Quantum Monte Carlo Calculations of Point Defects in Alumina

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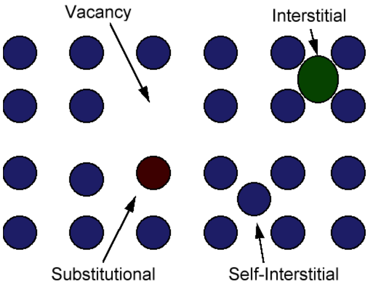
Outline

1. Point Defects
    - Thermodynamics of Defect Formation Energies
    - Point Defects in Alumina
    - Why DMC?
2. Results
    - Geometry
    - Formation Energies
    - Outlook
3. Coulomb Interactions
    - The Problem
    - Makov-Payne
    - Better Ideas
4. Summary

Outline

Point Defects & Background

Many types of point defect in crystals, “frozen” in during crystallisation:



Concentrations [X] of each species depend on formation energy G_f and entropy s_v per defect, according to Law of Mass Action:

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

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 (Corundum) 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:

$$\Delta E_{def} = E_{def} - E_{perf} - \Delta E_{\mathrm{atoms}}$$

Potentially misleading. Strongly dependent on accuracy of atomic calculation.
DMC would make this better but real concentrations depend on μ_i at time the crystal forms.

Gibbs Free Energies

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

Write formation energy in terms of defect supercell and chemical potentials of components:

$$\Delta G_f = E_{def} - \sum_{\text{species},i} n_i \mu_i$$

Energy of same supercell of bulk is $E_{perf} = \sum_i (n_i - \Delta n_i)\mu_i$. For neutral defects in Alumina we get

$$\Delta G_f = E_{def} - E_{perf} - \Delta n_{Al}\mu_{Al} - \Delta n_O \mu_O$$

So *e.g.* for an oxygen vacancy, charge 0 (an F centre):

$$\Delta G_f = E_{def}^{q=0} - E_{perf} + \mu_O$$

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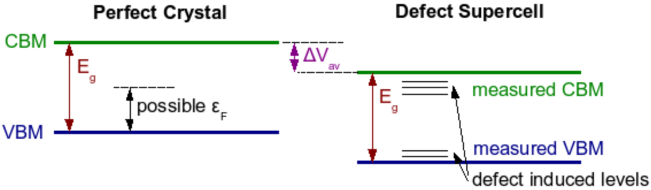
Charged Defects

For charged defects, consider system connected to electron reservoir at μ_e.

Zero of energy is arbitrary and is irrelevant in uncharged systems. End result contains E^q_{def} and $q\mu_e$ so is independent of zero of potential.

Can refer μ_e to the defect system, but E^{def}_{VBM} is obscured by levels of defect, which move VBM and CBM of defect cell:



Zhang-Northrup Formalism

Usual choice is

$$\mu_e = E_{VBM}^{perf} + (V_{av}^{def} - V_{av}^{perf}) + \epsilon_F$$

where

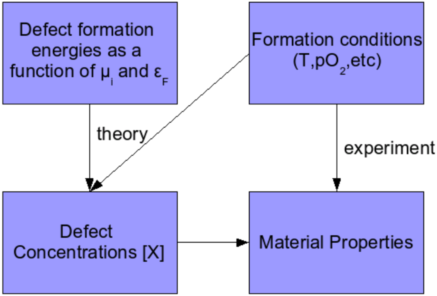
$$E_{VBM}^{perf} = E_{perf}^{q=0} - E_{perf}^{q=+1}$$

So e.g. for an oxygen vacancy, charge +1 (an F$^+$ centre):

$$\Delta G_f = E_{def}^{q=+1} - E_{perf} + \mu_O + 1 \times (E_{VBM}^{def} + \epsilon_F)$$

Formation Energies

Individual ΔG_f's contain μ_O, μ_{Al}, ϵ_F → not measurable



Defect formation energies as a function of μ_i and ε_F

Formation conditions (T, pO_2, etc)

theory

experiment

Defect Concentrations [X]

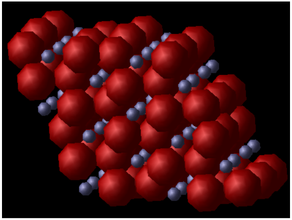
Material Properties

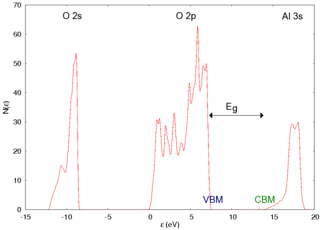
Some charge neutral combinations of defects are independent of these: (Schottky quintets $3V_O^{+2} + 2V_{Al}^{-3}$, Frenkel pairs $O_i^{-2} + V_O^{+2}$ and $Al_i^{+3} + V_{Al}^{-3}$)

Alumina

a k a Corundum / Aluminium Oxide / Al_2O_3

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

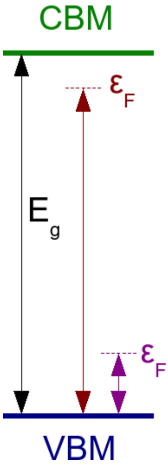




- Difficult to study point defects experimentally
- G_f's of all four main types of defect similar in value ($\sim$ 5eV)

Formation Energies

- Value of ϵ_F depends on presence or absence of conduction electrons
- Hence on *doping* by divalent or tetravalent impurities (*c.f.* trivalent Al^{3+})
- Alumina is amphoteric: Diffusion dominated by V_O, Al_I in presence of divalent impurities which lower ϵ_F (*e.g.* Mg^{2+})
- But dominated by O_I, V_{Al} in presence of tetravalent impurities (*e.g.* Ti^{4+}) which raise ϵ_F
- V_O (esp its diffusion) is of great technological importance



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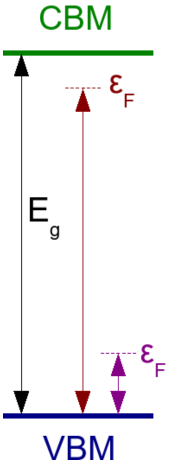


Point Defects in Alumina

- In general, one type of disorder dominates. Experimental determination relies on fitting coefficients to models → unreliable
- (Empirical) Pair potential methods get order of ΔG_f's depending strongly on potentials used
- More complex defect clusters such as $\mathrm{V_{AlO}}$ have also been suggested as significant
- Suggests need for Ab Initio calculation with high accuracy

Why DMC?

Table: Formation and Atomisation Energies (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. $\Delta_a H_0^{\mathrm{Al_2O_3}}$ and $\Delta_f H_0^{\mathrm{Al_2O_3}}$ are the atomisation and formation (cohesive) energies per formula unit of alumina.

Method	ΔH_0^{Al}	ΔH_0^{O}	$\Delta H_0^{\mathrm{AlO}}$	$\Delta_a H_0^{\mathrm{Al_2O_3}}$	$\Delta_f H_0^{\mathrm{Al_2O_3}}$
LDA-USP	4.05	3.62	0.91	-37.09	-18.15
LDA-DF	4.10	3.67	1.13	-36.48	-16.95
GGA-USP	3.41	2.82	0.74	-30.22	-14.94
DMC	3.47(1)	2.54(1)	0.68(1)	-32.62(3)	-18.04(3)
Experiment	3.42	2.58	0.69	31.95	-17.37

Why DMC?

Previous studies of defects:

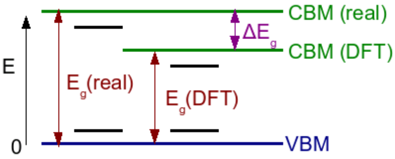
Phys. Rev. Lett. **83**, 2351 (1999) Leung, Needs, Rajagopal, Itoh, Ihara. *Calculations of Silicon Self-Interstitial Defects*: Interstitial formation energies 1-1.5eV higher in DMC than DFT.

Phys. Rev. Lett. **91**, 076403 (2003) Hood, Kent, Needs, Briddon. *Quantum Monte Carlo Study of the Optical and Diffusive Properties of the Vacancy Defect in Diamond*: Vacancy formation energy 1eV lower in DMC than DFT.

Suggests proper treatment of correlation crucial to correct treatment of defect electronic structure

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 is $m \times \Delta E_g$

or more precisely: $\sum_{i\ def}\sum_{j\ cond} |\langle\Psi_i|\Psi_j\rangle|^2 \times \Delta E_g = \sum_{i\ def}(1 - \sum_{j\ occ} |\langle\Psi_i|\Psi_j\rangle|^2) \times \Delta E_g$

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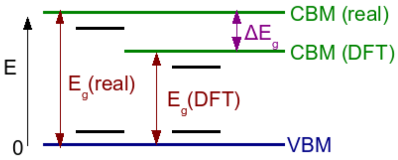

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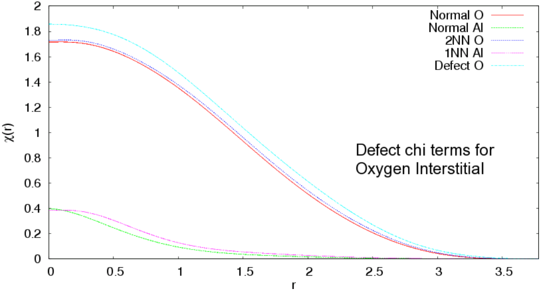
Why not VMC?

Inhomogeneity of defect locale renders VMC extremely challenging

Different χ-terms for 1NN, 2NN and defect site helps

Formation energies still uniformly several eV too large



Method

Run DMC in 2 × 2 × 1 hexagonal cell (still quite large as hexagonal unit cell contains 30 atoms).

$2 \times 2 \times 1 \Rightarrow$ 120 atoms, 576 electrons $\Rightarrow$ feasible.

$k-$point sample and extrapolate to large cell sizes in DFT, add correction to DMC results

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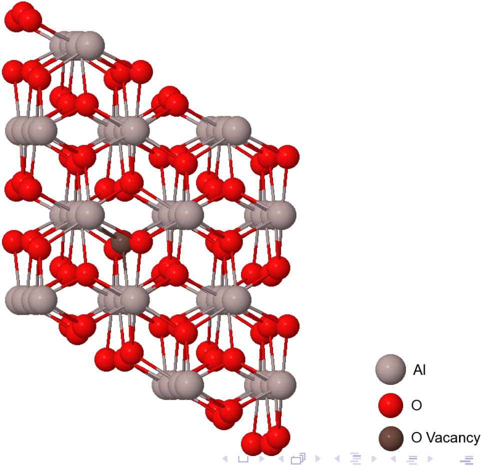
Outline

Geometry Relaxation - before

Bondlengths relax by up to 10% for 1NN. Gain from 0.05eV to 4eV, depending on charge state. Static lattice calculations clearly inaccurate.

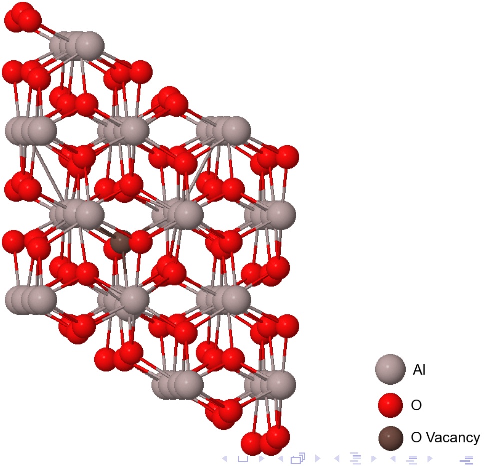
If defect site retains same charge, relaxation is minimal (< 1%)



Geometry Relaxation - after

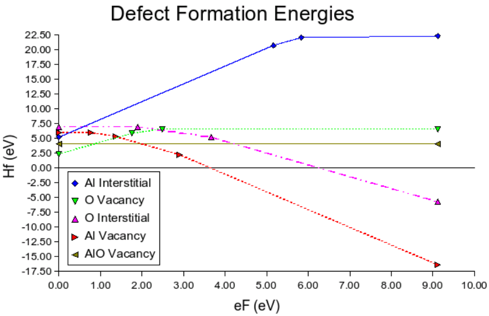
Sensitivity of geometry to DFT functional is small

Suggests it is mostly an electrostatic effect so DFT geometies should remain accurate in QMC.



DFT Formation Energies

Variation in previous DFT seems to be due to inconsistent formalism



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

DFT Formation Energies

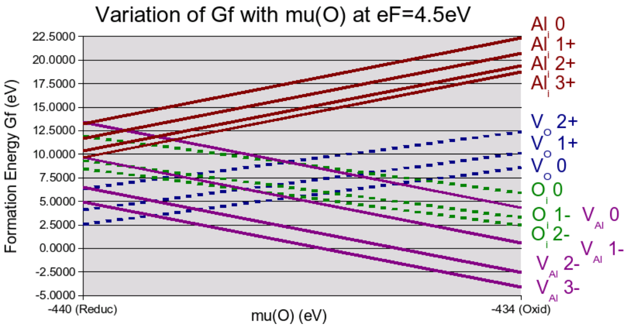
Full results at $T = 1400$K

Species	q=0	q=1	q=2	q=3
V_O^q	6.99	$4.03{+}\epsilon_F$	$1.81+2\epsilon_F$	
V_{Al}^{-q}	6.71	$7.47-\epsilon_F$	$8.84-2\epsilon_F$	$11.74-3\epsilon_F$
O_I^{-q}	7.47	$9.37-\epsilon_F$	$13.03-2\epsilon_F$	
Al_I^q	19.96	$13.86+\epsilon_F$	$8.02+2\epsilon_F$	$2.86+3\epsilon_F$
V_{AlO}^q	3.56	$20.37-\epsilon_F$		

AlO vacancy surprisingly stable!

DFT Formation Energies

As a function of μ_0:

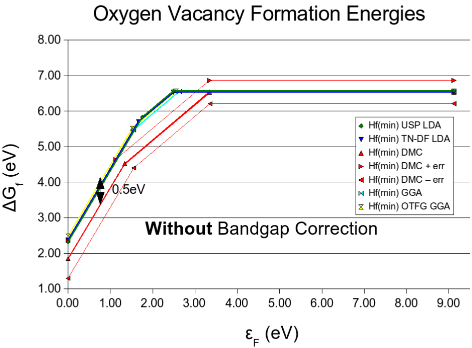


Oxygen vacancies dominate at low μ_0 (*i.e.* more favourable for O_2 to remain gaseous). Aluminium vacancies dominate at high μ_0.

Real solid could not explore this whole range.

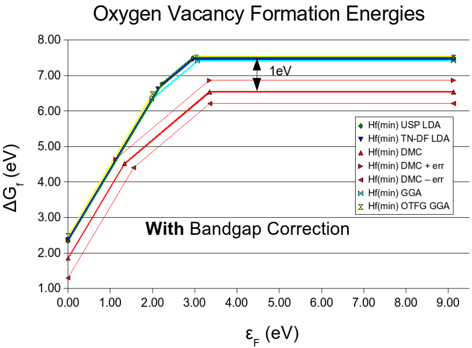
$T = 1400\text{K} \Rightarrow \mu_0 \simeq -435\text{eV}$.

DMC Formation Energies



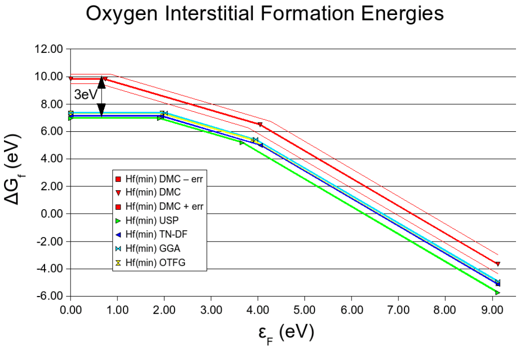
If no bandgap correction is applied, DMC results agree well with DFT except for correcting self interaction error of localised states

DMC Formation Energies



With bandgap correction, DFT 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.

Outlook

- Diffusion Monte Carlo shows significant differences in formation energies from DFT
- Accurate correlation very important for electronic structure around defects
- Computational demands are large but not unfeasible
- Outlook
  - Extend to more interesting oxides (*e.g.* TiO_2 - see Kilian's talk)
  - Defect migration barriers
  - Better defect-defect interaction corrections

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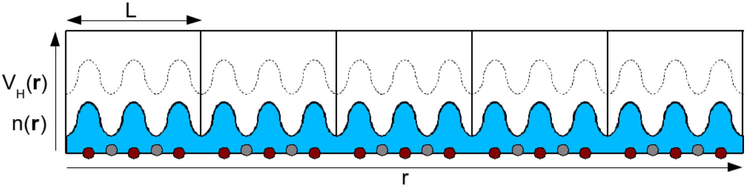
Defect-Defect Interactions

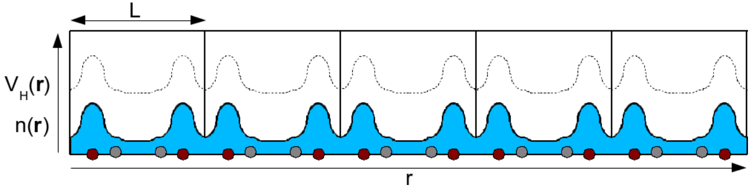
Perfect Crystal, full periodicity of lattice



Potential from $n(\mathbf{r})$ is $V_H(\mathbf{r}) = \frac{4\pi}{\Omega} \sum_{\mathbf{G}} \frac{n(\mathbf{G})}{G^2} e^{i\mathbf{G}.\mathbf{r}}$

Defect-Defect Interactions

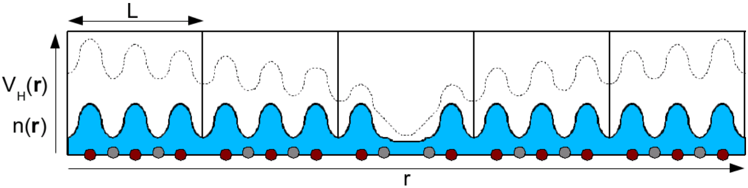
Introduce defect to supercell



If we use $V_H(\mathbf{r}) = \frac{4\pi}{\Omega}\sum_{\mathbf{G}} \frac{n(\mathbf{G})}{G^2} e^{i\mathbf{G}.\mathbf{r}}$ then defects feel potential from periodic replicas of themselves (and jellium background if $q \neq 0$)

Defect-Defect Interactions

Real situation is one defect supercell embedded in array of bulklike supercells



Difference of defect cell from perfect cell is $\Delta n(\mathbf{r})$.
Calculate $V_H(\mathbf{r})$ in real space: $V_H(\mathbf{r}) = \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'$

Possible Approaches

Ignore the problem and do nothing?

Commonly used - but greatly over-stabilises charged defects

Requires enormous supercells to converge ΔG_f

Average Potential Alignment

Use $\Delta V_{av} = V_{av}^{def} - V_{av}^{perf}$

Not on first sight intended for this purpose
Only addresses monopole correction

Works surprisingly well as it makes no assumptions about distribution of defect charge or polarisation

Dodgy in practice as “far from the defect” is very imprecise
Different choices to average over produce different results.
Not really feasible in QMC but DFT results should be applicable

Embedded Cluster Methods

Insert cluster with defect in field of point charges representing the ions, extending to infinity

Bypasses defect interactions entirely by changing boundary conditions

Edge effects, slow convergence with cluster size

Seems unlikely to work well in QMC

Makov-Payne Corrections

Makov-Payne Corrections: Approximate defects with lattice of point charges and remove spurious energy contributions

Result is $\Delta E_{MP} = -\frac{q^2\alpha}{2\epsilon L} - \frac{2\pi q Q}{3\epsilon L^3} + \mathrm{O}[L^{-5}]$

Hard to evaluate Q, hard to know what value of ϵ to use

Does not correctly account for polarisation effects

Great sometimes, very poor other times (often makes things worse).

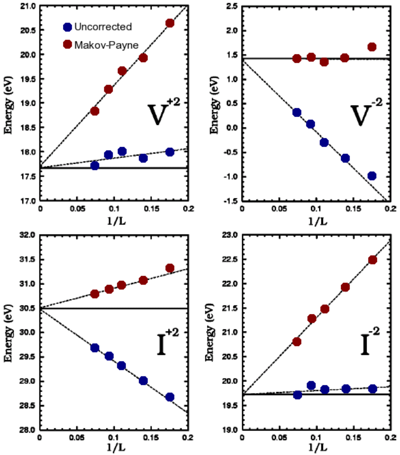
Makov-Payne Corrections

Accuracy depends on position of defect states relative to VBM & CBM

Generally speaking, if extra charge q returns density to more bulk-like state, MP works

If approximation of pointlike defect charge is bad, MP converges less quickly than uncorrected

Shim, Lee, Lee, Nieminen - Phys. Rev. B. 71 035206 (2005)



Correcting Just the Coulomb energy

Considering just the Hartree energy (similar arguments apply to psp terms):

$$n_{def}(\mathbf{r}) = n_{perf}(\mathbf{r}) + n_{loc}(\mathbf{r})$$

Since Poisson's Eq is linear we can write E_H as:

$$\begin{aligned} E_H^{def}[n] =& \frac{1}{2}\int_{cell} V_H^{per}(\mathbf{r}) n_{per}(\mathbf{r}) \mathrm{d}^3\mathbf{r} + \frac{1}{2}\int_{cell} V_H^{loc}(\mathbf{r}) n_{loc}(\mathbf{r}) \mathrm{d}^3\mathbf{r} \\ &+ \int_{cell} V_H^{per}(\mathbf{r}) n_{loc}(\mathbf{r}) \mathrm{d}^3\mathbf{r} \end{aligned}$$

Correcting Just the Coulomb energy

Can write this as

$$E_H = \frac{1}{2}\sum_{\mathbf{G}\neq 0}\frac{4\pi n_{per}(\mathbf{G})n_{per}(-\mathbf{G})}{\Omega G^2} + \frac{1}{2}\int_{cell}\int_{cell}\frac{n_{loc}(\mathbf{r}')n_{loc}(\mathbf{r})\mathrm{d}^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3\mathbf{r} + \int_{cell}\sum_{\mathbf{G}\neq 0}\frac{4\pi n_{per}(\mathbf{G})e^{i\mathbf{G}.\mathbf{r}}}{\Omega G^2}n_{loc}(\mathbf{r})$$

so

$$\Delta E_H[n] = \frac{1}{2}\int_{cell}\int_{cell}\frac{n_{loc}(\mathbf{r}')n_{loc}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3\mathbf{r}'\mathrm{d}^3\mathbf{r} - \frac{1}{2}\sum_{\mathbf{G}\neq 0}\frac{4\pi n_{loc}(\mathbf{G})n_{loc}(-\mathbf{G})}{\Omega G^2}$$

Correcting the boundary conditions on the potential

Does not solve the problem - equivalent sized error in KE due to polarization. Often this scheme makes convergence slower.

However... go back a step or two - put the correct form of V_H into the SCF loop

Run as a correction to the potential *inside* SCF loop

Boundary conditions on potential are a problem, esp for defects with low symmetry

Promising!

A Cunning Plan

Makov-Payne correction $\Delta E_{MP} = -\frac{q^2\alpha}{2\epsilon L}$ seems to describe most of the behaviour if ϵ is treated as a fitting parameter

Choose cell shapes (long and quite thin) for which $\alpha \simeq 0$?
e.g. $4 \times 4 \times 5$ has $v_M = -0.07$eV, compared to $v_M = -3.9$eV for $2 \times 2 \times 1$

Too big to be simulated with plane waves - perhaps with linear scaling?

Outline

Summary

- Formation energies for charged defects (first for QMC)
- Accuracy appears to beat DFT - but relies on DFT for geometries
- Points out overbinding and self-interaction errors present in DFT calculations

- Outlook
  - Work out how to correct defect-defect interactions
  - Extend to more interesting oxides (*e.g.* TiO_2)