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Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

Solids 2.

M. Foulkes
Imperial College London

Applications of Diffusion Quantum Monte Carlo to Solids

ICTP Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

Matthew Foulkes

Condensed Matter Theory Group
Imperial College London

Wednesday 23rd January 2008

Outline

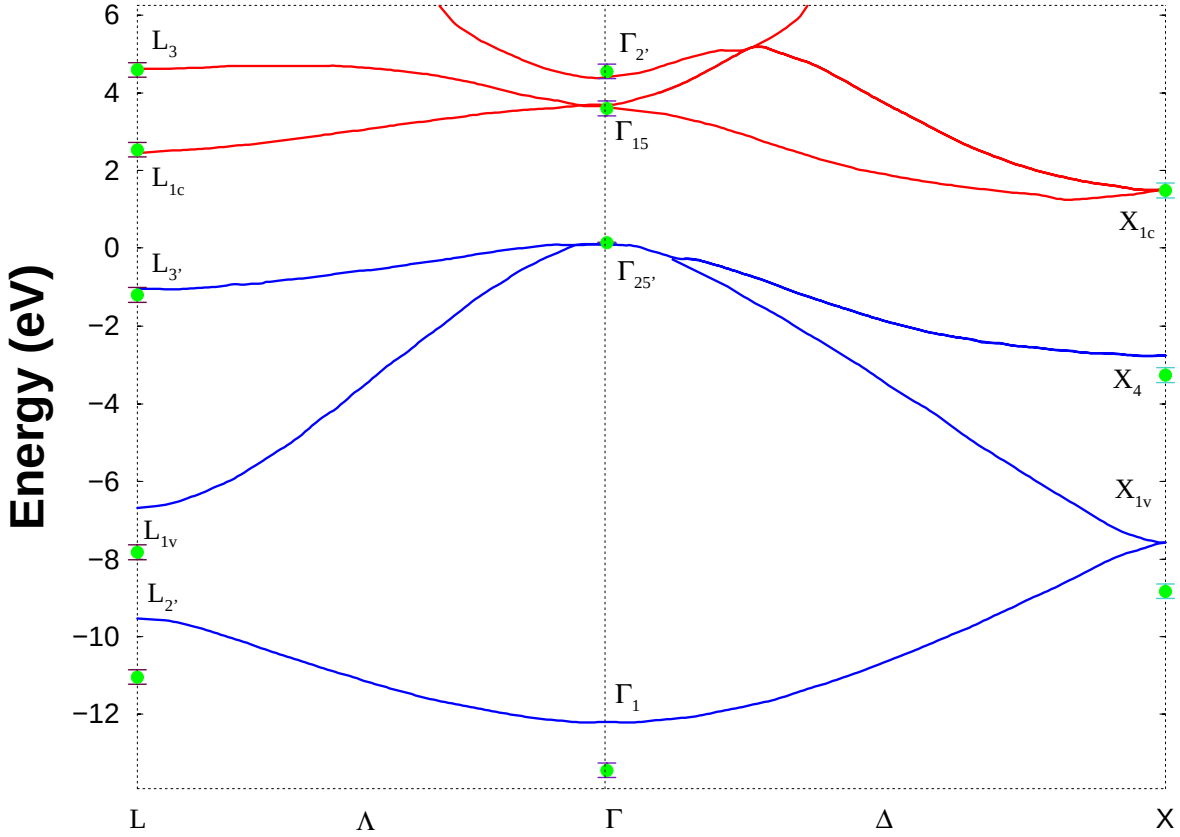
Outline

Cohesive Energies

Method	Si	Ge	C	BN	Al
Experiment	4.62	3.85	7.37	12.9	3.43
DFT	5.28	4.59	8.61	15.07	4.21
VMC	4.48	3.80	7.36	12.85	3.23
DMC	4.63	3.85	7.46		3.47

in eV per atom
statistical errors typically ± 0.04 eV/atom

Band Structure of Si



Outline

Finding out about Exchange and Correlation

DFT is a big deal!

- How accurate is it?
- How can we tell?
- Can we make it more accurate?

Describing Many-Electron Systems

Density

$$n(r)\,dr = \text{expected number of electrons in } dr$$

$$\int n(r)\,dr = N$$

Conditional Density

$$n(r'|r)\,dr' = \text{expected number of electrons in } dr' \text{ given that there is an electron at } r$$

$$\int n(r'|r)\,dr' = N - 1$$

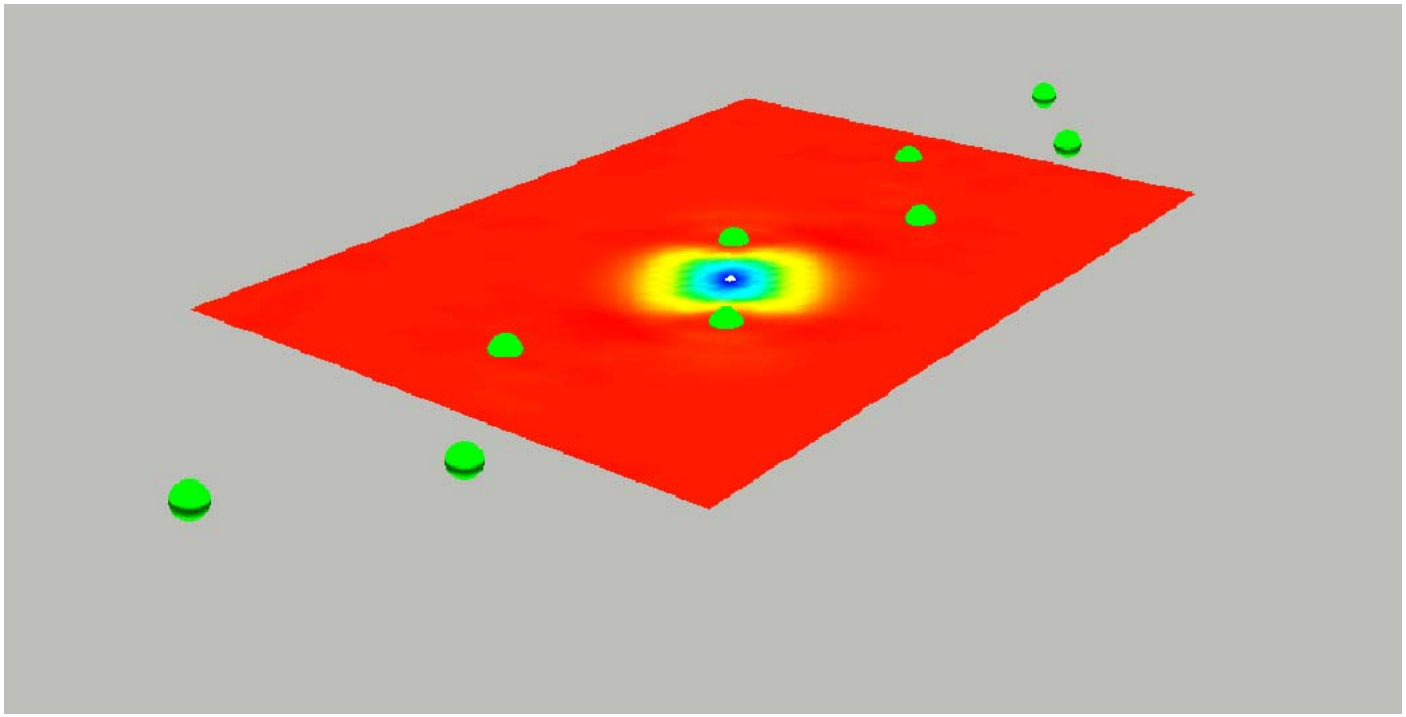
Exchange-Correlation Hole

$$
\begin{aligned}
n_{\mathrm{xc}}(r, r')\, dr' &= \text{change in expected number of electrons in } dr' \text{ caused by the presence of an electron at } r \\
n(r'|r) &= n(r') + n_{\mathrm{xc}}(r, r') \\
\int n_{\mathrm{xc}}(r, r')\, dr' &= -1
\end{aligned}
$$

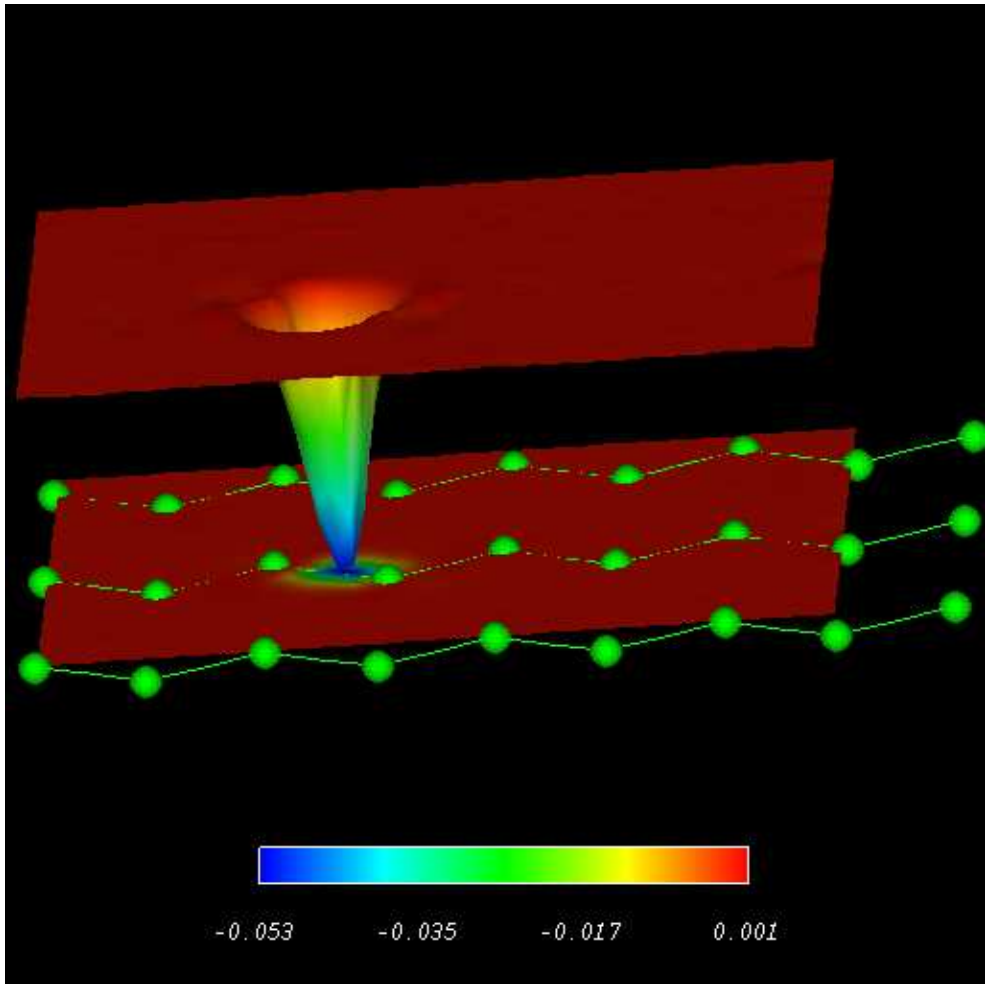
Electron-Electron Energy

$$
\begin{aligned}
E_{ee} &= \frac{1}{2} \iint \frac{n(r) n(r'|r)}{|r' - r|} dr dr' \\
&= \frac{1}{2} \iint \frac{n(r) n(r')}{|r - r'|} dr dr' + \frac{1}{2} \iint \frac{n(r) n_{\mathrm{xc}}(r, r')}{|r - r'|} dr dr' \\
&= E_{\mathrm{H}} + U_{\mathrm{xc}}
\end{aligned}
$$

The Exchange-Correlation Hole in Si



The Exchange-Correlation Hole in Si



The Energy Functional

- Define
$$E[n] \;=\; \mathrm{Min}_{\psi\to n(r)}\,\langle\psi|\;\hat{T}+\hat{V}_{\mathrm{ext}}+\hat{V}_{ee}\;|\psi\rangle\;.$$
  - Minimum E_0 of $E[n]$ attained when $n=n_0$ and $\psi=\psi_0$.
- $E \;=\; T+\int v_{\mathrm{ext}}\,n+E_{\mathrm{H}}+U_{\mathrm{xc}}$.
- Define the exchange-correlation functional $E_{\mathrm{xc}}[n]$ via
$$E[n]=T_s[n]+\int v_{\mathrm{ext}}n+E_{\mathrm{H}}[n]+E_{\mathrm{xc}}[n]\;,$$
where $T_s[n]$ is the KE of a *non-interacting* system with electron density $n(r)$.
- All terms in $E[n]$ are easy except for $E_{\mathrm{xc}}[n]$.

The Adiabatic Connection Formula

$$E_{\rm xc}[n] = \frac{1}{2}\iint \frac{n(r)\bar{n}_{\rm xc}(r,r')}{|r-r'|}\,dr\,dr'$$

where

$$\begin{aligned}
\bar{n}_{\rm xc}(r,r') &= \int_{\lambda=0}^{1} n^{\lambda}_{\rm xc}(r,r')\,d\lambda \\
\hat{H}^{\lambda}\psi^{\lambda} &= \left(\hat{T}+\lambda\hat{V}_{\rm ee}+\hat{V}^{\lambda}\right)\psi^{\lambda} = E^{\lambda}\psi^{\lambda} \\
n^{\lambda}(r) &= n(r)
\end{aligned}$$

- At $\lambda = 0$, $n^{\lambda}_{\rm xc}$ is the density-functional exchange hole.
- At $\lambda = 1$, $n^{\lambda}_{\rm xc}$ is the full exchange-correlation hole.

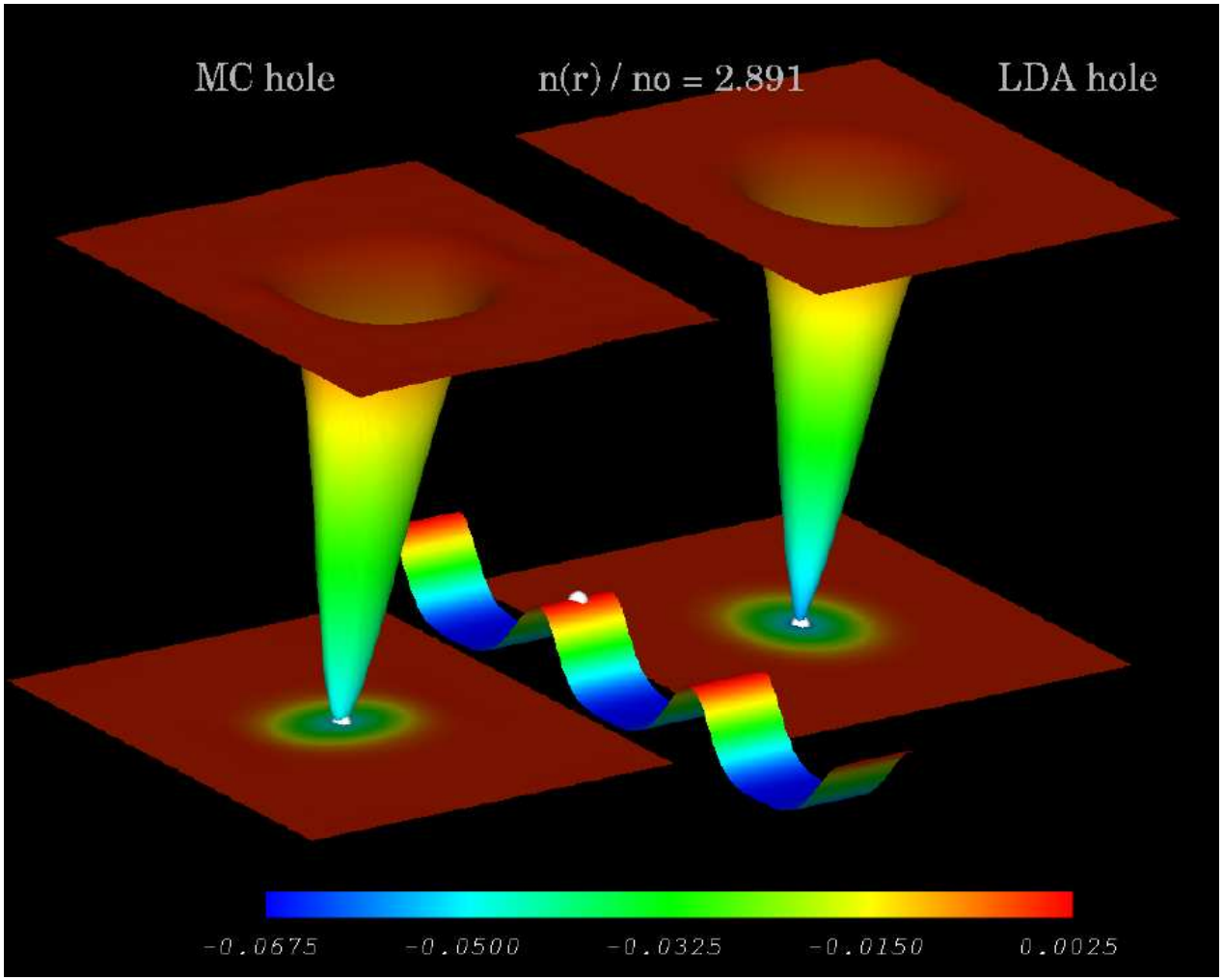
Exchange-Correlation Functionals

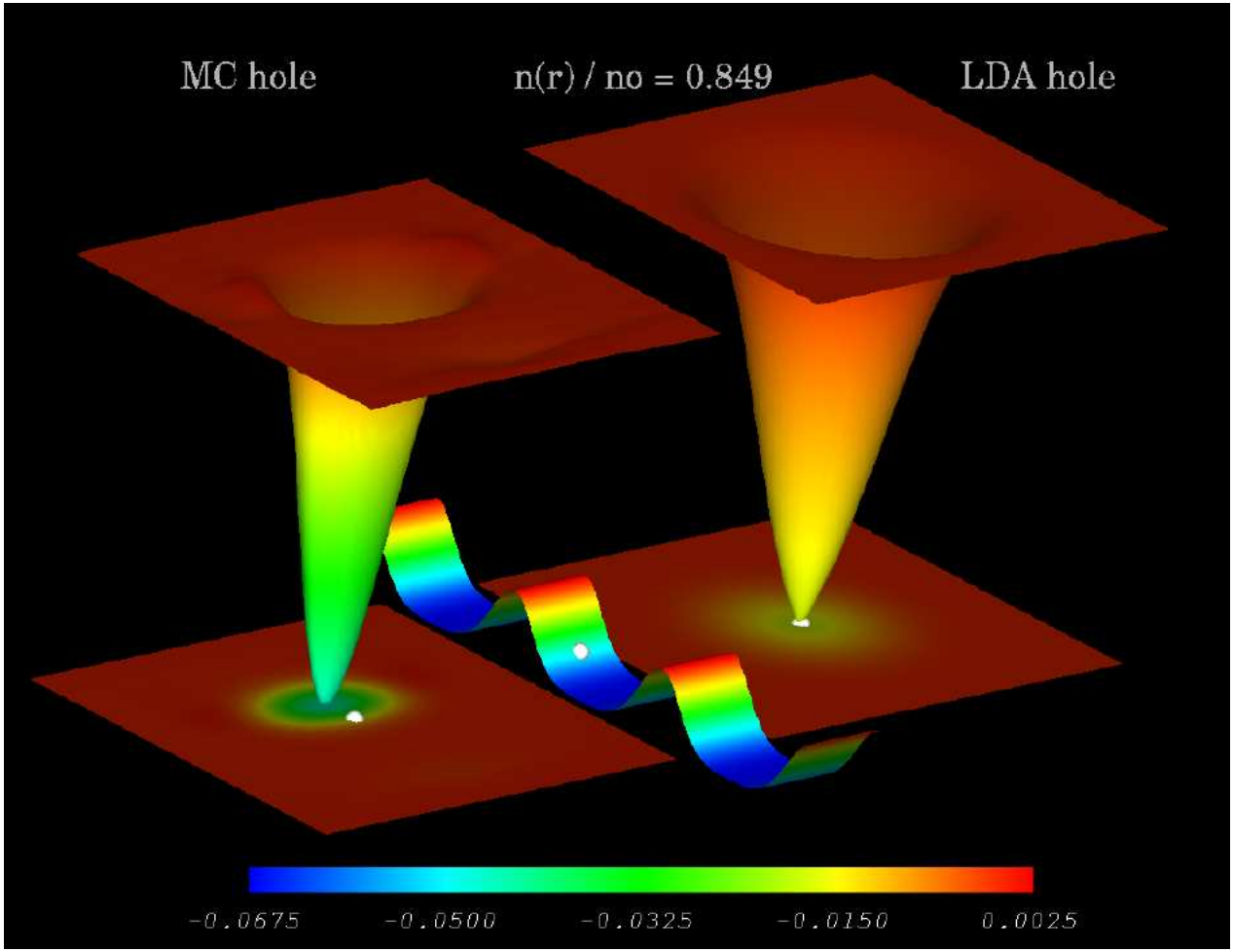
- In practice, $E_{\mathrm{xc}}[n]$ must be approximated.
- Standard approximations are LDA, GGA and MGGA:
  - $E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int e_{\mathrm{xc}}^{\mathrm{LDA}}(n(r))\,dr$
  - $E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int e_{\mathrm{xc}}^{\mathrm{GGA}}(n(r), |\nabla n(r)|)\,dr$
  - $E_{\mathrm{xc}}^{\mathrm{MGGA}}[n] = \int e_{\mathrm{xc}}^{\mathrm{MGGA}}(n(r), |\nabla n(r)|, \tau)\,dr$
- These simple approximations work surprisingly well, but seem unable to provide consistent *chemical accuracy*.
- Errors cannot be reduced systematically.

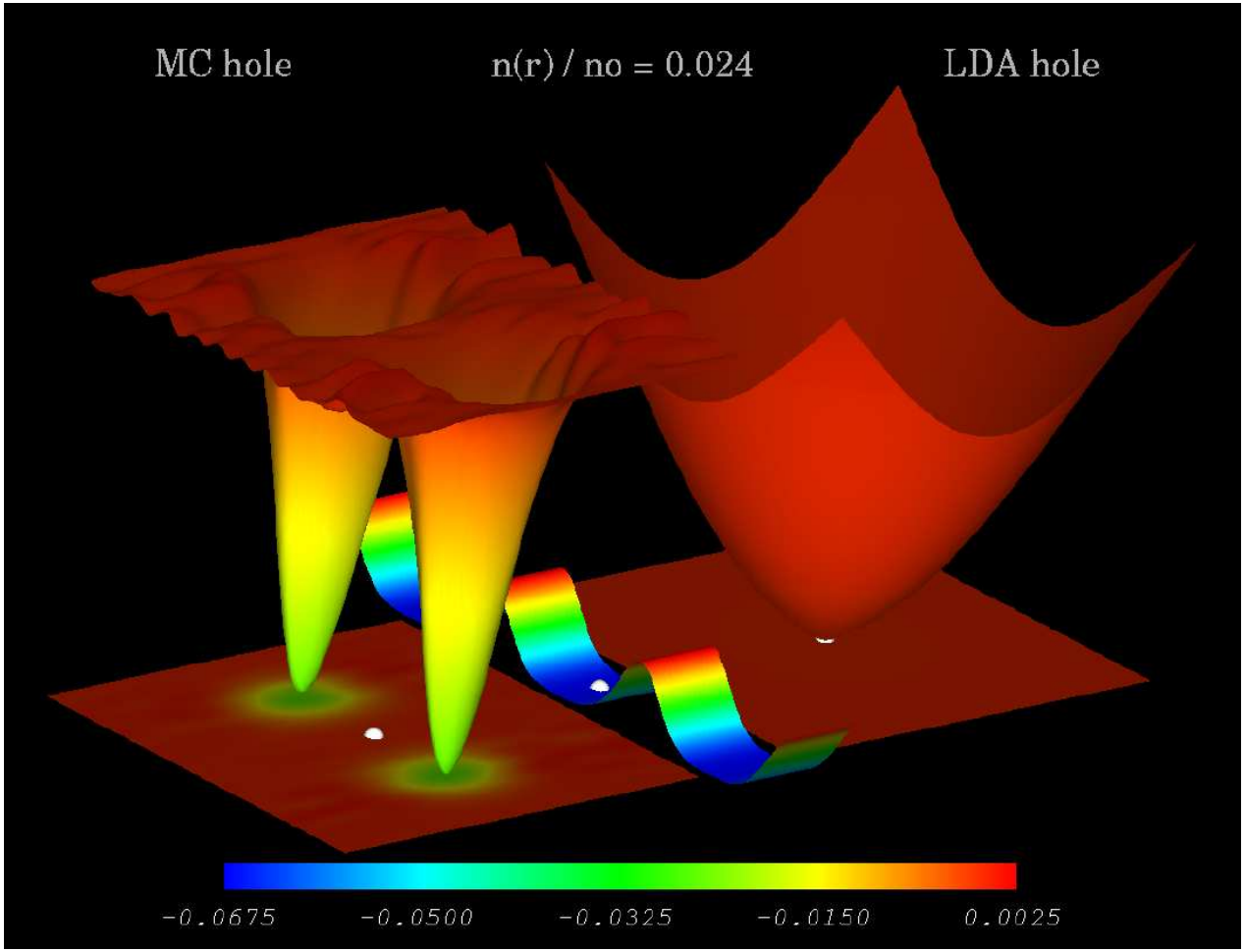
VMC Realisation of the Adiabatic Connection

$$E_{\mathrm{xc}} = \frac{1}{2}\iint \frac{n(r)\bar{n}_{\mathrm{xc}}(r,r')}{|r-r'|}\,dr'\,dr = \int e_{\mathrm{xc}}(r,[n])\,dr$$

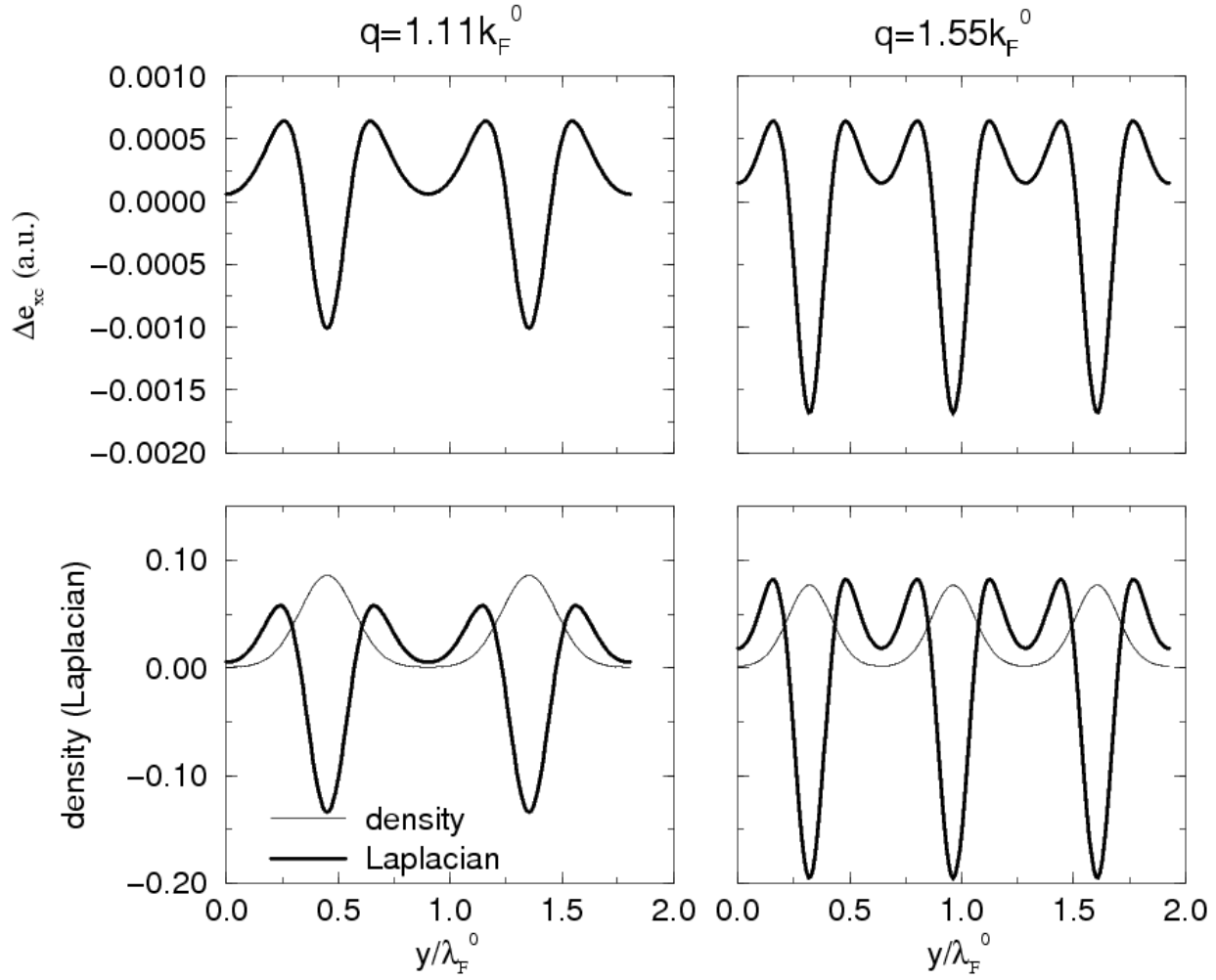
- Slater-Jastrow ansatz for many-body wavefunction.
- Integral over λ discretised.
- Variational parameters in ψ^{λ} and Fourier components of V^{λ} determined at every λ.
- Statistical errors small.
- Tried very hard to account for all the systematic errors (particularly finite-size errors).


MC hole
n(r) / no = 2.891
LDA hole
-0.0675
-0.0500
-0.0325
-0.0150
0.0025

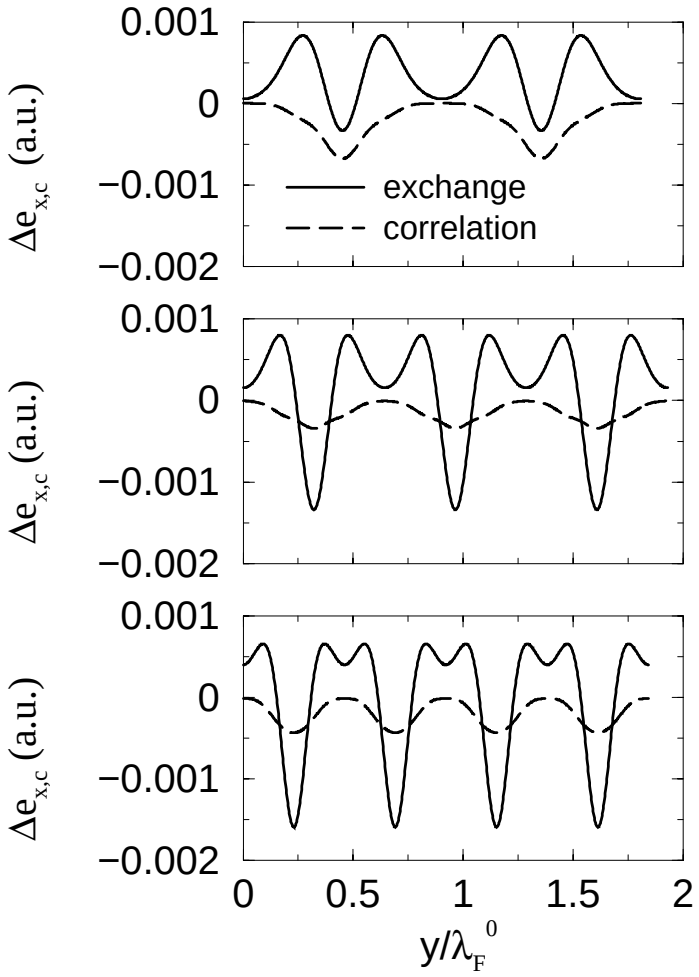

MC hole
n(r) / no = 0.849
LDA hole
-0.0675
-0.0500
-0.0325
-0.0150
0.0025


MC hole
n(r) / no = 0.024
LDA hole
-0.0675
-0.0500
-0.0325
-0.0150
0.0025

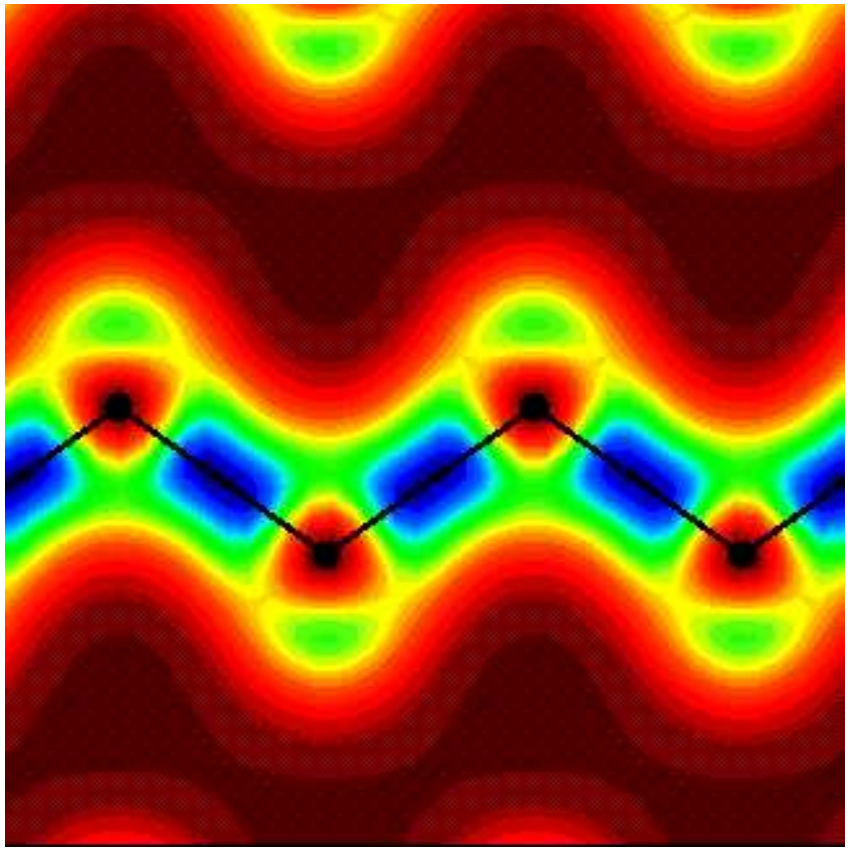
Errors in the LDA



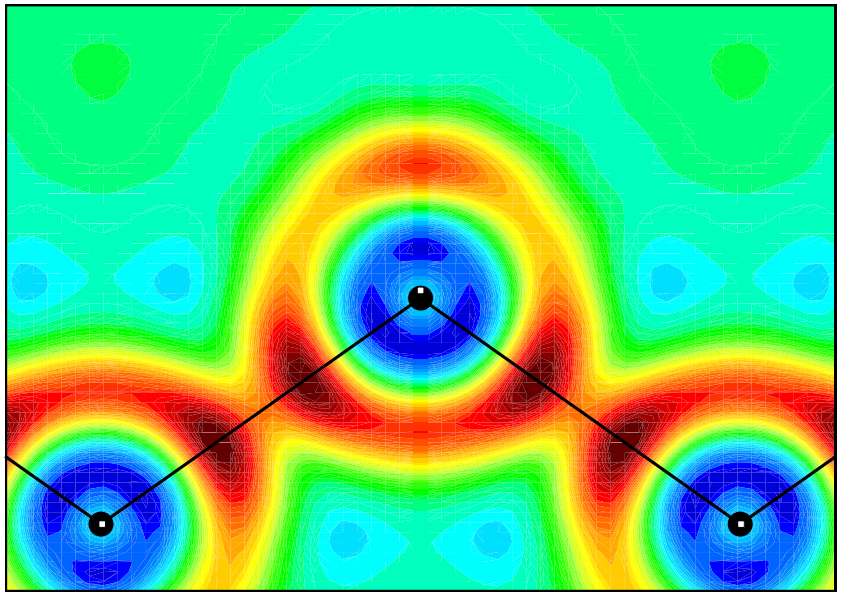
Exchange and Correlation Contributions to LDA Error



Exchange-Correlation Energy Density in Silicon



Error in LDA Exchange-Correlation Energy Density in Silicon



Exchange Functionals

The general form of the exact exchange functional is fixed by a scaling argument:

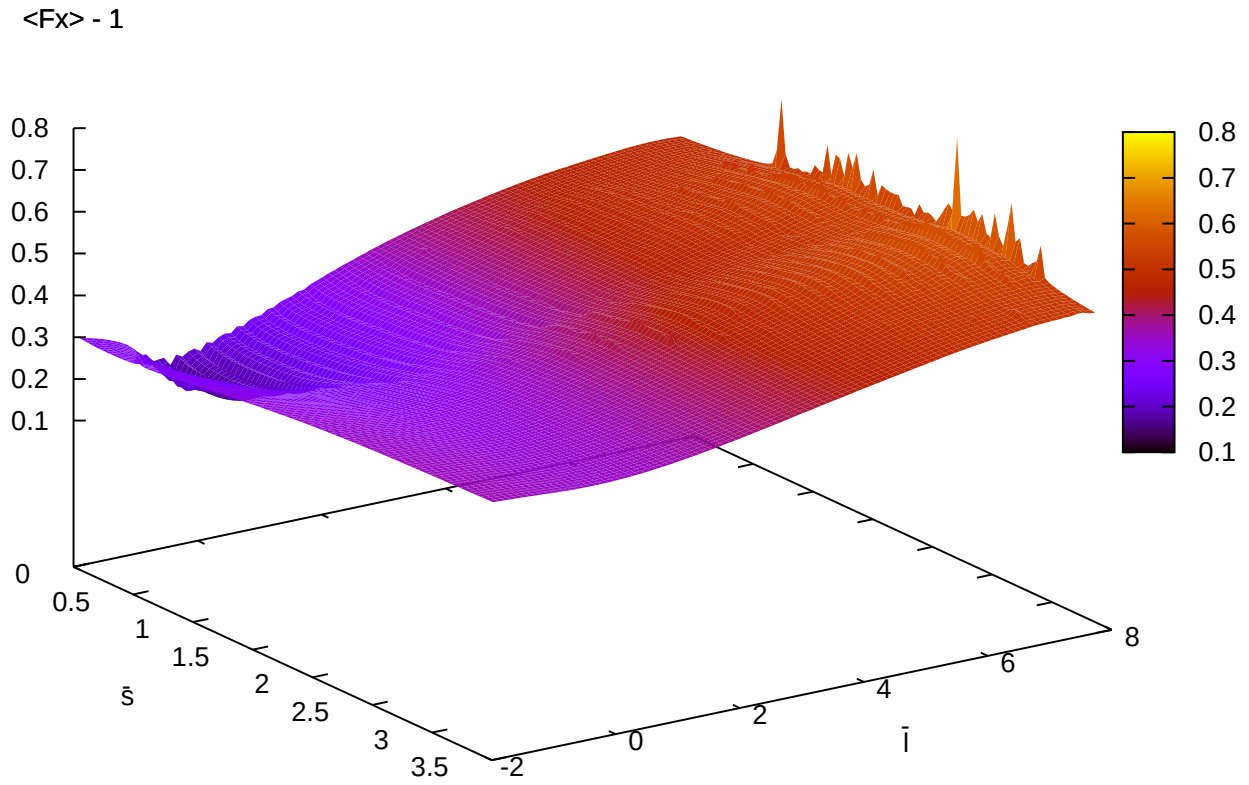
$$E_{\mathrm{x}}^{\mathrm{GGA}} = \int e_{\mathrm{x}}^{\mathrm{GGA}}(r)\,dr = -A_{\mathrm{x}} \int n^{4/3}(r) F_{\mathrm{x}}(s(r), l(r), \ldots)\,dr$$

where

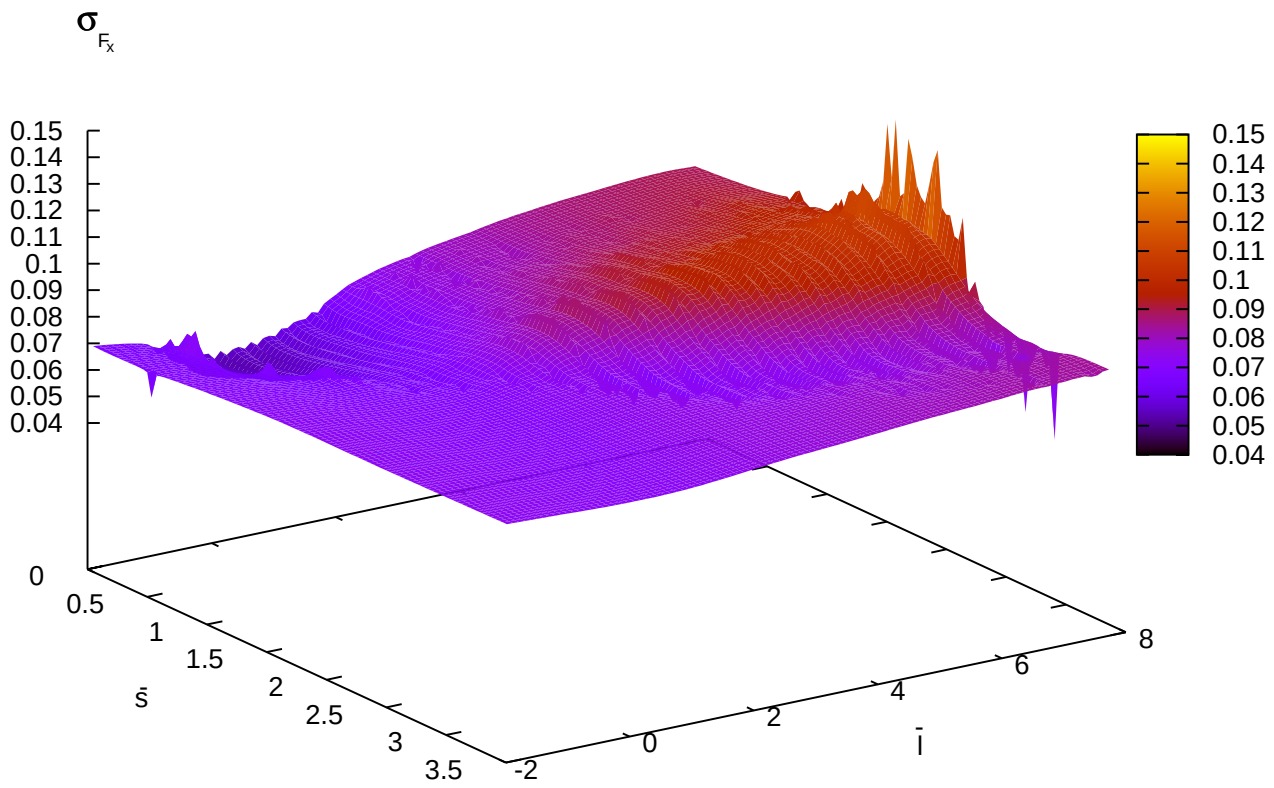
$$s(r) = \frac{|\nabla n(r)|}{2k_F(r)n(r)}$$

$$l(r) = \frac{\nabla^2 n(r)}{4k_F^2(r)n(r)}$$

$F_x - 1$ as a function of s and l

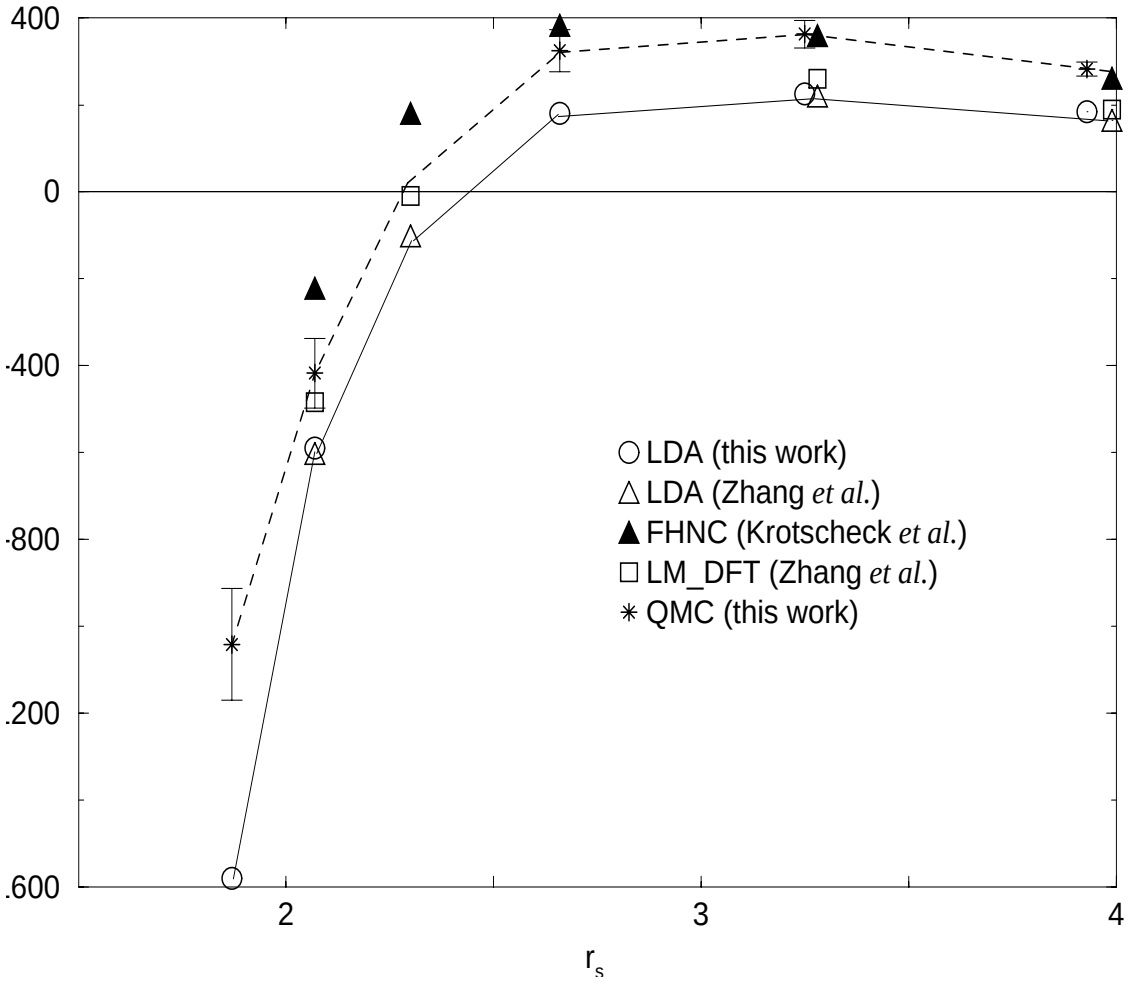


σ_{F_x} as a function of s and l



Outline

The Controversy



- Surface energies extrapolated from DMC simulations of jellium spheres,

$$E = N\epsilon_{\mathrm{bulk}} + 4\pi r^2\sigma + 2\pi r\gamma \ ,$$

  agree with DFT.
- RPA- and *GW*-based calculations agree with DFT.

For the surface energy of jellium at alkali-metal densities, the local-density approximation (LDA) and more advanced density-functional methods disagree strongly with the wave-function-based Fermi hypernetted-chain and diffusion Monte Carlo methods.

Z. Yan, J.P. Perdew, S. Kurth, C. Fiolhais and L. Almeida
Phys. Rev. B 61, 2595 (2000)

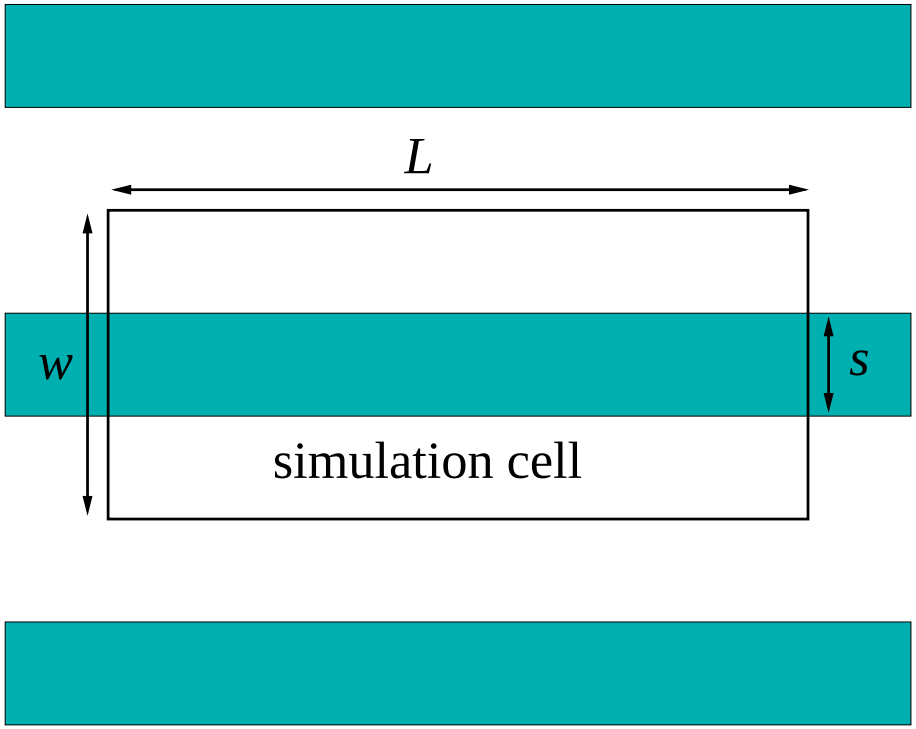
Are the slab DMC results wrong?

Surface Energies at (in erg cm^{-2}) when $r_s = 2.07$

Illinois (Li):	σ_{DMC}	$=$	-465 ± 50
Illinois (Acioli):	σ_{DMC}	$=$	-420 ± 80
Perdew *et al.*:	σ_{LDA}	$=$	-610
	σ_{GGA}	$=$	-690
	σ_{MGGA}	$=$	-567
	$\sigma_{\mathrm{LDA/RPA}}$	$=$	-553
	$\sigma_{\mathrm{GGA/RPA}}$	$=$	-587

$$
\begin{aligned}
1\ \mathrm{erg\,cm^{-2}} &= 6.25 \times 10^{-5}\ \mathrm{eV\,\AA^{-2}} \\
&= 6.42 \times 10^{-4}\ \mathrm{mHa\,Bohr^{-2}}
\end{aligned}
$$

Accuracy



$$N\epsilon_{\mathrm{slab}} = N\epsilon_{\mathrm{bulk}} + 2L^2\sigma$$
$$\sigma = \frac{N}{2L^2}(\epsilon_{\mathrm{slab}} - \epsilon_{\mathrm{bulk}}) = \frac{N}{2L^2}\Delta\epsilon_{\mathrm{slab}}$$

Assuming $r_s = 2.07$ and $s = 20$, require

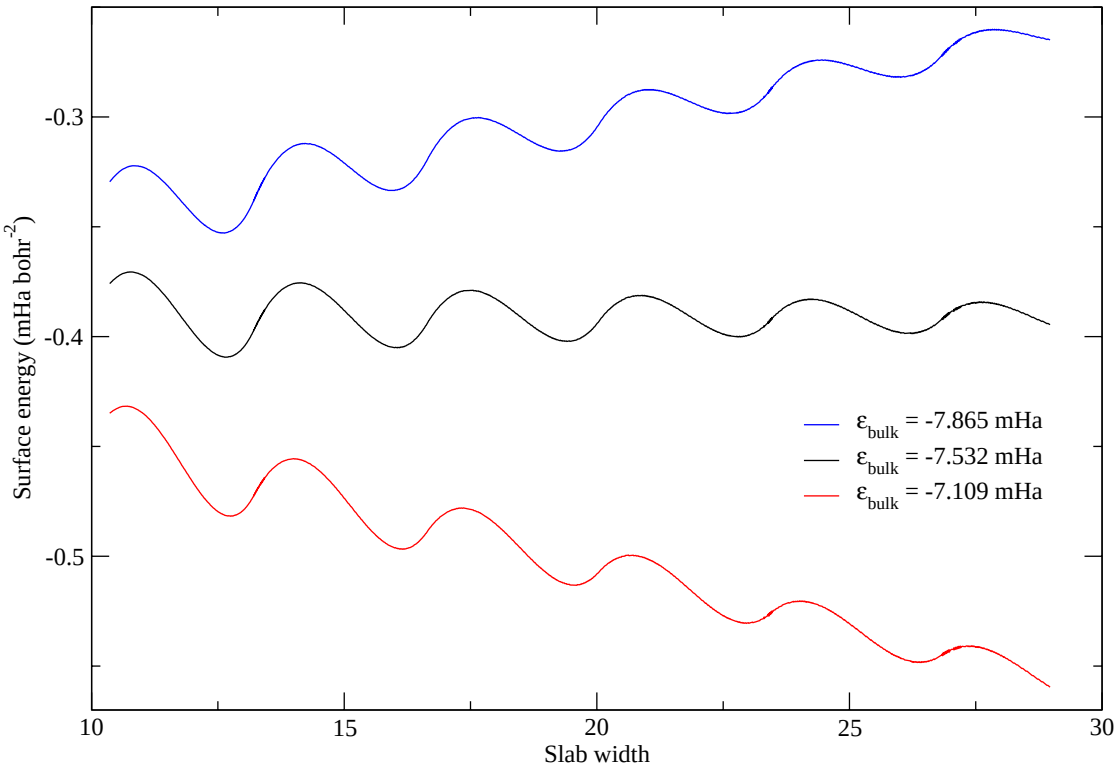
$$\delta(\Delta\epsilon_{\mathrm{slab}}) \sim 0.1 \text{ mHa} \quad (3 \text{ meV})$$

for resolution $\Delta\sigma \approx 50 \text{ erg cm}^{-2}$.

Possible Explanations

- DMC is right and other methods fail.
- Finite-size errors.
- Fixed-node errors.

Comparing Apples and Oranges



Effects of using different LDAs for the bulk calculation

Comparing Apples and Apples

Since

$$N = \frac{\text{Volume}}{\text{Volume per electron}} = \frac{L^2 s}{\frac{4}{3}\pi r_s^3} ,$$

the definition of σ,

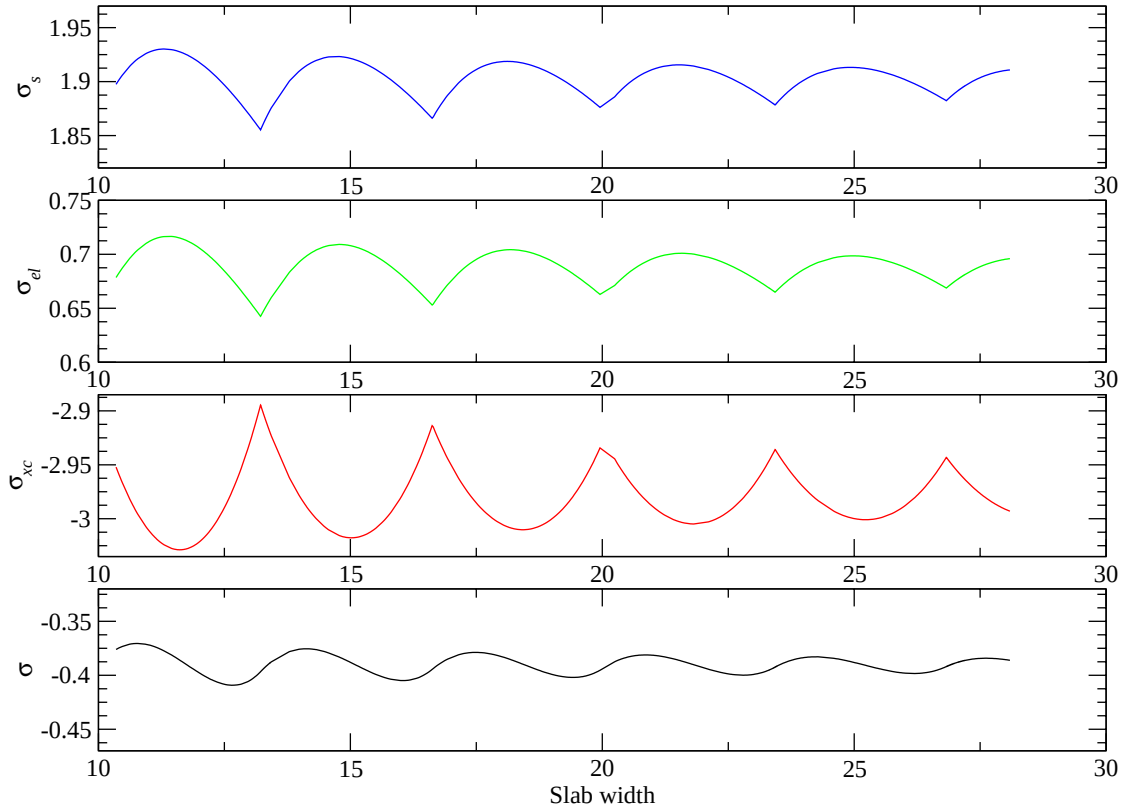
$$N\epsilon_{\text{slab}} = N\epsilon_{\text{bulk}} + 2\sigma L^2 ,$$

may be rewritten as

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + 2\left(\frac{4\pi r_s^3}{3s}\right)\sigma .$$

Can obtain σ from dependence of ϵ_{slab} on thickness s.

Slab-Width Oscillations



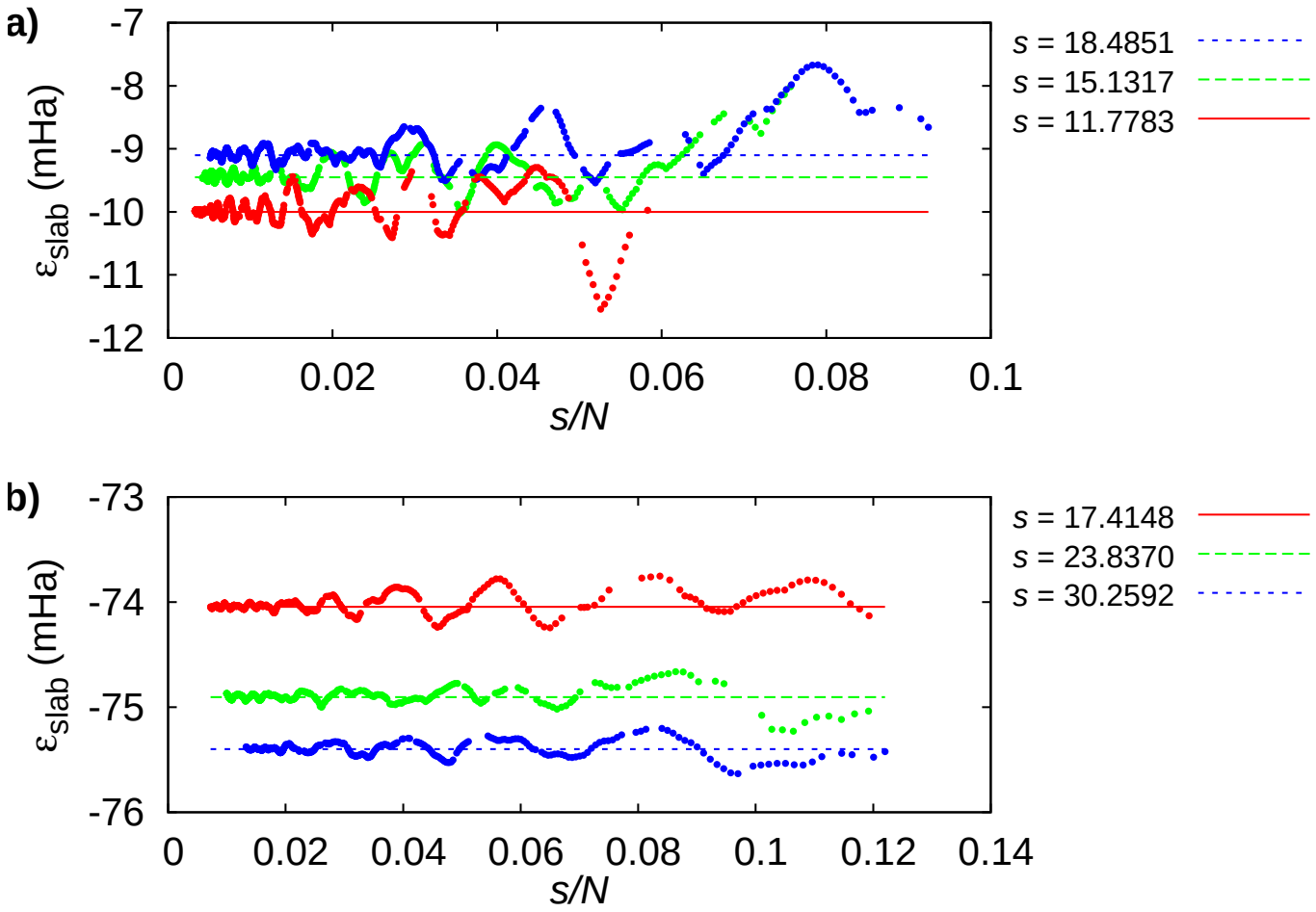
LDA surface energy as a function of slab thickness s

In-Plane Errors

- In DFT with a good in-plane k-point sampling,

$$\epsilon_{\text{slab}} = \epsilon_{\text{bulk}} + 2\left(\frac{4\pi r_s^3}{3s}\right)\sigma$$

  is a function of s only.
- In QMC, it also depends on the in-plane cell dimension L.

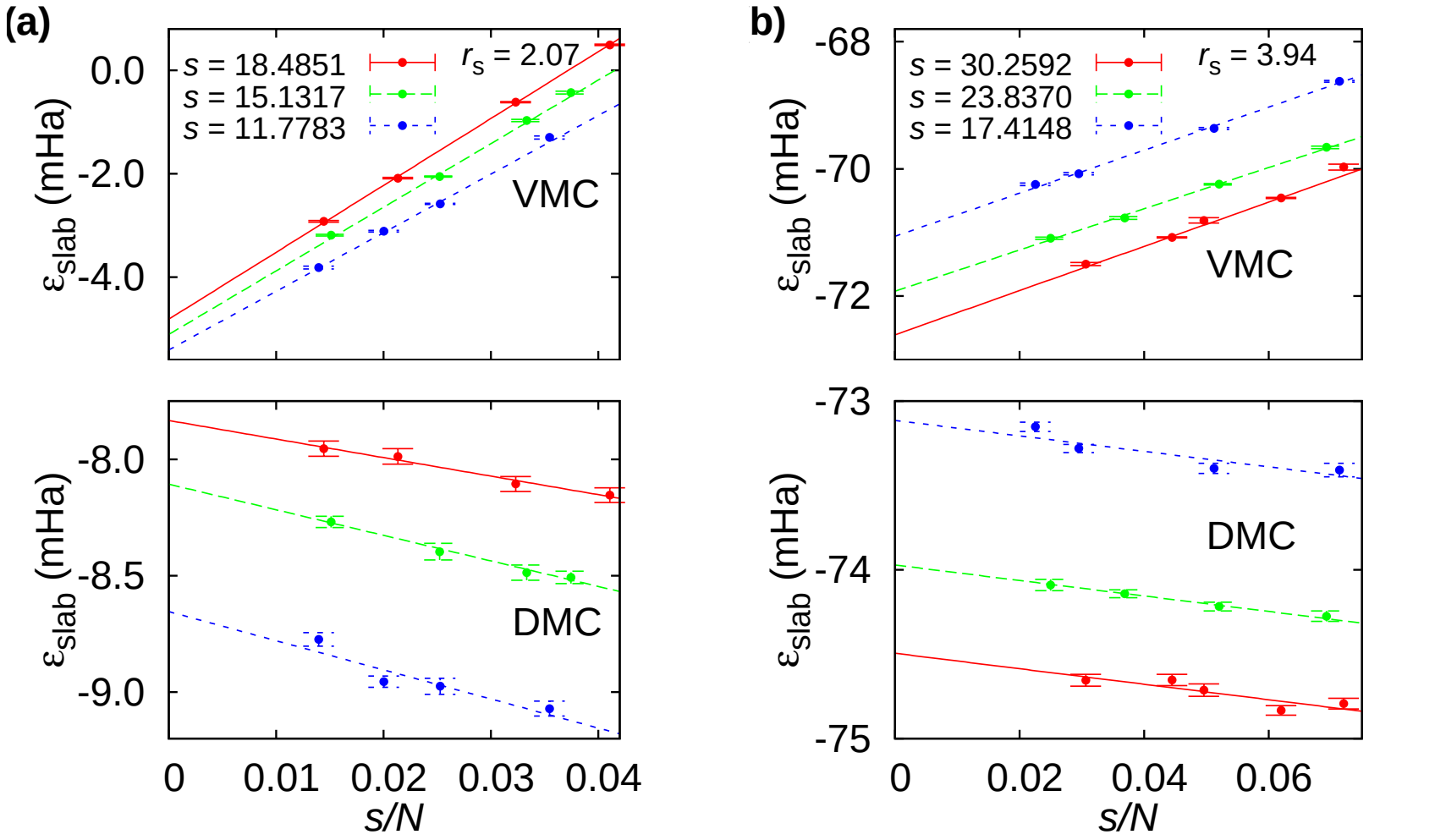


(s/N is proportional to $1/L^2$)

In-Plane Extrapolation

- Choose three consecutive values of s for which $\sigma_{\mathrm{LDA}}(s) = \sigma_{\mathrm{LDA}}(\infty)$.
- At each s, calculate DMC energy for a range of L values chosen such that LDA surface energy for the finite-L cell closely matches that for an infinite-L cell.

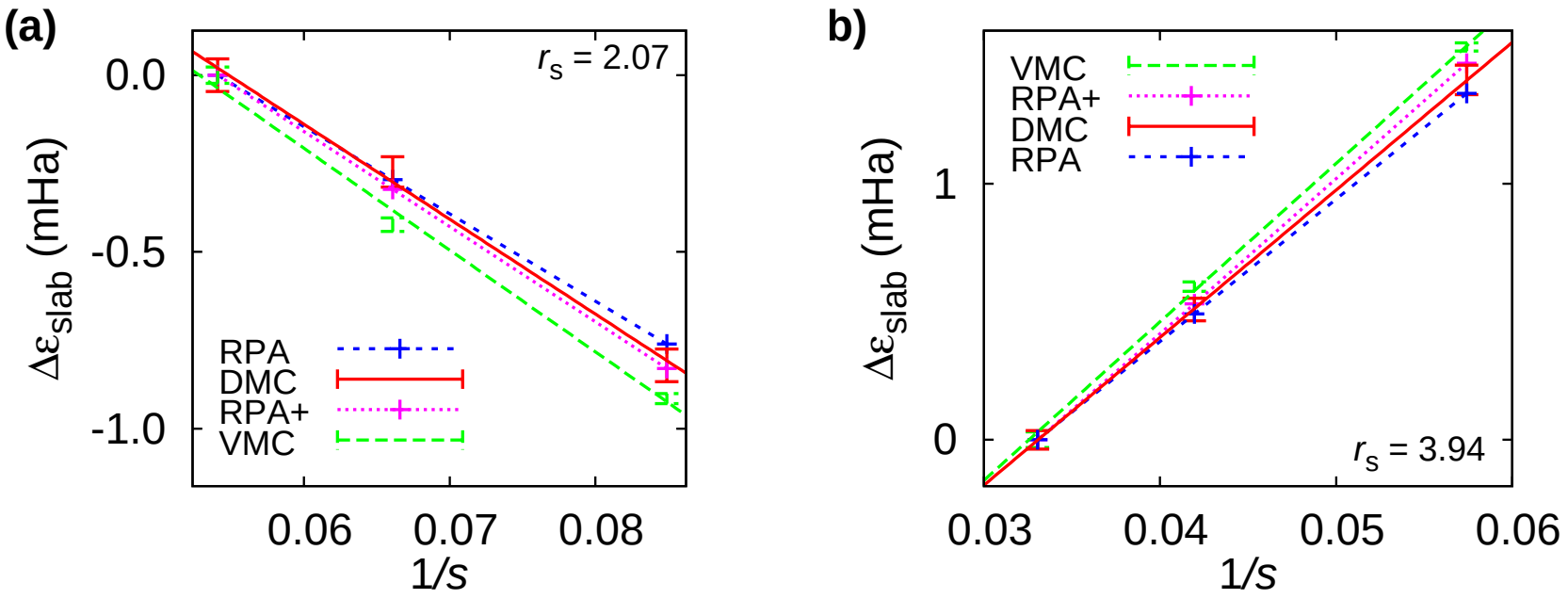
This procedure eliminates any “LDA" errors from our DMC energies



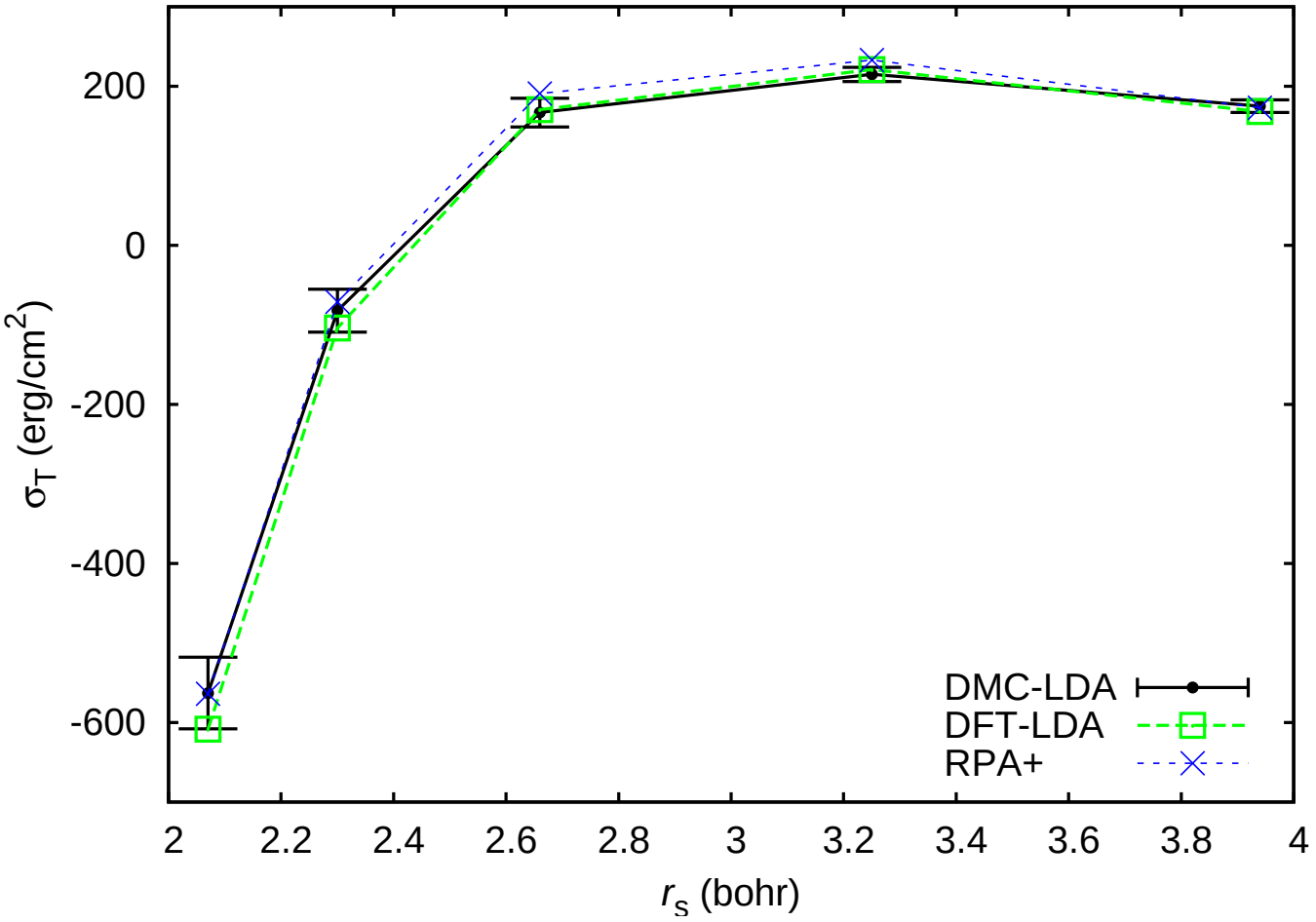
(s/N is proportional to $1/L^2$)

Dependence of ϵ_{slab} on $1/s$

For each s, extrapolate ϵ_{slab} energy to $L = \infty$. Then plot extrapolated values against $1/s$:



Surface Energy versus r_s



r_s	LDA	GGA	RPA	RPA+	DMC
2.07	−608.2	−690.6	−517	−564	-563 ± 45
2.30	−104.0	−164.1	−34	−71	-82 ± 27
2.66	170.6	133.0	216	191	179 ± 13
3.25	221.0	201.2	248	233	216 ± 8
3.94	168.4	158.1	182	173	175 ± 8

- DMC broadly consistent with LDA, mGGA, RPA+; inconsistent with GGA and RPA. DFT is *ridiculously* good.
- We get different (bad) results when we compare bulk and slab energies. Deduce that

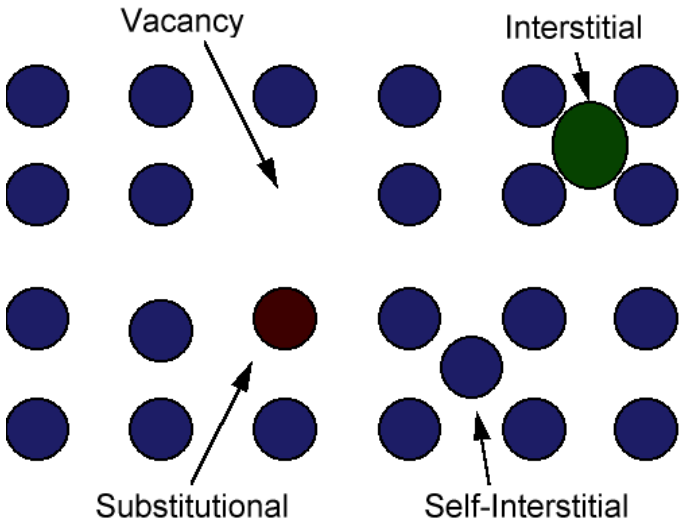
$$\text{(fixed-node error in slab)} - \text{(fixed-node error in bulk)} \sim 1\,\text{mHa}$$

  This difference does not decrease with s for the slab widths studied.
- Residual finite-size errors are about 0.3 mHa per electron.

Outline

Background

All crystals contain point defects “frozen” in during crystallization



Formation at constant P, $T \longrightarrow$ Minimise Gibbs Free Energy G.

Defect Concentration and Migration

Law of Mass Action gives concentrations $[X]$ of each species in formation energy E_f and entropy s_v per defect:

$$[X] \simeq e^{s_v/k} e^{-E_f/kT}$$

Formation energies also affect diffusion rates via Arrhenius Equation

$$\begin{aligned} \text{diffusion rate} &\propto \text{(number of defects)} \times \text{(rate of barrier hopping)} \\ &\propto e^{-E_a/kT} \end{aligned}$$

where activation energy $E_a = E_f + E_b$

Defect Properties

Defects can exist in multiple charge states. Free charges at defect sites form F-centres (Farbenzentrum) which interact strongly with light.

Defect concentrations strongly affect material properties (optical, electrical, mechanical, chemical etc).

Same mineral, different defects: Corundum, Ruby and Sapphire



Direct Comparison of Total Energies

Compare energy of supercell with and without defects, subtract energy of missing/added atoms:

$$\Delta E_{def} = E_{def} - E_{perf} - \Delta E_{\text{atoms}} \cdot$$

Potentially misleading. Real concentrations depend on μ_i at time the crystal forms.

Formation Energies

Formation at constant $P, T \rightarrow$ minimize Gibbs free energy G.

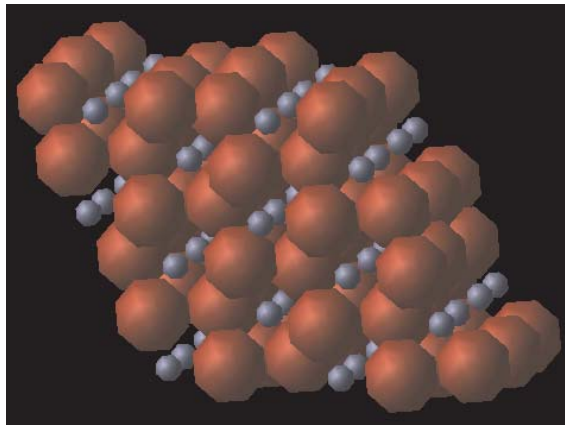
For defects in alumina of charge $q = -\Delta n_e$, we get

$$E_f = E^q_{def} - E_{perf} - \Delta n_{Al}\mu_{Al} - \Delta n_O \mu_O + q\mu_e \, .$$

Alumina

a k a Corundum / Aluminium Oxide / Al_2O_3

- Complex Structure due to 2:3 coordination. Bonding part ionic, part covalent.



- Difficult to study point defects experimentally.
- E_f's of all four main types of defect similar in value ($\sim$ 5eV).

Point Defects in Alumina

- In general, one type of disorder dominates. Experimental determination relies on fitting coefficients to models $\rightarrow$ unreliable.
- Pair potential methods get order of E_f's depending strongly on potentials used.
- Suggests need for ab Initio calculation with high accuracy.

Why DMC?

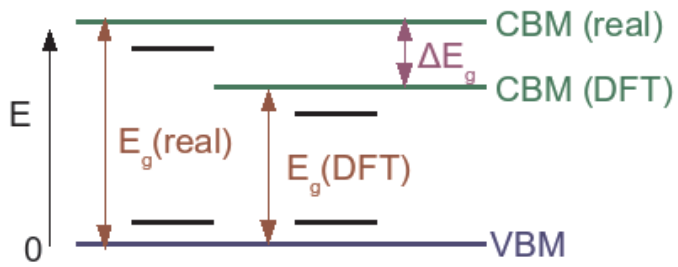
Table: Formation (all in eV). ΔH_0^{Al} and ΔH_0^{O} are the formation energies per atom of Al and O atoms in the gas phase. $\Delta H_0^{\mathrm{AlO}}$ is the formation energy of an AlO molecule.

Method	ΔH_0^{Al}	ΔH_0^{O}	$\Delta H_0^{\mathrm{AlO}}$
LDA-USP	4.05	3.62	0.91
LDA-DF	4.10	3.67	1.13
GGA-USP	3.41	2.82	0.74
DMC	3.47(1)	2.54(1)	0.68(1)
Experiment	3.42	2.58	0.69

Why DMC?

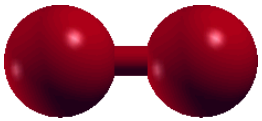
In case this is not yet convincing . . .

Occupied defect states deriving from conduction band states are too low energy because of DFT gap underestimation.

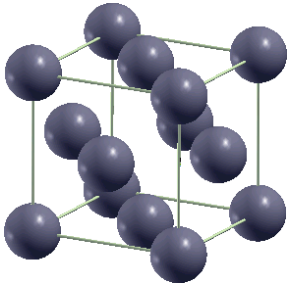


Correction $m \times \Delta E_g$ is normally applied to DFT formation energies.

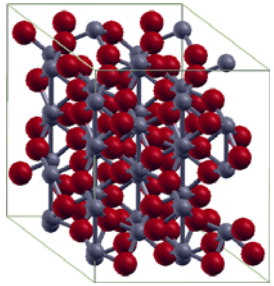
Ingredients



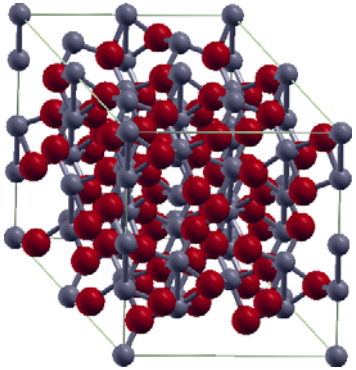
Oxygen molecule: $E_T[\mathrm{O}_2(g)]$



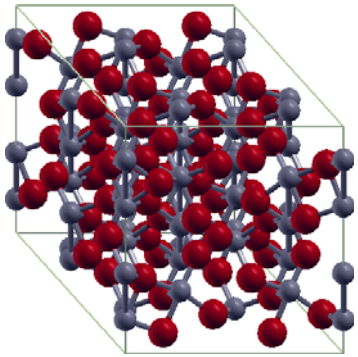
Aluminium metal: $E_T[\mathrm{Al}(s)]$



Alumina perfect crystal: $E_T[\mathrm{Al}_2\mathrm{O}_3(s)]$



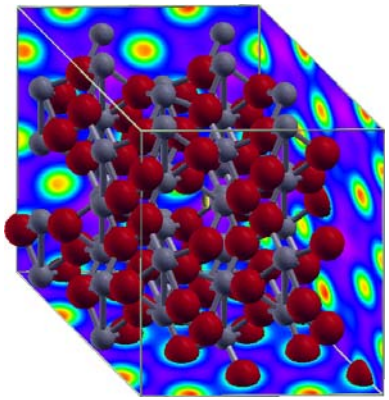
Aluminium Vacancy: $E_T^{def}[\mathrm{V}_{\mathrm{Al}}^q]$



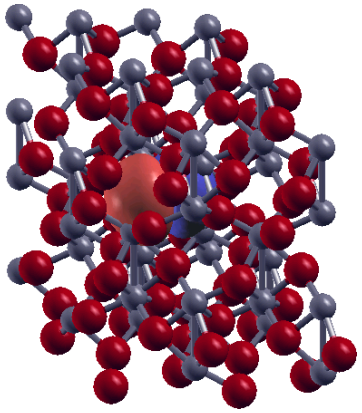
Aluminium interstitial: $E_T^{def}[\mathrm{Al}_{\mathrm{I}}^q]$

etc ...

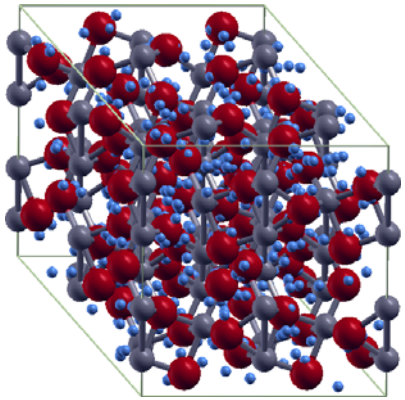
Methods



Plane Wave DFT — CASTEP



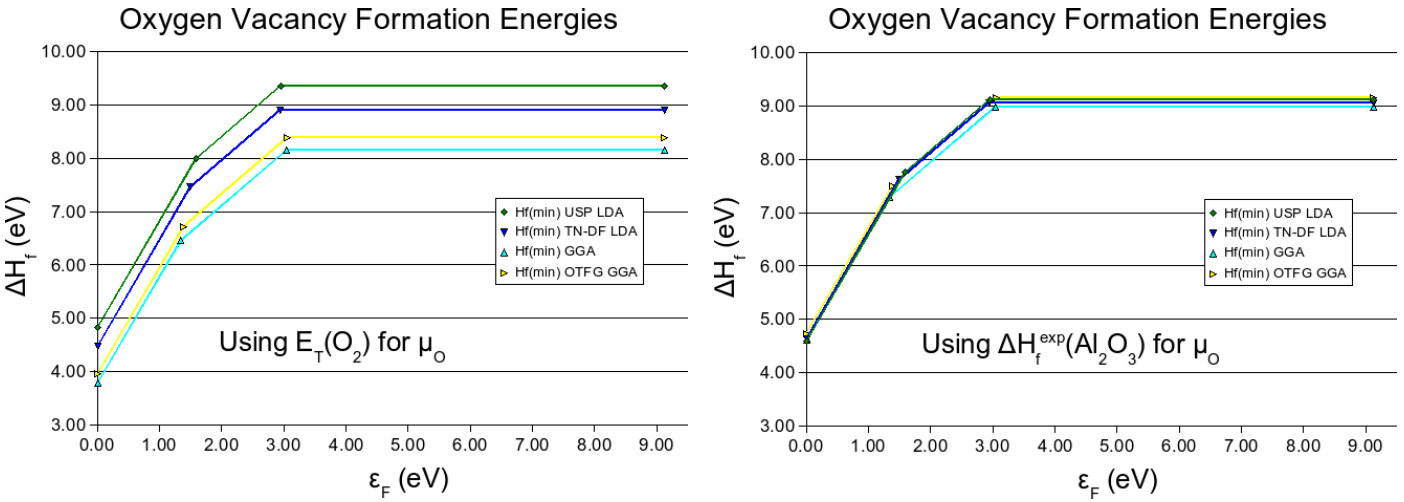
Linear Scaling DFT — ONETEP



Diffusion Monte Carlo — CASINO

DFT Formation Energies

Variation in previous DFT greatly reduced by avoiding Oxygen molecule $E_T(O_2)$ in calculation of Oxygen chemical potential μ_O

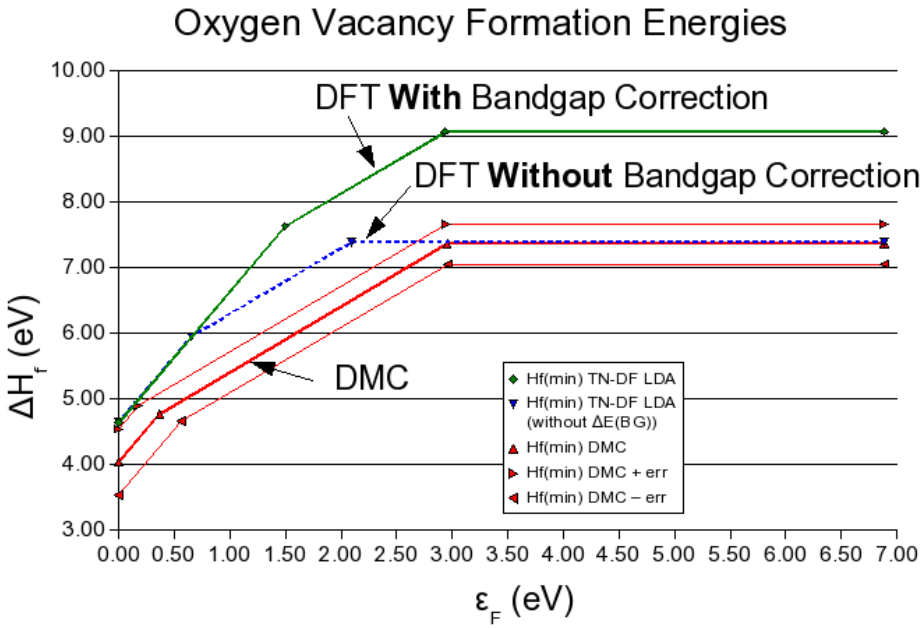


DFT results for different functionals and psps all agree to 0.1eV.

[Ref] M. W. Finnis, A. Y. Lozovoi, A. Alavi, Annu. Rev. Mater. Res **35**, 167 (2005).

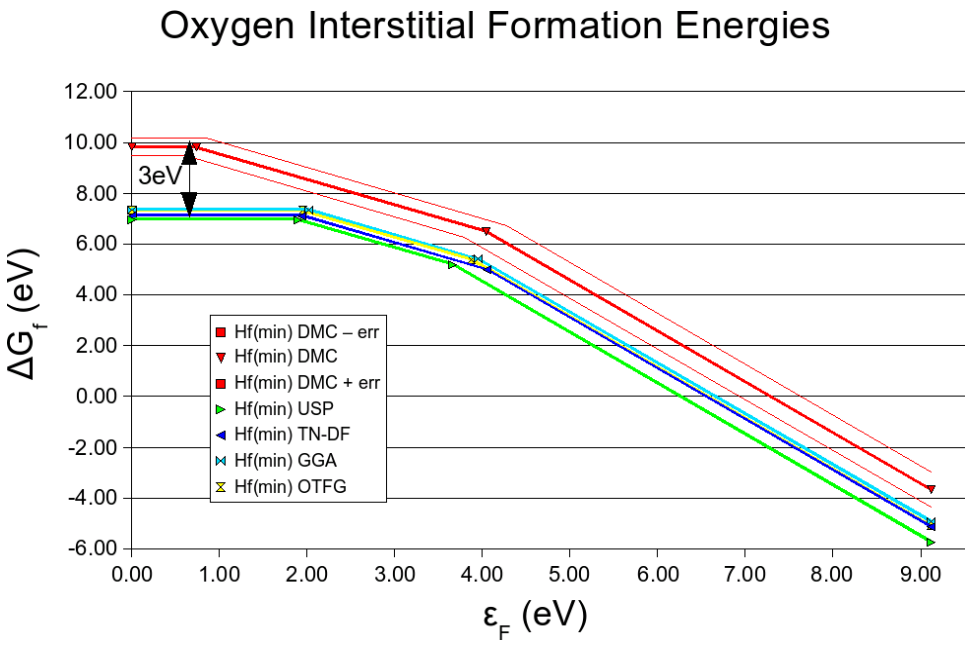
DMC Formation Energies

If no bandgap correction is applied, DMC results agree well with DFT except for correcting self-interaction error of localised states.



DFT (including bandgap correction) appears to be significantly overbinding. Real cost to break bonds is lower.

DMC Formation Energies



Interstitial is consistently harder to form, also suggesting DFT overbinds it.

Summary

- Diffusion Monte Carlo gives good results for defect formation energies in oxides.
- Resolves the “corundum conundrum”:
  - Defect formation energies previously believed to be much smaller (0.5–1eV).
  - Activation energies known to be all $\approx$ 6eV from diffusion expts.
  - Meant migration barriers must be $\approx$ 5eV — too high.
- Accuracy beats DFT — but relies on DFT for geometries.
- Computational demands are large but not unfeasible.
- New structure for Al vacancy identified.
- Migration barrier calculations underway.