



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

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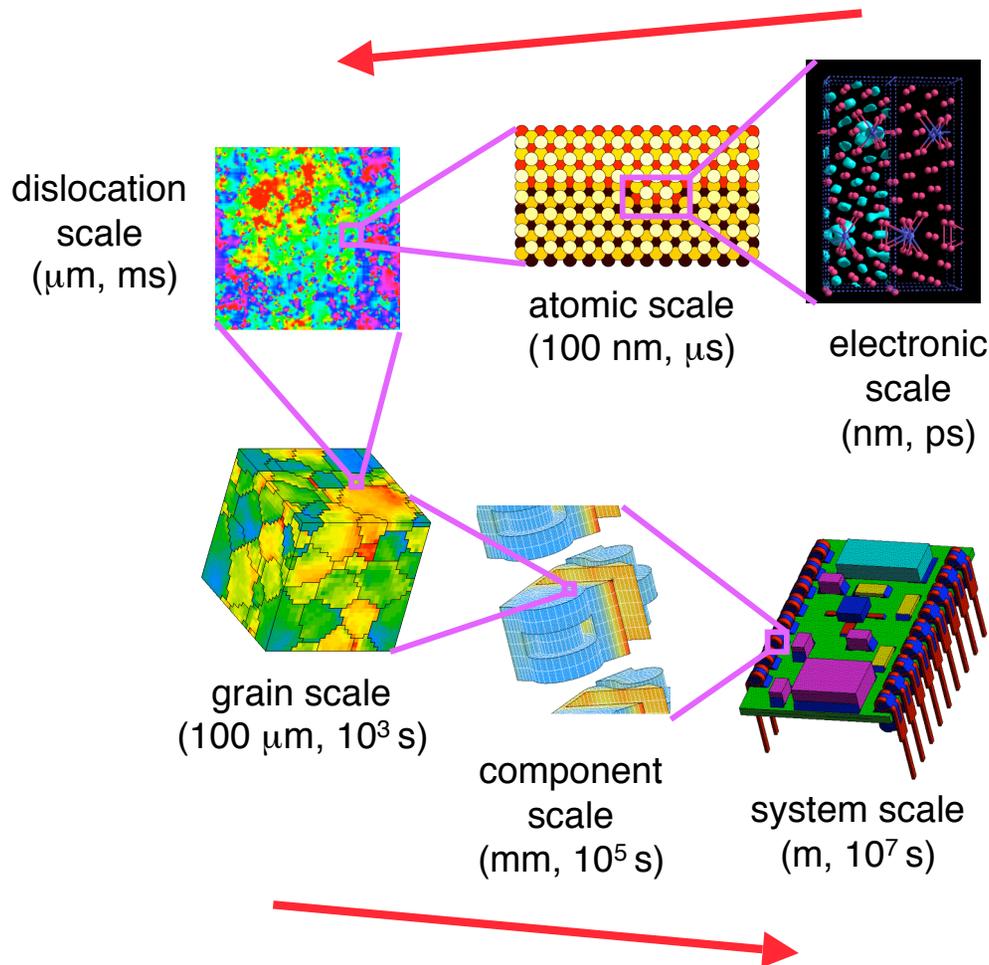


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# Density Functional Theory: The Underpinning of Predictive Multi-scale Efforts at Sandia

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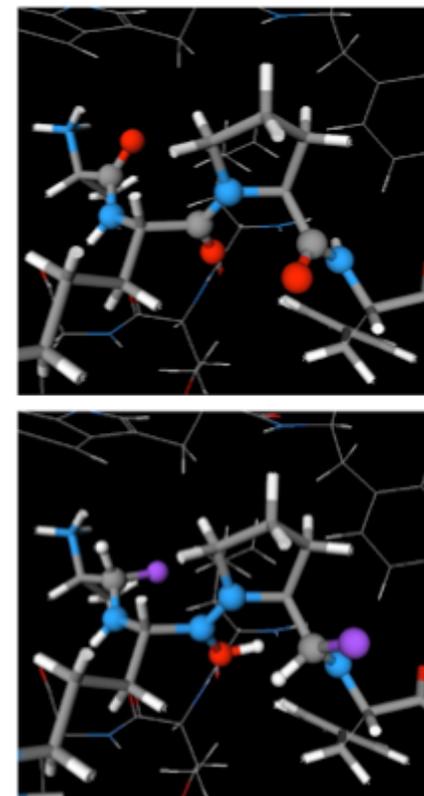
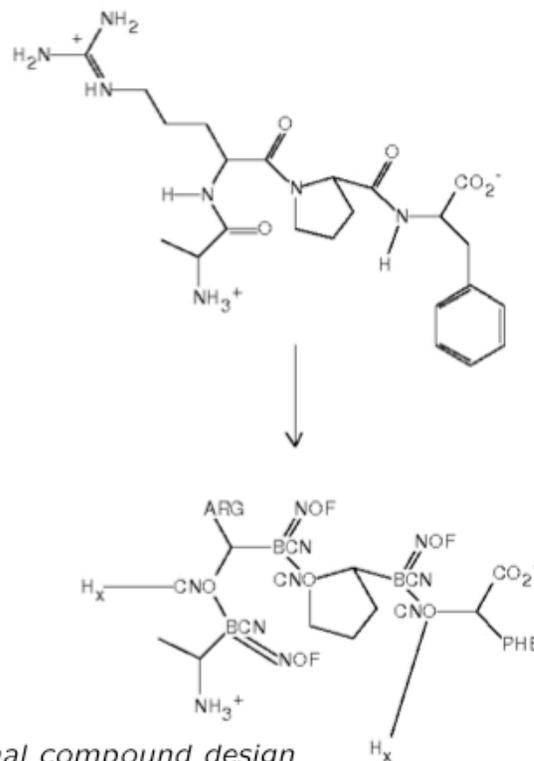


- **Goal:** Predict how materials age and perform under normal, adverse and extreme conditions.
- **Method:** Bridge length and time scales by using results from each scale as input on the next scale.
- **Foundation:** To get the fundamental processes right via DFT calculations at the electronic scale.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



# 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)

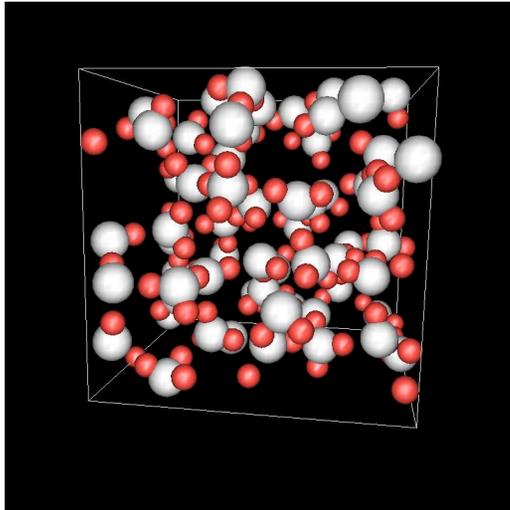
Crucial to have first principles methods that gives the right trends so that a target property can be calculated as a function of chemical composition.



# Speed is also very important

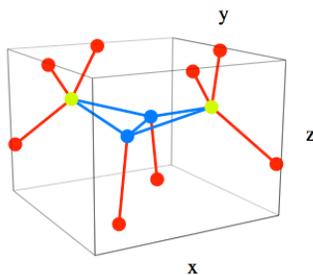
## DFT-MD (also called QMD)

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

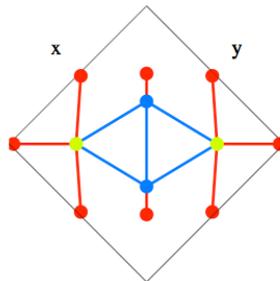


DFT is increasingly employed in quantum MD simulations of hundreds of atoms for tens of ps. This application demands functionals that are both accurate and fast. Every calculation with a temperature needs to be done with MD. Examples: Critical points and melting curves for EOS construction; Realistic calculations with water present.

## Large cells and diffusion:



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

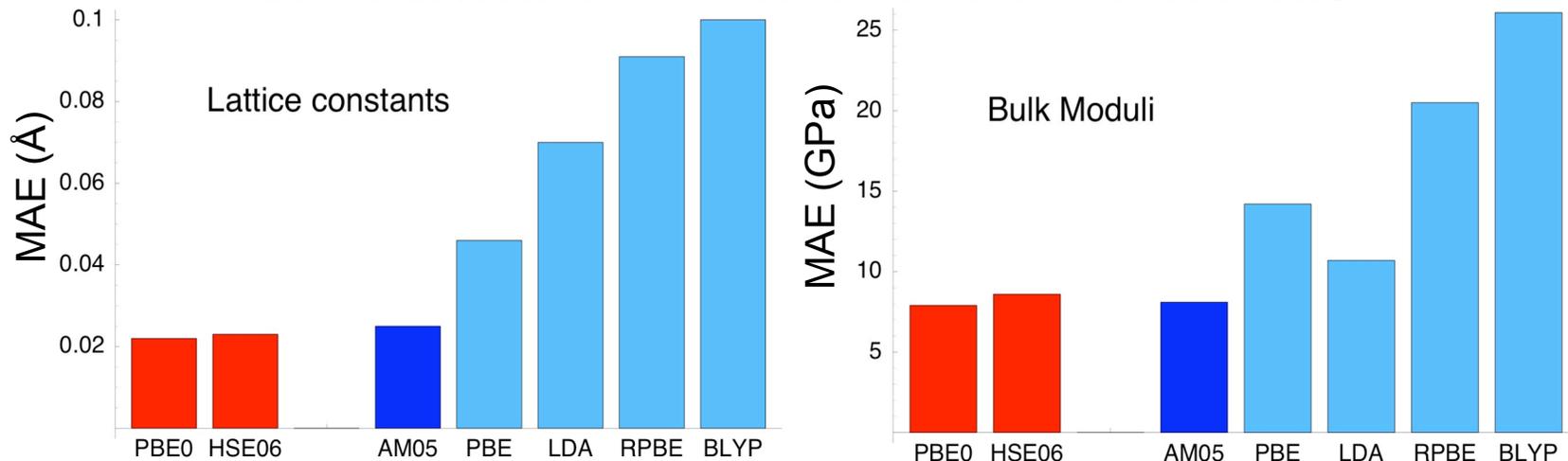


Since all solid state DFT calculations uses periodic boundary conditions, large supercells are required for defect simulations in order to avoid uncontrolled interactions between defects. Calculating diffusion coefficients also require nudge elastic band type calculations where several copies of the same systems are needed.



# 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.



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.



## So, why is AM05 so good?

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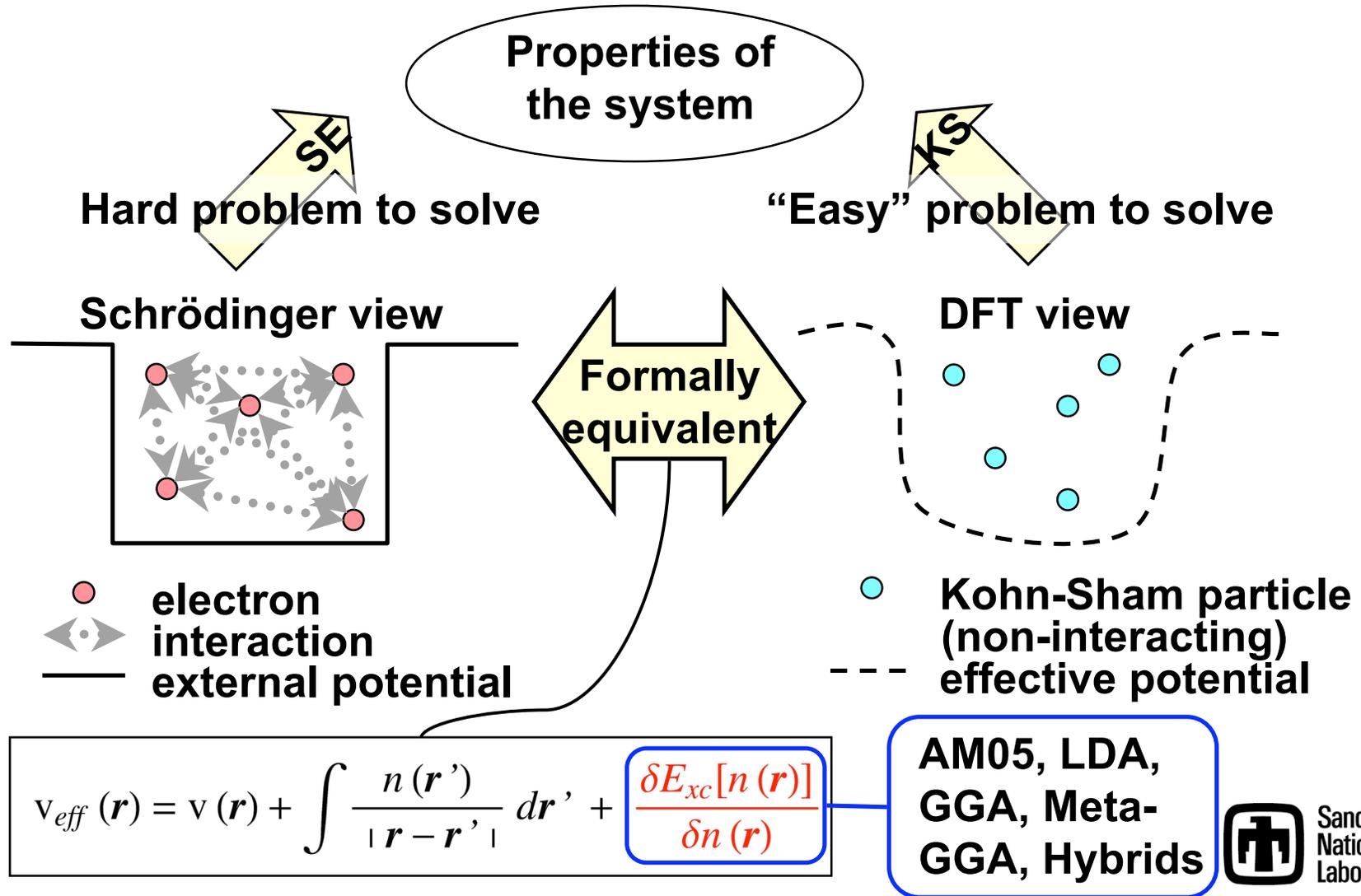
AM05 is based on a 'new' way of thinking about functionals that is actually based on how the first LDA was created already in 1965.

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

But let us start from the beginning:

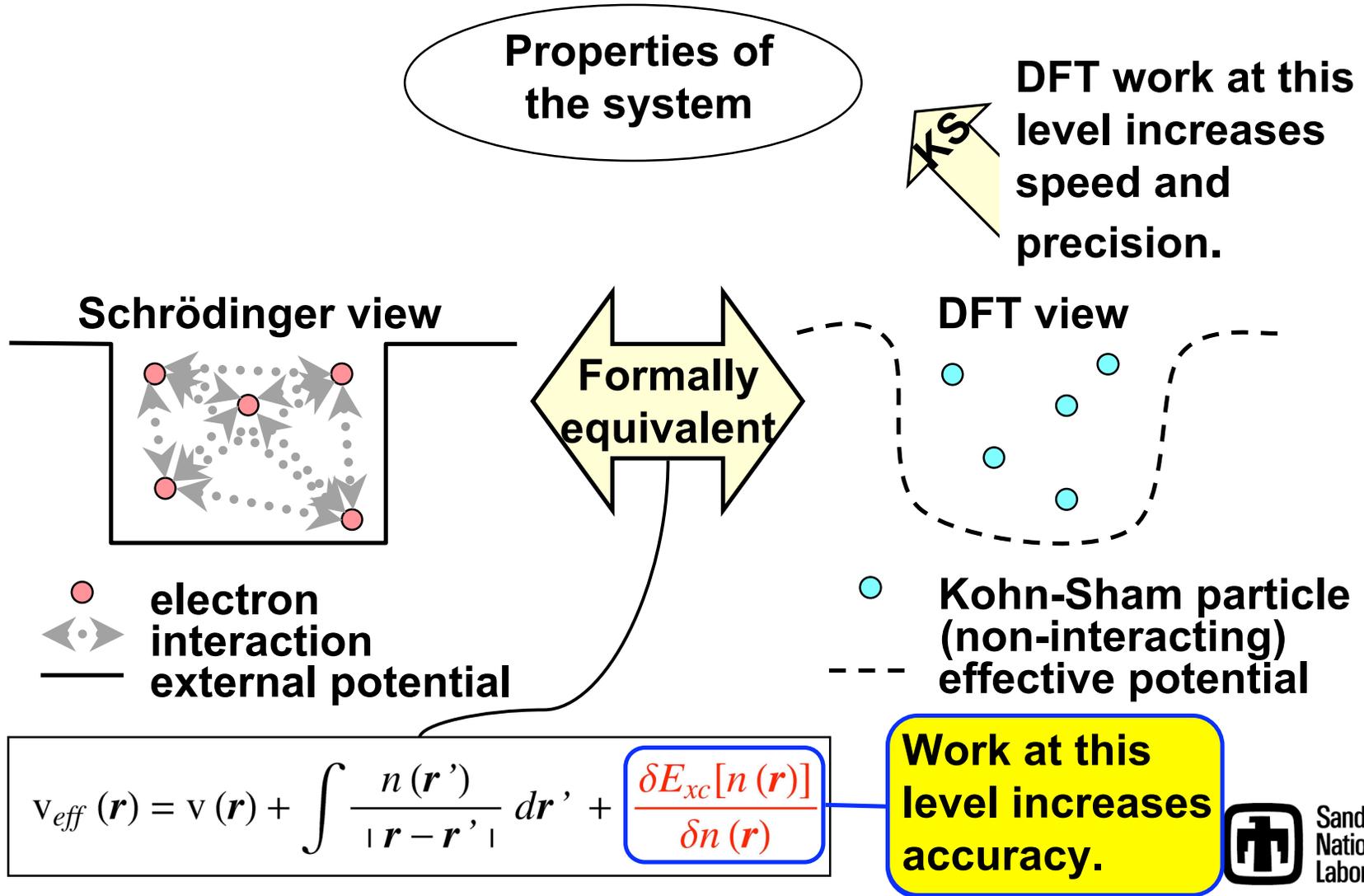


# DFT and functionals



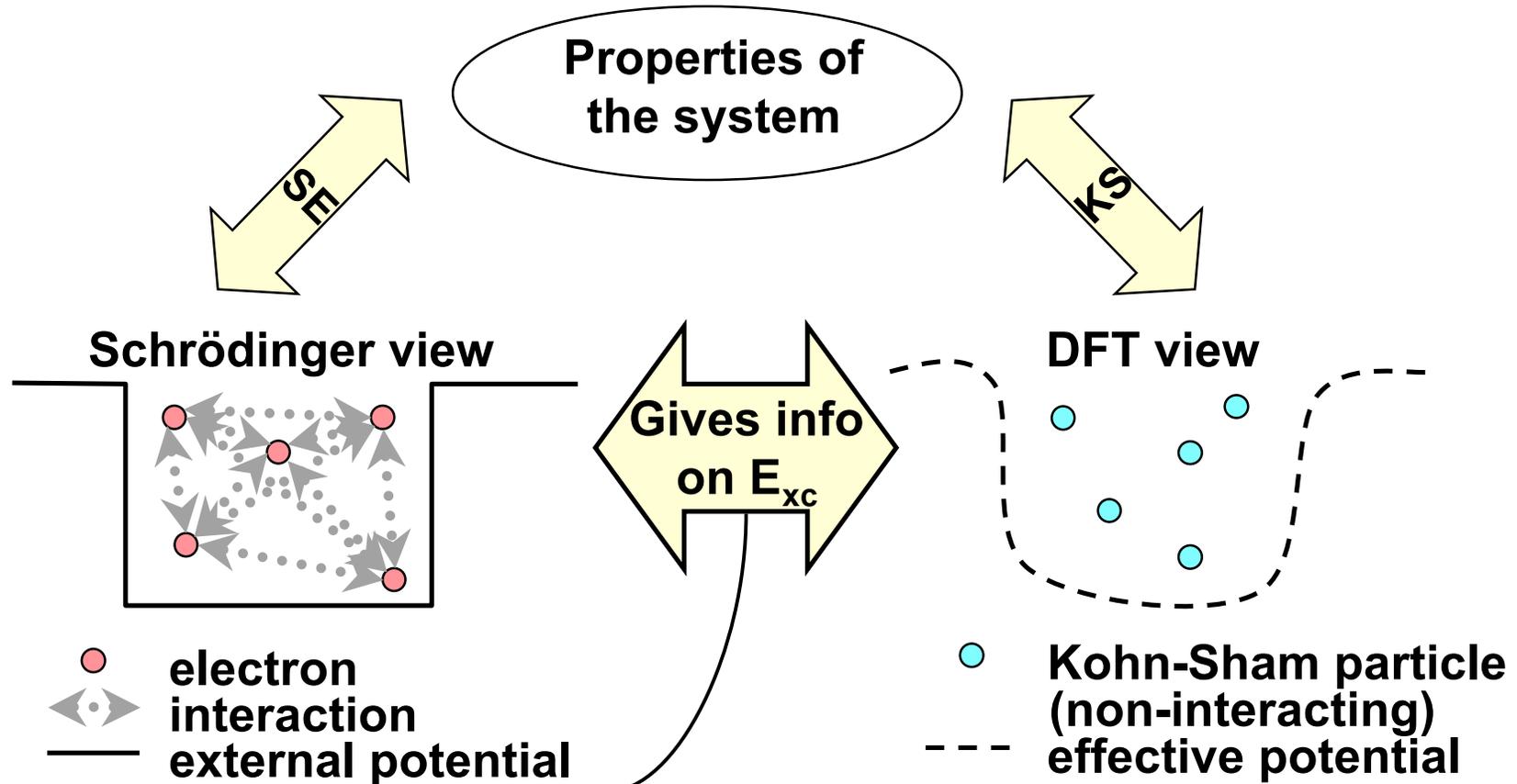


# DFT and functionals





# Functional development



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

**Work at this level increases accuracy.**



# Exchange-correlation functionals

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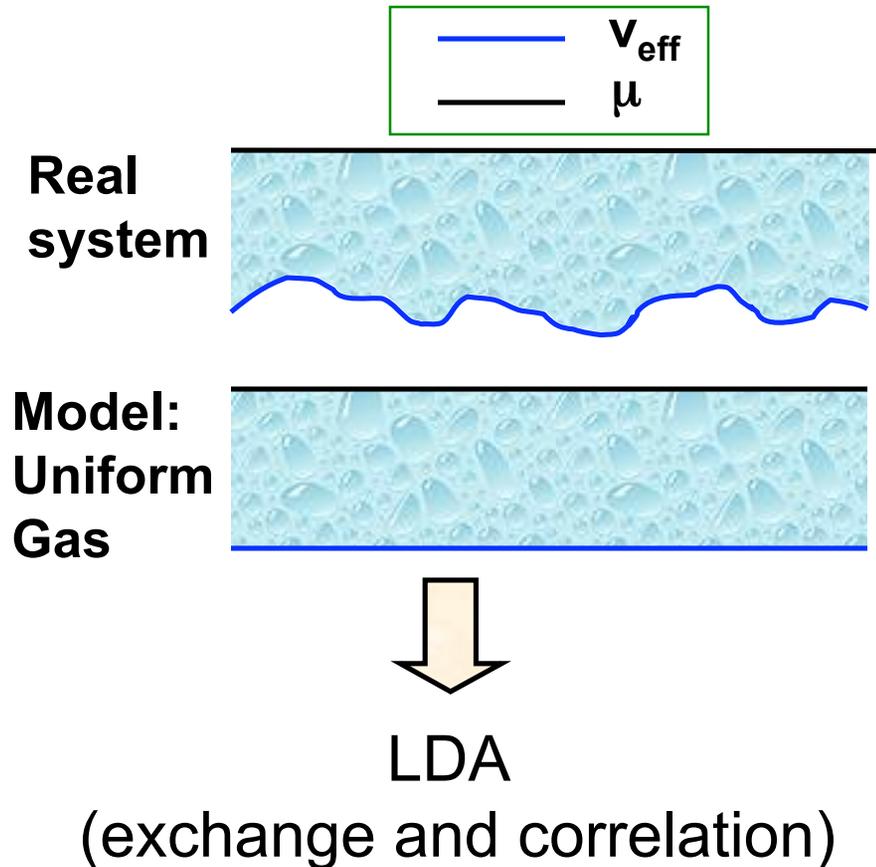
$$E_{xc} = \int_V n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}; [n]) dV$$

The *exchange-correlation energy density* 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).



## LDA and Ceperly-Alder

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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 use are based on their data.

(Before 1980, for example, Wigner correlation was used)



## **Beyond LDA: Constraints vs Model systems**

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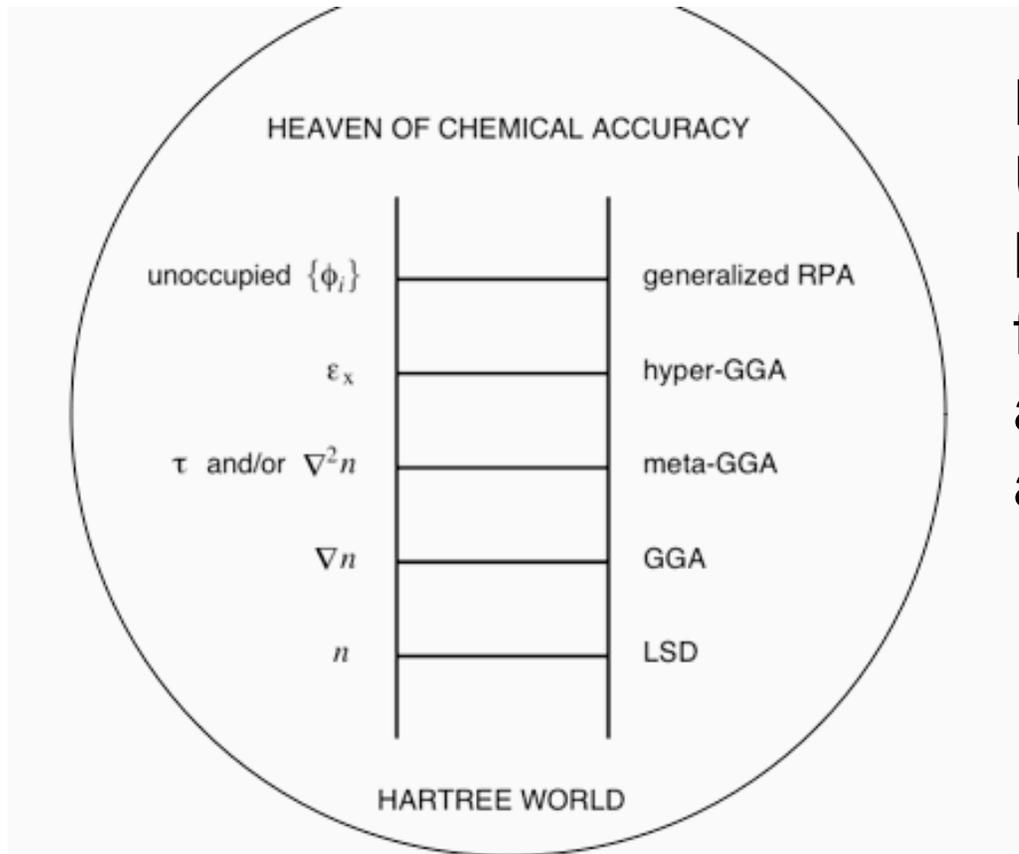
It was a large surprise that LDA worked so well.

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

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## Compatibility

Jellium surface exchange and correlation energies

Example:  $r_s=2.07$  (Al)

	$\sigma_x$	$\sigma_c$	$\sigma_{xc}$
Exact	2296	719	3015
LDA	2674	287	2961
GGA	2127	754	2881

In erg/cm<sup>2</sup>

(PBE)

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



## So, why is AM05 so good?

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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

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

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

LDA, GGA, meta-GGA, and AM05



# Subsystem functionals

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From  
general purpose functionals  
to  
specialized functionals

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

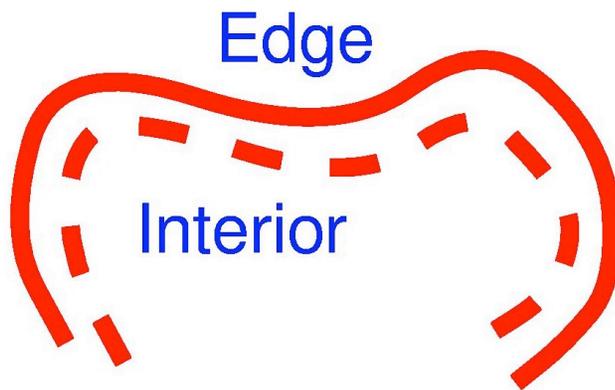
Use specialized functionals  
in the different subsystems

Divide integration over  $V$   
into integrations over subsystems



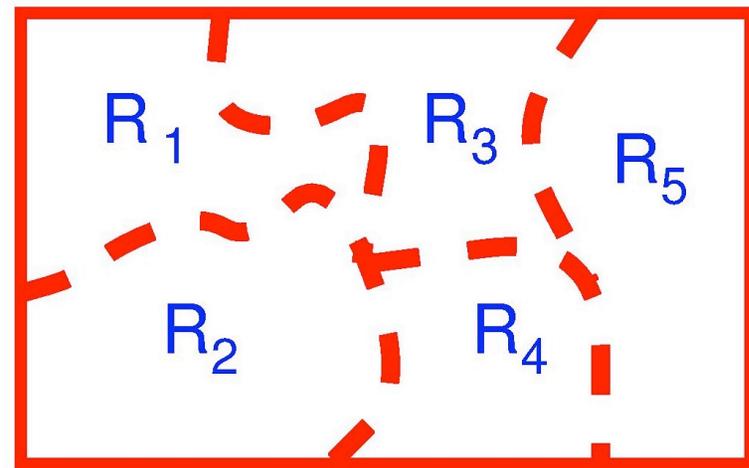
# Subsystem functionals

## Original Kohn and Mattsson approach



Kohn, Mattsson PRL 81, 3487 (1998)

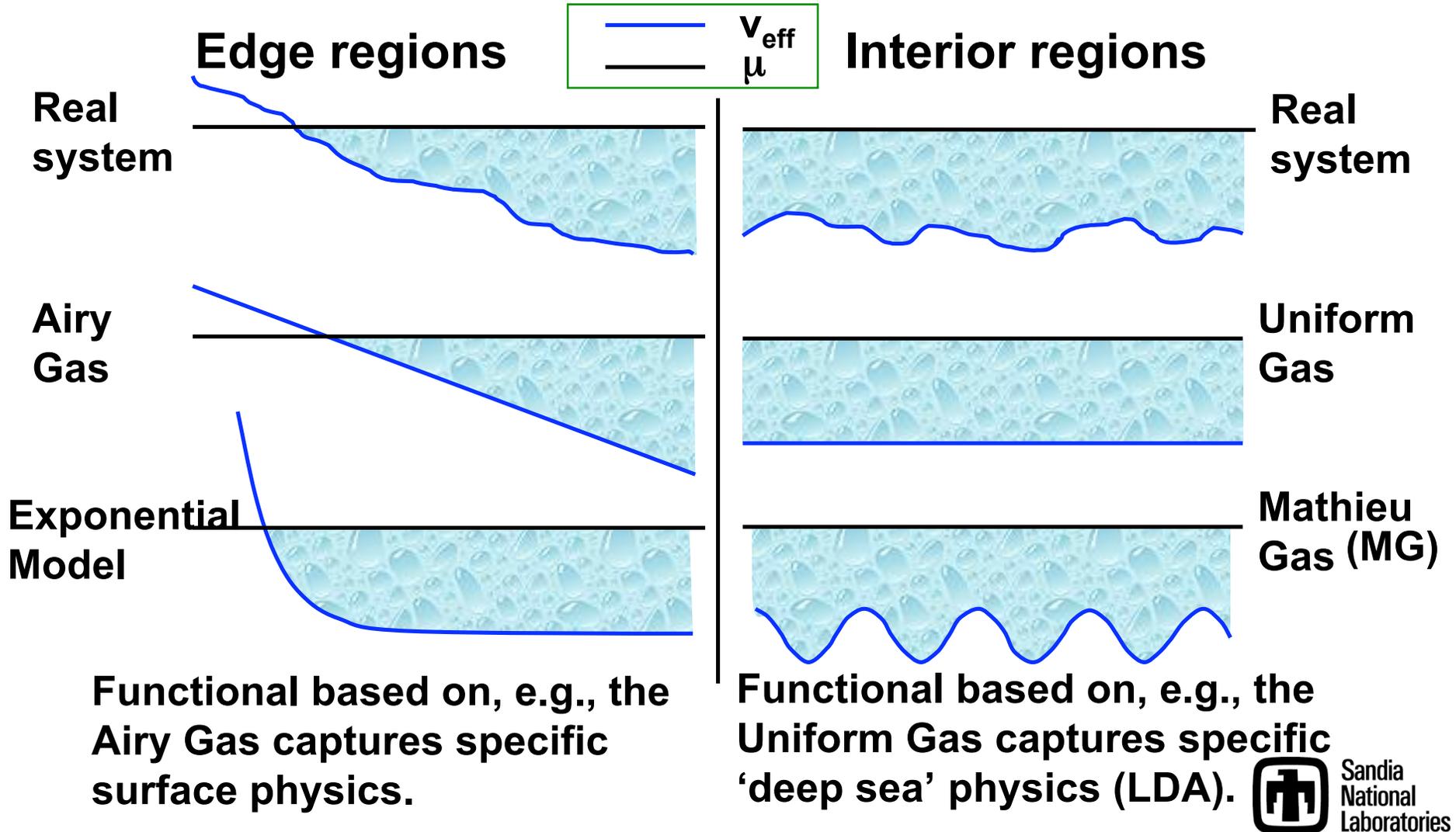
## Generalized Idea



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



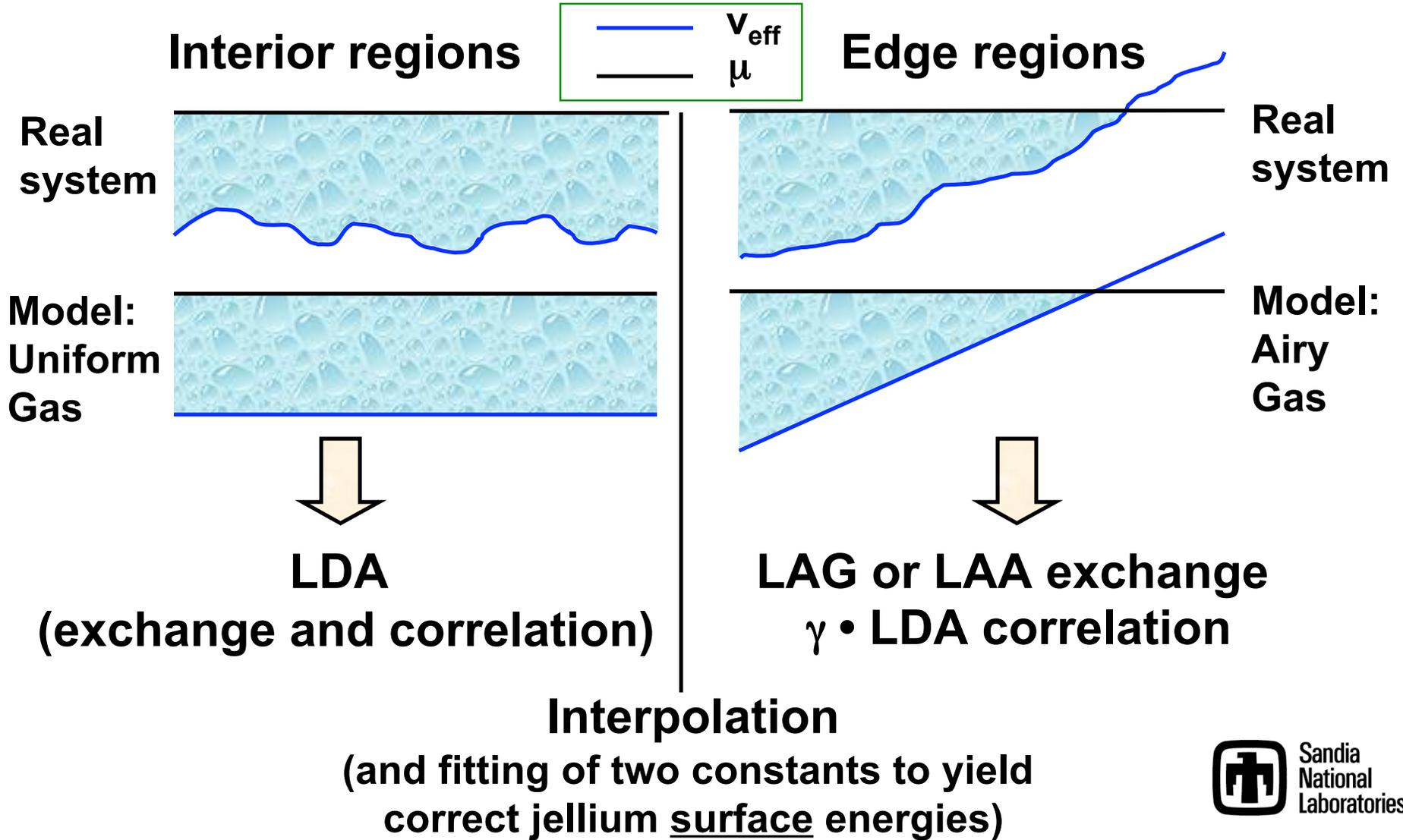
# Subsystem functionals





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

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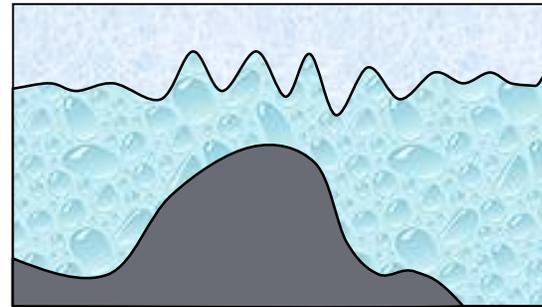
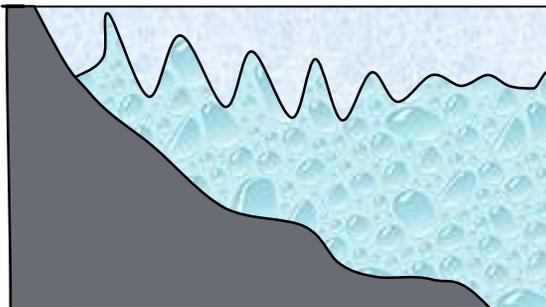


## AM05 for surfaces

AM05 is constructed to include the physics of surfaces in addition to the 'deep sea' physics included in LDA. So, what about AM05 and surfaces?

There are many types of surfaces and since we did not until recently have a code that could do proper surface problems we have explored 'internal surfaces' in bulk materials, mainly vacancies. The good performance of AM05 for bulk systems can actually also be explained from internal surfaces.

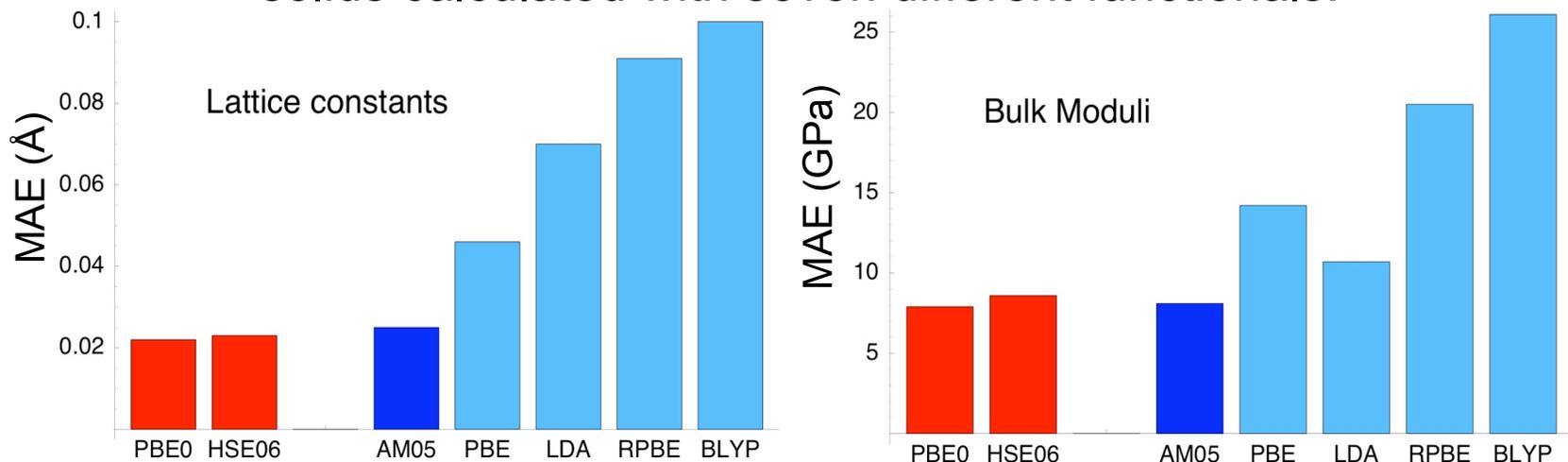
I like the picture of a sunken rock and the waves around it as a picture of that surface physics can be present also when no proper dry land island is present.





# 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.



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.



# Assessment published in JCP

Ann E. Mattsson

THE JOURNAL OF CHEMICAL PHYSICS 128, 084714 (2008)

## The AM05 density functional applied to solids

Ann E. Mattsson,<sup>1,a)</sup> Rickard Armiento,<sup>2,b)</sup> Joachim Paier,<sup>3,c)</sup> Georg Kresse,<sup>3,d)</sup>  
John M. Wills,<sup>4,e)</sup> and Thomas R. Mattsson<sup>5,f)</sup>

Other important results:

- VASP5 with existing PAW potentials can be used together with new functionals, greatly facilitating functional testing.
- By using two different codes we can put numerical error bars on our results. MAE error bars: 0.005 Å for lattice constants, and 3 GPa for Bulk Moduli.
- On average AM05 performs better than choosing the best of LDA or PBE for each solid.
- Assessment of experimental error bars now needed to resolve differences between state of the art functionals.



# RSPt and VASP results: Lattice constants

**VASP with AM05 on LDA or PBE core potentials give almost identical results! Very good for future testing of new functionals or more complicated properties.**

Solid	AM05			LDA		PBE		
	VASP		RSPt	VASP		RSPt	VASP	
	LDA PAW	PBE PAW		LDA PAW	RSPt		PBE PAW	RSPt
Li	3.4539	3.4559	3.456	3.359	3.362	3.433	3.434	
Na	4.2124	4.2125	4.222	4.052	4.053	4.201	4.196	
Al	4.0003	4.0076	4.008	3.984	3.986	4.041	4.043	
BN	3.6026	3.6071	3.604	3.583	3.583	3.627	3.625	
BP	4.5118	4.5203	4.520	4.491	4.495	4.548	4.553	
C	3.5497	3.5529	3.551	3.534	3.534	3.573	3.573	
Si	5.4306	5.4317	5.436	5.403	5.405	5.467	5.474	
SiC	4.3491	4.3514	4.361	4.330	4.337	4.377	4.386	
$\beta$ -GaN	4.4914	4.4921	4.506	4.460	4.465	4.548	4.553	
GaP	5.4385	5.4435	5.457	5.394	5.405	5.509	5.518	
GaAs	5.6689	5.6747	5.686	5.611	5.620	5.755	5.761	
LiF	4.0364	4.0420	4.041	3.908	3.912	4.065	4.065	
LiCl	5.1163	5.1223	5.114	4.962	4.966	5.150	5.149	
NaF	4.6860	4.6866	4.685	4.508	4.507	4.708	4.692	
NaCl	5.6844	5.6877	5.693	5.466	5.467	5.702	5.692	
MgO	4.2352	4.2291	4.221	4.168	4.164	4.259	4.253	
Cu	3.5641	3.5668	3.564	3.523	3.522	3.637	3.633	
Rh	3.7729	3.7729	3.786	3.757	3.769	3.833	3.845	
Pd	3.8713	3.8727	3.880	3.844	3.852	3.946	3.953	
Ag	4.0538	4.0549	4.062	4.002	4.010	4.150	4.155	
ME	-0.001	0.002	0.006	-0.070	-0.066	0.039	0.041	
MAE	0.026	0.025	0.022	0.070	0.066	0.046	0.048	
RMS	0.033	0.033	0.033	0.082	0.079	0.056	0.056	
MARE	0.6%	0.6%	0.5%	1.6%	1.5%	1.0%	1.1%	

**We estimate 0.003 Å error bars in ME, MAE, RMS**



# RSPt and VASP results: Bulk Moduli

**VASP with AM05 on LDA or PBE core potentials give almost identical results! Very good for future testing of new functionals or more complicated properties.**

Solid	AM05			LDA		PBE		
	VASP		RSPt	VASP		RSPt	VASP	
	LDA PAW	PBE PAW		LDA PAW	RSPt		PBE PAW	RSPt
Li	13.01	12.99	13.2	15.1	15.0	13.7	13.9	
Na	7.363	7.361	7.65	9.22	9.16	7.62	7.74	
Al	84.08	83.63	86.2	81.4	82.5	75.2	77.1	
BN	378.5	377.5	384	394	400	365	370	
BP	165.1	164.3	168	171	174	158	160	
C	442.5	441.4	450	456	465	424	431	
Si	90.30	90.11	92.0	93.6	95.4	86.4	87.5	
SiC	216.9	216.3	217	224	226	208	208	
$\beta$ -GaN	180.6	180.5	183	196	199	166	170	
GaP	80.31	80.13	81.1	87.0	88.2	74.3	75.1	
GaAs	65.08	65.07	65.4	71.8	72.4	59.7	59.4	
LiF	65.85	65.82	65.8	85.7	86.2	66.7	67.5	
LiCl	30.31	30.25	30.7	40.4	41.0	31.2	31.9	
NaF	43.27	43.08	42.4	60.1	60.4	44.5	45.6	
NaCl	22.04	21.99	21.0	31.4	31.5	23.4	23.7	
MgO	151.3	151.9	154	169	171	148	149	
Cu	157.4	157.3	165	180	187	134	140	
Rh	285.3	285.5	293	304	312	249	253	
Pd	194.2	193.9	202	216	224	165	167	
Ag	108.6	108.9	114	132	137	88.9	90.2	
ME	-4.38	-4.59	-1.80	7.48	10.4	-14.1	-12.1	
MAE	8.03	8.19	9.27	10.7	12.3	14.2	12.2	
RMS	11.2	11.3	11.9	15.2	18.4	18.3	16.2	
MARE	7.1%	7.2%	8.1%	10.8%	11.8%	10.4%	9.3%	

**We estimate 3 GPa error bars in ME, MAE, RMS**



# VASP results for bulk systems: Summary

Previous results by Paier et al

	$a_0$ (Å) <b>0.005 Å</b>			$B_0$ (GPa) <b>3 GPa</b>		
	ME	MAE	RMSE	ME	MAE	RMSE
AM05	0.001	0.025	0.033	-4.48	8.10	11.2
PBE0	0.007	0.022	0.029	-0.1	7.9	11.3
HSE06	0.010	0.023	0.030	-1.6	8.6	12.8
LoP ( $a_0$ )	0.006	0.040	0.048	-6.67	11.6	16.6
LoP ( $B_0$ )	-0.003	0.049	0.053	-2.45	7.26	9.79
PBE (*)	0.039	0.045	0.054	-12.3	12.4	16.4
PBE	0.039	0.046	0.056	-14.1	14.2	18.3
LDA	-0.070	0.070	0.082	7.48	10.7	15.2
RPBE	0.090	0.091	0.113	-17.9	20.5	24.7
BLYP	0.093	0.100	0.114	-26.0	26.1	32.2

Best of LDA or PBE with respect to lattice constant or bulk moduli.

Same functional and code, different points in Murnaghan fit.

Note that AM05's performance is obtained without tweaking, we have not fitted to any solid state system and no iterative procedure discarding bad choices is used.

**The fundament of the subsystem functional scheme is sound.**



# VASP results for bulk systems

## Lattice constants (Å)

Solid	Exp	AM05	LDA	PBE	BLYP	RPBE
Li	3.477	3.455	3.359	3.433	3.421	3.476
Na	4.225	4.212	4.052	4.201	4.210	4.295
Al	4.032	4.004	3.984	4.041	4.116	4.064
BN	3.616	3.605	3.583	3.627	3.647	3.646
BP	4.538	4.516	4.491	4.548	4.592	4.573
C	3.567	3.551	3.534	3.573	3.598	3.590
Si	5.430	5.431	5.403	5.467	5.532	5.499
SiC	4.358	4.350	4.330	4.377	4.411	4.398
$\beta$ -GaN	4.520	4.492	4.460	4.548	4.611	4.511
GaP	5.451	5.441	5.394	5.509	5.607	5.556
GaAs	5.648	5.672	5.611	5.755	5.871	5.812
LiF	4.010	4.039	3.908	4.065	4.084	4.146
LiCl	5.106	5.119	4.962	5.150	5.232	5.254
NaF	4.609	4.686	4.508	4.708	4.716	4.824
NaCl	5.595	5.686	5.466	5.702	5.763	5.847
MgO	4.207	4.232	4.168	4.259	4.281	4.302
Cu	3.603	3.565	3.523	3.637	3.711	3.682
Rh	3.798	3.773	3.757	3.833	3.905	3.857
Pd	3.881	3.872	3.844	3.946	4.034	3.984
Ag	4.069	4.054	4.002	4.150	4.262	4.215
ME	...	0.001	-0.070	0.039	0.093	0.090
MAE	...	0.025	0.070	0.046	0.100	0.091
RMS	...	0.033	0.082	0.056	0.114	0.113
MARE	...	0.6%	1.6%	1.0%	2.2%	2.0%

## Bulk Moduli (GPa)

Solid	Exp	AM05	LDA	PBE	BLYP	RPBE
Li	13.0	13.0	15.1	13.7	13.7	13.1
Na	7.5	7.36	9.22	7.62	7.08	6.94
Al	79.4	83.9	81.4	75.2	54.9	73.7
BN	400*	378	394	365	350	353
BP	165	165	171	158	146	152
C	443	442	456	424	399	410
Si	99.2	90.2	93.6	86.4	77.0	83.1
SiC	225	217	224	208	194	201
$\beta$ -GaN	210*	181	196	166	152	237
GaP	88.7	80.2	87.0	74.3	64.3	69.4
GaAs	75.6	65.1	71.8	59.7	50.6	55.2
LiF	69.8	65.8	85.7	66.7	65.5	59.3
LiCl	35.4	30.3	40.4	31.2	28.9	27.3
NaF	51.4	43.2	60.1	44.5	44.3	38.3
NaCl	26.6	22.0	31.4	23.4	22.0	20.1
MgO	165	152	169	148	145	139
Cu	142	157	180	134	112	120
Rh	269	285	304	249	214	232
Pd	195	194	216	165	137	148
Ag	109	109	132	88.9	71.2	74.4
ME	...	-4.48	7.48	-14.1	-26.0	-17.9
MAE	...	8.10	10.7	14.2	26.1	20.5
RMS	...	11.2	15.2	18.3	32.2	24.7
MARE	...	7.1%	10.8%	10.4%	18.7%	16.0%

369

190

**AM05:**  
**ME: -1.93 GPa**  
**MAE: 6.45 GPa**  
**RMS: 8.19 GPa**  
**MARE: 6.5 %**



# VASP results for bulk systems: Summary

Ann E. Mattsson

Previous results by Paier et al

	$a_0$ (Å) <b>0.005 Å</b>			$B_0$ (GPa) <b>3 GPa</b>		
	ME	MAE	RMSE	ME	MAE	RMSE
AM05	0.001	0.025	0.033	-1.93	6.45	8.19
PBE0	0.007	0.022	0.029	-0.1	7.9	11.3
HSE06	0.010	0.023	0.030	-1.6	8.6	12.8
LoP ( $a_0$ )	0.006	0.040	0.048	-6.67	11.6	16.6
LoP ( $B_0$ )	-0.003	0.049	0.053	-2.45	7.26	9.79
PBE (*)	0.039	0.045	0.054	-12.3	12.4	16.4
PBE	0.039	0.046	0.056	-14.1	14.2	18.3
LDA	-0.070	0.070	0.082	7.48	10.7	15.2
RPBE	0.090	0.091	0.113	-17.9	20.5	24.7
BLYP	0.093	0.100	0.114	-26.0	26.1	32.2

↑  
↑

Same functional and code, different points in Murnaghan fit.

We need to be very careful when comparing numbers generated with different settings and different codes. A new look at experimental values to compare with is needed. **Currently the performance of AM05, PBE0, and HSE06 cannot be distinguished.**



# RSPt, VASP, LAPW, and Gaussian PBE

Paier et al, JCP 124, 154709 (2006), Table V.

Solid	PAW		FP-(L)APW+lo		RSPt	
	$a_0$	$B_0$	$a_0$	$B_0$	$a_0$	$B_0$
Li	3.438	13.7	3.436	13.8	3.434	13.9
Na	4.200	7.80	4.195	7.76	4.196	7.74
Al	4.040	76.6	4.041	76.3	4.043	77.1
C	3.574	431	3.573	430	3.573	431
MgO	4.258	149	4.258	149	4.253	149
GaAs	5.752	59.9	5.756	60.5	5.761	59.4
Cu	3.635	136	3.630	139	3.633	140
Rh	3.830	254	3.832	255	3.845	253
Pd	3.943	166	3.944	168	3.953	167
Ag	4.147	89.1	4.154	90.6	4.155	90.2

RSPt gives results close to LAPW (differences might be my 'fault'). GTO does not.



# What about other systems?

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# Preliminary results: AM05 works as well as PBE for molecular chemical reactions

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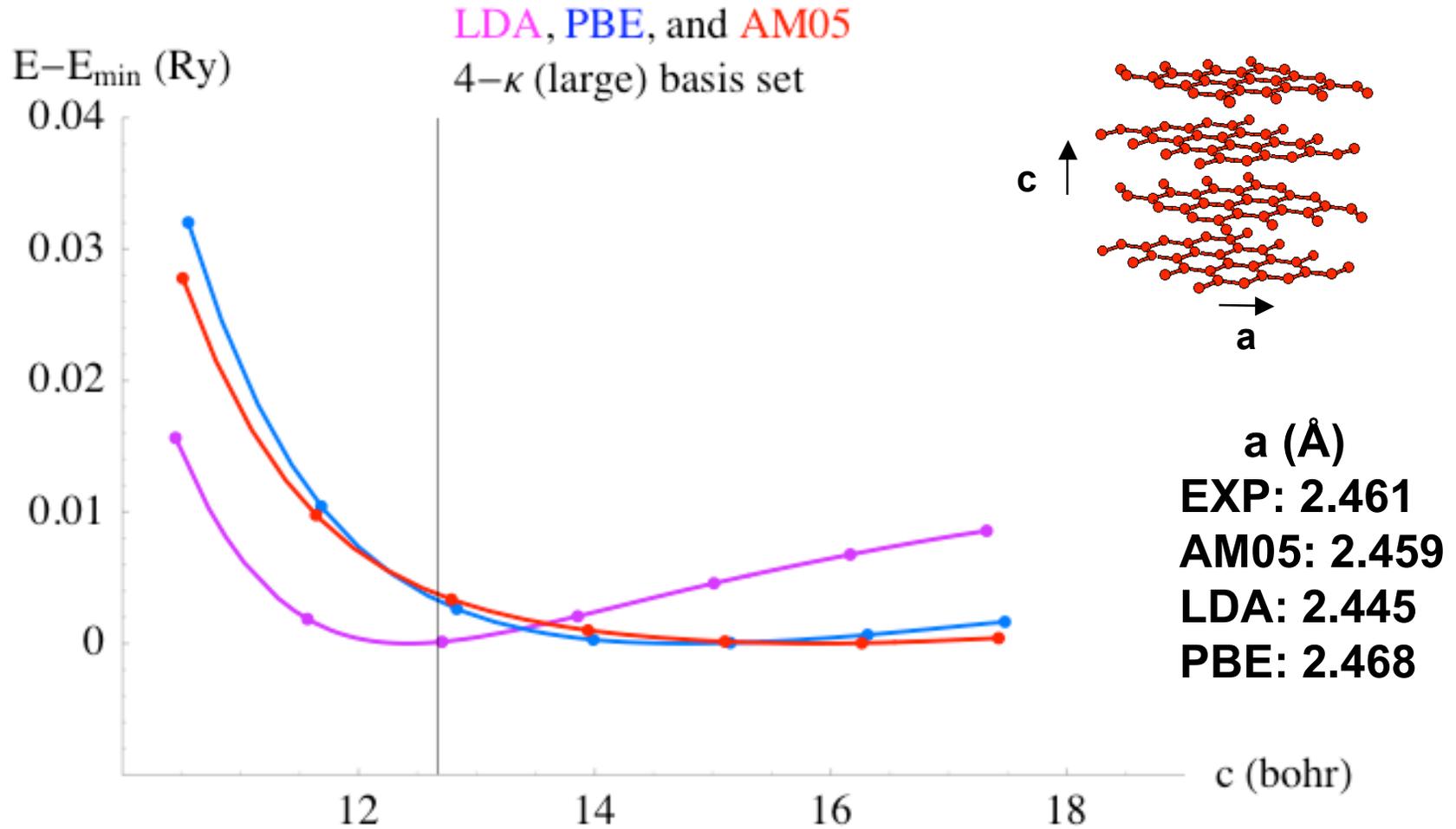
So far, 85 different chemical reactions:

	B3LYP	PBE on B3LYP structure	AM05 on B3LYP structure	Fully optimized PBE	Fully optimized AM05
Mean Absolute Error	5.38 kcal/mol	7.82 kcal/mol	8.11 kcal/mol	7.74 kcal/mol	8.17 kcal/mol

**AM05 finally gives us a functional  
to use for surface chemistry!**



# Graphite: distance between planes



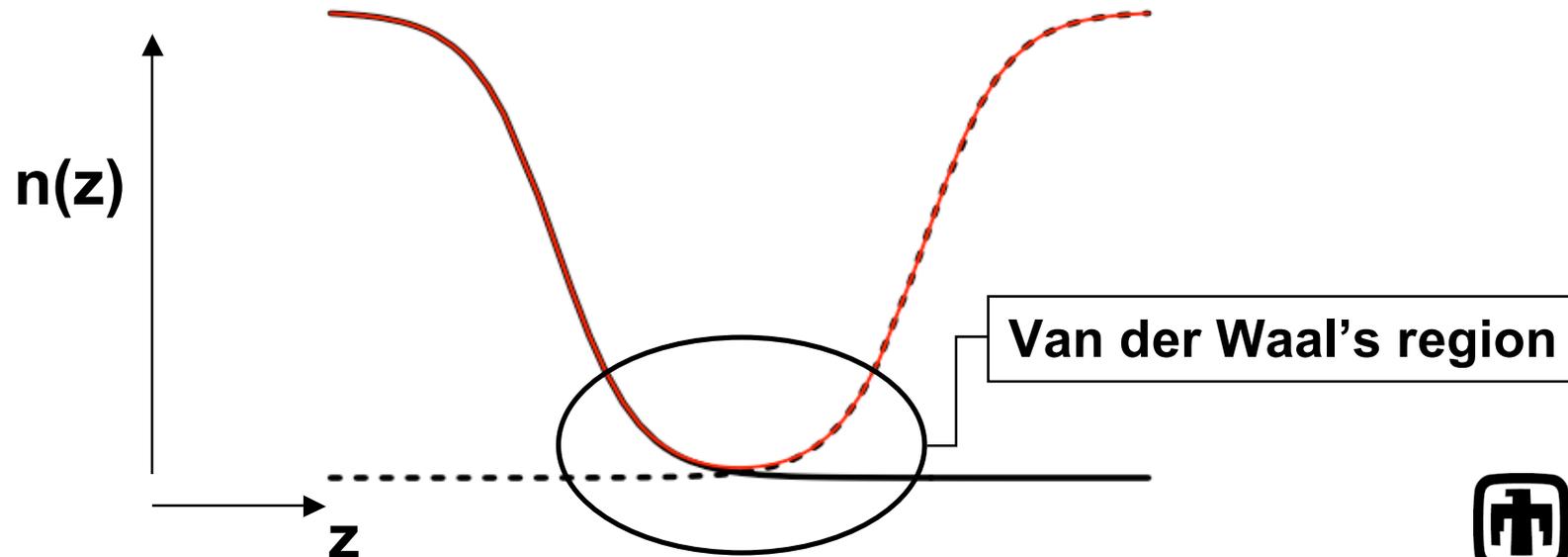


# Van der Waal's

AM05 is using the density and the density derivative. It does not include van der Waal's interactions. AM05 is behaving as the Airy gas in the 'edge' region. Density is probably good.

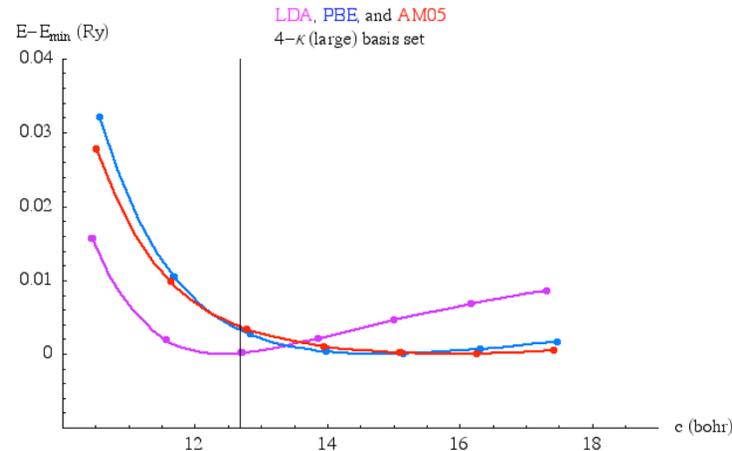
PBE and LDA are also using only the density and the gradient of the density and also cannot distinguish if one or two surfaces are present.

Any minima obtained is for the wrong reason.





# Very weak bonds: Lesson learned

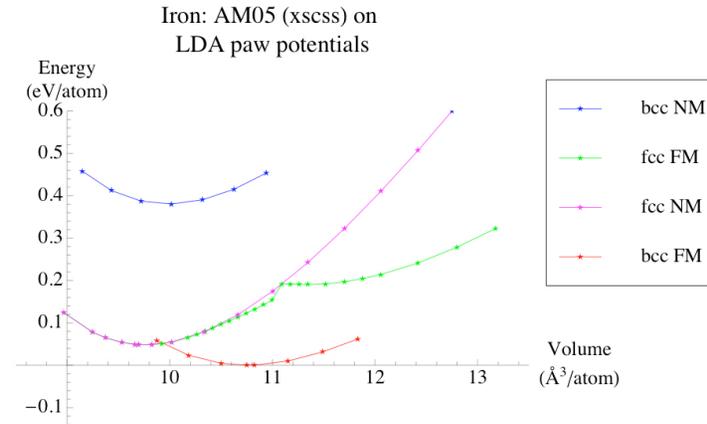
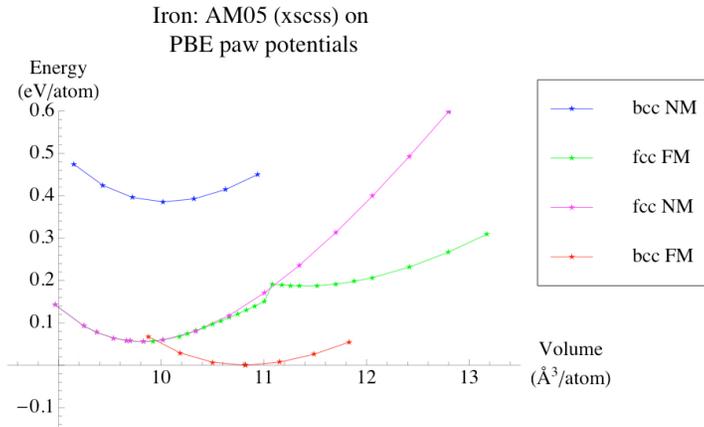


**AM05 includes no van der Waals attractions. LDA and PBE erroneously include something that looks like van der Waals attraction in, for example, graphite.**

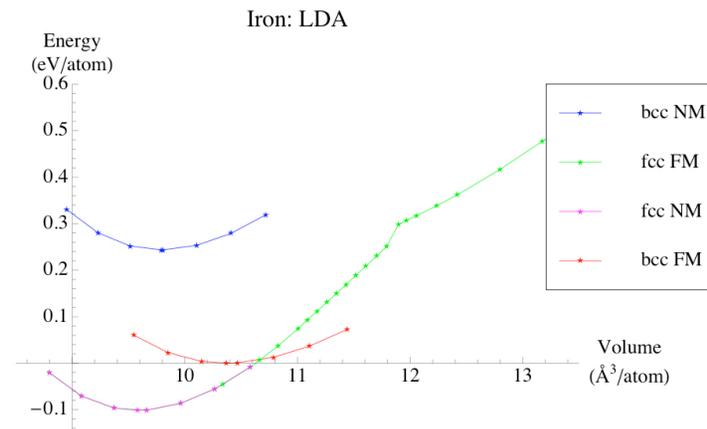
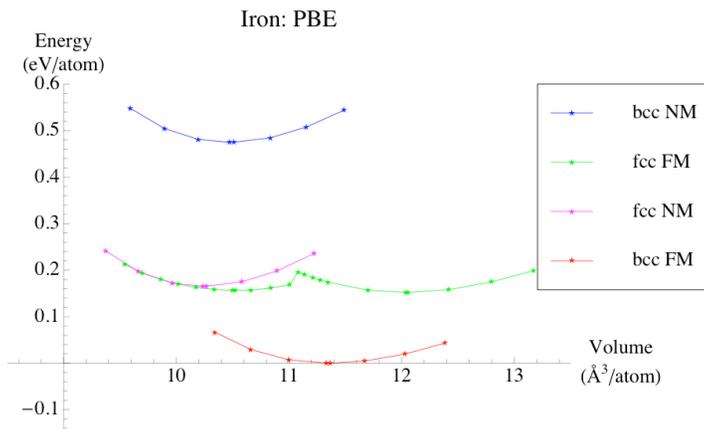
**Van der Waals needs to be included in a new functional. Work in progress.**



# Spin AM05: Fe, Energy vs volume



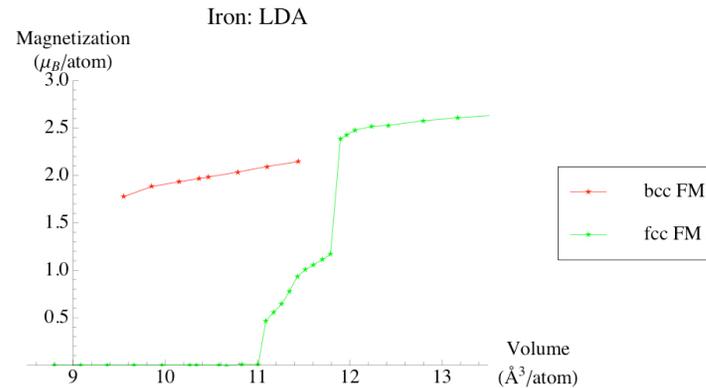
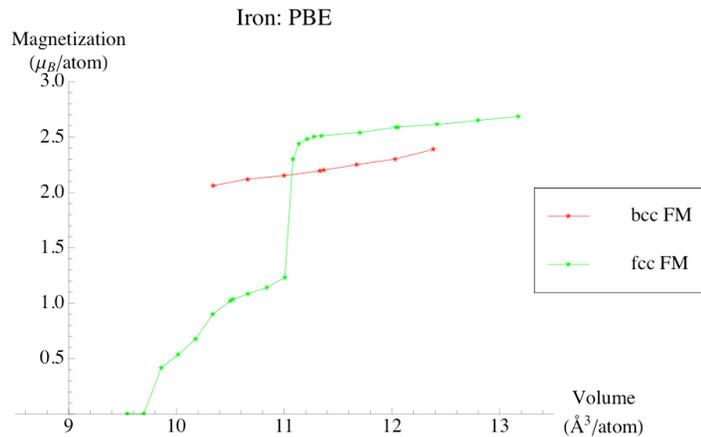
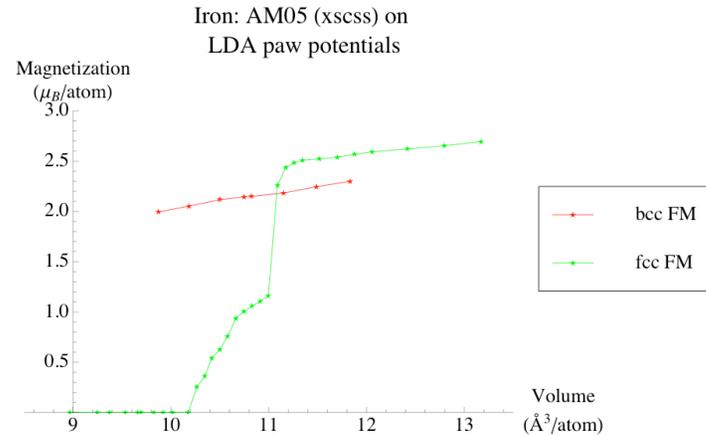
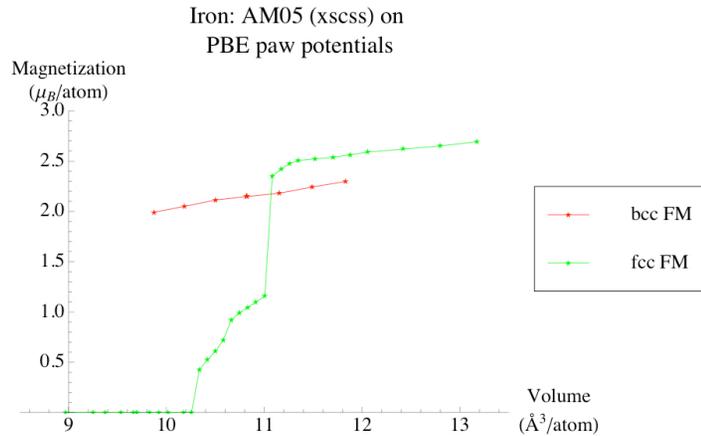
AM05 gives right bcc FM ground state.



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



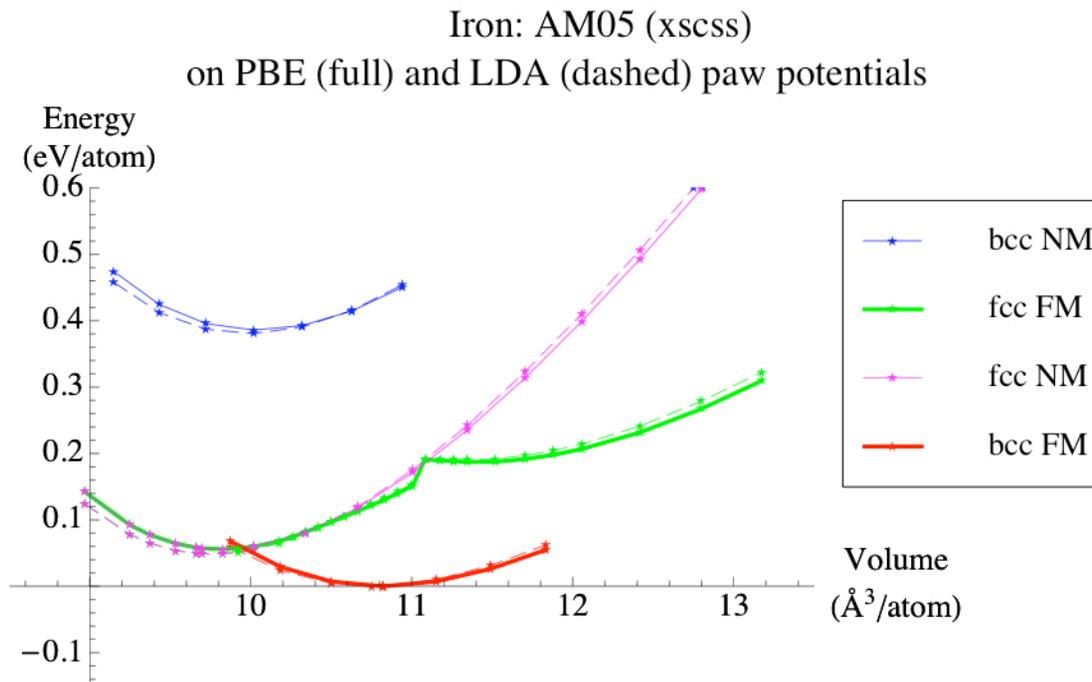
# Spin AM05: Fe, Magnetization vs volume



Magnetization: Exp  $2.20 \mu_B$ , PBE  $2.20 \mu_B$ , AM05  $2.15 \mu_B$ , LDA  $1.97 \mu_B$

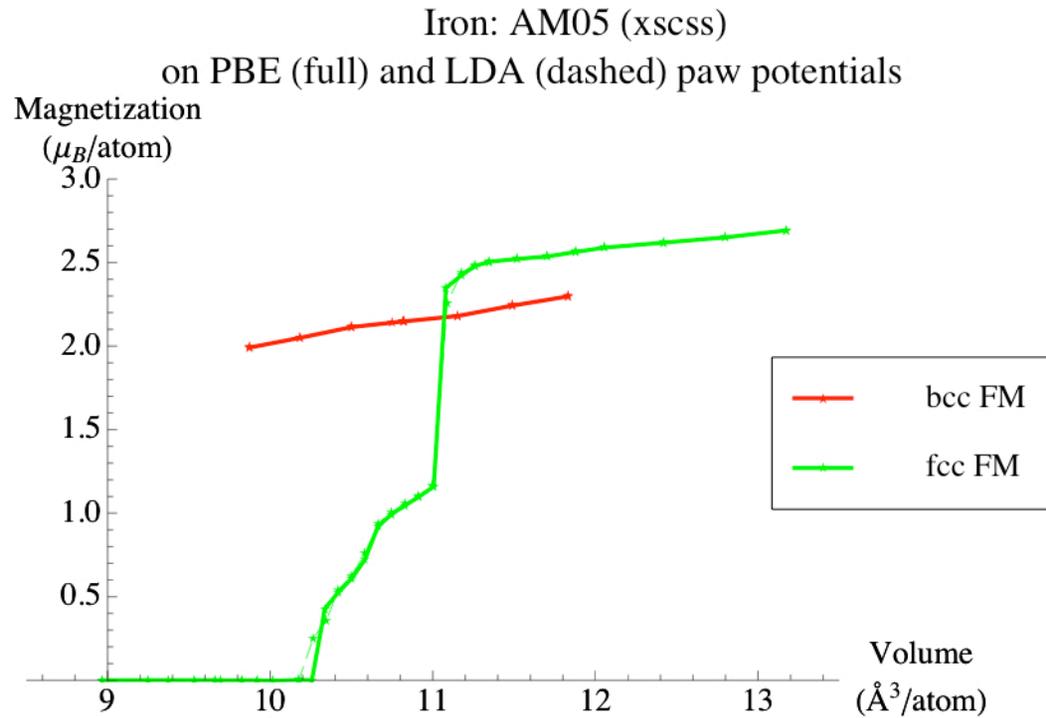


# Spin AM05: Fe, Energy vs volume





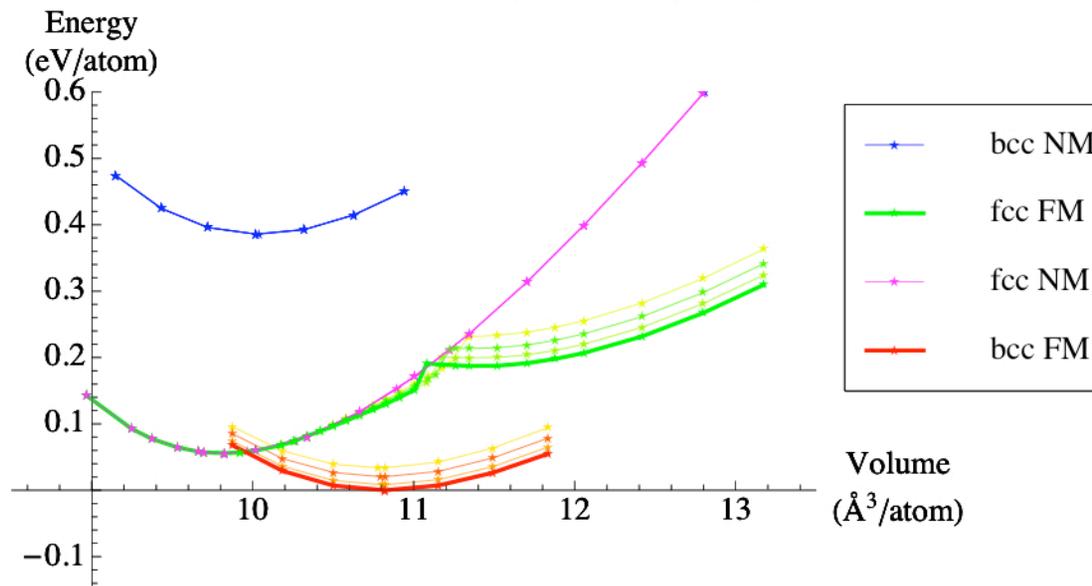
# Spin AM05: Fe, Magnetization vs volume





# Spin AM05: Fe, Energy vs volume

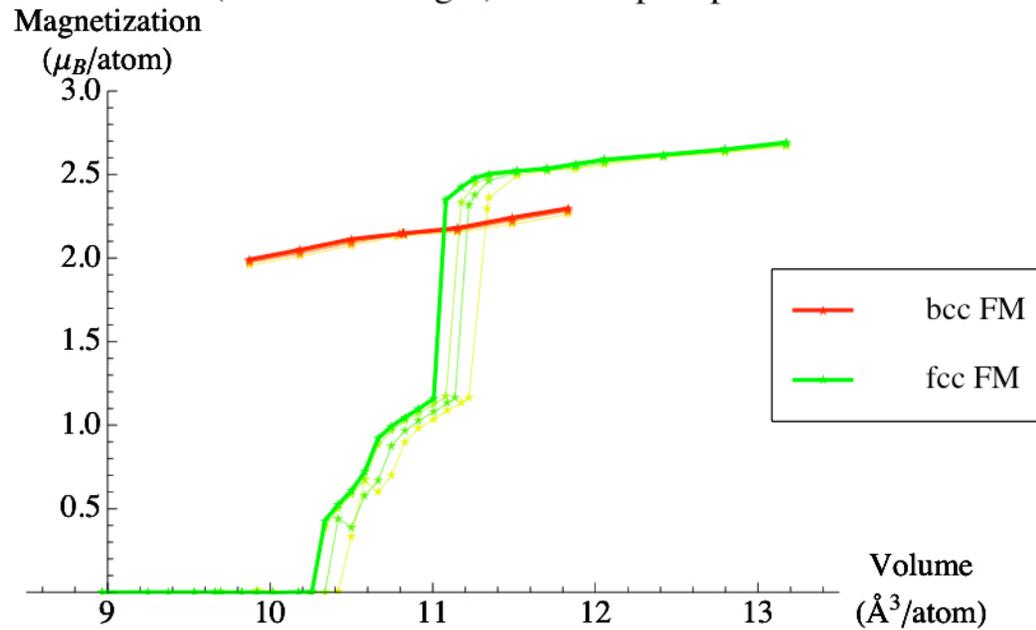
Iron: Comparison between AM05 (xscss) and xsctt, xscst, xtctt,  
(from bottom to top) on PBE paw potentials





# Spin AM05: Fe, Magnetization vs volume

Iron: Comparison between AM05 (xscss) and xscft, xscst, xtctt, (from left to right) on PBE paw potentials





# Functionals and Si interstitials

We usually use at least both LDA and PBE, to get estimate of functional errors. If large discrepancies we need to understand **WHY**.

Calculated formation energies in eV for the Si interstitials			
	Tetrahedral	Hexagonal	<110>-split
LDA	3.562	3.424	3.371
PBE	3.908	3.617	3.546
PW91	4.091	3.768	3.696
QMC1	5.40	4.82	4.96
QMC2	5.05	5.13	4.94

QMC1: Leung et al, PRL 83, 2351 (1999), 54 atom cell.

QMC2: Batista et al, PRB 74, 121102 (2006), 16 atom cell.

Our DFT calculations are state of the art, 216 atom cells. PW91 results compares within 0.03 eV with 256 atom cell results of Centoni et al, PRB 72, 195206 (2005).

Note: PBE and PW91 do not give the same, 0.1-0.2 eV differences. “Nonequivalence of the generalized gradient approximations PBE and PW91”, Ann E. Mattsson, Rickard Armiento, Peter A. Schultz, and Thomas R. Mattsson, PRB 73, 195123 (2006).



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**Unusually large differences between functionals.**

**Discrepancy with QMC results.**

**We need to understand **WHY**.**



## Si Interstitial Formation Energies (eV)

---

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	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**



# Monovacancy formation energies

---

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:

$$\text{AM05} > \text{LDA} > \text{PBE} > \text{PW91}$$



## Surface Intrinsic Errors

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

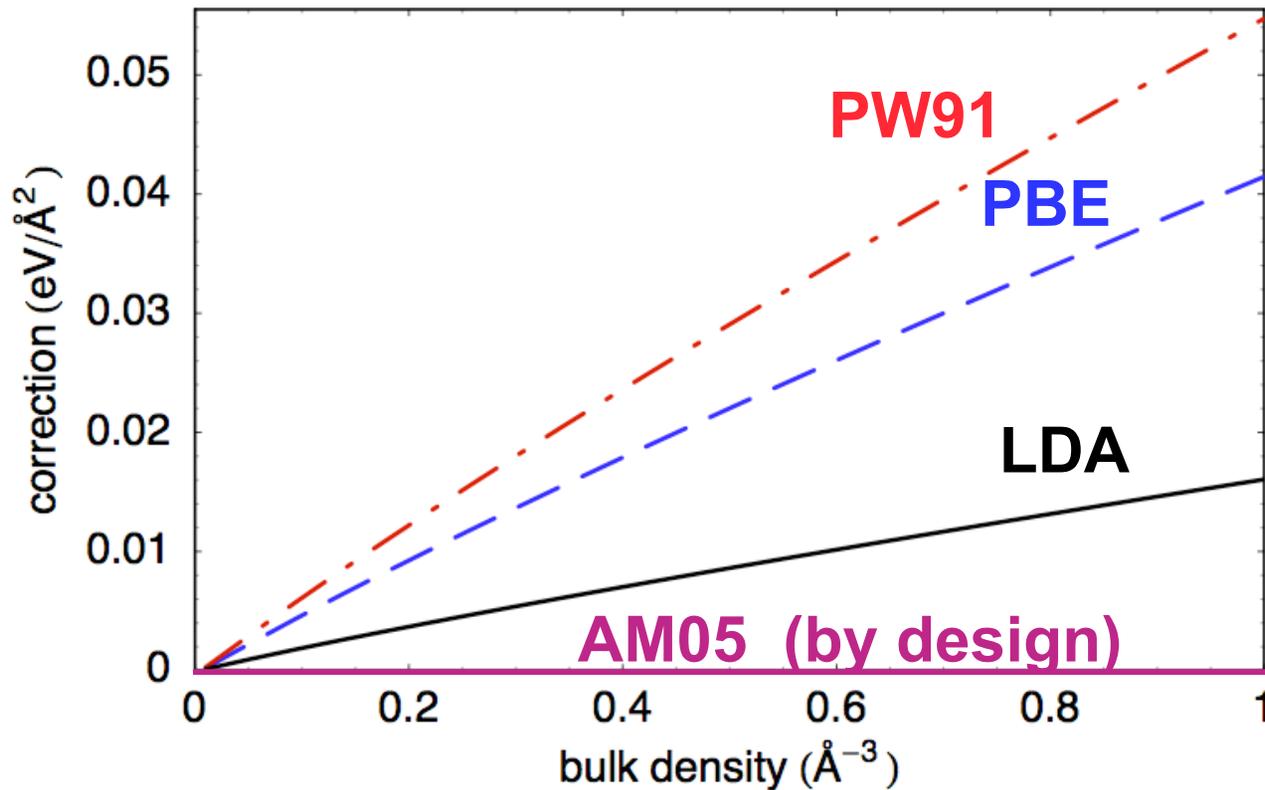
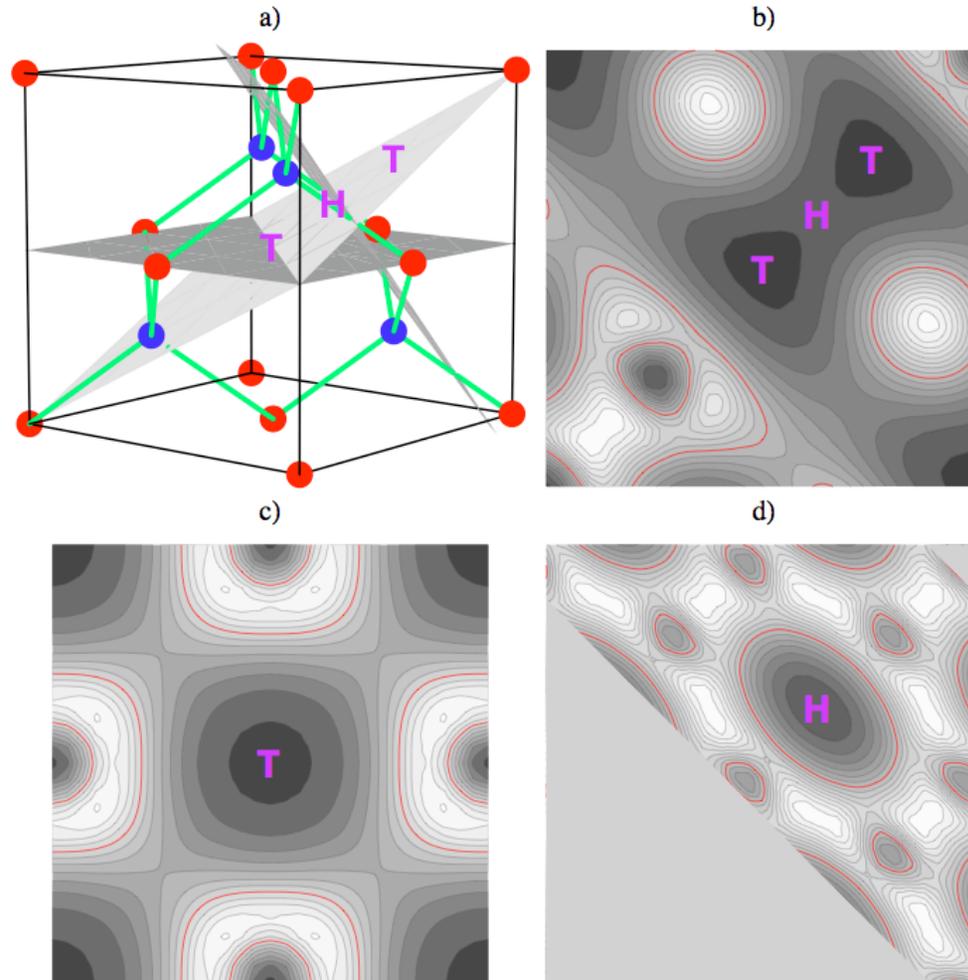


Fig. 2 in Mattsson et al, PRB 73,195123 (2006).



# Semiconductor bulk density: Holes

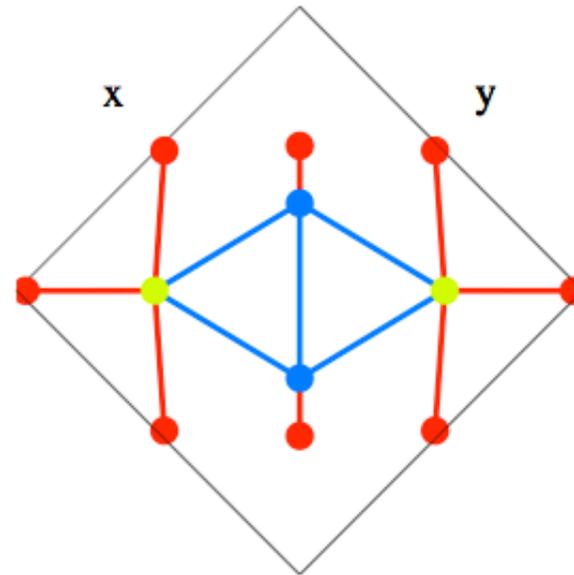
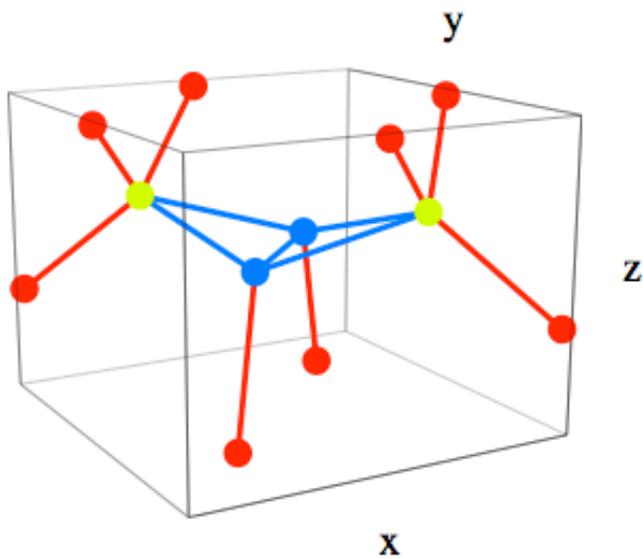
Ann E. Mattsson





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

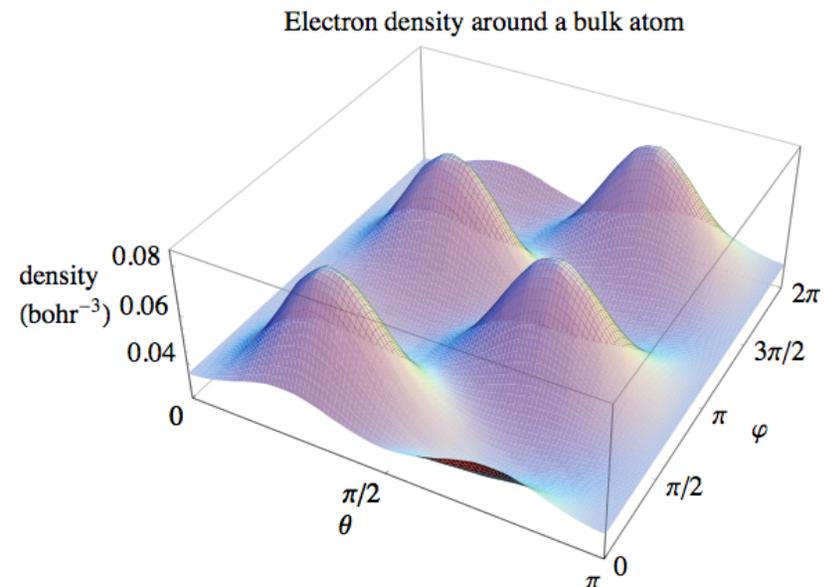
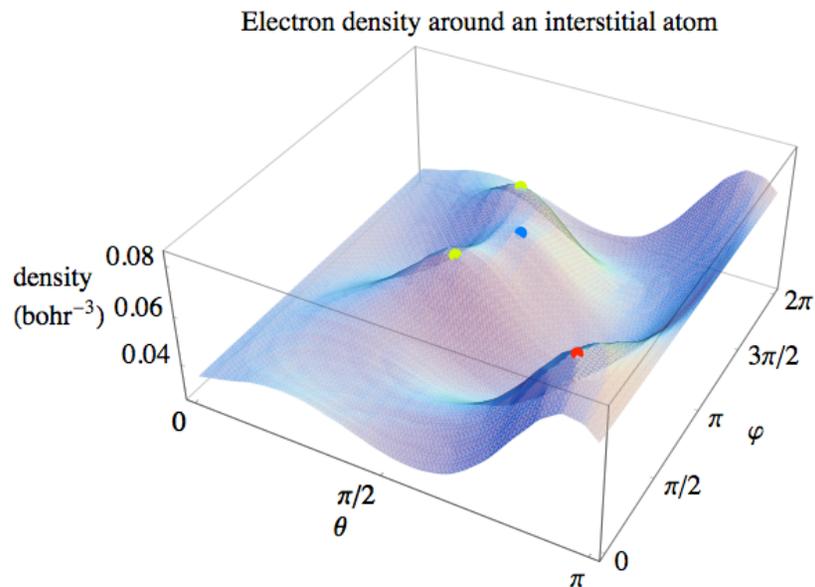
Ann E. Mattsson





# Bonds of 4-coordinated **interstitial** atom

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

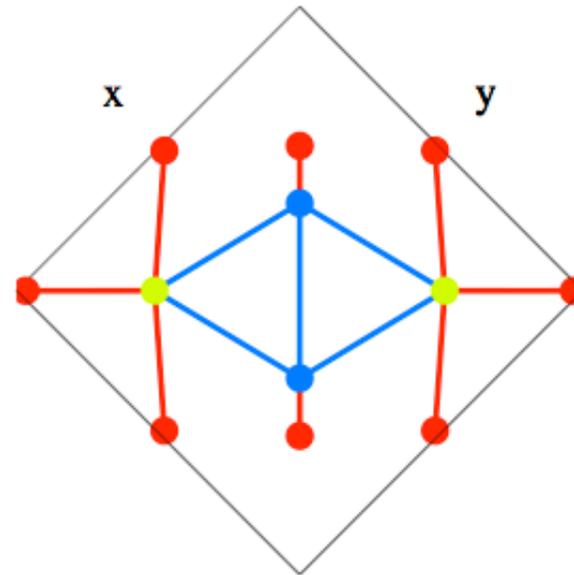
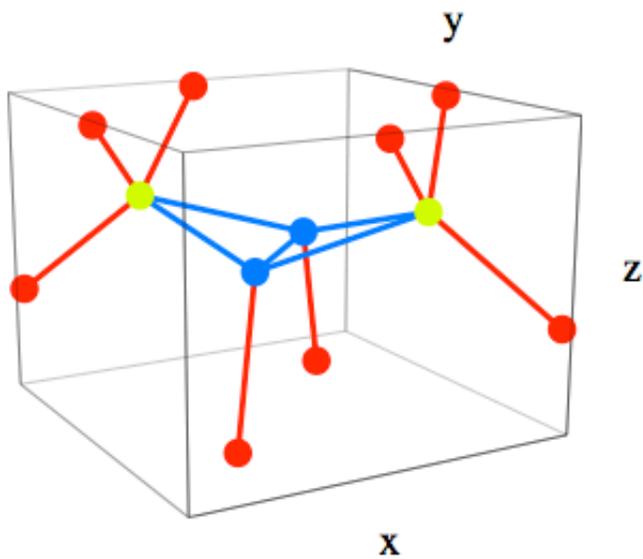


Very different from 4-coordinated **bulk** atom



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

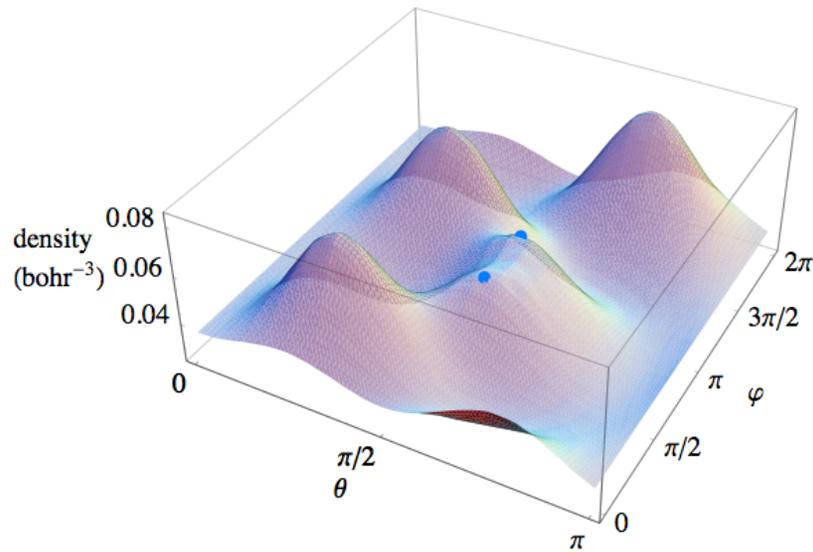
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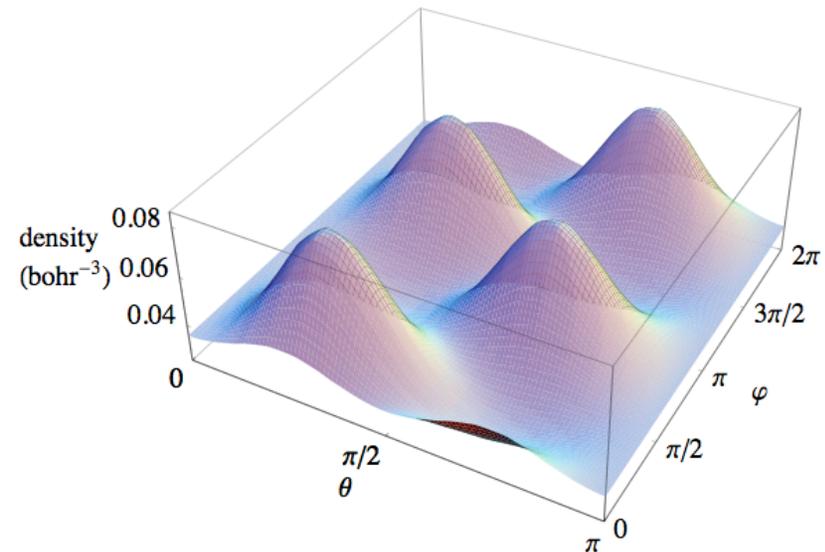


# Bonds of 5-coordinated atom

Electron density around a 5-coordinated atom



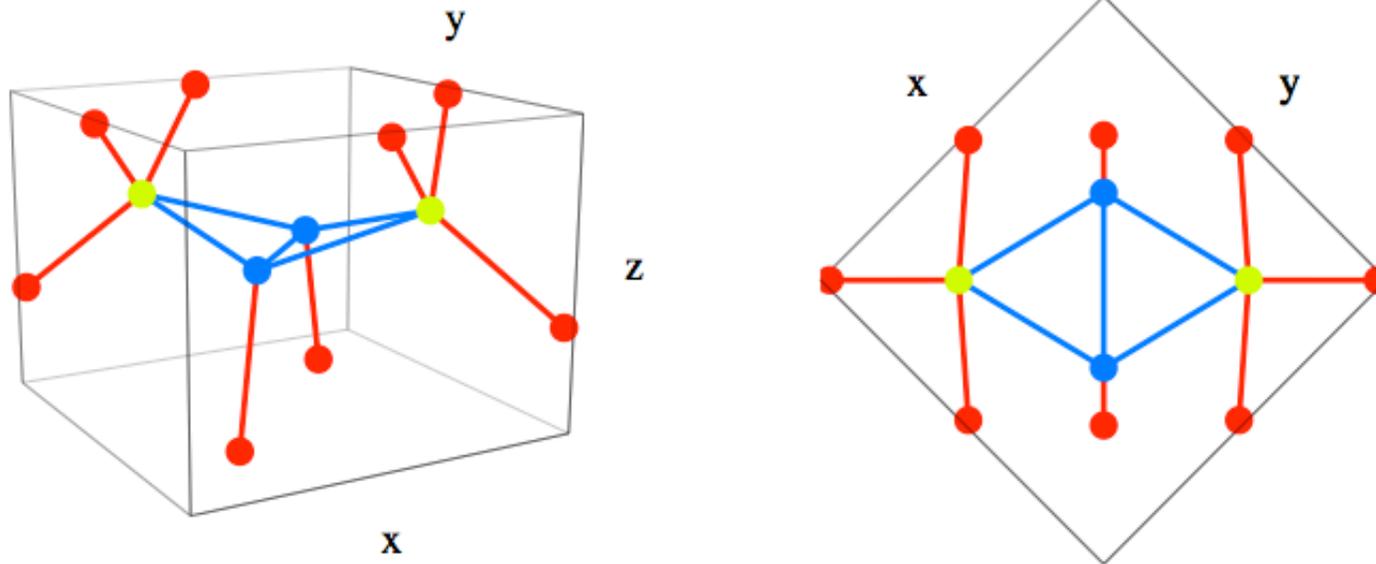
Electron density around a bulk atom



Three **bulk-like bonds**.



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



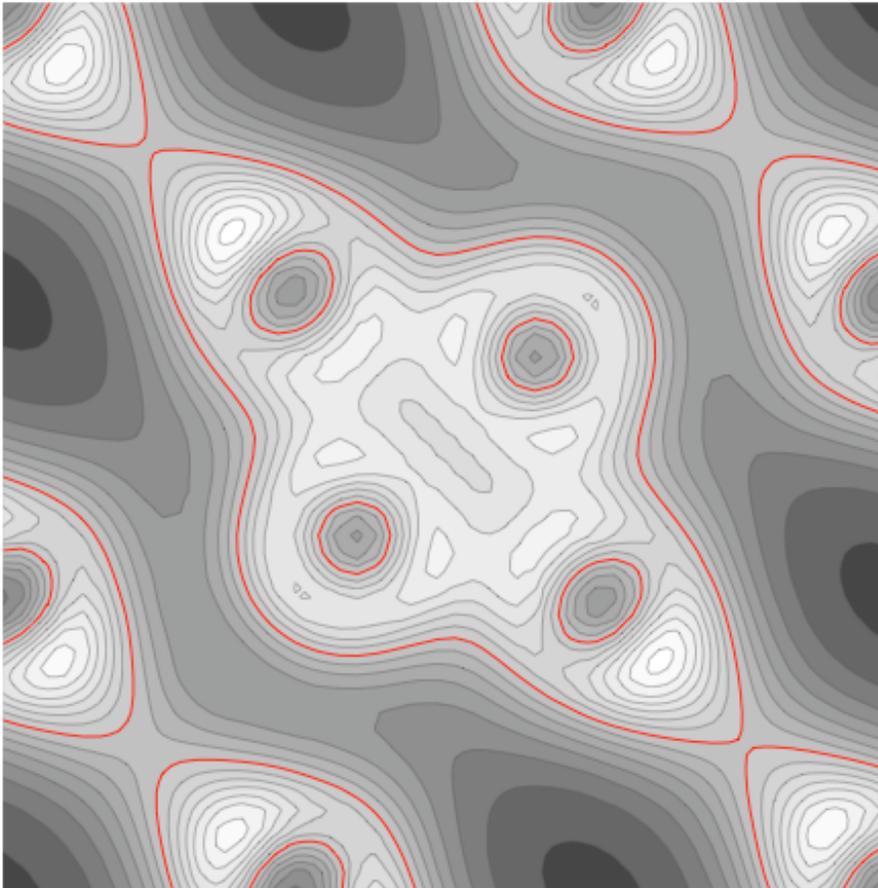
**Red bonds** are bulk-like. **Blue bonds** are weakened bonds with smeared out density, which take away surface area compared to bulk and surface effects will be present in the formation energy.



## **‘Homogeneous’ density around interstitial**

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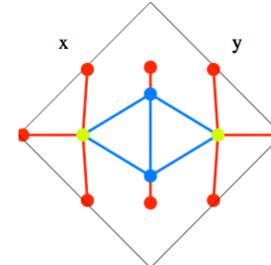
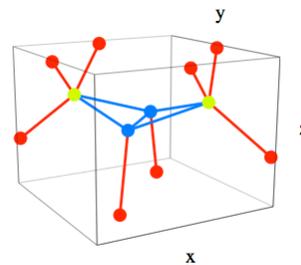
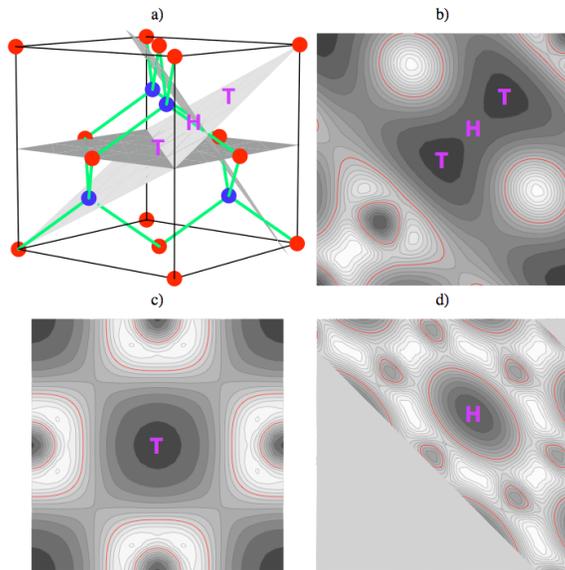


**Density contours in a plane through the 110-split interstitial, between blue and yellow atoms.**

**Clearly the density is more homogeneous than in the bulk.**



# Semiconductor bulk density: Holes



**<110>-split**

**Red bonds** are bulk-like. **Blue bonds** are weakened bonds with smeared out density, which take away surface area compared to bulk and surface effects will be present in the formation energy.

$$E_{\text{corr}} = E^{\text{DFA}} - A \Delta\sigma_{\text{xc}}^{\text{DFA}} \quad (\text{DFA: Density Functional Approximation})$$

$\Delta\sigma_{\text{xc}}^{\text{DFA}}$ : surface error correction. From PRB 73, 195123 (2006):



# Surface Intrinsic Errors

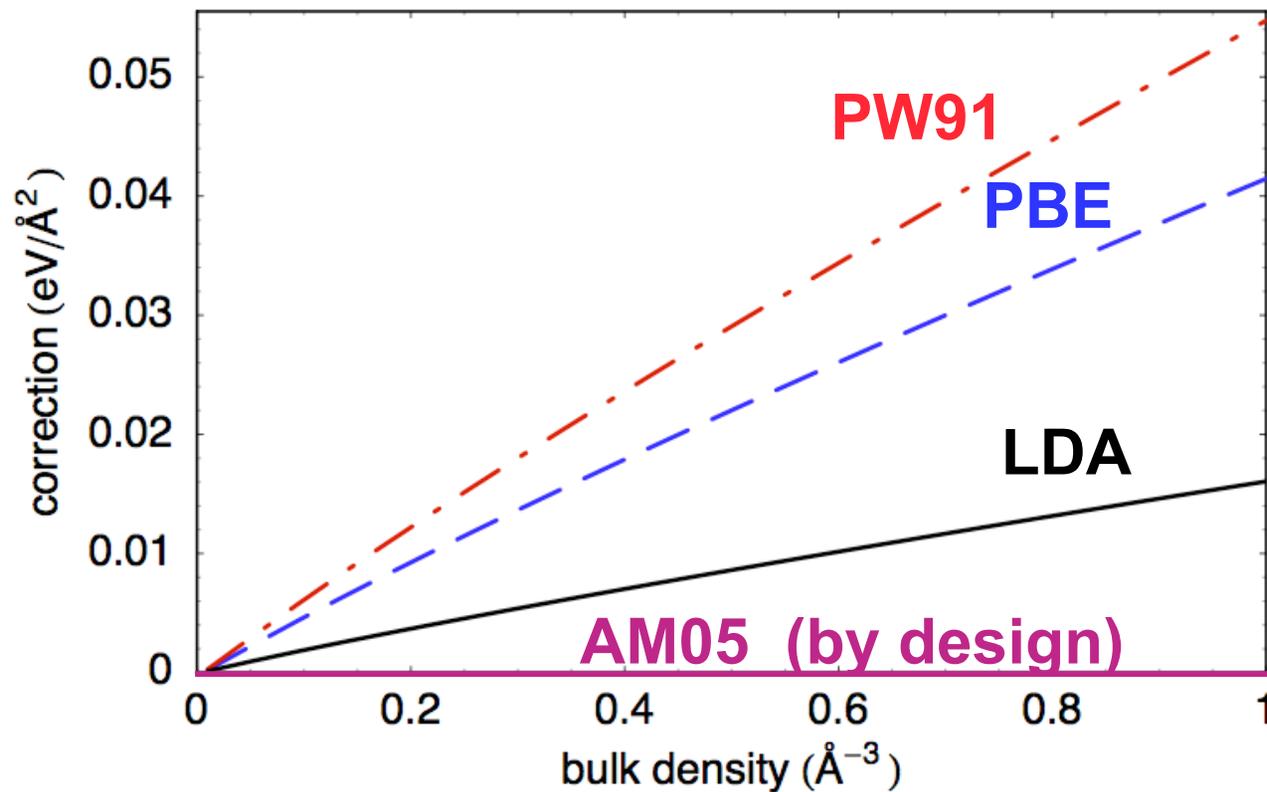
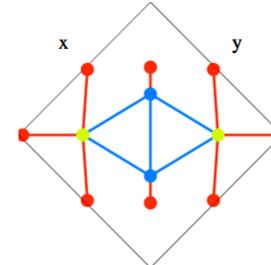
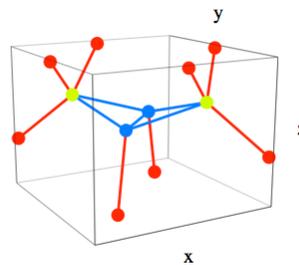
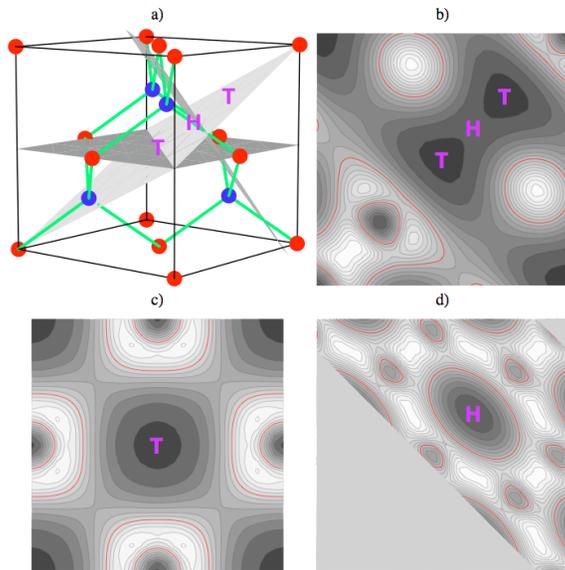


Fig. 2 in Mattsson et al, PRB 73,195123 (2006).



# Semiconductor bulk density: Holes



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$$\Delta\sigma_{\text{xc}}^{\text{LDA}} = 0.29 \Delta\sigma_{\text{xc}}^{\text{PW91}}, \Delta\sigma_{\text{xc}}^{\text{PBE}} = 0.76 \Delta\sigma_{\text{xc}}^{\text{PW91}}$$

Extract  $E_{\text{corr}}$  and  $(A\Delta\sigma_{\text{xc}}^{\text{PW91}})$  from least square fit.



# Correction for surface errors

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Calculated and surface corrected formation energies in eV for the Si interstitials						
	Tetrahedral		Hexagonal		<110>-split	
	Calc	Corr	Calc	Corr	Calc	Corr
LDA	3.56		3.42		3.37	
PBE	3.91		3.62		3.55	
PW91	4.09		3.77		3.70	
$E_{\text{corr}}$		3.35		3.28		3.23



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$E_{\text{corr}}$		3.35		3.28		3.23

$E_{\text{corr}}$  obtained from fitted value of  $A\Delta\sigma_{\text{xc}}^{\text{PW91}}$



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QMC1	5.40		4.82		4.96	

We have answered one **why**: Why different functionals give different results. **Taking surface effects into account all functionals give the same results.**

But the **WHY** all corrected DFT results disagree with QMC, remains.



## Si interstitials: Implications

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**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

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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 uniformly good performance for lattice constants and bulk modulus and perform as well as PBE for molecular chemical reactions.
- 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.
  - Spin?



# Thanks!

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Ann E. Mattsson

## For your attention.

Reprints available at:

[www.cs.sandia.gov/~aematts/publicationlist.html](http://www.cs.sandia.gov/~aematts/publicationlist.html)

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

**Questions? Comments?**



**End**

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Ann E. Mattsson