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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Density Functional Theory: The Bridge between Theoretical Condensed Matter Physics and Engineering.

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LANL CNLS Seminar 27 April 2011

National Nuclear Security Administration

Sandia National Laboratories

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.

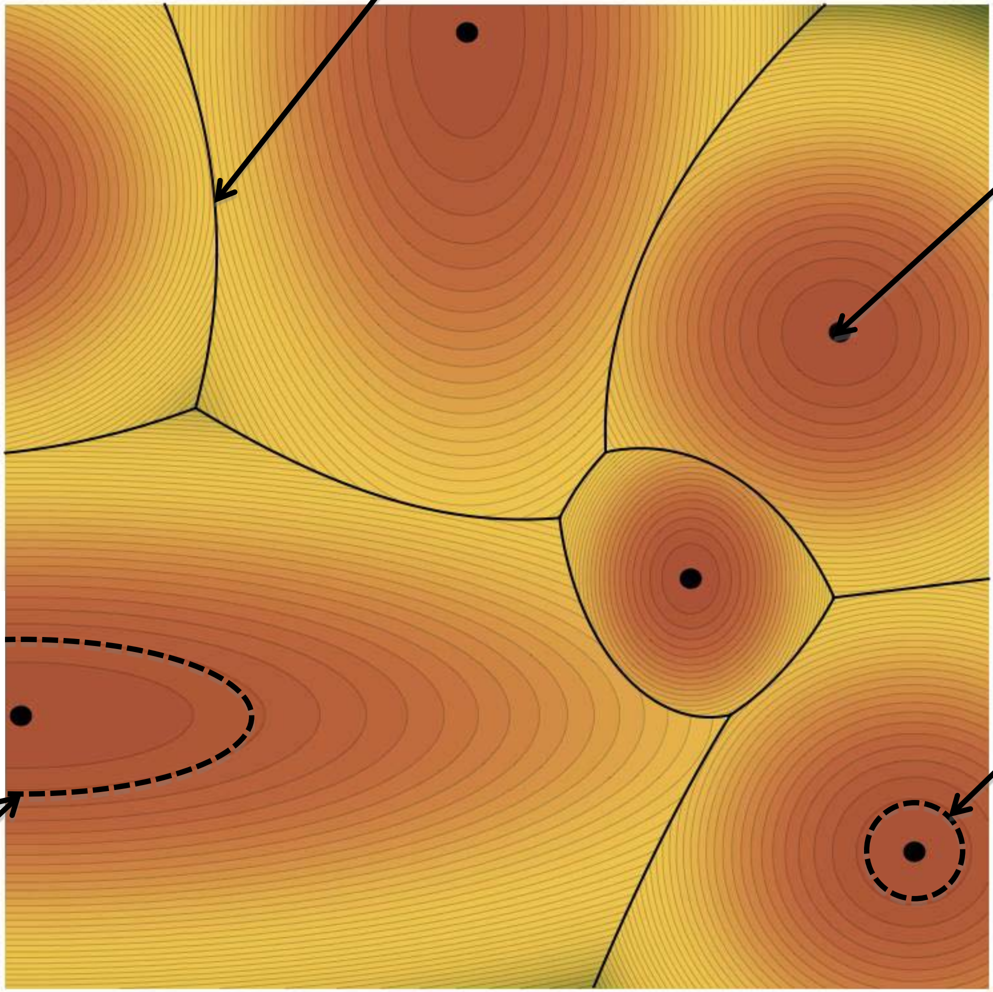
Approximate Hamiltonians with exact solutions.

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

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.



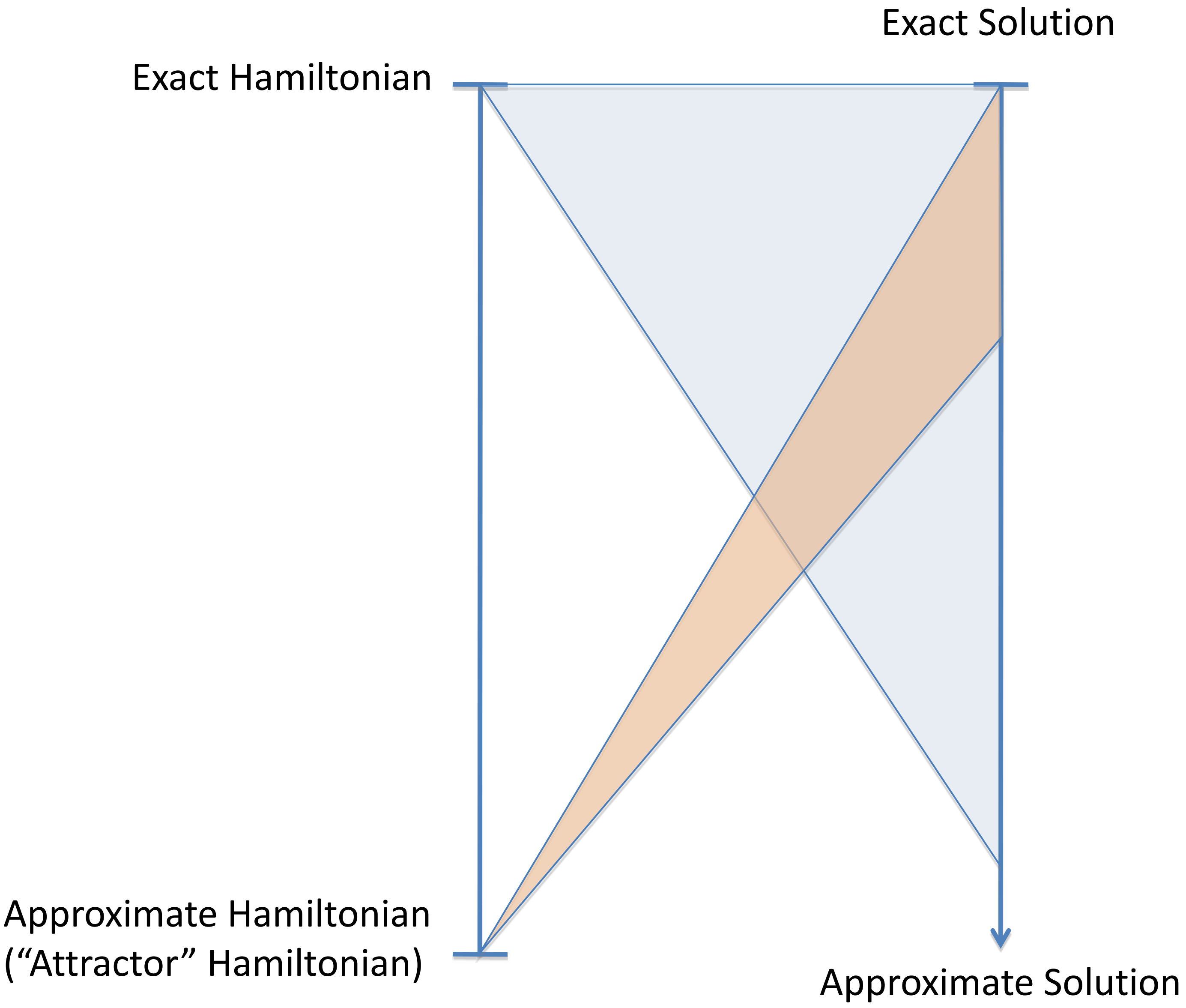
Marginal Physics is quite exciting.

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

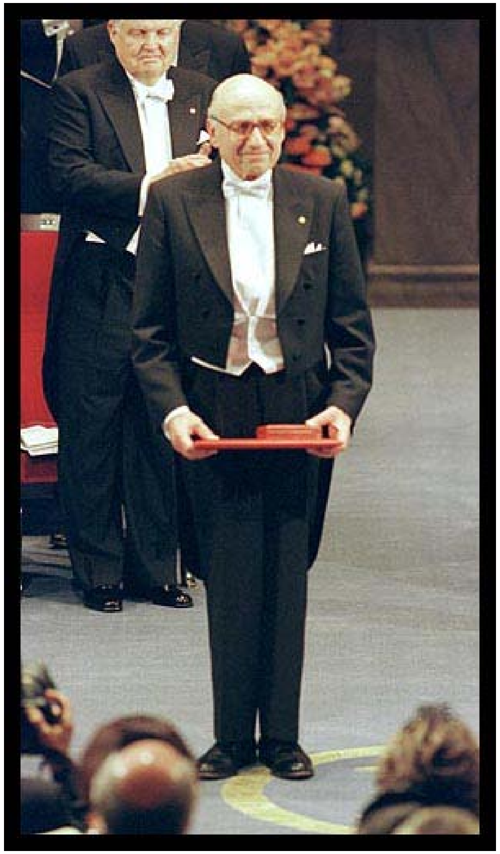
Perturbation Theory can take small influences from other types of physics into account.

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

How do we learn from the Quantum Mechanical equations?



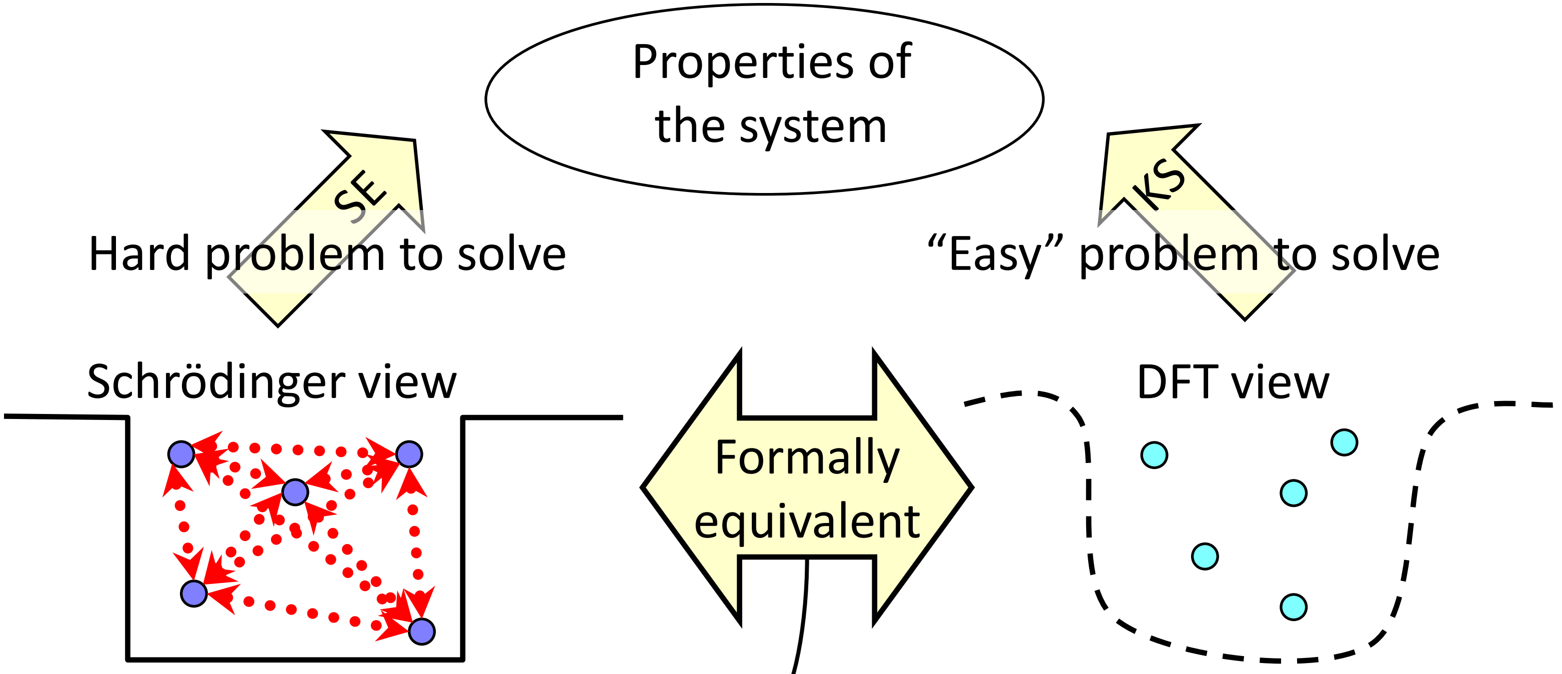
Walter Kohn awarded the Nobel Prize in Chemistry 1998 for Density Functional Theory



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



Properties of the system

SE

KS

Hard problem to solve

“Easy” problem to solve

Schrödinger view

Formally equivalent

DFT view

● electron
◄··► interaction
── external potential

○ Kohn-Sham particle (non-interacting)
- - - effective potential

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

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

Kohn-Sham equations:

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

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

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

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.

We do not need the many-body wave functions.

Approximations for the exchange-correlation functional

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

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

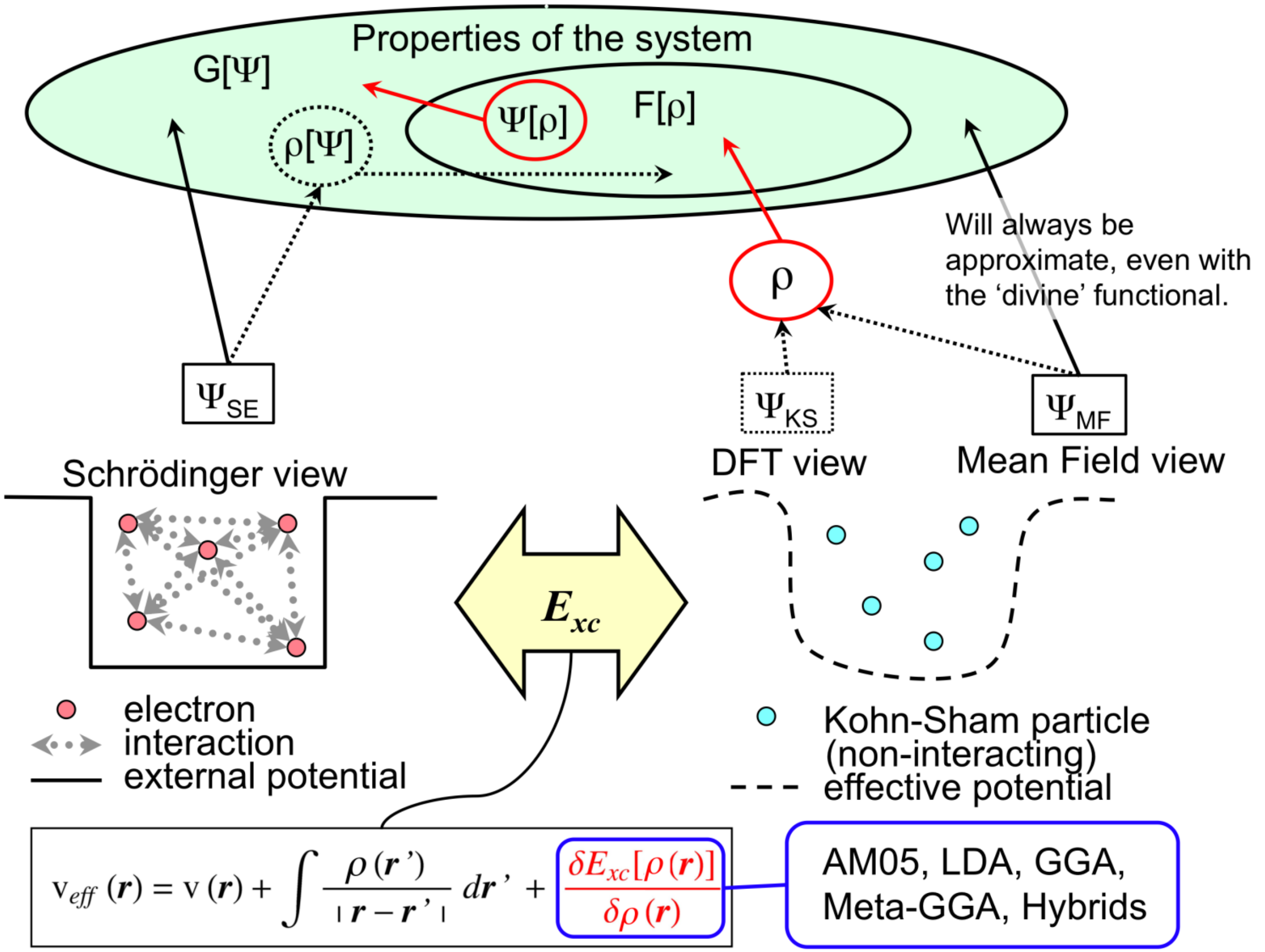
$$\mathrm{v}_{eff}(\mathbf{r}) = \mathrm{v}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|}\,d\mathbf{r}' + \boxed{\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}}$$

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

Density = ρ in chemistry
n in physics

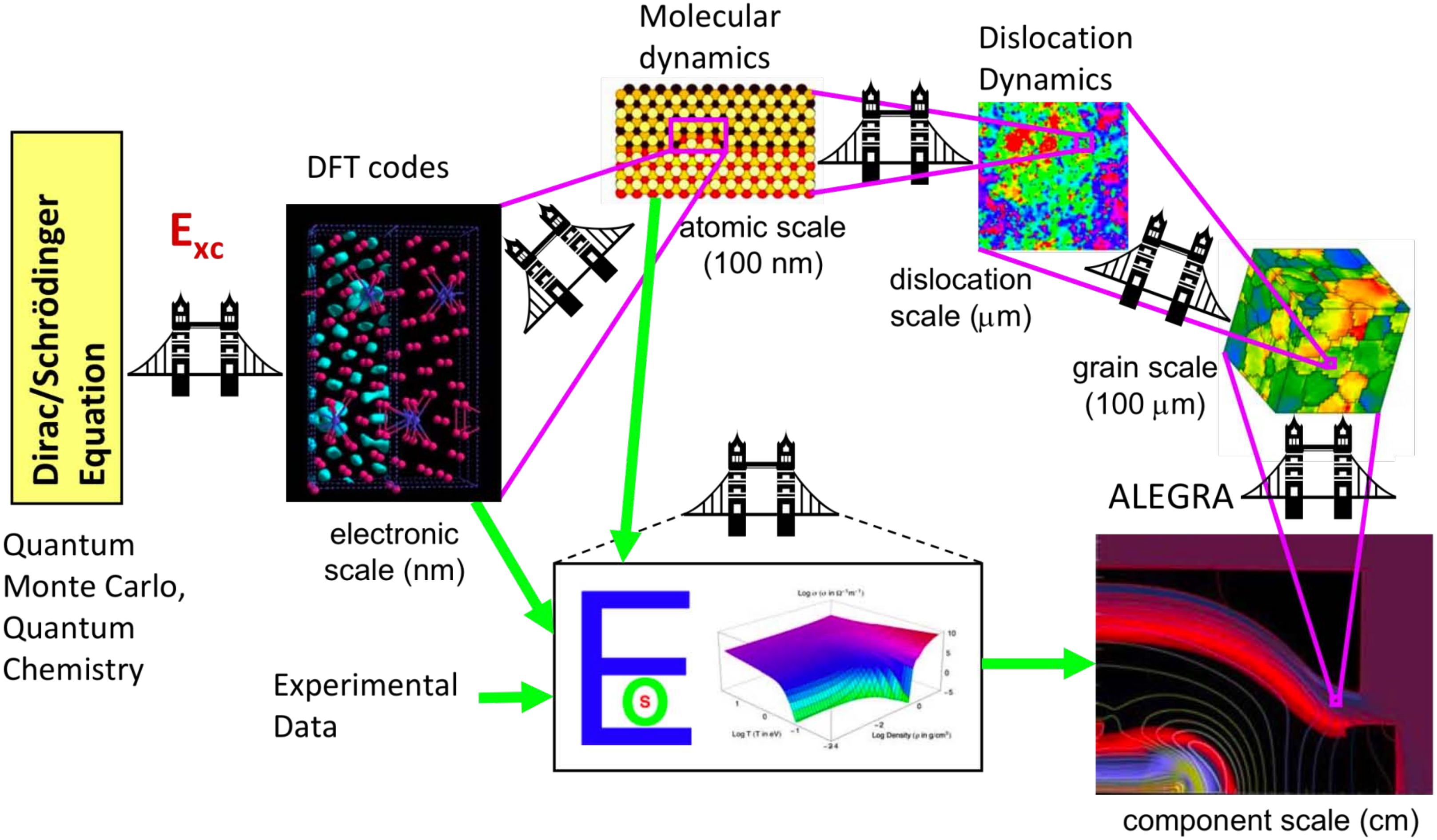


$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$

AM05, LDA, GGA, Meta-GGA, Hybrids

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

Bridges between Fundamental Law of Nature and Engineering



Dirac/Schrödinger Equation

E_{xc}

Quantum Monte Carlo, Quantum Chemistry

DFT codes

electronic scale (nm)

Molecular dynamics

atomic scale (100 nm)

Dislocation Dynamics

dislocation scale (μm)

grain scale (100 μm)

ALEGRA

component scale (cm)

Experimental Data

Predictive DFT calculations for EOS construction: Example of Xe

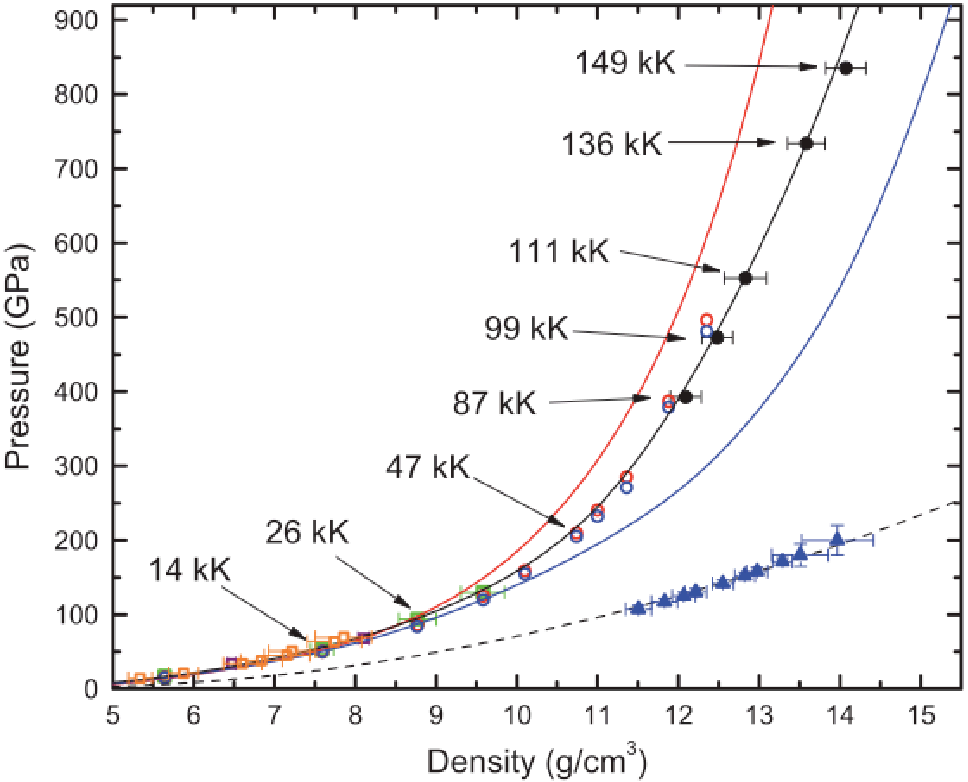


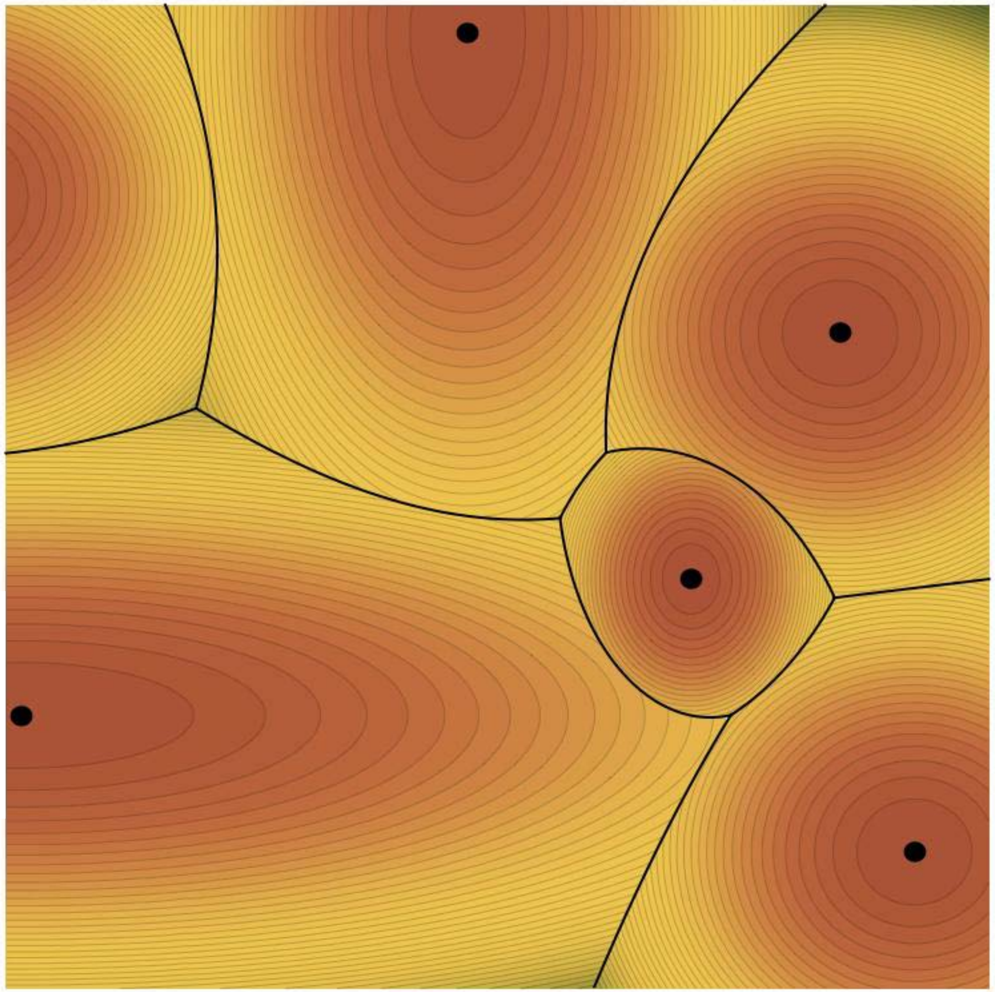
FIG. 3 (color). P-ρ Hugoniot plot. Lines and symbols as in Fig. 2. Black dashed line, 5191 298 K isotherm; blue triangles, solid xenon compression data [17]. Also indicated are Hugoniot temperatures calculated using 5191. Our DFT calculated isotherm [37] agrees with the experimental data [17].

Seth et al. PRL 105, 085501 (2010)

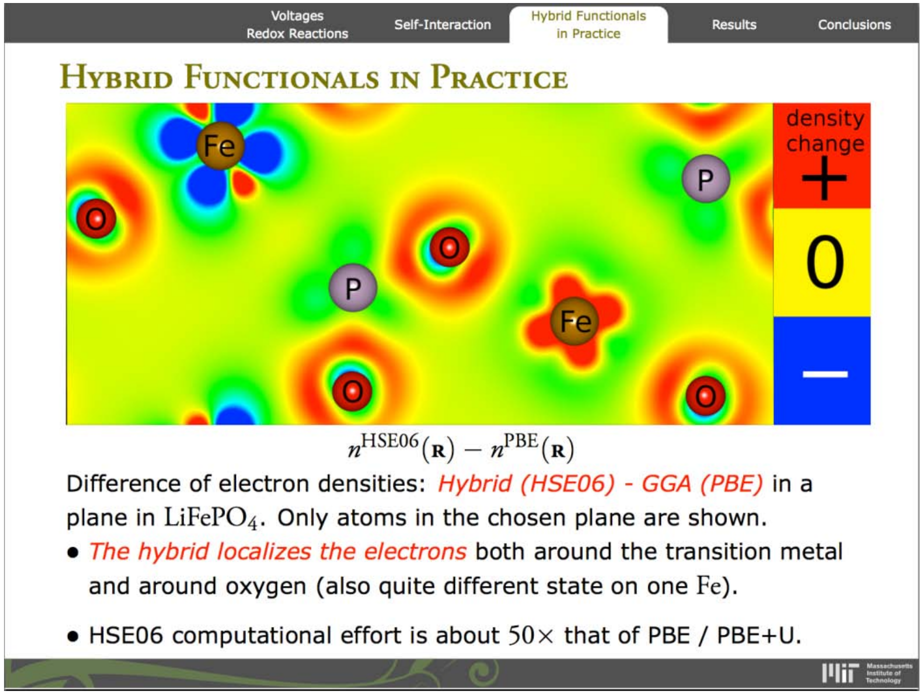
Red circle: LDA
Blue circle: AM05
Black circles: Z data
Black line: New EOS 5191
Blue line: SESAME 5190
Red line: LEOS 540

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).

For functional development we need info from the Dirac/Schrödinger Equation



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

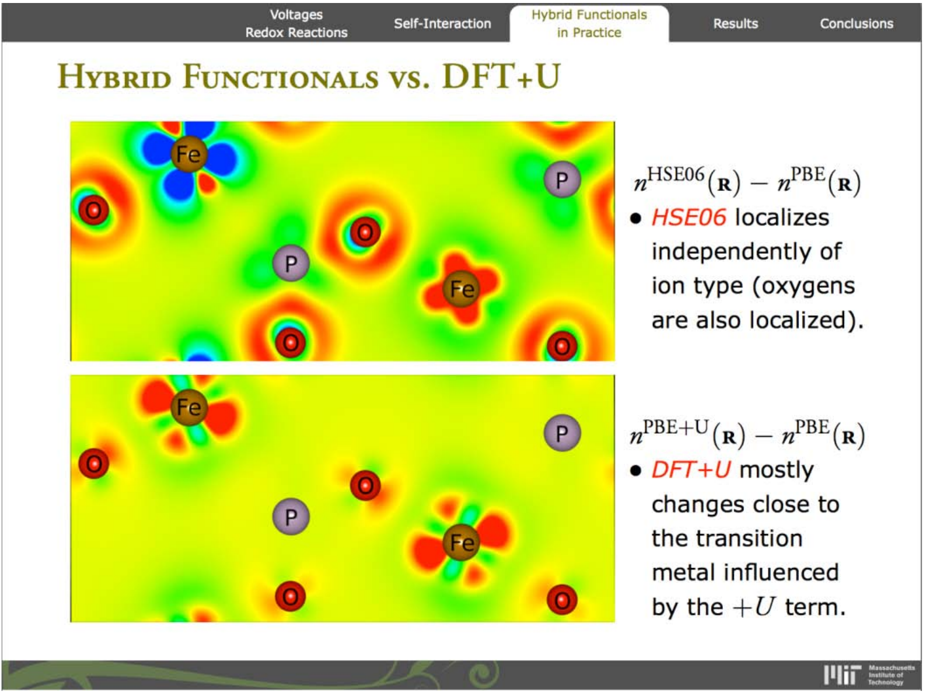


HYBRID FUNCTIONALS IN PRACTICE

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

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).

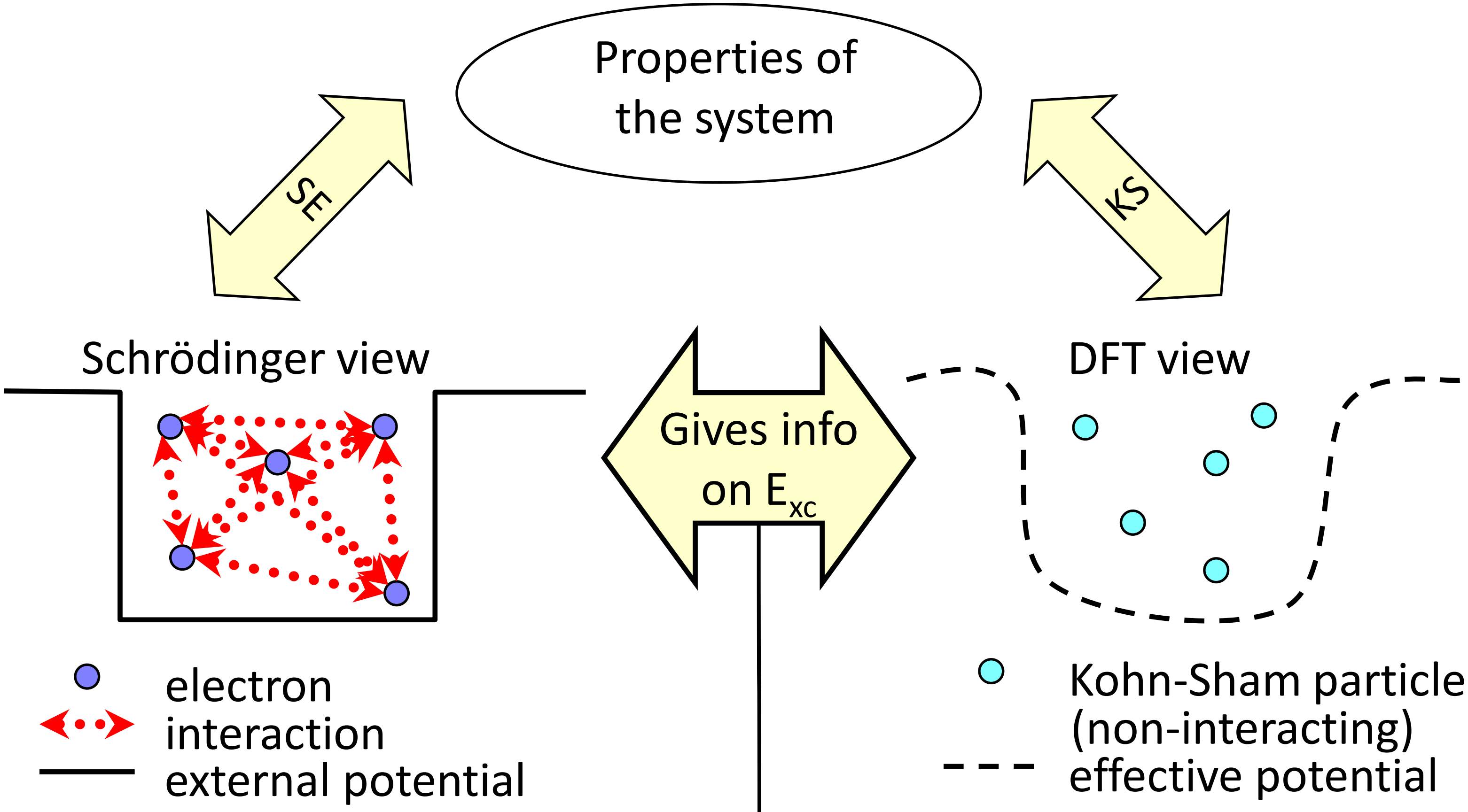
$n^{\mathrm{PBE+U}}(\mathbf{R}) - n^{\mathrm{PBE}}(\mathbf{R})$

- *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.

Functional development



Properties of the system

SE

KS

Schrödinger view

Gives info on E_{xc}

DFT view

● electron

◄•••► interaction

— external potential

○ Kohn-Sham particle (non-interacting)

- - - effective potential

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

LDA and Ceperly-Alder

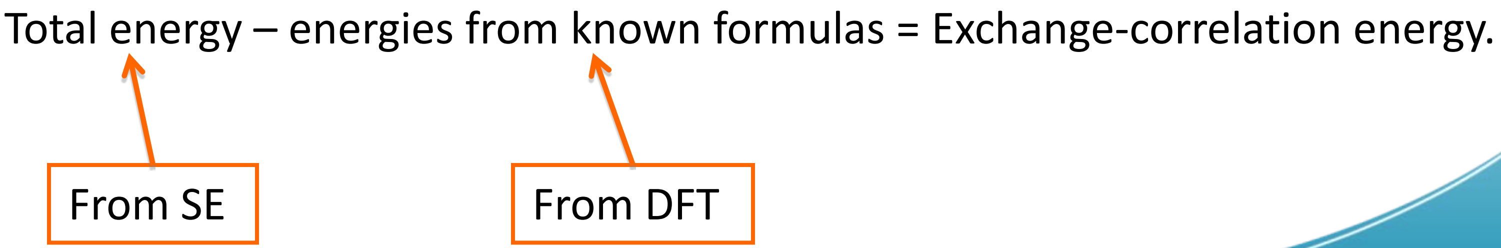
Ceperly and Alder, PRL 45, 566 (1980).

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)

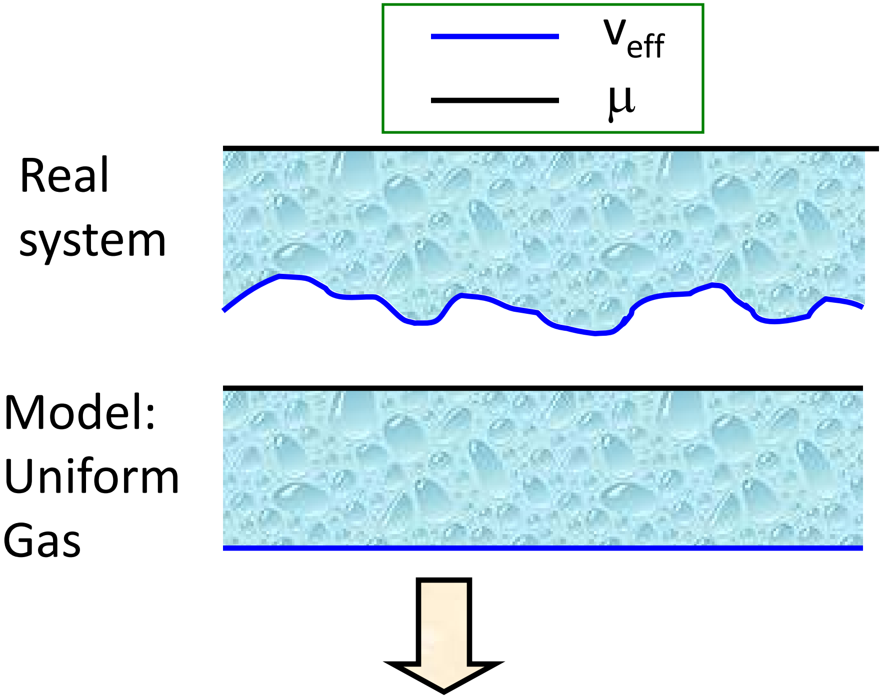


Total energy – energies from known formulas = Exchange-correlation energy.

From SE

From DFT

The LDA functional



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.

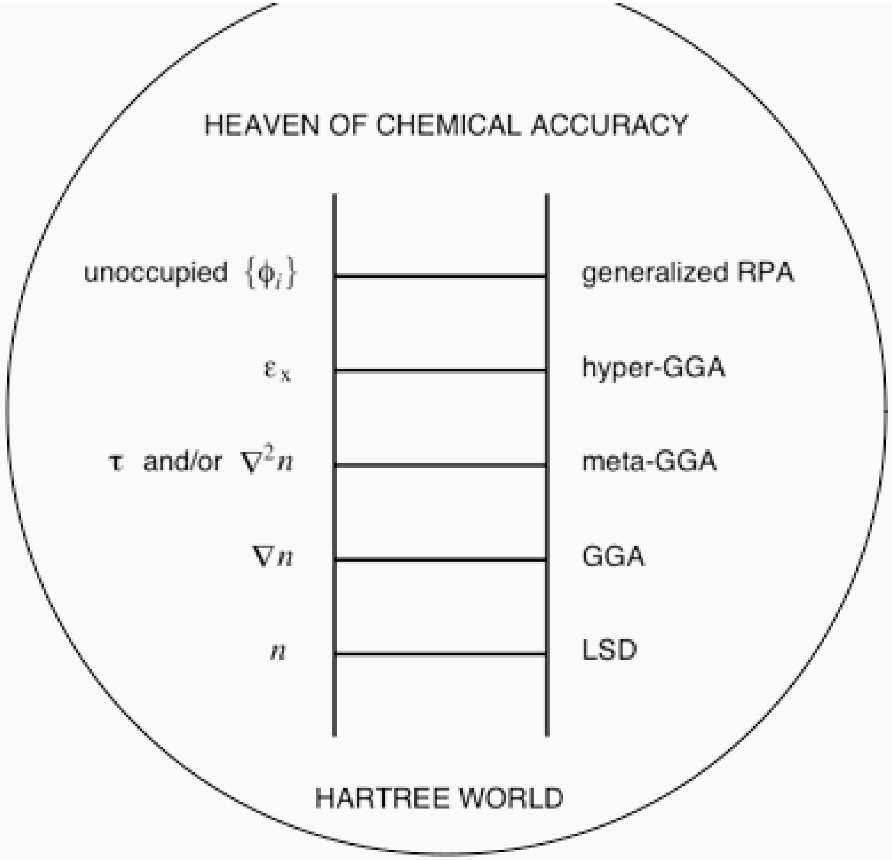
Basic concept and first explicit LDA published in 1965 (Kohn and Sham).

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 constraints 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 model system: 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



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

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

Compatibility: Using model systems

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

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

The *exchange-correlation energy per particle*

is modeled in DFT.

LDA, GGA, meta-GGA, and AM05

Subsystem functionals

From
general purpose functionals
to
specialized functionals

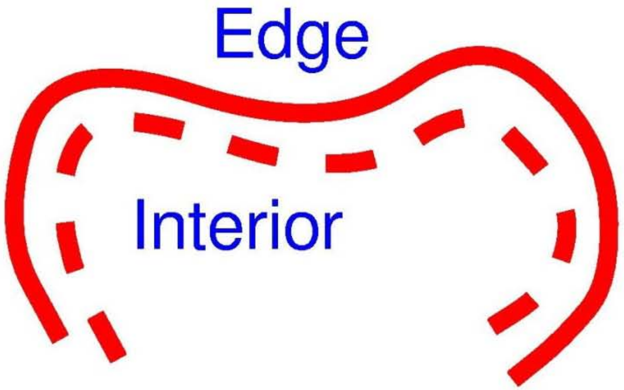
$$E_{xc} = \int_V n(\boldsymbol{r})\, \epsilon_{xc}(\boldsymbol{r};[n])\, dV$$

Use specialized functionals
in the different subsystems

Divide integration over V
into integrations over subsystems

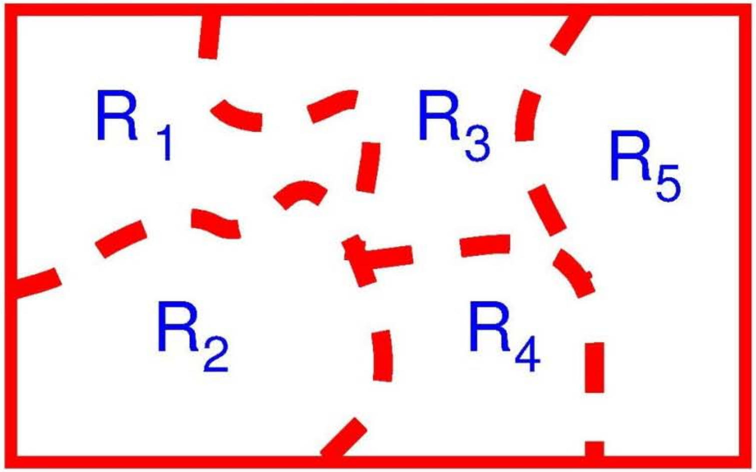
Subsystem functionals

Original Kohn and Mattsson approach



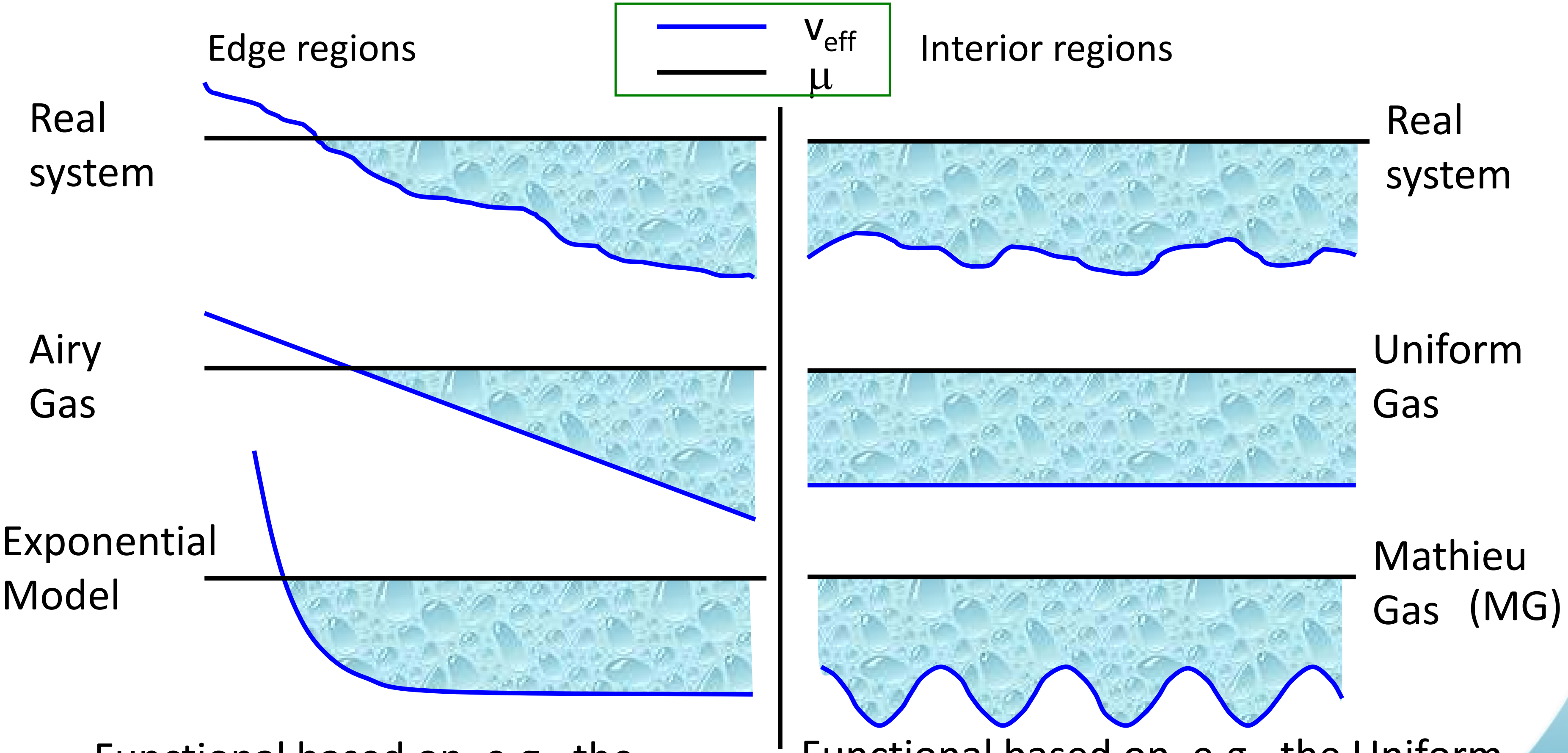
Kohn, Mattsson PRL 81, 3487 (1998)

Generalized Idea



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

Subsystem functionals



Edge regions

Interior regions

v_{eff}

μ

Real system

Airy Gas

Exponential Model

Real system

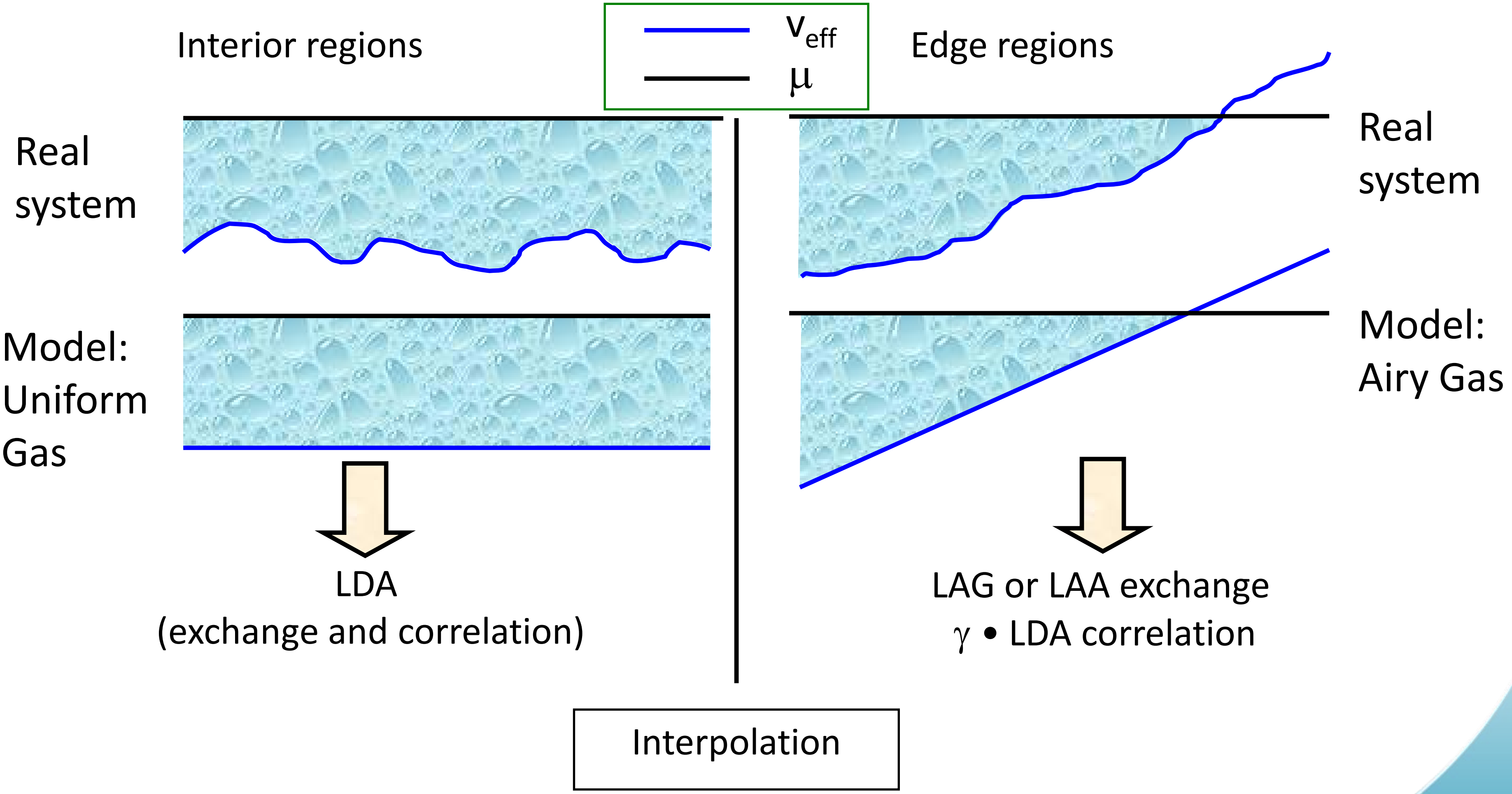
Uniform Gas

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).

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



Interior regions

Edge regions

— v_{eff}

— μ

Real system

Model: Uniform Gas

LDA
(exchange and correlation)

Real system

Model: Airy Gas

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.

Practical information about AM05

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

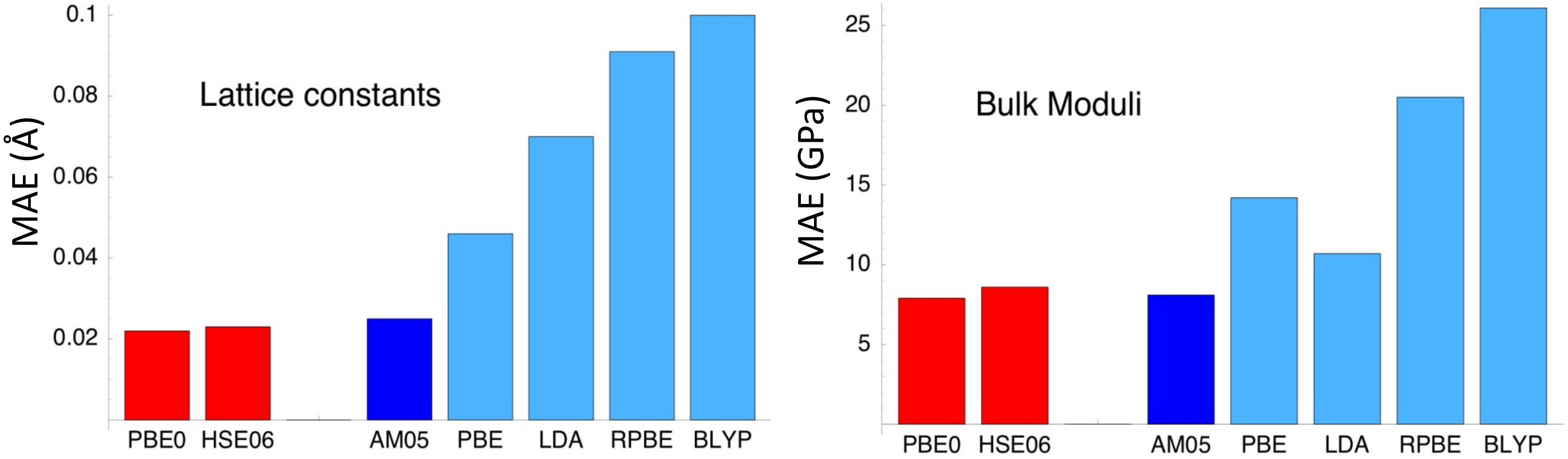
- AM05 can be implemented into any code that can run a GGA. Already implemented in VASP5 and many other codes.

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

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

AM05 is as accurate as a hybrid, but much faster

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 <u>one to three order of magnitudes faster</u> to use than hybrids (red). AM05 has the same accuracy as hybrids for solids and thus enable <u>accurate and fast</u> 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.

PBEsol vs AM05

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

Surface energies for a number of metals

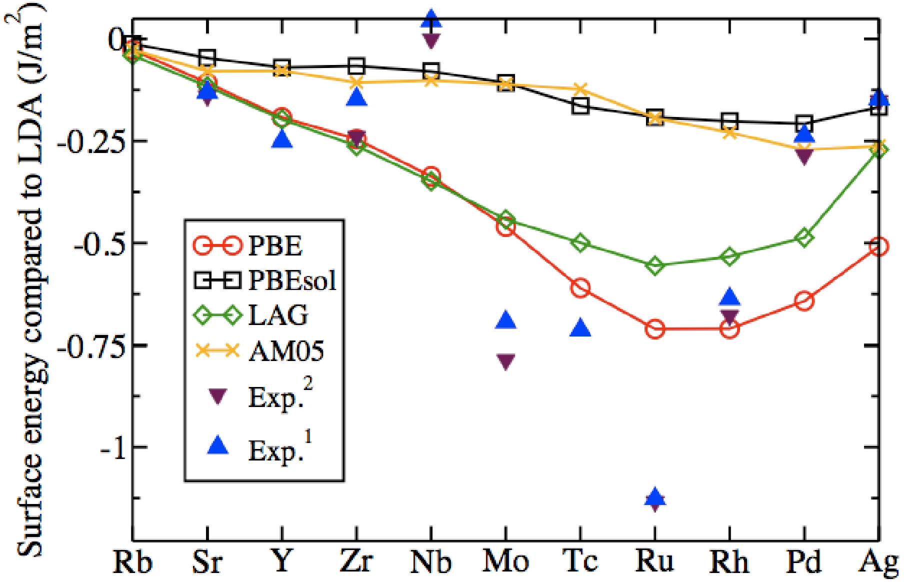
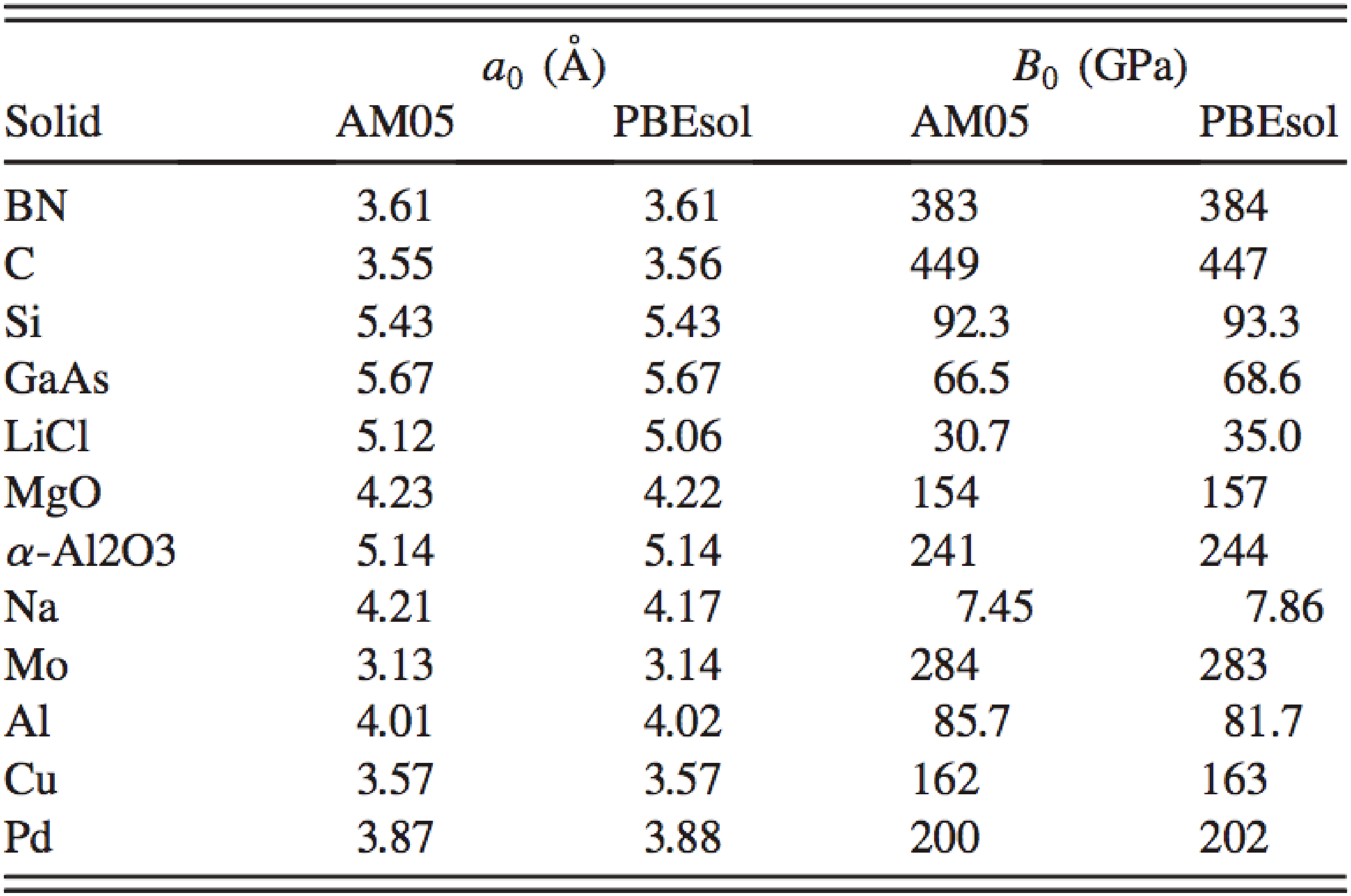


FIG. 1: (Color online) The effect of PBE (red circles), PBEsol (black squares), LAG (green diamonds) and AM05 (yellow crosses) gradient corrections on the LDA surface energies for Rb, Sr and 4*d* transition metals (in J/m^2). For comparison, the differences between the experimental surface energies (blue 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).



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?

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

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.

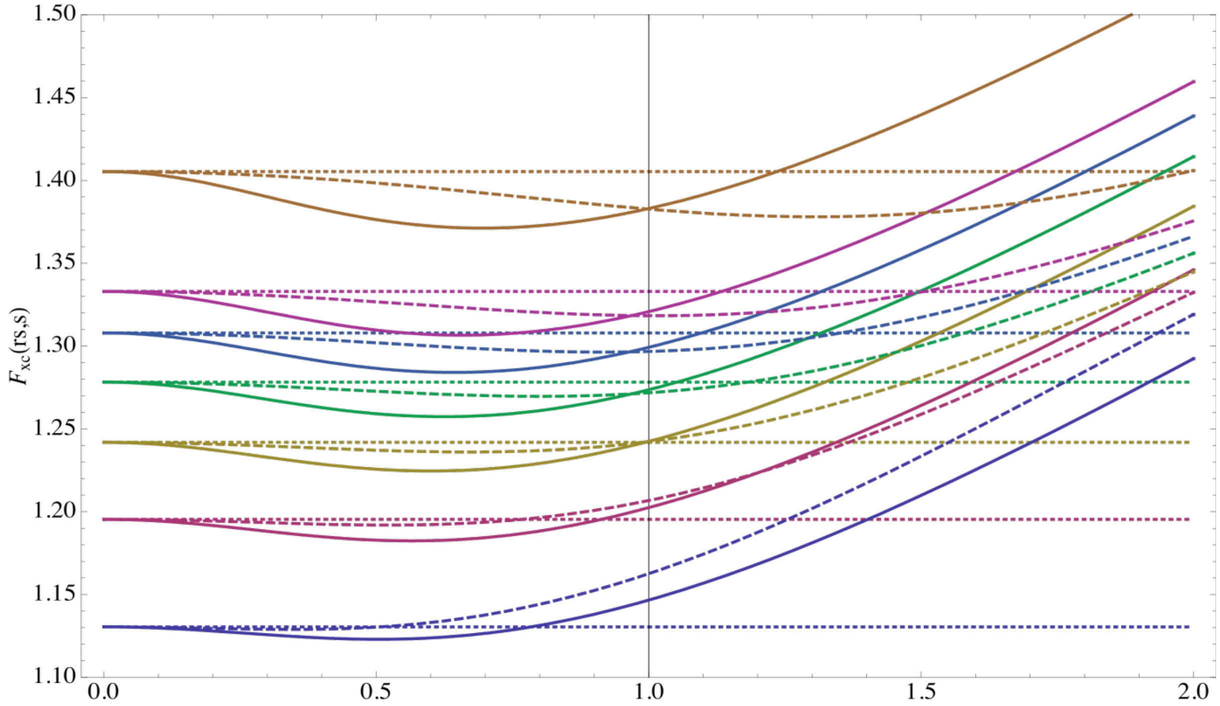
Gradient expansion of exchange (used in PBEsol)
derived from "alternative definition of exchange".
(Discussed in PRB 66, 165117 (2002)).

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 not give similar results as LDA)

PBEsol and AM05 are locally different but globally similar.

What is next?

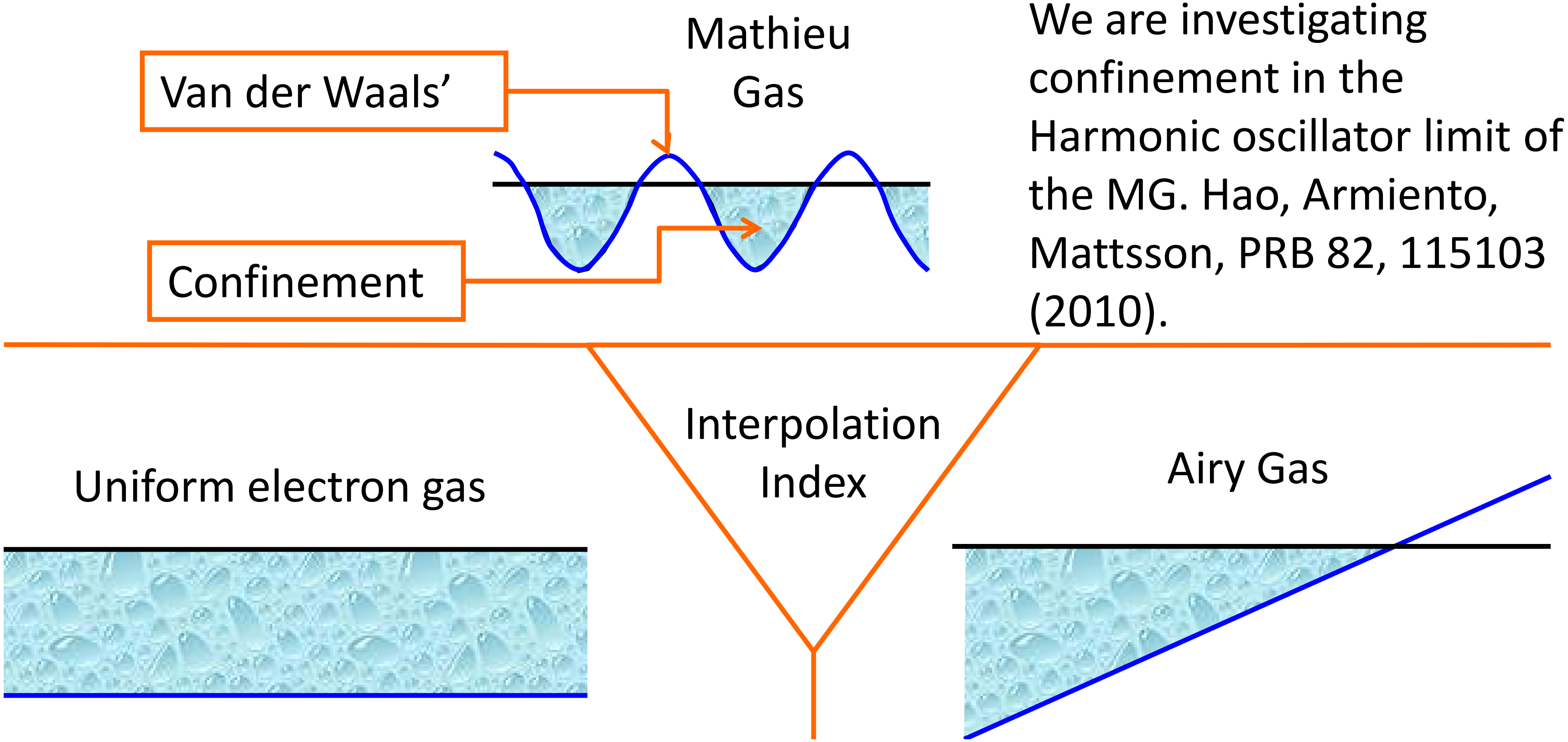
The construction of AM05 shows that the subsystem functional scheme can be a fruitful way of constructing exchange-correlation functionals.

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.

A functional for confined and van der Waals' systems



Van der Waals'

Confinement

Mathieu Gas

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

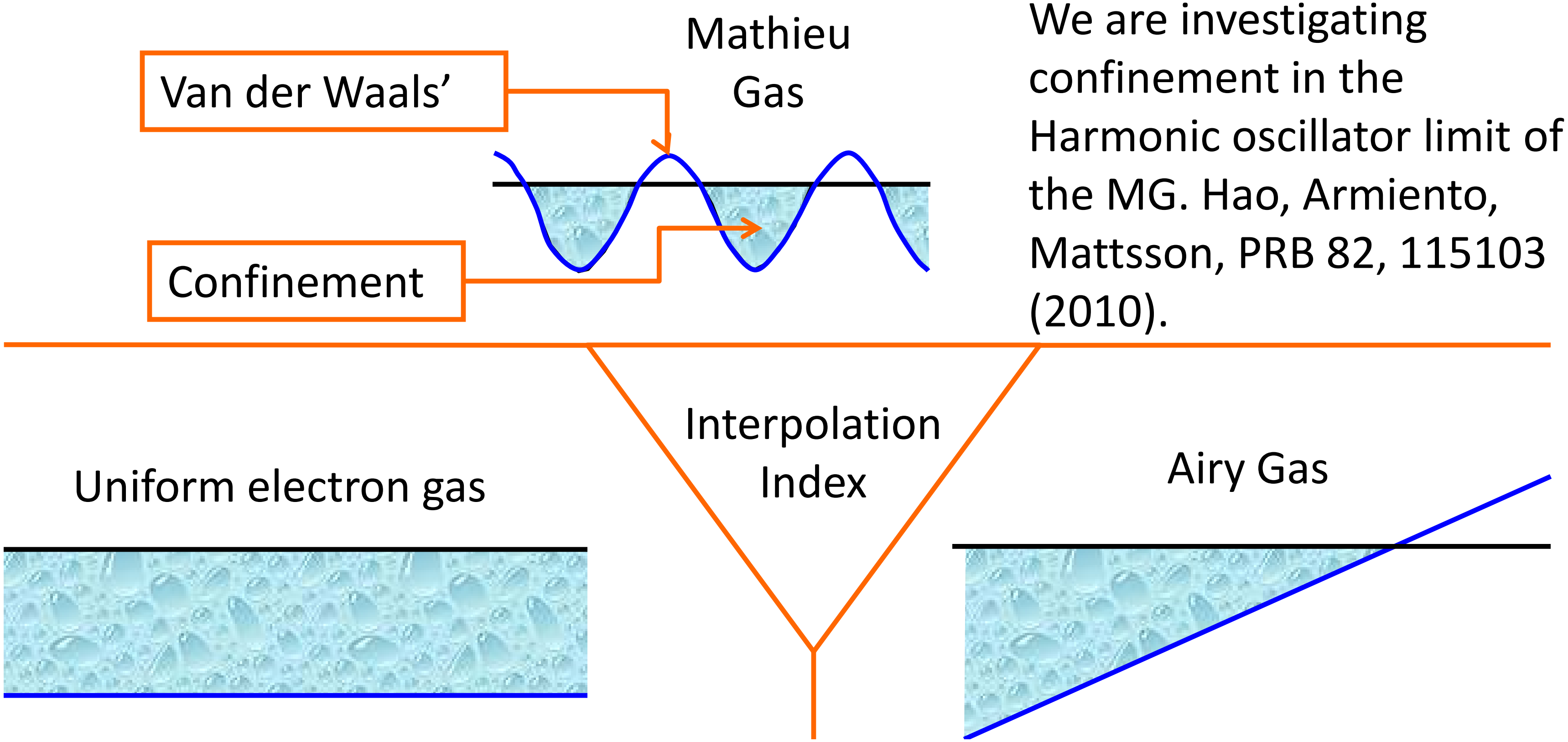
Interpolation Index

Uniform electron gas

Airy Gas

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).

A functional for confined and van der Waals' systems



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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. 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.

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

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Schrödinger based Kohn-Sham Equations

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

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.

From currents to spin densities

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

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

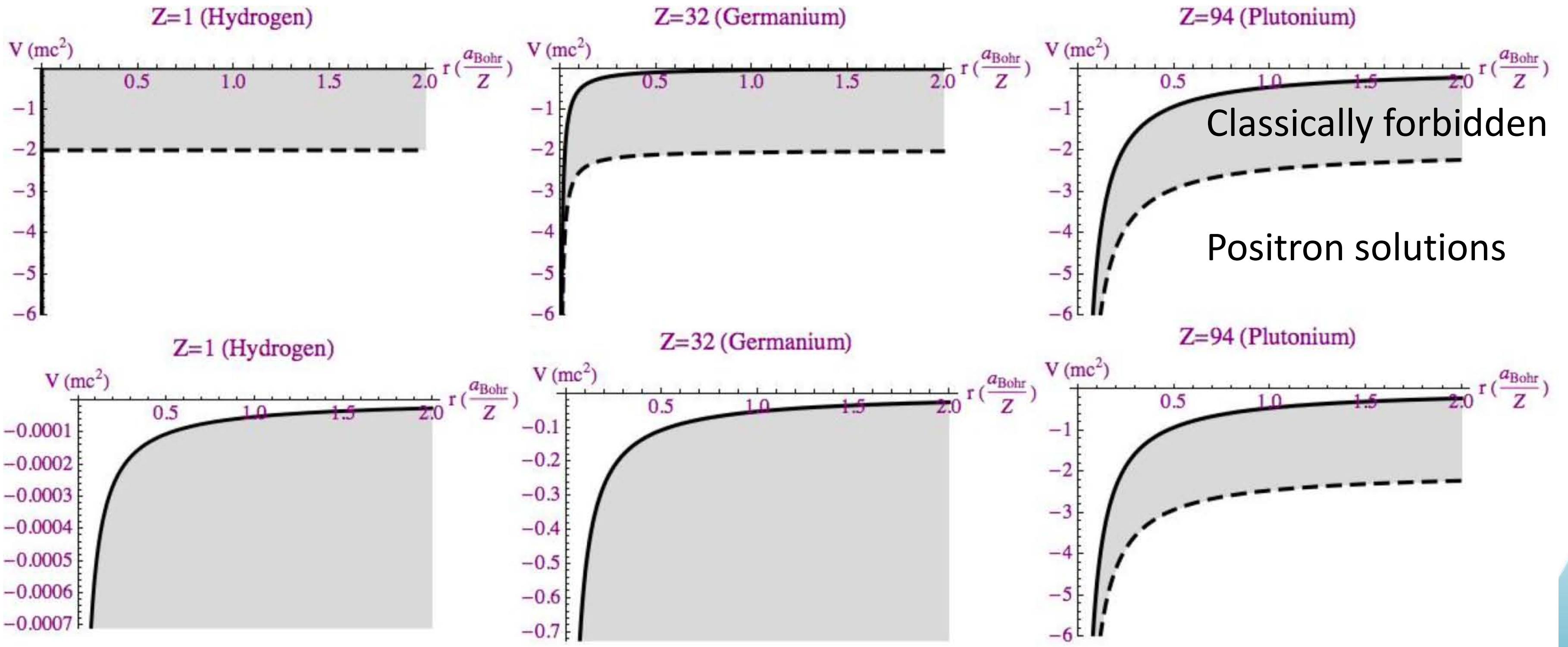
$$\boldsymbol{I} = \frac{e}{2mc} \sum_{-mc^2<E_n<E_F} \left\{ \psi_n^\dagger \, \beta \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\text{eff}}}{c} \right) \psi_n \right] + \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\text{eff}}}{c} \right) \psi_n \right]^\dagger \beta \, \psi_n \right\}$$

Orbital current: Neglecting this gives…

When do we have relativistic effects?

Non-relativistic limit is:

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



Electron solutions

Classically forbidden

Positron solutions

Violated near nuclei for high Z materials.

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?

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.

Intramolecular structure: Example of bond lengths

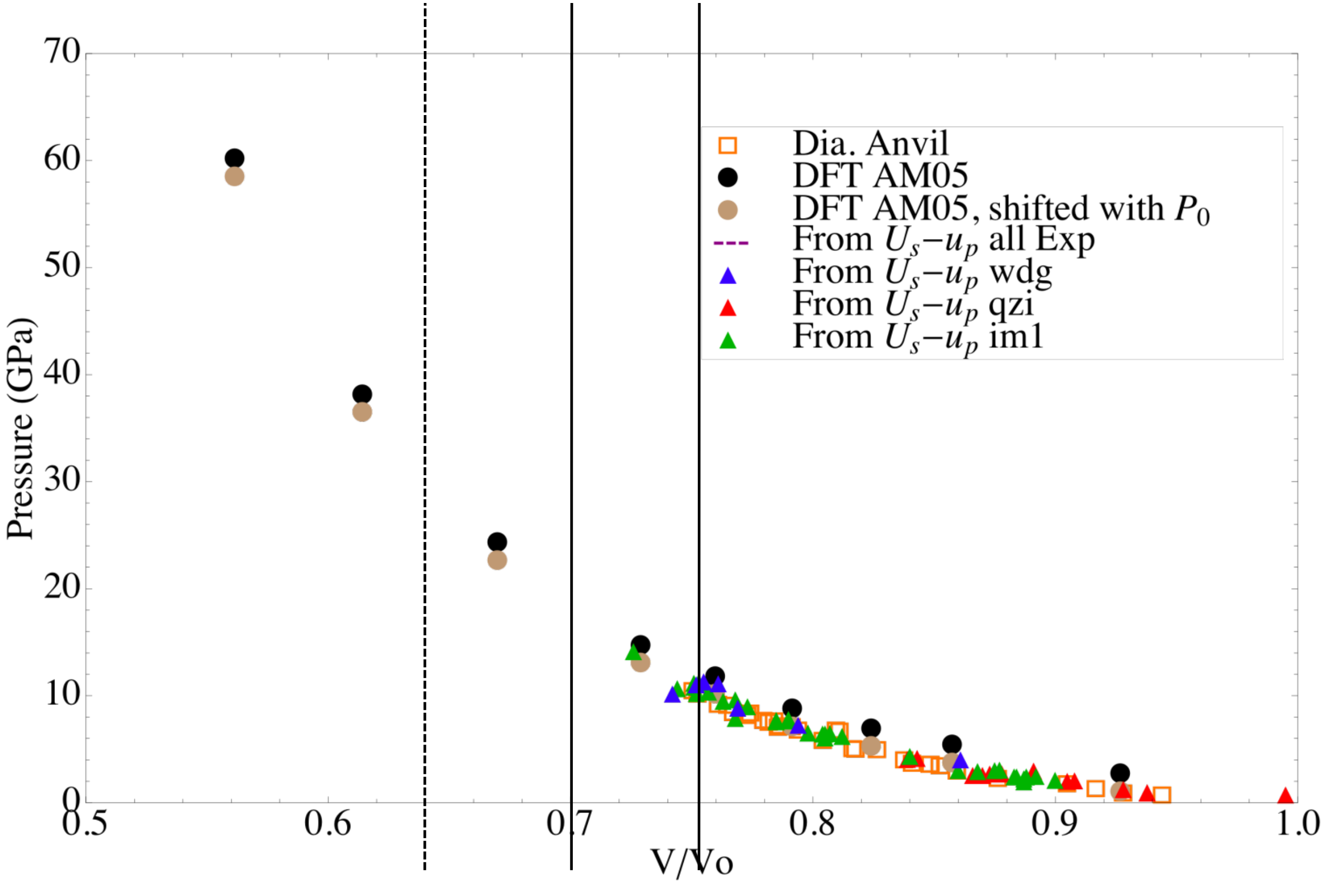
Exp at ~298 K.

	Exp	LDA	LDA	HSE	AM05	PBE	HSE	PBE	AM05
a	9.38 Å	9.00 Å	9.38 Å	9.38 Å	9.38 Å	9.38 Å	9.60 Å	9.90 Å	10.80 Å
c/a	0.715	0.710	0.715	0.715	0.715	0.715	0.720	0.720	0.780
C--C	1.531	1.518	1.523	1.528	1.530	1.538	1.531	1.543	1.535
C--O	1.446	1.428	1.427	1.438	1.436	1.449	1.438	1.449	1.434
O--N	1.403	1.400	1.409	1.381	1.417	1.439	1.385	1.452	1.436
O(2)--N	1.198	1.211	1.210	1.206	1.213	1.218	1.206	1.217	1.209
O(1)--N	1.193	1.208	1.208	1.204	1.212	1.217	1.204	1.217	1.213

The intramolecular bond lengths are not sensitive to the crystal environment with the possible exception of the O—N bond. For this bond HSE is also breaking the usual trend of bond lengths LDA < HSE, AM05 < PBE.

Compared to the intermolecular distances, all functionals give a good description of the intramolecular distances.

PETN

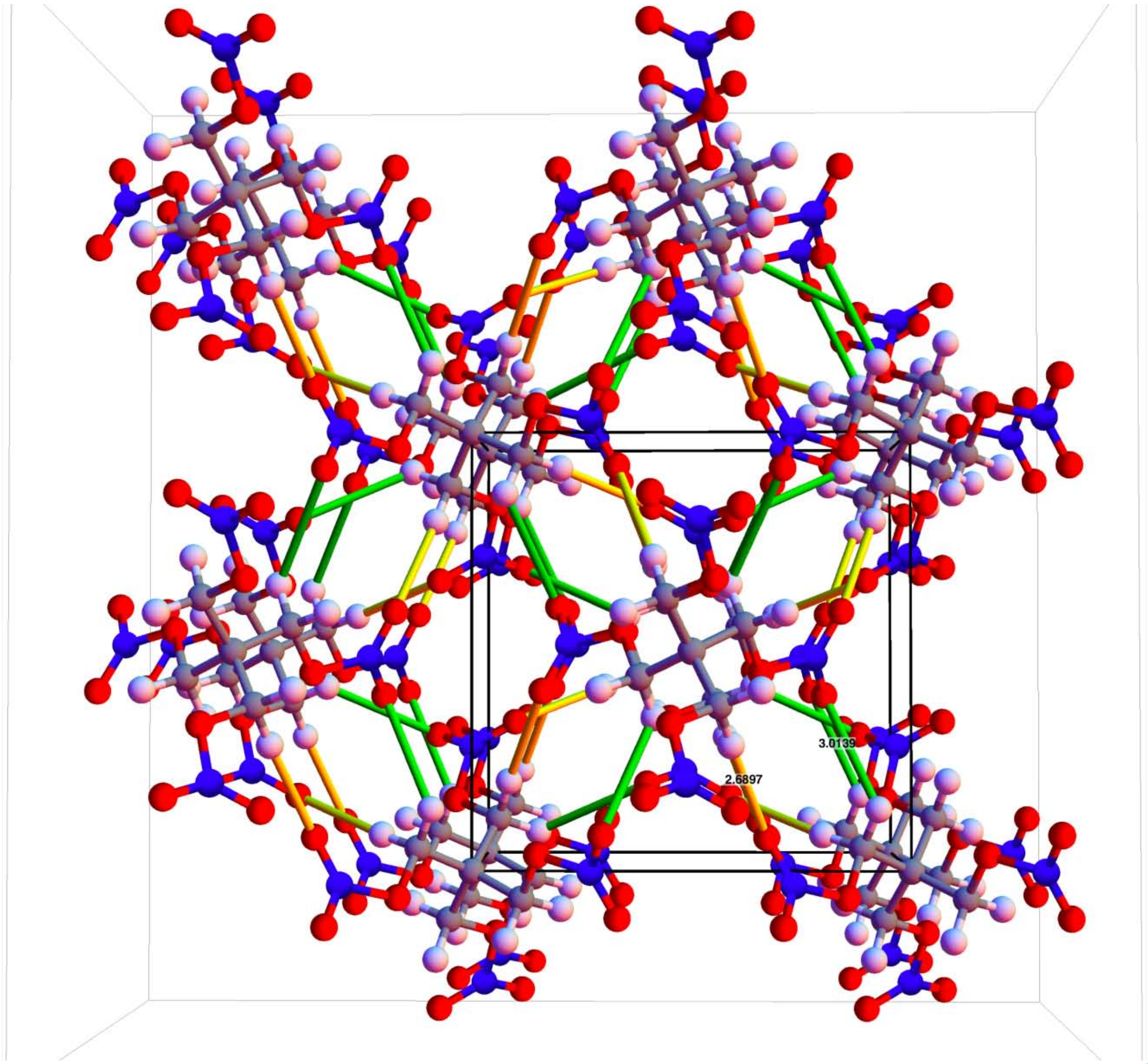


DFT-AM05 can NOT be trusted for less compression than 0.75. DFT-AM05 can probably be trusted for larger compression than 0.7, but at least 0.64.

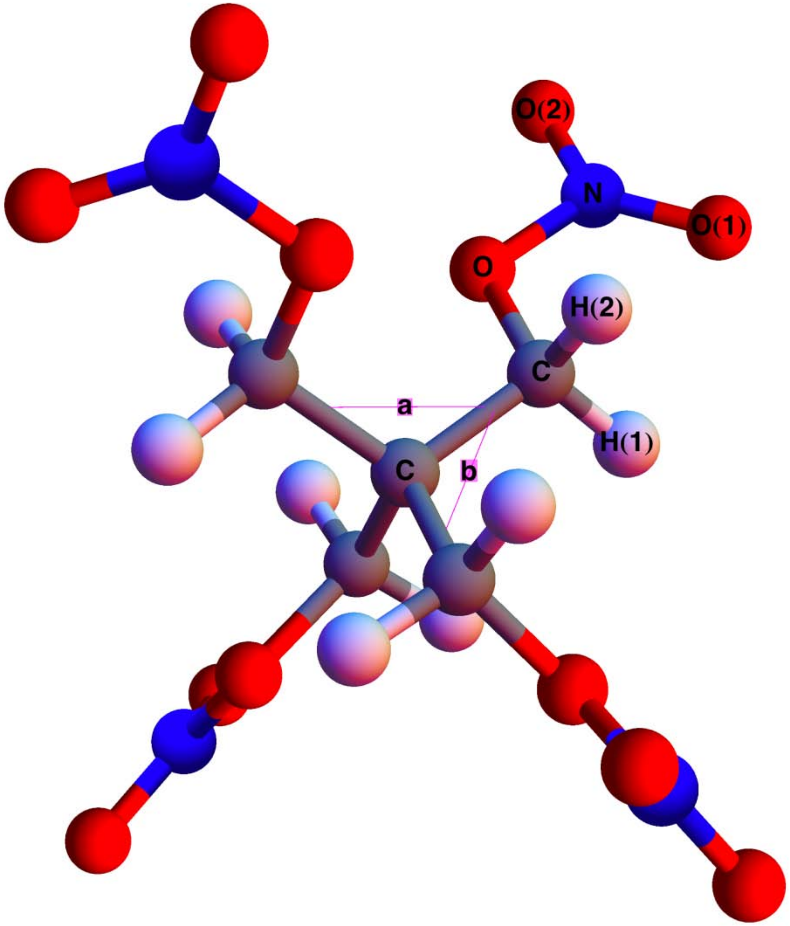
Interesting fact: experimental data hard to obtain below 0.7.

Triangles are single crystal shock data.

Sensitive and non-sensitive directions



The good news: Intramolecular structure



We have calculated the molecule structure (bond lengths and angles) in the crystal environment at theoretical equilibrium and experimental lattice parameters. Functionals follow the usual trends but all give a good description. This means the large differences in equilibrium volumes stem from the poor description of the intermolecular van der Waals' bonds.