# Improving the Predictive Power of Density Functional Theory Calculations

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# Bridges between Fundamental Law of Nature and Engineering

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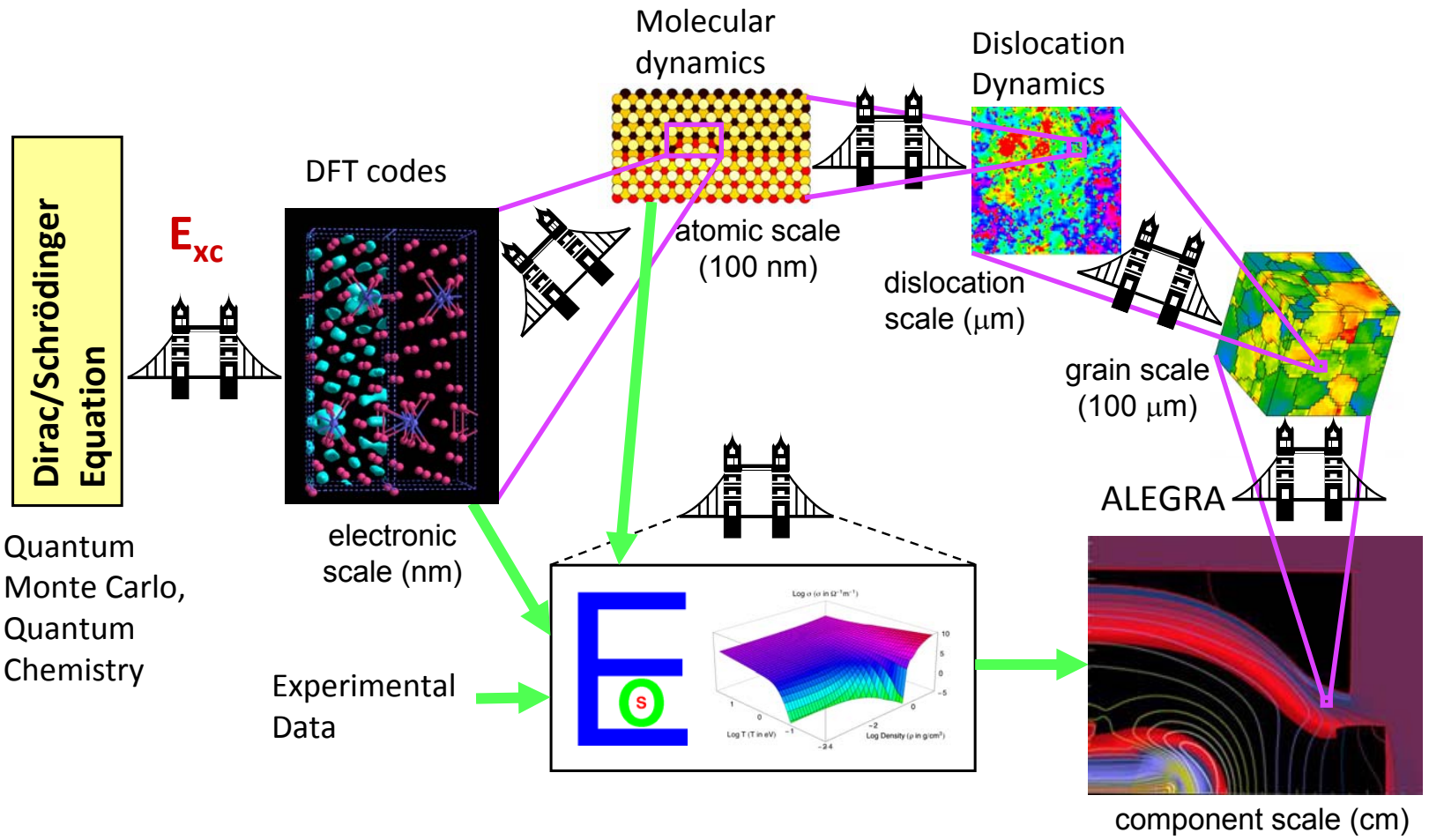

# Equation of State: Example of Material input

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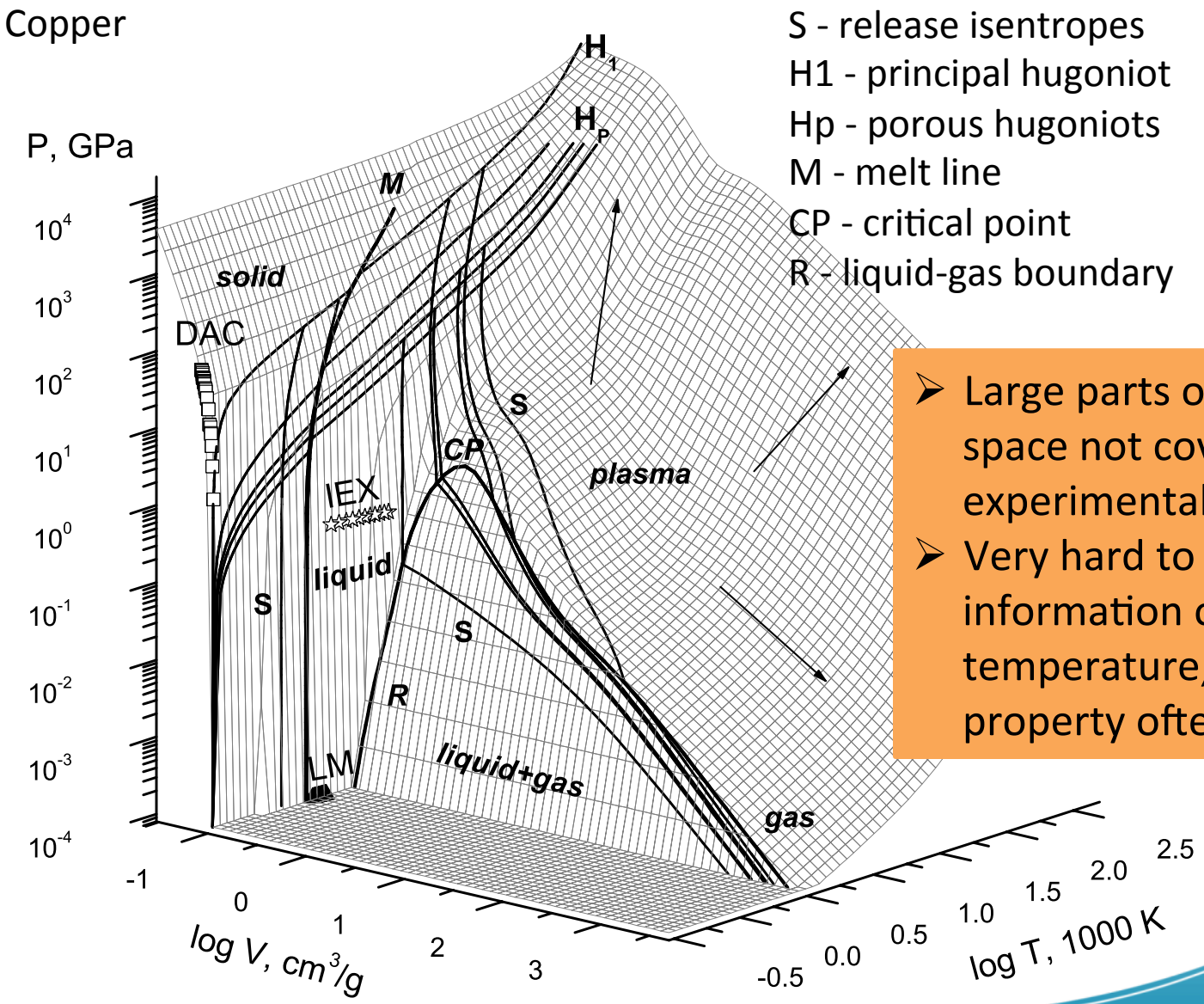
DAC - diamond anvil cell measurements
IEX - isobaric expansion experiments
S - release isentropes
H1 - principal hugoniot
Hp - porous hugoniots
M - melt line
CP - critical point
R - liquid-gas boundary




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

# Two Ti EOS: Kerley (2003) and Pecker (2005)

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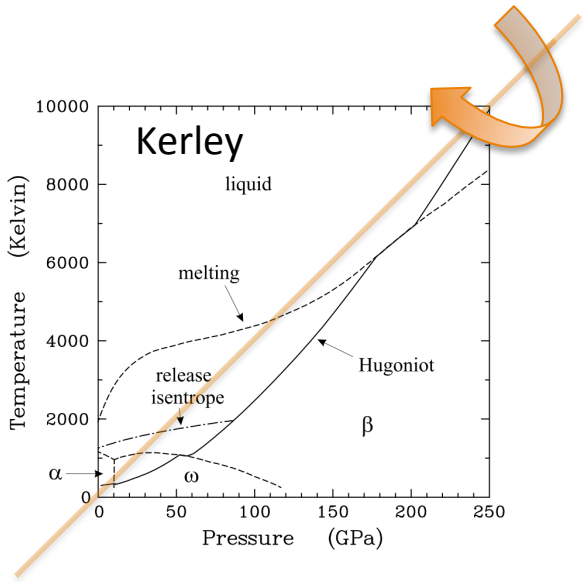
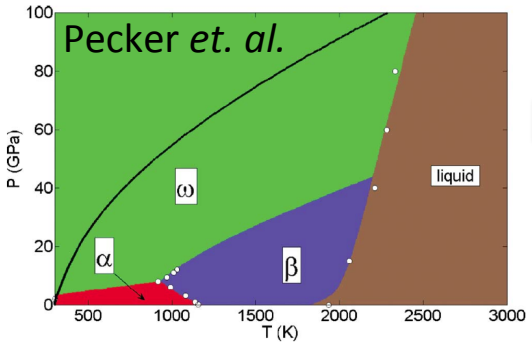
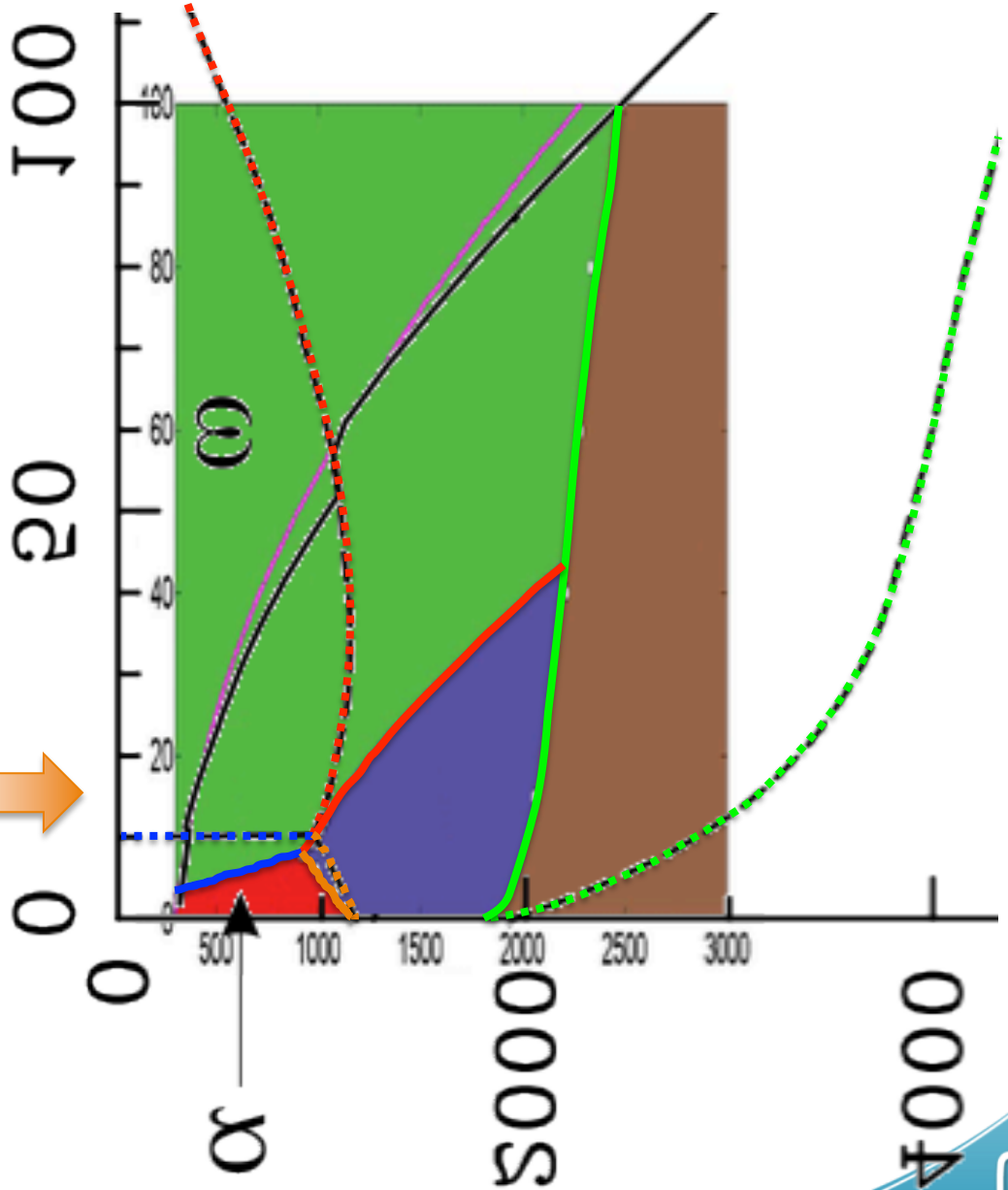


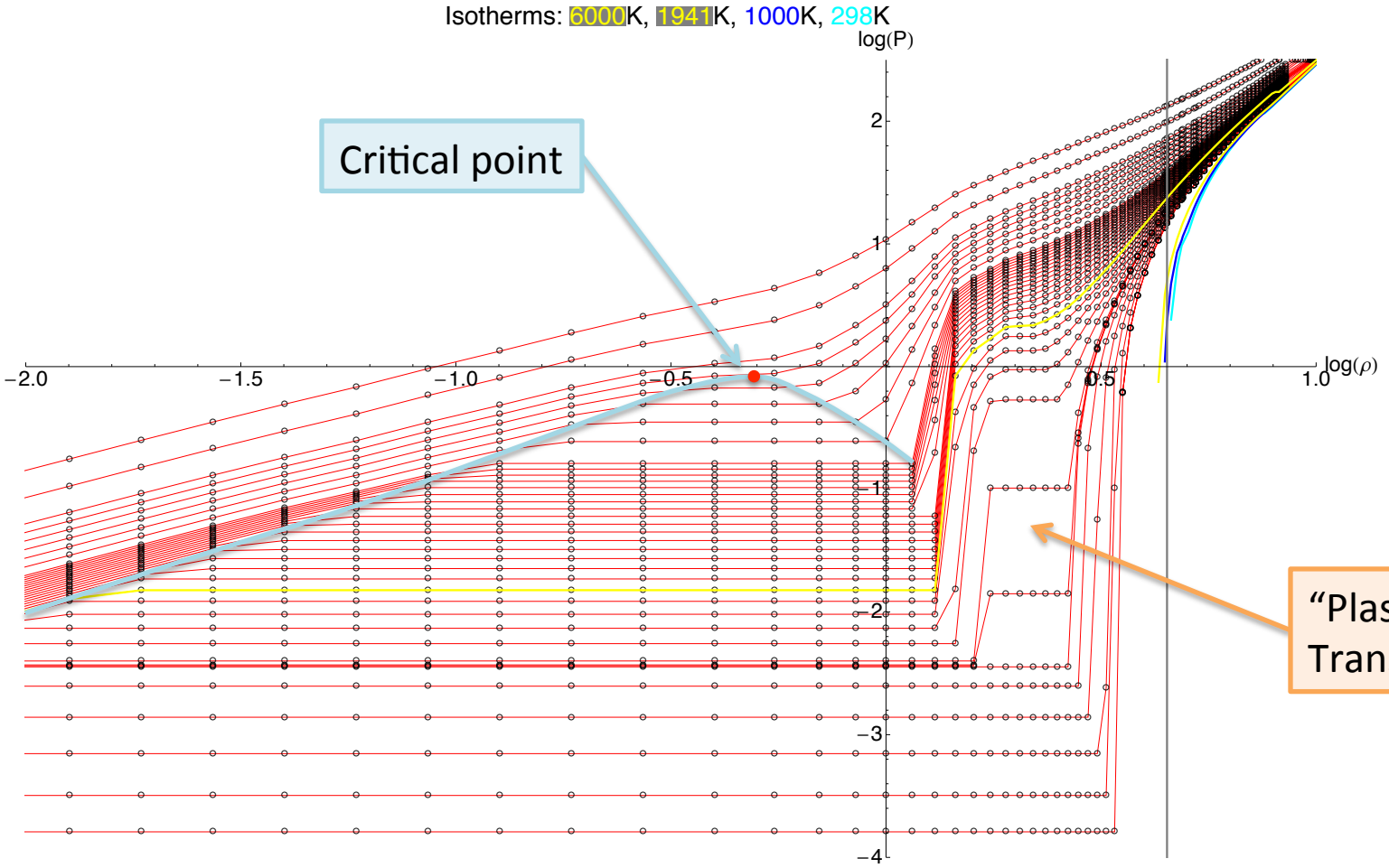

α→β

ω→β

α→ω

melting

# More …




Kerley critical point at 0.5 g/cc and 15500K,
Pecker et al at same density but 9000K.

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# Equation of State: Example of Material input

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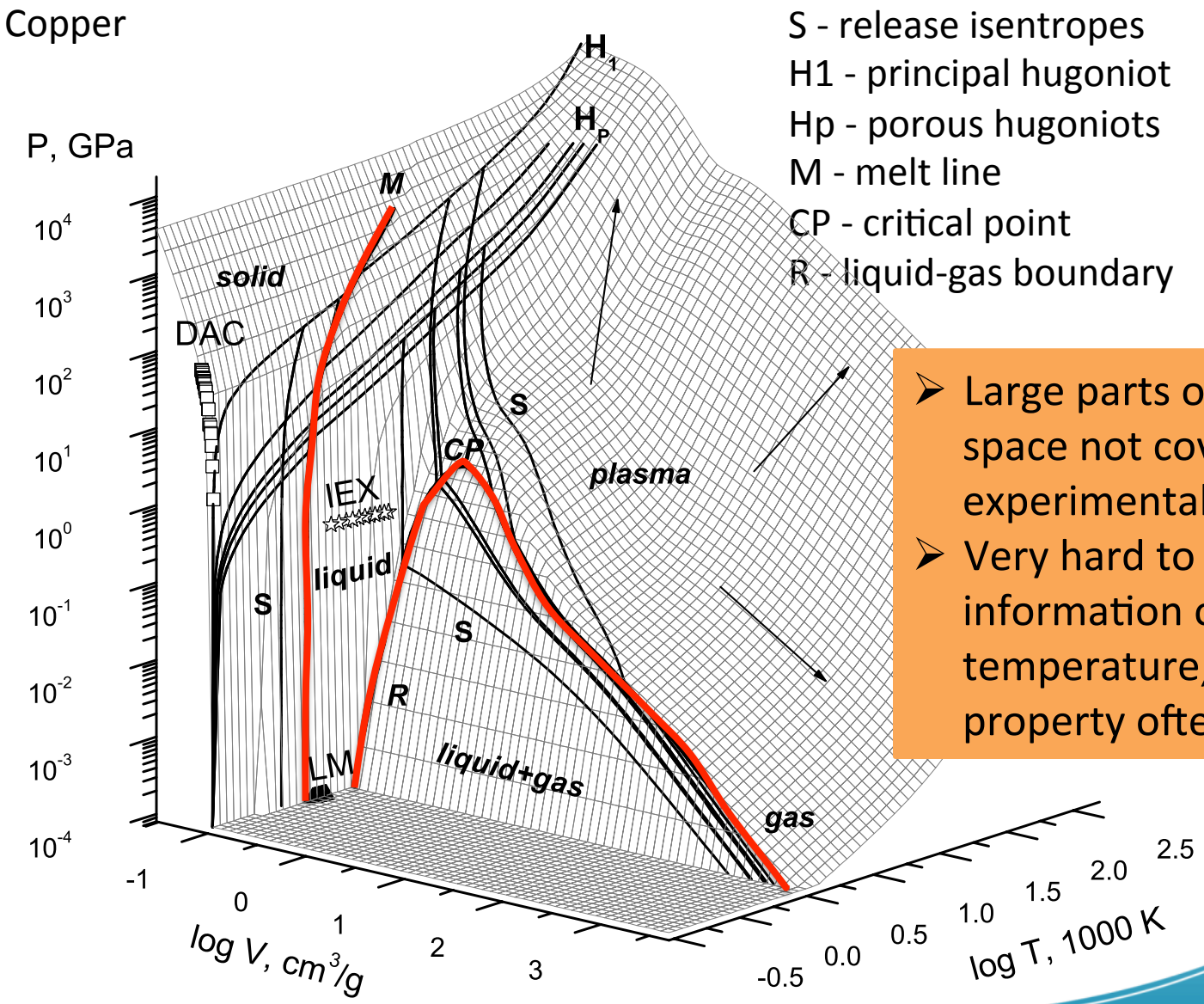


- Large parts of parameter space not covered by any experimental technique.
- Very hard to get information on temperature, this property often inferred.

# Molecular Dynamics

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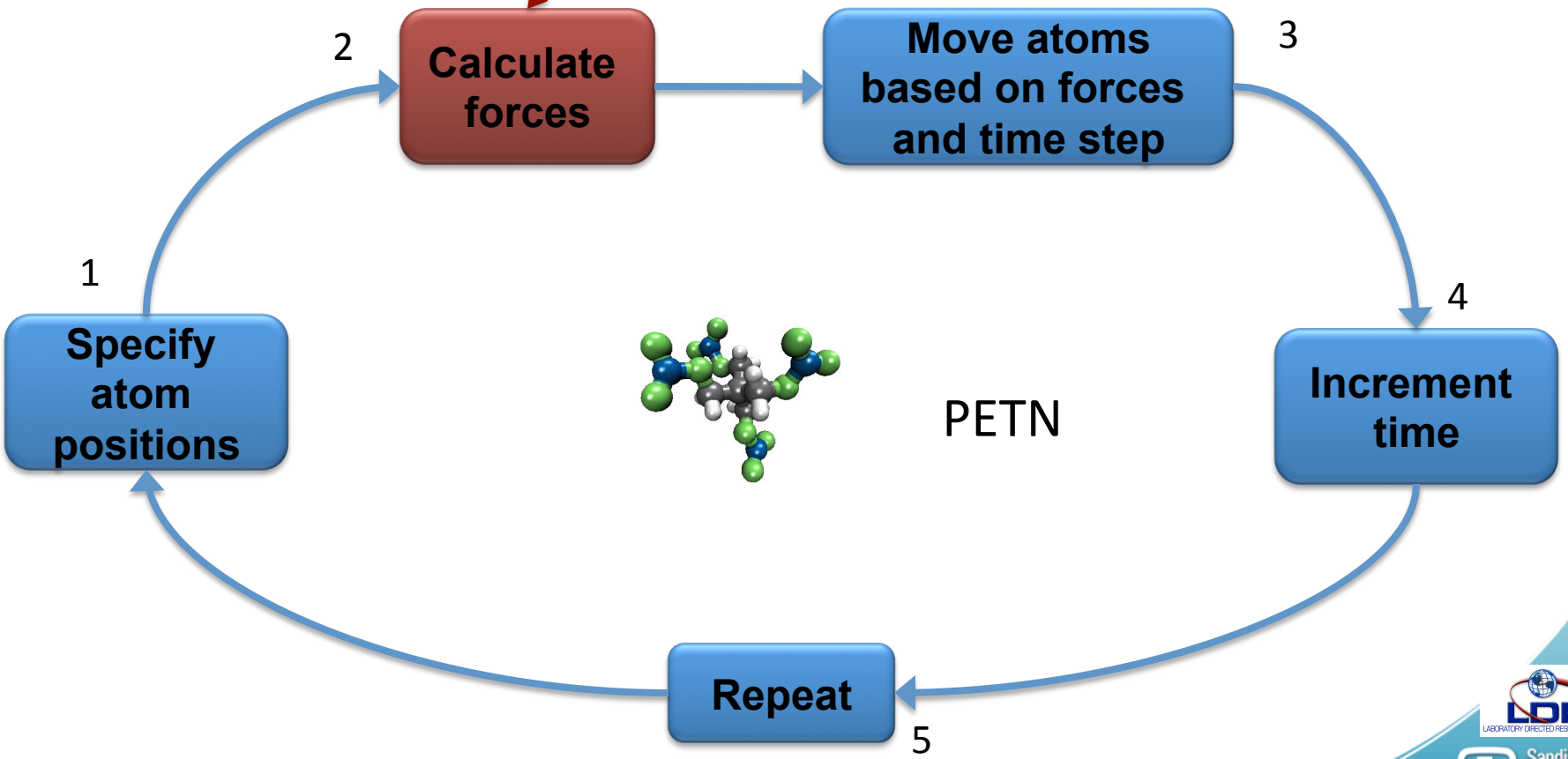
DFT-MD (or a AIMD or QMD): Forces calculated with DFT.
Classical MD: Forces calculated with force fields or potentials.




Adapted from slides by Ryan Wixom, SNL.

# Bridges between Fundamental Law of Nature and Engineering

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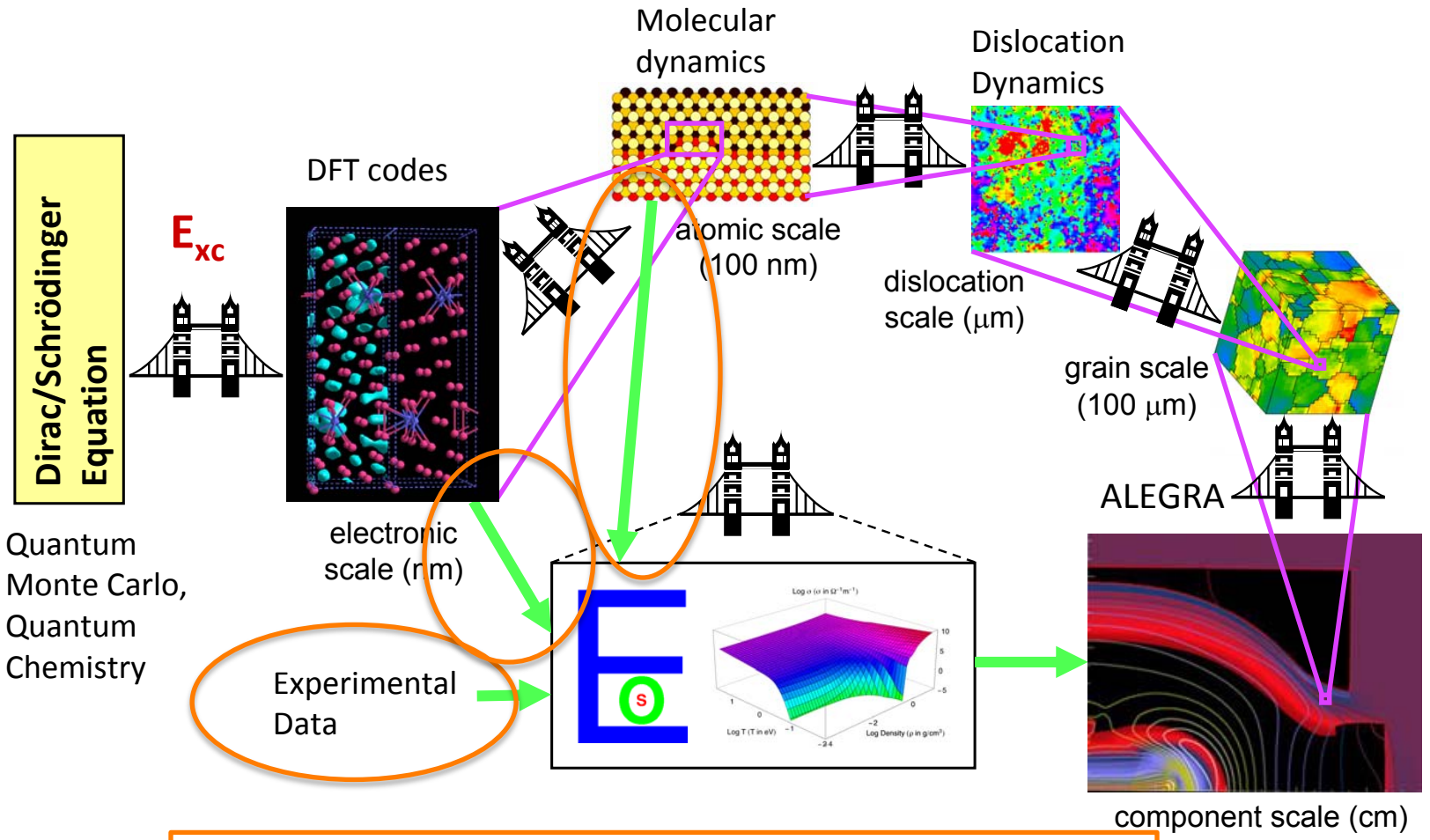



The ability to perform high-fidelity calculations is most important for cases where experiments are impossible, dangerous, and/or prohibitively expensive to perform.

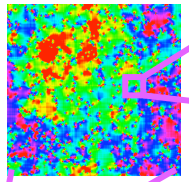
# Example: Modeling and simulation of Nuclear Energy related systems

Upscaling needed. In each step, reality that cannot be modeled is resulting in error bars.

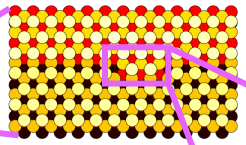
We cannot solve the Dirac Equation for the Nuclear power plant.

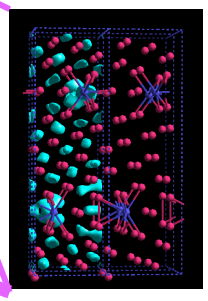
Dirac/Schrödinger Equation

dislocation scale (μm, ms)

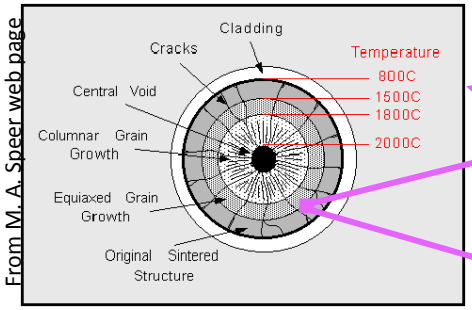


atomic scale (100 nm, μs)

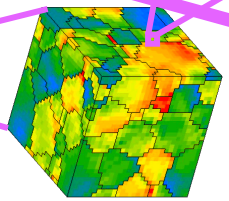




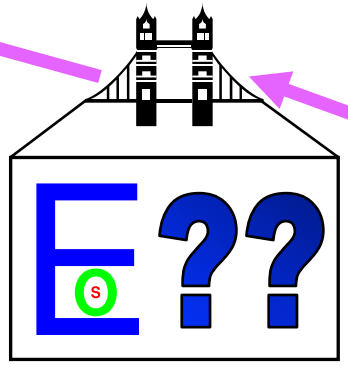
$E_{xc}$




component scale (cm, days)

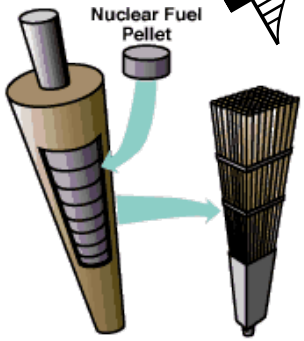


grain scale (100 μm, $10^3$ s)

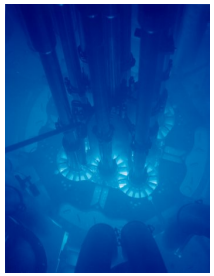


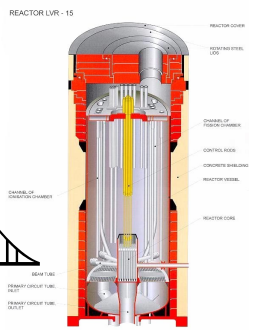

electronic scale (nm, ps)

Are these safe?




system scale (dm, years)





Facility scale (m, many years)

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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. 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.

# Relativistic effects



Notably present in Au (Z=79), its color, and Hg (liquid).
Similar color effect as in Au already in Cs (Z=55).
Indications some effects in Fe (Z=26) is due to relativistic effects.

# 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.

# 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

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

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

Orbital current: Neglecting this gives…

# Approximate Dirac for spin density functionals

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

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

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

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

Now ordinary DFT spin functionals can be used.

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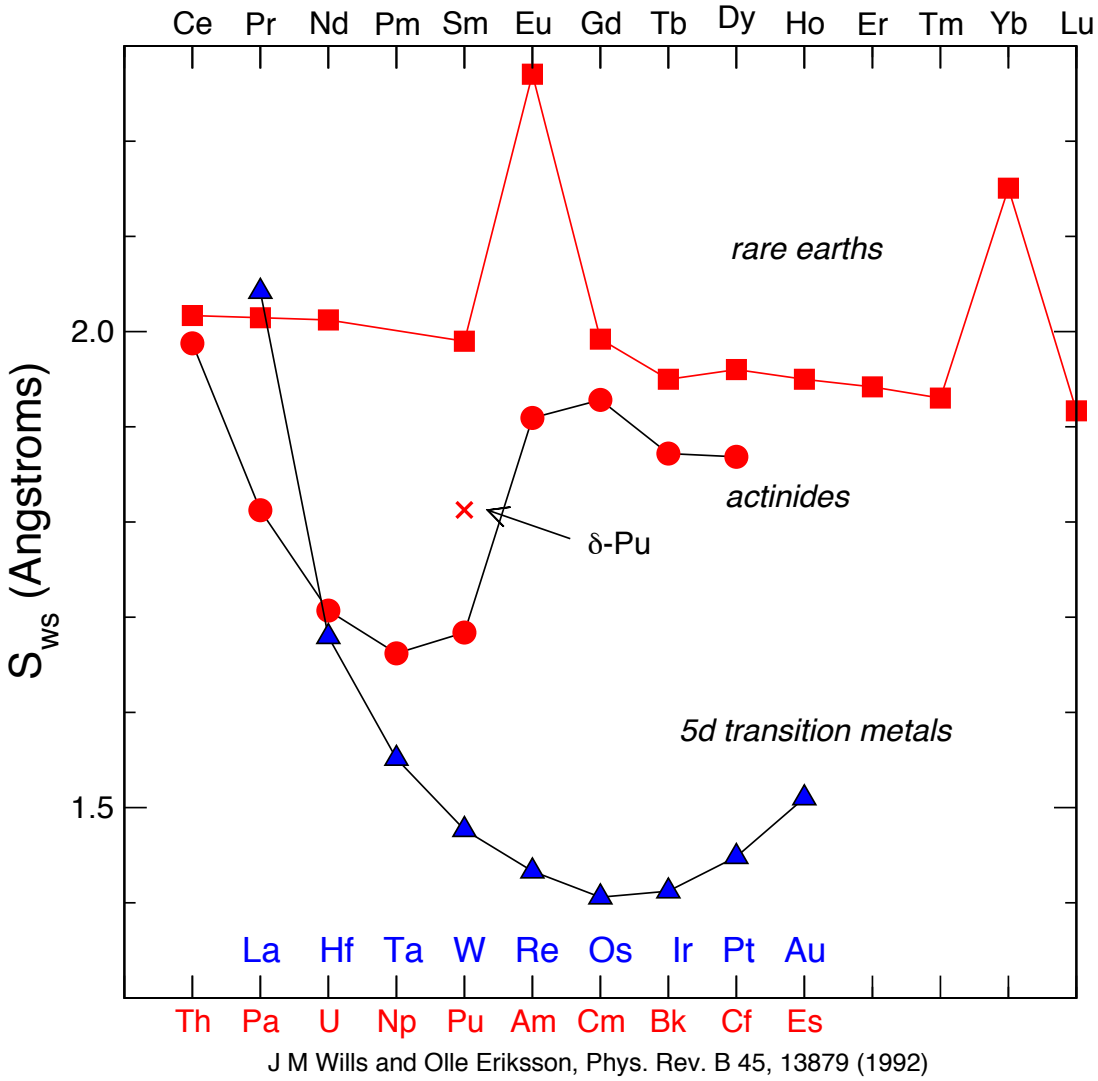
# Confinement physics




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

Experimental equilibrium volumes.

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

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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…

# Actinide Physics: Competition between localization and delocalization

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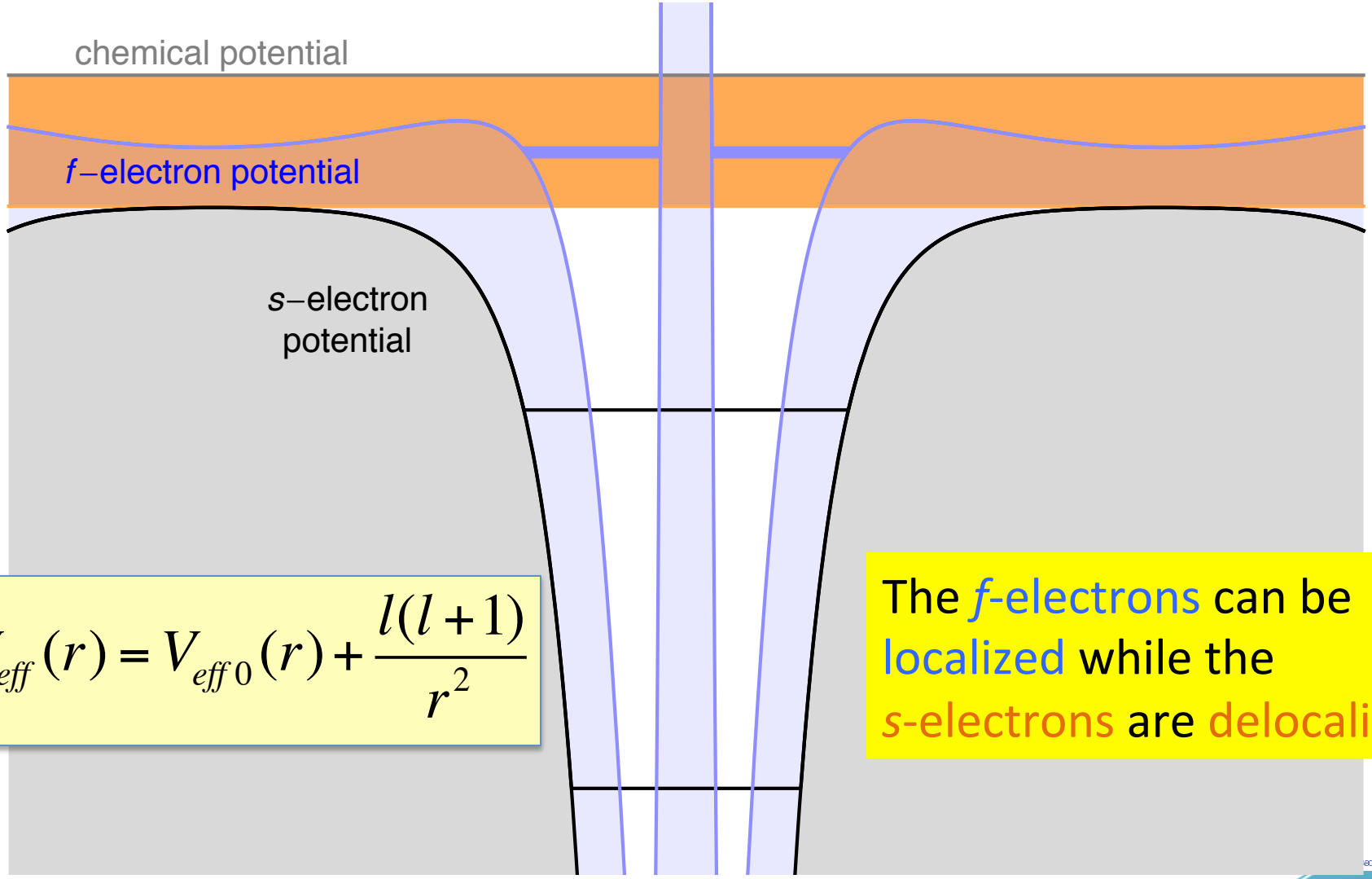


$$V_{eff}(r) = V_{eff\,0}(r) + \frac{l(l+1)}{r^2}$$

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

# Actinide Physics: Competition between localization and delocalization

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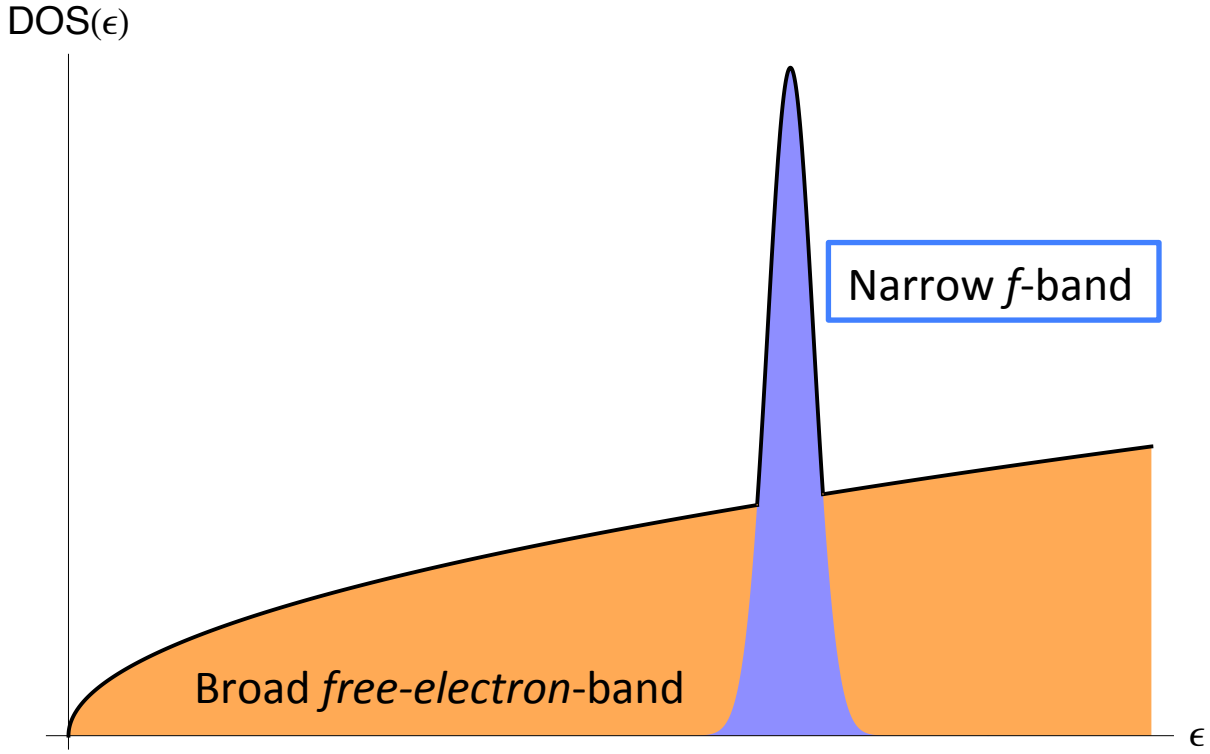


The delocalized electrons in the broad *free-electron* band and the localized electrons in the narrow *f*-electron band are behaving very differently. The interesting physics and chemistry of *f*-electron materials are governed by a competition between these two different pictures.

# Actinide Physics: Density Functional Theory

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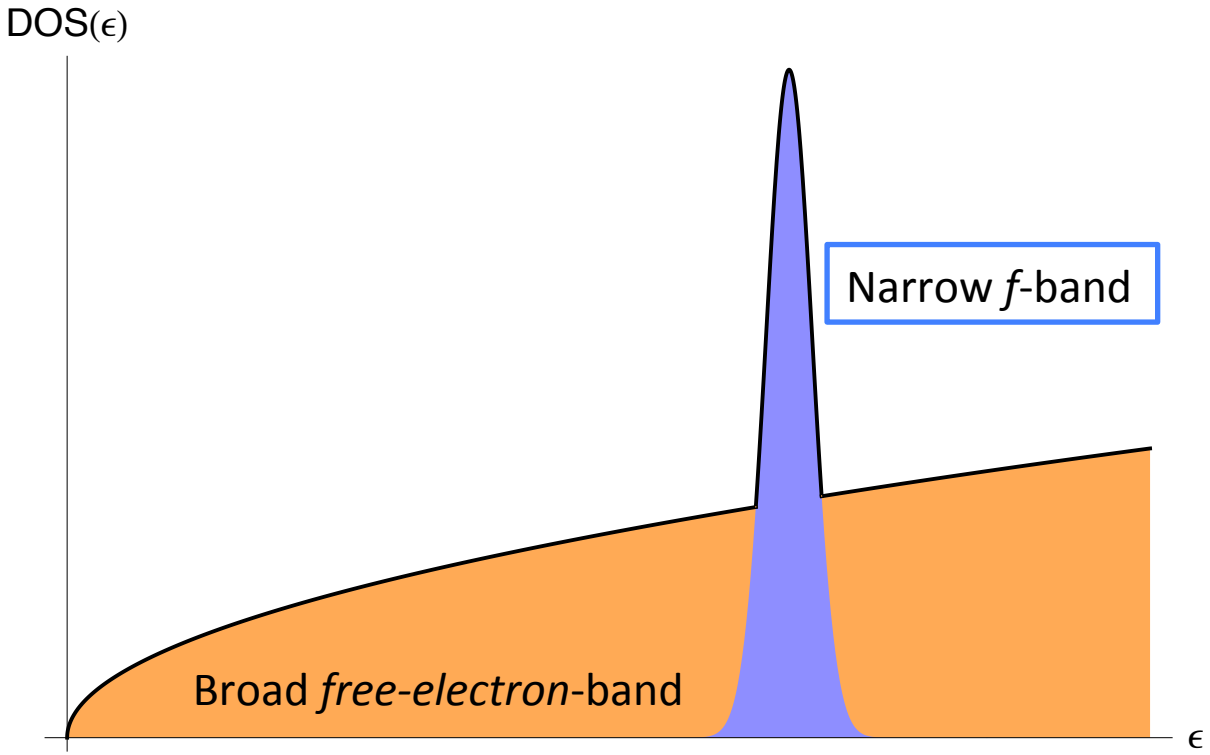


LDA and other functionals based on the uniform electron gas can be expected to work on the broad free-electron band.

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

Since the physics of actinides is due to the competition between these two types of states, a functional need to be able to describe the two situations equally well.

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

# Actinide Physics: Electrons are fermions

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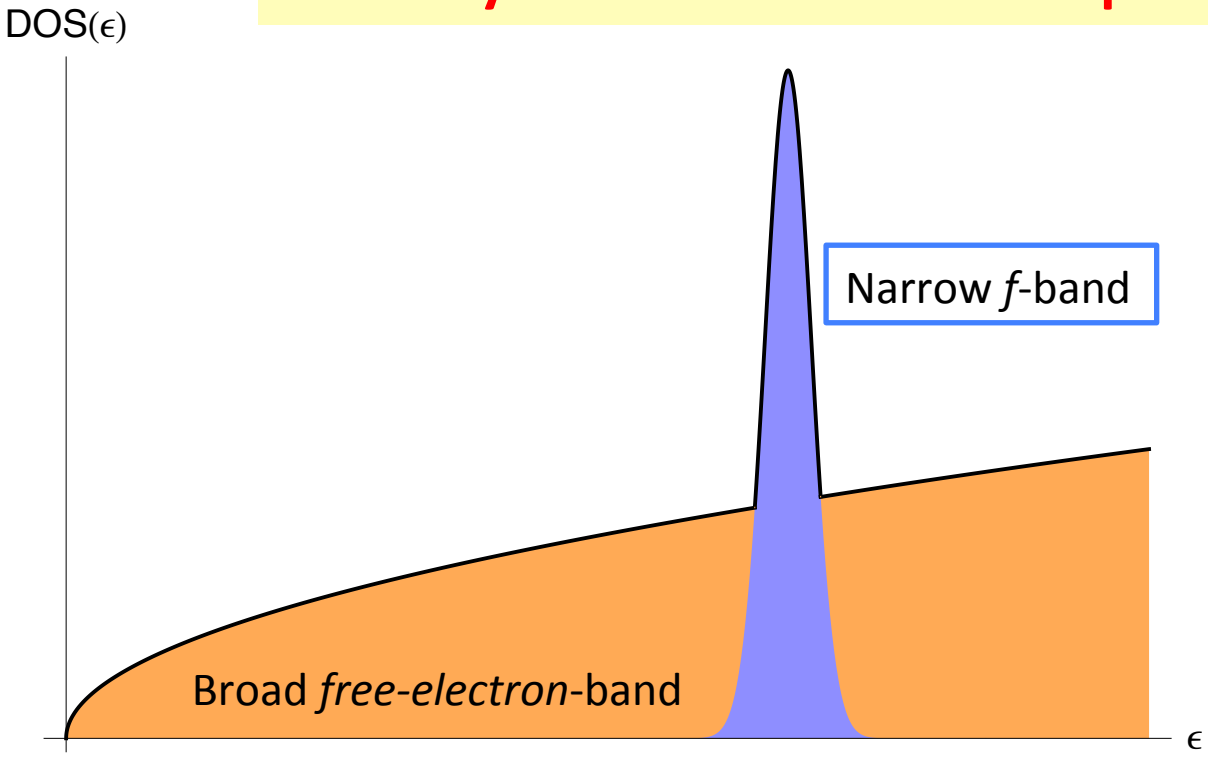
Electrons are fermions,
**they each need their own quantum state**.




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

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

# 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.

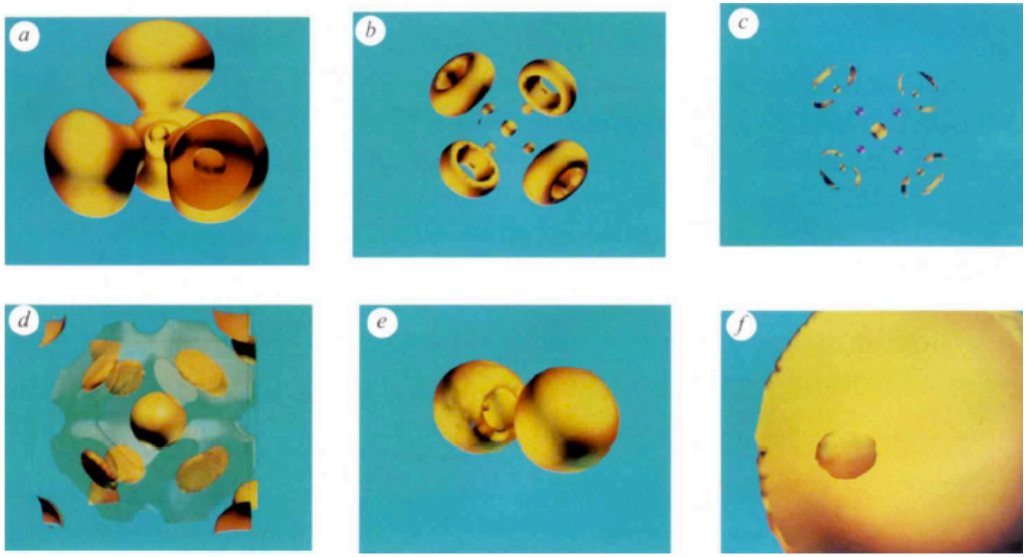



FIG. 1 Localization domains of $CF_4$ (*a*–*c*), Li (*d*), LiF (*e*) and LiH (*f*). *a*–*c*, Reduction of the localization domains of $CF_4$. Below ELF = 0.37 (where ELF is the localization function; see text) there are six localization domains: five core and one valence. The bifurcation at ELF = 0.37 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)

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

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# Subsystem Functional Scheme:

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

Dividing V into sub-regions where different subsystem functionals apply

Specialized functionals in different subsystems

?

Interpolation Index:

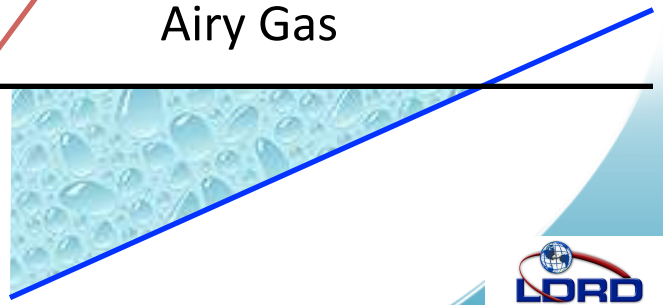
**ELF**

Interior physics:

Uniform electron gas

Surface physics:

Airy Gas



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# 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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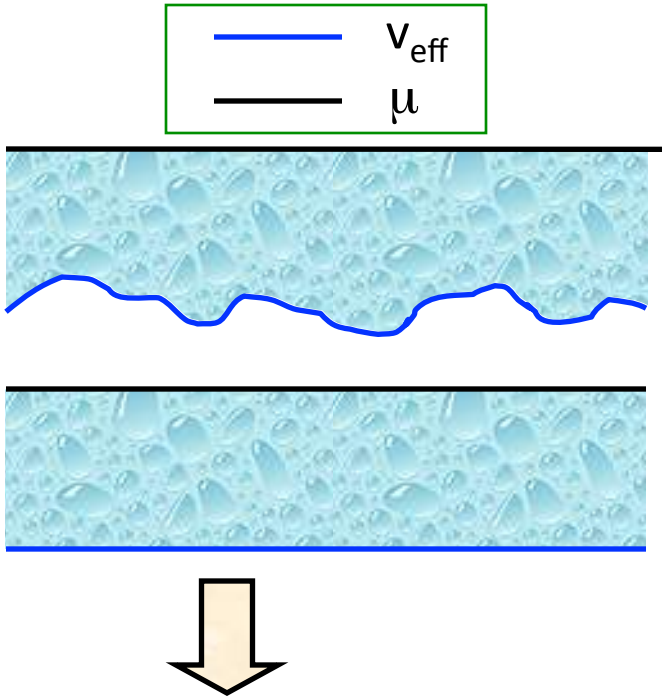


Assume each point in the real system contribute the amount of exchange-correlation energy as would a uniform electron gas with the same density.

Obviously exact for the uniform electron gas.

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

# 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

# Subsystem functionals

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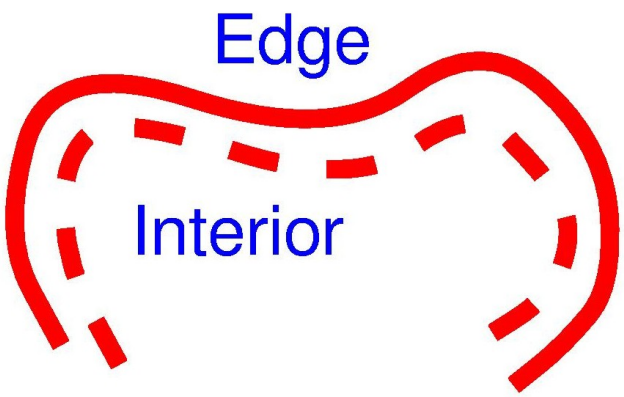
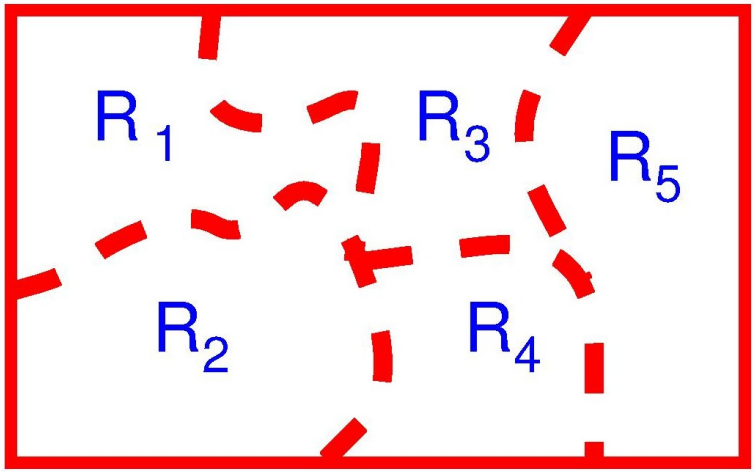
## Original Kohn and Mattsson approach




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.

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

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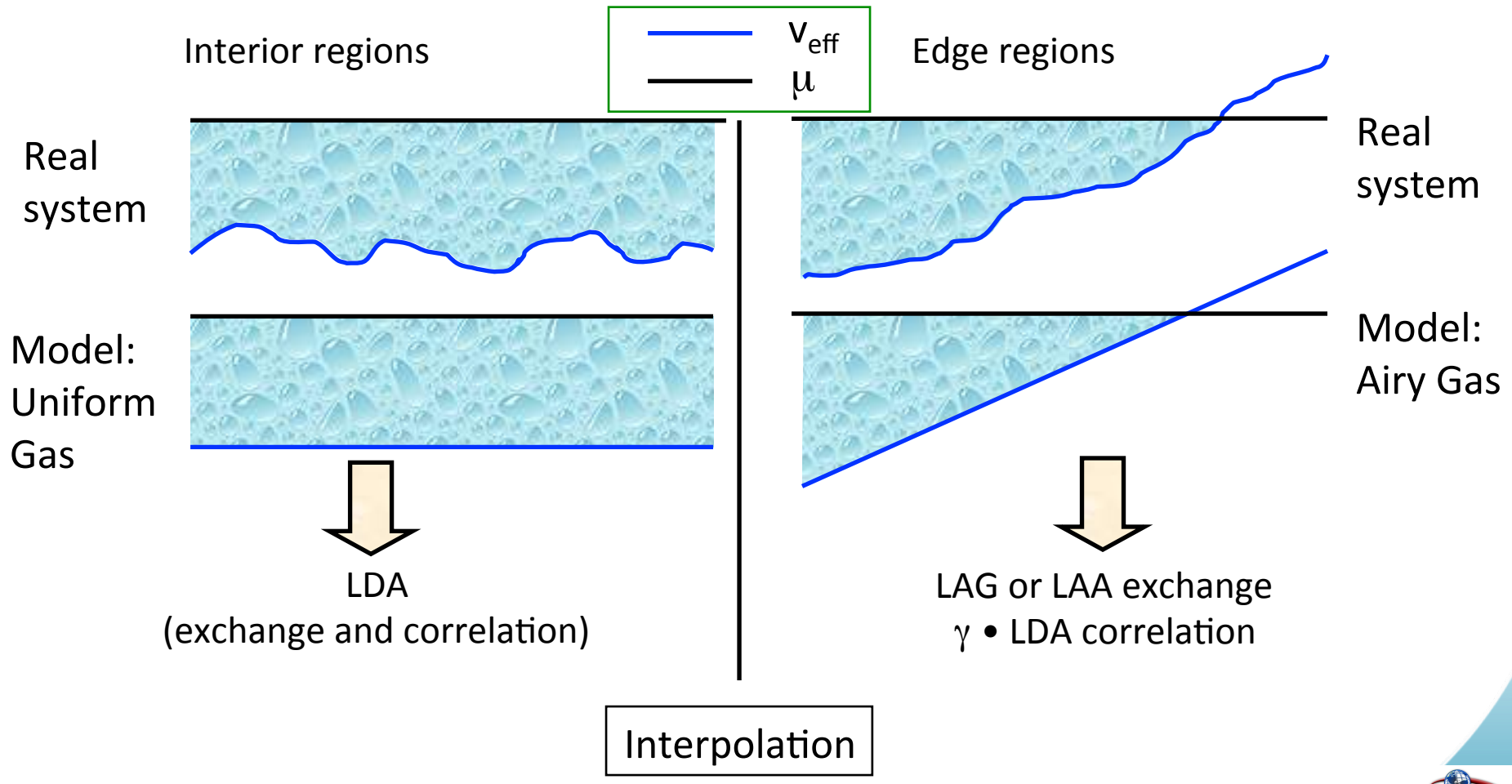


Two constants (one is $\gamma$ above, one is in interpolation index) are determined by fitting to yield correct jellium surface energies.

# AM05 is as accurate as a hybrid, but much faster

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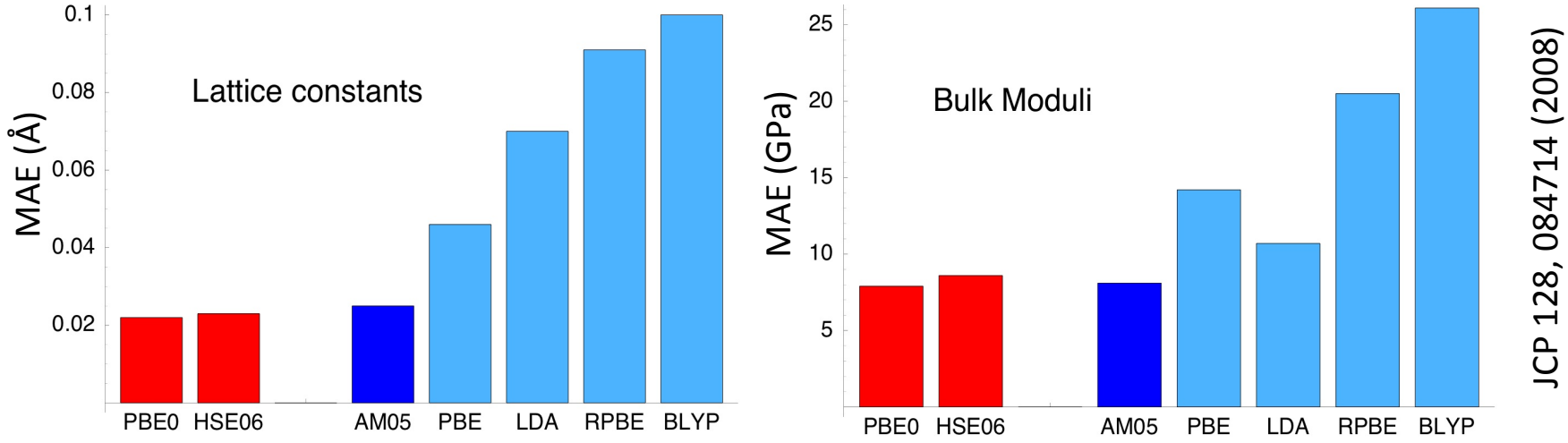
Comparison of mean absolute errors (MAE) for properties of 20 solids calculated with seven different functionals.




JCP 128, 084714 (2008)

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.

# Side note: Large N vs slowly varying limit

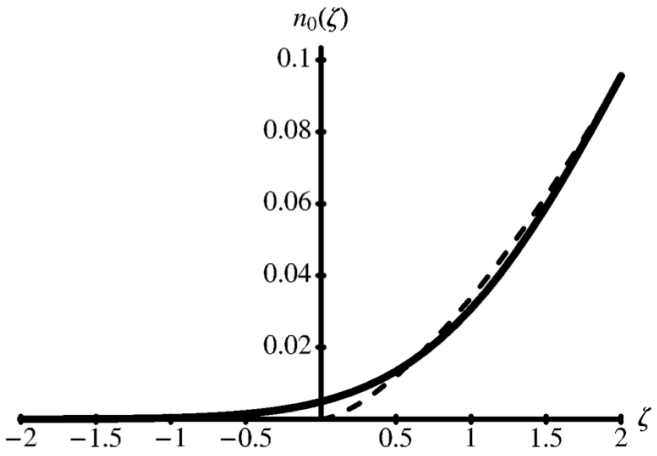



FIG. 5. The density of the Airy gas, exact (solid line) and i the Thomas Fermi approximation (dashed line).

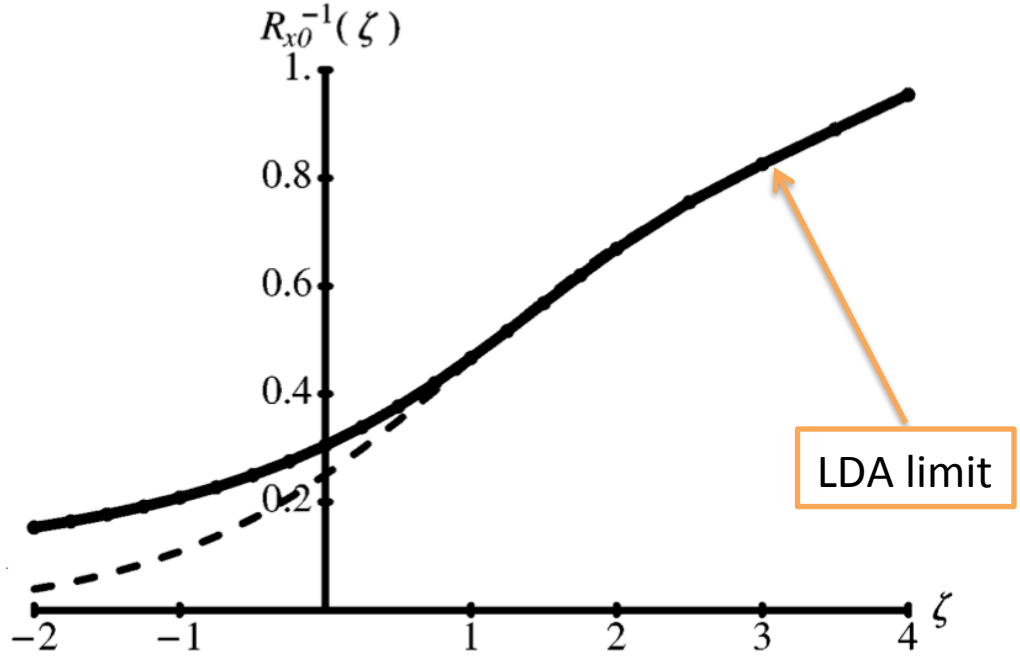



FIG. 6. The inverse radius of the exchange hole of the Airy gas: (solid line) exact, (dashed line) LDA.

AG goes to large N limit, not slowly varying limit. AG exchange energy does not fulfill gradient expansion for slowly varying density.

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# Subsystem Functional Scheme:

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

Dividing V into sub-regions where different subsystem functionals apply

Specialized functionals in different subsystems

?

Interpolation Index:

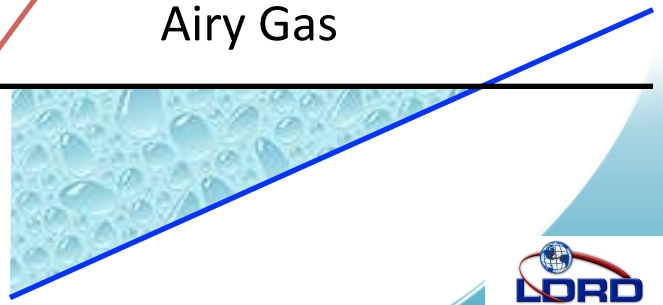
**ELF**

Interior physics:

Uniform electron gas

Surface physics:

Airy Gas



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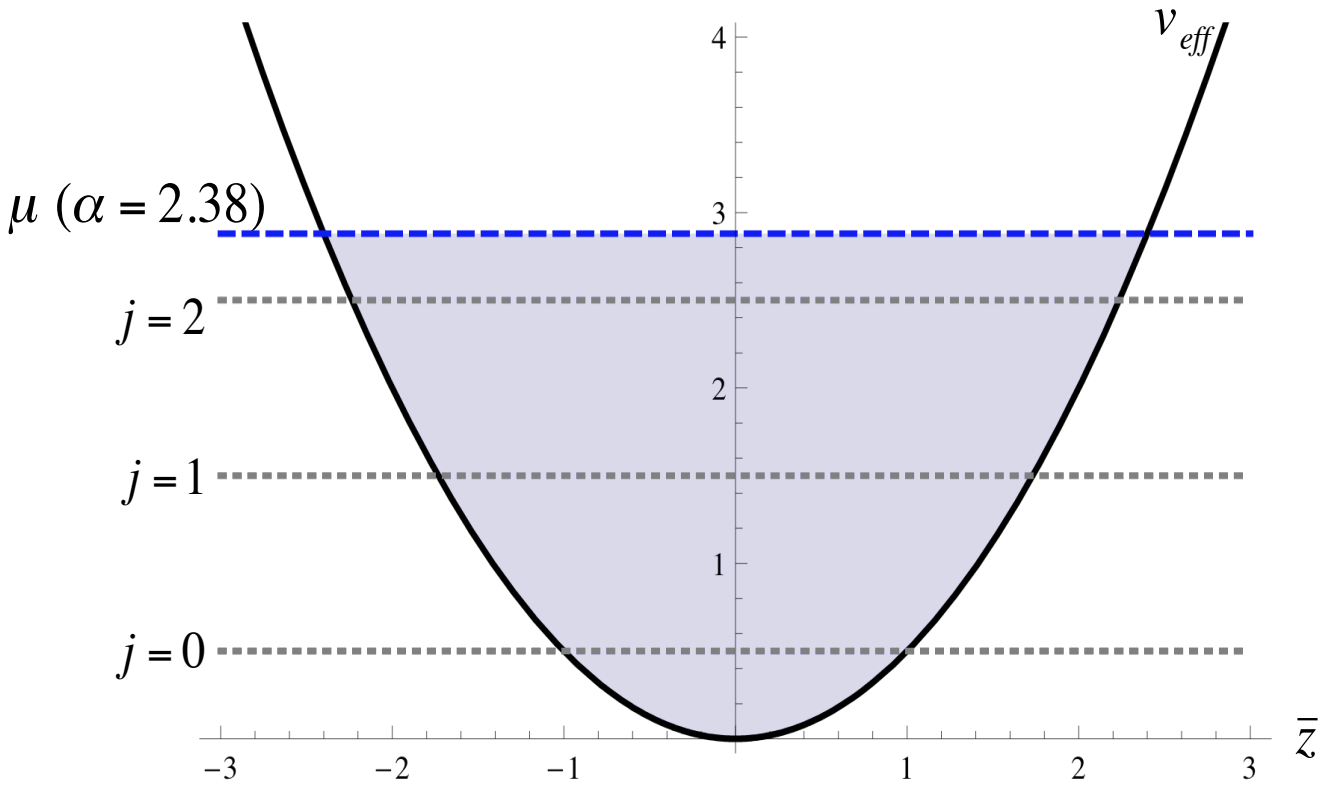
# Harmonic Oscillator model (HO)

Ann E. Mattsson

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

HO model: Localized electron levels in a continuum.

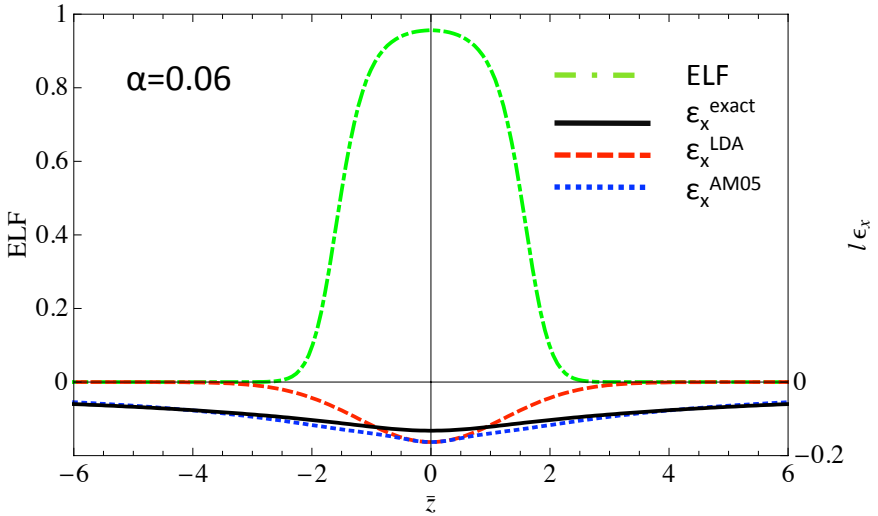


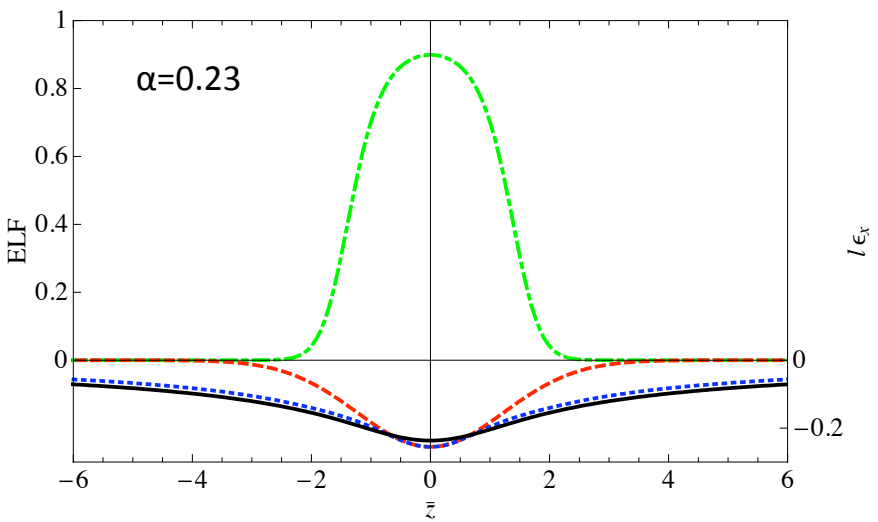

Energy of subbands $\varepsilon_j = (j + \frac{1}{2})\frac{1}{l^2}$

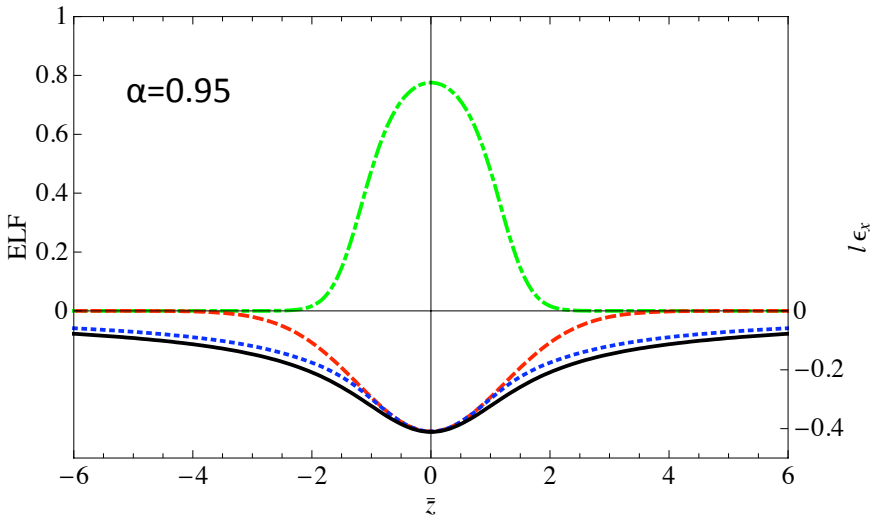
Chemical potential $\mu = (\alpha + \frac{1}{2})\frac{1}{l^2}$

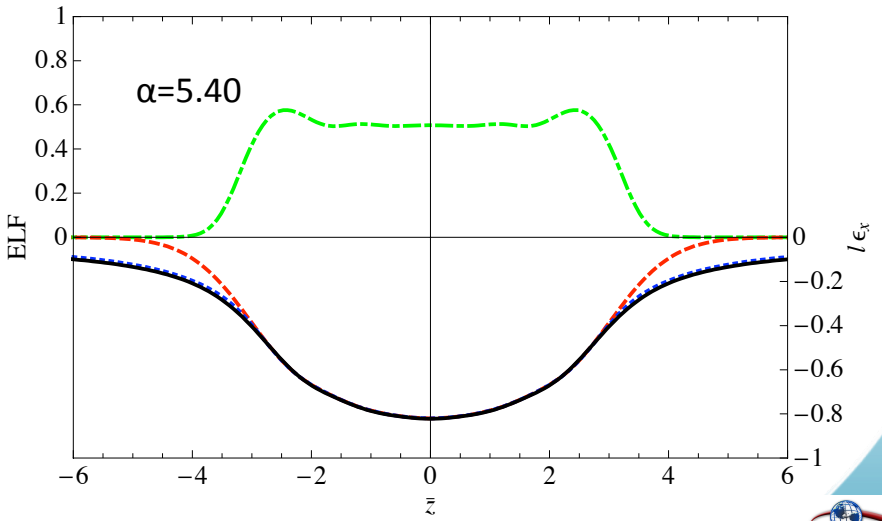
$\alpha$ characterizes how many subbands have been occupied, and determines the level of confinement.

# ELF in HO systems versus Exchange Energy




**ELF is correlated with the exchange energy errors!**

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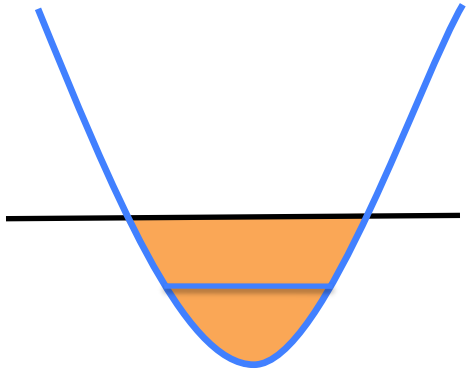
# Subsystem Functional Scheme:

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

Dividing V into sub-regions where different subsystem functionals apply

Specialized functionals in different subsystems

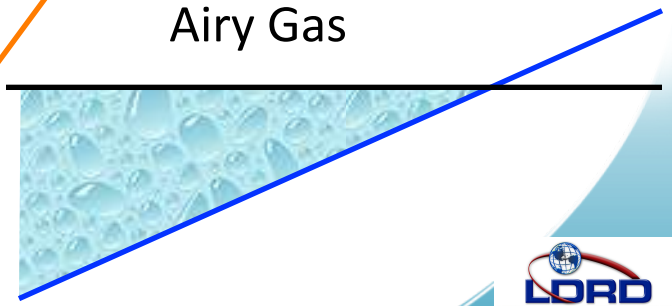
Confinement physics:
Harmonic oscillator gas



Interpolation Index:
**ELF**

Interior physics:
Uniform electron gas

Surface physics:
Airy Gas



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

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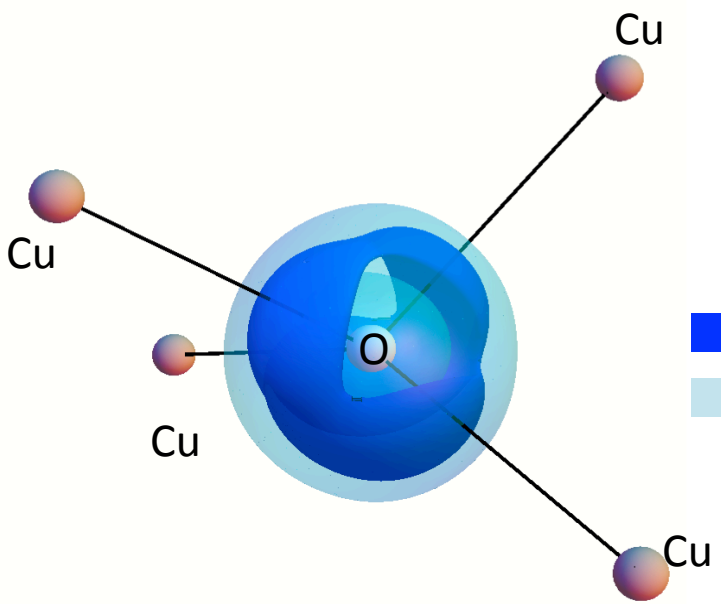



ELF ≈ 1/2: uniform electron gas like

ELF ≈ 1: strong localization, discrete levels

ELF > 0.83

ELF > 0.77

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

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

# Si from QMC

ANTONIO C. CANCIO AND M. Y. CHOU

PHYSICAL REVIEW B **74**, 081202(R) (2006)

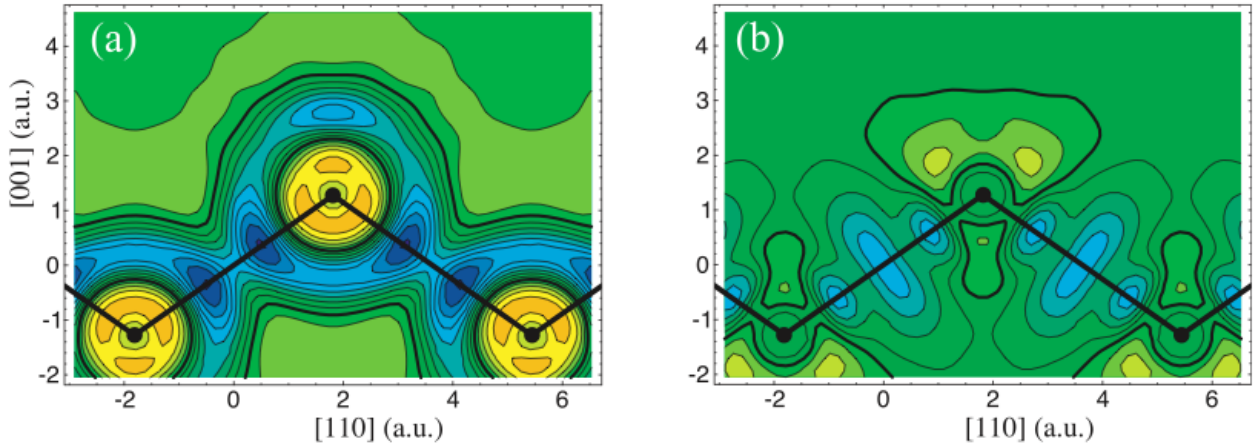
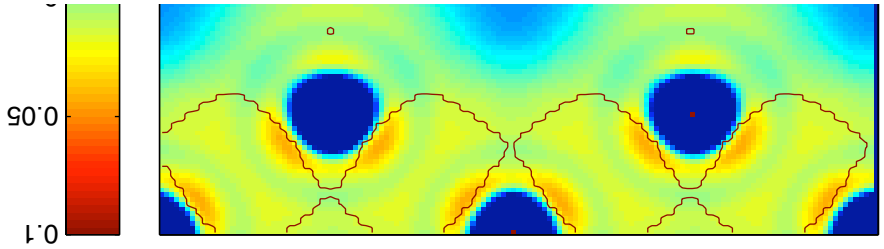



FIG. 1. (Color) Comparison of DFT and VMC $e_{xc}$'s on the (110) plane of the Si crystal. (a) Difference between the LDA $e_{xc}$ and that of VMC data (Ref. 10). Difference between that of the GGA$^{++}$ model described in the text and the VMC result. Contours in increments of $0.2\times10^{-3}$ a.u., with thicker contour that for zero difference. Bluer (darker) regions show negative difference and redder (lighter) regions, positive.



# Si from QMC

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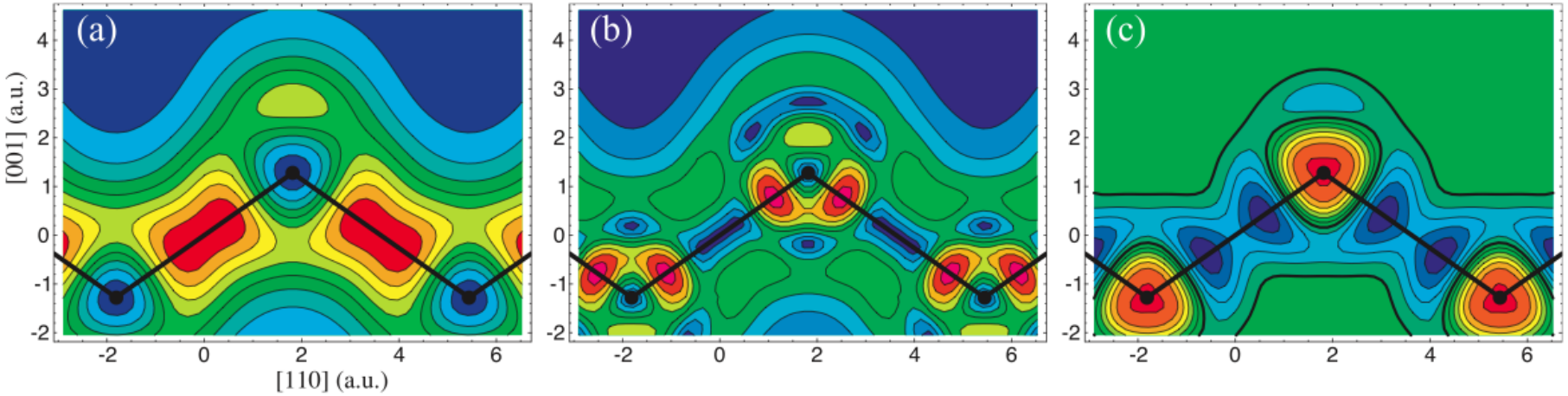
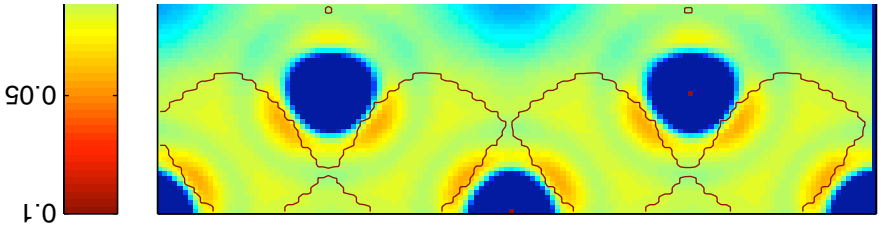



FIG. 2. (Color) Gradient analysis of the density of crystalline Si. The density $n$ (a), $|\nabla n|$ (b), and $\nabla^2 n$ (c) on the (110) plane of the Si crystal. Atoms and bonds outlined in black. Shading varies from blue (dark gray) (low) to red (light gray) (high) and contours are in increments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



# Summary

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

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# Kinetic energy functionals

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

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

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

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

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

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# Kinetic energy functionals

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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.

$$\left.\begin{aligned} \tau_{UEG} &= k_F^5/5/\pi^2 \\ n_{UEG} &= k_F^3/3/\pi^2 \end{aligned}\right\} \longrightarrow \tau_{TF} = 3/5\ (3\pi^2)^{2/3}\ n^{5/3}$$

This is corresponding to LDA for exchange-correlation functionals

# Kinetic energy functional for surface system

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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 $\tau$ for the Airy gas. We have n for an Airy gas.

We need to express $\tau$ 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

Ann E. Mattsson

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 $\tau$ for the Harmonic Oscillator (HO) gas. We have n for a HO gas.

We need to express $\tau$ 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.

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

# Kinetic energy functional for confined systems

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For a HO system with α < 1:

$$t = \underbrace{\frac{5}{3}\frac{\alpha + \bar{z}^2}{(3\pi^{1/2}\alpha e^{-\bar{z}^2})^{2/3}}}$$

$$\begin{cases} s = \dfrac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}} = \dfrac{|2\bar{z}|}{2(3\pi^{1/2}\alpha e^{-\bar{z}^2})^{1/3}} \\ q = \dfrac{\nabla^2 n}{4(3\pi^2)^{2/3} n^{5/3}} = \dfrac{4\bar{z}^2 - 2}{4(3\pi^{1/2}\alpha e^{-\bar{z}^2})^{2/3}} \end{cases}$$

$$\begin{cases} \alpha = \left[\dfrac{1}{2(s^2 - q)}\right]^{3/2} / (3\pi^{1/2} e^{-\frac{s^2}{2(s^2-q)}}) \\ \bar{z}^2 = \dfrac{s^2}{2(s^2 - q)} \end{cases}$$

$$t = \frac{5}{3}\left(\frac{1}{\sqrt{2(s^2 - q)}} \frac{1}{3\pi^{1/2} e^{-\frac{s^2}{2(s^2-q)}}} + s^2\right)$$

Not final answer…