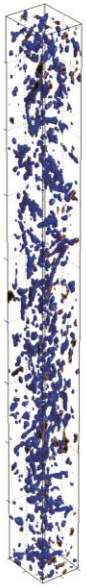


Nanotomography: 25 nm slices



80,000 pores





R.R. Wixom et al. J. Mater. Res. 25 (2010) 1362

Experimentally determined computational model of microstructure of explosives.

Single crystal Equation of State needed.

Bridges between Fundamental Law of Nature and Engineering

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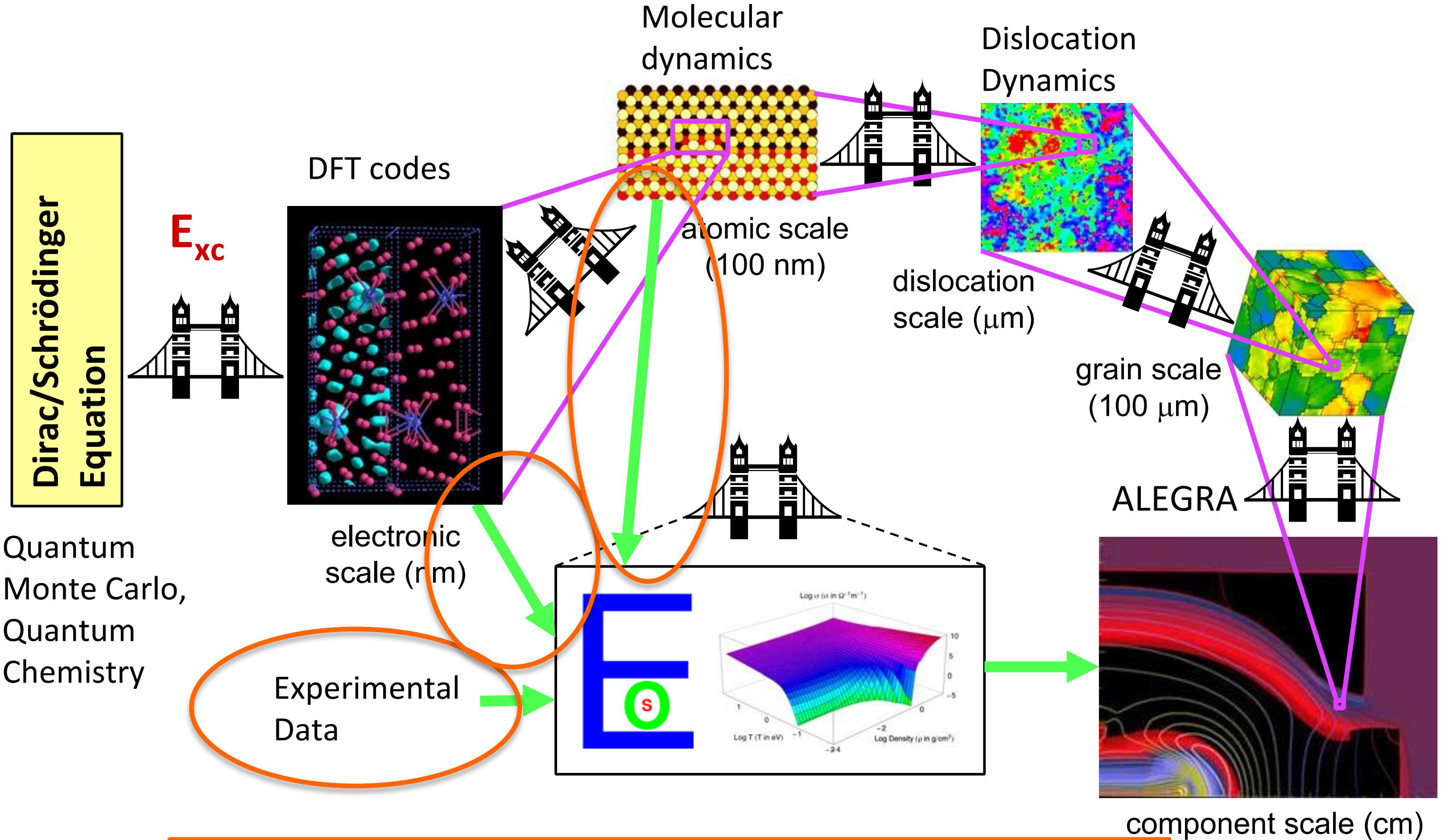

Dirac/Schrödinger Equation

E_{xc}

DFT codes

electronic scale (nm)

Molecular dynamics

atomic scale (100 nm)

Dislocation Dynamics

dislocation scale (μm)

grain scale (100 μm)

ALEGRA

component scale (cm)

Quantum Monte Carlo, Quantum Chemistry

Experimental Data

The ability to perform high-fidelity calculations is most important for cases where experiments are impossible, dangerous, and/or prohibitively expensive to perform.

PETN: The bad news: Equilibrium structure

Functional	a (Å)	c/a	Comment
LDA	8.961	0.710	
HSE	9.69	0.718	estimated
PBE	9.888	0.718	
AM05	---	---	no binding
Experiment	9.38	0.715	at ~298K

LDA, PBE, AM05: Energies calculated in a grid of 0.1 Å spacing in a and 0.01 spacing in c/a, extending at least 4 points on each side of minima (AM05 covering the PBE minima).

HSE: Because of the computational cost only three energies are calculated, from which the lattice parameter is estimated.

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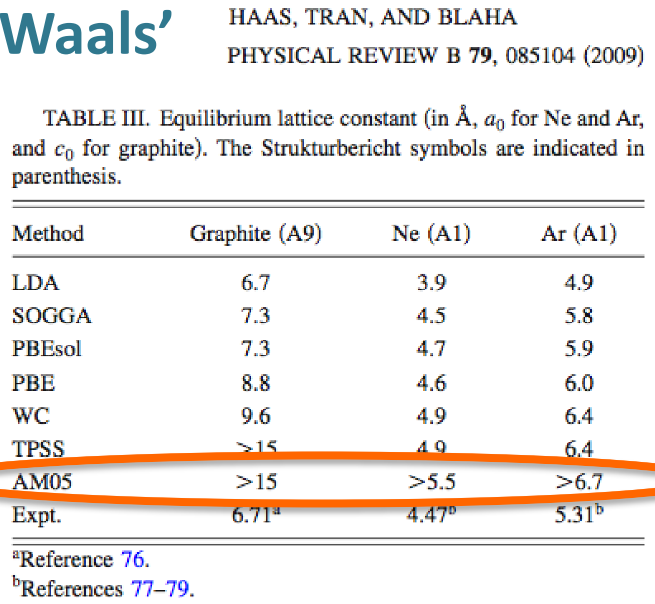
Van der Waals’



HAAS, TRAN, AND BLAHA

PHYSICAL REVIEW B **79**, 085104 (2009)

TABLE III. Equilibrium lattice constant (in Å, a_0 for Ne and Ar, and c_0 for graphite). The Strukturbericht symbols are indicated in parenthesis.

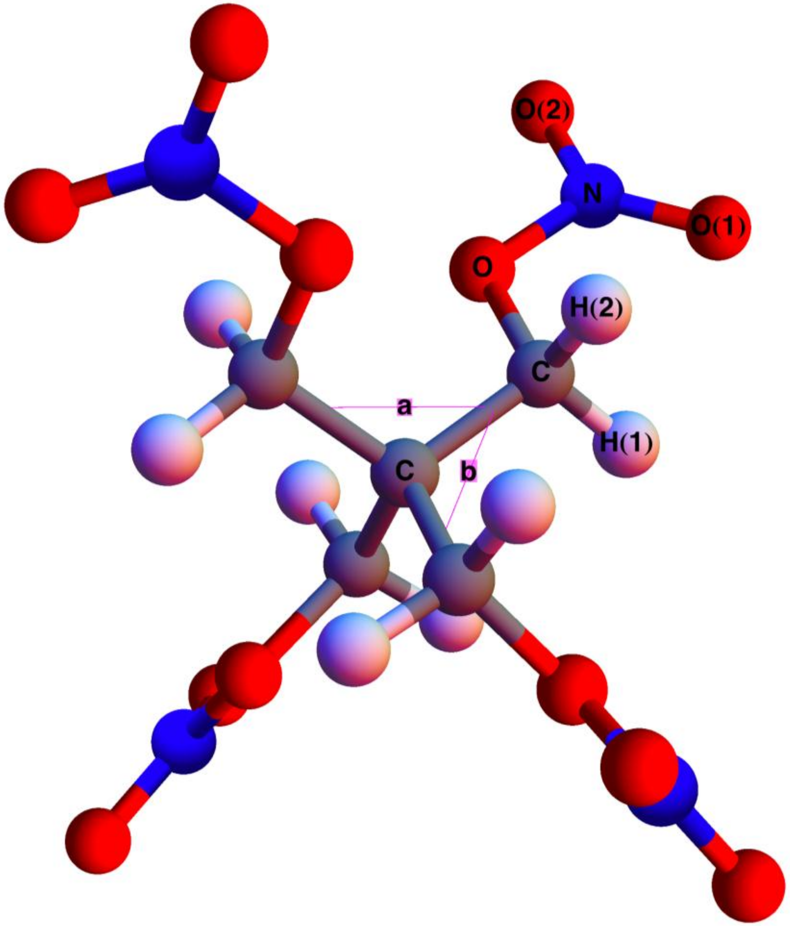
Method	Graphite (A9)	Ne (A1)	Ar (A1)
LDA	6.7	3.9	4.9
SOGGA	7.3	4.5	5.8
PBEsol	7.3	4.7	5.9
PBE	8.8	4.6	6.0
WC	9.6	4.9	6.4
TPSS	>15	4.9	6.4
AM05	>15	>5.5	>6.7
Expt.	6.71[a]	4.47[b]	5.31[b]

[a] Reference 76.

[b] References 77–79.

- LDA sometimes gives good minimum but for the wrong reasons, and not consistently.
- AM05 might be better off than other functionals since it contains no van der Waals’, not even faulty.

PETN:
The good news: Intramolecular structure



- We have calculated the molecule structure (bond lengths and angles) in the crystal environment.

- Functionals follow the usual trends but all give a good description compared to experiments.

- The large differences in equilibrium volumes thus stem from the poor description of the intermolecular van der Waals' bonds.

Hugoniots: Circumvent problems at equilibrium

So, we know AM05 does not include any van der Waals' forces but that it treats compressed matter very accurately.

Idea: Use experimental equilibrium volume for the ambient reference but use the theoretical pressure at this volume (and room temperature) as pressure reference. (This methodology has been used for polymers before: AM05 does not bind any of them. However, the effect is small in the polymers, that is, the theoretical pressure is small).

Easy to motivate this using AM05, but harder when you have a functional that gives a faulty minima.

Molecular Dynamics

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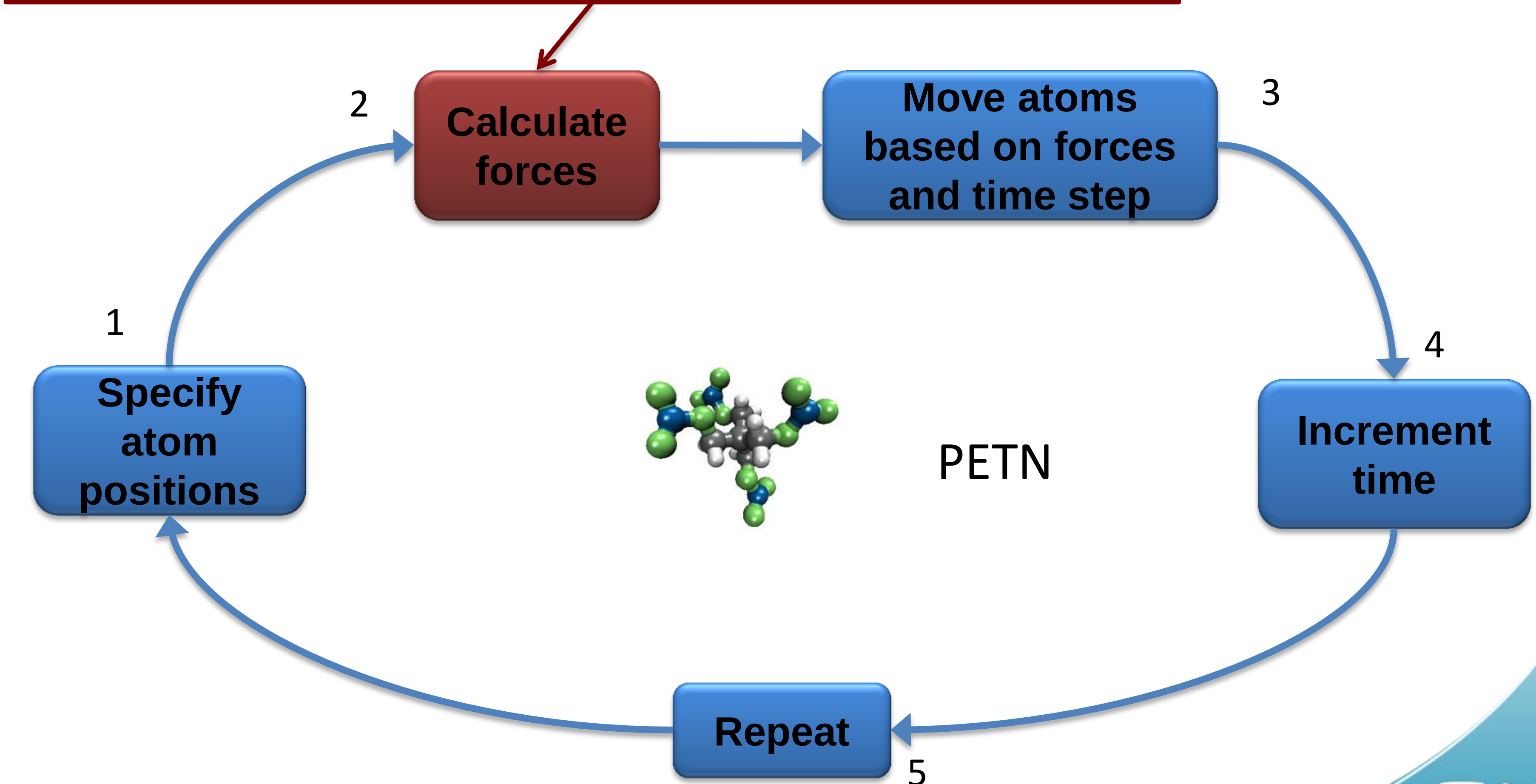
DFT-MD (or a AIMD or QMD): Forces calculated with DFT.
Classical MD: Forces calculated with force fields or potentials.



Adapted from slides by Ryan Wixom, SNL.

Finding the Hugoniot State (P,T,E) for any V.

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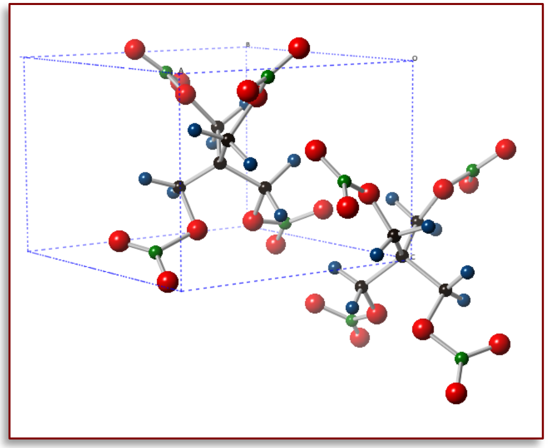
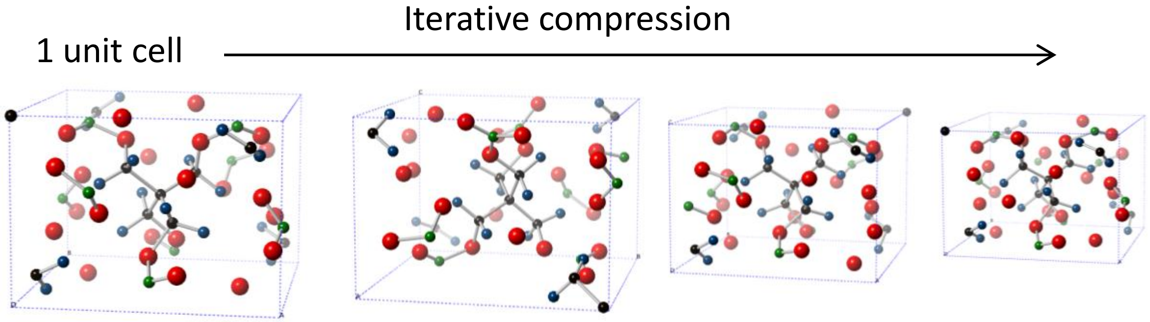
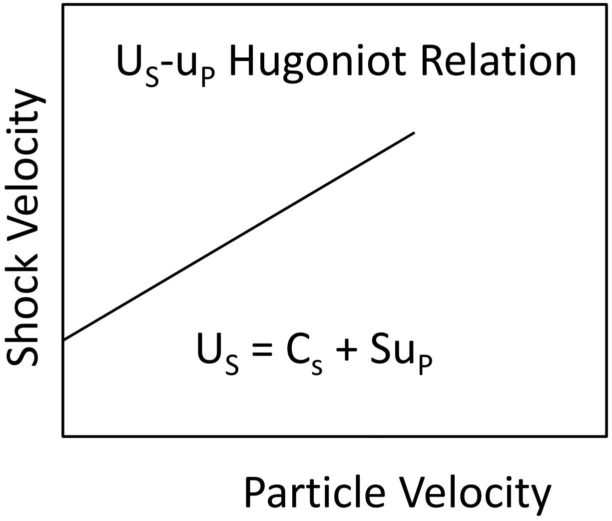


PETN, V_o at 300K



1.0 a	0.95 a	0.90 a	0.85 a
1.0 V	0.85 V	0.72 V	0.61 V



Mass $\boxed{\rho_o D = \rho_1 (D - u_1)}$

Momentum $\boxed{P_1 = \rho_o D u_1}$

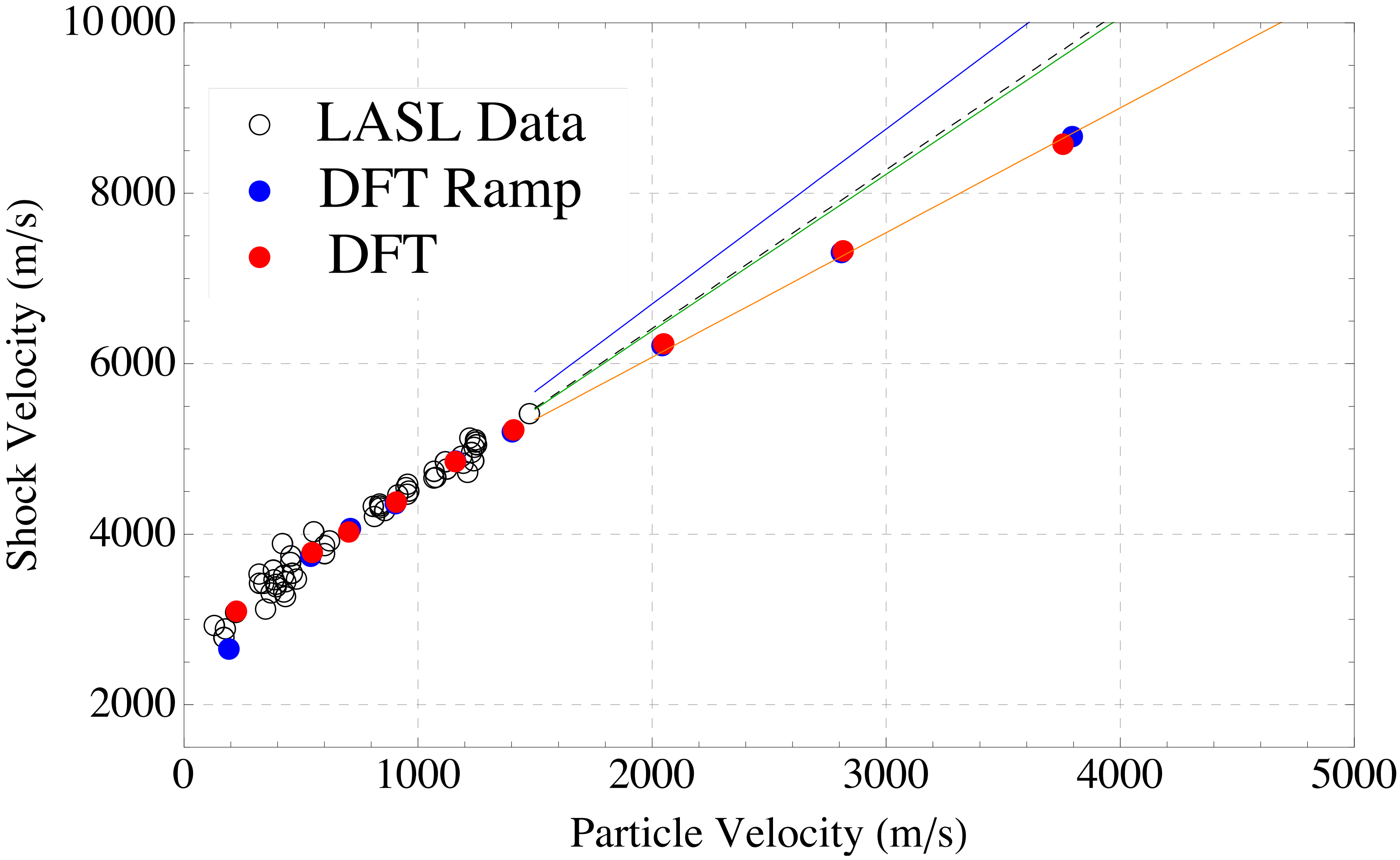
Energy $\boxed{E - E_o = \frac{1}{2}(P + P_o)(V_o - V)}$ R.H. equation

Key Point: jump conditions are only valid on the Hugoniot

Approach 1:
Set V, ramp T, and solve for where above is true.
Approach 2:
Set V, run several Ts, fit to P(T) and E(T) and solve.

PETN

DFT-MD calculated single crystal Hugoniot



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Epsilon CL-20

DFT-MD calculated single crystal Hugoniot

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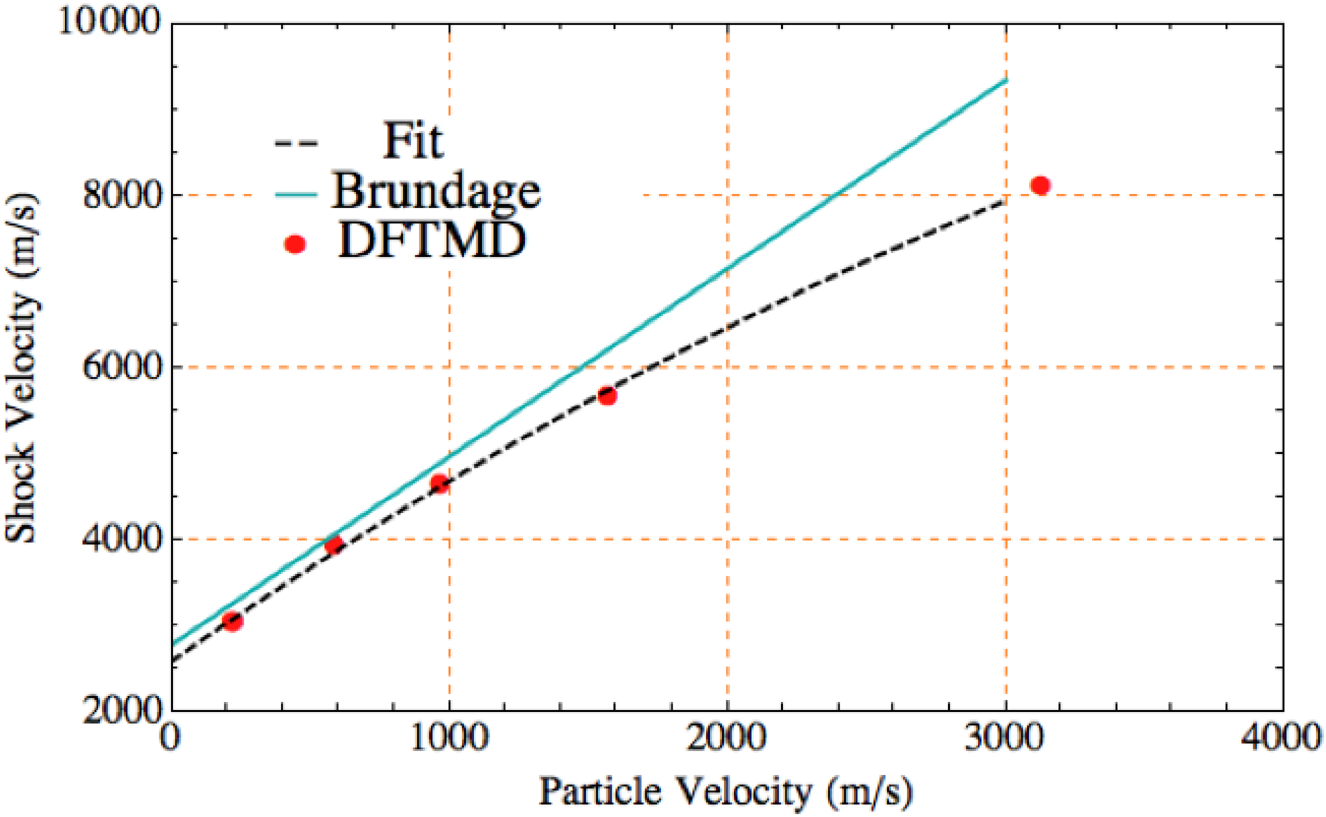

Brundage: 2770 + 2.19x (2009 APS SCCM Proceedings)

Second order fit to DFTMD: 2580.55+ 2.25161 x - 0.000155591 x^2

Epsilon CL-20

DFT-MD calculated single crystal Hugoniot –

… and comparison with Gump’s DAC experiments

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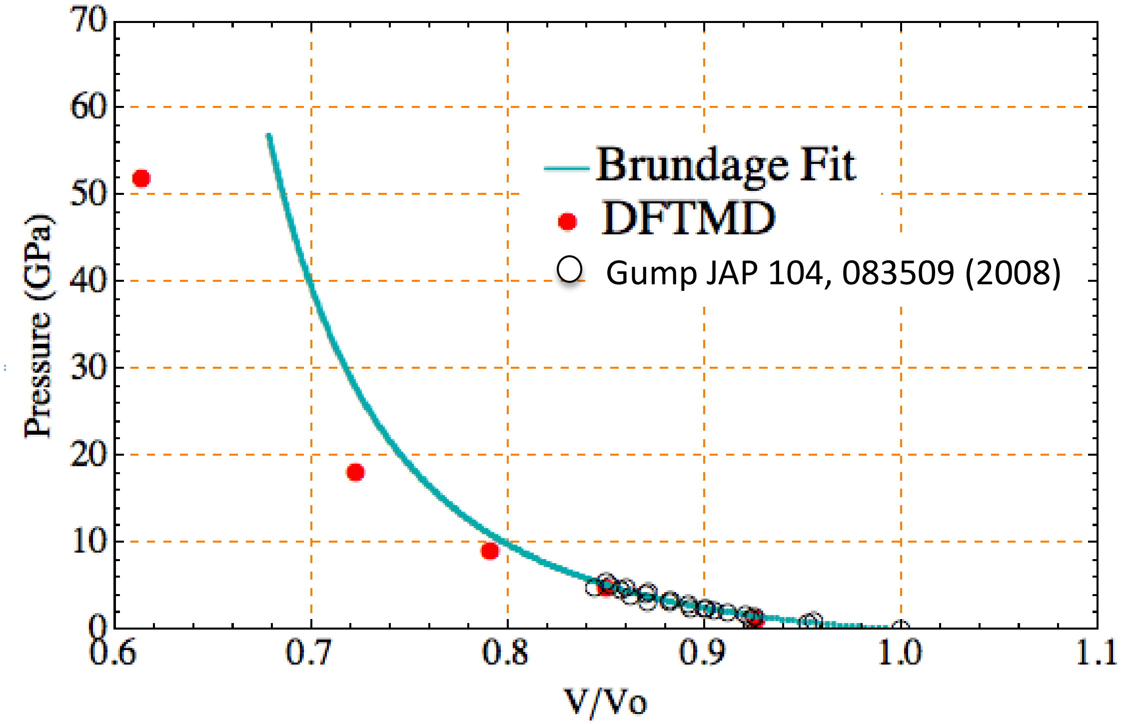

Brundage: 2770 + 2.19x (2009 APS SCCM Proceedings)

Experimental volume of CL-20 from Nielsen et al, Tetrahedron 54 (1998) 11793-11812. P21/n A=8.852, B=12.556, C=13.386, β=106.82°

HNS

DFT-MD calculated single crystal Hugoniot and Isotherm

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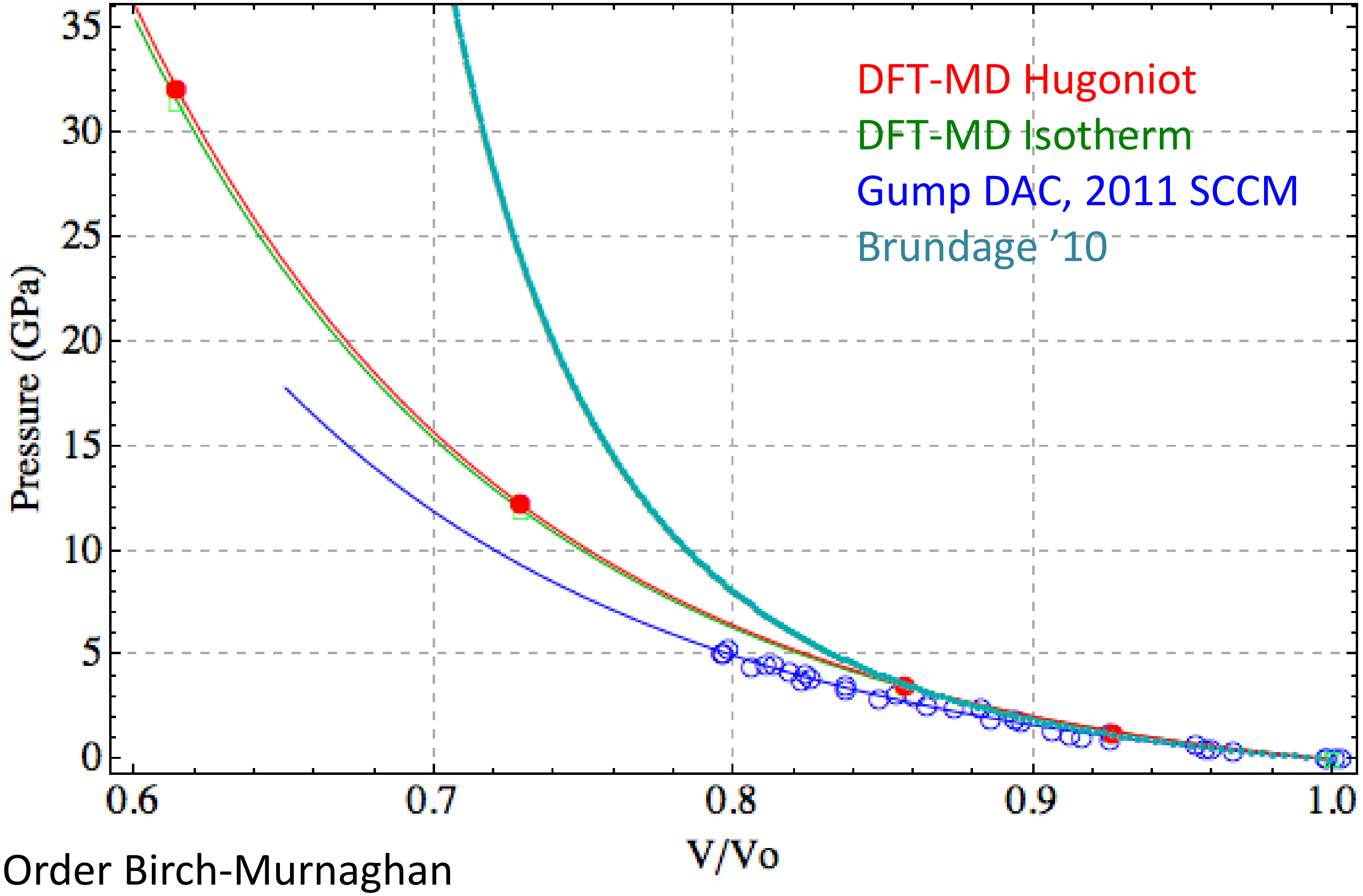

Fits: 3rd Order Birch-Murnaghan

Hugoniot → Bo: 13.7849, Bo': 6.74949

Isotherm → Bo: 13.4739, Bo': 6.77552

Gump DAC → Bo: 11.217, Bo': 6.2174

HNS

DFT-MD calculated single crystal Hugoniot

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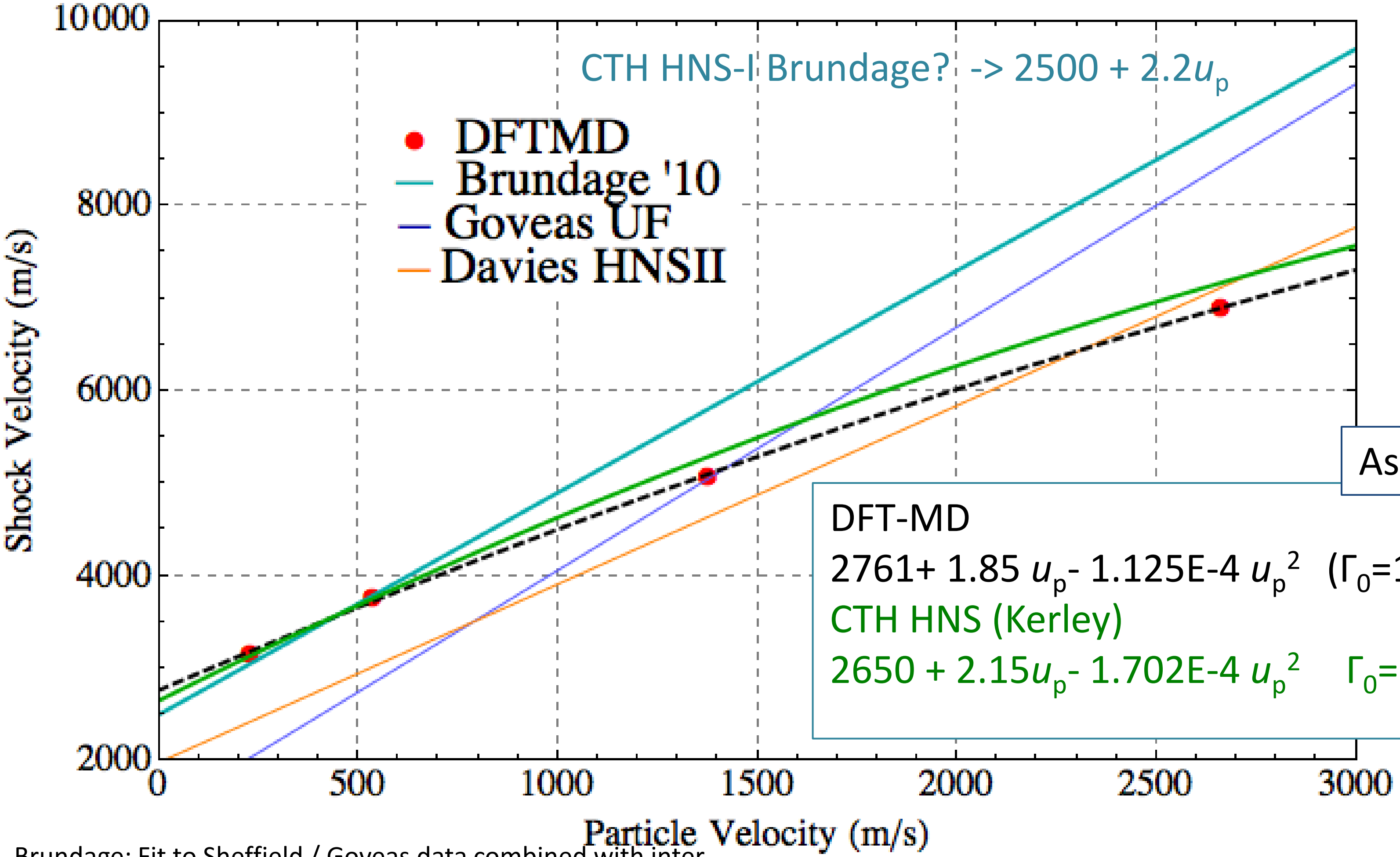

CTH HNS-I Brundage? -> 2500 + 2.2u_p

Assumed

DFT-MD

2761+ 1.85 u_p- 1.125E-4 u_p^2 (Γ_0=1 C_v=1.35)

CTH HNS (Kerley)

2650 + 2.15u_p- 1.702E-4 u_p^2 Γ_0=2 C_v=1.12

Brundage: Fit to Sheffield / Goveas data combined with inter-granular stress measurements (2010 IDS).
Goveas/Davies: fits to 91% TMD pressings APS SCCM 2005

Experimental volume from Gerard and Hardy, Acta Cryst. C4 (1998) 1283-1287. Monoclinic P21/c, A=22.326, B=5.5706, C=14.667, β=110.04°

We can and will calculate C_v and Γ

Does it matter?

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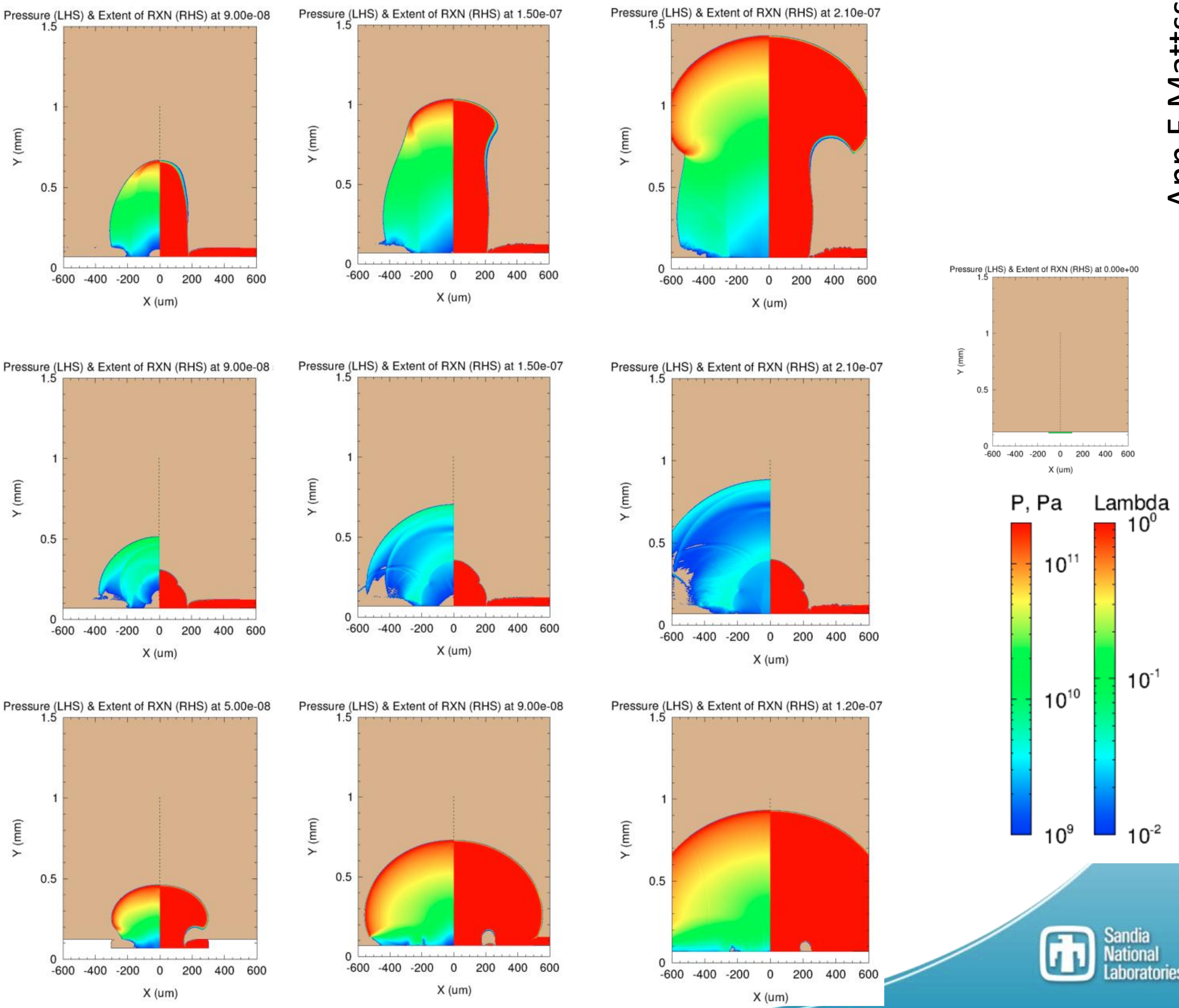
HNS-I
(CTH ?)
Γ_0=1.0, C_v=1.35E+11

DFT-MD
(p-alpha)
Γ_0=1.0, C_v=1.35E+11

HNS
(Kerley)
Γ_0=2.0, C_v=1.12E+11



Kinetic energy functionals

Ann E Mattsson

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

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

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

$$E[n]=T_s[n]+E_{ext}[n]+E_{hartree}[n]+E_{xc}[n]$$

Minimize wrt density: $\delta E/\delta n = 0$

Kinetic energy functionals

Calculate the kinetic energy density $\tau = T_s/V$ for a uniform electron gas.
Calculate the electron density n for a uniform electron gas.

Express T_s as a functional of the density n, $T_s[n]$.

This is the Thomas-Fermi approximation for the kinetic energy.

$$\left.\begin{array}{l} \tau_{UEG} = k_F{}^5/5/\pi^2 \\ \\ n_{UEG} = k_F{}^3/3/\pi^2 \end{array}\right\} \xrightarrow{\hspace{3cm}} \tau_{TF} = 3/5\ (3\pi^2)^{2/3}\ n^{5/3}$$

This is corresponding to LDA for exchange-correlation functionals

Kinetic energy functional for surface system

Calculate the kinetic energy density for a surface system
Calculate the electron density for a surface system

Express T_s as a functional of the density n

This is a surface approximation for the kinetic energy.

We can easily calculate τ for the Airy gas. We have n for an Airy gas.

We need to express τ as a function of n and its derivatives.

Possibly we need to use an interpolation index to interpolate between TF and Airy. Need to remember to use same definition for all subsystems.

Vitos et al have made a parameterization: PRA **61**, 052511 (2000).

This is corresponding to LAA and LAG for exchange functionals.

Kinetic energy functional for confined systems

Calculate the kinetic energy density for a confined system
Calculate the electron density for a confined system

Express T_s as a functional of the density n

This is a confined system approximation for the kinetic energy.

We can easily calculate τ for the Harmonic Oscillator (HO) gas. We have n for a HO gas.

We need to express τ as a function of n and its derivatives.

Possibly we need to use an interpolation index to interpolate between HO, TF, and Airy. Need to remember to use same definition for all subsystems.

Temperature

There is no additional problem to add temperature to this scheme. Just one more parameter to account for in the parameterization procedure.

VASP PAW potentials: Standard (old) Kr

=

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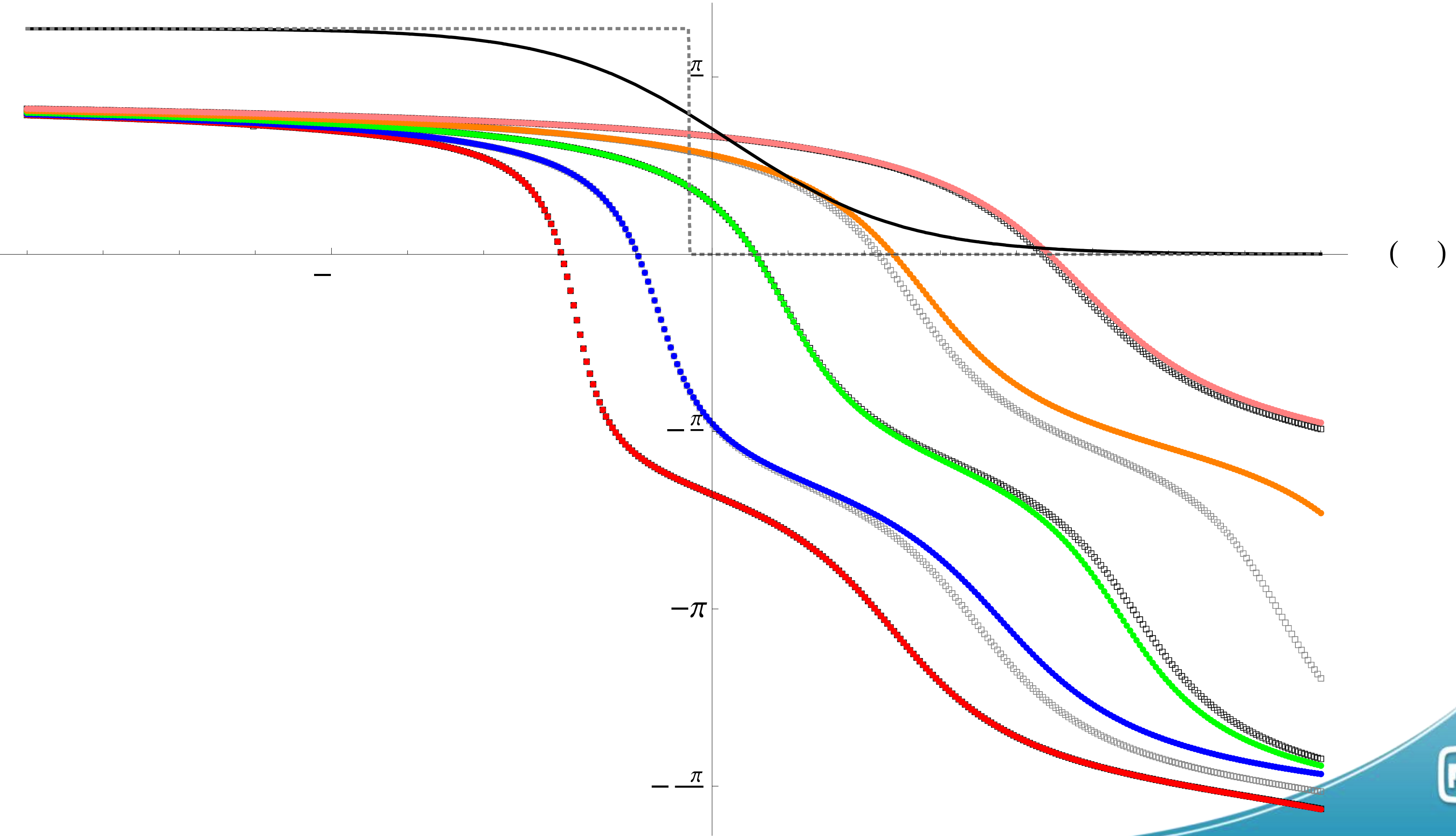

PAW potentials: Still 8 electrons

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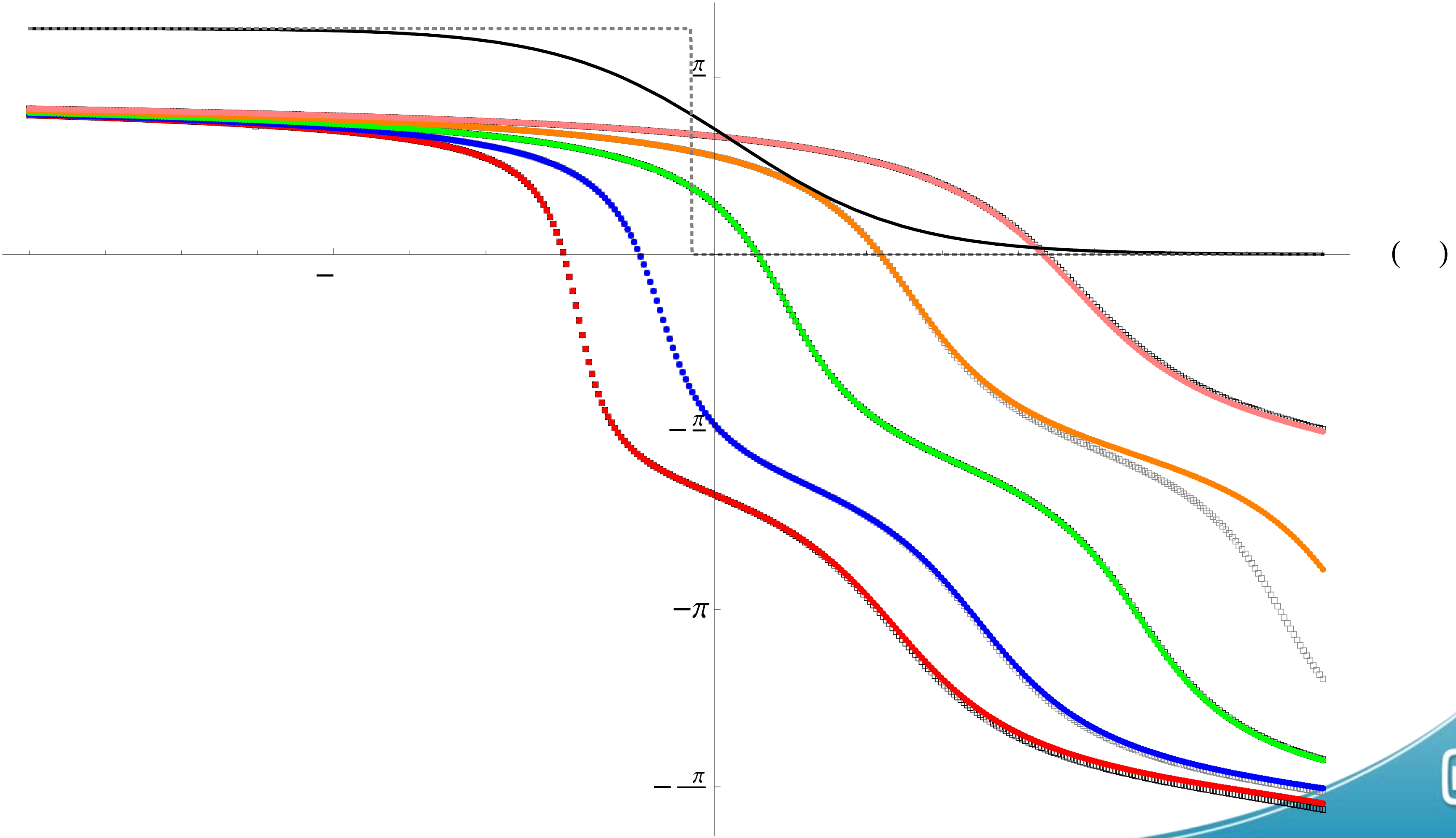
$=$

$\ell = (\quad)\quad(\quad)\quad(\quad)\quad(\quad)\quad(\quad)$

$(\quad)$



PAW potentials: Now 18 electrons

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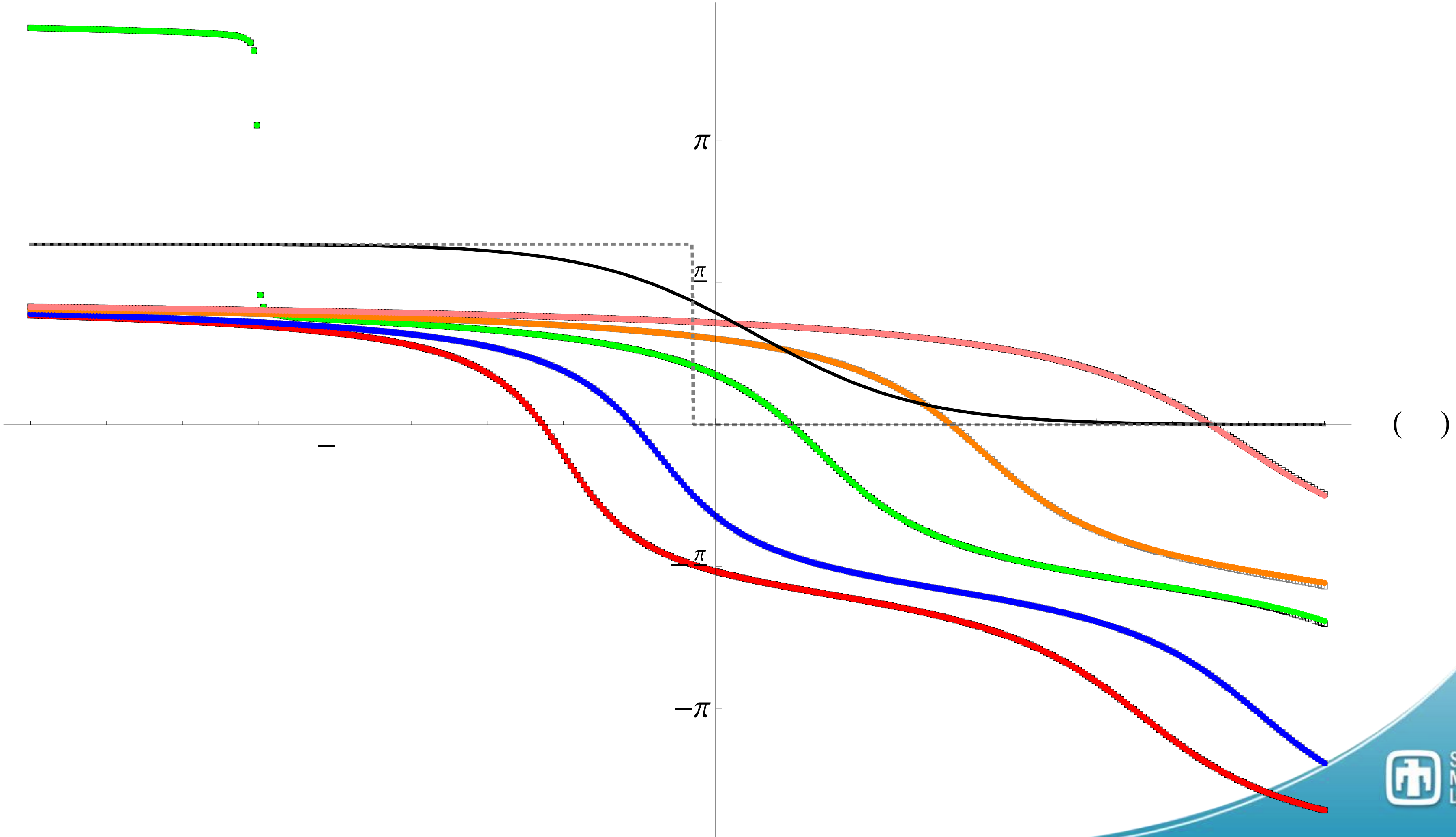
$=$

$\ell = (\quad)\quad(\quad)\quad(\quad)\quad(\quad)\quad(\quad)$

$(\quad)$



Summary

- The warm dense matter region poses a particular challenge with its multitude of phases and competing physical processes.
- Experiments are of limited usefulness due to limitations in accessible parameter space. Accurate computational tools would be valuable complements.
- Even the largest and fastest computer will give us useless results if the equations implemented are the wrong ones or if the computational approach has limited accuracy.
- Density Functional Theory has the potential to provide us with the generally accurate and fast computational tool we need.
- We have implementing the DFT-Dirac equations needed to describe actinide materials.
- We are working on a general functional that would allow us to incorporate the confinement physics of the HO model system in a self-consistent way.
- The subsystem functionals scheme is a promising approach also for kinetic energy functionals.

Ann E Mattsson

Thank you for your attention.

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Website with publications: http://www.cs.sandia.gov/~aematts/

Summary

- In order to search for new materials with desired functionality, a computational capability with reliable accuracy is highly desirable.
- Experiments are of limited usefulness due to difficulties in synthetizing new materials and their limitations in accessible parameter space.
- Even the largest and fastest computer will give us useless results if the equations implemented are the wrong ones or if the computational approach has limited accuracy.
- Density Functional Theory has the potential to provide us with the generally accurate and fast computational tool we need.
- We are implementing the DFT-Dirac equations needed to describe actinide materials.
- We are working on a general functional that would allow us to incorporate the confinement physics of the HO model system in a self-consistent way.

Thank you for your attention.

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Good modeling and simulation methods needed for materials models. Example: Nuclear Energy

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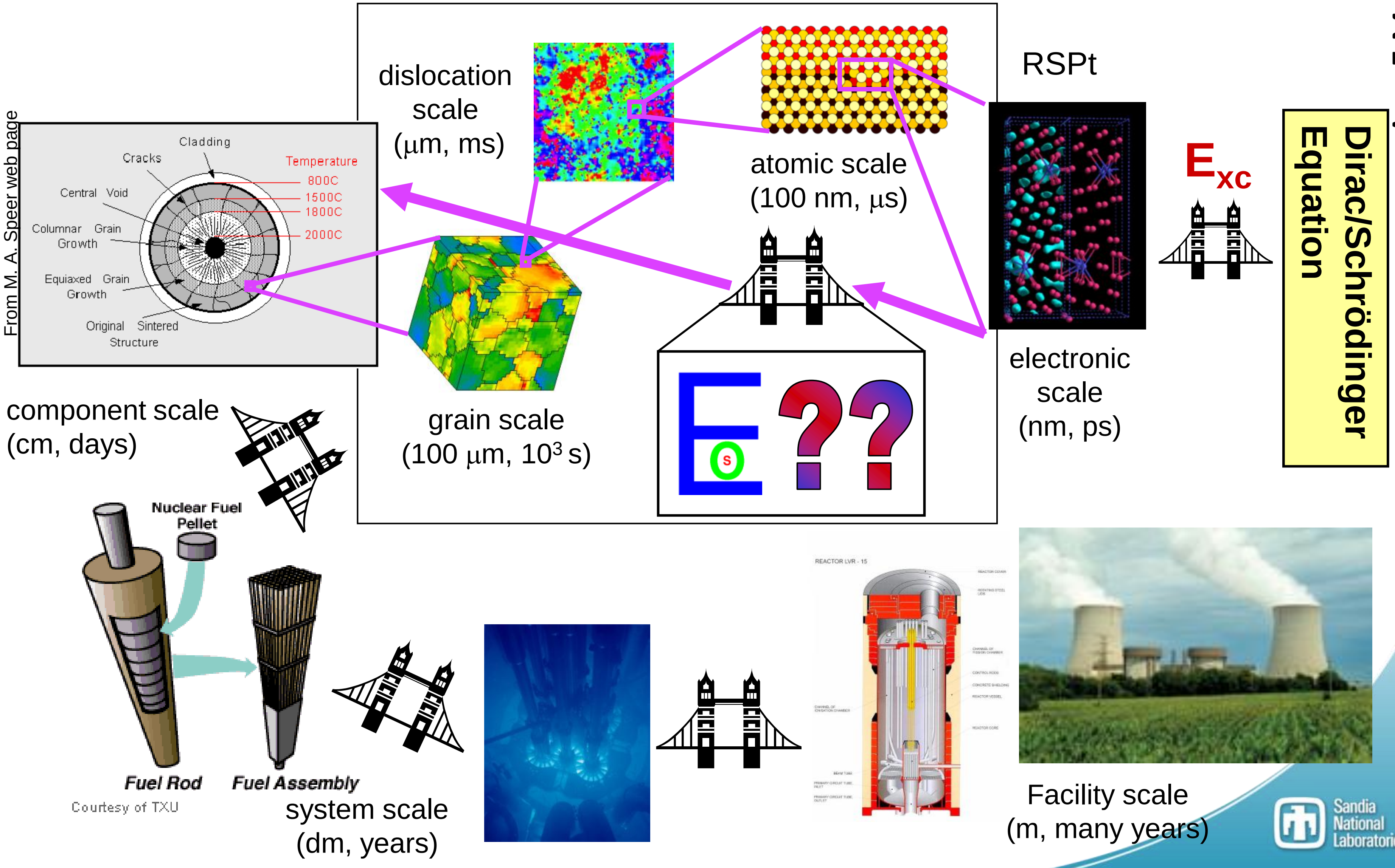


From M. A. Speer web page

dislocation scale (μm, ms)

atomic scale (100 nm, μs)

RSPt

E_{xc}

Dirac/Schrödinger Equation

component scale (cm, days)

grain scale (100 μm, 10^3 s)

electronic scale (nm, ps)

Courtesy of TXU

system scale (dm, years)

Facility scale (m, many years)

Practical information about AM05

- The division into subsystems is done automatically via the interpolation index.

- AM05 can be implemented into any code that can run a GGA. Already implemented in VASP5 and many other codes.

- AM05 is as fast and easy to use as LDA and PBE.

- Subroutines and information at http://dft.sandia.gov/functionals/AM05.html

Relativity

Questions:

- How much does the Dirac equation help in itself?

- Is using spin density functionals enough (possibly with LDA relativistic corrections that are already worked out)?

- Will we need vector current functionals?

John Wills (LANL) and I are working together to answer these questions with the help of a Dirac implementation into the RSPt code.

Note: If a vector current functional is needed I believe only our subsystem functional scheme can be at all successful.

Relativity

Summary:

- I discuss the basics of relativity in DFT in more detail in the review article, “Modeling and Simulation of Nuclear Fuel Materials” by Devanathan et al. in Energy Environ. Sci., 3, 1406 (2010).

- Dirac Equation is definitely needed to describe the $p_{1/2}$ states in high-Z materials.

- Dirac Equation needs vector current functional.

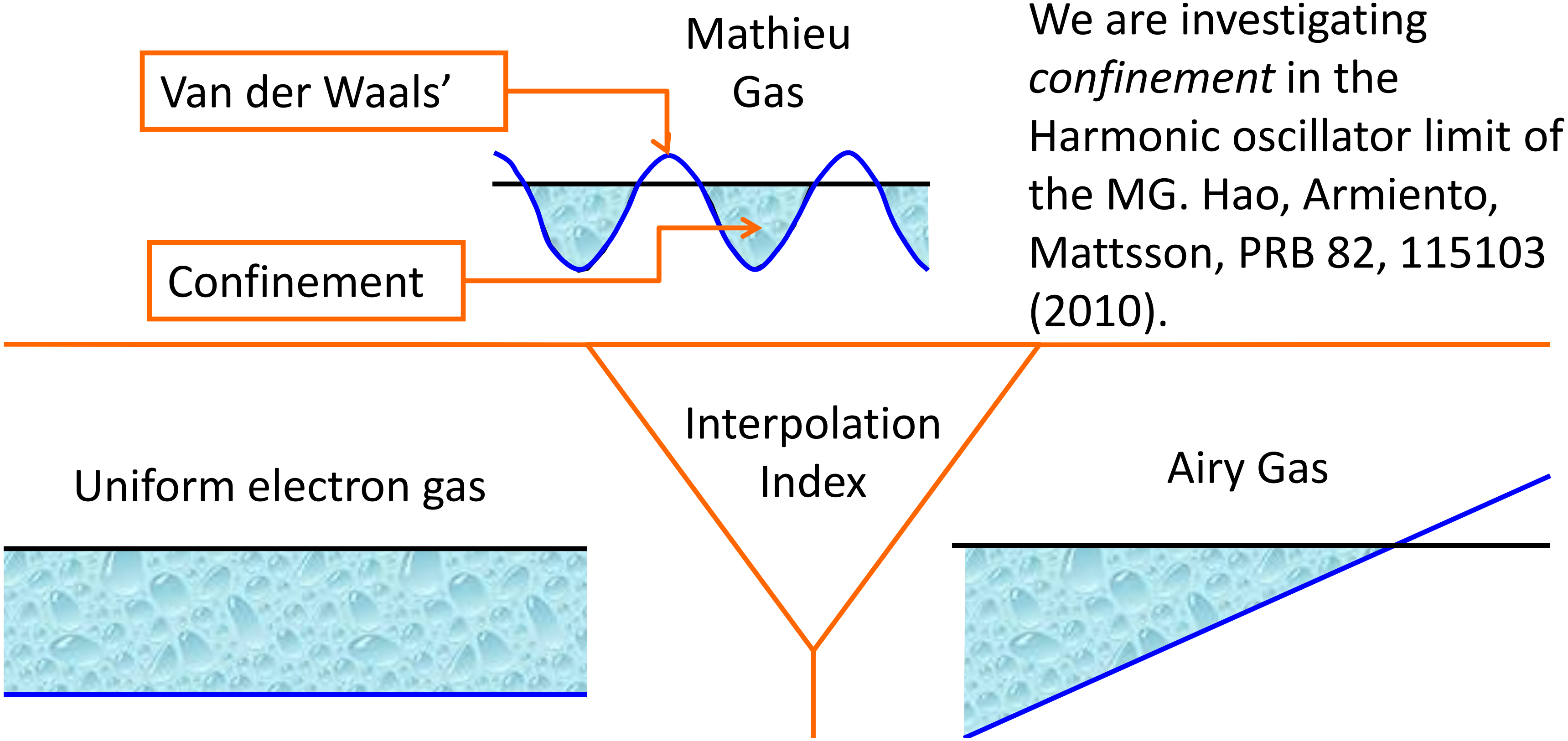
- An approximation can be made, to formulate in terms of spin densities instead.

What is ‘localization’ really?

Why do we have a high ELF, and thus corrections, on the oxygens, when the common belief is that the *d*-electrons on the copper ions are the ones that are not well treated with DFT?
Could it be two different effects?

A functional for confined and van der Waals’ systems

Ann E Mattsson



Van der Waals’

Mathieu Gas

Confinement

Interpolation Index

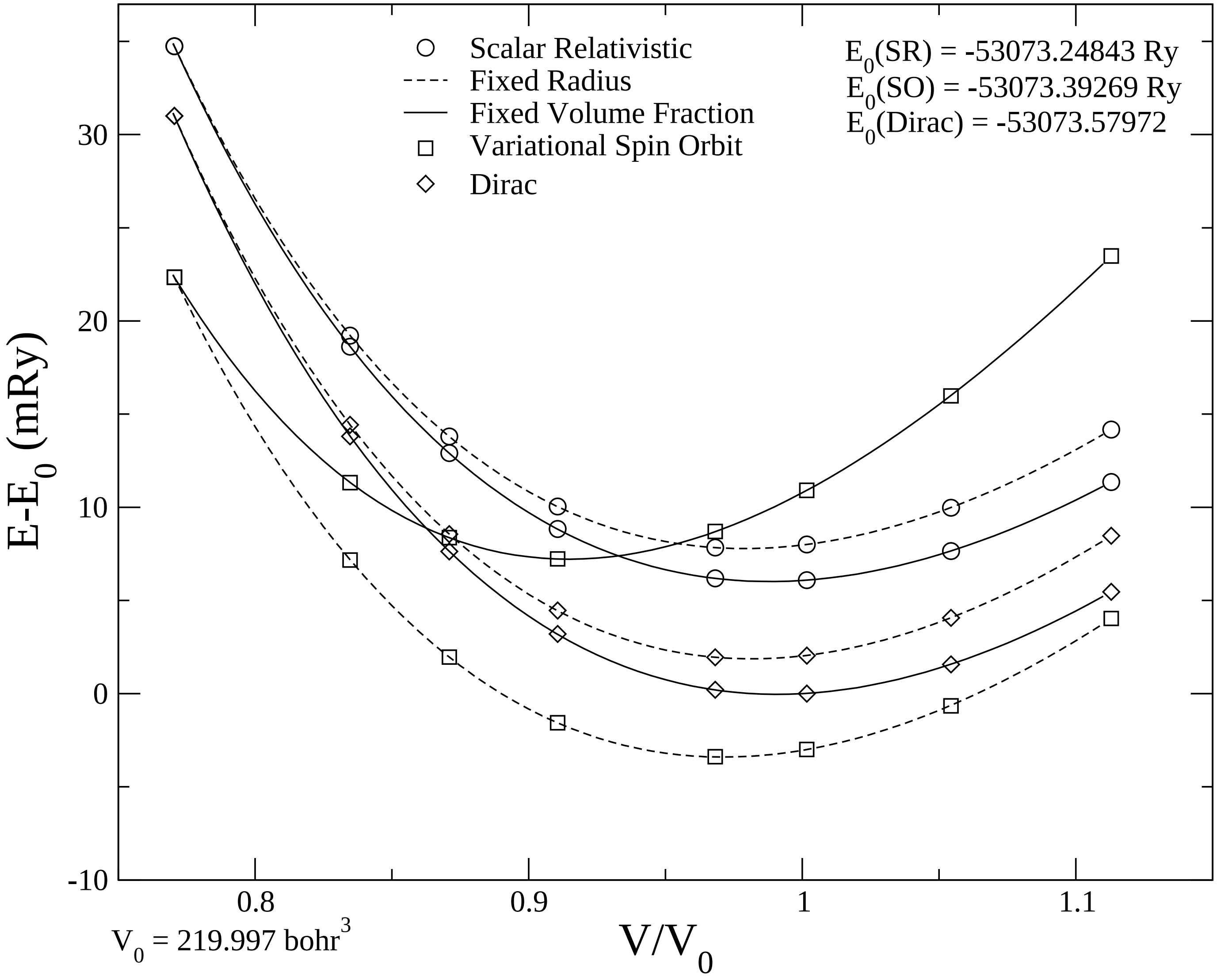
Uniform electron gas

Airy Gas

We are investigating *confinement* in the Harmonic oscillator limit of the MG. Hao, Armiento, Mattsson, PRB 82, 115103 (2010).

Want to know more?: “The Subsystem Functional Scheme: The Armiento-Mattsson 2005 (AM05) Functional and Beyond”, Mattsson and Armiento, International Journal of Quantum Chemistry 110, 2274 (2010).

Thorium PBE results



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A functional for confined systems via the subsystem functional scheme

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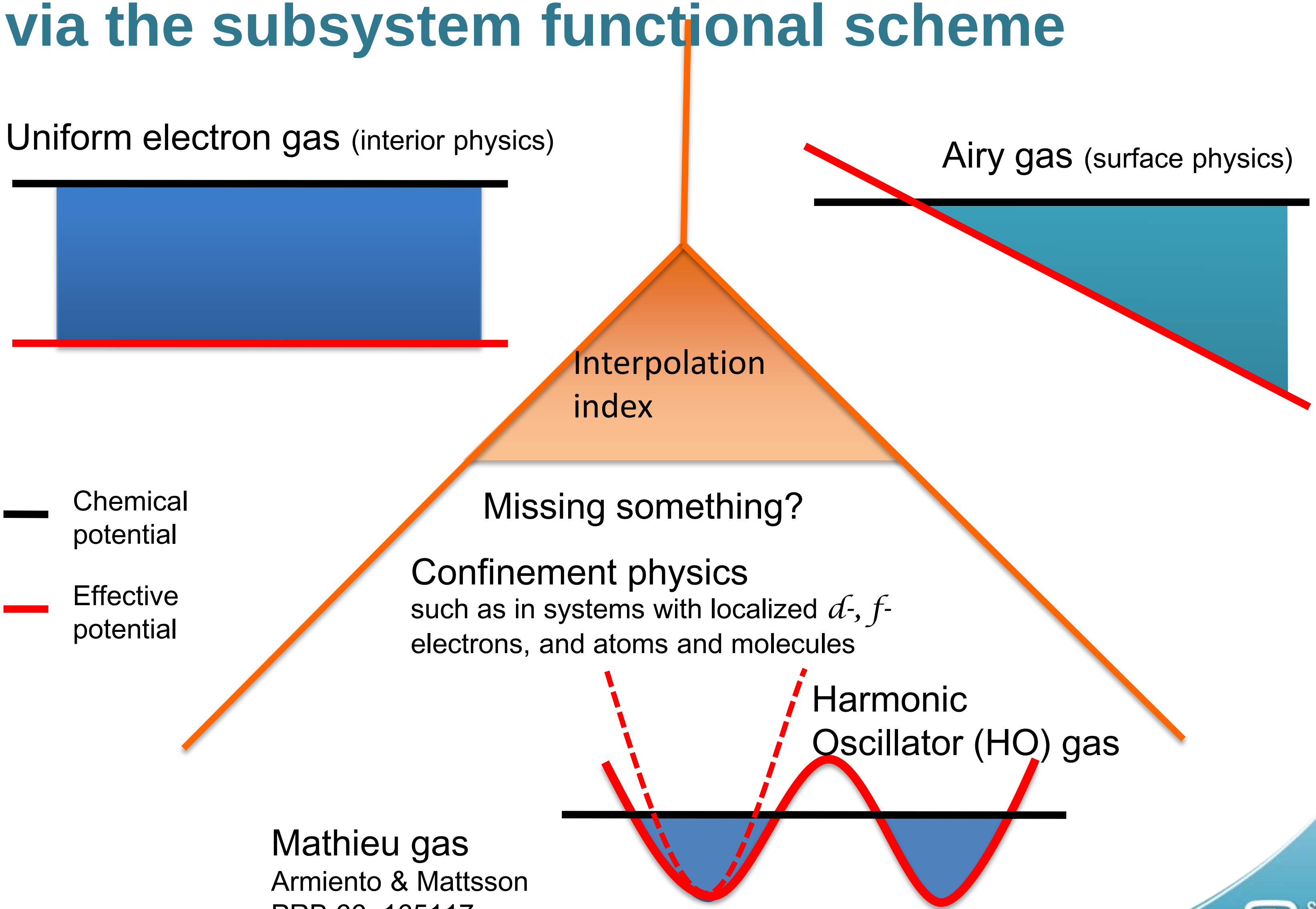


Uniform electron gas (interior physics)

Airy gas (surface physics)

Interpolation index

Missing something?

Confinement physics
such as in systems with localized *d*-, *f*-electrons, and atoms and molecules

Harmonic Oscillator (HO) gas

▬ Chemical potential

🟥 Effective potential

Mathieu gas
Armiento & Mattsson
PRB 66, 165117
(2002)

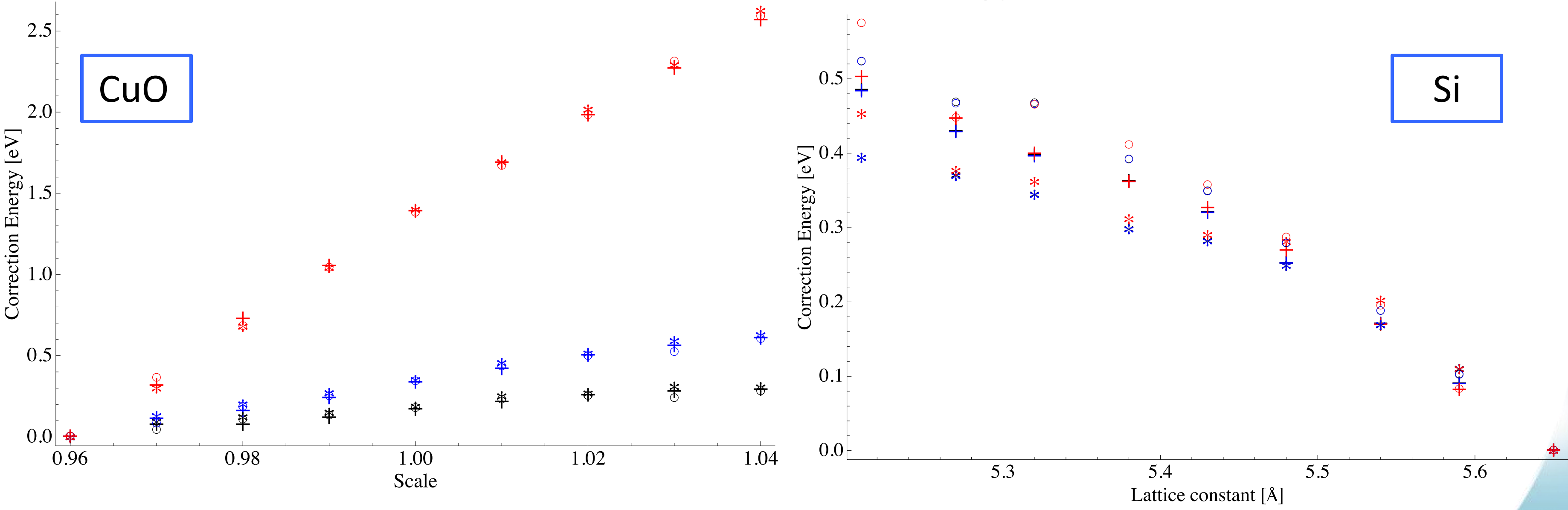
Confinement error correction for Si

Ann E Mattsson

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

Interpolation Index

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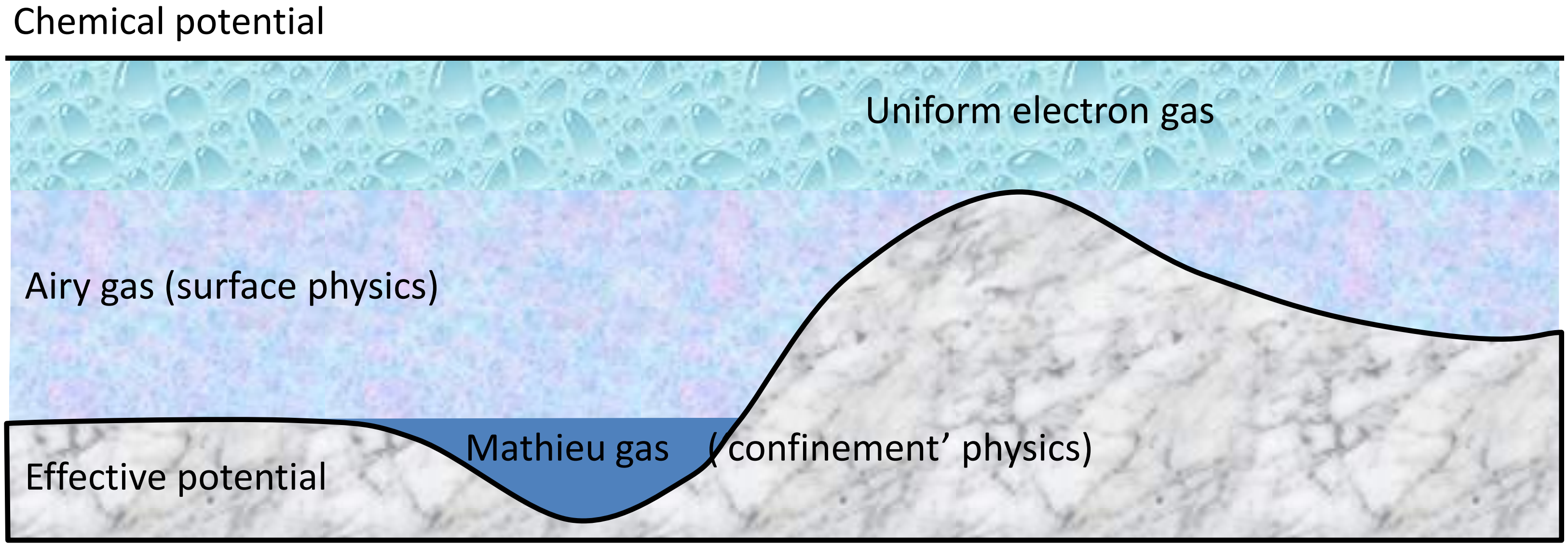
The Subsystem Functional (SSF) Scheme



How to make a general functional using the SSF scheme:

- One specialized SSF for each type of physics.
- An interpolation index to decide how much of each type of physics should be included in each point of the system.

Functional development

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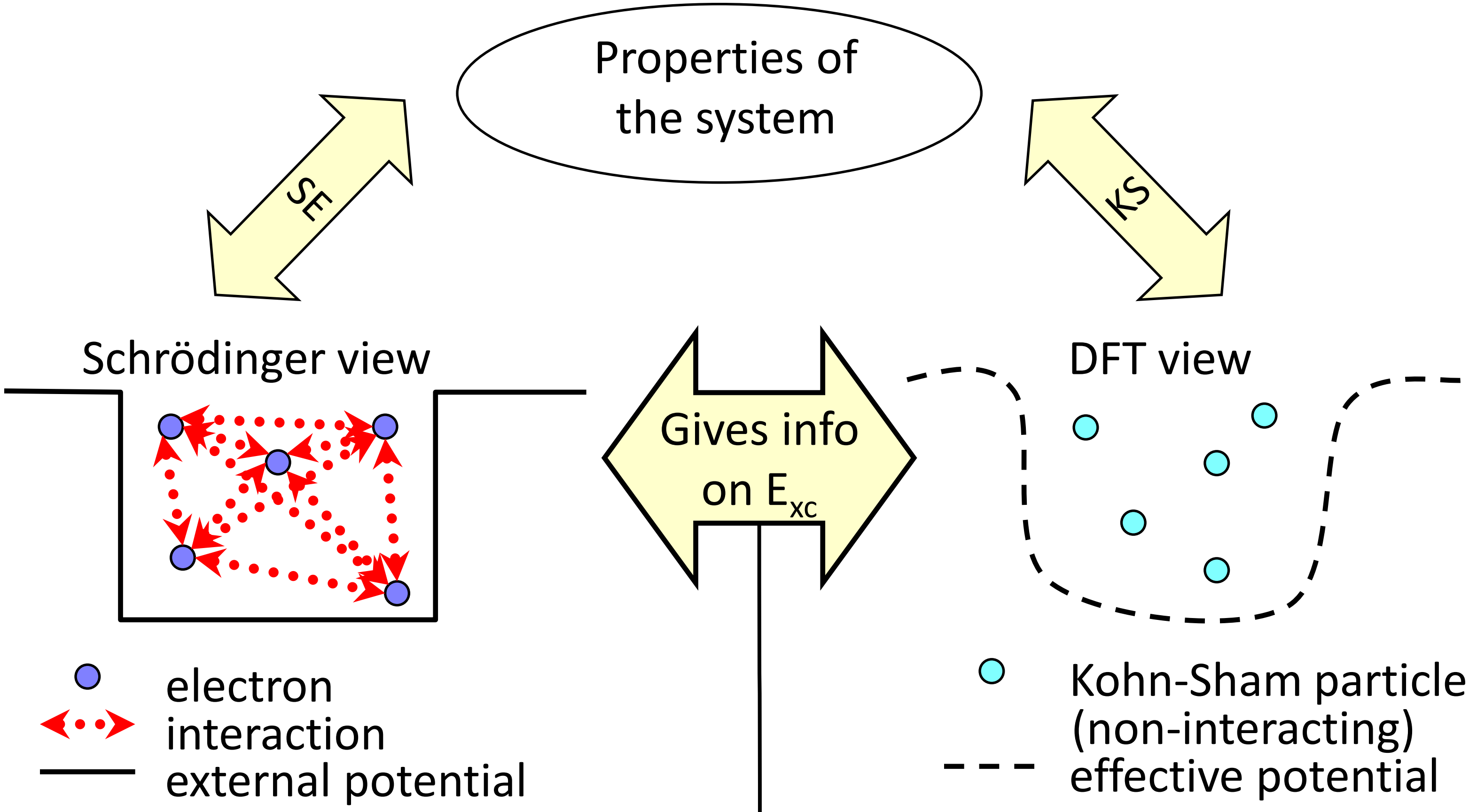

$$\mathrm{v}_{eff}(\boldsymbol{r}) = \mathrm{v}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}' + \boxed{\frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}}$$

Beyond LDA: Constraints vs Model systems

It was a large surprise that LDA worked so well.
Two views developed:

- LDA works because it fulfills a number of <u>constraints</u> that also the exact (or ‘divine’) functional fulfills. Led to Perdew’s way of constructing functionals, and GGA’s and other functionals in the Jacob’s ladder. Emphasis on improving exchange and correlation separately.
- LDA works because of the compatibility-based error cancellation attributed to its foundation on a <u>model system</u>: the uniform electron gas. Kohn transferred his belief in this explanation to me. Led to the subsystem functional scheme and AM05. Emphasis on the total, combined, exchange-correlation.

Jacob’s ladder

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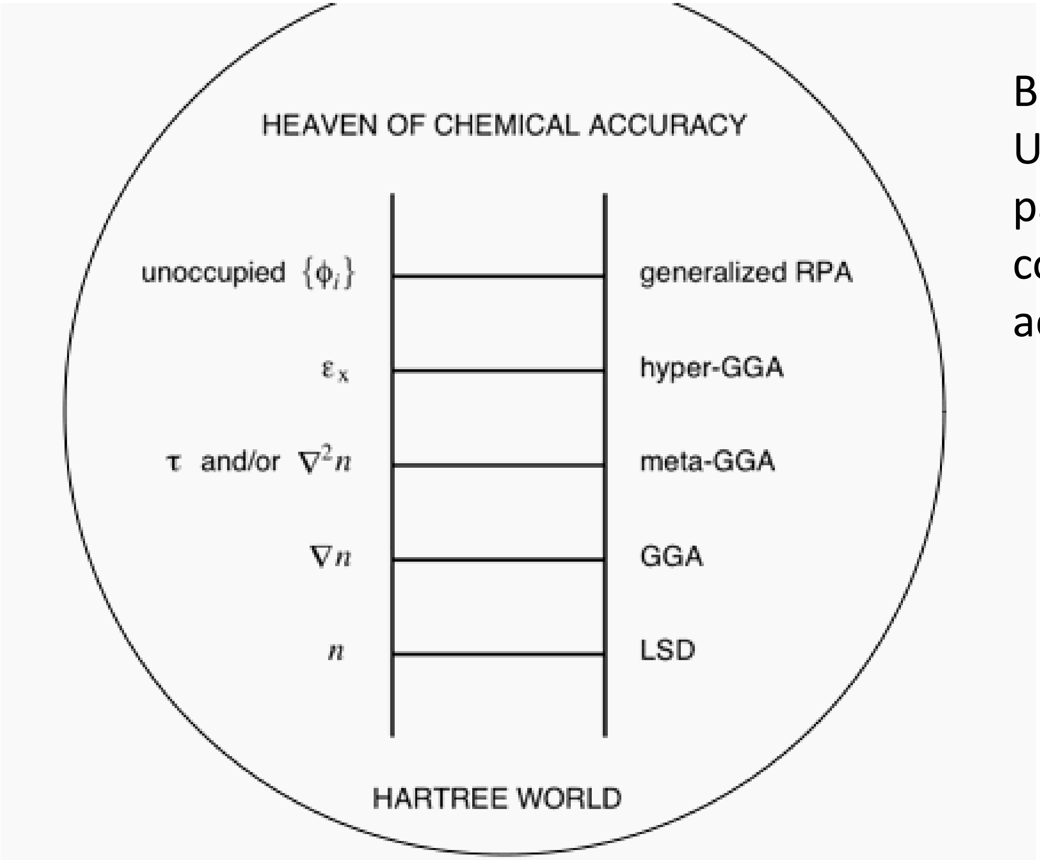

From Perdew et al. JCP 123, 062201 (2005).

Basic principle:
Use added density based parameters to fulfill more constraints and thus get a more accurate functional.

Compatibility: Using model systems

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Compatibility

Jellium surface exchange and correlation energies

Example: r_s=2.07 (Al)

	σ_x	σ_c	σ_{xc}
Exact	**2296**	**719**	**3015**
LDA	**2674**	**287**	**2961**
GGA	**2127**	**754**	**2881**

In erg/cm^2

(PBE)

LDA correlation constructed from remaining energy of the uniform electron gas.

Exchange-correlation functionals

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

The *exchange-correlation energy per particle*

is modeled in DFT.

LDA, GGA, meta-GGA, and AM05

Subsystem functionals

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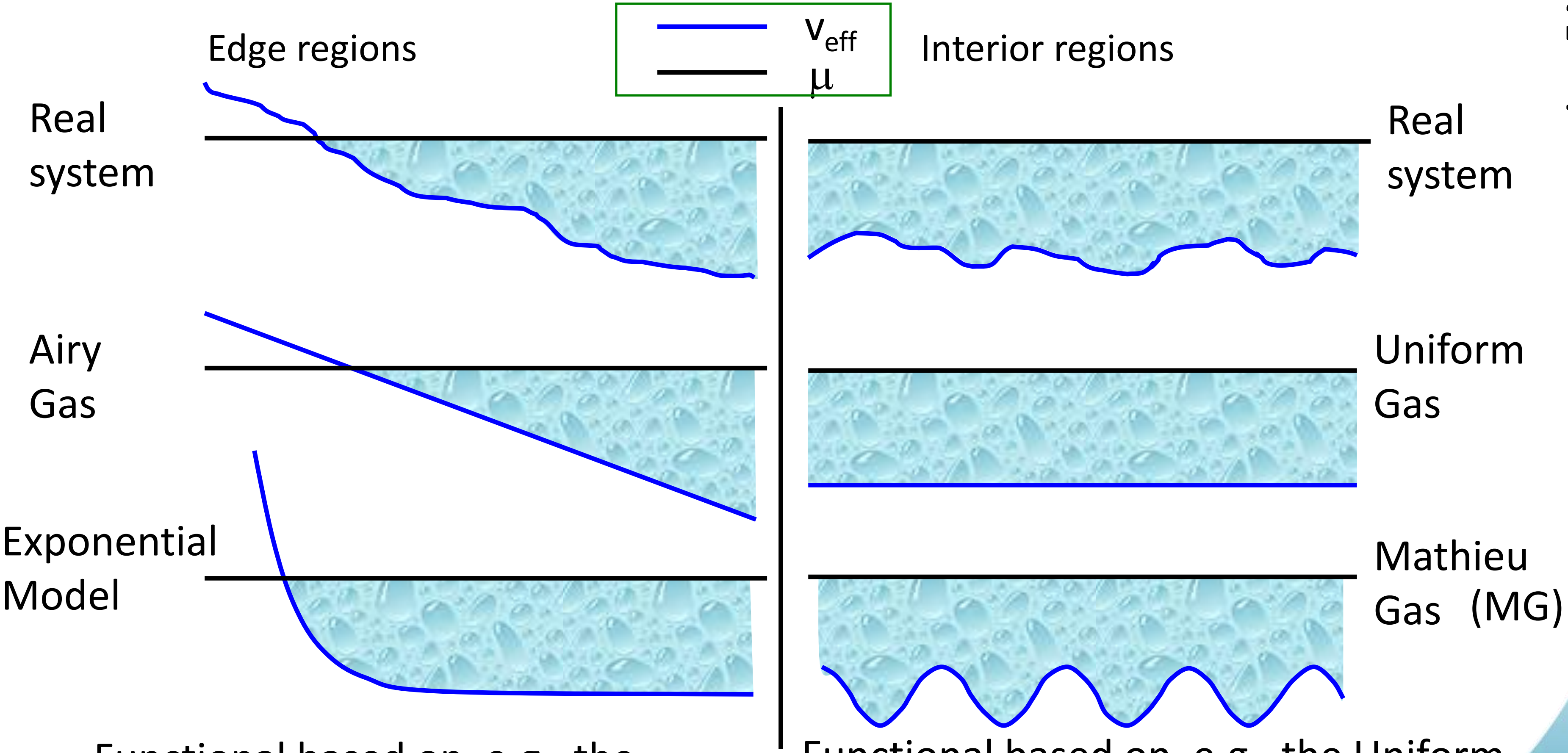


Edge regions

v_{eff}

μ

Interior regions

Real system

Airy Gas

Exponential Model

Real system

Uniform Gas

Mathieu Gas (MG)

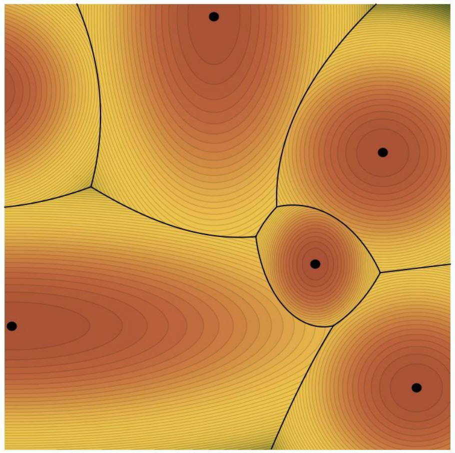
Functional based on, e.g., the Airy Gas captures specific surface physics.

Functional based on, e.g., the Uniform Gas captures specific 'deep sea' physics (LDA).

Summary

- Density Functional Theory based calculations have already proven to be important for developing Equation of State tables for use in Engineering codes.
- DFT calculations are routinely used in all of Materials Science.
- The achievable accuracy for DFT based calculations are fully determined by the quality of the exchange-correlation functional.
- The exchange-correlation functional needs to incorporate all essential many-body effects present in the system.
- The development of better functionals needs to be informed from theories outside of DFT.
- We need information about how density and energy are related.

- We need all help you can give us!



PBEsol vs AM05

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PBEsol: (PRL 2008)

Fulfills the gradient expansion of exchange.

Uses the "AM05 constraint" for correlation: Fitting the total exchange-correlation to jellium surface energies.

Argues that the important factor is the gradient expansion of exchange.

AM05: (PRB 2005)

Uses a surface system, the Airy Gas, for exchange.

Fits total exchange-correlation to another surface system, the jellium surface system.

We argue that the important factor is the consistent use of surface systems for the total exchange-correlation.

From our compatibility viewpoint, PBEsol and AM05 would give very similar results <u>for cases where surface effects are important.</u>

If gradient expansion was the key, PBEsol and AM05 would not give the same results.

Surface energies

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Surface energies for a number of metals

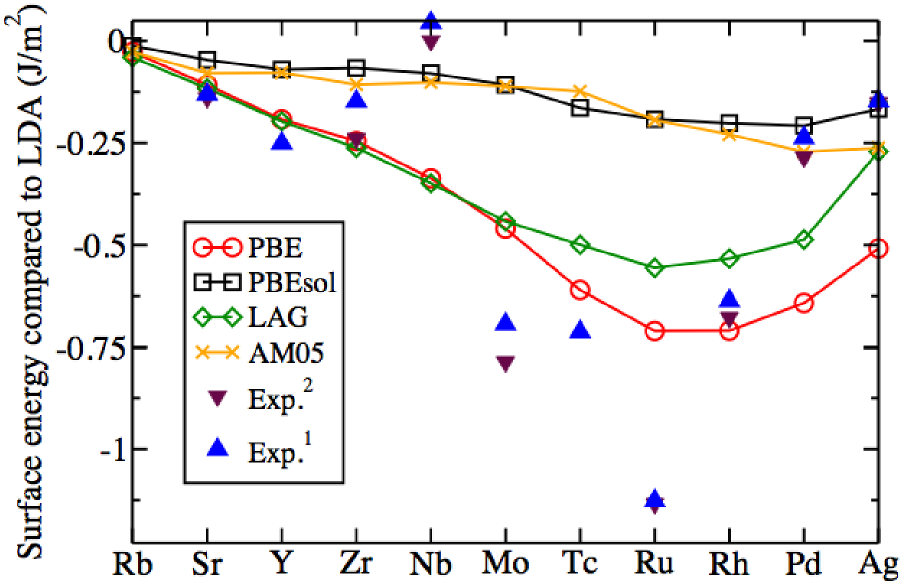

FIG. 1: (Color online) The effect of PBE (red circles), PBEsol (black squares), LAG (green diamonds) and AM05 (yellow crosses) gradient corrections on the LDA surface energies for Rb, Sr and 4*d* transition metals (in J/m^2). For comparison, the differences between the experimental surface energies (blue triangle up: Expt.^{1} Ref. [38]; maroon triangle down: Expt.^{2} [39]) and LDA values are also shown.

Ropo, Kokko, and Vitos, PRB 2008.

PBEsol and AM05 give the same surface energies

PBEsol gives very similar results as AM05 for most solids (Comment PRL 2008).

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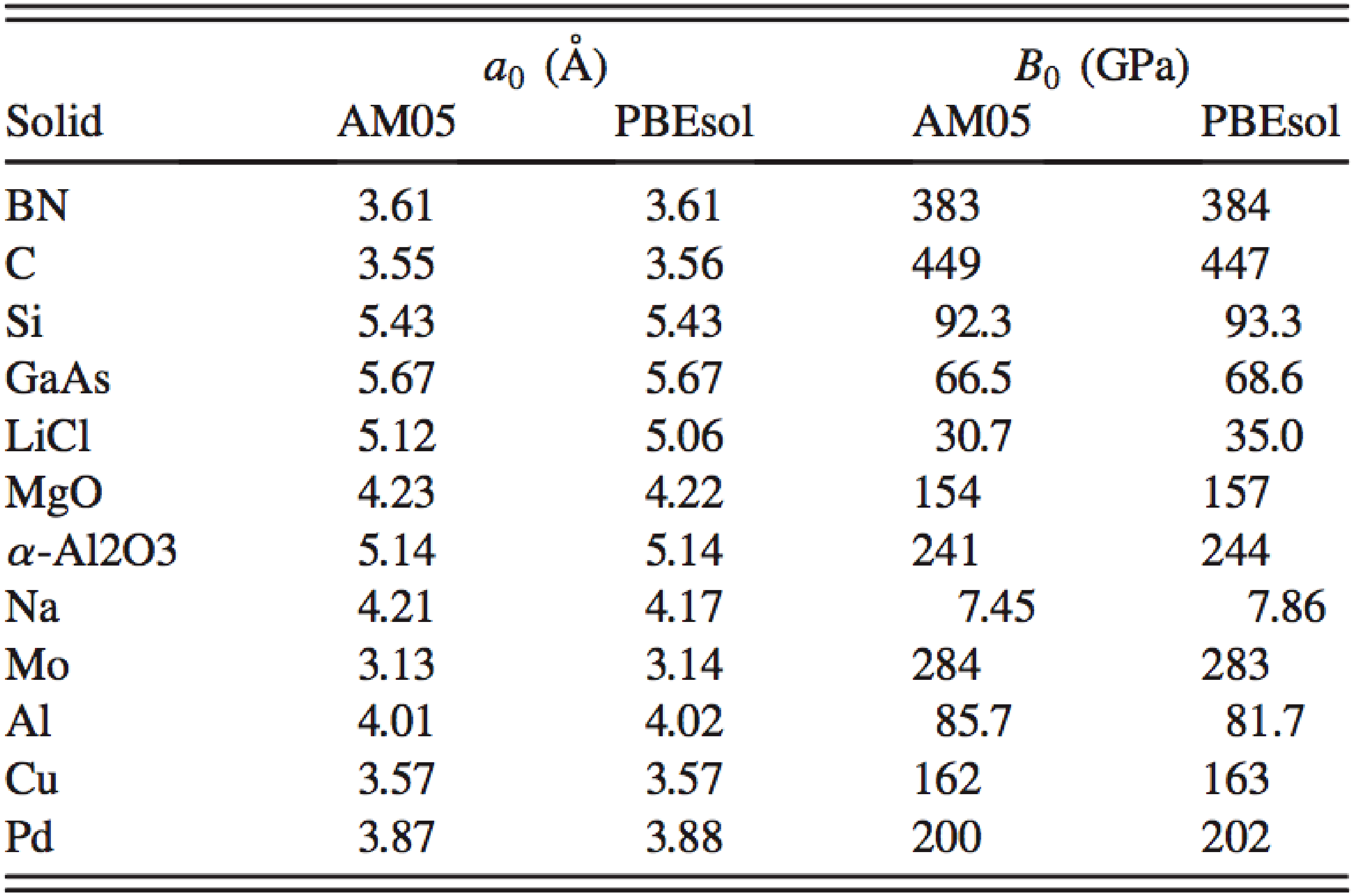

Solid	a_0 (Å) AM05	a_0 (Å) PBEsol	B_0 (GPa) AM05	B_0 (GPa) PBEsol
BN	3.61	3.61	383	384
C	3.55	3.56	449	447
Si	5.43	5.43	92.3	93.3
GaAs	5.67	5.67	66.5	68.6
LiCl	5.12	5.06	30.7	35.0
MgO	4.23	4.22	154	157
α-Al2O3	5.14	5.14	241	244
Na	4.21	4.17	7.45	7.86
Mo	3.13	3.14	284	283
Al	4.01	4.02	85.7	81.7
Cu	3.57	3.57	162	163
Pd	3.87	3.88	200	202

Extended list of examples available at
http://dft.sandia.gov/functionals/AM05.html

Why are AM05 and PBEsol giving so similar results?

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

exchange-correlation energy

exchange-correlation energy per particle

Two facts based on this formula:

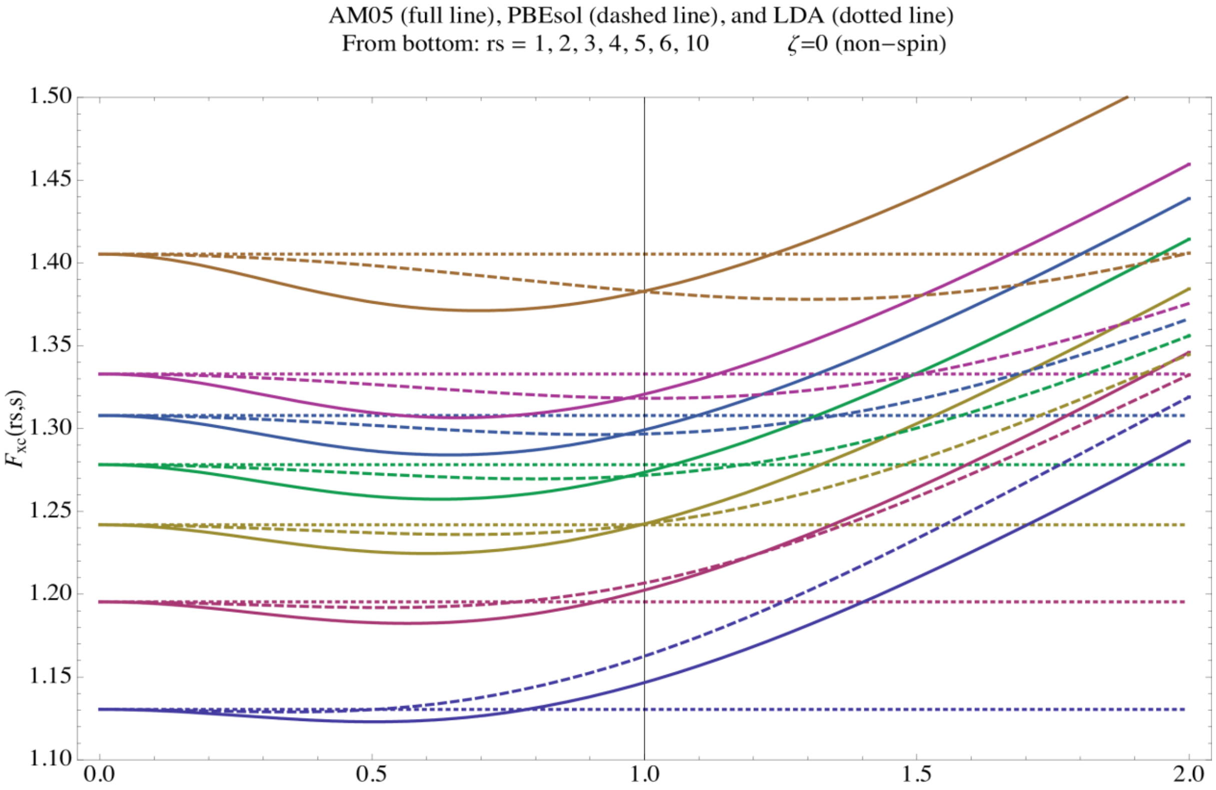
1) In every point, exchange and correlation per particle can be different as long as they add up to the total exchange-correlation energy per particle in this point. *"Alternative separation of exchange and correlation"* *(Published in PRB 68, 245120 (2003)).*

2) The exchange-correlation energy per particle can be different in every point as long as the integral gives the same total exchange-correlation energy.

Gradient expansion of exchange (used in PBEsol)
derived from "alternative definition of exchange".
(Discussed in PRB 66, 165117 (2002)).

Differences and similarities between PBEsol and AM05

Exchange built on different definitions, but total exchange-correlation energies the same for jellium surfaces.


AM05 (full line), PBEsol (dashed line), and LDA (dotted line)
From bottom: rs = 1, 2, 3, 4, 5, 6, 10 ζ=0 (non−spin)

$$\frac{\varepsilon_{xc}^{GGA}}{\varepsilon_{x}^{LDA}}$$

LDA (s=0)

s=dimensionless gradient

F_{xc} of AM05 and PBEsol no more similar than PBEsol and LDA (and PBEsol does <u>not</u> give similar results as LDA)

PBEsol and AM05 are locally different but globally similar.

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When do we have relativistic effects?

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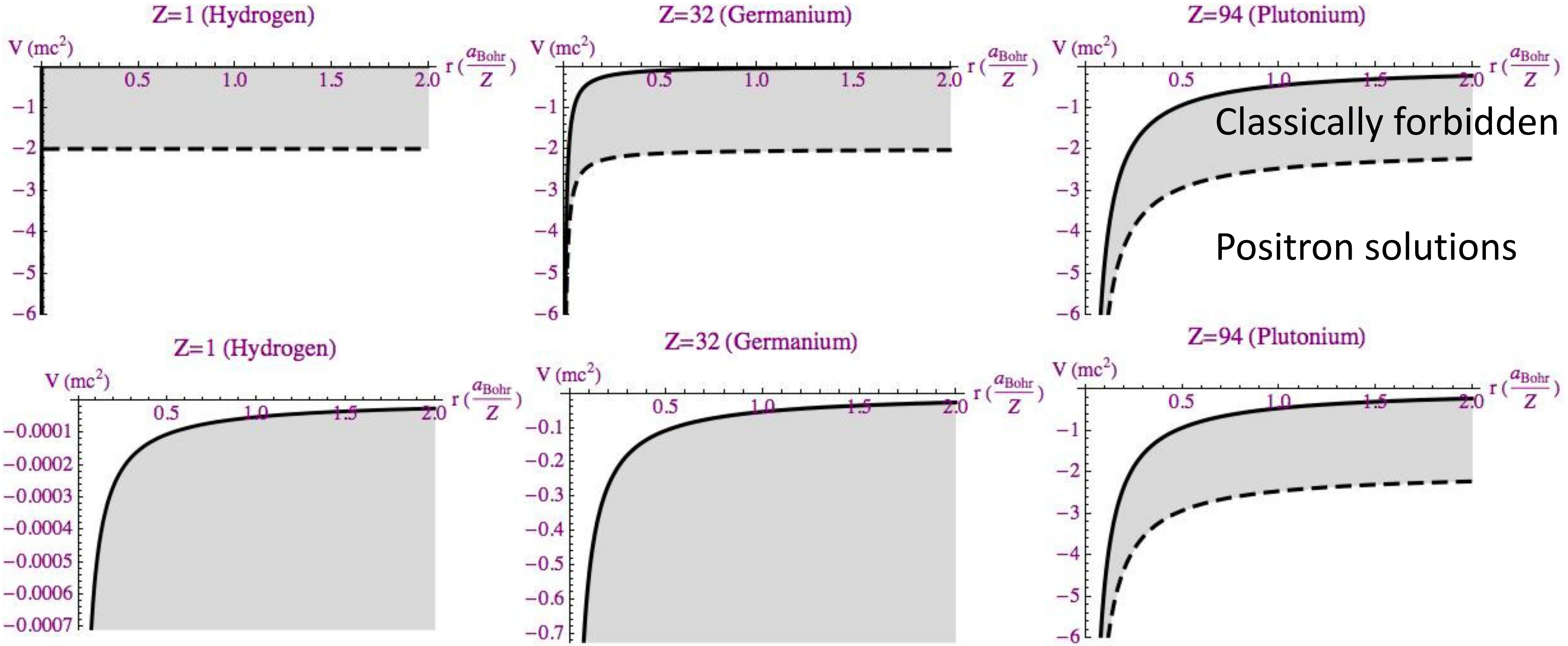
Non-relativistic limit is: $$|E_n^{(NR)} - V_{eff}(\boldsymbol{r})| << 2mc^2$$



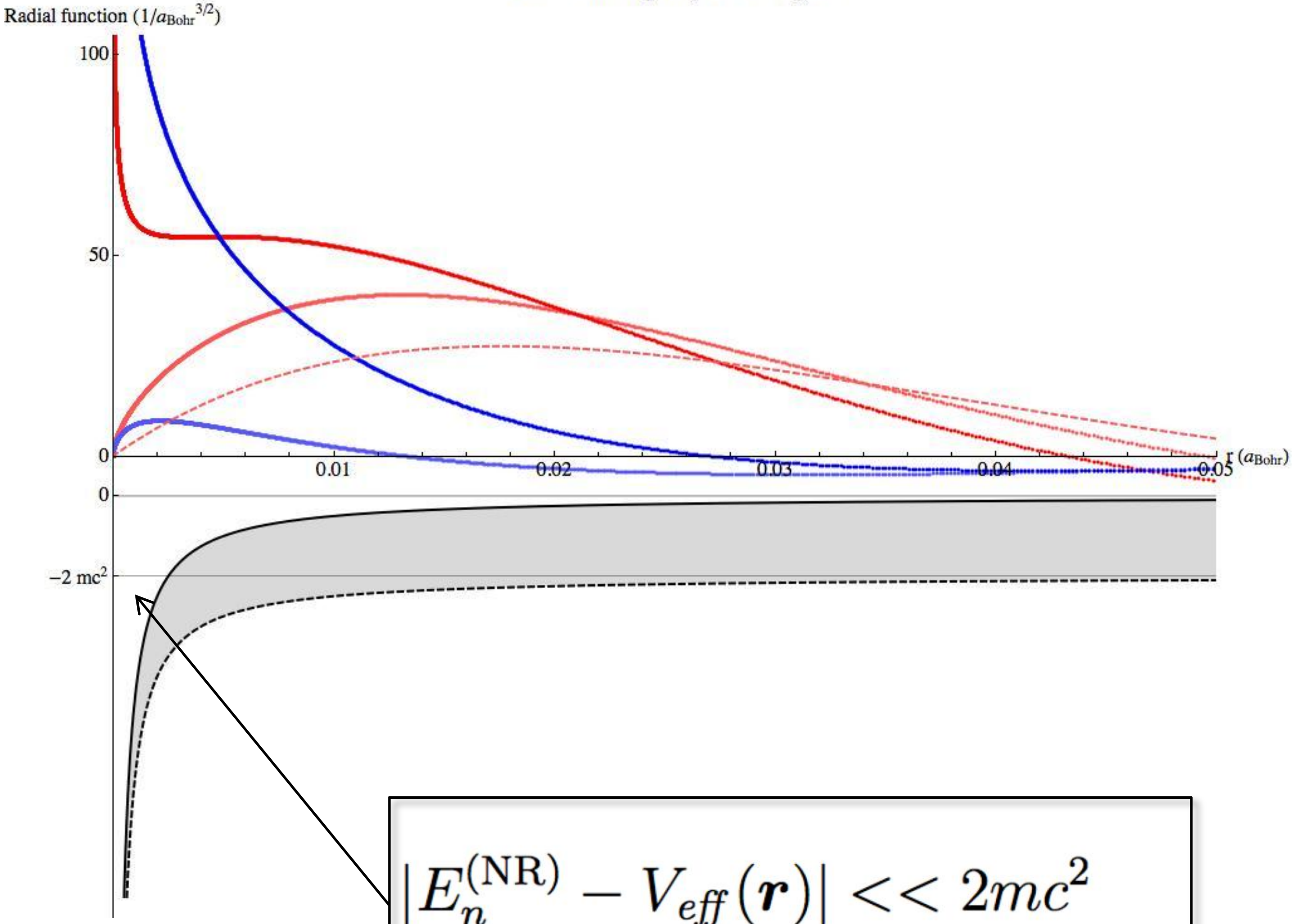
Electron solutions

Classically forbidden

Positron solutions

Violated near nuclei for high Z materials.

The $p_{1/2}$ states (κ=1) and potential



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.

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

violated

Dirac Equation:
Relativistic Kohn-Sham equations

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$$\left(c\,\boldsymbol{\alpha}\cdot\left(\boldsymbol{p}-\frac{e\boldsymbol{A}_{\mathit{eff}}}{c}\right) + \begin{pmatrix} I & 0\\ 0 & I\end{pmatrix} V_{\mathit{eff}}(\boldsymbol{r}) + \beta\, m c^2 \right)\psi_n(\boldsymbol{r}) = E_n\,\psi_n(\boldsymbol{r})$$

$$V_{\mathit{eff}}(\boldsymbol{r}) = -e\left(A^0_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{J^0(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^\mu]}{\delta J^0(\boldsymbol{r})}\right)$$

$$e\boldsymbol{A}_{\mathit{eff}}(\boldsymbol{r}) = -e\left(\boldsymbol{A}_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{\boldsymbol{J}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^\mu]}{\delta \boldsymbol{J}(\boldsymbol{r})}\right)$$

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k\\ \sigma_k & 0\end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0\\ 0 & -I\end{pmatrix} \qquad I = \begin{pmatrix} 1 & 0\\ 0 & 1\end{pmatrix} \qquad \psi_n = \begin{pmatrix} \psi_{1,n}\\ \psi_{2,n}\\ \psi_{3,n}\\ \psi_{4,n}\end{pmatrix}$$

2x2 Pauli Matrices

$$J^\mu = (J^0, \boldsymbol{J}) = -e\sum_n \left(\psi_n^\dagger\psi_n,\ \psi_n^\dagger\boldsymbol{\alpha}\,\psi_n\right)$$

Summary

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- Present exchange-correlation functionals fail to give correct equilibrium structure of CuO from DFT calculations.
- This failure is connected to errors due to an incorrect description of the physics for regions with highly localized electrons (high ELF).
- We have presented a confinement error correction scheme to quantify and correct for these errors. The main ingredients of the scheme are the electron localization function (ELF) and the Harmonic Oscillator (HO) model system.
- The scheme has been applied to the CuO system, and a promising trend of improvement for the equilibrium structure calculation of CuO is shown.
- We are working on a general functional that would allow us to incorporate the confinement physics of the HO model system in a self-consistent way.

Thank you for your attention.

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Rational Compound Design

- Finding a non-peptidic inhibitor

PHYSICAL
REVIEW
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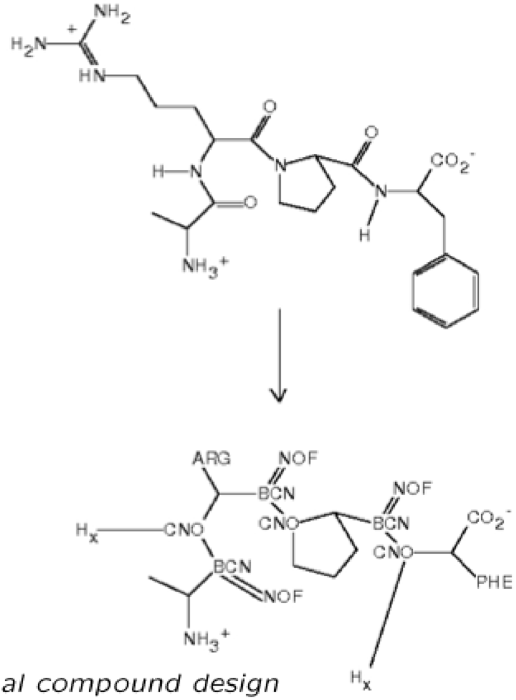
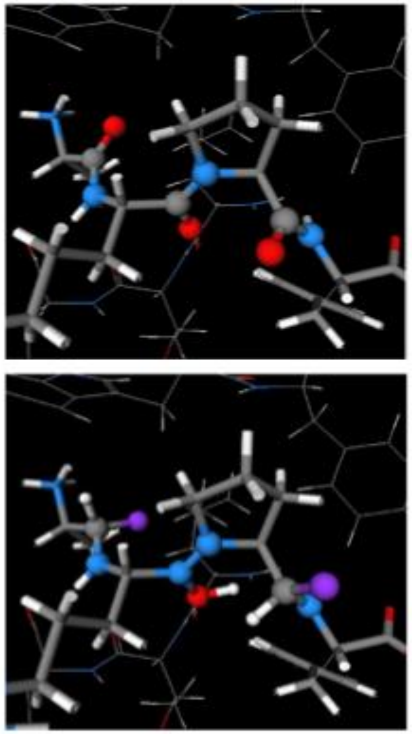
7 October 2005

Volume 95, Number 15

APS Published by The American Physical Society





Variational particle number approach for rational compound design

OAvL, R. Lins, U. Rothlisberger, *Phys Rev Lett* **95** 153002 (2005)

Crucial to have first principles methods that gives the right trends so that a target property can be calculated as a function of chemical composition. Note that new, previously unknown, compounds need ab initio methods.

DFT calculations of CuO structure

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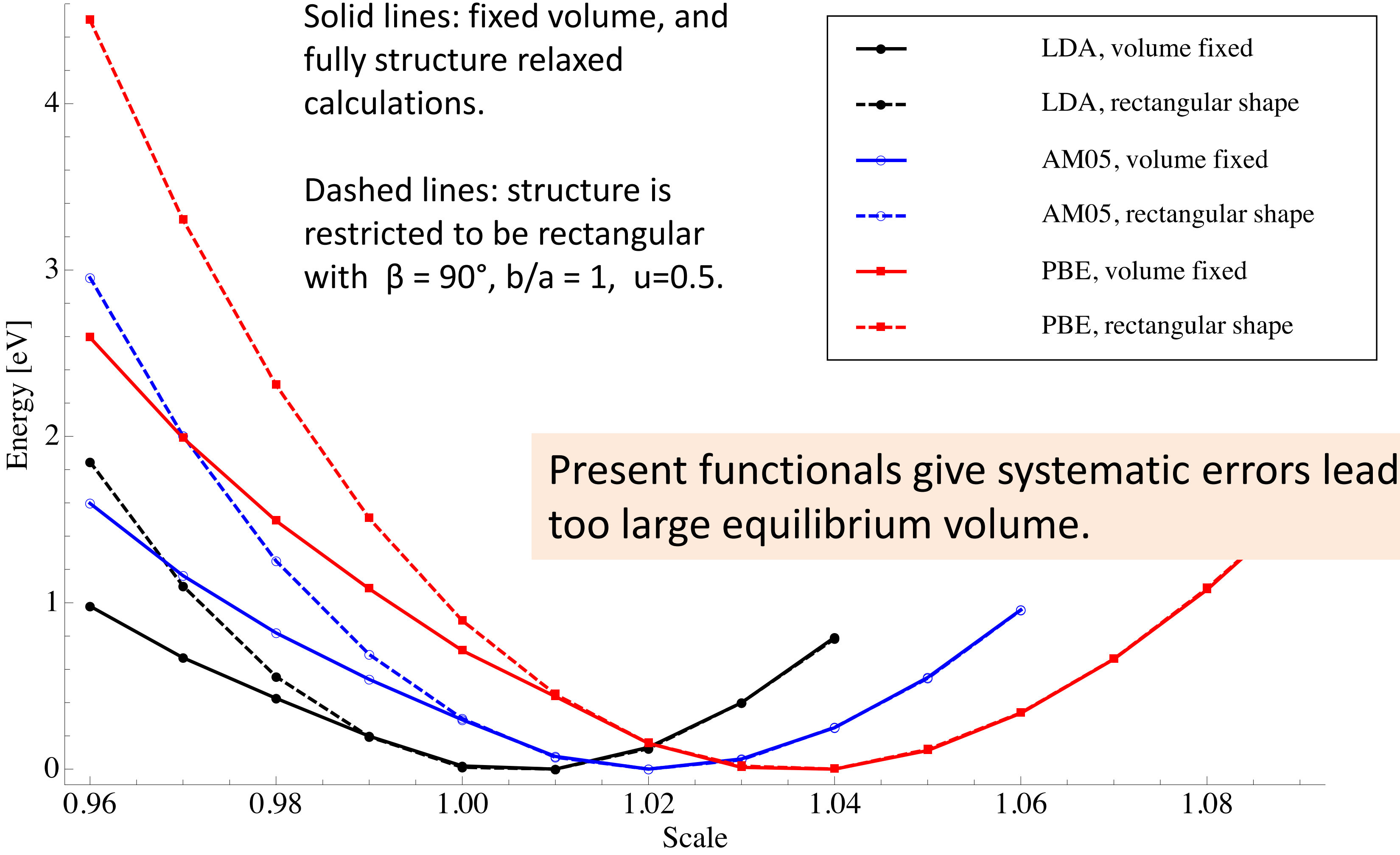


Solid lines: fixed volume, and fully structure relaxed calculations.

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

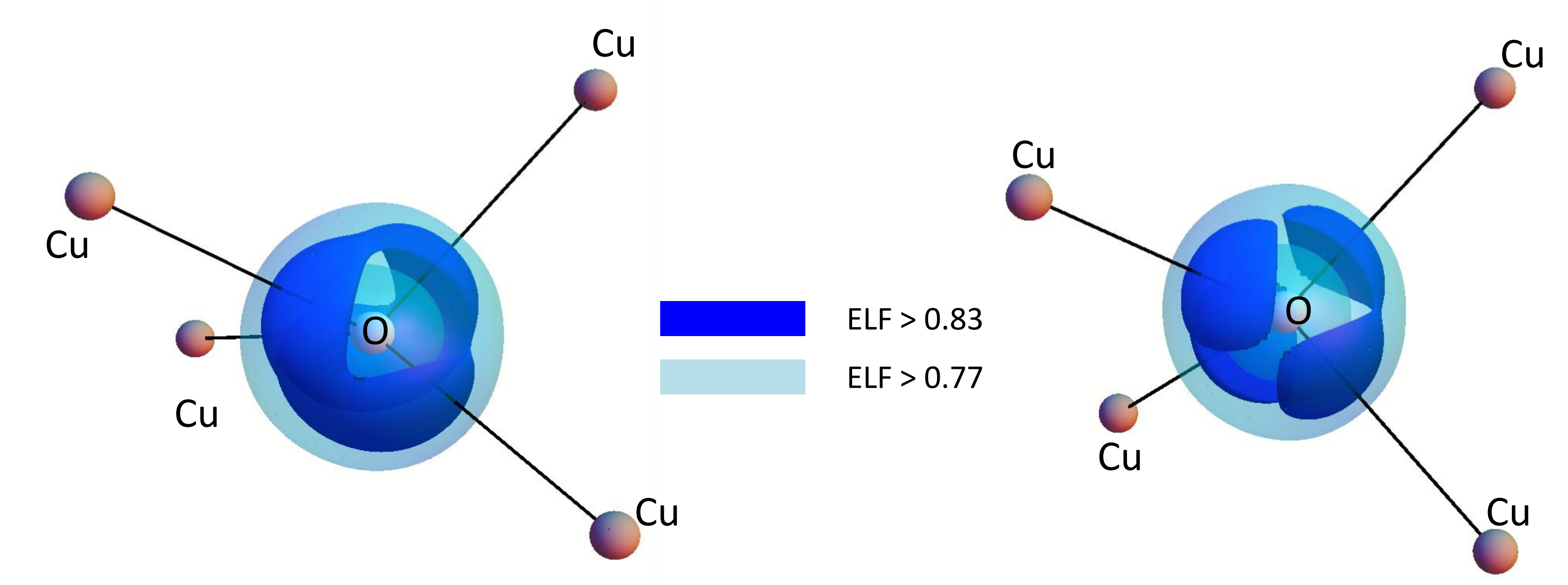
V_0 is the lattice volume of the experimental structure

Electron localization function (ELF)

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

Ann E Mattsson

ELF ≈ 1/2: uniform electron gas like
ELF ≈ 1: strong localization



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

Rectangular structure with the same volume as the left one but with c/a = 1.23, b/a=1, β=90°, u=0.5

Note: High ELF regions are around the oxygen atoms.