Calibration of the DFT/GGA+U Method for Determination of Reduction Energies for Transition and Rare Earth Metal Oxides of Ti, V, Mo, and Ce

Suzanne Lutfalla, Vladimir Shapovalov, and Alexis T. Bell*

Department of Chemical and Biomolecular Engineering, University of California-Berkeley, Berkeley, California 94720-1462, United States

ABSTRACT: GGA+U calculation were performed for oxides of Ti, V, Mo, and Ce with the objective of establishing the best value of the parameter $U_{\text{eff}}$ to use in order to match the calculated reduction and oxidation energies of each oxide with experimental values. In each case, the reaction involved the hydrogen reduction of an oxide to its next lower oxide and the formation of water. Our calculations show that the optimal value of $U_{\text{eff}}$ required to match calculated and experimental values of the reaction energy are significantly different from those reported in the literature based on matching lattice parameters or electronic properties and that the use of these values of $U_{\text{eff}}$ can result in errors in the calculated redox energies of over 100 kJ/mol. We also found that, when an element exhibits more than two oxidation states, the energy of redox reactions between different pairs of these states are described by slightly different values of $U_{\text{eff}}$.

INTRODUCTION

The oxides of transition and rare earth metals, such as Ti, V, Cu, La, and Ce, are often used as catalysts for industrially important reactions. Consequently, quantum chemical calculations for such elements are of much interest, and density functional theory (DFT) is one of the tools commonly applied to such systems. The catalytic properties of these materials are attributed to their reducibility, to such systems. The catalytic properties of these materials are attributed to their reducibility, where lower oxidation states correspond to occupied d and f orbitals. At the same time, d and f electrons also present difficulties for DFT calculations, because this method tends to delocalize d and f electrons excessively. These difficulties affect a broad spectrum of oxide properties, including crystal lattice parameters, conductivity, and energies of oxide reduction and oxidation.

The difficulty in obtaining accurate property predictions for transition metal oxides from DFT calculations has been recognized for some time. Despite attempts to use hybrid functionals and dynamical mean-field theory to treat the problem, DFT with generalized gradient approximation (GGA) functionals remains an economical choice, and therefore, corrections directed at specific drawbacks of the method are introduced.

It is generally understood that the main source of error in DFT for d and f electrons is their correlated nature. A commonly used ad hoc method for improving the description of d and f electrons is the DFT+U method, in which an “on-site” potential is added to introduce intra-atomic interactions between the strongly correlated electrons. Most recent articles have used the potential proposed by Dudarev et al., which has the form

$$E = \frac{(U - J)}{2} \sum_{\sigma} (n_{m,\sigma} - n_{m,\sigma}^0)^2$$  \hspace{1cm} (1)

where $U$ and $J$ are the effective Coulomb and exchange parameters, respectively, and $n$ is the occupation number of a d orbital number $m$ with spin $\sigma$. $U$ and $J$ can, in principle, be computed from first principles. In reality, however, the theoretical values of $U$ and $J$ give poor results, and therefore, these parameters are adjusted by fitting to experimental data, such as the oxide band gap or the lattice parameters. Because eq 1 depends on only the difference, $U - J$, can be replaced with one variable $U_{\text{eff}} = U - J$ for the sake of brevity.

The value of $U_{\text{eff}}$ is element-specific, and at least one study has suggested that it is transferable between different oxidation states of a given element. $U_{\text{eff}}$ is usually determined empirically, to fit some specific physical property, most often the crystal lattice parameters or the band gap between the occupied and unoccupied states. The principal problem with this approach is that no two properties are described well by the same value of $U_{\text{eff}}$, and therefore, a value is picked that minimizes the average error in several properties.

Application of the on-site interaction term to transition metal oxides has been recognized as necessary because of its strong influence on the orbital energies of the occupied d and f states and, as a consequence, on the formation energy of oxygen vacancies formed during reactions that proceed through a Mars–van Krevelen mechanism. For the purposes of catalytic chemistry, we are interested in values of $U_{\text{eff}}$ that accurately describe redox reactions. Several authors have shown that the oxygen vacancy formation energy depends strongly on the value of $U_{\text{eff}}$. A notable problem with this approach is that experimental formation energies of oxygen vacancies are difficult to evaluate, and consequently, different authors have reported different values of $U_{\text{eff}}$ for the same element.

Chemisorption energies for probe molecules can serve as a more reliable test of the value of $U_{\text{eff}}$. For example, CO can react with an oxide to form CO$_2$, which remains adsorbed as a surface carbonate. The net effect of this reaction is that the metal oxide is...
reduced. As the d band of the oxide becomes partially filled, the value of $U_{\text{eff}}$ will have an effect on the computed adsorption energy. Huang and Fabris21 analyzed the energetics of CO adsorption on ceria when surface reduction is involved, whereas the values $U_{\text{eff}} = 2\text{--}3\ eV$ are more appropriate. Still, experimental adsorption energies tend to have a large range, depending on the condition of the surface and the experimental technique used to measure them. Therefore, the effect of $U_{\text{eff}}$ on the redox reaction energies has not been settled.

In this work, we consider the redox pairs TiO$_2$/Ti$_2$O$_3$, V$_2$O$_5$/V$_2$O$_3$, MoO$_3$/MoO$_2$, and CeO$_2$/Ce$_2$O$_3$. We used bulk oxides in order to avoid the need to determine surface structures. To avoid the difficulties associated with the description of O$_2$ by DFT,13 we chose H$_2$ as the reducing agent and gas-phase H$_2$O as the oxidizing agent. The reduction energy of each oxide was measured them. Therefore, the value of $U_{\text{eff}}$ on the redox reaction energies has not been settled.

### COMPUTATIONAL APPROACH

All calculations were performed using the VASP 4.6 package.22,23 We used the revised Perdew–Burke–Ernzerhof (PBE) functional24 and the projector-augmented wave (PAW) potentials.25,26 The plane-wave cutoff was set to 500 eV. For integration over the Brillouin zone, Γ-centered sets of $k$ points were tested to achieve convergence better than 1 meV/atom. The resulting sets are $17 \times 17 \times 7$ for TiO$_2$, $5 \times 5 \times 5$ for Ti$_2$O$_3$, $3 \times 9 \times 9$ for V$_2$O$_5$, $5 \times 5 \times 11$ for V$_2$O$_3$, $7 \times 7 \times 7$ for V$_2$O$_5$, $6 \times 1 \times 6$ for MoO$_3$, $13 \times 13 \times 13$ for MoO$_2$, $11 \times 11 \times 7$ for Ce$_2$O$_3$, and $7 \times 7 \times 7$ for CeO$_2$. Integration was performed using the tetrahedron method with Bloch corrections.27 The crystal symmetry and magnetic properties of each oxide are listed in Table 1. The corundum structures of Ti$_2$O$_3$ and V$_2$O$_3$ have two choices of the unit cell in use: the primitive rhombohedral unit cell with compositions V$_4$O$_8$ and Ti$_4$O$_8$ and the hexagonal unit cell with compositions V$_{12}$O$_{18}$ and Ti$_{12}$O$_{18}$. The transformation of the lattice vectors and coordinates between the rhombohedral and hexagonal unit cells was described by Cousins.28 We used the rhombohedral cell for our calculations, but the lattice parameters discussed in the text correspond to the hexagonal lattice, as it is the one more commonly discussed. The oxide structures were fully optimized for each value of $U_{\text{eff}}$ tested. All calculations were tested to achieve convergence better than 1 meV/atom.

### Table 1. Symmetry and Magnetic Properties of the Oxides

| Oxide   | Symmetry     | Magnetic Arrangement at STP
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>$P4_1//mnm$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>$R3\bar{m}$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>$Pmmn$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>$P2_1//c$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>V$_2$O$_3$</td>
<td>$R3$</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>$Pmmn$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Mo$_2$O$_3$</td>
<td>$P2_1//c$</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>$Fm3m$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>$P3m1$</td>
<td>Antiferromagnetic</td>
</tr>
</tbody>
</table>

*STP = standard temperature and pressure.

### Table 2. Experimental Enthalpy of Formation and Enthalpy Change between 0 and 298.15 K

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\Delta H_{\text{f},0}$ (kJ/mol)</th>
<th>$H_{\text{f},298.15} - H_{\text{f},0}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>8$^{35}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$-243$</td>
<td>$-36$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>$-944$</td>
<td>$-97$</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>$-1521$</td>
<td>$-15$</td>
</tr>
<tr>
<td>V$_2$O$_3$</td>
<td>$-1551$</td>
<td>$-21$</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>$-714$</td>
<td>N/A</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>$-1217$</td>
<td>$-17$</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>$-745$</td>
<td>$13$</td>
</tr>
<tr>
<td>Mo$_2$O$_3$</td>
<td>$-589$</td>
<td>$8$</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>$-1090$</td>
<td>$10$</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>$-1800$</td>
<td>$21$</td>
</tr>
</tbody>
</table>

### Table 3. Dependence of Lattice Parameters (in Å) on $U_{\text{eff}}$

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$U_{\text{eff}}$ (eV)</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0</td>
<td>4.594</td>
<td>4.687</td>
<td>4.701</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.16</td>
<td>5.20</td>
<td>5.24</td>
</tr>
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<td></td>
<td>5</td>
<td>13.61</td>
<td>13.78</td>
<td>13.88</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4.368</td>
<td>5.339</td>
<td>5.382</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>0</td>
<td>5.743</td>
<td>5.861</td>
<td>5.969</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.517</td>
<td>4.609</td>
<td>4.665</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.375</td>
<td>4.585</td>
<td>4.506</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>0</td>
<td>3.963</td>
<td>4.047</td>
<td>4.020</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.855</td>
<td>17.184</td>
<td>17.180</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.696</td>
<td>3.682</td>
<td>3.704</td>
</tr>
<tr>
<td>Mo$_2$O$_3$</td>
<td>0</td>
<td>5.611</td>
<td>5.657</td>
<td>5.671</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.856</td>
<td>4.896</td>
<td>4.908</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.623</td>
<td>5.675</td>
<td>5.689</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>0</td>
<td>3.891</td>
<td>3.88</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.059</td>
<td>6.04</td>
<td>6.11</td>
</tr>
</tbody>
</table>

$^a$ $\theta = 122.61^\circ, 122.61^\circ, 121.961^\circ, 121.808^\circ$, and 121.841$ for experiment and $U_{\text{eff}} = 0.0, 2.0, 5.0$, and $8.0$ eV, respectively. $^b$ Value computed for $U_{\text{eff}} = 1.0$ eV.
initiated with the experimentally known values of the lattice parameters (see Table 3 below). The effect of \( U_{\text{eff}} \) on the oxide lattice parameters was determined, as well as the redox energy for each of the oxide pairs of interest.

Experimental enthalpies of formation used in this work are listed in Table 2. Because the energy changes determined by our calculations correspond to 0 K, to compare energies of reactions, it is necessary to subtract the enthalpy difference between 0 and 298.15 K. Unfortunately, we were not able to find the change in entropy of formation for VO\(_2\) between 0 and 298.15 K. We note, however, that for the overall redox reactions, this correction is below 6 kJ/mol, which is comparable to the error inherent in our theoretical method. Therefore, we chose not to make the correction in the enthalpy change with temperature.

\section*{RESULTS AND DISCUSSION}

\textbf{Oxidation Energy}. The effect of \( U_{\text{eff}} \) on the energy of reduction of TiO\(_2\) to Ti\(_2\)O\(_3\) according to the reaction

\[ 2\text{TiO}_2 + \text{H}_2 = \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \quad (2) \]

is shown in Figure 1. The experimental energy, 125 kJ/mol, is matched for \( U_{\text{eff}} = 2.3 \) eV. This value is significantly smaller than that suggested by Morgan and Watson, \( U_{\text{eff}} = 4.2 \) eV, which was obtained by optimizing the position of the oxygen vacancy states in the electronic spectra of rutile.\(^{14}\) Our finding is similar to the conclusion of Hu and Metiu in a recent publication.\(^{29}\) They recommended using a \( U_{\text{eff}} \) value between 2 and 3 eV. The authors used this value of \( U_{\text{eff}} \) to compare the concentration of oxygen vacancies in rutile and anatase.\(^{30}\) We note, however, that the value of \( U_{\text{eff}} \) determined by Morgan and Watson overestimates the enthalpy change for reaction 2 by 17 kJ/mol.

Vanadium is the only element for which we considered more than two oxides. Therefore, it is an instructive example of the limitations of the DFT+U methodology. Figures 2 and 3 summarize the dependence on \( U \) of the reactions

\[ \text{V}_2\text{O}_5 + \text{H}_2 = 2\text{VO}_2 + \text{H}_2\text{O} \quad (3) \]

\[ \text{V}_2\text{O}_5 + 2\text{H}_2 = \text{V}_2\text{O}_3 + 2\text{H}_2\text{O} \quad (4) \]

The two reactions also can be combined to obtain

\[ 2\text{VO}_2 + \text{H}_2 = \text{V}_2\text{O}_3 + \text{H}_2\text{O} \quad (5) \]

The experimental reaction enthalpies are −119 kJ/mol for reaction 3, −150 kJ/mol for reaction 4, and −31 kJ/mol for reaction 5. From Figures 2 and 3, one can see that, although the optimal values of the on-site repulsion term are similar for the three reactions, they are not identical. The optimal values of \( U_{\text{eff}} \) for reactions 3 and 4 are 2.3 and 1.8 eV, respectively. The difference between these two values is in line with that reported by Wang et al.\(^{13}\) The optimal value for reaction 5 is \( U_{\text{eff}} = 1.1 \) eV. Therefore, although the equilibrium between V\(_2\)O\(_5\) and V\(_2\)O\(_3\) seems to be described reasonably well, VO\(_2\) is artificially destabilized by the same choice of the parameter. By contrast, Scanlon et al. suggested \( U_{\text{eff}} = 4.0 \) eV based on a comparison of the computed electronic spectra with the experimental ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) data.\(^{7}\) This value results in enthalpies that are lower than those observed experimentally by about 100 kJ/mol for each of the reactions. Figures 2 and 3 also show that the relative energies of the reactions diverge, rather than shifting by a
constant value, which makes calculations for metals with multiple oxidation states particularly sensitive to the choice of $U_{\text{eff}}$.

The energy of reduction for the reaction

$$\text{MoO}_3 + \text{H}_2 = \text{MoO}_2 + \text{H}_2\text{O}$$ (6)

is $86 \text{ kJ/mol}$ and can be matched using a value of $U_{\text{eff}} = 8.6 \text{ eV}$, as can be seen from Figure 4. Once again, this value differs from those previously reported. Coquet and Willock$^5$ used the DFT + U method with the PBE functional to study the formation of oxygen defects on the (010) surface of $\alpha$-MoO$_3$. From comparison of periodic plane-wave and cluster calculations, they arrived at the value of $U_{\text{eff}} = 6.3 \text{ eV}$. On the other hand, in a study of magnetism in MoO$_2$, Wang et al.$^17$ used a range of values for $U_{\text{eff}}$ between 1 and $-1 \text{ eV}$, citing weak correlation in Mo.

Cerium dioxide (CeO$_2$) is used as an oxygen-storage material for the three-way control of automotive emissions. Consequently, a number of authors have examined the issue of parametrization of the DFT+U method. Fabris et al.$^{10}$ suggested that the optimal value of $U_{\text{eff}}$ required to match the energy for the reaction

$$2\text{CeO}_2 = \text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2$$ (7)

is around $1 \text{ eV}$ for GGA+U with atomic-like orbital projectors. Jiang et al.$^{18}$ used GGA+U to compute the effects of oxygen partial pressure on the CeO$_2$ surfaces. They calibrated $U_{\text{eff}}$ to the electronic spectra and arrived at a value of $6.3 \text{ eV}$. Skorodumova et al.$^{16}$ have published several articles on cerium oxides, and in a recent publication, they dealt with the choice of the Coulomb repulsion parameter for reaction 7. The raw data suggested an optimal value of $U_{\text{eff}}$ for the GGA functional of about $2 \text{ eV}$; however, the authors noted that the binding energy of O$_2$ used in their calculations was overestimated, and hence, they recommended the value of $U_{\text{eff}} = 5 \text{ eV}$. Nolan et al.$^{19}$ obtained a value of $U_{\text{eff}}$ in their study of ceria surfaces based on the degree of delocalization of the f electrons. They observed that, for $U_{\text{eff}} < 5$, the electrons were partly delocalized, but at $U_{\text{eff}} = 5 \text{ eV}$, localization became complete, leading them to conclude that the appropriate value was $U_{\text{eff}} = 5 \text{ eV}$. This value of $U_{\text{eff}}$ was later used for a study of NO$_2$ adsorption on ceria.$^{31}$ Castleton et al. optimized the value of $U_{\text{eff}}$ for electronic spectra and structure and recommended $U_{\text{eff}} = 5.5 \text{ eV}$ for GGA+U, conceding it as a compromise between several properties. Da Silva et al.$^{32}$ compared the performances of the hybrid and GGA functionals, including GGA+U. They noted the large deviation of the oxidation energy with a typical estimation of $U_{\text{eff}} = 4.5 \text{ eV}$ from the experimental values and suggested that the value of $2 \text{ eV}$ be used instead. This conclusion coincides with the results of Loschen et al.$^{33}$ Huang and Fabris$^{21}$ also suggested a value for $U_{\text{eff}}$ of $2-3 \text{ eV}$ based on their calculations of the energy for CO adsorption.

The reaction considered in the present study is

$$2\text{CeO}_2 + \text{H}_2 = \text{Ce}_2\text{O}_3 + \text{H}_2\text{O}$$ (8)

As seen in Figure 5, varying the value of $U_{\text{eff}}$ from 0 to $6 \text{ eV}$ changes the enthalpy of reaction 8 by more than 200 kJ/mol, as well as its sign. The experimental value of $138 \text{ kJ/mol}$ is matched with $U_{\text{eff}} = 0.2 \text{ eV}$. However, if one uses the commonly recommended value of $4.5 \text{ eV}$, the reaction enthalpy becomes $-31 \text{ kJ/mol}$, which is almost $170 \text{ kJ/mol}$ lower than the experimental value.

**Lattice Parameters.** The GGA in general produces inaccurate lattice constants, and we would not suggest using these parameters to fit the value of $U_{\text{eff}}$. However, we include a discussion of lattice parameters for two reasons. First, the data are already available from the present calculations. Second, because lattice parameters are sometimes used as one of several parameters to justify the selection of the value of $U_{\text{eff}}$, it is important to discuss what sort of errors should be expected from a given choice of $U_{\text{eff}}$.

The effect of $U_{\text{eff}}$ on the lattice parameters of the oxides investigated in this study is shown in Table 3. In all cases, the lattice parameters are overestimated using the GGA functional, and the extent of overestimation increases as the Coulomb repulsion term grows. Therefore, GGA+U worsens the description of the crystal lattice compared to that obtained with GGA. By contrast, the local density approximation (LDA) functional typically underestimates lattice constants, so the use of LDA+U is a viable means for determining values of $U_{\text{eff}}$ required to match calculated and observed lattice parameters.

The single exception to the trend in lattice parameters with $U_{\text{eff}}$ is MoO$_3$, for which the lattice parameters $a$ and $b$ generally decrease with increasing values of $U_{\text{eff}}$ and the parameter $c$ increases. This structure is characterized by well-defined layers perpendicular to the $b$ axis. The interactions between the layers are weak and presumably largely of van der Waals in character. Studies by
Coquet and Willock\textsuperscript{a} and Scanlon et al.\textsuperscript{34} indicated that the effect of such weak binding was the absence of a minimum in the plot of energy versus the length of the b lattice parameter. These two studies worked around the problem by freezing the b vector at its experimental value and then relaxing the a and c parameters so as to minimize the total energy. In our study, we were able to locate such a minimum, by frequent updates to the plane wave basis set. The optimized b vector was overestimated by a much larger amount than is typical of GGA. Nevertheless, we decided against using the DFT+U method, the value of U of MoO\textsubscript{3}, all atoms should be allowed to contribute due to relaxation of the lattice. We believe that, for the MoO\textsubscript{3}/MoO\textsubscript{2} pair, to about 100 kJ/mol of enthalpy per Bader electron charge. Laubach et al.\textsuperscript{123} indicated that the e\textsubscript{ff} energy versus the length of the lattice parameter. These two edges the support of the French Ministry of Research through the master’s program at ENS Lyon. We also thank Andrew Getsoian at University of California-Berkeley for his contribution to calculations for MoO\textsubscript{2}.

\section*{REFERENCES}


\section*{AUTHOR INFORMATION}

\section*{Corresponding Author}

*E-mail: bell@chem.berkeley.edu.

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