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Towards predictive power of density functional theory based calculations: Understanding exchange-correlation functionals

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

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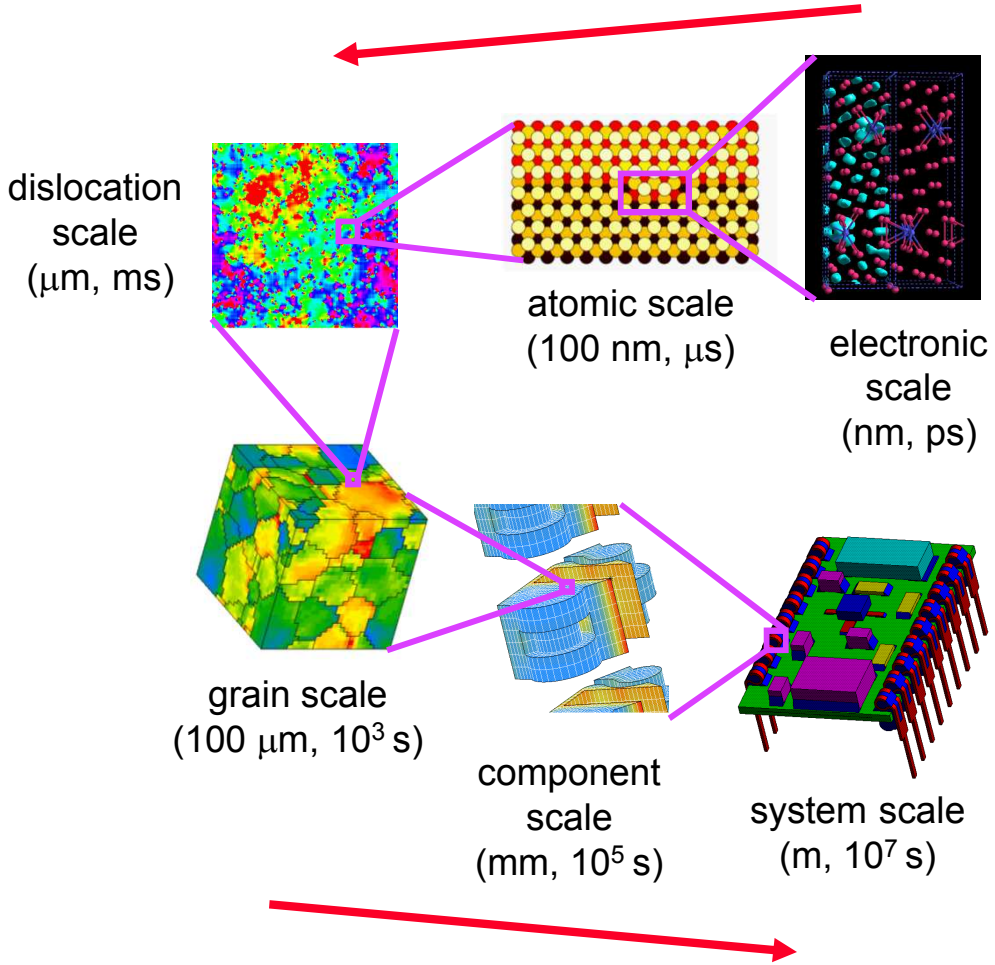

- Goal: Predict how materials age and perform under normal, adverse and extreme conditions.
- Method: Bridge length and time scales by using results from each scale as input on the next scale.
- Foundation: To get the fundamental processes right via DFT calculations at the electronic scale.

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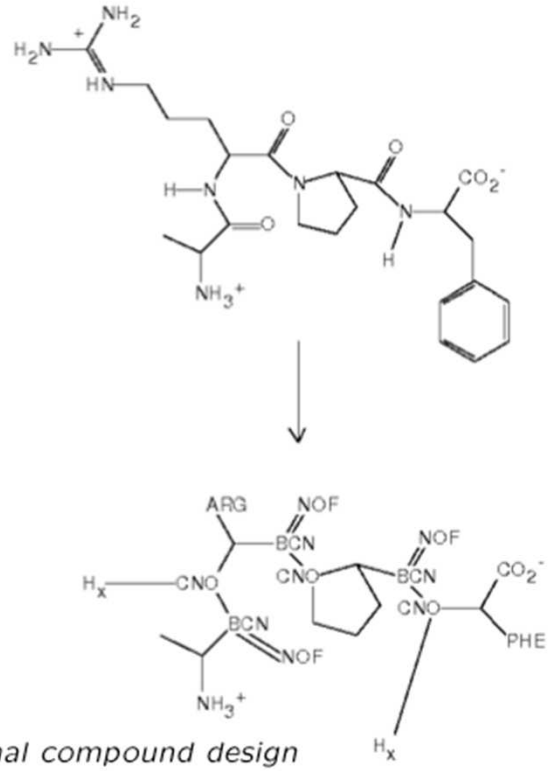
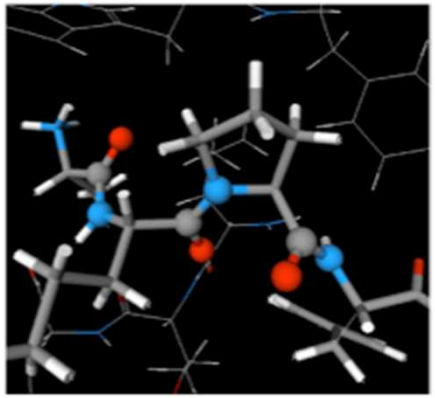
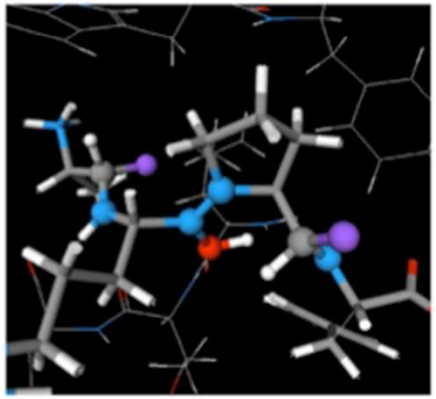
Rational Compound Design

- Finding a non-peptidic inhibitor







Variational particle number approach for rational compound design
OAvL, R. Lins, U. Rothlisberger, *Phys Rev Lett* **95** 153002 (2005)

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DFT and functionals

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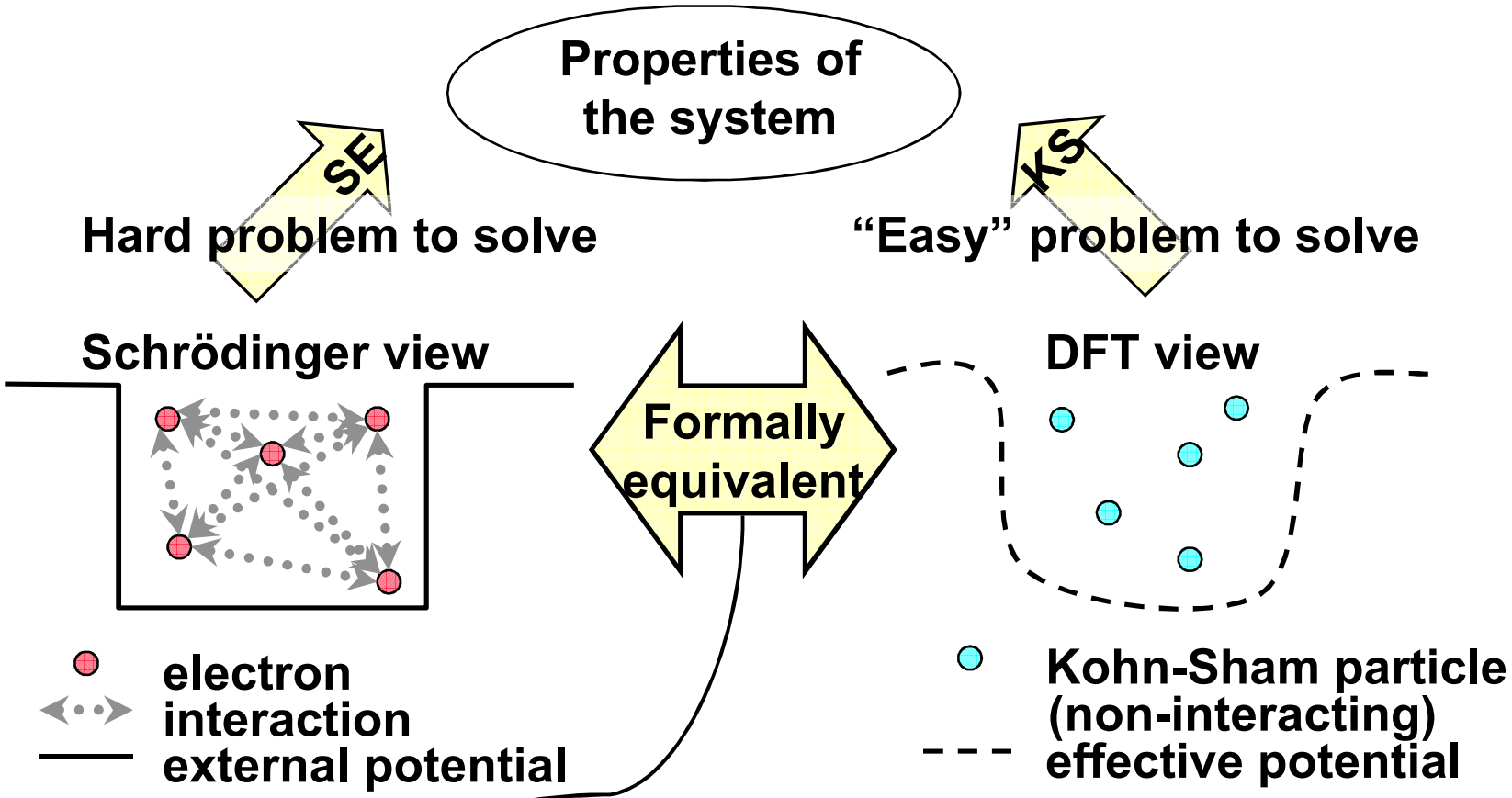

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

LDA, GGA, Meta-GGA, Hybrids, …

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DFT and functionals

Properties of the system

KS

DFT work at this level increases speed and precision.

Schrödinger view

Formally equivalent

DFT view

electron

interaction

external potential

Kohn-Sham particle (non-interacting)

effective potential

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

Work at this level increases accuracy.

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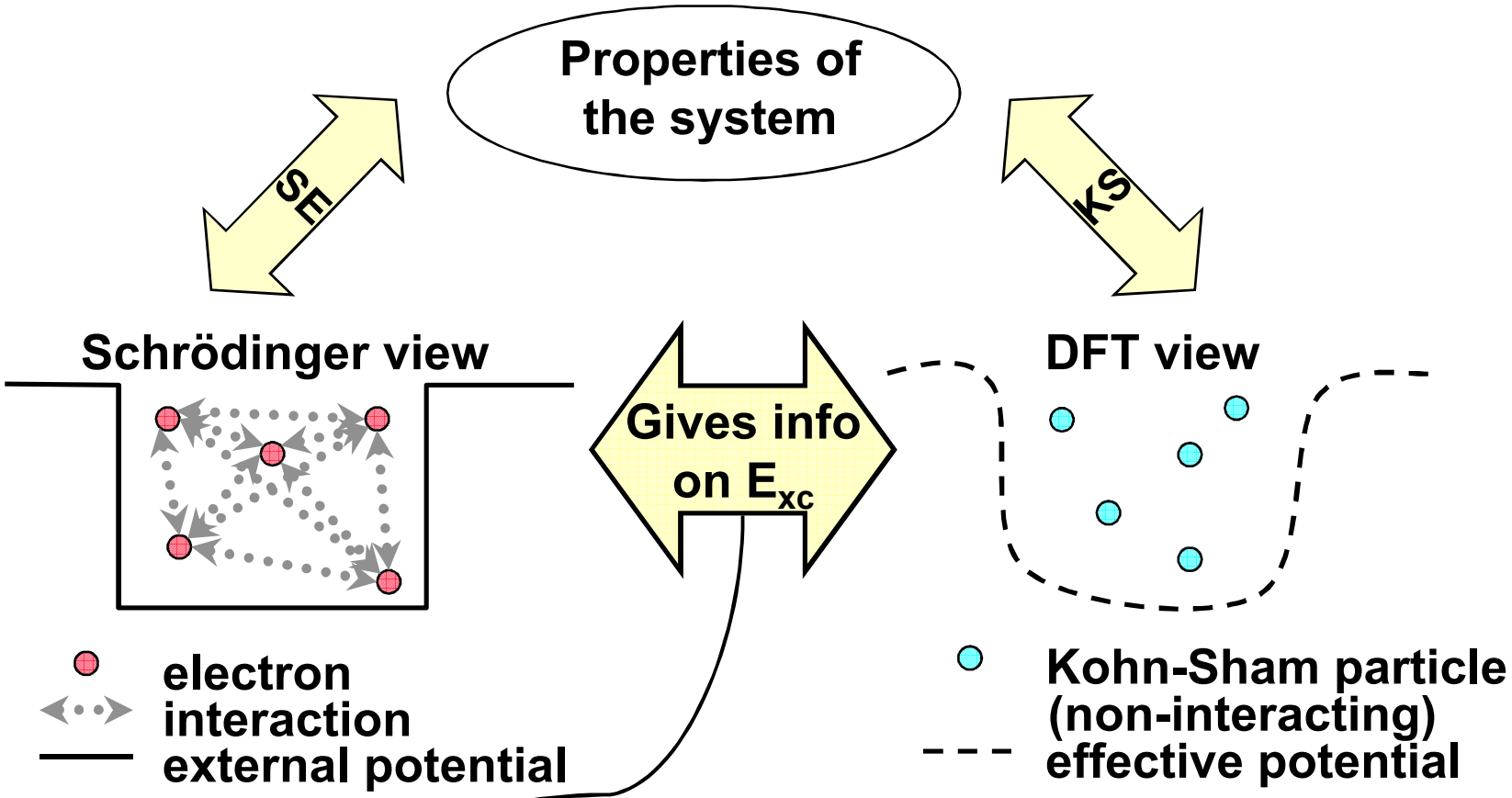
Functional development



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

Work at this level increases accuracy.

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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 of different densities.

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

ALL LDA correlation functionals in use are based on their data.

(Before 1980, Wigner correlation was used)

Using model systems

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Compatibility

Jellium surface exchange and correlation energies

Example: r_s=2.07 (Al)

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

In erg/cm^2

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

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Exchange-correlation functionals

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

The ***exchange-correlation energy density*** is modeled in DFT.

LDA, GGA, and meta-GGA

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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

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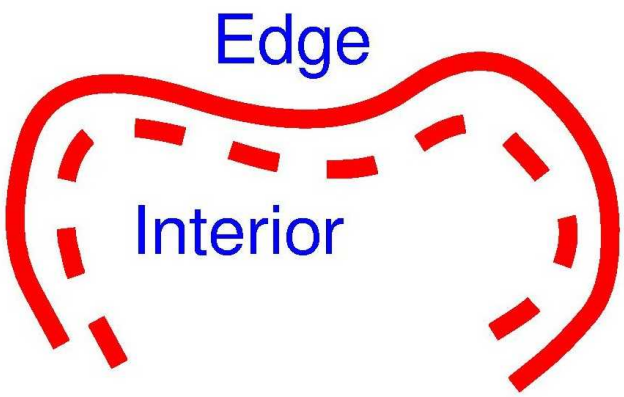
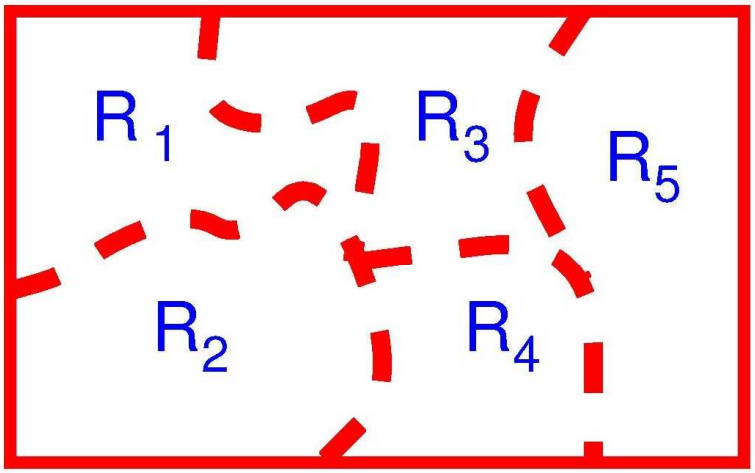
Subsystem functionals

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.

Subsystem functionals

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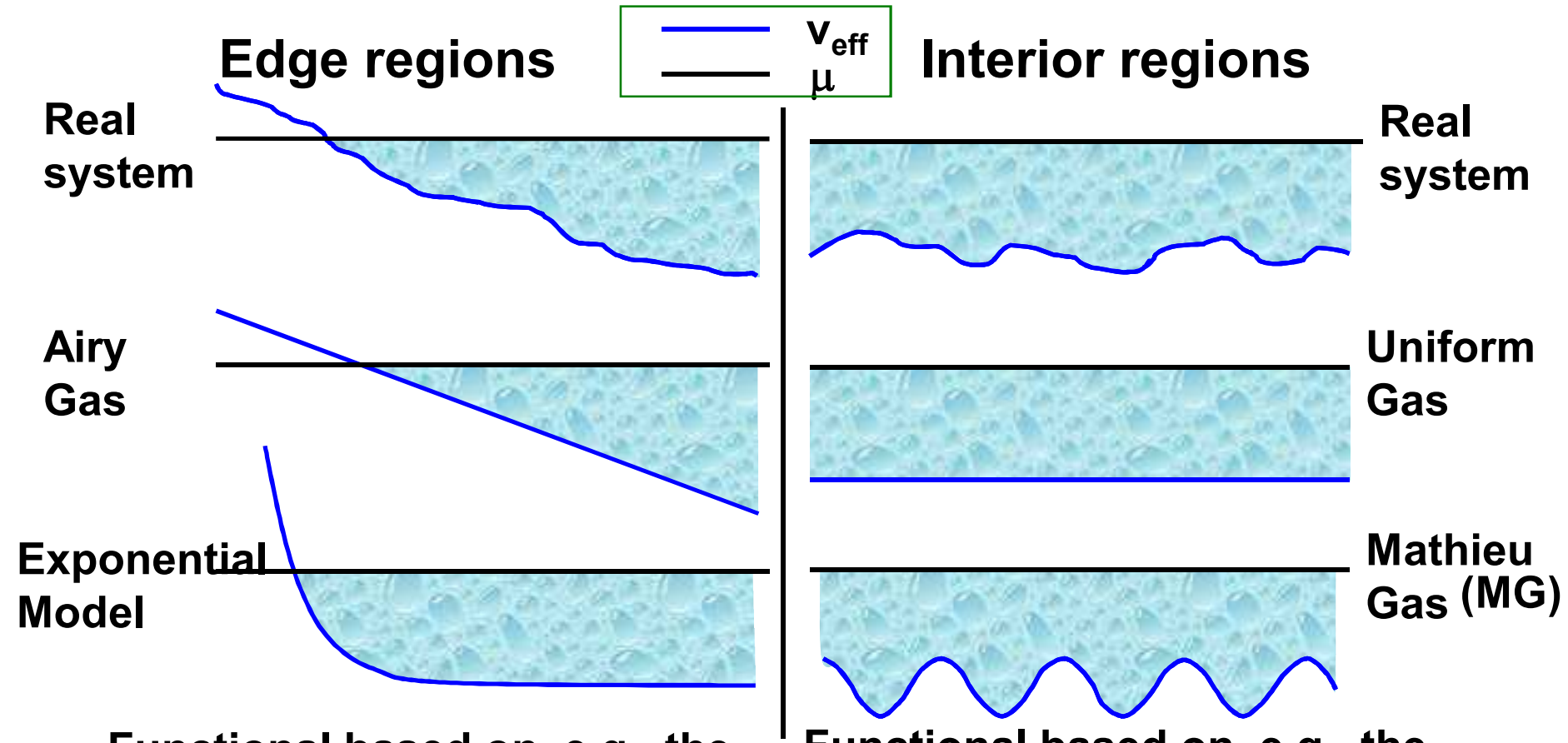

Functional based on, e.g., the Airy Gas captures specific surface physics.

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

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

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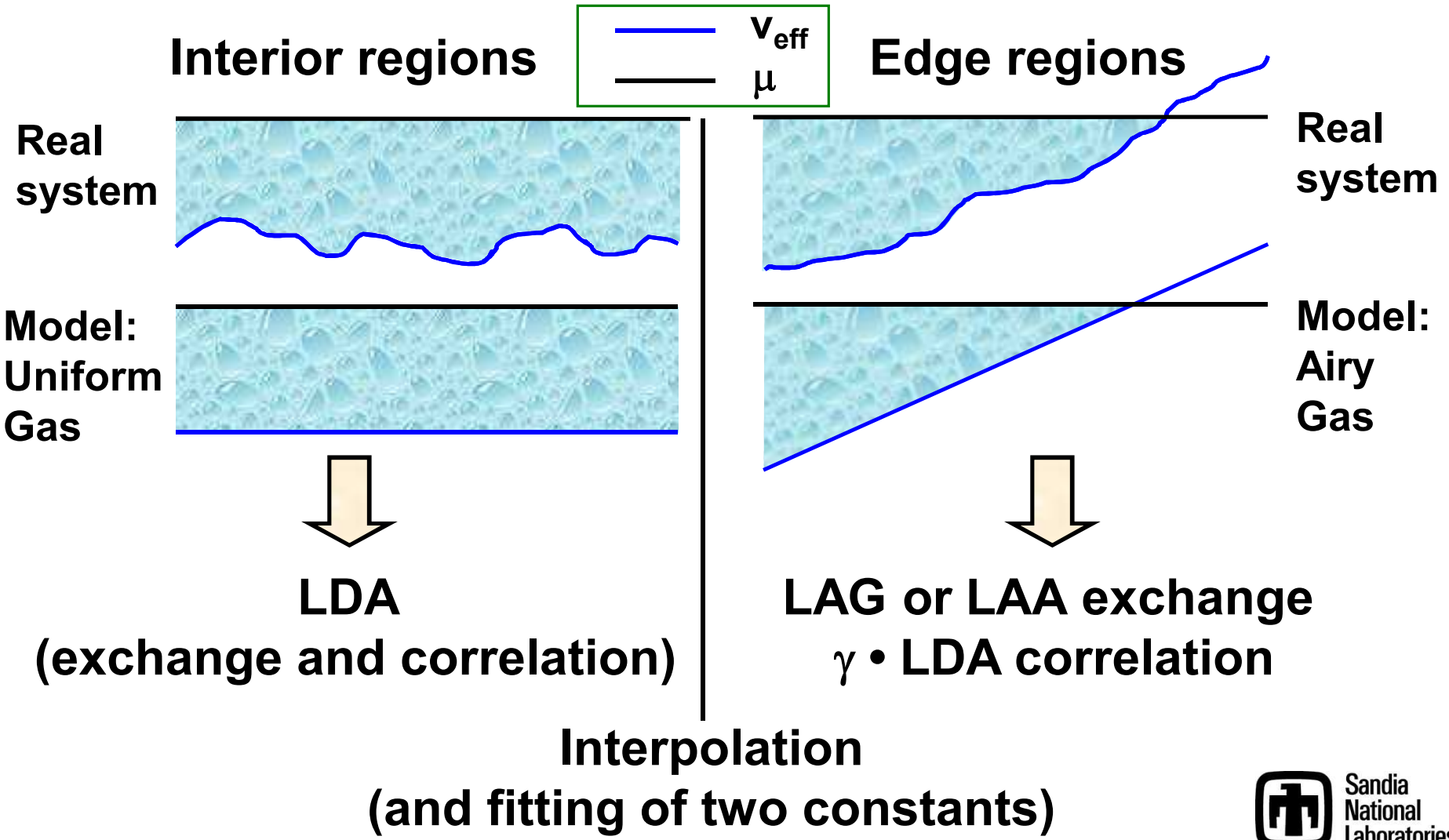

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Testing functionals

We have a new functional, AM05. Now we need to test it. What tests should we do? Why?

First step: Does it work at all?

Next step: Depends on outcome of first step.

AM05 is designed to work on surfaces, correcting surface intrinsic errors. We had access to solid state codes. Most appropriate and easiest to start testing on bulk materials with an eye towards vacancy formation energies.

Previous work: Al, Pt, Pd, and Mo vacancies

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Correcting vacancy formation energies via the surface correction scheme, Mattsson and Kohn, JCP 115, 3441 (2001).

Vacancy formation energies (eV)					
	E_{LDA}	E_{LDA}^{corr}	E_{GGA}	E_{GGA}^{corr}	Experiment
Al	(0.70)	**0.76**	(0.54)	**0.67**	**0.67±0.03**
Pt	(0.95)	**1.15**	(0.68)	**1.18**	**1.24, 1.32, 1.35, 1.45**
Pd	(1.50)	**1.71**	(1.20)	**1.70**	**1.5, 1.7, 1.85**
Mo	(2.89)	**3.00**	(2.67)	**2.96**	**1.6, 2.24, 3.0, 3.0, 3.6**

Carling, et al., PRL 85, 3862 (2000) and Mattsson and Mattsson, PRB 66, 124110 (2002).

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Results for bulk systems

Lattice const. (Å)	Exp.	LDA	PBE	PW91	AM05
Pt	3.92	3.90 (0.5)	3.99 (1.7)	3.99 (1.7)	3.94 (0.5)
Al	4.03	3.98 (1.2)	4.04 (0.2)	4.05 (0.5)	4.01 (0.5)
Si	5.430	5.404 (0.5)	5.475 (0.8)	5.473 (0.8)	5.437 (0.1)
GaAs	5.653	5.619 (0.6)	5.762 (1.9)	5.756 (1.8)	5.686 (0.6)
C diam.	3.567	3.533 (1.0)	3.573 (0.2)	3.573 (0.2)	3.551 (0.4)
C graphite a	2.461	2.445 (0.7)	2.468 (0.3)	----	2.459 (0.1)

Percent deviation from experiment in parenthesis

Unlike LDA and the GGAs, AM05 has consistent performance for the stronger bonds governing the lattice constant in common bulk materials.

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Results for bulk systems

Bulk Mod (GPa)	Exp.	LDA	PBE	PW91	AM05
Pt	283	312 (10)	254 (10)	252 (11)	291 (3)
Al	77	86 (11)	80 (3)	76 (1)	87 (13)
Si	99	96 (3)	87 (12)	87 (12)	92 (7)
GaAs	76	72 (4)	60 (21)	60 (21)	65 (14)
C diam.	443	464 (5)	430 (3)	430 (3)	449 (1)

Percent deviation from experiment in parenthesis

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Graphite

Lattice const. (Å)	Exp.	LDA	PBE	PW91	AM05
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C graphite a	2.461	2.445 (0.7)	2.468 (0.3)	----	2.459 (0.1)

Percent deviation from experiment in parenthesis

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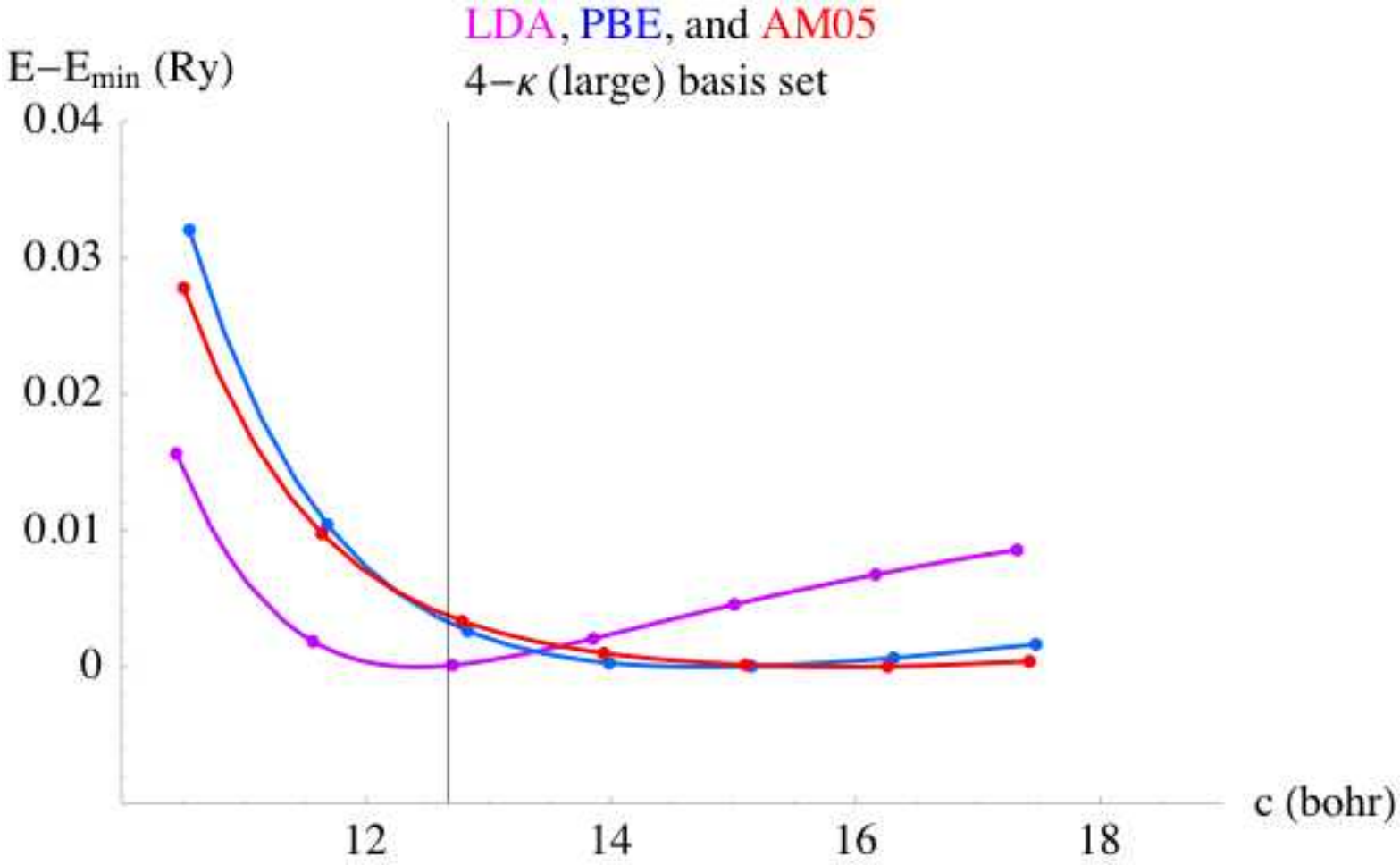
Graphite: distance between planes



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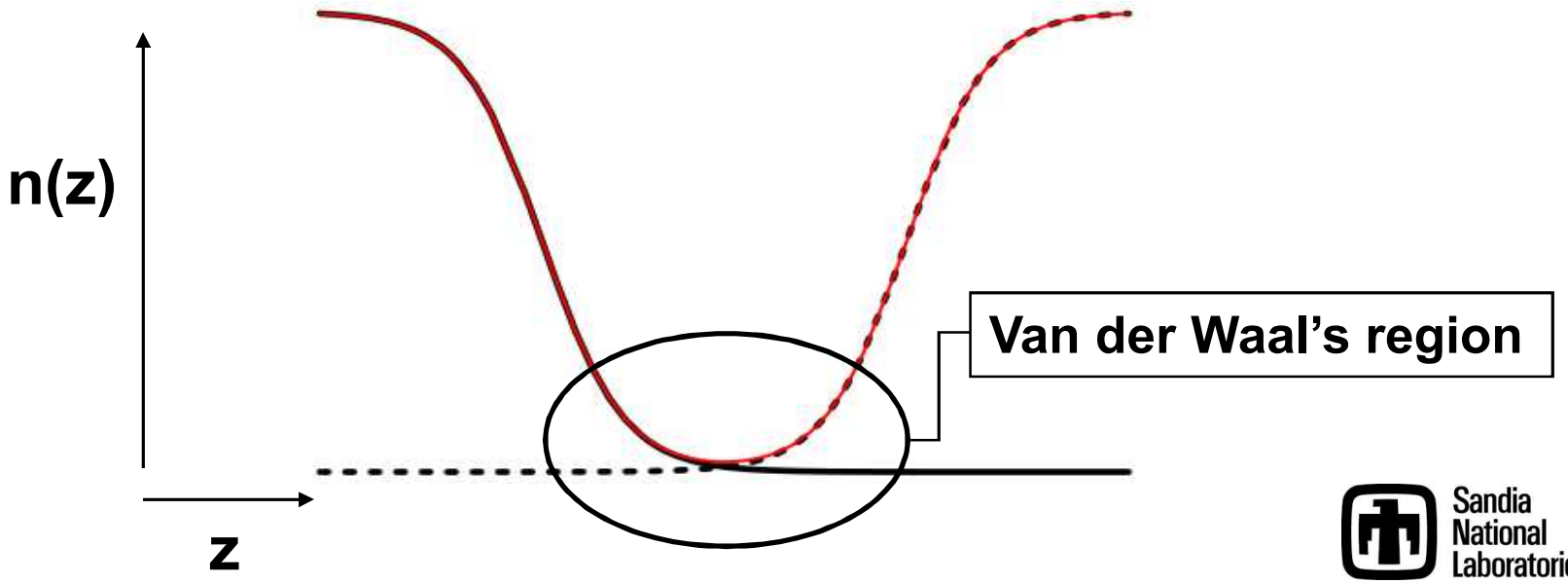
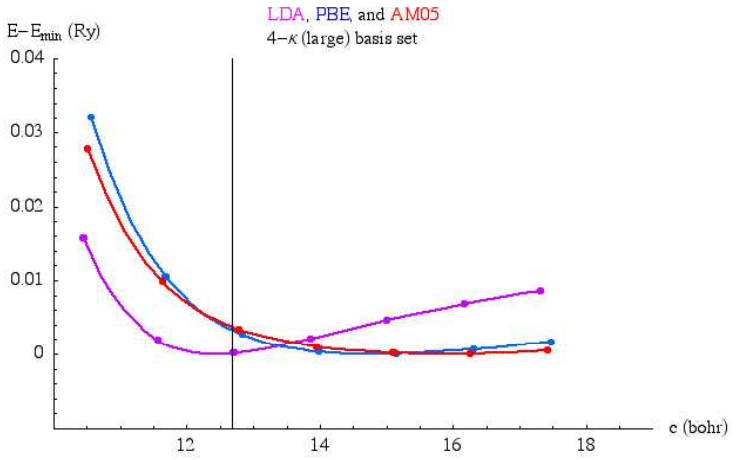
Van der Waal's

AM05 is a local functional. It does not include van der Waal's interactions. AM05 is behaving as the Airy gas in the 'edge' region. Density is probably good.

PBE and LDA are also local. Any minima obtained is for the wrong reason.



Very weak bonds: Lesson learned



AM05 includes no van der Waals attractions. LDA and PBE erroneously include something that looks like van der Waals attraction in, for example, graphite.

Van der Waals needs to be included in a new functional. We have expertise in how to do this.

Designing a functional

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Current situation: No functional performs with the same accuracy on all parts of a system.

Needed: A functional that treats weak and strong interactions equally well.

Our plan: 1) Investigate the performance of AM05 and other functionals for a wide variety of systems in order to 2) understand what physics is included or not in the different functionals. 3) Include missing physics in a new functional designed by the subsystem functional scheme.

Ultimate goal: A general functional that treats all subsystems with the same accuracy.

Silicon ad-dimer diffusion on Si(001)

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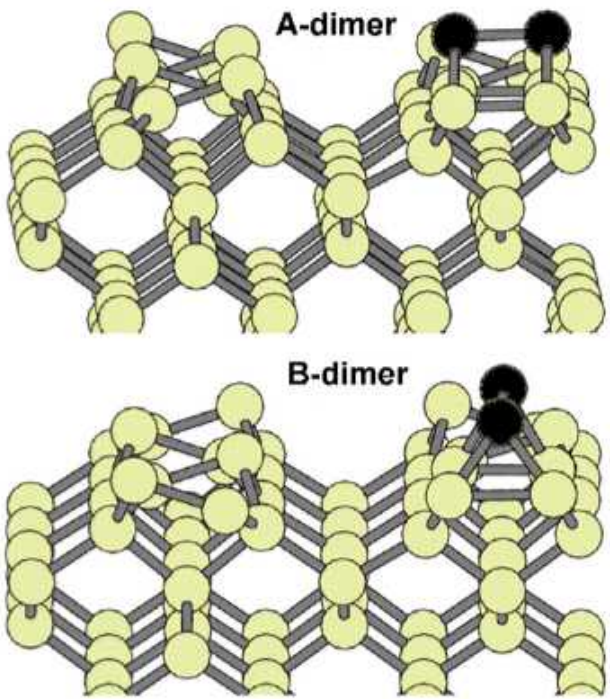

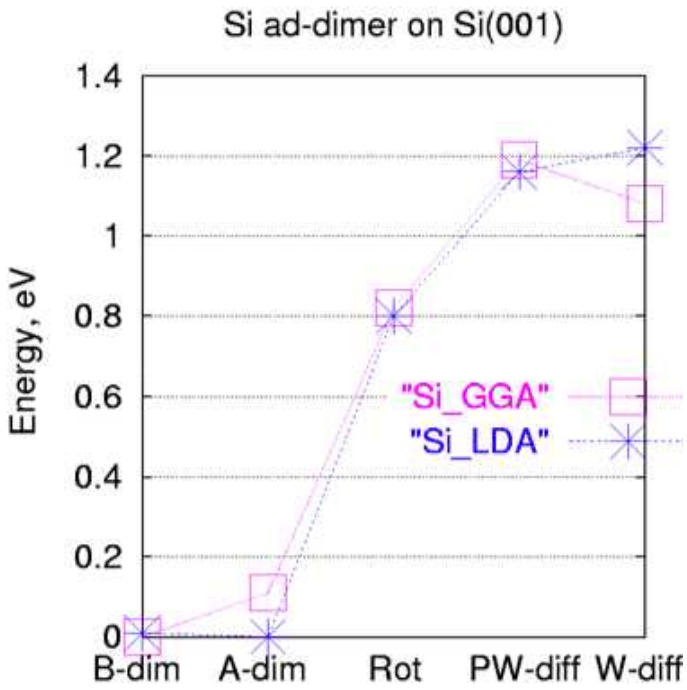

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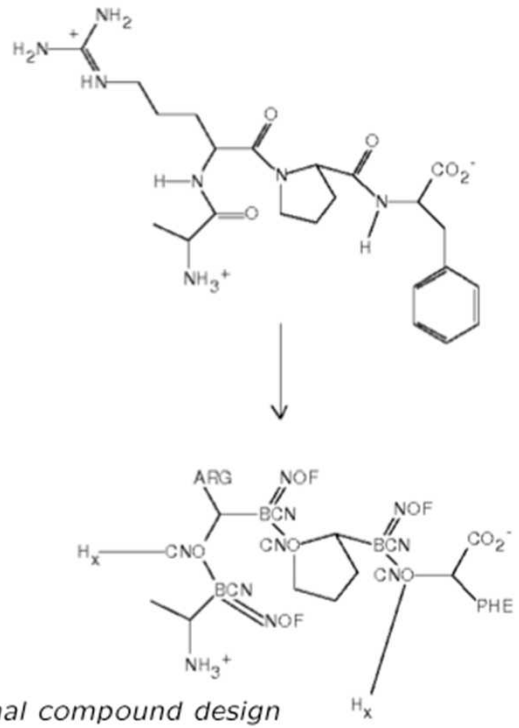
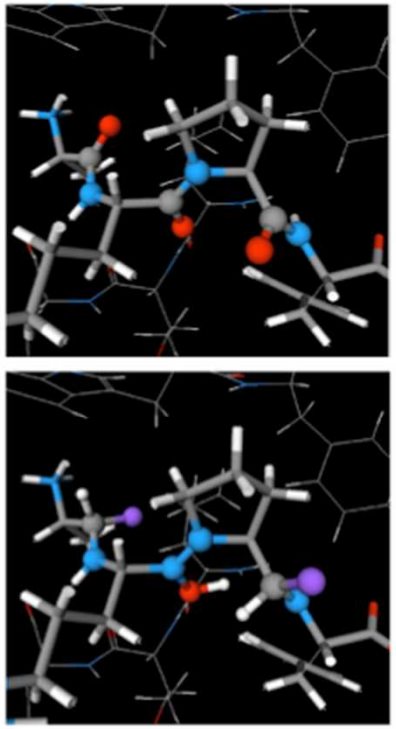
Rational Compound Design

- Finding a non-peptidic inhibitor





Variational particle number approach for rational compound design

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

Very important to get trends right:
Either choose functional automatically or use one that has same accuracy for everything.

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The trend LDA → LAG → LDA/LAA(LAG)

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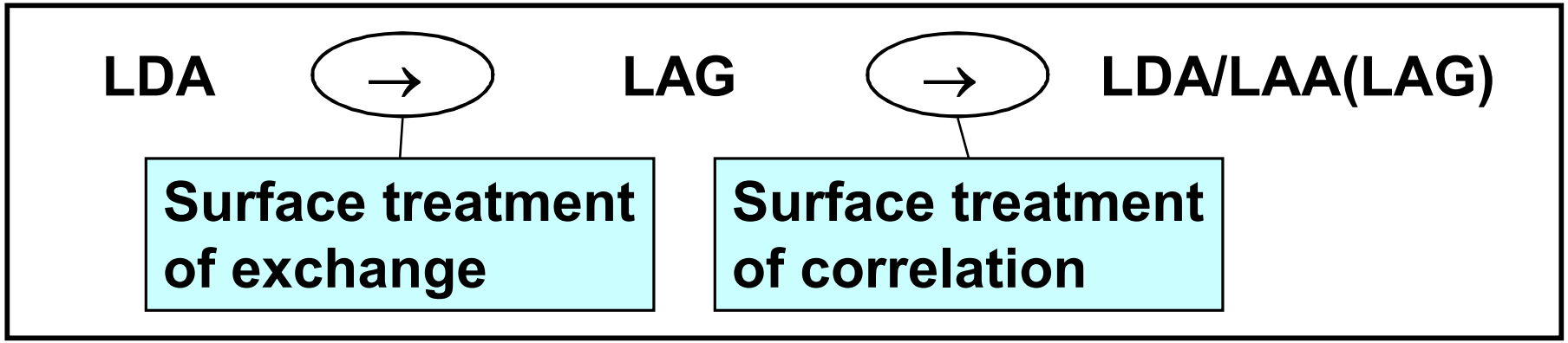

LDA/LAA is what we now call AM05.

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Results for bulk systems

Lattice constant (Å)	Exp.	LDA	LAG	LDA/LAG	LDA/LAA
Pt	3.92	3.90	3.96	3.93	3.94
Al	4.03	3.96	4.02	4.01	4.02
Si	5.43	5.38	5.44	5.42	5.43

Bulk Mod. (GPa)	Exp.	LDA	LAG	LDA/LAG	LDA/LAA
Pt	283	312	272	294	291
Al	77.3	81.7	76.8	82.1	81.7
Si	98.8	95.1	88.7	91.5	90.5

Results for monovacancy formation energies

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Formation energy (eV)	Exp.	LDA	LAG	LDA/LAG	LDA/LAA
Pt	(1.35)	0.91	0.73	1.00	0.99
Al	0.68	0.67	0.59	0.83	0.84
Si	(3.6)	3.58	3.69	3.57	3.59

64-atom cells, full relaxation (volume and geometry). Still we do not trust these values for experimental comparison for Pt and Si. Larger cells are needed for these.

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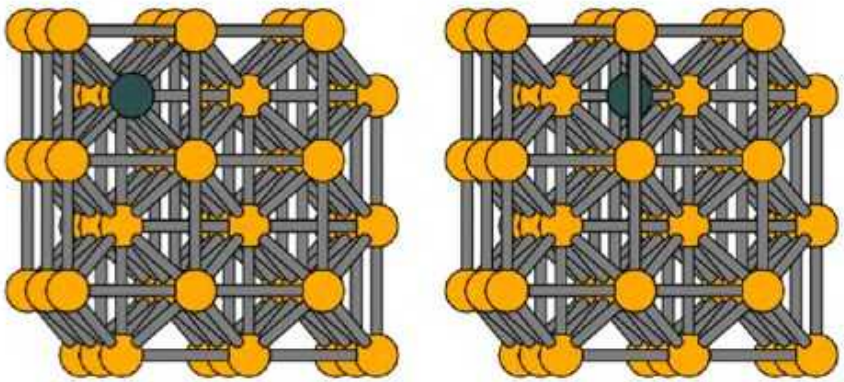
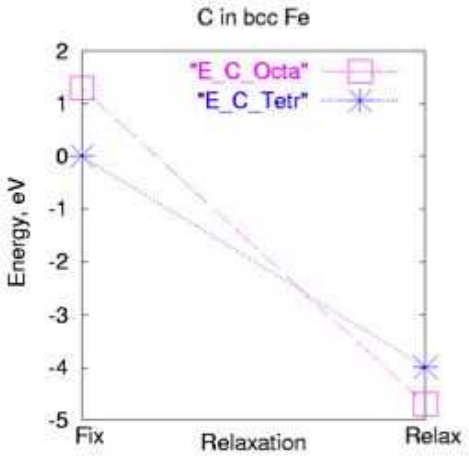
Carbon impurities in bcc iron

The importance of relaxation





Just one example from "Designing meaningful density functional theory calculations in materials science---a primer" by Mattsson, Schultz, Desjarlais, Mattsson, and Leung, Modelling Simul. Mater. Sci. Eng. 13 R1-R31 (2005).

Results for monovacancy formation energies

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Formation energy (eV)	Exp.	LDA	LAG	LDA/LAG	LDA/LAA
Pt	(1.35)	0.91	0.73	1.00	0.99
Al	0.68	0.67	0.59	0.83	0.84
Si	(3.6)	3.58	3.69	3.57	3.59

Why is AM05 overcorrecting for Al?
Gradient treatment probably needed in interior region.
Experimental value might be somewhat low.

Previous work: Al, Pt, Pd, and Mo vacancies

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Previous work applied PBE correction to PW91 results.

Vacancy formation energies (eV)					
	E_{LDA}	E_{LDA}^{corr}	E_{GGA}	E_{GGA}^{corr}	Experiment
Al	(0.70)	**0.74**	(0.54)	**0.67** 0.74/ 0.78	**0.67±0.03**
Pt	(0.95)	**1.15**	(0.68)	**1.32** 1.34	**1.24, 1.32, 1.35, 1.45**
Pd	(1.50)	**1.71**	(1.20)	**1.76** 1.85	**1.5, 1.7, 1.85**
Mo	(2.89)	**3.00**	(2.67)	**2.96** 3.06	**1.6, 2.24, 3.0, 3.0, 3.6**

Mattsson, Armiento, Schultz, and Mattsson, PRB 73, 195123 (2006).

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Monovacancy formation energies

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Formation energy (eV)	AM05	LDA	PBE	PW91
Pt	0.99	0.91	0.72	0.64
Al	0.84	0.67	0.61	0.53
Si	3.59	3.58	3.65	3.68

Clear trend in metal monovacancy formation energies:

AM05 > LDA > PBE > PW91

Surface Intrinsic Errors

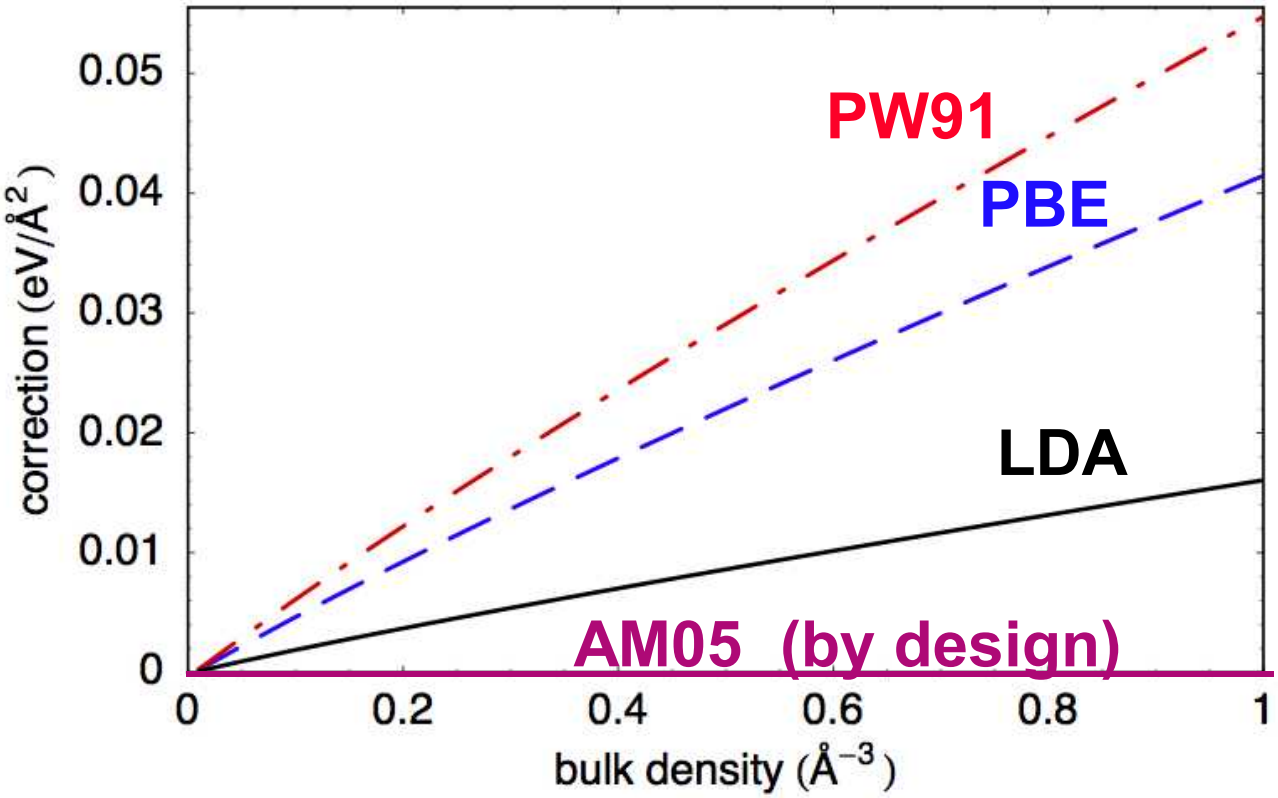

Fig. 2 in Mattsson et al, PRB 73,195123 (2006).

Monovacancy formation energies

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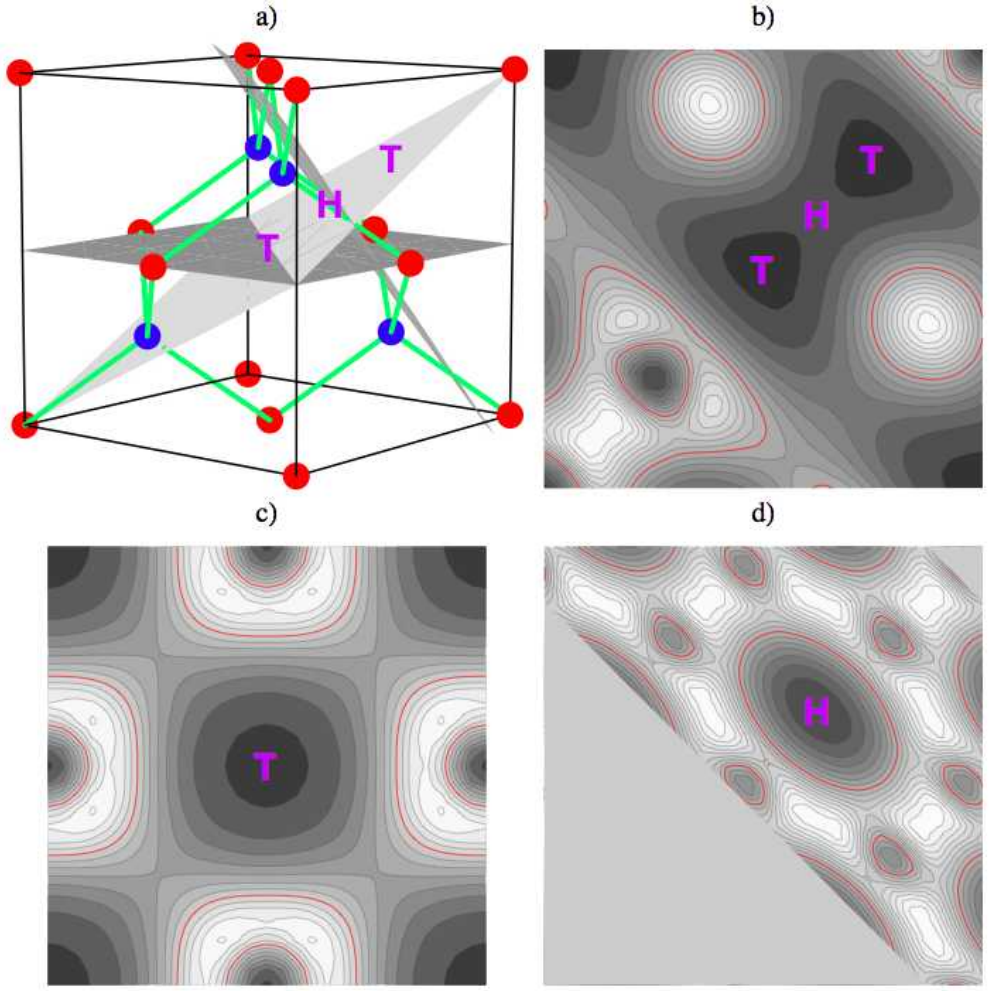
Formation energy (eV)	AM05	LDA	PBE	PW91
Pt	0.99	0.91	0.72	0.64
Al	0.84	0.67	0.61	0.53
Si	3.59	3.58	3.65	3.68

Clear trend in metal monovacancy formation energies:

AM05 > LDA > PBE > PW91

What about Si?

Semiconductor bulk density: Holes



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Si Interstitial Formation Energies (eV)

	AM05	LDA	PBE	PW91
Tetrahedral	3.399	3.562	3.908	4.091
Hexagonal	3.253	3.424	3.617	3.768
110-split	3.160	3.371	3.546	3.696

Clear trend: AM05 < LDA < PBE < PW91

Surface Intrinsic Errors

Opposite trend for metal vacancy formation energies.
Same trend for surface intrinsic error correction.

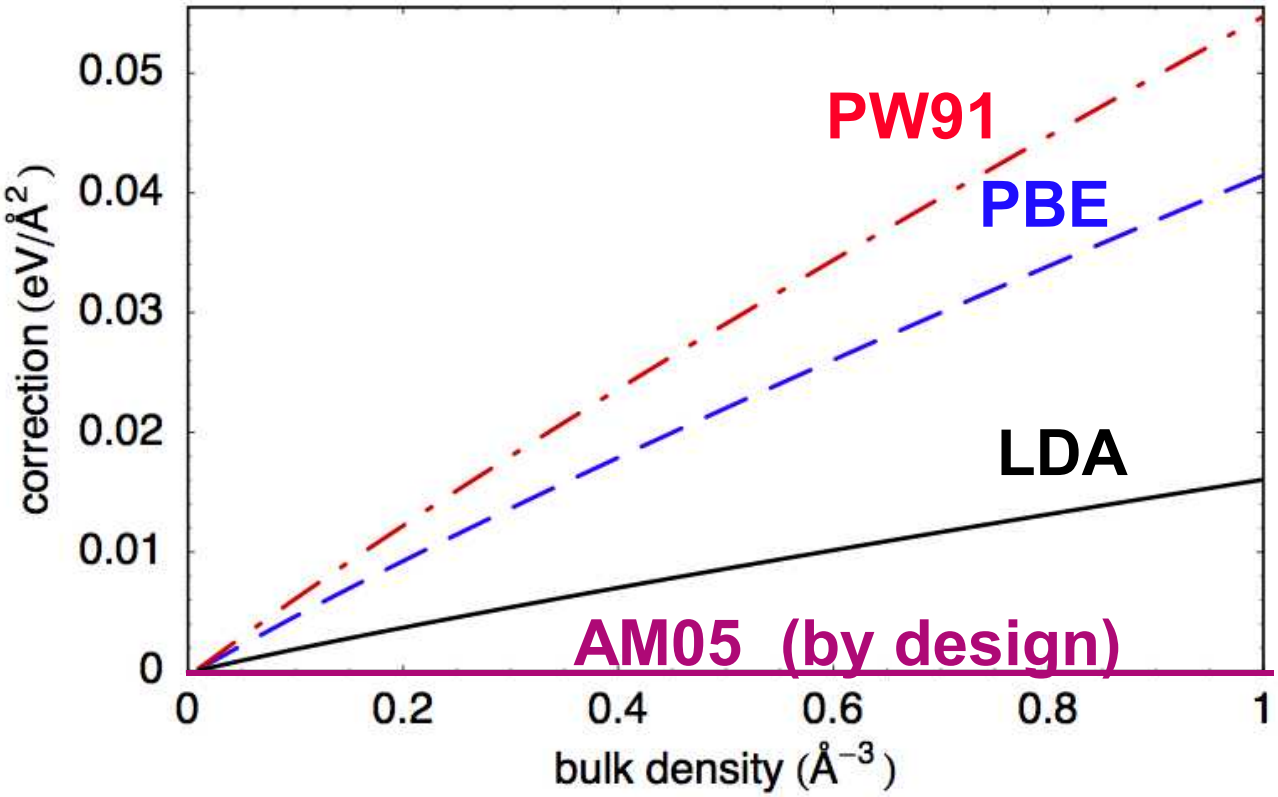

Fig. 2 in Mattsson et al, PRB 73,195123 (2006).

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The ⟨110⟩ - split interstitial

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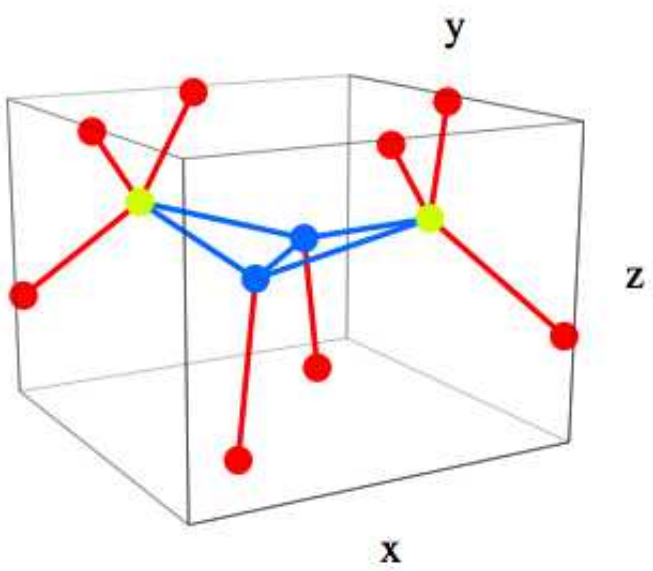

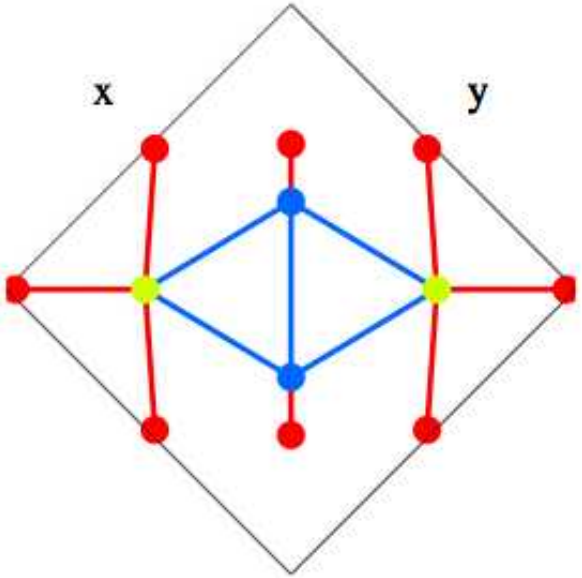

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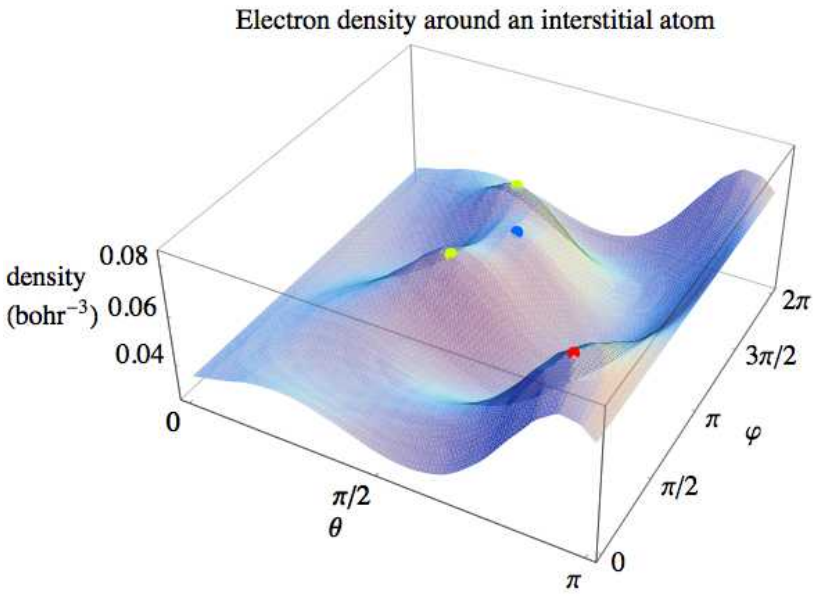
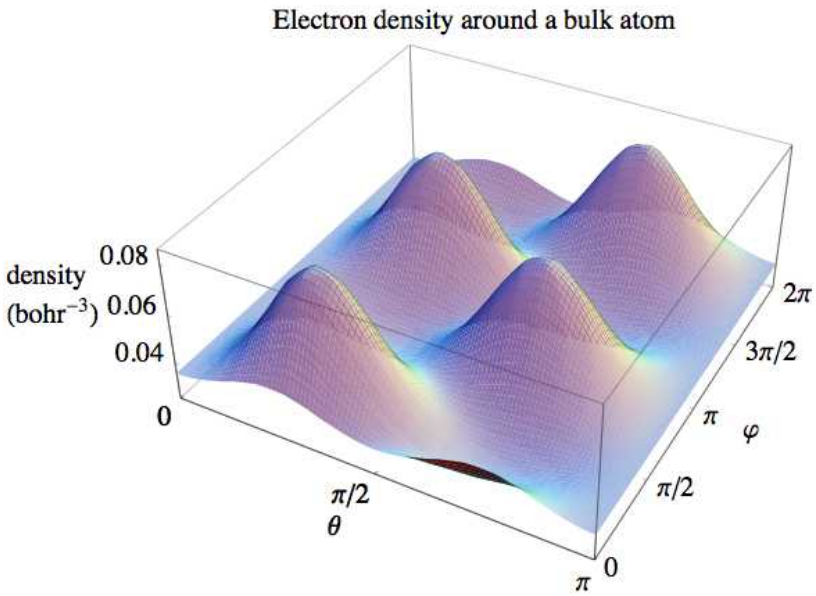
Bonds of 4-coordinated interstitial atom

Density on a sphere around an atom.
Radius half interatomic distance.





Very different from 4-coordinated bulk atom

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The ⟨110⟩ - split interstitial

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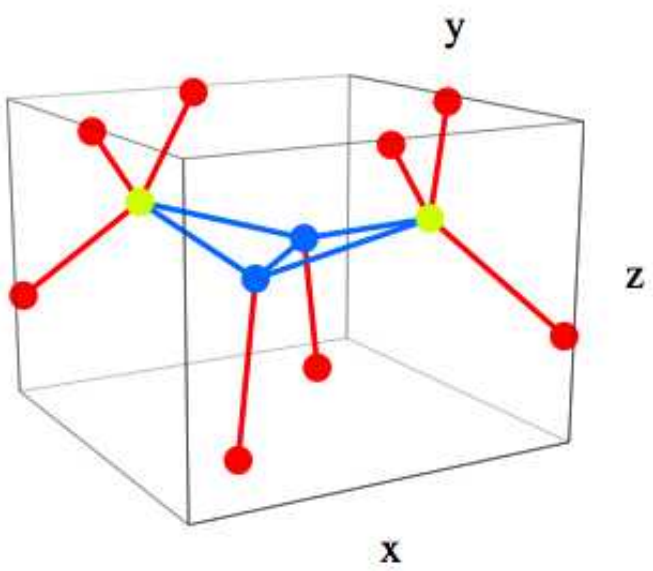

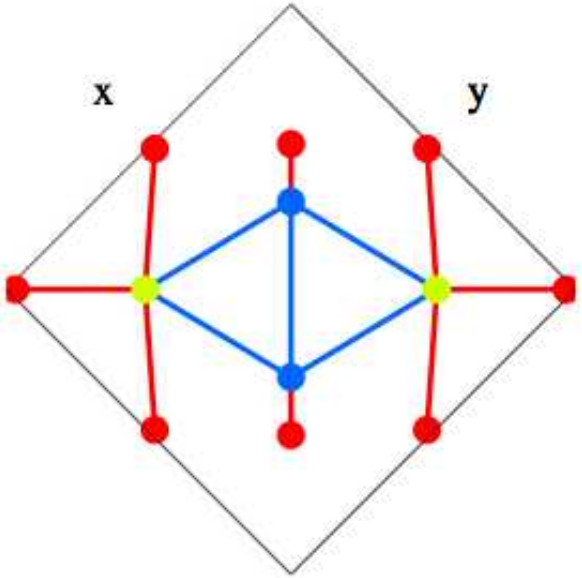

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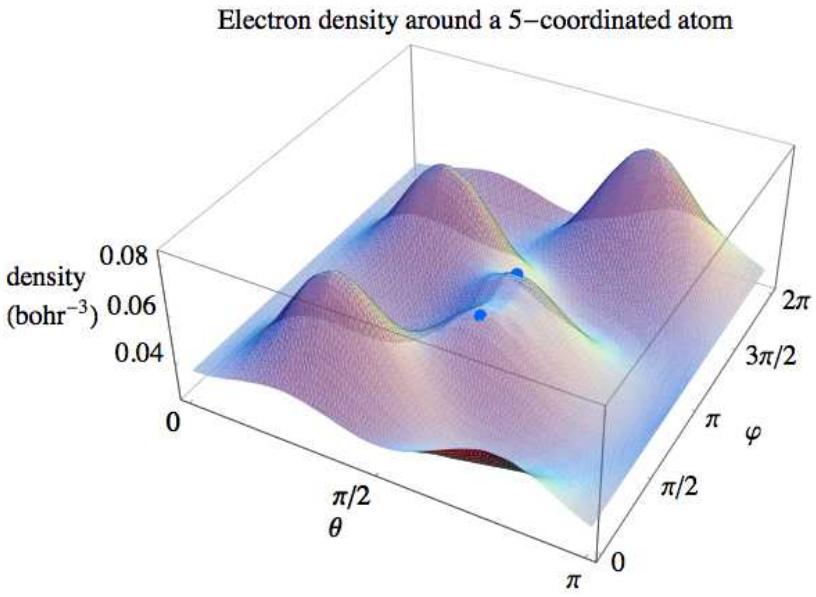
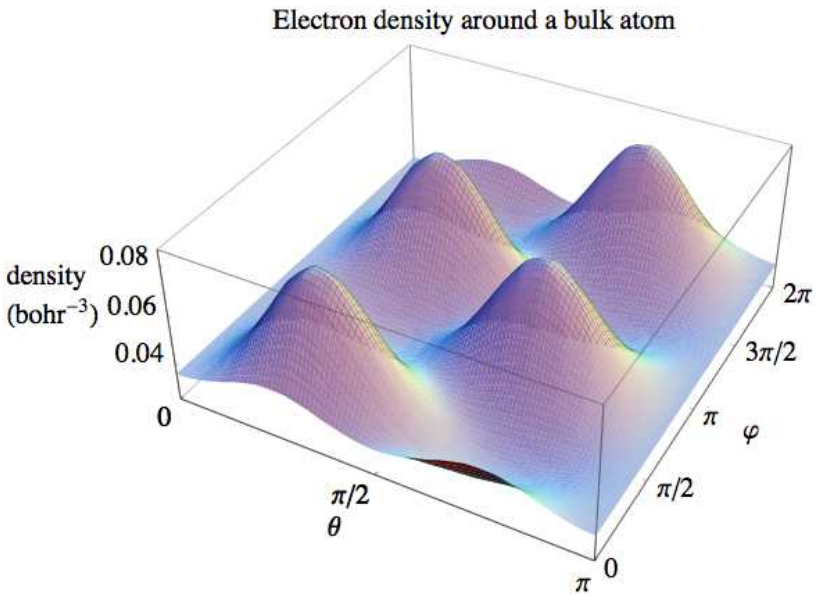
Bonds of 5-coordinated atom





Three bulk-like bonds.

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The ⟨110⟩ - split interstitial

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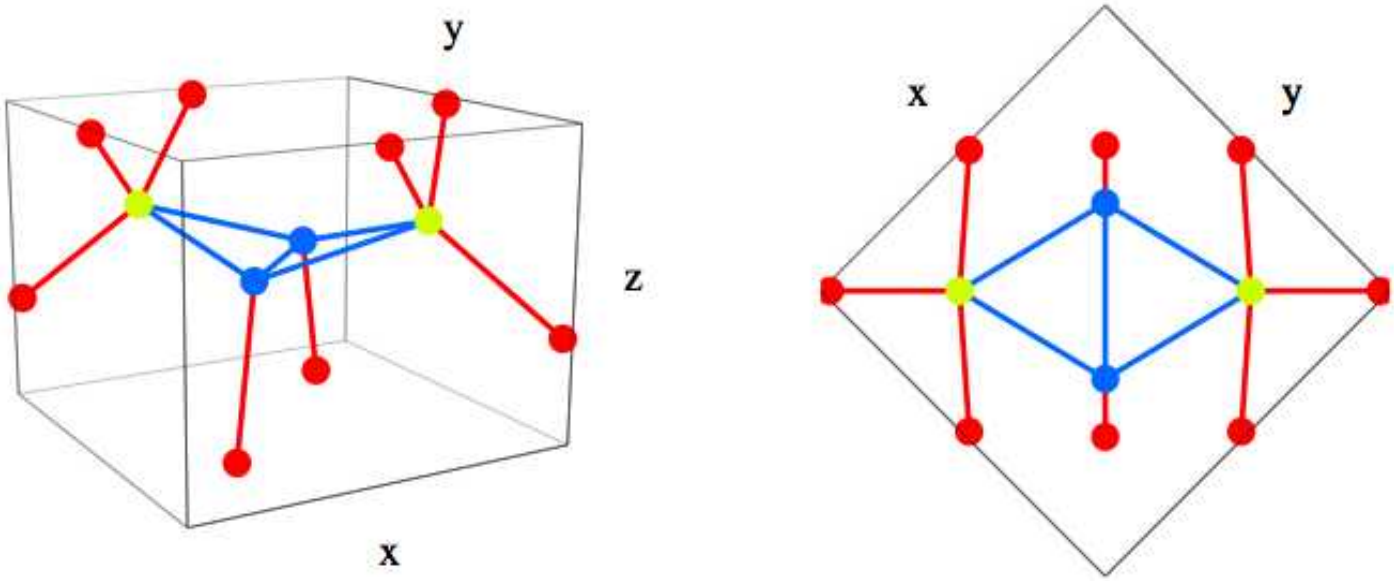

Red bonds are bulk-like. **Blue bonds** are weakened bonds with smeared out density. Surface effects arise from these smeared out bonds.

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‘Homogeneous’ density around interstitial

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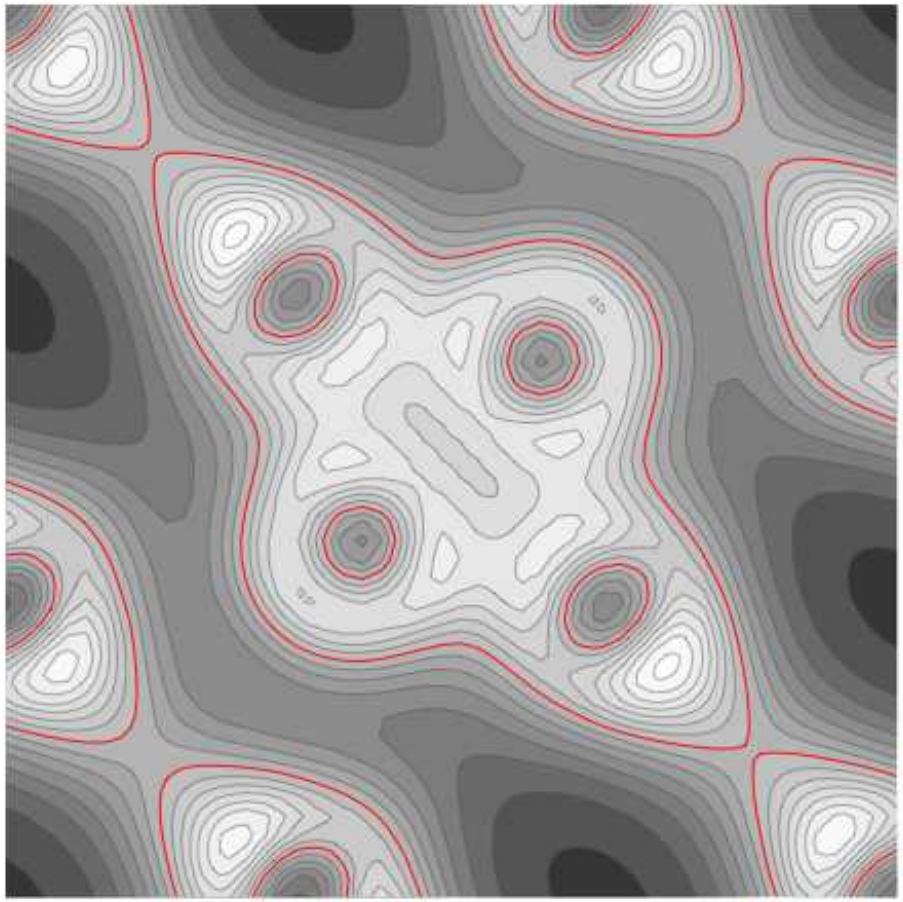

Density contours in a plane through the 110-split interstitial, between blue and yellow atoms.

Clearly the density is more homogeneous than in the bulk.

Si Interstitial Formation Energies (eV)

	DFT/AM05
Tetrahedral	3.40
Hexagonal	3.25
110-split	3.16

Si interstitials: Implications

If QMC right: Some unknown, large, error, the same for all pure functionals, is plaguing interstitial formation energy calculations. PW91 results get closest to QMC results because they have largest surface intrinsic error to cancel.

If DFT right: Some error in QMC give too high interstitial formation energies. Correcting wrong pseudo-potentials and relaxation probably not enough to explain the difference.

Summary and conclusions

There are two reasons we want to UNDERSTAND the performance of functionals:

- For a DFT based simulation to be truly predictive, the choice of functional needs to be based on objective criteria founded on theoretical insight (right answer for the right reason).
- We need to understand the performance of existing functionals in order to be able to construct new, better, ones.

I have presented results and insights about LDA, PBE, PW91, and AM05 obtained when testing the latter.

- AM05 has uniform performance for lattice constants (and maybe bulk modulus).
- AM05 seems to be a good starting point for further development.
    - Van der Waals should be included.
    - Probably some gradient corrected treatment for interior regions needed for better performance for metal systems.

Thanks!

For your attention.

Preprints/Reprints available at:

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

Collaborators: Rickard Armiento, Peter Schultz, Thomas Mattsson, Ryan Wixom

Questions? Comments?

End

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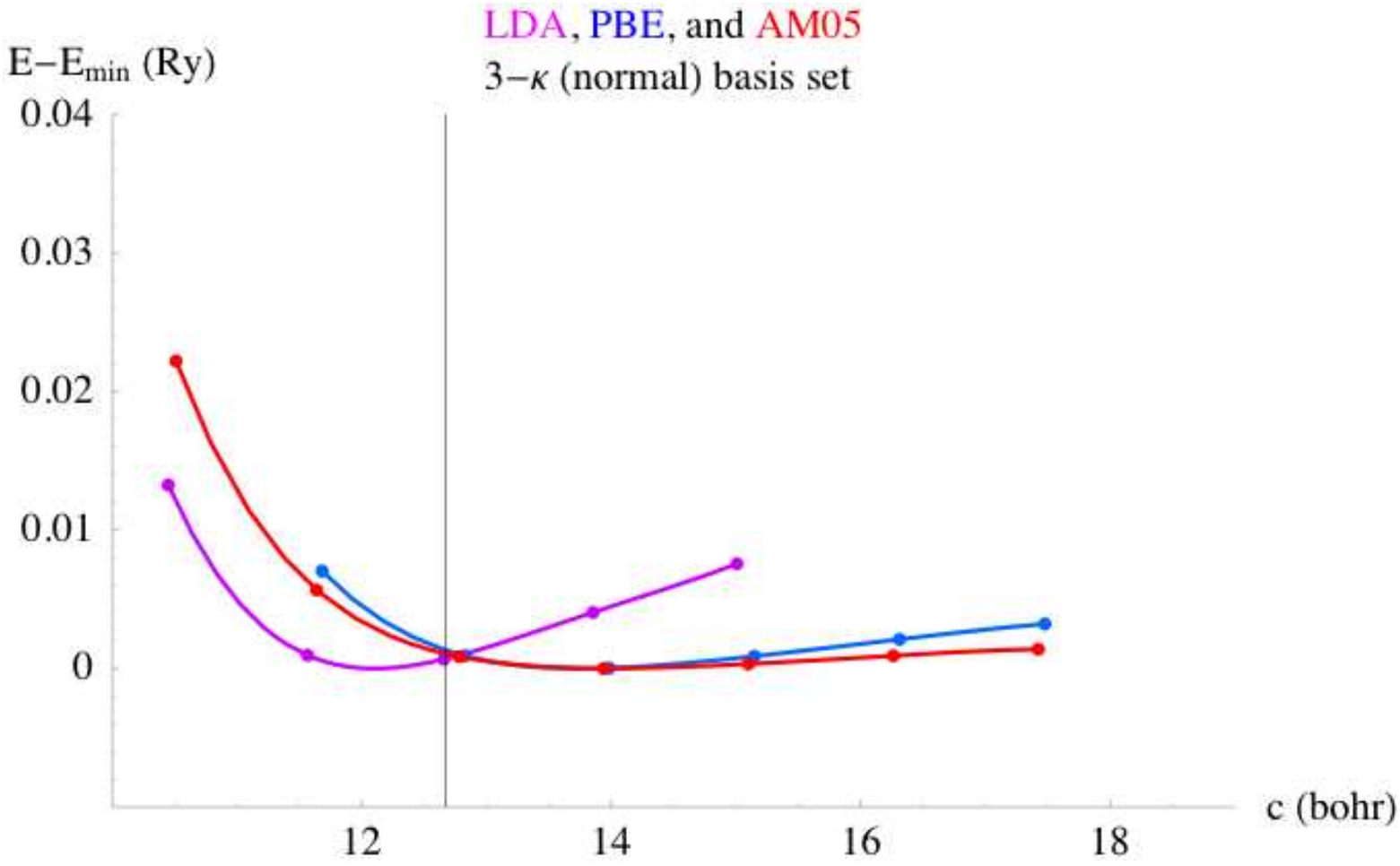
Graphite summary



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