

# Accurate electronic and chemical properties of 3d transition metal oxides using a calculated linear response $U$ and a DFT+ $U(V)$ method

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We validate the usage of the calculated, linear response  $U$  for evaluating accurate electronic and chemical properties of bulk 3d transition metal oxides. We find calculated values of  $U$  leads to improved band gaps. For the evaluation of accurate reaction energies, we first identify and eliminate contributions to the reaction energies of bulk systems due only to changes in  $U$  and construct a thermodynamic cycle that references the total energies of unique  $U$  systems to a common point using a DFT+ $U(V)$  method, which we recast from a recently introduced DFT+ $U(R)$  method for molecular systems. We then introduce a semi-empirical method based on weighted DFT/DFT+ $U$  cohesive energies to calculate bulk oxidation energies of transition metal oxides using density functional theory and linear response calculated  $U$  values. We validate this method by calculating 14 reactions energies involving V, Cr, Mn, Fe, and Co oxides. We find up to an 85% reduction of the mean average error (MAE) compared to energies calculated with the PBE functional. When our method is compared with DFT+ $U$  with empirically derived  $U$  values and the HSE06 hybrid functional, we find up to a 65% and 39% reduction in the MAE, respectively.

Keywords: DFT+ $U$ , transition metal oxides, oxidation energy, linear response calculation

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## I. INTRODUCTION

The electronic and chemical properties transition metal oxides (TMOs) is of central importance in heterogeneous catalysis, electrochemistry, photocatalysis, and sensors<sup>1-3</sup>. Standard exchange-correlation functionals (LDA and GGA) in density functional theory (DFT) often fail to calculate either of these properties of TMOs accurately, which hinders our ability to identify and discover new TMOs for these applications. This failure has been partially attributed to a lack of cancellation of the self-interaction error produced by localized  $d$ -electrons.<sup>4-6</sup> The two most common ways to account for this error is incorporation of exact exchange via hybrid functionals,<sup>7</sup> or the addition of a Hubbard  $U$  to the  $d$ -electrons of the transition metal.<sup>8,9</sup> Although more accurate than DFT results, hybrid functionals have not shown significant improvement on top of the computationally cheaper DFT+ $U$  method for calculating accurate bulk reaction energies.<sup>5,10,11</sup> A majority of studies using DFT+ $U$  for evaluating chemical properties of a large number of TMOs use an empirically determined Hubbard  $U$ .<sup>12-14</sup> This strategy has been successful at capturing accurate known properties but it requires experimental data. This limitation is especially relevant regarding chemical properties of surfaces, such as the adsorption energies on well defined oxide surfaces,<sup>15</sup> which are more difficult to measure than bulk properties.

In contrast to using empirically derived  $U$  values, the Hubbard  $U$  is system specific and can be calculated via a linear response method.<sup>16</sup> The linear response  $U$  has been used in studies for evaluating a number of properties of a wide variety of materials,<sup>17-21</sup> but relative stabilities between TMO materials are more difficult to capture using calculated linear response  $U$  values. One reason for this is that the correction,  $E_U$ , leads to offsets in the total energy that include both the desired physical correction as well as an arbitrary contribution, shown in Figure 1, that makes comparisons between total energies with different  $U$  values meaningless.<sup>5,8,22</sup> This difficulty is highlighted in one of the first papers employing linear response  $U$  values for the calculation of redox potentials, where it was unclear whether the reactant or product's  $U$  values should have been used in reaction energy calculations.<sup>22</sup> Further studies use global  $U$  values that are averages of the linear response  $U$  values of intermediates along a reaction path, but the accuracy of this method is dependent on small differences between unique  $U$  values.<sup>23,24</sup> For example, in their paper on the addition of molecular  $H_2$  to  $FeO^+$ , Kulik et al. found certain reaction energies and transition state

barriers we're more accurately described by a locally averaged  $U$ .<sup>24</sup> A more recent study addressed this limitation of using averaged  $U$  values by constructing a DFT+ $U(\mathbf{R})$  method takes into account derivatives of  $U$  with respect to a specific reaction path.<sup>25</sup>

In this study, we use linear response  $U$  values to calculate accurate electronic and chemical properties of a number of pure 3d TMOs. We show that calculated linear response  $U$  values leads to more accurate band gaps of most materials we calculated. We adapt a recently developed DFT+ $U(\mathbf{R})$  method for calculating potential energy landscapes of molecular reaction paths to be suitable for bulk reaction paths, which we call DFT+ $U(V)$ .<sup>25</sup> We then use the DFT+ $U(V)$  method to eliminate contributions to reaction energies due only to changes in  $U$ . We then construct a thermodynamic pathway that goes through isolated atoms and allows us to compare relative stabilities of unique  $U$  bulk transition metal oxides using linear response  $U$  and semi-empirical DFT+ $U(V)$  method. We show our method is predictive and accurate for the calculation of oxidation energies of V, Cr, Mn, Fe, and Co TMOs.

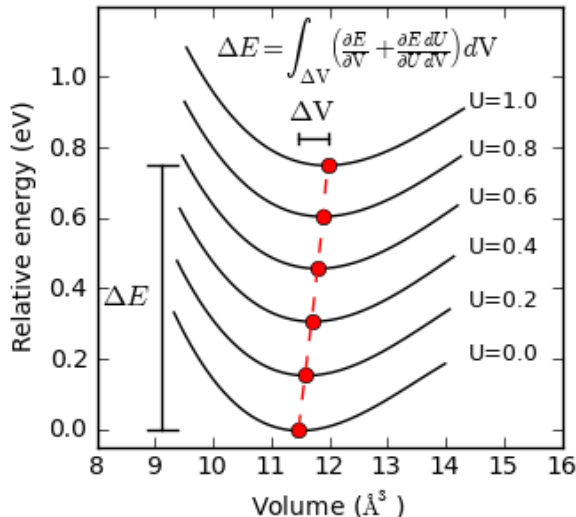


FIG. 1. Illustration of the arbitrary offset imposed upon comparing one structure at different  $U$  values. The energy difference  $\Delta E$  can be evaluated as a path integral over changing  $U$  and  $V$  space. Black curves show the energy versus volume behavior near the ground state volume of bulk Fe. The red points show the ground state volumes calculated at different Hubbard  $U$  values. The dashed red line shows a path over  $U$  and  $V$  space that is constrained to ground state structures.

## II. METHODS

All DFT calculations were performed with QUANTUM-ESPRESSO (QE).<sup>26</sup> The exchange correlation functional used was the Perdew-Burke-Ernzerhof (PBE)<sup>27,28</sup> generalized gradient approximation (GGA). The procedure for calculating the linear response  $U$  in bulk systems can be found in a previous paper by Cococcioni and de Gironcoli.<sup>16</sup> A list of the transition metal oxides, their atomic and magnetic structure, and their calculated linear response  $U$  values are shown in Table I.

In QUANTUM-ESPRESSO, the projection  $\mathbf{P}^I$  of the extended wavefunction on localized set of atomic orbitals determines the Hubbard  $U$  correction,<sup>29,30</sup> and shape of the atomic orbitals depends how the pseudopotential was generated, such as the charge state for which the pseudopotential was generated. To show that the performance of the calculated linear response  $U$  is independent of  $\mathbf{P}^I$ , we perform all calculations using ultrasoft pseudopotentials from two libraries: the original QE pseudopotential library<sup>31</sup> and the Garrity-Bennet-Rabe-Vanderbilt (GBRV) pseudopotentials.<sup>32</sup> The uniqueness of each PP is highlighted in the different atomic  $E_U(U)$  behavior (see supporting information<sup>33</sup>) and the calculated linear response  $U$  values (Table I). While we cannot explain the precise source of pseudopotential dependent linear response  $U$  value, the important observation is that they generate different calculated  $U$  values. This highlights the complexity of the transferability of specific  $U$  values and emphasizes the need for calculated linear response  $U$  values, which has shown to be able to adjust accordingly to different pseudopotentials.<sup>23</sup>

TABLE I. All oxides we used in this study along with their corresponding structure, magnetic ordering, and calculated linear response  $U$  values using both the original QUANTUM-ESPRESSO library ( $U_{QE}$ ) and GBRV high-throughput PPs ( $U_{GBRV}$ ) set of PPs.<sup>31,32</sup>  $U$  values of compounds with inequivalent metal ions ( $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ) were taken as a weighted average of the  $U$  value of each metal ion.

Compound	Crystal Structure	Magnetic Structure	$U_{QE}$	$U_{GBRV}$
VO	$F\bar{m}3m$	AFM	4.12	3.61
$\text{V}_2\text{O}_3$	$\bar{R}3c$	AFM	4.99	4.64
$\text{VO}_2$	$P\bar{2}_1/c$	NM	5.14	5.02
$\text{V}_2\text{O}_5$	$Pm\bar{m}n$	NM	5.12	4.67
$\text{Cr}_2\text{O}_3$	$\bar{R}3c$	AFM	2.73	4.86
$\text{CrO}_3$	$C2cm$	NM	4.99	7.42
MnO	$F\bar{m}3m$	AFM	4.94	5.52
$\text{Mn}_3\text{O}_4$	$I4_1/amd$	FM	4.05	6.11
$\text{MnO}_2$	$P2_1/c$	AFM	4.78	4.20
FeO	$F\bar{m}3m$	AFM	4.10	5.80
$\text{Fe}_3\text{O}_4$	$F\bar{d}3m$	FM	3.72	6.07
$\text{Fe}_2\text{O}_3$	$\bar{R}3c$	AFM	3.47	5.21
CoO	$F\bar{m}3m$	AFM	4.89	5.86
$\text{Co}_3\text{O}_4$	$F\bar{d}3m$	AFM	5.43	7.44

### III. RESULTS AND DISCUSSION

We first demonstrate that the application of linear response  $U$  values gives improved electronic properties such as band gaps in Figure 2. In almost all cases when a band gap is experimentally observed, DFT without the Hubbard  $U$  predicts a smaller or non-existent band gap, and the application of  $U$  opens up and increases the band gap to give improved agreement with experimental values. We note two exceptions, VO and  $\text{Mn}_3\text{O}_4$ , where the calculated Hubbard  $U$  leads to worse agreement and not much improvement, respectively. Near stoichiometric VO is difficult to synthesize, and the lack of vanadium or

oxygen vacancies in our VO model likely leads to differences between the experimental and calculated band gap.<sup>34</sup> Studies measuring the band gap of  $\text{Mn}_3\text{O}_4$  are scarce, and the only experimental source we could find was taken of  $\text{Mn}_3\text{O}_4$  nanorods,<sup>35</sup> which could be a source of the disagreement.

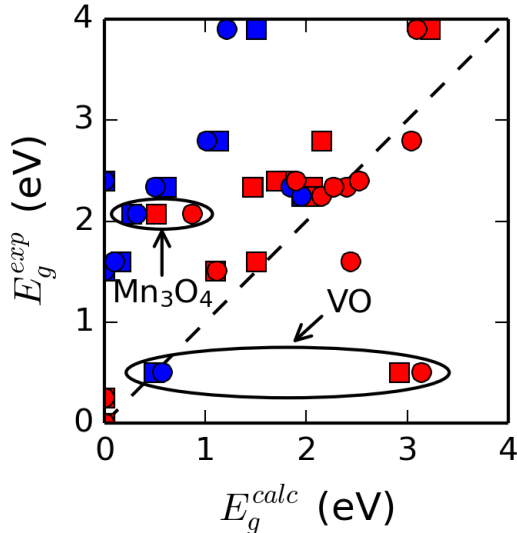


FIG. 2. Comparison between experimental and calculated band gaps of all 3d transition metal oxides included in this study. DFT and DFT+ $U$  results are shown by blue and red markers, respectively. Results using the original QANTUM-ESPRESSO and Garrity-Bennet-Rabe-Vanderbilt (GBRV) pseudopotentials are shown by  $\square$  and  $\circ$  markers, respectively. Experimental values are taken from a number of sources.<sup>34–43</sup>

In contrast to electronic properties, evaluating accurate reaction energies requires us to identify and eliminate the arbitrary offset in the total energy, shown in Figure 1. The ground state structures of Fe calculated at  $U = 0$  and  $U = 1.0$ , though electronically inequivalent, both represent reference states in a thermodynamic framework. The application of  $U$  produces an arbitrary shift in the total energy of these reference points, given by  $\Delta E$  that is not physically meaningful in calculating reaction energies. We decompose  $\Delta E$  into a path integral over the total derivative over  $U$  and  $V$  space shown in Equation (1). This approach, coined as DFT+ $U(\mathbf{R})$ , was used in a previous study that looked at the potential energy surface of a number of dissociating diatomic molecules and a chemical reaction.<sup>25</sup> We extend this method to bulk systems by replacing the interatomic distance of molecule  $\mathbf{R}$  with the volume of a bulk unit cell  $V$ , which essentially captures the changing bond distances between

atoms.

$$\Delta E = \int_V \frac{dE}{dV} dV = \int_V \left( \frac{\partial E}{\partial V} + \frac{\partial E}{\partial U} \frac{dU}{dV} \right) dV. \quad (1)$$

Because  $E$  depends on both  $V$  and  $U$ , the total derivative contains changes in the total energy produced by both changes in  $V$  ( $\frac{\partial E}{\partial V}$ ) and changes in  $U$  ( $\frac{\partial E}{\partial U} \frac{dU}{dV}$ ). Note, this derivation implies some  $U(V)$  relationship. If we assume that  $E$  is continuous with respect to  $U$  and  $V$ , the entire integral is path independent, but the contributions of each differential are not path independent. If we choose a path through  $U$  and  $V$  space that is constrained to the ground state structure (Figure 1), the entire arbitrary offset  $\Delta E$  is contained within the ( $\frac{\partial E}{\partial U} \frac{dU}{dV}$ ) term.

This analysis shows that if one has an appropriate  $U(V)$  relationship, the physically meaningful contribution to differences in the total energies of different structures is captured by the  $\frac{\partial E}{\partial V}$  term and is shown in Equation (2). We call this formalism the DFT+ $U(V)$  method.

$$\Delta E_{\text{DFT}+U(V)} = \int_V \frac{\partial E}{\partial V} dV \quad (2)$$

Theoretically, as long as one can determine a simple reaction path and derive a meaningful  $U(V)$  relationship, Equation (2) be used to evaluate the relative energetics of any two systems with different applied  $U$  values. To make this method practical for evaluating relative stabilities of bulk systems, which have complex crystal structures and no simple reaction paths between systems, we construct a scheme where the total energies of all bulk systems calculated at different  $U$  values reference total energies of isolated metal atoms and molecular oxygen at  $U = 0$ . This is illustrated in Figure 3 and derived in Equations (3) - (5) below.

$$\Delta H_{rxn} = E_{\text{MO}_y}^{U=b} - E_{\text{MO}_x}^{U=a} - \frac{y-x}{2} E_{\text{O}_2} \quad (3)$$

$$\begin{aligned} \Delta H_{rxn} = & (E_{\text{MO}_y}^{U=b} - E_{\text{M}_{\text{atom}}}^{U=0} - \frac{y}{2} E_{\text{O}_2}) \\ & - (E_{\text{MO}_x}^{U=a} - E_{\text{M}_{\text{atom}}}^{U=0} - \frac{x}{2} E_{\text{O}_2}) \end{aligned} \quad (4)$$

$$\Delta H_{rxn} = \Delta E_{\text{DFT}+U(V), \text{MO}_y} - \Delta E_{\text{DFT}+U(V), \text{MO}_x} \quad (5)$$

This allows the reaction path to be a simple isotropic expansion of the bulk cell, which only requires a single, one-dimensional reaction coordinate,  $V$ , in Equation (2). We will discuss

our rationale for picking  $U = 0$  in the following paragraphs.

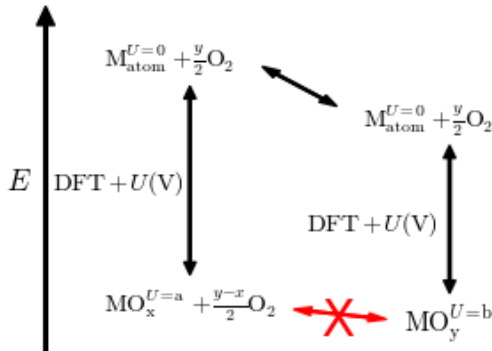


FIG. 3. Method for calculating oxidation energies by referencing cohesive energies using the  $DFT+U(V)$  method. Consider the oxidation reaction  $MO_x + \frac{y-x}{2}O_2 \rightarrow MO_y$ , where  $M$  is a transition metal. Total energies of  $MO_x$  and  $MO_y$  cannot be directly compared due to having different linear response  $U$  values. We construct a thermodynamic cycle that goes through a common reference system to compare the relative energetics at different  $U$  values. The  $DFT+U(V)$  method eliminates the unphysical contribution to the total energy produced by applying the Hubbard  $U$ .

To determine the meaningful  $U(V)$  relationship, we again turn to a study by Kulik et al.<sup>25</sup> They derived a similar method for determining how the total energy of molecular systems changed when breaking a single bond. The relationship they used for  $U(V)$  was the system specific, linear response calculated  $U$  value along the reaction coordinate  $\mathbf{R}$ , which was the length of the breaking bond. This approach yielded improved bond dissociation energies. We now hypothesize that the calculated linear response  $U$  values used in conjunction with the  $DFT+U(V)$  method should also yield improved reaction energies between different bulk systems. We note that many previous studies have used a linear response  $U$  derived  $U(V)$  relationship for the calculation of a variety of bulk properties of  $3d$  TMOs,<sup>18,44,45</sup> but our study is the first to use such a relationship for the calculation of reaction energies.



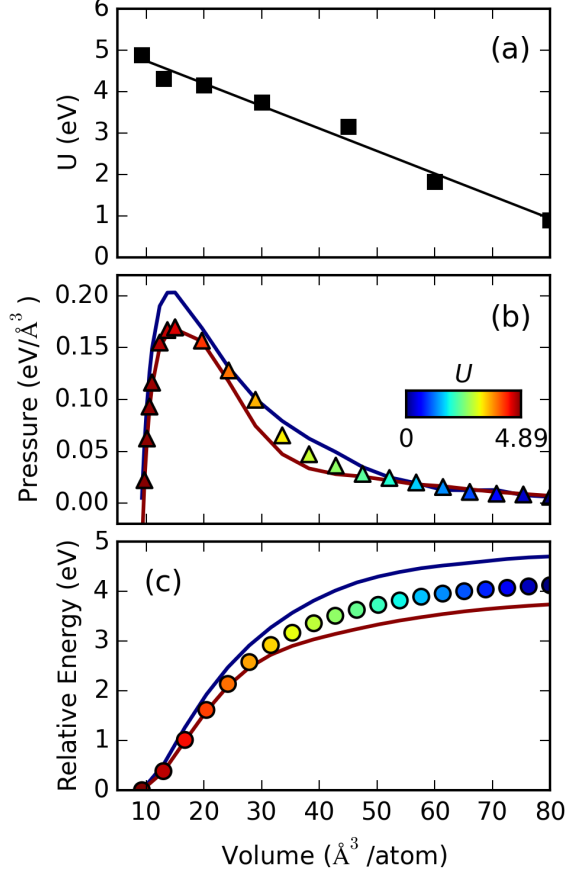


FIG. 4. (a) The behavior of the calculated linear response  $U$  of CoO as a function of volume. (b) The negative pressure of CoO as a function of both volume using the linear response  $U = 4.89$  eV of the bulk (red line),  $U = 0$  eV (blue line), and the  $U(V)$  relationship ( $\Delta$ ). (c) The potential energy surface of isotropically expanding CoO using  $U = 4.89$  eV (red line),  $U = 0$  eV (blue line), and the  $U(V)$  relationship ( $\Delta$ ) calculated by integration of the pressures shown in (b). In both the  $U(V)$  calculated stress and energy in (b) and (c), value of  $U$  is parametric within the calculation and is shown by the color of  $\Delta$  and  $\bigcirc$ , respectively.

To assess the feasibility and validity of this approach, we first tested the DFT+ $U(V)$  method by calculating the reference energy of a simple bulk system. The procedure we used is taken from the original detailed usage of DFT+ $U(\mathbf{R})$  method on the  $\text{FeO}^+$  diatomic molecule. The primary difference is that we are looking at a bulk system, so that instead of interatomic distance ( $\mathbf{R}$ ) and force ( $\frac{dE}{d\mathbf{R}}$ ), we use volume ( $V$ ) and pressure ( $\frac{dE}{dV}$ ). We chose bulk CoO, and the behavior of the total energy and calculated linear response  $U$  is shown below in Figure 4 (a). There is a clear trend of the calculated linear response  $U$  decreasing

from the bulk value of 4.89 eV to  $\sim 1$  eV. We then calculated the linear response  $U$  of all other atoms and found that they were all near 0 eV and less than the linear response  $U$  values of their corresponding bulk structures. This led us to choose  $U = 0$  for all atoms as the common reference point. Because this choice is taken at the high volume limit where most bulk structures of the same element will have similar  $U(V)$  behavior, it is likely that errors produced by this choice will be canceled in energy differences.

With the information of how  $U$  varies with  $V$ , we choose a path through  $U$  and  $V$  space to calculate  $(\frac{\partial E}{\partial V})$  necessary to evaluate Equation (2). We then integrate along  $V$  to find the DFT+ $U(V)$  reference energy. Figure 4 (b) shows the negative pressure calculated by the Hellmann-Feynman theorem<sup>46</sup> implemented in QUANTUM-ESPRESSO using the  $U(V)$  relationship shown in Figure 4 (a) and Equation 2. In Figure 4 (c), we integrate the negative pressure to calculate the potential surface. This gives us the DFT+ $U(V)$  energy for this specific material, which can be now used in meaningful comparisons with the total energies of systems calculated with unique Hubbard  $U$  values in equations 3 - 5.

Figure 4 shows that though possible, the calculation of a single DFT+ $U(V)$  reference energy is quite expensive, requiring total energy and linear response  $U$  calculations at numerous points along the isotropically expanding volume. Therefore, it would be impractical to perform the DFT+ $U(V)$  method for many systems. Figure 4 also shows that the DFT+ $U(V)$  reference energy lies between the cohesive energy calculated at  $U_{\text{bulk}}$  and  $U_0$  and therefore can be written as a weighted average between the cohesive energies at  $U_{\text{bulk}}$  and  $U_0$ . This quantity, which we call the semi-empirical DFT+ $U(V)$  energy, is shown in Equation 6,

$$\Delta E_{\text{DFT}+U(V)} = x\Delta E_{\text{coh}}^{U=U_{\text{bulk}}} + (1-x)\Delta E_{\text{coh}}^{U=U_0}, \quad (6)$$

where  $x$  is a material specific weighting factor that can be calculated directly by the method shown above, which for CoO was found to be 0.600. Physically,  $x$  is a measure of how the self-interaction error of a transition metal produced by its  $d$  electrons is retained as its bonds are broken. Alternatively, the  $x$  value can also be fit by minimizing errors produced by the complete DFT+ $U(V)$  method for calculating bulk oxidation energies using equations 5 and 6. The set of TMOs along with their calculated linear response  $U$  values we will use in these fits is shown in Table I.

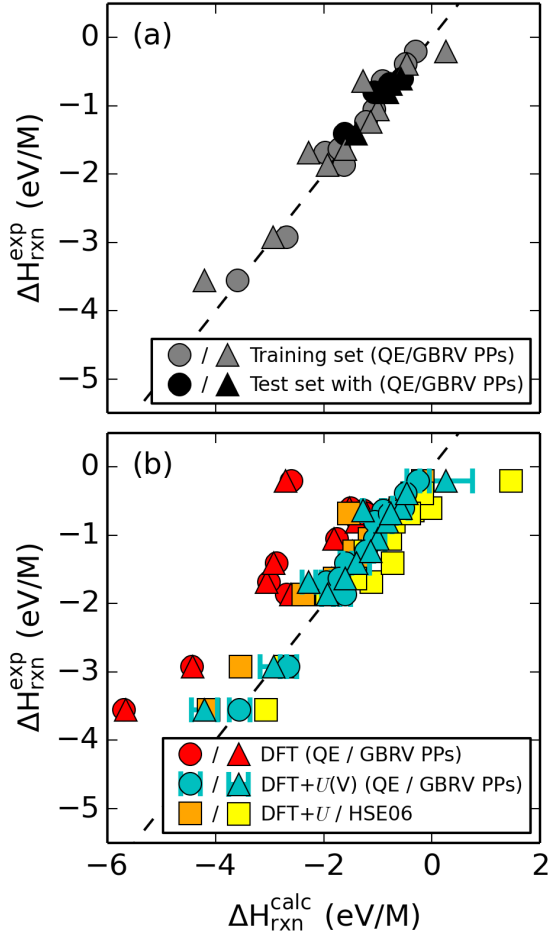


FIG. 5. (a) Use of the DFT+ $U(V)$  on calculating oxidation energies of a test set (Cr, Mn, Co oxide reactions) with an  $x$  parameter fitted from the oxidation energies of a training set (V, Fe oxide reactions). Gray markers are training set data. Black markers are test set data. (b) All oxidation energies were calculated using a single  $x$  parameter per PP.  $x = 0.599 \pm 0.053$  ( $x = 0.487 \pm 0.08$ ) fitted to all reactions involving species in Table I with QE (GBRV) PPs and confidence intervals on the  $x$  and the calculated reaction energies. Red markers are DFT energies. Teal markers are semi-empirical DFT+ $U(V)$  energies. Orange and yellow squares are reaction energies calculated using DFT+ $U$  with empirically determined, element specific  $U$  values and HSE06, respectively. DFT+ $U$  and HSE06 data taken from the literature.<sup>10,13,47</sup> In both (a) and (b), results calculated using QE (GBRV) PPs are  $\circ$  ( $\triangle$ ).

We now demonstrate the predictive power and accuracy of using energies calculated using the semi-empirical DFT+ $UV$  method for calculating relative stabilities of  $3d$  transition metal

oxides by calculating reaction energies of the transition metal oxides shown in Table I. We also calculated formation energies of these TMOs using the semi-empirical DFT+ $U(V)$  method, but found mixed results (see supporting information<sup>33</sup>). Figure 5 (a) shows the reaction energies of a test set of reactions calculated with an  $x$  value fitted to a training set of reactions. The training set is made up of oxidation reactions involving V, Cr, and Fe oxides, while the test set is made up of oxidation reactions involving Mn and Co oxides. A low mean average error (MAE) in both the training and test set of 0.139 eV/M (0.267 eV/M) and 0.157 eV/M (0.037 eV/M) with the QE (GBRV) PPs demonstrates the predictive power of our method.

Figure 5 (b) shows energies of all oxidation reactions calculated with the semi-empirical DFT+ $U(V)$  method at an optimized value of  $x$  compared to experiments and DFT without the application of the Hubbard  $U$ . With the QE (GBRV) PPs, we find that the MAE using our method is 85% (79%) lower than the MAE using DFT using a fitted  $x$  value of 0.599 (0.487). Uncertainty analysis of the fitted parameter  $x$  produces confidence intervals in reaction energies that include experimental values, again demonstrating the improved accuracy using the semi-empirical DFT+ $U(V)$  method. The similar performance and  $x$  parameter of both the QE and GBRV PPs demonstrate that the improvement our method gives is independent of how the  $d$ -orbitals and occupations are defined. The excellent agreement between the overall fitted (0.599) and calculated (0.600)  $x$  value for CoO using the QE PPs further demonstrates a calculated, first-principles selection of the Hubbard  $U$  is responsible for the improved reaction energies.

It is also important that we compare our method to the current widely used methods we discussed in the introduction, which are namely an empirical DFT+ $U$  method with element specific  $U$  values and hybrid functionals. Because many of these calculations have already been done, we compiled total energy data calculated using DFT+ $U$  and the HSE06 hybrid functional<sup>7</sup> from a number of sources (see supporting information).<sup>10,13,47</sup> The oxidation energies and MAE values can be seen in Figure 5 (b) and Table II. Consistent with previous work comparing empirical DFT+ $U$  and hybrid functionals, DFT+ $U$  outperforms hybrid functionals.<sup>5,10,11</sup> We show that our semi-empirical DFT+ $U(V)$  method with a single fitted  $x$  value outperforms either DFT+ $U$  or HSE06, which again attests the success of the linear response determined Hubbard  $U$  in correcting the self-interaction error inherent in TMO systems.

TABLE II. Computed mean average errors (MAEs) of oxidation energies calculated using DFT, a fully empirical DFT+ $U$ , the HSE06 functional, and the DFT+ $U(V)$  method combined with our thermodynamic framework. All reaction energies are normalized with respect to the number of metal ions involved.

Method	MAE (eV/M)
DFT (QE PPs)	0.96
DFT (GBRV PPs)	0.98
DFT+ $U$ <sup>13,47</sup>	0.23
HSE06 <sup>10</sup>	0.40
DFT+ $U(V)$ (QE PPs)	0.14
DFT+ $U(V)$ (GBRV PPs)	0.20

We note that the  $x$  value we calculated for CoO using DFT+ $U(V)$  (0.600) and empirically by fitting reaction energies (0.599 and 0.487) and are similar and close to 0.5, suggesting a mere average of linear response  $U$  values is sufficient. This idea has already been used in a number studies on molecular systems,<sup>23,24</sup> and our work further validates the applicability of this method onto TMO bulk systems, which have a number of important technological applications listed in the introduction. Furthermore, the theoretical framework of referencing atomic states allow us to directly compare total energies calculated at their linear response  $U$  values and bypasses the need to re-calculate total energies at globally or locally averaged  $U$  values. Finally, we point out the inherent difference in calculating reaction energies using our thermodynamic framework than using a reaction specific  $U$  that was averaged between the reactant and product linear response calculated  $U$  value. By going through cohesive energies, the average is taken between the dissociative limit  $U = 0$  and bulk value  $U = U_{\text{MO}_x}$ , not the between the linear response values of the product  $U = U_{\text{MO}_x}$  and reactant  $U = U_{\text{MO}_y}$ . It is unclear whether the two averages would produce similar results in relative stabilities.

#### IV. CONCLUSION

In summary, we have shown how the calculated, linear response Hubbard  $U$  value leads to improved electronic and chemical properties of 3d transition metal oxides. We developed

a semi-empirical DFT+ $U$ (V) model for accurately predicting relative stabilities of bulk TMOs. This model requires a minimum number of DFT calculations and incorporates the first-principles calculated linear response  $U$ . We find reaction energies of transition metal oxides calculated using our method show improvement over not only DFT but also empirical DFT+ $U$  and hybrid functional methods.

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