# Choice of U for DFT+U Calculations for Titanium Oxides

Zhenpeng Hu and Horia Metiu*

Department of Chemistry and Biochemistry, and Department of Chemical Engineering, University of California, Santa Barbara, California 93106, United States

ABSTRACT: Many recent articles have suggested that density functional theory (DFT) with the generalized-gradient approximation does not provide the correct electronic structure for the oxides of titanium. The current opinion is that a Hubbard U correction improves the DFT results. There is no generally accepted method for deciding what the value of the U parameter should be, and we propose that, if one intends to study catalysis, U should be chosen to fit the reaction energy for the oxidation of Ti_2O_3 to TiO_2. We show that the value of U derived in this manner provides additional improvements in the description of the electronic structure.
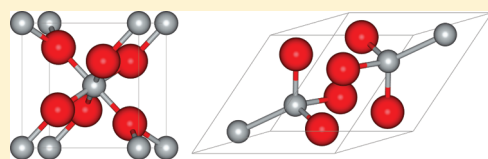
1. INTRODUCTION

The study of catalysis by oxides benefits from calculations using density functional theory (DFT) to find possible intermediates, to help assign spectra, or to determine the activation energies and reaction mechanism. In the past few years it has been repeatedly pointed out that DFT with the generalized-gradient approximation (GGA), or with the local density approximation (LDA), has some shortcomings when used to calculate the properties of transition metals or rare-earth oxides (see reviews by Pacchioni[1] and Ganduglia-Pirovano, Hoffmann and Sauer[2]). Since the objections stem from the manner in which DFT deals with the cations, the same shortcomings ought to be present when the theory is applied to sulfides, halides, or other solid compounds of these metals.

As is well-known, in DFT, the difference between the bottom of the conduction band and the top of the valence band is smaller than the measured band gap. This is true for all oxides, but it is particularly severe for Ti_2O_3; normal DFT calculations find that Ti_2O_3 is a metal[3] while the experiments show that it is an insulator[4−6] with a band gap[7] of 1 eV. Moreover, it is expected[1,2] that when oxygen vacancies are formed in TiO_2 the unpaired electrons left behind after removing an oxygen atom should be housed in orbitals that are localized on the Ti atoms and whose energy is in the band gap; GGA-DFT calculations[8−13] do not fulfill these expectations. It is believed that the main reason for these difficulties is the electron self-interaction in DFT. Methods that remove the self-interaction, such as exact-exchange or self-interaction corrected DFT, require too much computer power to be useful for computations on catalysis. A possible, practical cure may be provided by the GGA+U theory. This prevents the unwanted delocalization of the d- or f-electrons, by adding to the Hamiltonian a term that increases the total energy when two d- or f-electrons are located on the same cation. Hybrid functionals are also an improvement over ordinary GGA-DFT, because they use some Hartree−Fock exchange for a partial cancellation of the self-interaction; unfortunately this gain in quality is at the expense of efficiency, and the hybrid functionals are of limited usefulness in heterogeneous catalysis research.
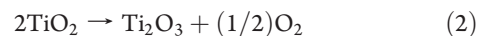
Most oxidation reactions, in which TiO_2 is involved as a catalyst or as a support, occur through a Mars−van Krevelen mechanism,[14−16] in which the oxide is reduced and reoxidized during the catalytic cycle; the Ti atoms involved in catalysis change their valence from IV to III and back to IV. Therefore, it is necessary to find a suitable U value for DFT+U calculation on catalysis reactions involving titanium oxide.

Previous work[17−27] has recommended a variety of values for U. Depending on the quantity fitted, the U values were in a wide range from 2.5 to 10 eV. There is no consensus regarding the procedure by which U is chosen or the best value for U. Most of the previous work determined U so that the energies of some of the Kohn−Sham orbitals match the excitation energies measured by "one-electron spectroscopy", such as the band gap[17−19] of TiO_2, the energy of the states in the band gap[20−22] of partially reduced TiO_2, or the XPS spectrum.[28] In other papers U was calculated by a variety of methods.[24−26,29]

In this article, we propose a choice of U for TiO_2 that is designed to make the DFT+U method useful for calculations aimed at understanding catalysis. Because catalysis is controlled exclusively by energy differences, it is natural to choose U to fit the energy of the "redox" reactions

$$2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O \qquad (1)$$

and

$$2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2 \qquad (2)$$
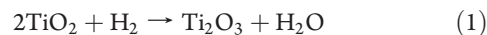
These are relevant to catalysis because most oxidation reactions involving TiO_2 take place thorough a mechanism in which Ti is reduced and then reoxidized.

Our confidence in the value of U given by this fitting is increased if other criteria are also satisfied. While we do not believe that the KS energies should coincide with the ones measured by one-electron spectroscopy, it is reasonable to
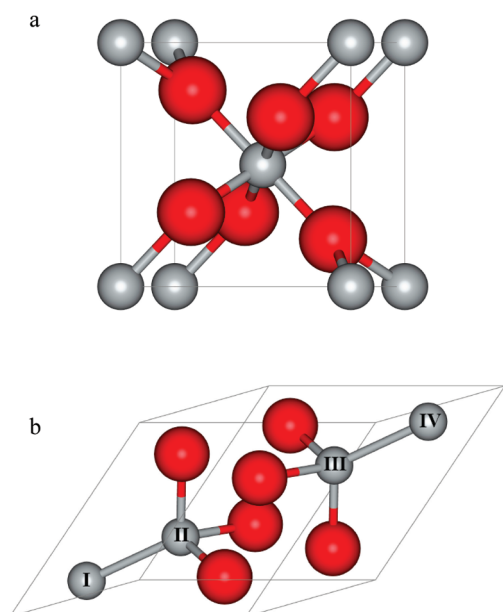
Figure 1. Unit cell used in the bulk calculations: (a) rutile TiO_2 and (b) Ti_2O_3. The red spheres are O atoms; the gray spheres are Ti atoms.

require that they should be qualitatively similar. Thus, we expect that if U is "correct", Ti_2O_3 should be an insulator (normal DFT calculations find that it is a metal) and that the formation of oxygen vacancies should create KS orbitals in the gap of TiO_2.

We also perform hybrid functional calculations (B3LYP, B3PW, and PBE0) for bulk Ti_2O_3 and TiO_2 to test whether this method of self-interaction removal gives satisfactory energies for these reactions.

In principle, more data should be fitted, but the structure of TiO is not well established, the energy differences between rutile, anatase, and brookite are smaller than the expected accuracy of DFT, Ti halides are not solids, and the sulfides have an ill-defined structure. Furthermore, reliable desorption energies for molecules on titanium oxides are not available because of the difficulty of preparing well-defined surfaces in ultrahigh vacuum (steps and oxygen vacancies are always present).

We find that a U value between 2 and 3 eV, used with the PW91 or the PBE functional but not with LDA, satisfies all these criteria. The hybrid functionals give remarkably accurate reaction energies and reasonable band gaps, as compared to GGA or GGA+U.

2. METHODOLOGY

The primitive unit cell for bulk rutile TiO_2 calculations is a rectangular box containing two Ti atoms and four O atoms with $P4_2/mnm$ symmetry (Figure 1a). For bulk Ti_2O_3 calculations, the primitive cell is a rhombohedral box (Figure 1b) containing four Ti atoms (I, II, III, and IV along the [111] direction) and six O atoms, with $R\bar{3}c$ symmetry.

The GGA-DFT and the DFT+U calculations were performed with the VASP code.[30−32] We used three functionals (LDA,[33] PW91,[34] and PBE[35]) and the projector augmented wave[36,37] (PAW) pseudopotential. The electrons in the 3p, 4s, and 3d shells of Ti and in the 2s, 2p shells of O were included explicitly in all calculations. The parameter U for Ti was varied between 0 and 6 eV. All "+U" calculations used Dudarev's approximation[38] with

Table 1. Energies of the Reactions $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$ and $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$ (in eV) Calculated by Various Methods[a]

	$2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$, exp = 3.81 eV					
U	LDA+U	PW91+U	PBE+U	B3LYP	B3PW	PBE0
0	3.90	3.69	3.62	4.045	3.901	**3.852**
1	4.06	**3.83**	**3.77**	(4.163)	(3.992)	
2	4.20	3.93 S	3.83 S			
3	4.26 S	**3.74 SG**	**3.60 SG**			
4	4.06 SGL	3.39 S	3.25 S			
5	**3.72 S**	2.99 S	2.84 S			
6	3.32 S	2.56 S	2.40 S			

	$2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$, exp = 1.30 eV					
U	LDA+U	PW91+U	PBE+U	B3LYP	B3PW	PBE0
0	1.00	1.11	1.08	**1.39**	1.18	1.06
1	1.15	**1.26**	**1.23**	(1.54)	(**1.31**)	
2	**1.29**	**1.36 S**	**1.30 S**			
3	**1.35 S**	1.16 SGL	1.07 SGL			
4	1.15 SG	0.82 S	0.99 S			
5	0.81 S	0.42 S	0.31 S			
6	0.41 S	0.02 S	.			

[a] The experimental standard heats of reactions are 3.81 and 1.30 eV, respectively. The values in parentheses, for the hybrid functionals, were obtained by using 15% Hartree−Fock exchange. S indicates that the calculations give the correct spin ordering for Ti_2O_3. G indicates that the calculation gives good values for the band gap of Ti_2O_3. L indicates that a calculation gives correct values for the lattice parameter ratio c/a of Ti_2O_3. The numbers in bold are the calculated heats of reaction that are closest to the standard reaction enthalpy.

U equivalent to the U_{eff} parameter ($U_{eff} = U - J$). For geometry optimization, the plane-wave cutoff was 500 eV, and the convergence criteria were 10^{-4} eV for energy and 0.01 eV/Å for stress. Once the optimum energy was found, we used a plane-wave cutoff of 400 eV with an energy convergence criterion of 10^{-5} eV, to get the single-point energy and see the effect of different U values. In all calculations, we used a gamma-centered $13 \times 13 \times 13$ k-point mesh for Ti_2O_3 and a gamma-centered $13 \times 13 \times 17$ k-point mesh for rutile TiO_2. A finer $21 \times 21 \times 21(25)$ k-point mesh was also tested, which allowed us to conclude that the $13 \times 13 \times 13(17)$ k-point mesh was good enough.

The lattice parameter of the supercell has been optimized for each value of U. We also performed calculations with different values of U that used the lattice parameters obtained with GGA-DFT, as has sometimes been done.[26,28] The difference between the energies calculated in this way and those obtained by optimizing the geometry is less than 0.2 eV.

The hybrid functional calculations, using the B3LYP,[39−41] B3PW,[34,39,41] and PBE0[42] functionals, were performed with the Crystal06 code.[43] These spin-polarized calculations used the following Gaussian basis sets: 8-411G*, for O the atoms, and 8-6-411G, for the Ti atoms.[44] The five tolerances for Coulomb and exchange integrals were set to 10^{-8}, 10^{-8}, 10^{-8}, 10^{-8}, and 10^{-16} atomic units, respectively. An extra large grid (XXLGRID) for numerical integrals, the shrink factor 10 10 for Ti_2O_3 (8 8 for TiO_2), and the single-point energy convergence of 10^{-6} au were used to improve the accuracy of the results.
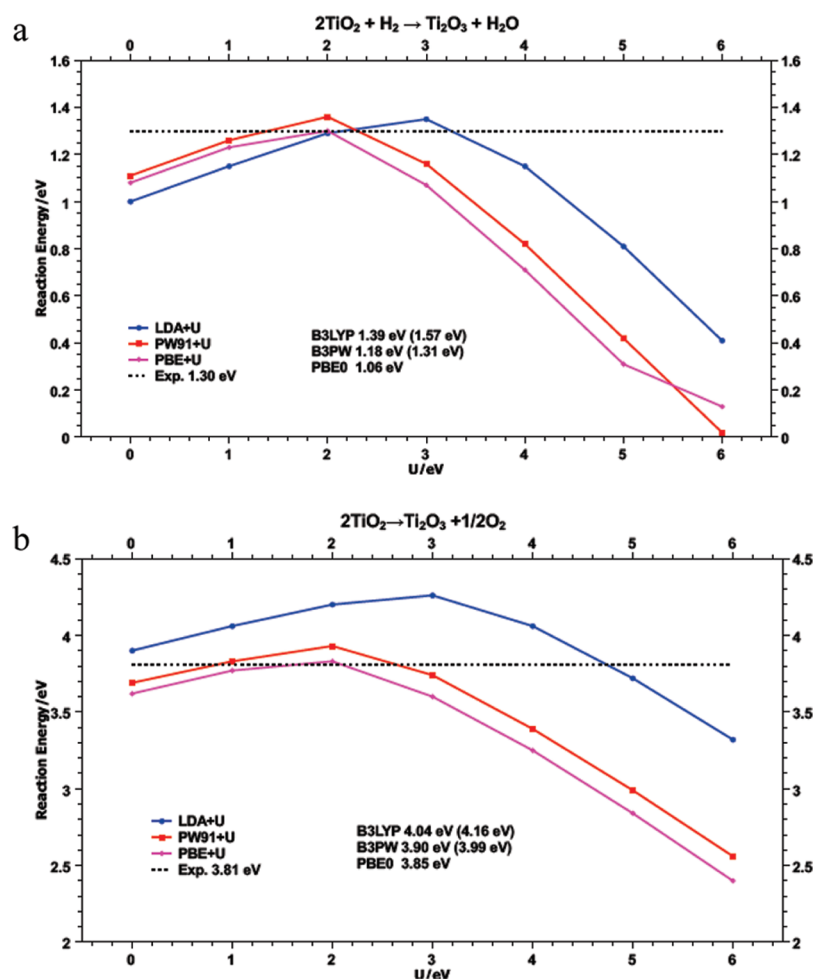
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dx.doi.org/10.1021/jp111350u |J. Phys. Chem. C 2011, 115, 5841–5845

Figure 2. (a) Energy of the reaction $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$ as a function of U. (b) Energy of the reaction $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$ as a function of U.

3. RESULTS FOR GGA AND GGA+U

3.1. The Energy of Reaction. As explained in section 1, we wish to find a value of U for which DFT+U describes well the energies of the reactions $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$ and $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$, and for which Ti_2O_3 is an insulator with the correct magnetic ordering. We place a greater emphasis on the reduction of TiO_2 with H_2 because that reaction does not involve O_2, a molecule for which DFT does not give the correct bond energy.

The energy of the reactions, calculated with LDA+U, PW91+U, and PBE+U, for U varying, in increments of 1, from 0 to 6, are given in Table 1 and are plotted in Figure 2.

Since we trust most the results obtained for the reduction of TiO_2 with hydrogen, we recommend using U between 2 and 3 eV for PW91+U or for PBE+U. The same values of U give good results for the energy of oxidation of Ti_2O_3 with oxygen. We recommend against using LDA+U, for the following reason: the reaction energy for $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$ is close to experiment if $U = 5$ eV, but reasonable energies for $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$ are obtained for $U = 3$ eV. We believe that it is not acceptable to use different values of U, for a given functional, when dealing with two reactions involving the reduction of the same oxide.

It is reasonable to expect that the value of U might depend on the Ti−Ti distance and the environment of the Ti atoms. If this dependence is strong, it would be very difficult to determine a value of U that is entirely atom-dependent and the GGA+U method would have limited usefulness. It is therefore comforting to see that using the same U for Ti_2O_3 and TiO_2 leads to reasonable results.

3.2. Lattice Parameters. It is well-known that GGA-DFT does not give accurate values for lattice parameters.[20,26,28,45,46] We cannot find a value of U for which the GGA+U calculations give a good agreement with both the lattice constants and the heats of the two reactions considered here.

3.3. Band Gaps. Figures 3a and b show the dependence of the band gaps of Ti_2O_3 and TiO_2, respectively, on U. Ti_2O_3 is an insulator[4−6] with a band gap[7] of 1 eV. Like previous calculations,[3] our LDA and GGA calculations (with the PW91 and PBE functionals) give no band gap: according to LDA or GGA, Ti_2O_3 is a metal. A gap opens when $U \geq 2$ eV, and it is close to the experimental value when $U = 3$ eV. As U increases the band gap of rutile TiO_2 increases, but it never reaches the experimental value[47] of 3 eV. Previous work[17,19] has shown that to obtain a band gap of 3 eV one must use $U = 10$ eV. As we have already stated, we believe that DFT calculations need not give the correct band gap, but it is important that Ti_2O_3 is no longer a metal when $U > 2$ eV.

3.4. The Spin States of Ti_2O_3. The primitive unit cell of Ti_2O_3 has four Ti atoms, each having one d-electron. Several electronic states, which differ through the orientation of the spins on these four atoms, are possible. We find that for $U \geq 2$ the spin state
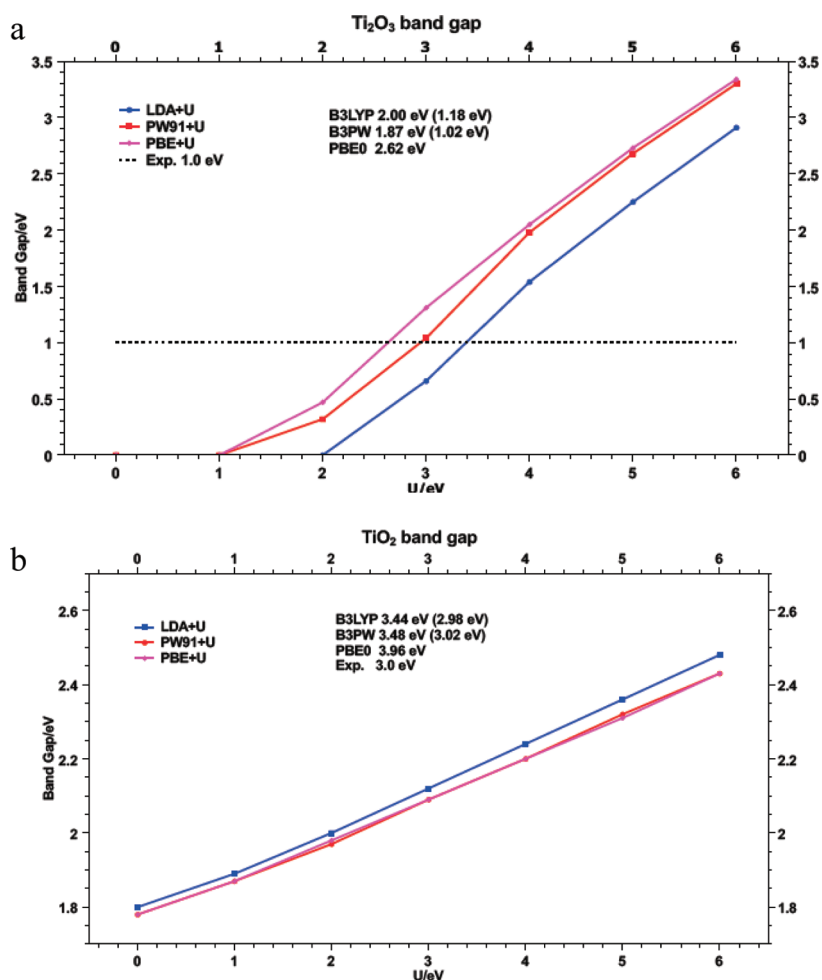
Figure 3. (a) Band gap of Ti_2O_3 as a function of U. (b) Band gap of rutile TiO_2 as a function of U.

having the lowest energy is $(+, -, -, +)$, where atom I in Figure 1b has spin up, atom II in Figure 1b has spin down, etc. This is in agreement with previous reports.[4,44] However, the energy differences between various spin states are very small, and, given the errors expected in DFT calculations, it is questionable whether obtaining the correct spin-ordering is significant.

4. RESULTS FOR HYBRID FUNCTIONALS

The hybrid functionals counteract the ill effects of electron self-interaction by using some Hartree−Fock (HF) exchange. They are expected to do better with titanium oxides than GGA. To test this belief we calculated the energies of the reactions $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$ and $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$ by using B3LYP, B3PW, and PBE0. While the original derivation of the hybrid functionals fixed the amount of Hartree−Fock exchange to 20%, this percentage can be viewed as an adjustable parameter. To explore what happens if we change it, we performed a few calculations with 15% Hartree−Fock exchange.

For the reaction $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$, the difference between the calculated heats of reaction and the reaction enthalpy is 0.09 eV (a 6.9% deviation) for B3LYP, −0.12 eV (a 9.2% deviation) for B3PW, and −0.24 eV (a 18.5% deviation) for PBE0. Changing the percentage of Hartree−Fock exchange to 15% (values in bracket, in Figure 2a) makes the calculated energies worse. For the reaction $2TiO_2 \rightarrow Ti_2O_3 + (1/2)O_2$,

the results are 4.04 eV for B3LYP, 3.90 eV for B3PW, and 3.85 eV for PBE0, while the standard enthalpy of reaction is 3.81 eV. This leads to the following errors: 6% for B3LYP, 2.6% for B3PW, and 1.04% for PBE0. The agreement with the experiment is remarkable, considering that there is no adjustable parameter in these procedures. Changing the amount of Hartree−Fock exchange to 15% makes the agreement with the experiment worse (but the error is not large). As far as the reaction energies are concerned, there is no preferred hybrid functional, and, as a rule of thumb, we should expect errors of 0.2 eV or less.

The calculated band gap of rutile TiO_2 (see Figure 3b) is 3.44, 3.48, and 3.96 eV, for B3LYP, B3PW, and PBE0, respectively. These values are larger than the measured value[47] of 3.0 eV. The calculated band gap for Ti_2O_3 is 2.00 eV for B3LYP, 1.87 eV for B3PW, and 2.62 eV for PBE0. The experimental value is 1 eV. Using 15% Hartree−Fock exchange improves the band gaps but gives worse energies than the conventional value of 20%.

A further test was performed for B3PW with 15% Hartree− Fock exchange. We calculated the band gap of a system in which a Ti atom, out of the 16 atoms in the TiO_2 supercell, was replaced with a V atom. The presence of the V dopant shifts the band gap to[7] 0.80 eV, and the calculated band gap for this system is 0.76 eV. The good agreement is probably accidental, but it is satisfying to see that the trend is correct: doping with V lowers the gap.

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dx.doi.org/10.1021/jp111350u |*J. Phys. Chem. C* 2011, 115, 5841–5845

5. SUMMARY

We propose that, if one is interested in redox catalysis by TiO_2, one should use either PBE+U or PW91+U, with $U = 2-3$ eV, because such calculations give reasonable values for the energy of reduction of TiO_2 to Ti_2O_3. While we do not expect the Kohn−Sham orbital energies to give the correct band gap, we are gratified that with our choice of U, Ti_2O_3 is no longer a metal and it has the correct spin state. Since calculations using hybrid functionals consume more computer power, we recommend using DFT+U for studying catalysis by the oxides of the transition metals and rare-earth metals. While the calculations are not highly accurate, many questions in catalysis can be settled reliably if the error in total energy differences are less than ~0.2 eV.

■ AUTHOR INFORMATION

Corresponding Author
*Tel (805) 893-2256; fax (805) 893-4120; e-mail metiu@chem.ucsb.edu.

■ ACKNOWLEDGMENT

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