## **Point Defects in TiO<sub>2</sub>**

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#### Outline



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#### **Motivation**



- Nick has been researching Al<sub>2</sub>O<sub>3</sub>, I am currently looking into TiO<sub>2</sub>, and have begun exploring the possibilities of research into ZrO<sub>2</sub>, all having numerous technological applications
- TiO<sub>2</sub>'s optical properties render it a popular white pigment, and it is also used in electrical applications such as gas sensors or in electrocatalysis, as a semiconductor photocatalyst, or corrosion-protective coating
- Many properties, such as catalytic behaviour and the growth and dissolution rates of the oxide in electro-chemical cells, depend critically on the electronic density of states in the band gap
- The properties and performance of TiO<sub>2</sub> have been seen to be affected by changes in the electronic structure when point defects are created in the bulk or at the surface<sup>1</sup>
- Defect formation energies can tell us what the most stable defects are at certain temperatures, pressures, and at differing chemical potentials
- Very few quantitative predications of point defect energies exist for TiO<sub>2</sub>
- Only very few QMC calculations have been done for metal oxides, and those that have been done promise improvement over DFT<sup>2</sup>

## TiO<sub>2</sub>



- Three phases: Rutile, Anatase, Brookite
   Rutile phase: tetragonal structure, whereby Ti is surrounded by 6 O atoms in an octahedral configuration and the stacking of octahedra results in threefold coordinated O atoms
- High oxidising power results in *n*-type doping and high conductivity
- Very durable
- High refractive index and very white (pigment)
- Bandgap ~3.2eV
- Naturally occurring is almost always reduced
   General agreement that reduced rutile is oxygen deficient<sup>1</sup>
- Ti interstitials prefer to diffuse along [001] channel rather than in the [100] or [010] directions

#### **Method**

- 2x2x1 72 atom supercell containing 384 electrons
- DFT

 CASTEP, LDA with 3000eV plane-wave cutoff, Trail and Needs DF pseudopotentials

QMC

•CASINO, VMC and DMC with Jastrow factor including separate  $\chi$  terms for each NN, defect site



### TiO<sub>2</sub> - Bulk Geometry





	a(Å)	c(Å)	Ti-O short (Å)	Ti-O long (Å)
LDA 400eV	4.547	2.927	1.933	1.952
	(-1.0%)	(-1.1%)	(-0.8%)	(-1.4%)
LDA 1000eV	4.603	2.976	1.953	1.989
	(+0.2%)	(+0.6%)	(+0.3%)	(+0.5%)
GGA-PBE	4.629	2.963	1.957	1.996
400eV	(+0.7%)	(+0.1%)	(+0.5%)	(+0.8%)
Experiment <sup>3</sup>	4.594	2.959	1.948	1.98

Jmel

## TiO<sub>2</sub> - Defects





#### **TiO<sub>2</sub> - Geometry Relaxation**







	First NN Relaxation	Second NN Relaxation	
	Distance (Å), %-change	Distance (Å), %-change	
V <sub>o</sub> original	1.996(Ti <sub>1NN</sub> ), 0%; 1.957 (Ti <sub>1NN</sub> ), 0%	2.964 (O <sub>2NNa</sub> ), 0%; 2.795 (O <sub>2NNb</sub> ), 0%	
V <sub>o</sub> X	+13.9%; +14.2%	-0.8%; -2.4%	
V <sub>o</sub> ·	+12.8%; +12.9%	-0.8%; -3.2%	
v <sub>o</sub> "	+13.8%; +13.6%	-1.0%; -2.4%	

#### **Defect Formation Energies**



- Concentration of a defect species can be expressed in terms of the Gibbs free energy of defect formation  $\Delta G_f$  and the accompanying entropy  $s_v$
- We want to find and minimise  $\Delta G_f$
- For crystal formation at constant *P*, *T*:

$$\Delta G_f = E^{total}(\alpha, q) - \sum_{\alpha} n_{\alpha} \mu_{\alpha}(T, P)$$

We substitute for the energy of a perfect supercell of bulk crystal:

$$E^{total}(perfect) = \sum_{\alpha} (n_{\alpha} - \Delta n_{\alpha}) \mu_{\alpha}(T, P)$$

 We then obtain the Gibbs free energy of defect formation as a function of defect species α in charge state q, at temperature T and oxygen partial pressure P:

$$\Delta G_f(\alpha, q, T, P) \cong E^{total}(\alpha, q) - E^{total}(perfect) - \Delta n_{\alpha} \mu_{\alpha}(T, P) + q\varepsilon_F$$

we want to find and minimise this, as a function of  $\varepsilon_F$ 

• The last term in  $\Delta G_{f}$ .

 $\varepsilon_F = \varepsilon_F^{from VBM} + \left(E^{total}(perfect) - E^{total}(+1) + V^{av}(defect) - V^{av}(perfect)\right)$ 

is used to define the arbirtrary zero in the potential for the case of a charged defect and incorporates the average potential scheme

• We determine the oxygen chemical potential according to the work of Finnis et al.:

$$\mu_O(T,P) = \frac{1}{2} \Big[ \mu_{TiO_2}^0 - \mu_{Ti}^0 - \Delta G_{f,TiO_2}^0 \Big] + \Delta \mu_O^0(T) + \frac{1}{2} k_B T \ln \Big( \frac{P}{P^0} \Big) \Big]$$

- We can calculate the Ti chemical potential from Ti pure metal,  $\mu_{TiO_2}$  is the calculated total energy per TiO<sub>2</sub> unit, we get  $\Delta G^{o}_{f,TiO_2}$  (the Gibbs formation energy of the oxide per mole in the standard state) from thermodynamic data, and we work at standard pressure
- The chemical potentials must fulfill the equilibrium dependency:

$$\mu_{Ti} + 2\mu_O = \mu_{TiO_2}$$

 Due to PBCs, we introduce an artificial long-range interaction between the defect and its periodic images

#### **Results - DFT**



- Most stable charge state dependent on ε<sub>F</sub>
- Confirmed previous calculations that highest charge states are not necessarily the most stable at  $\varepsilon_F = E_d/2$
- Oxygen Vacancy
   +1 state most stable for half of bandgap, afterwards neutral defect, verifying published results<sup>1</sup>
- Oxygen Interstitial
   Neutral state lowest-lying



**Oxygen Vacancy Formation Energy** 



**Oxygen Interstitial Formation Energy** 

#### **Results - DFT**



- Titanium Vacancy
   Agrees with previous prediction that -4 charged vacancy most stable for large section of bandgap
- Titanium Interstitial
   +4,+3,+2 charged Titanium interstitials all low-lying defect states
   Disagrees with photoelectron spectroscopy where +3 state is found 0.7-0.9eV below CBE



Titanium Interstitial Formation Energy

#### **Results - DFT**





Shifting  $\mu_0$  from the oxidation to the reduction limit, while  $\varepsilon_F = E_q/2$  and based on the equilibrium condition of:

$$\mu_{Ti} + 2\mu_O = \mu_{TiO_2}$$

the formation energies of Ti<sub>i</sub> and V<sub>o</sub> are found to decrease, while those of V<sub>Ti</sub> and O<sub>i</sub> increase For the entire range of  $\mu_o$ , the neutral charged O<sub>i</sub> and the +1 charged V<sub>o</sub> are found to be the most stable defects

Reduced TiO<sub>2</sub> known to be oxygen deficient

#### **Issues - Semi-core Electrons**





- Neglecting 6 3p semi-core electrons for Ti results in quite uniform error of ~0.5eV in formation energy of separate defect states, without majorlyshifting transition between stable defect charge states
- This error is relatively large compared with the defect formation energies of ~7-8.5eV
- Treatment would require adequate Ti pseudopotential for use within CASINO which includes these electrons

•For 72-atom supercell used, this would mean 144 extra electrons

Ideally need larger supercell to keep defects further apart, but this would then mean the inclusion of even more electrons

#### **Issues - Supercell Approximation**







#### **Issues - Supercell Approximation**



- PBCs introduce artificial long-range electrostatic and strain interactions between periodic defect images and do not produce the right polarisation energy in the bulk surrounding the defect
- Tails of potentials generated by local electrostatic moments of the defect overlap cell boundaries, corrupting the local potential of an "isolated" defect
- Can compute formation energies in different sized supercells and extrapolate to an infinite sized supercell, corresponding to an isolated defect, however computationally costly as we require at least 3 separate calculations
- Alternatively, compute formation energy in a single supercell and use an analytic correction formula to remove the spurious electrostatic contributions
  - These correction formula differ between methods used to circumvent the Coulomb divergence. Most commonly, the Uniform Background Charge (UBC) method is used. Schultz<sup>6</sup> has also presented the Local Moment Counter Charge (LMCC) method.



Both display different dependences on supercell size, and different analytic formula have been proposed to remove their spurious electrostatic energy contributions

	UDC		
•	<ul> <li>Jellium background used to artificially screen the <i>q</i>/<i>r</i> potential from the charge <i>q</i> in the defect</li> <li>Overscreening overestimates the stability of the charged defect as the</li> </ul>	•	Separate aperiodic model defension $n_{LM}(r)$ from supercell charge, we electrostatic moments match t to a certain order $\rho(r) = \rho_{LM}(r) + \rho'(r)$

Corresponds to metallic screening

#### 

ect charge whose the system's up

$$\rho(r) = \rho_{LM}(r) + \rho'(r)$$

- Coulomb energy of remaining periodic charge is neutral and momentless
- $\phi_{LM}(r)$  solved with local BCs  $(q/r \rightarrow 0$  as  $r \rightarrow \infty$ )
- $\phi'_{def}(r)$  solved from neutral defect density  $\rho'_{def}(r)$  in PBCs
- Potential due to net charge truncated at Wigner-Seitz cell around defect so it doesn't corrupt the potential of neighbouring cells
- Corresponds to limit where screening is present ourside the supercell



 Both display different dependences on supercell size, and different analytic formulae have been proposed to remove their spurious electrostatic energy contributions

UBC	LMCC		
	• Problem: net charge at defect induces screening in bulk crystal that is not cont in supercell, can estimate using simple dielectric continuum: $E_P = \left(1 - \frac{1}{\varepsilon}\right) \frac{q^2}{R_{Jost}}$ This can then be reformulated to be inc in the fitting parameter $A_1$ for a polynom	ained luded nial fit	
	$\oplus$		

#### Fitting to Polynomial (for UBC: Makov-Payne)

• For both methods, applying a correction formula of the form:

$$E^{f}[D;L,E_{F}] = E^{f}[D;L \rightarrow \infty,E_{F}] + \frac{A_{1}}{L} + \frac{A_{3}}{L^{3}} + \frac{A_{5}}{L^{5}}$$

provides extrapolations to the infinite supercell which are in agreement

- The fitted parameters, however, differ from defect to defect, appearing to reduce the chances that a simple, analytic formula can accurately correct supercell formation energies<sup>4</sup>
- In addition, the success of the fits is also defect specific
- Many studies have used relaxed defect structures, which may be incorrect as they are influenced by strain effects
- When Makov-Payne is used together with potential realignment, the two schemes usually produce a large overestimate of the required correction<sup>5</sup>

#### **Conclusions and future work**



- Found very strong lattice relaxations for both neutral and charged defects
- Found usual LDA underestimation of bandgap (2.55eV cf. 3.2eV experimentally)
- Found dominant defect species to be the +1 charged V<sub>O</sub> and the neutrally charged O<sub>i</sub>
- Found V<sub>Ti</sub> formation energies to be several eV higher than either Oxygen defect
- Disagreement between calculated Ti<sub>i</sub> +3 charged defect state and experimental observations from photoelectron spectroscopy
- Found that semi-core electrons cannot be neglected in Titanium pseudopotential as they result in a 0.5eV error in the defect formation energies
- Current QMC calculations will provide more insight into what the most stable defect charge states are and their ordering, as well as whether DFT is, for example, overbinding (Al<sub>2</sub>O<sub>3</sub>)
- For accurate absolute values of the defect formation energy, will need to include semi-core electrons in Ti pseudopotential, as well as use larger supercell
   But:
  - ■For 2x2x1 supercell containing 72 atoms, this means N<sub>e</sub>=384+144=528
  - •For 2x2x2 supercell containing 144 atoms, this means  $N_e$ =768+288=1056
- Energies of migration barriers are the next step
- Much work is to be done on understanding and potentially creating a more universal correction scheme to be applied after circumventing the Coulomb divergence in the supercell approximation





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