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Project Title: DNI: High-temperature Corrosion Resistance From First Principles
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Research progress: In the first year of this project, we focused on computing defect formation energies for a multitude of point defects in Al_2O_3. In order to ensure accurate results, we use density functional theory and started this project by approximating exchange and correlation using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation. These type of calculations are ideally suited to systematically investigate convergence of our results with respect to super-cell size, **k**-point sampling, and plane-wave basis energy cutoff, while investigating a large number of defects and charge states. While we are planning to explore hybrid exchange-correlation functionals that are computationally more expensive but more accurate than DFT-PBE, we delayed this for now, because their applicability is more limited.

Instead, before assessing the influence of exchange and correlation on defect formation energies, we use DFT-PBE to evaluate formation energies for a very extensive list of point defects, comprising of V_{Al}, V_O, Al_I, O_I, Ti_{Al}, Ti_I, Ti_O, Y_{Al}, Y_O, Y_I, Mg_{Al}, Mg_O, and Mg_I. For each of these defects, we study at least three different charge states and we took the influence of spin polarization into account in these calculations. The Freysoldt correction scheme was applied to compute accurate formation energies of charged defects, for several of these cases. We found that those corrections can be sizable and are on the order of 0.3 eV, e.g. for negatively charged Ti_{Al} and even more for higher charge states. While we are still analyzing the results from these simulations, this part of the project will provide us with a comprehensive view of point defects in alumina, needed for further progress. We will then compute, for specific examples, how large the influence of the description of exchange and correlation is on these formation energies, by comparing to hybrid-functional calculations.

		octahedral				displaced			
	electrons	total energy (eV)	magnetization	shortest Al_I – Al (Å)	shortest Al_I – O (Å)	total energy (eV)	magnetization	shortest Al_I – Al (Å)	shortest Al_I – O (Å)
Al_I^x	387	-590.9729	1	2.2675	2.1936	-591.2236	0	2.1910	1.9656
Al_I^{+1}	386	-602.5174	2	2.3114	2.0719	-603.8444	0	2.1941	1.9670
Al_I^{+2}	385	-615.4136	0	2.3419	1.8878	-615.3336	1	2.2689	1.9352
Al_I^{+3}	384	-627.7956	0	2.3378	1.8777	-627.7956	0	2.3378	1.8776

Figure 1: Total energies (in eV), magnetization, and two geometrical parameters (in Å) for Al_I defects in different charge states. The relaxed octahedral geometry is compared to the relaxed displaced geometry and the lowest-energy configuration is highlighted in green.

Even our early analysis of the DFT-PBE data has already shown interesting results: In particular, we reproduced earlier findings from the computational literature, that showed that for charge-neutral O_I, the initial octahedral configuration of the defect is not the actual ground-state geometry. Furthermore, this octahedral geometry leads to non-vanishing magnetization in the presence of the defect. However, it was observed and reported for charge-neutral O_I before that there is a lower-energy, non-magnetic atomic geometry, that represents the actual ground-state. In this project, we extended this study by investigating similar behavior for different charge states of another intrinsic defect, Al_I (see Fig. 1). These results clearly show that for low-charge states (0, +1), the displaced geometry is favorable, and for higher charge states the octahedral configuration is lower in energy (+2, +3). In the +3 case, the displaced geometry actually relaxes to the octahedral configuration. This indicates that for 0, +1, and +2 there may an energy barrier between the two geometries, but there is none for +3. The data in Fig. 1 also shows that the lowest-energy configuration is the one with zero net magnetization for Al_I.

Thus, from the data in Fig. 1 it becomes clear that these relaxations have a significant effect on the total energies as well as defect formation energies. Hence, we have already started and are continuing to investigate whether similar effects occur for the other defects we studied in alumina. This will allow us to obtain a reliable picture of point defects in alumina and, more importantly, it also constitutes necessary input to study both migration barriers for defect diffusion and defect clusters in alumina next.

We have already started computing formation energies of a large set of defect clusters involving Mg, Ti, and Y dopants, including $V_{Al} + Al_I$, $V_{Al} + V_O$, $V_O + O_I$, $Ti_{Al} + V_{Al}$, $Ti_{Al} + V_O$, $Ti_O + V_{Al}$, $Ti_O + 2V_{Al}$, $2Ti_{Al} + V_{Al}$, $3Ti_{Al} + V_{Al}$, $Mg_{Al} + V_O$, $Mg_O + V_{Al}$, $2Mg_{Al} + V_O$, $Y_{Al} + V_O$, and $Y_O + V_{Al}$. While we are still analyzing these simulations, we have found for the specific case of $V_O + O_I$ that the structural relaxation leads to recombination of this defect. This implies that this cluster is unstable and in the final relaxed geometry, the distance between O_I and the first three sets of nearest-neighbor Al and O atoms differs from pure Al_2O_3 by less than 0.1 %. To explore this further, we started investigating the influence of the $V_O - O_I$ separation (see Fig. 2). This data shows that this defect cluster recombines for short as well as large initial separations, but is stable for intermediate $V_O - O_I$ distances. Our early tests showed that no recombination occurs for $V_{Al} + Al_I$. We are currently focusing on understanding this relaxation mechanism and whether this effect occurs for other defect clusters. Once this is understood, the next step, as described in the original proposal, will be the computation of migration barriers of defects and defect clusters.

cluster	charge	V_O site	V_O -- O_I distance (Å)	supercell	total energy (eV)	formation energy (eV)
V_O + O_I	0	34	1.4822	2x2x2	-598.6569	0.0005
		12	2.2370	2x2x2	-598.6568	0.0006
		43	2.4708	---	---	---
		27	2.4780	2x2x2	-598.6569	0.0005
		6	2.4830	---	---	---
		20	2.6394	2x2x2	-588.0542	10.6032
		45	2.6624	---	---	---
		19	2.8484	2x2x2	-588.0541	10.6033
		32	2.9870	2x2x2	-588.1625	10.4949
		26	3.1473	---	---	---
		10	3.1960	2x2x2	-598.6564	0.0010
		23	3.2795	---	---	---
		42	3.5705	2x2x2	-598.6567	0.0007
		2	3.5946	---	---	---

Figure 2: Formation energies of $V_O + O_I$ clusters (in eV) for different $V_O - O_I$ separations.

Career impact: Computational materials science is an exciting field on a stellar rise owing to powerful super computers. In order for academia and industry to benefit from highly parallel machines such as *Blue Waters*, highly trained researchers with a diverse set of skills are needed. In this project the PI has trained and is continuing to train a graduate student in using high-performance computer cluster to run a large number of density-functional theory simulations. This student is split (50 %) with another project that requires mastering a different computational approach. For this reason, the present project significantly extends the student's skill set by providing training in defect calculations, including charge-corrections such as the Freysoldt scheme. In addition, the student is receiving training in physics and materials science to achieve a deep understanding of the background and theoretical framework. The student is part of an active collaboration with Prof. Shen Dillon and is also getting experience in presenting their results in front of local researchers and at national conferences. This project provides the student with excellent presentation and communication skills needed to become a highly capable individual that can take on excellent positions in academia, national labs, or industry.

This project allows the PI to expand their research portfolio into a completely new direction. Due to the broad applicability of the approaches used here, we expect that this will be very important in the future of the PI's career. In addition, this project involves another collaboration with Prof. Dallas Trinkle, in order to study diffusivity of defects, which also will be beneficial for the PI's career.