



The subsystem functional scheme: The Armiento-Mattsson 2005 (AM05) functional and beyond

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Multiscale Dynamic Materials Modeling

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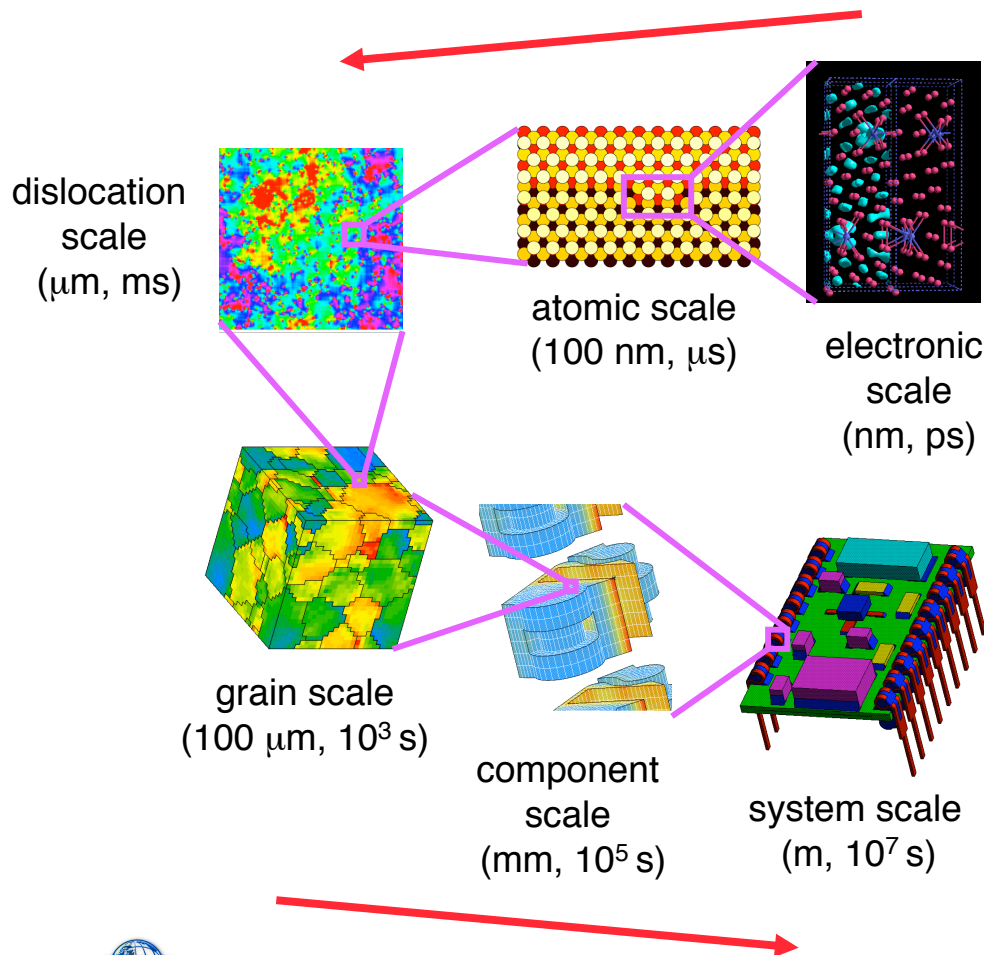
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Density Functional Theory: The Underpinning of Predictive Multi-scale Efforts at Sandia



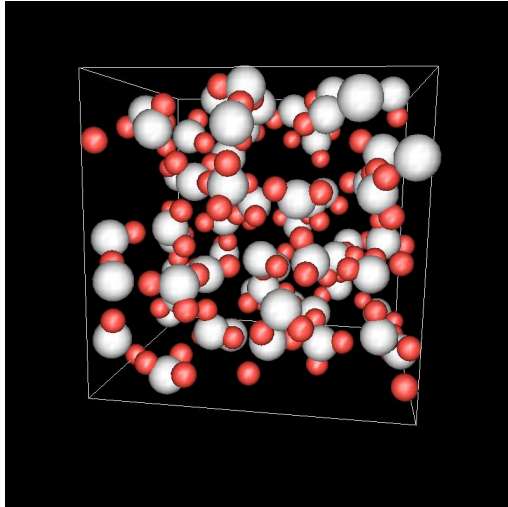
- **Goal:** Predict how materials age and perform under normal, adverse and extreme conditions.
- **Method:** Bridge length and time scales by using results from each scale as input on the next scale.
- **Foundation:** To get the fundamental processes right via DFT calculations at the electronic scale.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



Speed is also very important

DFT-MD (also called QMD)

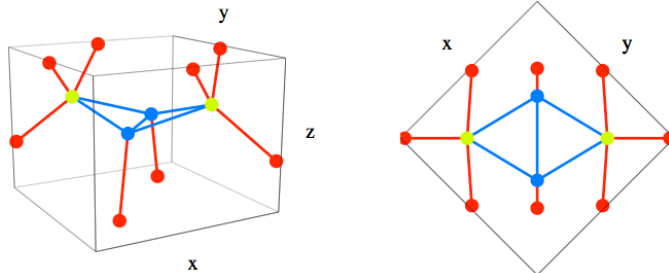
Snap shot of water simulation
(64 molecules) done with
AM05. Thomas Mattsson.



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:

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.

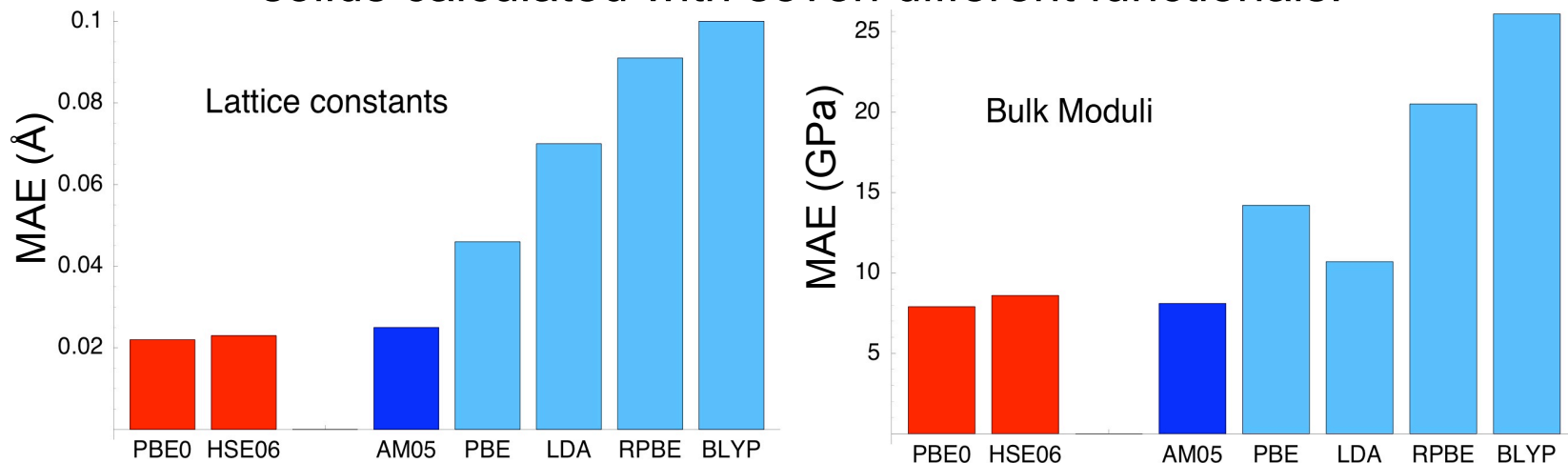


The Si $\langle 110 \rangle$ - split interstitial

AM05 is as accurate as a hybrid, but much faster, for 'normal' solid state systems

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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.

Most important:
AM05 proves that fast AND accurate is possible.



AM05 works as well as PBE for molecular chemical reactions

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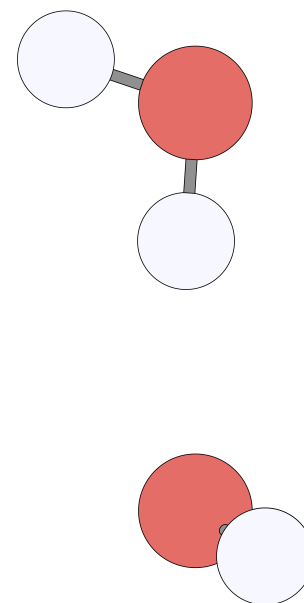
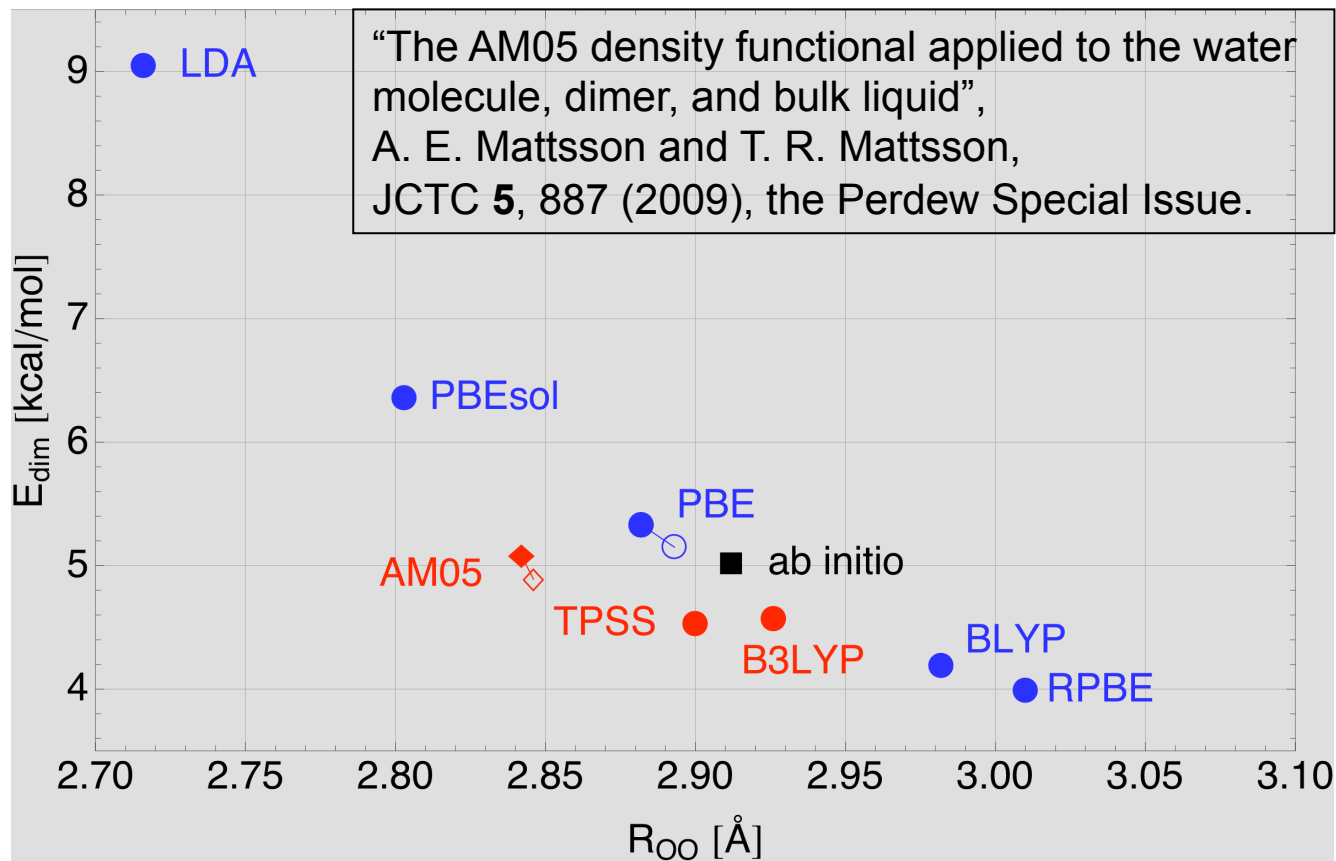
85 different chemical reactions between
molecules from the G2 set:

	B3LYP	BLYP	PBE	AM05
Mean Absolute Error	5.32 kcal/ mol	7.30 kcal/ mol	7.63 kcal/ mol	8.08 kcal/ mol

Note: AM05 is constructed without any reference to
molecular systems.

To appear in Journal of Computational
Chemistry. Preprint at arXiv:0908.1744
<http://arxiv.org/abs/0908.1744>

The binding energy and O--O distance of the water dimer



TPSS from Santra et al JCP **127**, 184104 (2007)

B3LYP from Xu et al JPCA **108**, 2305 (2004)

Best ab initio is CCSD(T)



So, why is AM05 working?

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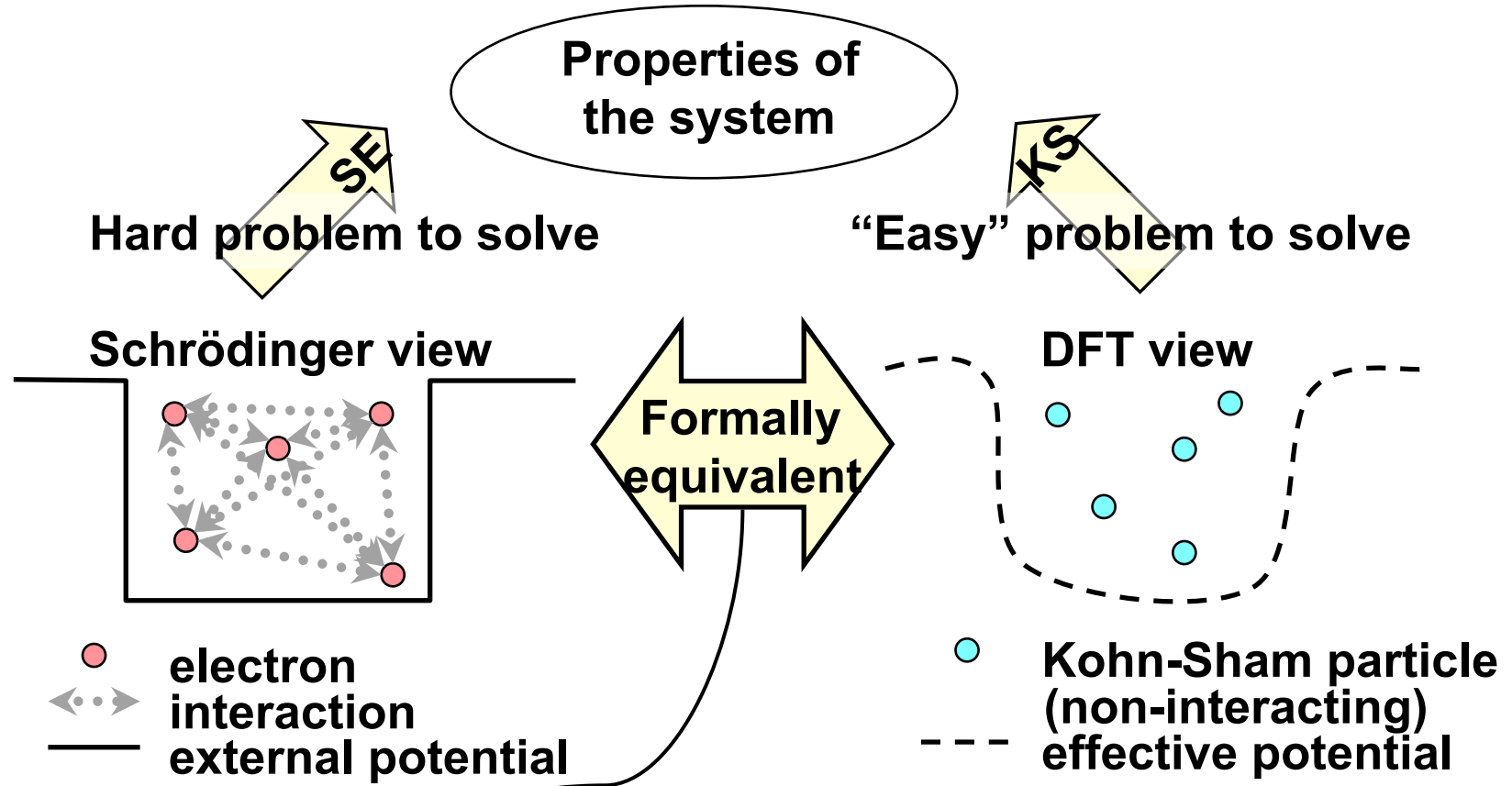
AM05 is based on a 'new' way of thinking about functionals that is actually based on how the first LDA was created already in 1965.

AM05 is constructed via the sub-system functional scheme using model systems which emphasizes COMPATIBILITY.

But let us start from the beginning:



DFT and functionals



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

AM05, LDA,
GGA, Meta-
GGA, Hybrids





Exchange-correlation functionals

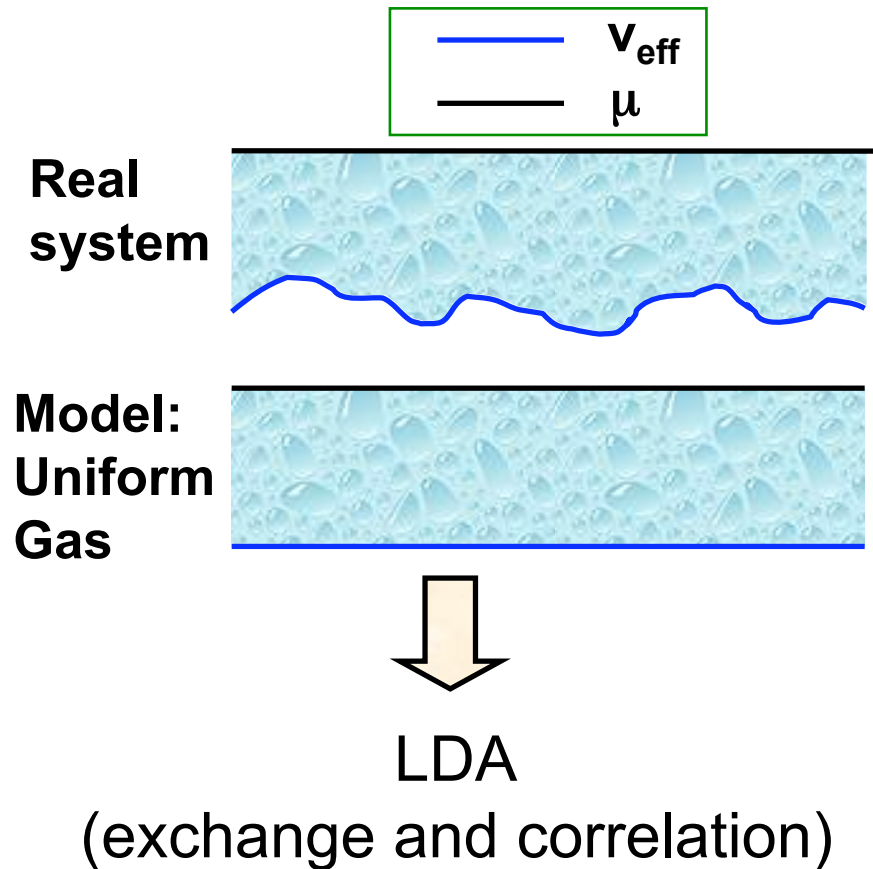
$$E_{xc} = \int_V n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}; [n]) dV$$

The *exchange-correlation energy per particle* is modeled in DFT.

LDA, GGA, meta-GGA, and AM05



The LDA functional



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.

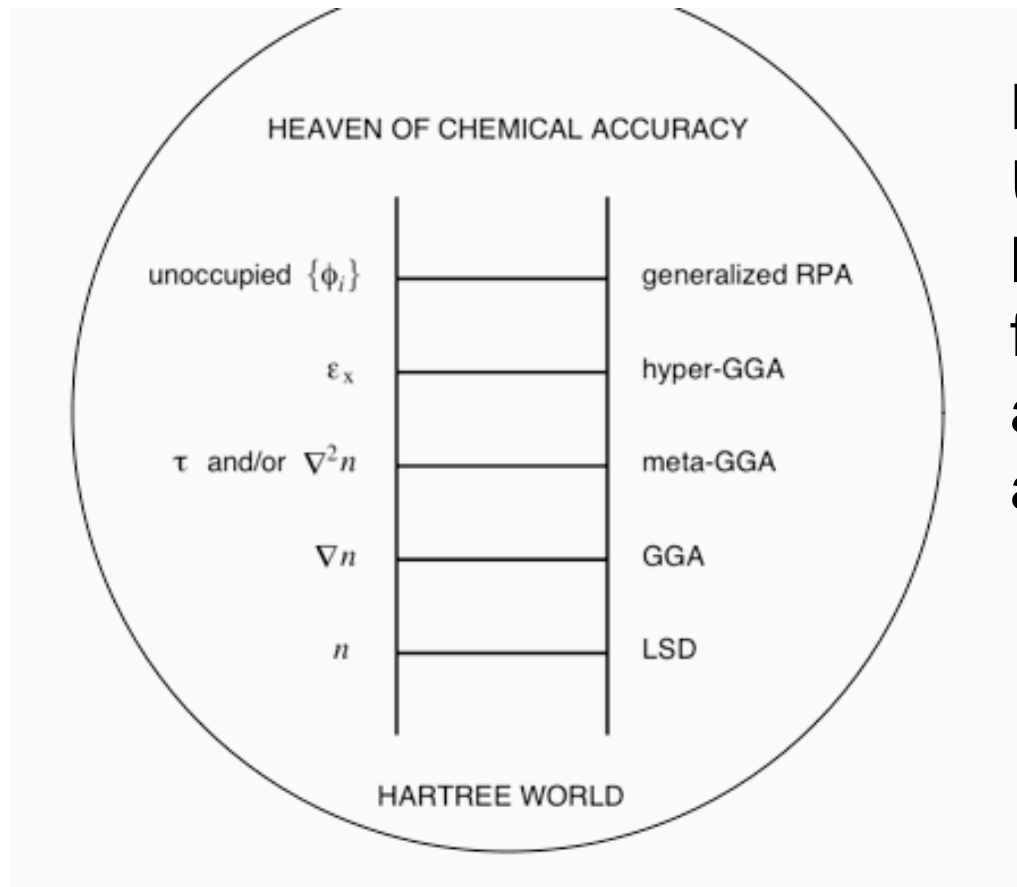
Two views developed:

- 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

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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/cm²

(PBE)

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



So, why is AM05 working?

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AM05 is based on a 'new' way of thinking about functionals that is actually based on how the first LDA was created already in 1965.

AM05 is constructed via the sub-system functional scheme using model systems which emphasizes COMPATIBILITY.



Exchange-correlation functionals

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

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Subsystem functionals

From
general purpose functionals
to
specialized functionals

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

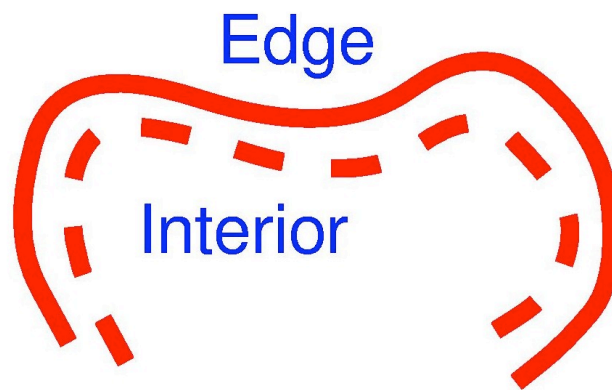
Use specialized functionals
in the different subsystems

Divide integration over V
into integrations over subsystems



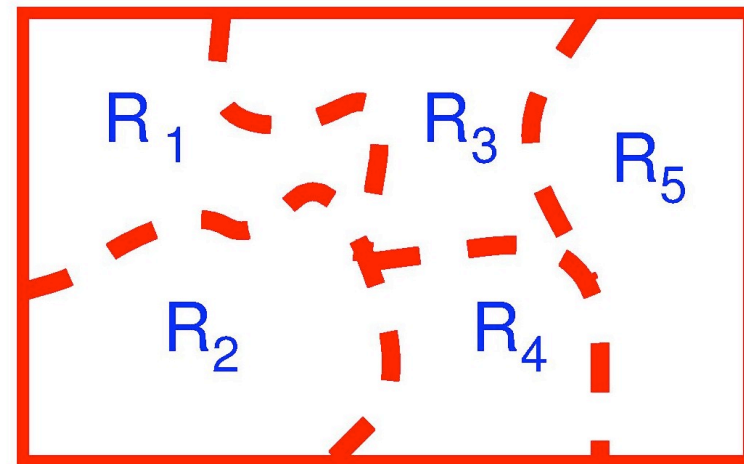
Subsystem functionals

Original Kohn and Mattsson approach



Kohn, Mattsson PRL 81, 3487 (1998)

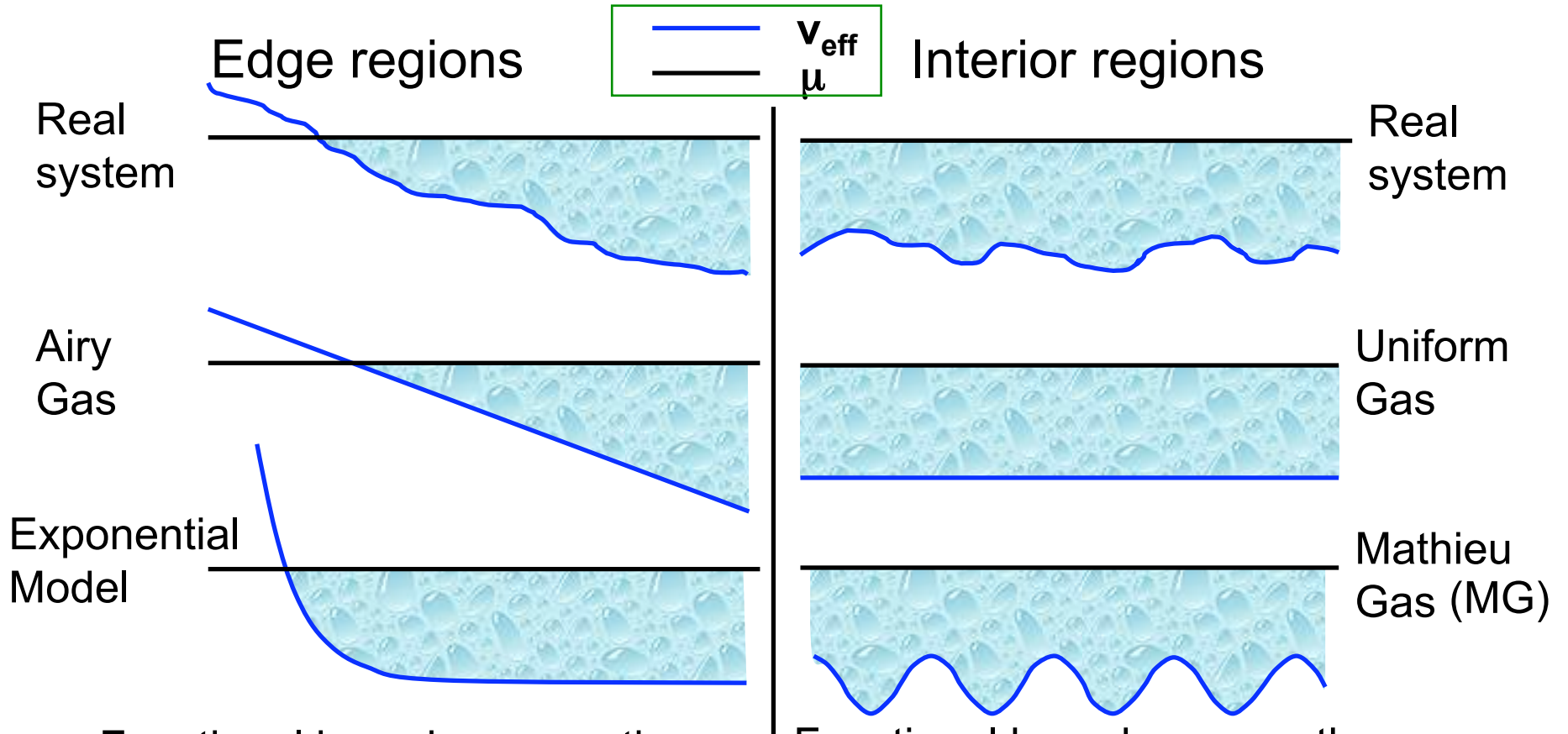
Generalized Idea



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



Subsystem functionals



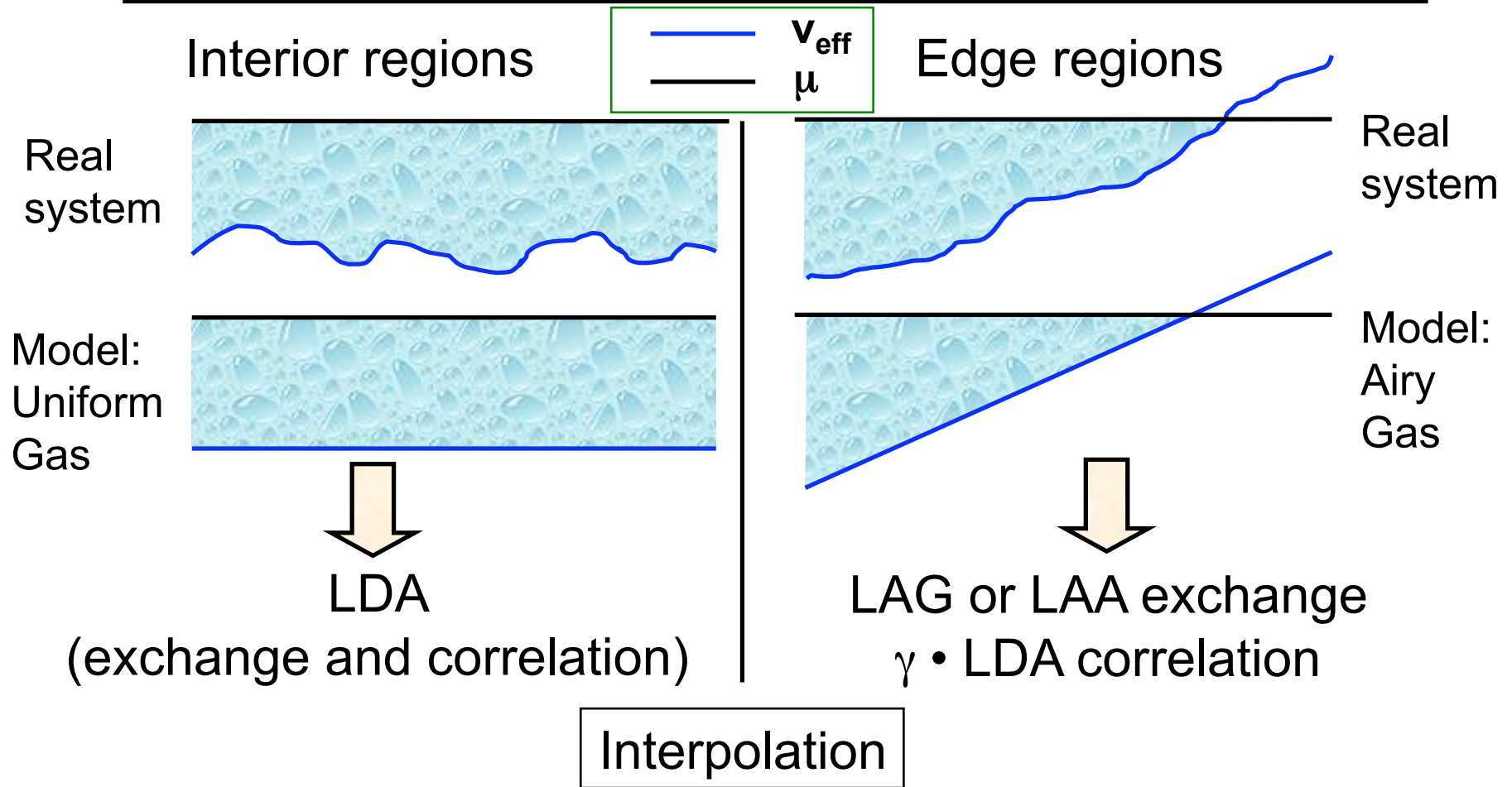
Functional based on, e.g., the Airy Gas captures specific surface physics.

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



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

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The AM05 functional

$$\epsilon_{xc}^{\text{AM05}}(n(\mathbf{r}), s(\mathbf{r})) = \epsilon_{xc}^{\text{interior}}(n)X(s) + \epsilon_{xc}^{\text{edge}}(n, s)(1 - X(s))$$

The results for the uniform electron gas ($X(s=0)=1$) are exactly recovered, as are the 'exact' results for the jellium surface model systems.



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>



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 (vs exchange) surface system, the jellium surface system.

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

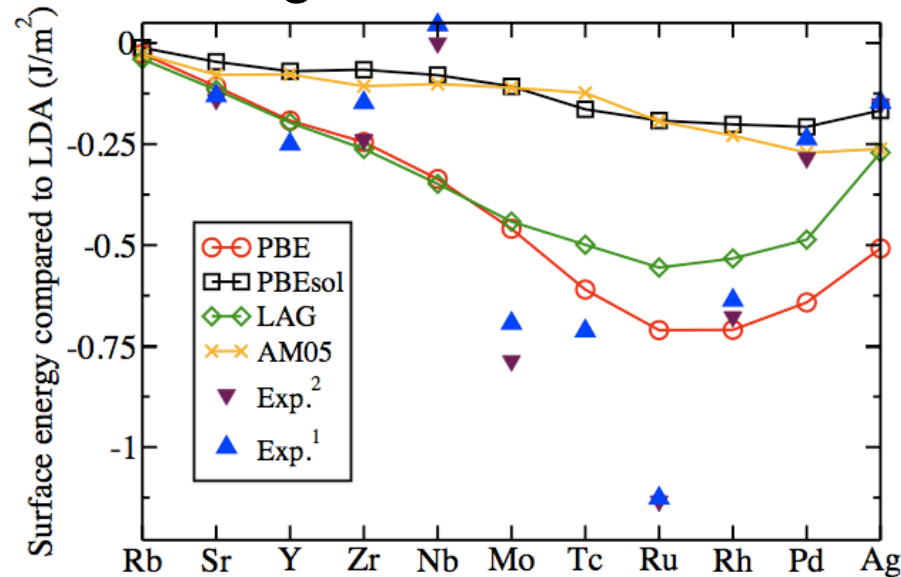
From our compatibility viewpoint, PBEsol and AM05 would give very similar results for cases where surface effects are important.

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



Surface energies

Surface energies for a number of metals



Ropo, Kokko, and Vitos, PRB 2008.

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 4d transition metals (in J/m²). 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.

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)		B_0 (GPa)	
	AM05	PBEsol	AM05	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 -Al ₂ O ₃	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?

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

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”.*

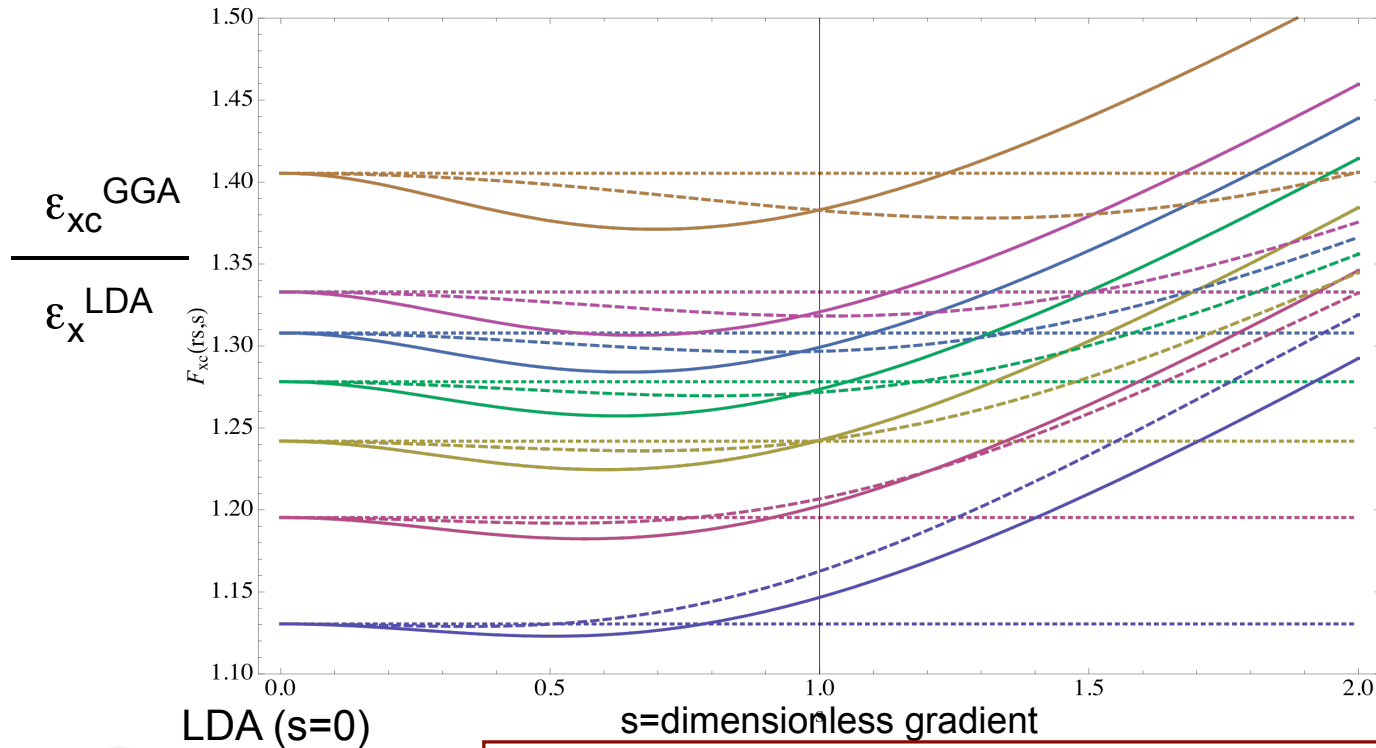
(Discussed in PRB 66, 165117 (2002)).



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: $r_s = 1, 2, 3, 4, 5, 6, 10$ $\zeta=0$ (non-spin)



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.



Improving upon AM05

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WC, PBEsol, and SOGGA, show that the AM05 accuracy can be obtained in different ways. Once you know that you can get something better than PBE using just the density and the gradient of the density, it can be done. In fact, the Capelle group has recently shown that the two parameter values changed between PBE and PBEsol, can be re-fitted further to give even better results than PBEsol (PRB **79**, 201106(R) (2009)). So, it is clear that AM05 can be improved upon by fine tuning details in the construction.

However, it is our strong belief that a major improvement in accuracy can only be achieved by including new physics into a functional via an additional model system.



Van der Waals'

HAAS, TRAN, AND BLAHA

PHYSICAL REVIEW B 79, 085104 (2009)

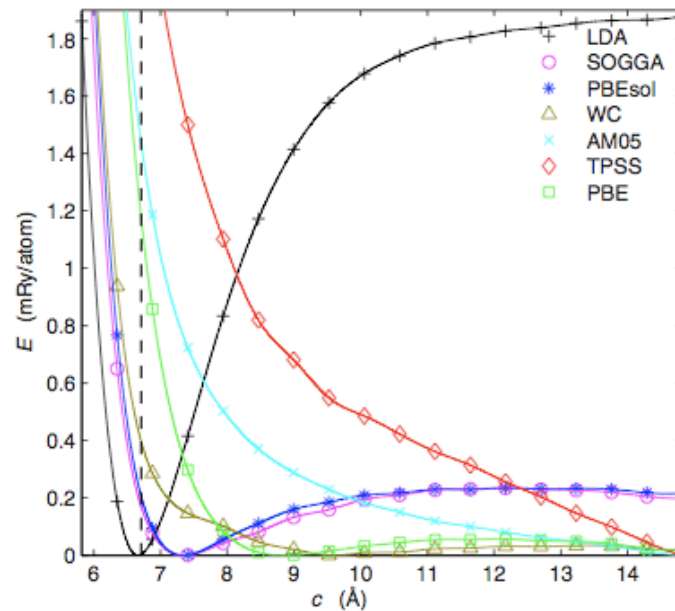


FIG. 3. (Color online) Total energy of graphite vs the lattice constant c (the interlayer distance is $c/2$). The in-plane lattice constant a was kept fixed at the experimental value (2.464 Å) for all values of c . The minima for the AM05 and TPSS functionals are either much larger than 15 Å or absent. The vertical dashed line represents the experimental lattice constant ($c_0=6.71$ Å).

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

^aReference 76.

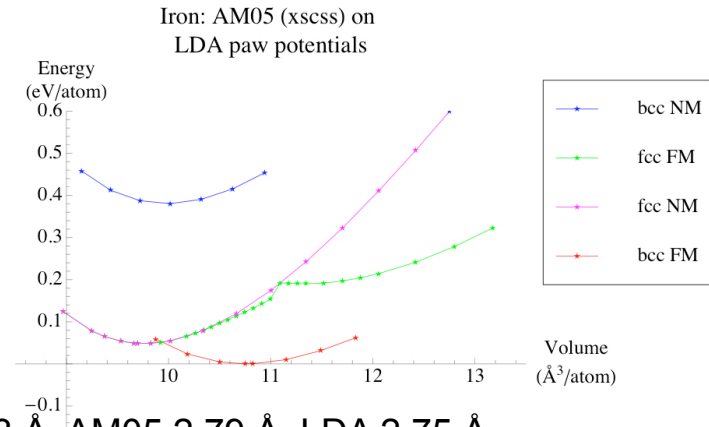
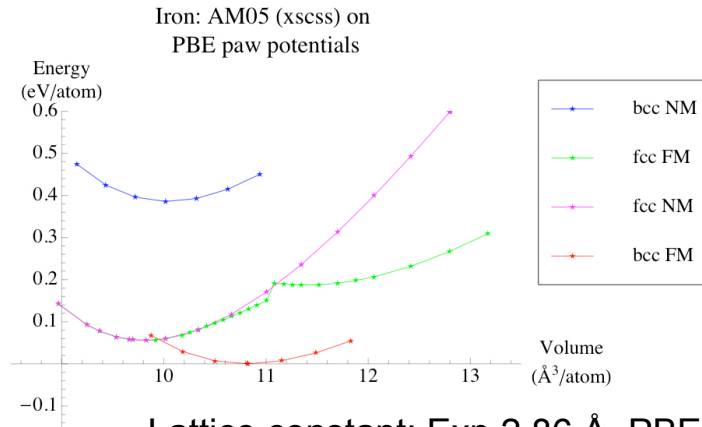
^bReferences 77–79.

Even though AM05 might be better off than other functionals since it contains no van der Waals', not even faulty, the fact remains that no functional does van der Waals' well.

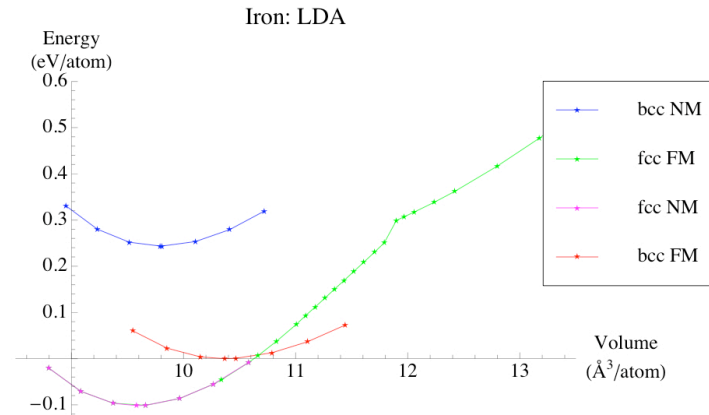
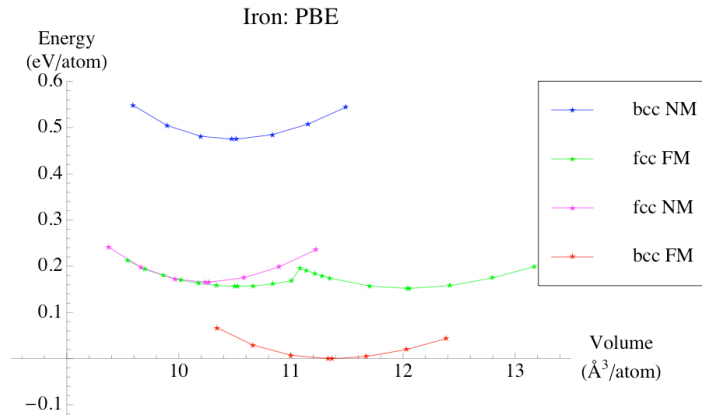


Spin AM05: Fe, Energy vs volume

“Implementing and testing the AM05 spin density functional”,
Ann E. Mattsson and Rickard Armiento,
Physical Review B **79**, 155101 (2009)



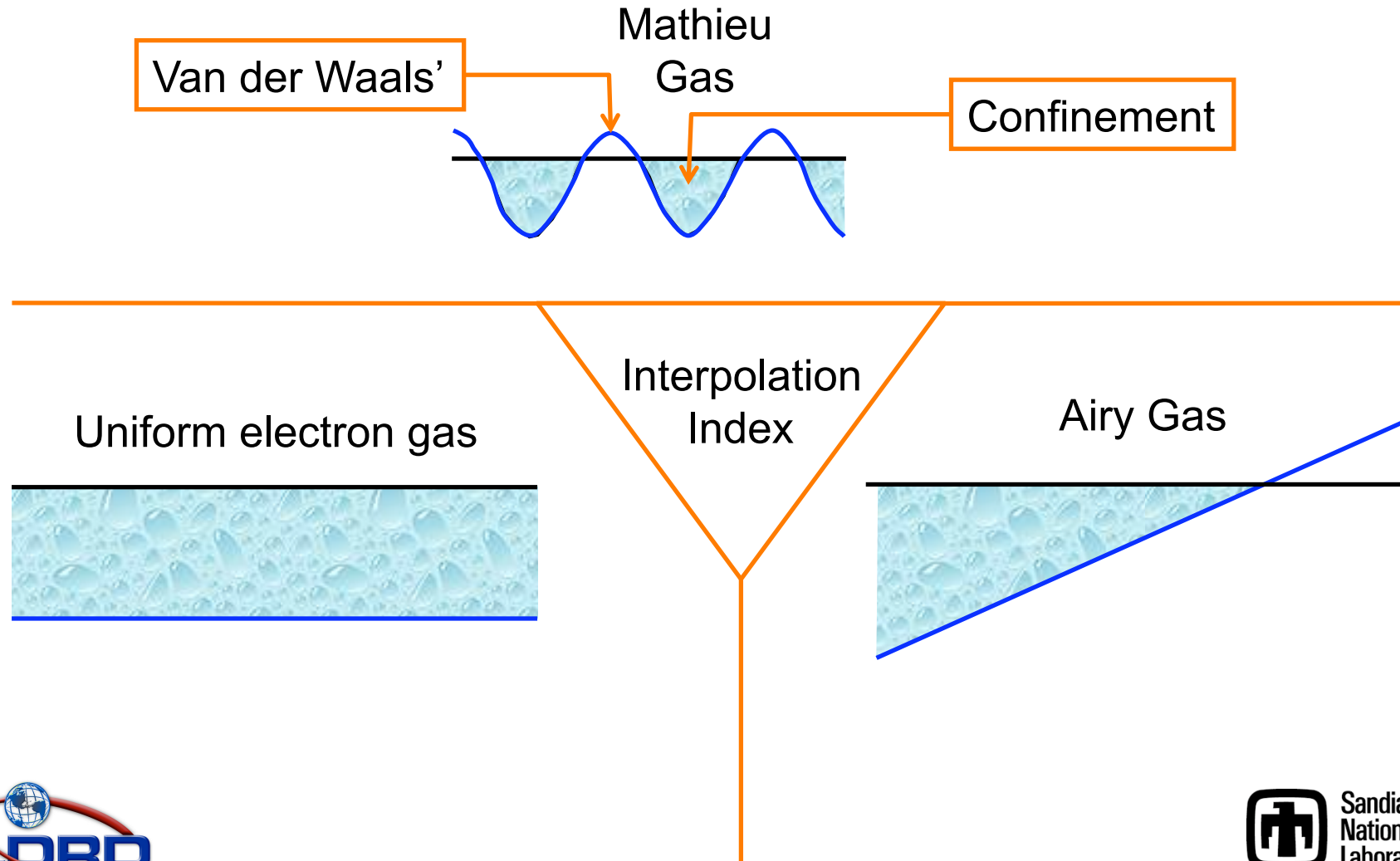
Lattice constant: Exp 2.86 Å, PBE 2.83 Å, AM05 2.79 Å, LDA 2.75 Å
 Bulk modulus: Exp 174 GPa, PBE 185 GPa, AM05 218 GPa, LDA 252 GPa



AM05 gives right bcc FM ground state, but uncharacteristically large errors in lattice constant and bulk modulus.

A functional for confined and van der Waals' systems

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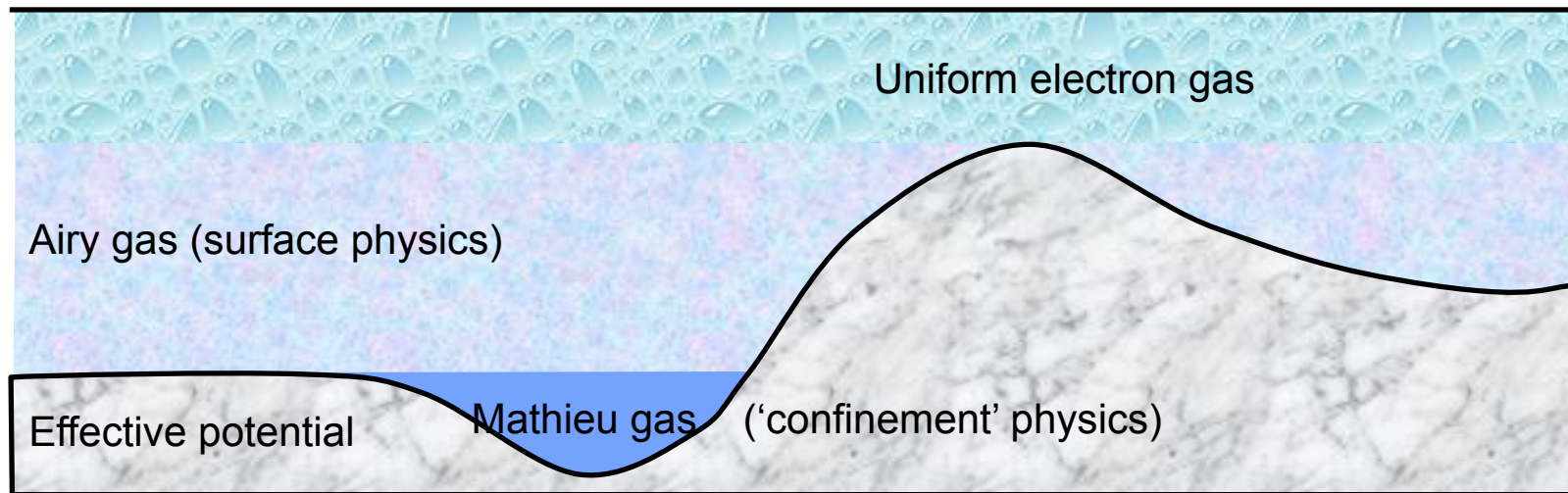


Interpolation Index

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The Subsystem Functional (SSF) Scheme

Chemical potential



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.



A New functional

$$\begin{aligned}\epsilon_{xc}^{\text{new}}[n(\mathbf{r})] &= \epsilon_{xc}^{\text{interior}}(n) X1[n] (1 - X2[n]) \\ &+ \epsilon_{xc}^{\text{edge}}(n, s) (1 - X1[n]) (1 - X2[n]) \\ &+ \epsilon_{xc}^{\text{confined}}[n] (1 - X1[n]) X2[n].\end{aligned}$$

Will give exact results for uniform electron gas, and jellium surfaces, but also a new set of model systems describing ‘confinement’ physics.

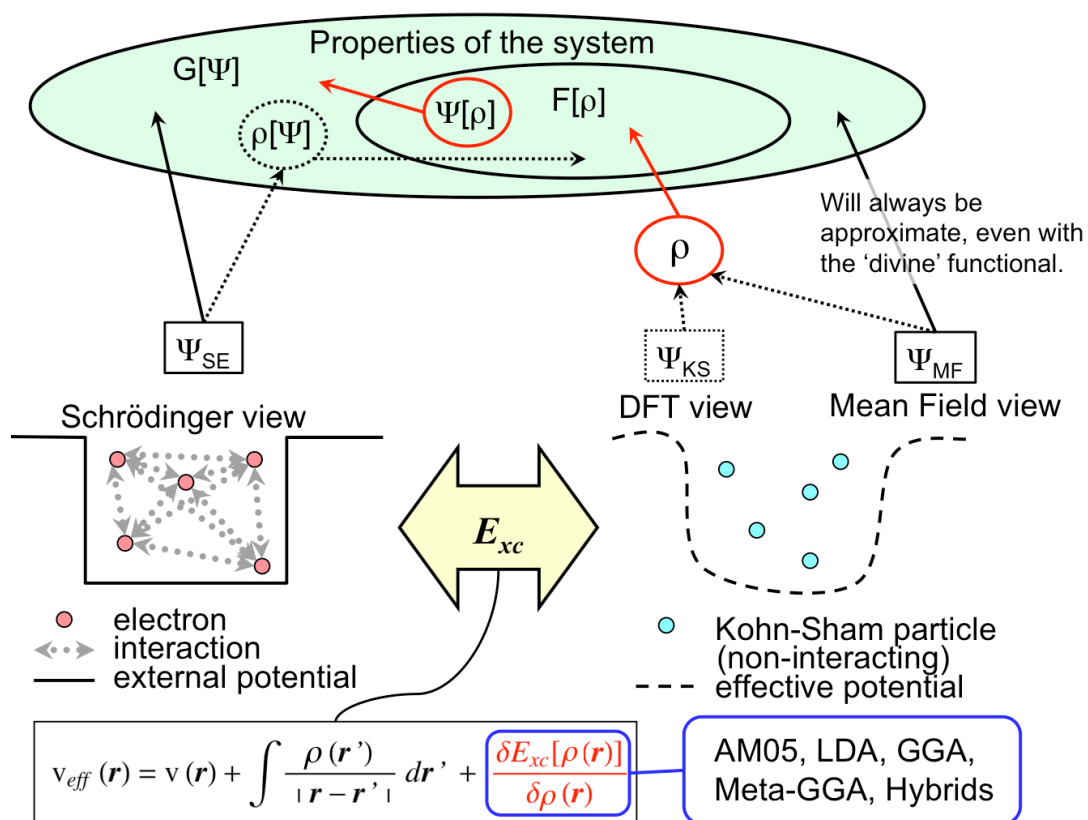


Summary

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- AM05 is an accurate and fast functional for solids.
- AM05 works well for matter in compression but not for van der Waals.
- AM05 works OK for molecules and liquids if confinement errors cancel.
- The subsystem functional scheme used to create AM05 promises to be valuable for creating functionals for problematic areas of DFT, such as for Molecular Crystals (van der Waals'), transition metal oxides, and Actinides (d- and f-electrons, confined systems). This is our focus now.
- Since AM05 is so different it is a good complement to more standard functionals like LDA and PBE for estimating error bars.
- With improved accuracy of functionals, new standards for acceptable numerical errors will emerge. (You cannot blame the functional any more).

But only DFT properties will be good





Thanks!

Ann E. Mattsson

For your attention.

Reprints available at:

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

Collaborators: Rickard Armiento, Feng Hao, Thomas Mattsson

Subroutines for implementation of AM05 into several types of DFT codes are available at:

<http://dft.sandia.gov/functionals/AM05.html>

Questions? Comments?



End

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