

Quantum Monte Carlo Calculations of Point Defects in Alumina

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Outline

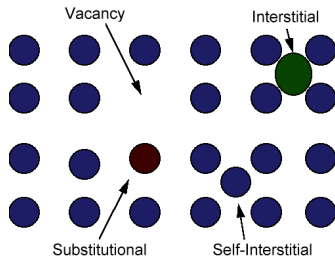
- 1 Point Defects
 - Thermodynamics of Defect Formation Energies
 - Point Defects in Alumina
 - Why DMC?
- 2 Results
 - Geometry
 - Formation Energies
- 3 Summary

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Point Defects & Background

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



Formation at constant $P, T \rightarrow$ Minimise Gibbs Free Energy G .
Law of Mass Action shows concentrations $[X]$ of each species depend on formation energy ΔH_f and entropy s_v per defect:

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

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:

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

Potentially misleading: Strongly dependent on accuracy of atomic calculation.

DMC can improve this but real concentrations depend on chemical potentials μ_j at time the crystal forms not just

True Formation Energies

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

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

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

$$\Delta H_f = E_{def} - E_{perf} - \Delta n_{Al} \mu_{Al} - \Delta n_{O} \mu_{O}$$

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

$$\Delta H_f = E_{def}^{q=0} - E_{perf} + \mu_{O}$$

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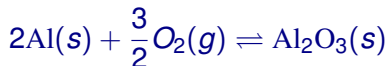
So e.g. for an oxygen vacancy, charge 0 (an F centre):

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

Oxygen Chemical Potentials

Total energy calculation of $E_T(O_2)$ for Oxygen molecule is unreliable, especially in DFT: $\Delta E \simeq 1.5\text{eV}$.

Circumvent need for calculated $E_T(O_2)$ in μ_O by substituting experimental energy of formation $\Delta G_f(Al_2O_3)$:



so at standard temperature and pressure:

$$\mu_O(T^0) = \frac{1}{3} \left(\mu_{Al_2O_3}^0(T^0) - 2\mu_{Al}^0(T^0) + \Delta G_{Al_2O_3}^0(T^0) \right)$$

Oxygen Chemical Potentials

Then correct for temperature and pressure via:

$$\begin{aligned}\mu_{\text{O}}(p_{\text{O}_2}, T) = & \frac{1}{3} (\mu_{\text{Al}_2\text{O}_3}^0(T^0) - 2\mu_{\text{Al}}^0(T^0) + \Delta G_{\text{Al}_2\text{O}_3}^0(T^0)) \\ & + \Delta\mu_{\text{O}}^0(T) + \frac{1}{2} k_B T \log(p_{\text{O}_2}/p^0)\end{aligned}$$

$\Delta\mu_{\text{O}}^0(T)$ can be approximated by ideal gas of rigid dumbbells:

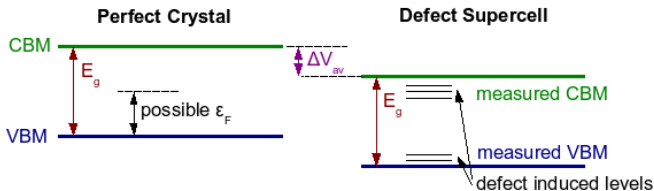
$$\Delta\mu_{\text{O}}^0(T) = -\frac{1}{2} ((S_{\text{O}_2}^0 - C_P^0)(T - T^0) + C_P^0 T \log(T/T^0))$$

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_{def}^q and $q\mu_e$ so is independent of zero of potential.

Can refer μ_e to the defect system, but E_{VBM}^{def} 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):

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

Makov-Payne Corrections

Makov-Payne corrections for defect-defect interactions

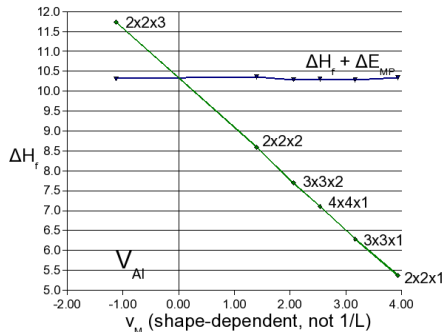
$$\Delta E_T^{def} = \frac{\alpha q^2}{2\epsilon_0 L} + O[L^{-3}]$$

Fit of ϵ_0 to $E_{def}(v_M)$ works better than experimental ϵ_0

$\epsilon_0^{exp} \simeq 9.1$ whereas

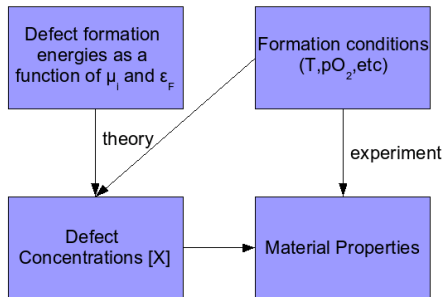
$\epsilon_0^{fit} \simeq 3.57$

Can interpolate to infinite size by taking long, thin cells to get $v_M < 0$, which is safer than extrapolating.



Formation Energies

Individual ΔH_f 's contain $\mu_O, \mu_{Al}, \epsilon_F \rightarrow$ not measurable

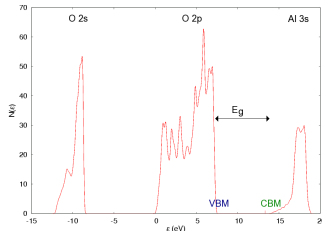
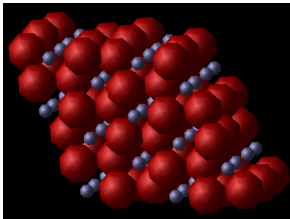


Some charge neutral combinations of defects are independent of these: (Schottky quintets $3V_O^{+2} + 2V_{Al}^{-3}$, Frenkel pairs $O_i^{-2} + V_O^{+2}$ and $Al_i^{+3} + V_{Al}^{-3}$)

Alumina

a.k.a Corundum / Aluminium Oxide / Al_2O_3

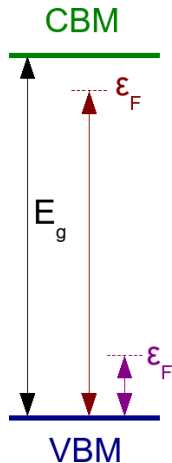
- Complex Structure due to 2:3 coordination. Complex bonding: part ionic, part covalent



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

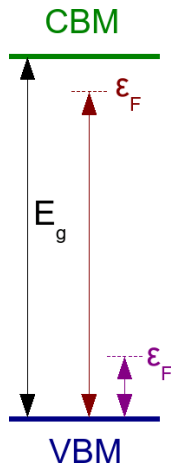
Formation Energies

- 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 V_{AlO} have also been suggested as significant
- Suggests need for high accuracy *Ab Initio* calculation

Why DMC?

Table: Formation and Atomisation Energies in eV of O, Al, AlO and Al₂O₃

Method	ΔH_0^{Al}	ΔH_0^{O}	ΔH_0^{AlO}	$\Delta_a H_0^{\text{Al}_2\text{O}_3}$	$\Delta_f H_0^{\text{Al}_2\text{O}_3}$
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

Previous QMC 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.*

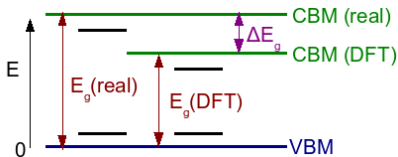
Phys. Rev. Lett. **91**, 076403 (2003) Hood, Kent, Needs, Briddon. *Quantum Monte Carlo Study of the Optical and Diffusive Properties of the Vacancy Defect in Diamond: Vacancy formation energy 1eV lower in DMC than DFT.*

Phys. Rev. B **71**, 220101 (2005) D. Alfè, M. J. Gillan *Schottky defect formation energy in MgO calculated by diffusion Monte Carlo: DMC on vacancies in metal oxides.*

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.

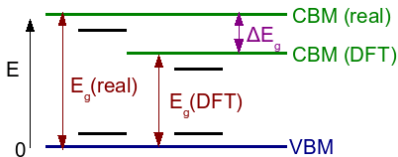


Correction is $m \times \Delta E_g$

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

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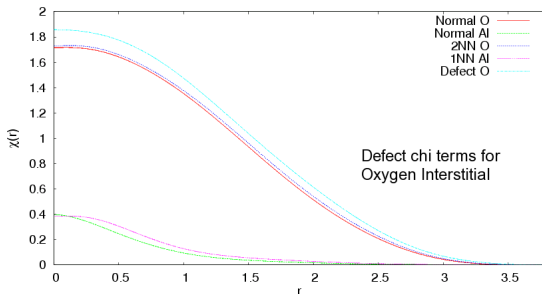
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Why not VMC?

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

DMC with CASINO in $2 \times 2 \times 1$ hexagonal cell (still large: hexagonal unit cell contains 30 atoms).

$2 \times 2 \times 1 \Rightarrow 120$ atoms $\Rightarrow 576$ electrons

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

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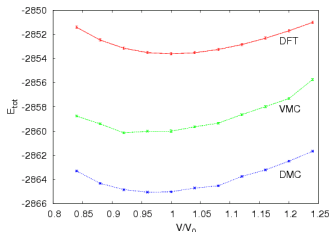
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Bulk Alumina in DMC

DFT geometry and lattice parameter work well:



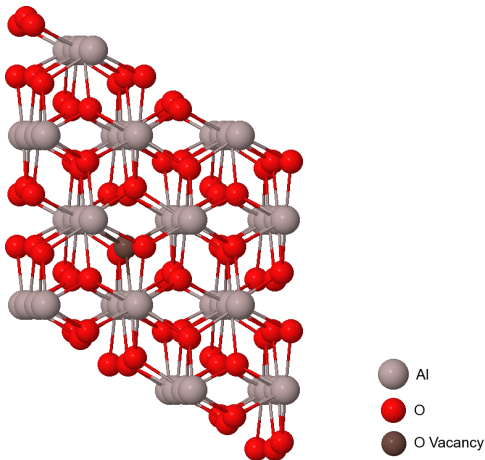
Energy Gap much closer to experiment than DFT:

Method	Excitation Gap (eV)	Charging Gap (eV)
LDA-USP	6.9	6.5
DMC	9.4(3)	10.6(5)
Experiment	9.1	-

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.

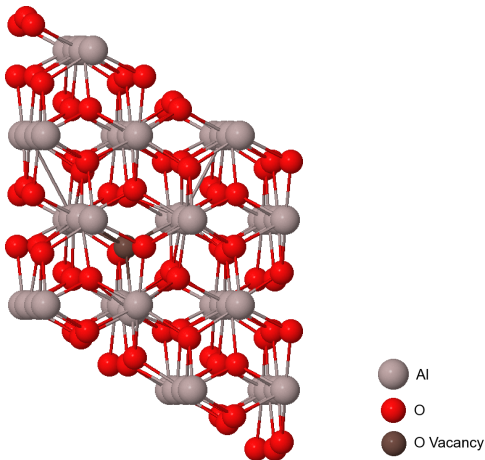
If defect site retains same charge, relaxation is minimal (< 1%)



Geometry Relaxation - after

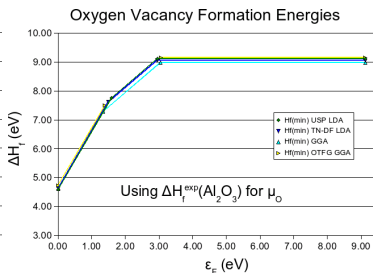
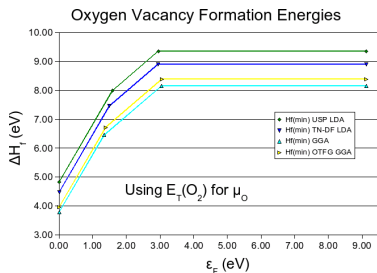
Sensitivity of geometry to DFT functional is small

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



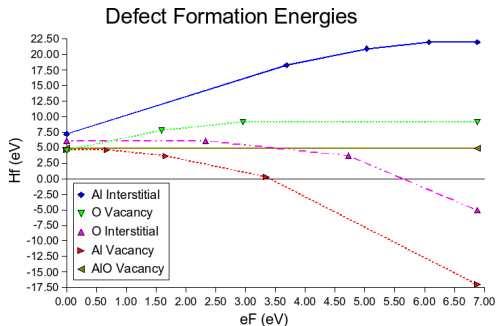
DFT Formation Energies

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 psp's all agree to 0.1 eV.

DFT Formation Energies

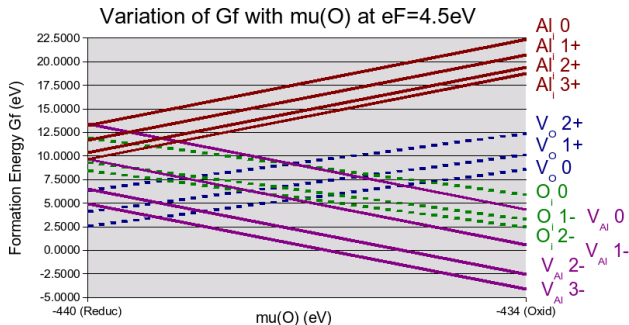


As expected, trend is from V_O (Al_I) at low ϵ_F to V_{Al} (O_I) at high ϵ_F

AlO vacancy surprisingly stable!

DFT Formation Energies

As a function of μ_{O} (remember $\mu_{\text{Al}} = \frac{1}{2}(\mu_{\text{Al}_2\text{O}_3} - 3\mu_{\text{O}})$):

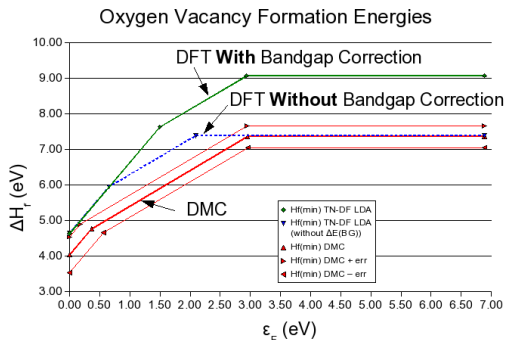


Oxygen vacancies dominate at low μ_{O} (*i.e.* more favourable for O_2 to remain gaseous). Aluminium vacancies dominate at high μ_{O} .

Real solid could not explore this whole range.

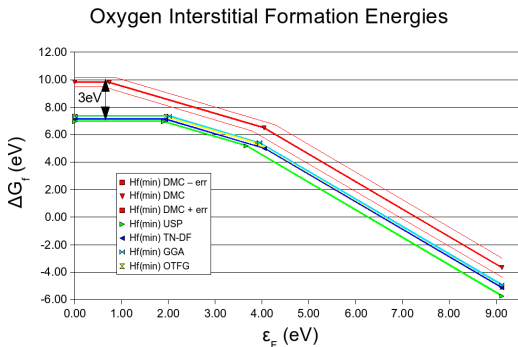
$T = 1400\text{K} \Rightarrow \mu_{\text{O}} \simeq -435\text{eV}$.

DMC Formation Energies



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

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- Overbinding and self-interaction errors both highlighted
- 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)
 - Defect migration barriers
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