The *f*-electron Problem: Approach to Improving Accuracy of Density Functional Theory for Actinide Materials

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Modeling and simulation of Nuclear Energy related systems: Science based engineering

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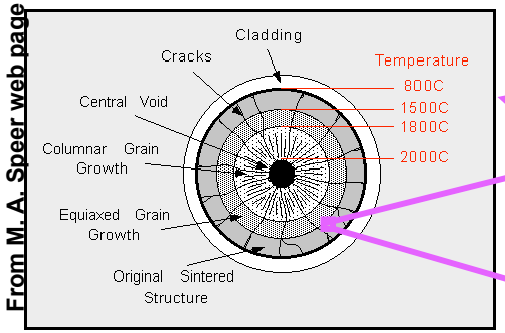
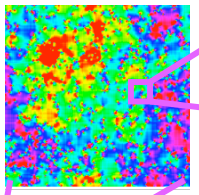
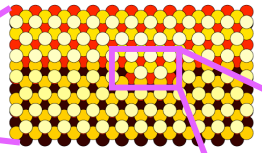


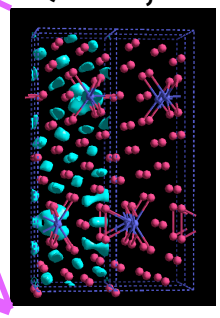
dislocation scale (μm, ms)





atomic scale (100 nm, μs)

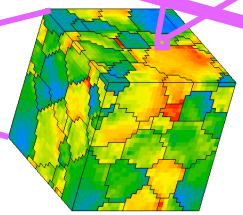
VASP, RSPt, Quest, Socorro



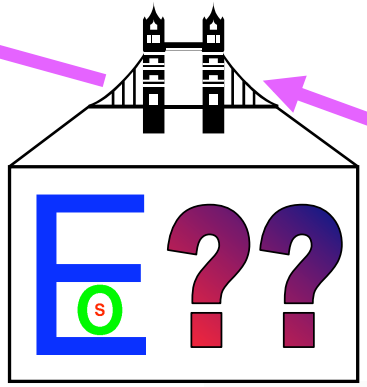
electronic scale (nm, ps)

E_{xc}

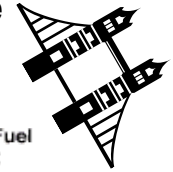
Schrödinger Equation

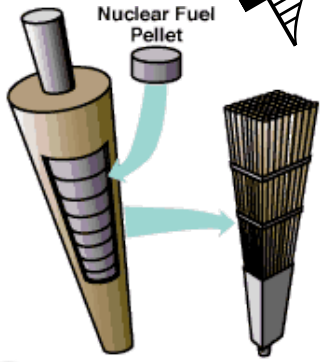


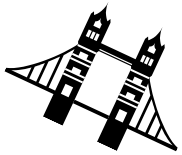
grain scale (100 μm, 10^3 s)



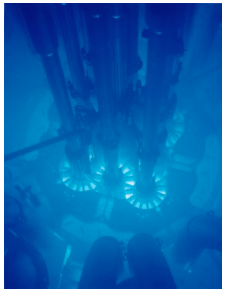
component scale (cm, days)

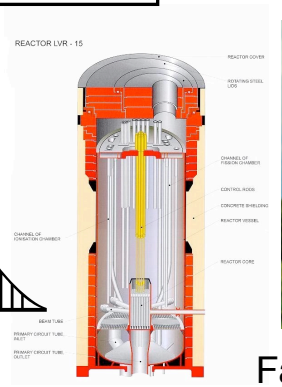






system scale (dm, years)





Facility scale (m, many years)

Courtesy of TXU

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Predictive DFT calculations for EOS construction: Example of Xe

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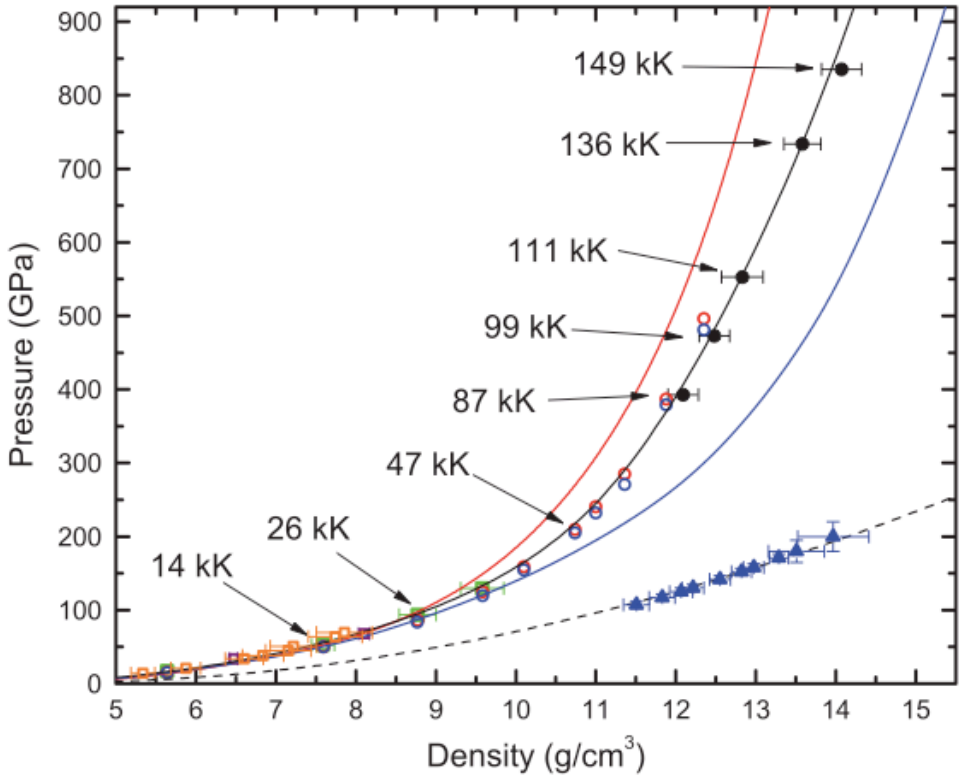

FIG. 3 (color). P-ρ Hugoniot plot. Lines and symbols as in Fig. 2. Black dashed line, 5191 298 K isotherm; blue triangles, solid xenon compression data [17]. Also indicated are Hugoniot temperatures calculated using 5191. Our DFT calculated isotherm [37] agrees with the experimental data [17].

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).

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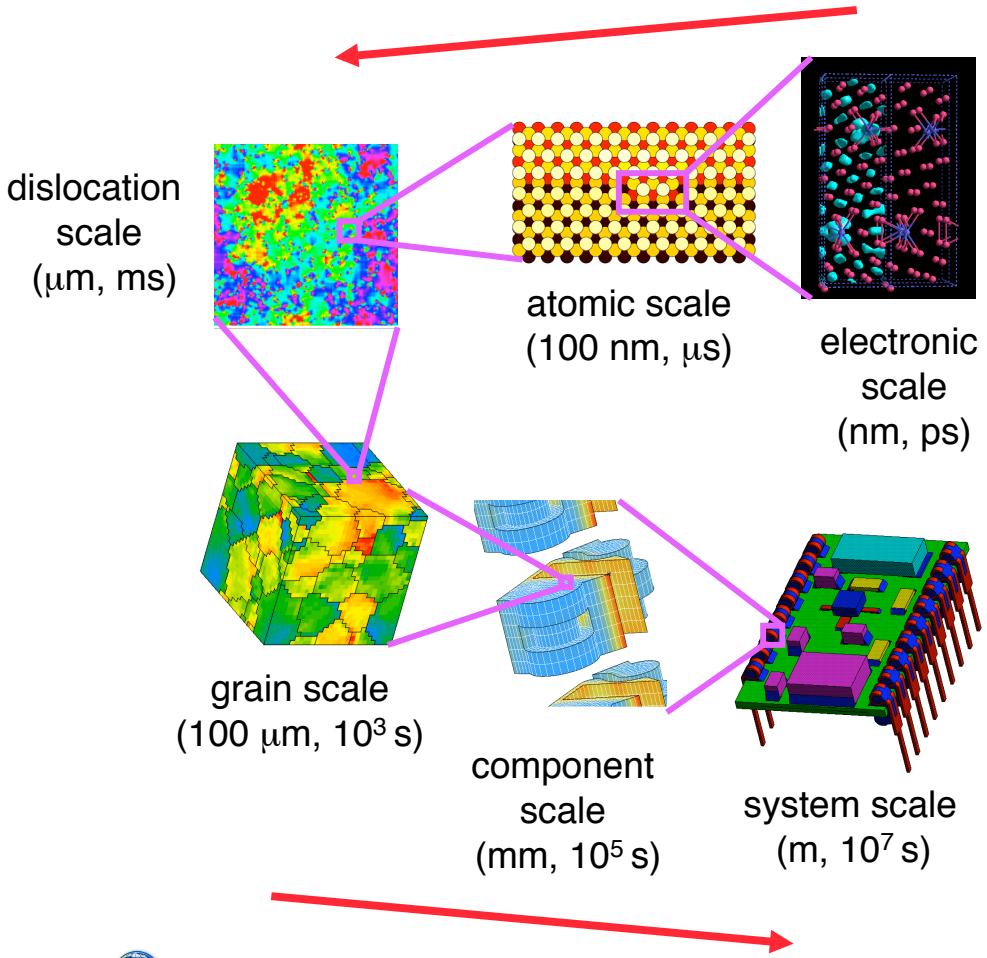
Density Functional Theory: The Underpinning of Predictive Multi-scale Efforts

Ann E. Mattsson



- Goal: Predict how materials age and perform under normal, adverse and extreme conditions.
- Method: Bridge length and time scales by using results from each scale as input on the next scale.
- Foundation: To get the fundamental processes right via DFT calculations at the electronic scale.
- Examples: DFT based EOS for continuum simulations. DFT investigations of Si and GaAs defects important for electronics modeling.

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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. In this talk I will focus on actinides. I am leading the effort at Sandia to improve DFT for this class of materials.

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

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

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

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. See for example Chris Stanek's and Enrique Batista's talks.

When do we have relativistic effects?

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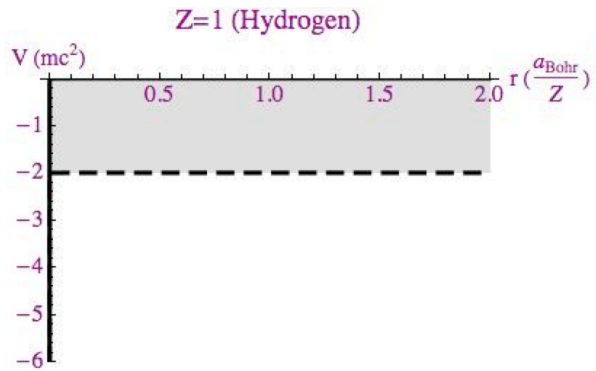
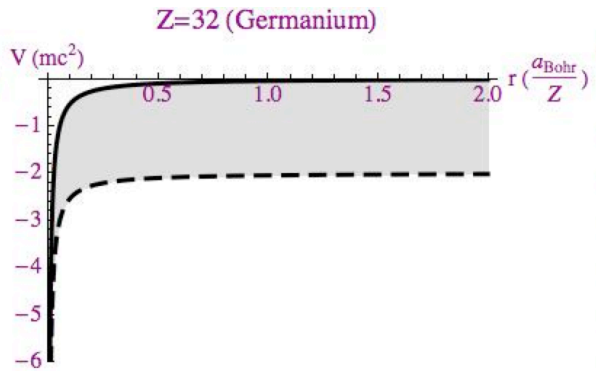
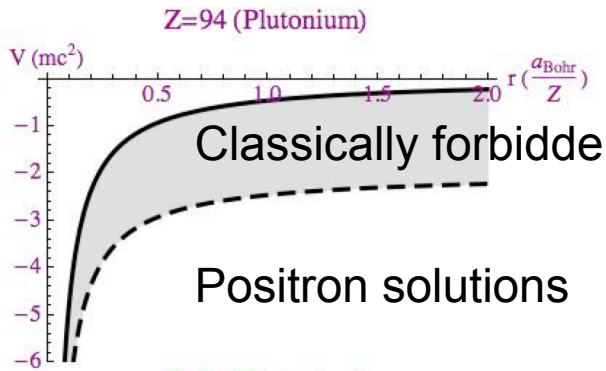
$$|E_n^{(\mathrm{NR})} - V_{eff}(\boldsymbol{r})| > 2mc^2$$

Electron solutions

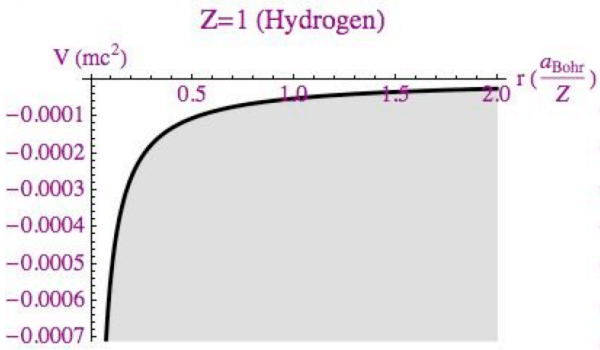


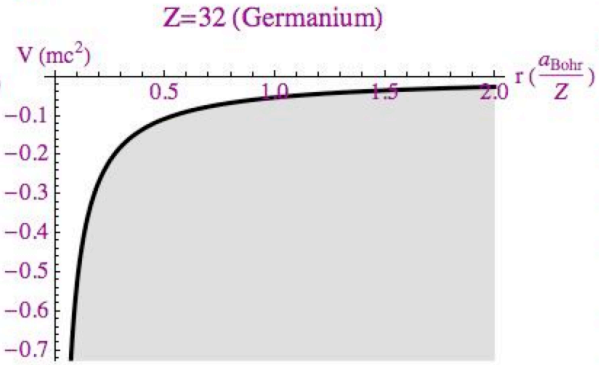


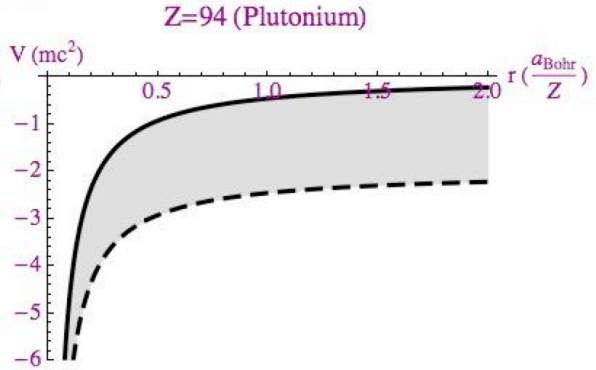


Classically forbidden

Positron solutions







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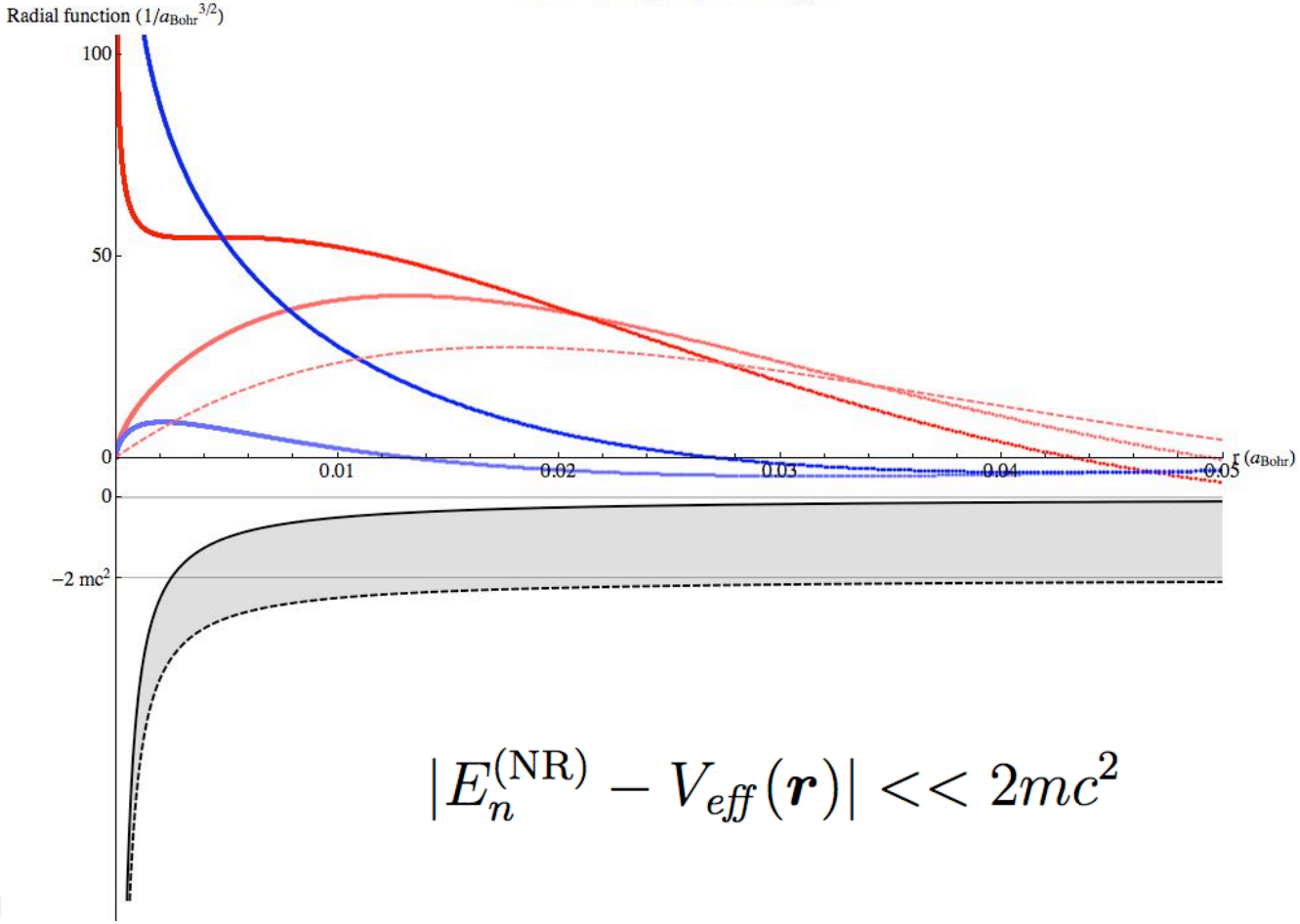
The $p_{1/2}$ states (κ=1) and potential

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.



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

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Relativistic Kohn-Sham equations: Functionals

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

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

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

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

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.

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Approximate Dirac for spin density functionals

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

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

$$\mu_B \boldsymbol{B}_{eff}(\boldsymbol{r}) = \left(\mu_B \boldsymbol{B}_{ext}(\boldsymbol{r}) + \int d^3r' \frac{\boldsymbol{M}(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|} + \frac{\delta E_{xc}[J^0, \boldsymbol{M}]}{\delta \boldsymbol{M}(\boldsymbol{r})} \right)$$

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

Now ordinary DFT spin functionals can be used.

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Relativity

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Summary:

• I discuss this 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 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.

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Relativity

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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?

I am working together with John Wills (LANL) and Torey Semi (CSM) to answer these questions.

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

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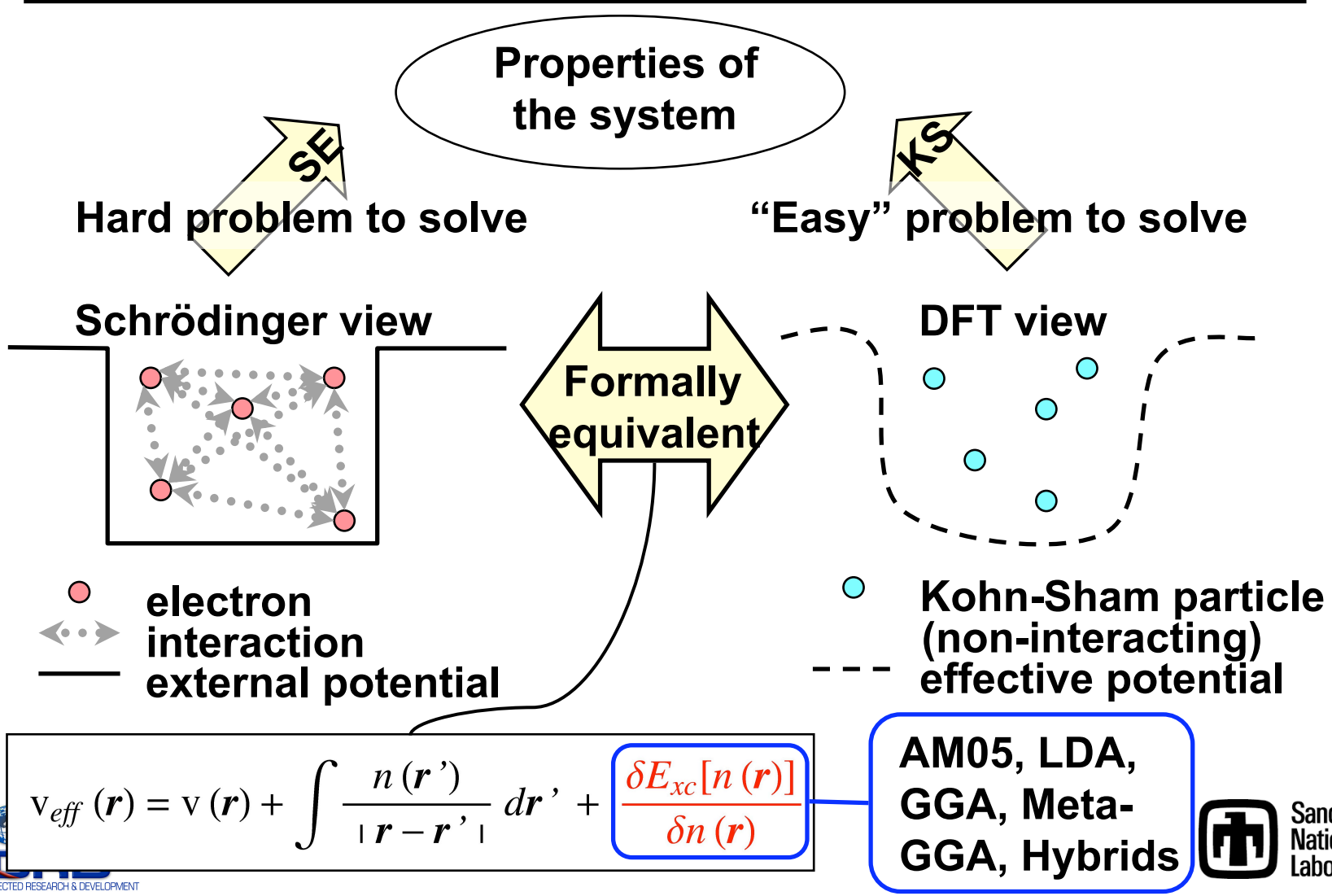
DFT and functionals



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Subsystem functionals

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From
general purpose functionals
to
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

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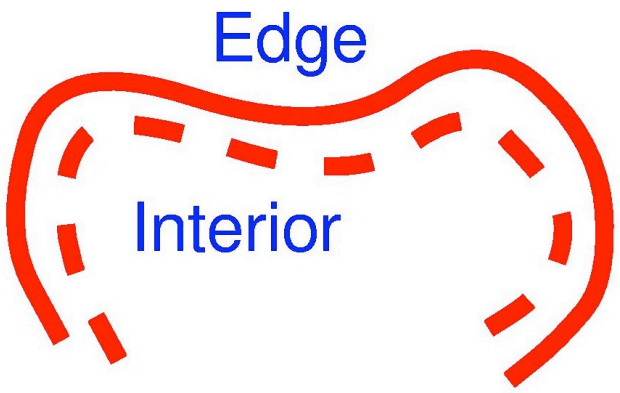
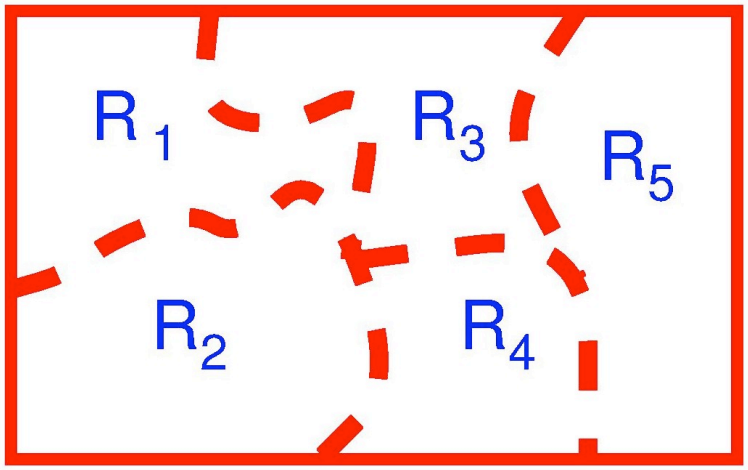
Subsystem functionals

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.

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The LDA functional

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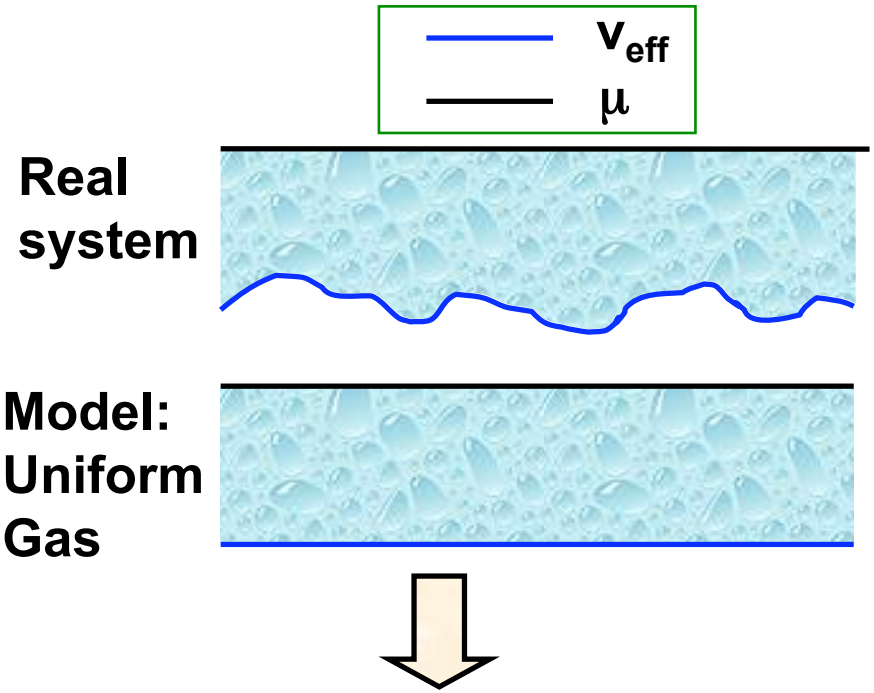

LDA
(exchange and correlation)

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).

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

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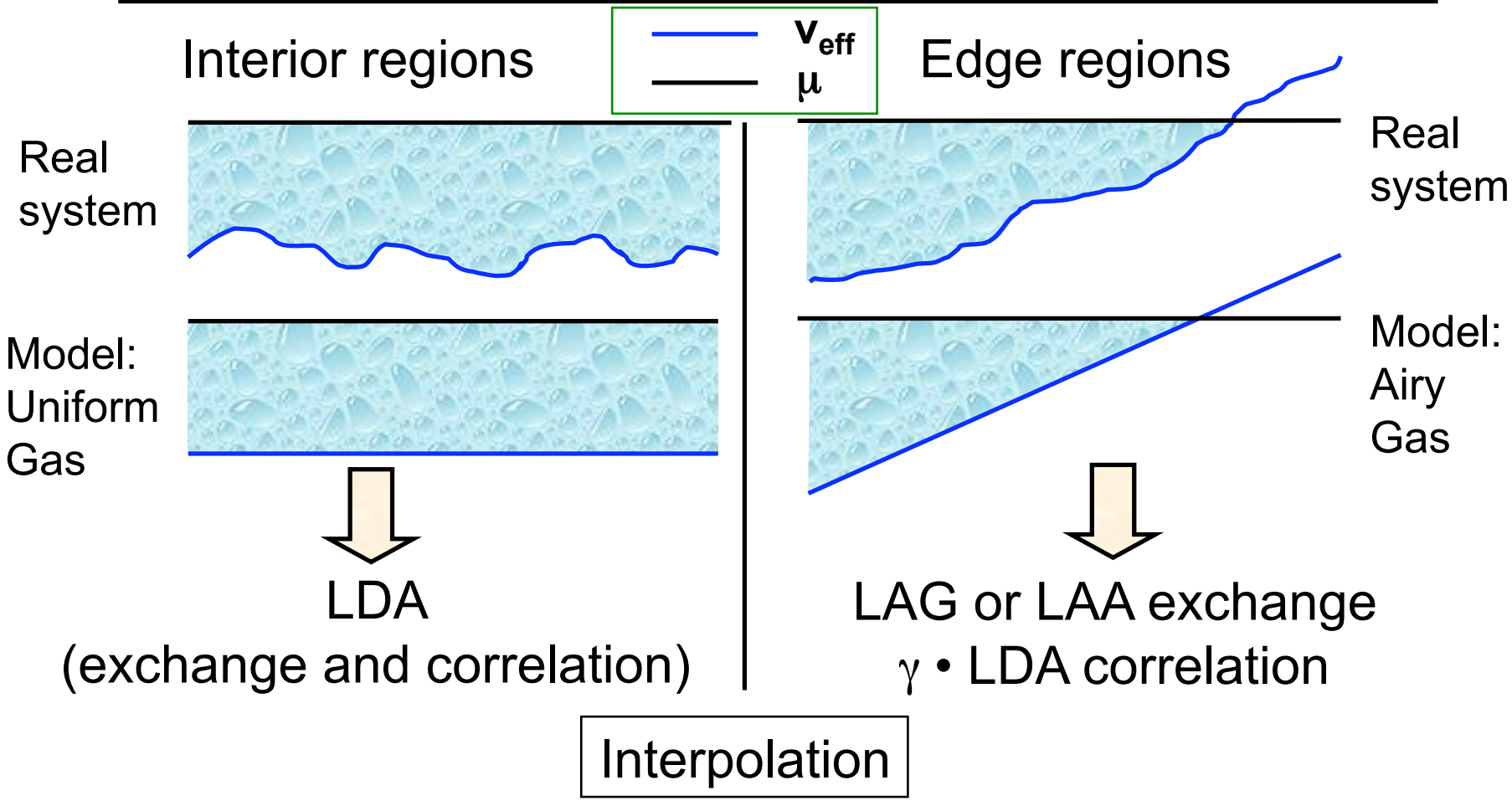

Interpolation

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

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AM05 is as accurate as a hybrid, but much faster

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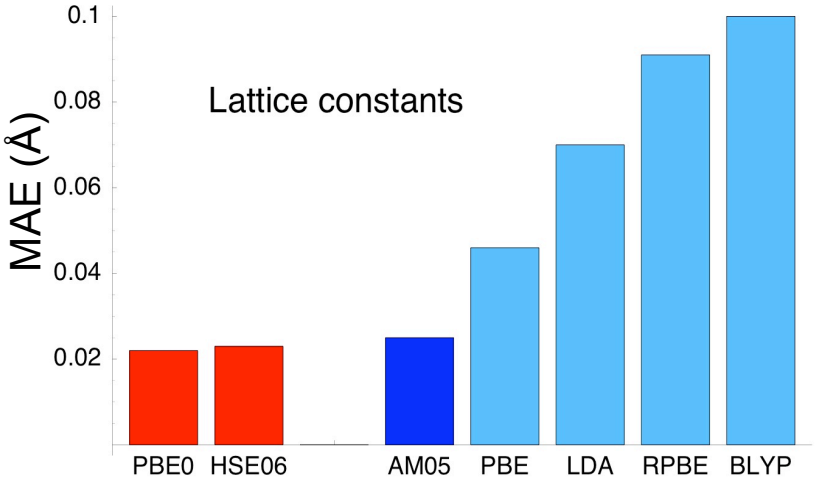
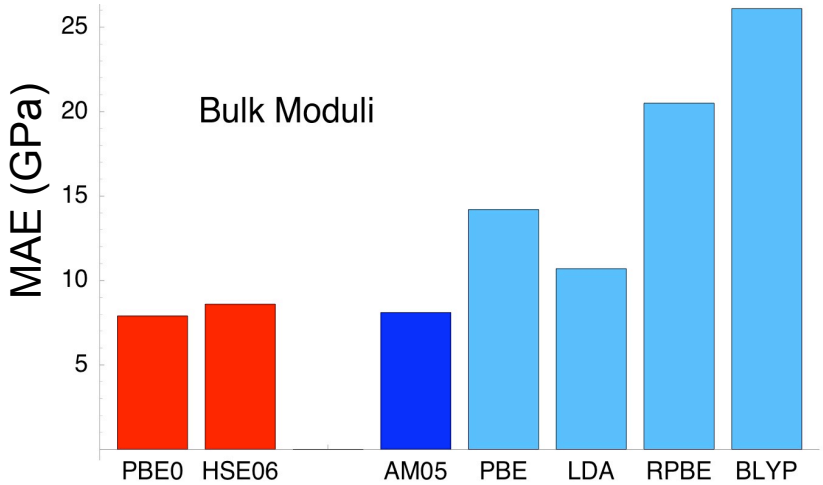
JCP **128**, 084714 (2008)

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.

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A functional for confined and van der Waals' systems

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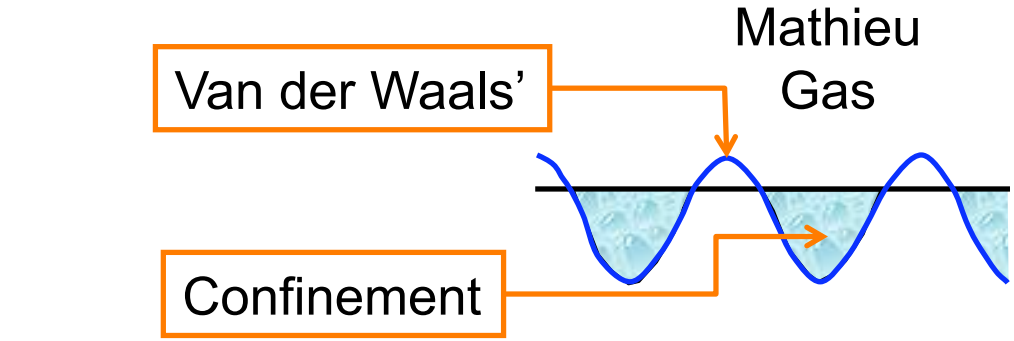
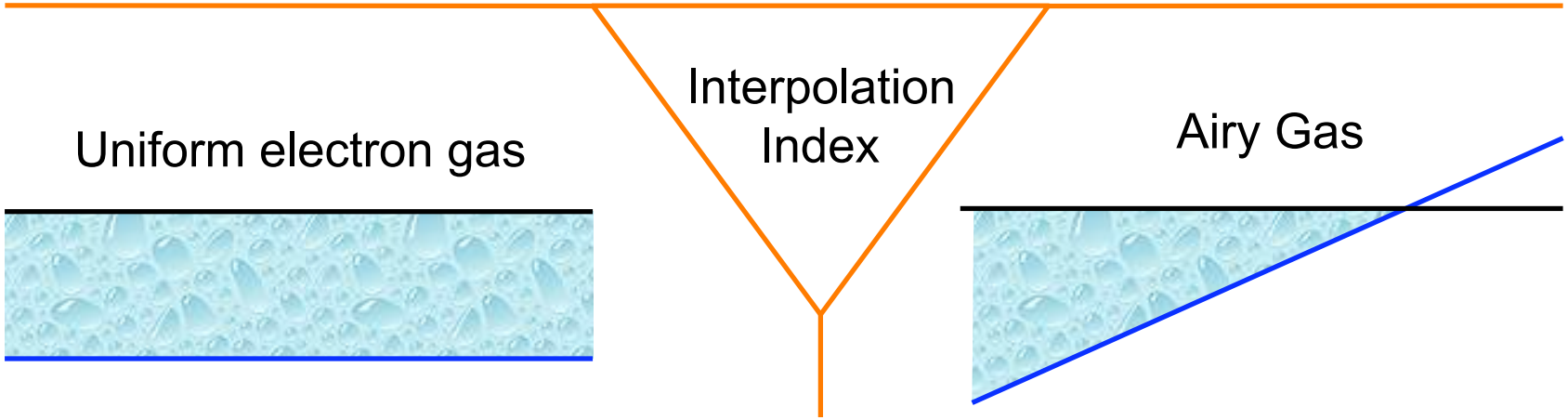


We are investigating the Harmonic oscillator limit of the MG. Hao, Armiento, Mattsson, PRB **82**, 115103 (2010).



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).

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A functional for confined systems via the subsystem functional scheme

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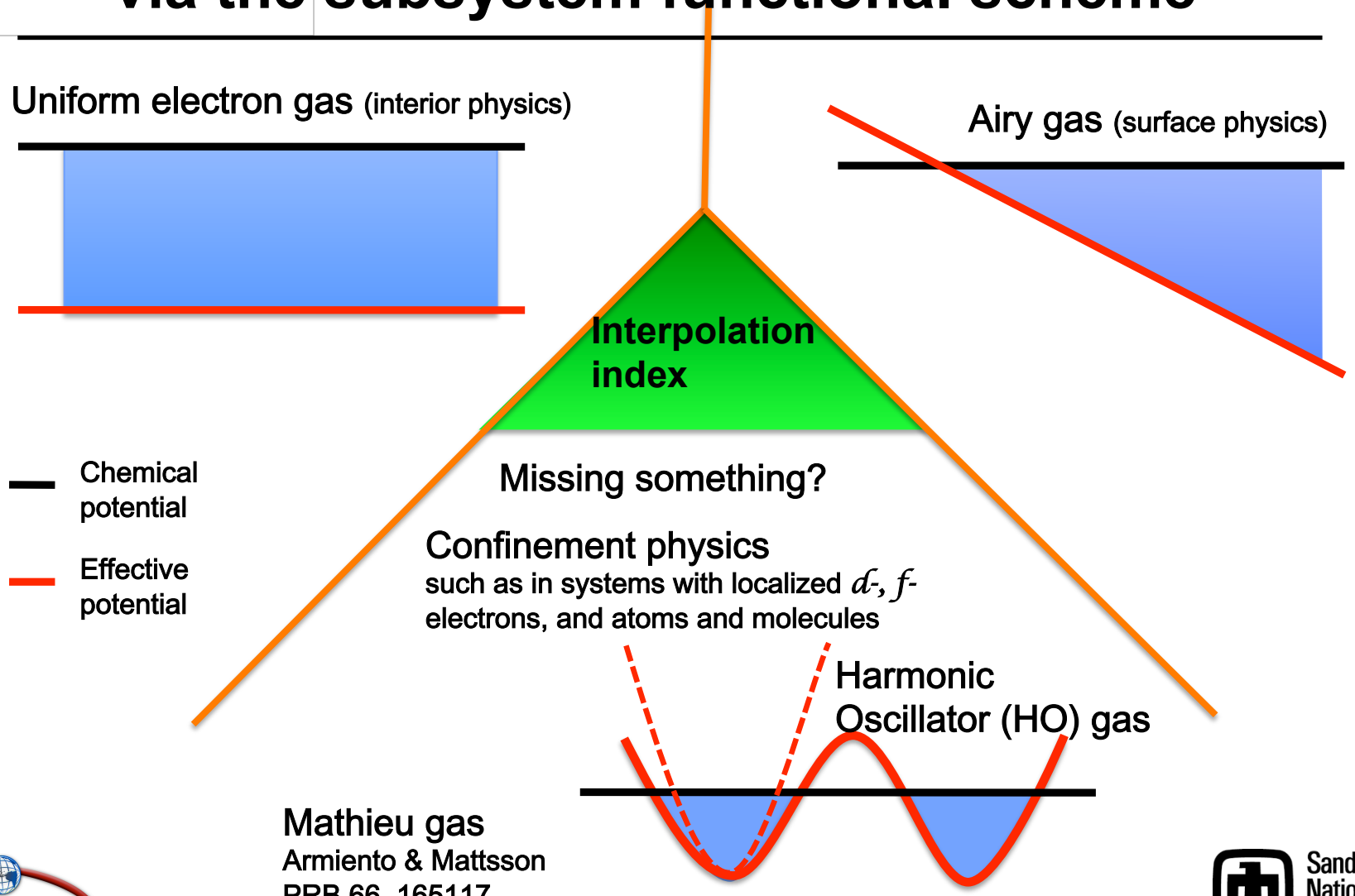

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Harmonic Oscillator (HO) gas

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KS equation

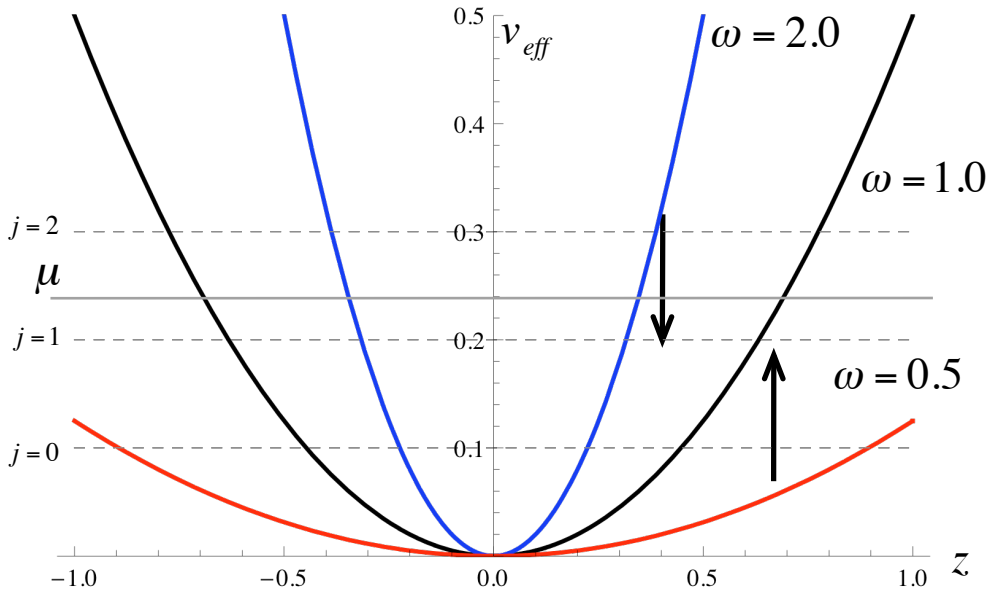
$$\left(-\frac{1}{2}\nabla^2 + \frac{\omega^2}{2}z^2\right)\psi_\nu(\vec{r}) = E_\nu\psi_\nu(\vec{r})$$

Effective potential

If we set

$$l = \frac{1}{\sqrt{\omega}},\ \bar{z} = z/l$$

HO gases with different potential strength fall into one representation



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Harmonic Oscillator (HO) gas

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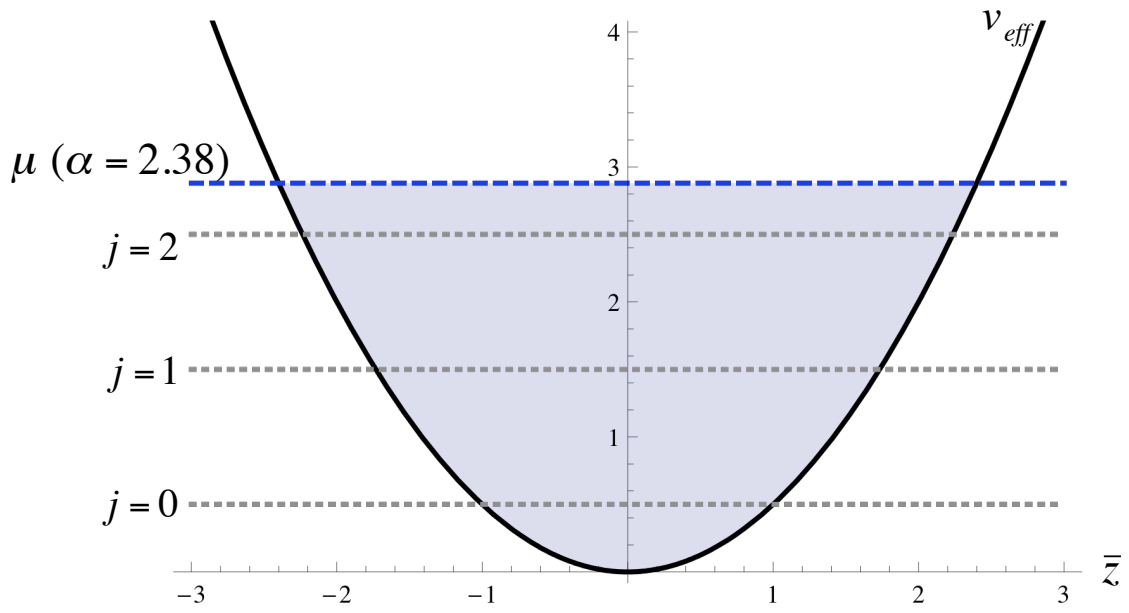
Energy of subbands

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

Chemical potential

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

α **characterizes how many subbands that are occupied**



Dimensionless density

$$(l^3 n)\ (\bar{z},\ \alpha)$$

Dimensionless exchange energy per particle

$$(l\varepsilon_x^{conv})\ (\bar{z},\ \alpha)$$

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Potential → density (*V*→n) mapping

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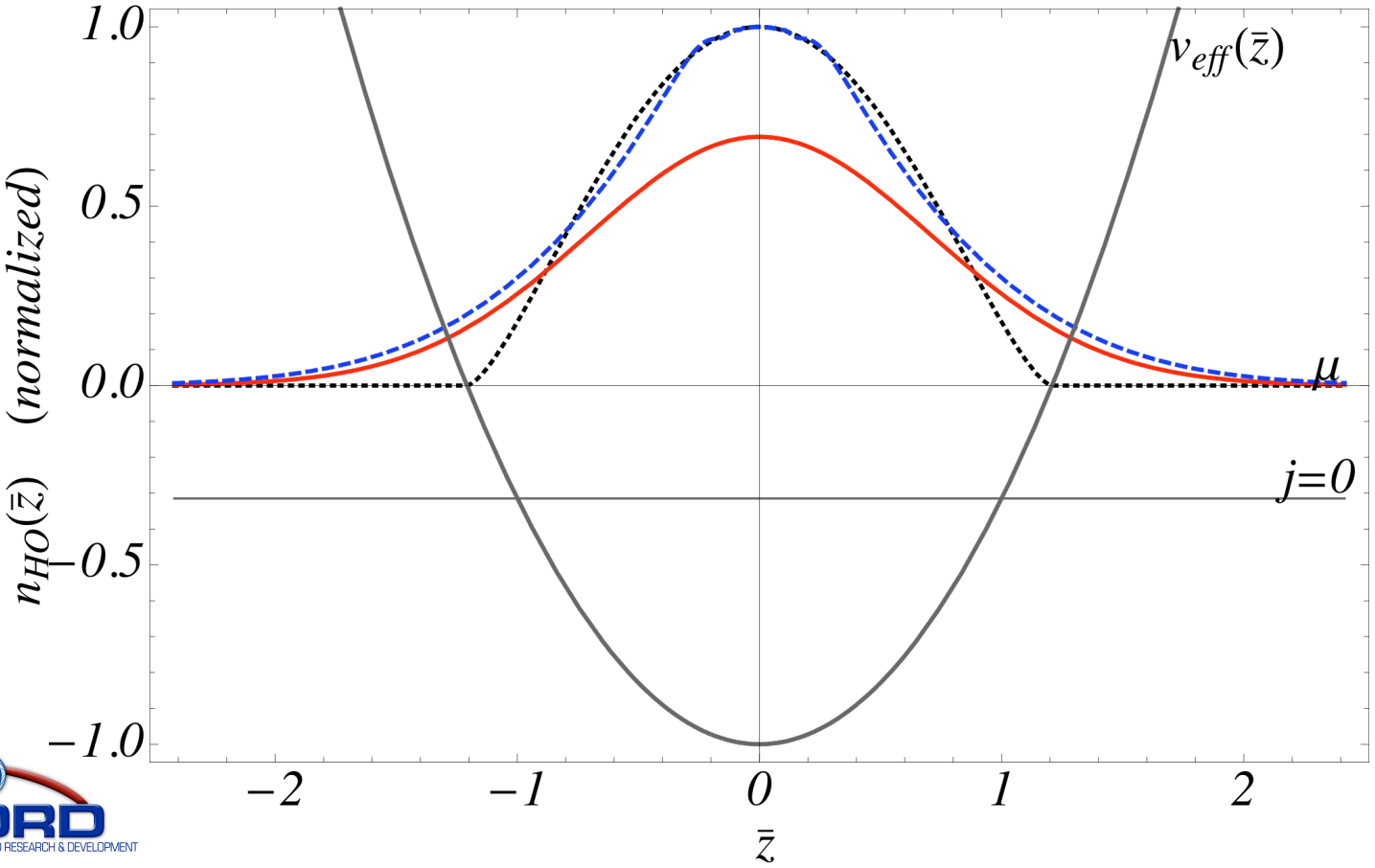
UEG *V*→n
AG *V*→n
exact

$\alpha = 0.23$ HO gas



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Summary density

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In the high density regions in confined systems, the exact density is lower than expected from both uniform electron gas and Airy gas based potential to density mappings.

This is due to that the electrons have fewer states to occupy than in a uniform electron gas or an Airy gas due to the discretization of the spectrum from the confinement.

The AG mapping is OK at edges as it should.

Question: Is the density change taking care of the change in exchange energy density as well?

Density → exchange energy ($n \rightarrow \varepsilon_x$) mapping

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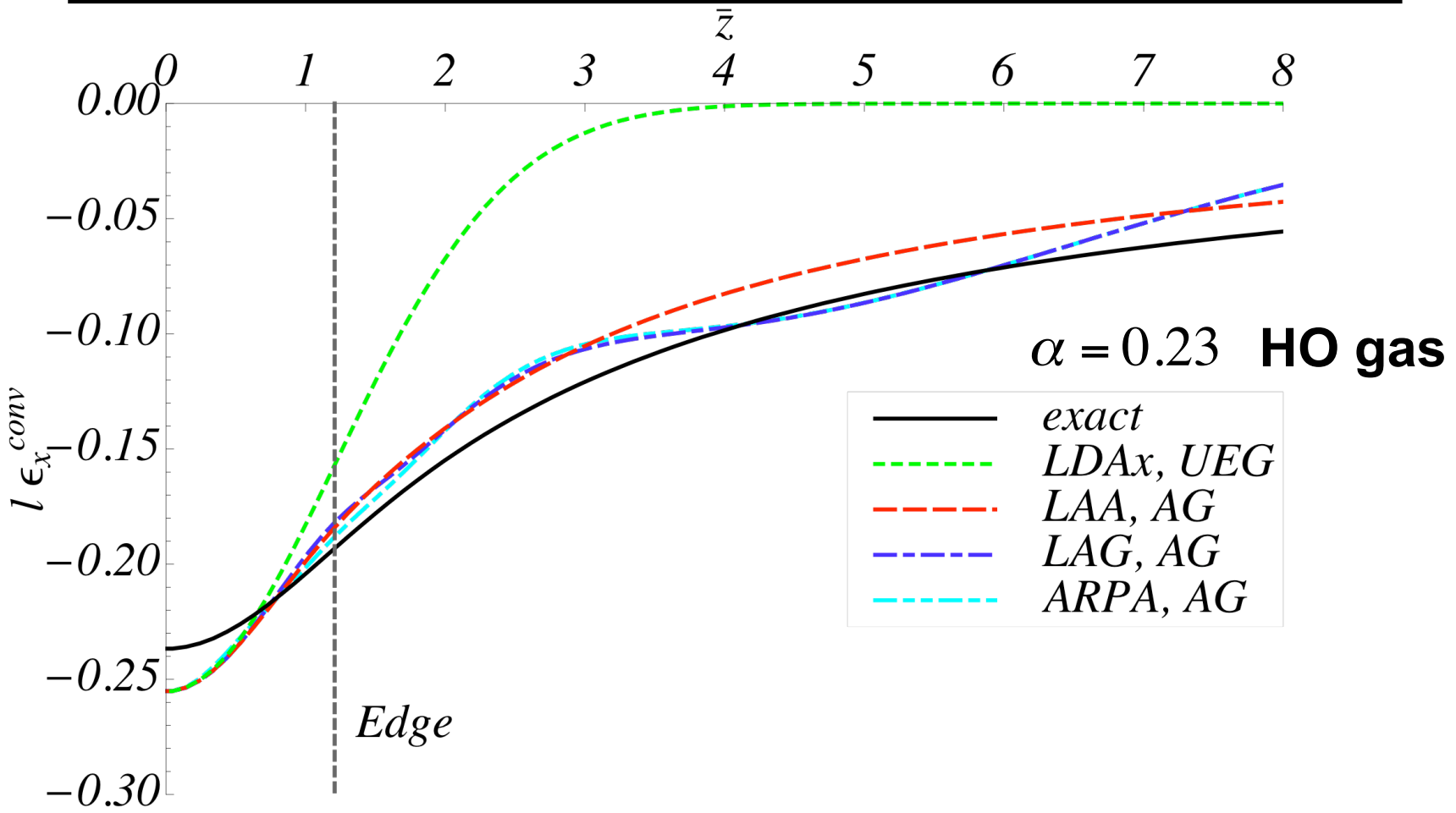

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Summary exchange energy per particle

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In the high density regions in confined systems, the exact exchange energy per particle is less negative than expected from both uniform electron gas and Airy gas based density to exchange energy per particle mappings.

The AG mapping is OK at edges as it should.

It is not only the density that changes from the expected at confinement, then LDAx would be giving the correct exchange, but also the relation between the density and the exchange.

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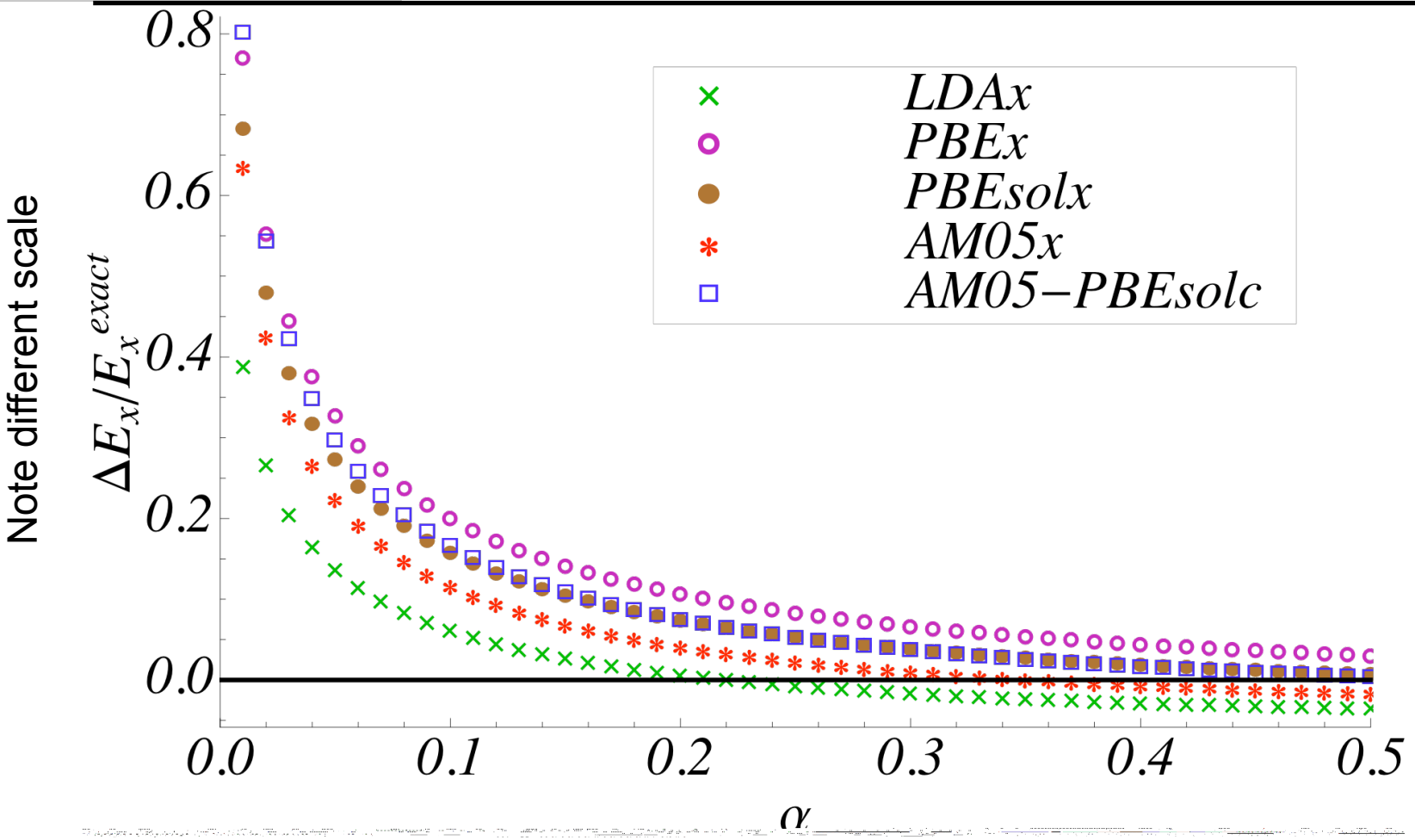
Relative errors of E_x for the HO gas for different density functionals



Confinement physics is not well described by traditional density functionals.

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Conclusions and outlook

Ann E. Mattsson

The errors presently available exchange energy functionals make are dependent on how confined the system is. For highly confined systems the error can be substantial.

What is next?

- Parameterize the exchange of the HO gas for use in a functional.
- Find an interpolation index that can determine the character of the system, that is, how confined the system is in a point.
- Find an, at least partially, compatible correlation.

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Thanks!

For your attention.

E-mail: aematts@sandia.gov

Web: http://dft.sandia.gov/

Preprints/Reprints available at:

www.cs.sandia.gov/~aematts/publicationlist.html

Subroutines for implementation of AM05 into several types of DFT codes are available at http://dft.sandia.gov/functionals/AM05.html

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End

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