Critical Assessment of the DFT + U Approach for the Prediction of Vanadium Dioxide Properties

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In a previous study (Stahl and Bredow, Chem. Phys. Lett. 2018, 695, 28–33), we have studied structural, energetic, and electronic properties of two vanadium dioxide VO₂ polymorphs with modified global and range-separated hybrid functionals. Since hybrid methods are computationally demanding, we evaluate the computationally more efficient DFT + U method in the present study. We assessed the widely used Dudarev PBE + U approach with a literature value of the effective Hubbard parameter \( U_{\text{eff}} = 3.4 \text{ eV} \). We compared the PBE + U results for the two VO₂ polymorphs with our previous results, a self-consistent hybrid functional sc-PBE0, and the \( \text{meta-GGA} \) functional SCAN. It was found that the PBE + U method yields a strongly distorted monoclinic phase and does not reproduce the metal-to-insulator transition of VO₂ correctly, even with modified values of \( U_{\text{eff}} \). On the other hand, sc-PBE0 and SCAN describe the relative stability and the electronic structure of both polymorphs correctly and also provide reasonable lattice parameters. The functional SCAN yields the optimal balance between computational efficiency and accuracy.

Introduction

The DFT + U approach is nowadays widely applied to model strongly correlated systems, in particular open-shell transition metals compounds, in order to overcome known shortcomings of standard local and semi-local Kohn–Sham density-functional theory (DFT). The main reason for this failure is the self-interaction error and, consequently, the artificial electron delocalization.\(^{[1,2]}\) In order to diminish these problems, the DFT + U approach has been introduced as a computationally efficient correction of DFT. The DFT + U method is a combination of DFT and the Hubbard model.\(^{[3,4]}\) Intra-atomic Coulomb and exchange integrals are replaced by parameters \( U \) and \( J \), respectively. In this article, we focus on the DFT + U implementation by Dudarev et al.\(^{[5]}\) This simplified approach employs an effective parameter \( U_{\text{eff}} = U - J \). The energy is calculated as follows:

\[
E_{\text{DFT} + U} = E_{\text{DFT}} + \frac{(U-J)}{2} \sum_{\sigma} \left[ \left( \sum_{m_1} n_{m_1m_2}^{\sigma} \sigma \right) - \left( \sum_{m_1,m_2} n_{m_1m_2}^{\sigma} n_{m_2m_1}^{\sigma} \sigma \right) \right].
\]

This equation is derived from the Hubbard Hamiltonian with occupation numbers \( n \) of selected electronic states \( m_1 \) and \( m_2 \) with spin \( \sigma \). It is known that the simplified approach may be inaccurate for the description of magnetic states.\(^{[6]}\) Another well-known problem of the DFT + U approach is that, in principle, individual \( U_{\text{eff}} \) parameters have to be obtained for every compound and element.\(^{[1,2,7,8]}\) The optimal parameters are usually obtained in an empirical way by adjusting calculated electronic band gaps to experimental reference values. A previous study\(^{[9]}\) that tried to calibrate the \( U_{\text{eff}} \) parameters for various transition metal oxide reductions including the reduction of \( V_2O_5 \) to VO₂ and VO₂ to \( V_2O_3 \) it was found that a \( U_{\text{eff}} \) parameters optimized to fit the band gap or lattice parameters, does not yield accurate energies. Many approaches have been developed to calculate the effective \( U \) parameter non-empirically. One of these is based on linear response theory,\(^{[10]}\) first developed by Anisimov and Gunnarsson.\(^{[11]}\) Another approach is based on a local-orbital expansion.\(^{[12]}\) The constrained random-phase approximation has also been used to calculate the effective \( U \) parameter.\(^{[13,14]}\) More recently, self-consistent methods to obtain \( U_{\text{eff}} \) parameters from the local electron density based on the Thomas–Fermi screening model\(^{[15]}\) or linear response theory\(^{[16]}\) have been introduced.

In the present study, the accuracy of the widely used Dudarev DFT + U approach is assessed for the calculation of bulk properties of vanadium dioxide. VO₂ was chosen as an example because it has been extensively studied, both experimentally and theoretically, for example, with diffusion quantum Monte Carlo (DQMC)\(^{[17]}\) and dynamical mean field theory (DMFT).\(^{[18,19]}\) Therefore, accurate reference values are available for structural, energetic, electronic, and magnetic properties.

At 340 K, VO₂ exhibits a transition from a monoclinic semiconductor (\( \text{M}_{1} \)) phase to a metallic phase with rutile structure (\( \text{R} \)).\(^{[20]}\) The phase transition is accompanied by a change from
an antiferromagnetic to a paramagnetic spin state.\cite{17,21,22} The heat of transition from R to M$_1$ was measured as $-0.044$ eV.\cite{23} The relative energy $\Delta E_{M_1-R}$ has been calculated as $-0.008$ eV with DQMC.

The results of the DFT + U method obtained for the two VO$_2$ polymorphs are compared with those obtained in our previous study.\cite{24} For comparison, we additionally perform self-consistent hybrid and meta-GGA (general gradient approximation) functional calculations in this study. A nonempirical self-consistent hybrid functional based on the static electronic dielectric constant $\varepsilon_{\infty}$ [eq. (3)] is employed here in continuation of our previous work in which we empirically adjusted the amount $\alpha$ [eq. (2)] of Fock exchange in hybrid functionals.\cite{24} Adjustment of $\alpha$ is necessary because standard hybrid functionals describe both VO$_2$ phases as insulators. The meta-GGA functional SCAN\cite{25} was considered because it has been shown to yield accurate structure parameters as well as the correct energetic order of the two VO$_2$ phases.\cite{17}

In this study, we will analyze the quality of these methods with respect to the phase transition of VO$_2$, which is relevant for the practical applications.\cite{26}

**Methodology**

GGA + U and meta-GGA calculations were performed with the plane-wave program VASP (version 5.4.4).\cite{27-29} The simplified, rotationally invariant Hubbard correction introduced by Dudarev et al.\cite{5} was applied to the GGA functional PBE.\cite{30}

After convergence tests, a $9 \times 9 \times 9$ k-point mesh and a cutoff energy $E_{\text{cut}} = 900$ eV were used. The RMM-Diis algorithm was employed for structure optimizations. The Methfessel–Paxton smearing with $\tau = 0.05$ eV was used for the optimizations. The band gaps and relative energies were calculated using the tetrahedron method with Blöchl corrections.

In line with our previous work, the program CRYSTAL17 (version 1.0.2)\cite{31} was used for self-consistent hybrid calculations based on the functional PBE0.\cite{32} The revised pob-def2-TZVP basis sets\cite{33} were selected for V and O. The amount $\alpha$ of Fock exchange in the exchange functional was calculated iteratively from the inverse of the dielectric constant $\varepsilon_{\infty}$.\cite{34}

$$E_{\text{hyb}} = \alpha E_{\text{Fock}} + (1-\alpha)E_{\text{GGA}}$$

$$\alpha = 1/\varepsilon_{\infty}$$

The dielectric constant is calculated using coupled-perturbed Kohn–Sham (CPKS) theory based on the wave function obtained with updated $\alpha$ from eq. (3). After convergence, $\alpha = 12.7\%$ was obtained for the monoclinic phase. For the metallic rutile VO$_2$ phase, the converged value of $\alpha$ is close to zero, 0.0032%, which essentially reduces sc-PBE0 to the standard PBE functional. Since we are interested in the relative phase stability, the M$_1$ phase value of $\alpha = 12.7\%$ was used in all calculations if not noted otherwise. The CRYSTAL hybrid DFT calculations employed a $12 \times 12 \times 12$ k-point mesh and strict values of the integral truncation tolerances ($10^{-6}$, $10^{-9}$, $10^{-15}$, $10^{-16}$, $10^{-18}$).

For both polymorphs, a diamagnetic (dm) and a ferromagnetic (fm) states were considered. Additionally, every possible antiferromagnetic spin distribution in the primitive unit cell was computed in the broken symmetry approximation. In the initial guess, local magnetizations (up, u and down, d) were assigned to the four V atoms of the unit cell. Unless specified otherwise, the calculations were done in the antiferromagnetic udud state to compare the results to our previous investigations, where only this spin state was considered. In Table 1, the four symmetry inequivalent combinations are given.

**Results**

For better comparison, the rutile phase was calculated not only in the original space group (P4$_2$/mnm, No. 136) but also in the space group (P2$_1$/c, No. 14) of the monoclinic phase. The latter approach is important for the consistent calculation of antiferromagnetic spin states in both phases. The lattice transformation was performed using the Bilbao crystallography server.\cite{37-39} The transformation matrix and origin shift the program uses to transform the structure are shown in the Supporting Information section. For diamagnetic (dm) and ferromagnetic (fm) states, the crystal structures obtained with both unit cells are essentially the same (see Table S1 in the Supporting Information).

The main difference between the rutile and the monoclinic phases is the V–V distance along the quasi-linear chains (see Figs. 1a and 1b). In the rutile structure, all V atoms are equidistant, while there is a pronounced bond alternation in the monoclinic phase. These distances are therefore listed in the following section, together with calculated band gaps and relative energies.

**PBE + U**

The dependence of the calculated band gaps and the relative energy $\Delta E_{M_1-R}$ from $U_{\text{eff}}$ was investigated. This was carried out using the experimental structures, taken from Ref. [49] and Ref. [50]. The results are shown in Figures 2 and 3.

| Spin states | Band gap | V–V distances | $(M_1)$ | Band gap | V–V distance | $\Delta E_{M_1-R}$ |
|-------------|----------|---------------|--------|----------|--------------|-------------------|
| dm          | 0.65     | 2.52, 3.16    |        | 0.00     | 2.79         | 0.38              |
| uudud       | 1.32     | 3.04, 3.04    |        | 0.87     | 2.92         | 0.20              |
| uuddu       | 1.17     | 3.02, 3.02    |        | 1.17     | 3.02         | 0.00              |
| uuuddu      | 1.17     | 3.03, 3.02    |        | 1.17     | 3.02         | 0.00              |
| fm          | 0.98     | 3.04, 3.04    |        | 0.71     | 2.92         | 0.82              |
| Exp.        | 0.60 (Ref. [35]) | 2.65, 3.12 (Ref. [36]) |        | 0.0 (Ref. [35]) | 2.87 (Ref. [36]) | $-0.044$ (Ref. [23]), $-0.008$ (Ref. [17]) |

Table 1. Calculated band gaps, relative phase stability $\Delta E_{M_1-R}$ in eV, and V–V distances in Å obtained with PBE + U, $U_{\text{eff}} = 3.4$ eV.
For both phases, a metallic ground state is predicted for $U_{\text{eff}} < 1.5$ eV. The band gap of the R phase is zero up to $U_{\text{eff}} = 2.5$ eV and then increases linearly. In the range $U_{\text{eff}} = 1.5$–2.5 eV, the monoclinic phase has a small band gap of 0.2 eV. Beyond $U_{\text{eff}} = 2.5$ eV, the band gap increases non-monotonically. The experimental value of 0.6 eV\[35\] is approximately obtained for $U_{\text{eff}} = 3.0$–3.5 eV. As a consequence, there is no common value for $U_{\text{eff}}$ which yields the correct band gap for both phases.

$\Delta E_{M_1-R}$ is positive in the whole investigated range of $U_{\text{eff}}$ (Fig. 3). This means it is impossible to calculate the correct phase stability with a single value for the Hubbard parameter. In the region between $U_{\text{eff}} = 2.5$–3.5 eV, where the band gap in the monoclinic phase strongly increases, also the relative energy shows fluctuations. This behavior of the band gap and relative energies with the parameter $U_{\text{eff}}$ has already been observed in previous theoretical studies on MnO$_2$ and MnO.[1] The magnetic moments of the V-atoms were analyzed to find an explanation of the observed band gap dependence from $U_{\text{eff}}$. Our hypothesis was that spin localization on the V atoms steeply increases for $U_{\text{eff}} > 2.5$ eV, and that this is responsible for the band gap increase. However, this behavior was not found. The magnetic moments steadily increase to 0.9 $\mu_B$ for $U_{\text{eff}} > 1.5$ eV. This shows the difficulties in choosing the correct $U_{\text{eff}}$ value to describe different polymorphs of the same compound, which was also found in previous studies.[2,7] Application of different $U_{\text{eff}}$ values to the two polymorphs would be favorable for the electronic structure; however, this does not allow to calculate relative energies. It would also not be possible to calculate the phase transition between M$_1$ and R.

In the following, we will discuss results for $U_{\text{eff}} = 3.4$ eV, a value that is well established in the literature to describe VO$_2$.[40–47] The resulting band gaps, relative energy, and V–V distances after geometry optimization are shown in Table 1. The magnetization of the V atoms and the relative energies of the spin states are given in Table 2. More details of the calculated structure parameters are given in the Supporting Information Table S2. The closed-shell (dm) calculation correctly reproduces the experimental band gaps and provides reasonable V–V distances (2.52 and 3.16 Å compared to the experimental values 2.65 and 3.12 Å, respectively) for the monoclinic phase.[17] However, the relative energy $\Delta E_{M_1-R}$ is qualitatively wrong (+0.38 eV instead of −0.044 eV\[23\]). It has to be noted that the diamagnetic state is not the ground state of both compounds and was considered mainly for comparison. All methods considered in this article yielded the ferromagnetic (fm) state to be the ground state of the rutile phase and the antiferromagnetic state with the uudd or uddu spin distribution to be the ground state of the monoclinic phase.

![Figure 1](https://wileyonlinelibrary.com)

**Figure 1.** (a) V–V chains with alternating bond distances in monoclinic and (b) equidistant V–V chains in tetragonal VO$_2$. V: light blue, O: red. [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 2](https://wileyonlinelibrary.com)

**Figure 2.** Band gaps (eV) as a function of $U_{\text{eff}}$ with both phases in the udud spin state. [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 3](https://wileyonlinelibrary.com)

**Figure 3.** Relative energy $\Delta E_{M_1-R}$ (eV) as a function of $U_{\text{eff}}$ with both phases in the udud spin state. [Color figure can be viewed at wileyonlinelibrary.com]
Different from the dm state and at variance with experiment, all fm and afm states have large band gaps for both phases with the PBE + U method. Unexpectedly, the relative energy $\Delta E_{M_1, R}$ is strongly dependent from the spin configuration, with variations from -0.81 to +0.38 eV. The correct sign of the relative energy is obtained only with the spin distribution udud and the ferromagnetic state. The energy difference between the diamagnetic and the antiferromagnetic state $\Delta E_{dm, afm}$ is quite large, 1.28–1.75 eV. The most stable antiferromagnetic state was obtained with the uddu spin distribution. The GGA + U lattice parameters show slightly larger deviations from experiment than the modified hybrid functionals. During optimization, the atom positions of the monoclinic structure become similar to the rutile structure. The optimized atom positions strongly deviate from experiment (see Supporting Information Table S2 and Fig. S11). As a consequence, the V–V distances are almost equal for the monoclinic phase in both fm and afm states, contradicting the experiment. In particular, for the uddu and uddu spin distributions, the results of $M_1$ structure optimizations are almost indistinguishable from the R phase. The relative energy $\Delta E_{M_1, R}$ is correspondingly essentially zero.

Our results support the conclusions by Bell et al. that $U_{eff}$ parameters, which are optimized for the band gap, do not yield accurate energies. In this study, we even found that there is no appropriate value of $U_{eff}$ for obtaining accurate thermodynamic properties for both VO$_2$ polymorphs.

Optimizations were performed with varying values of $U_{eff}$ to analyze the effect of the on-site correction on the structure. These calculations showed that the distortion of the $M_1$ phase takes place if $U_{eff}$ is larger than 2.0 eV. The cause of this phenomenon is further analyzed by calculating the projected density of states (pDOS) for various $U_{eff}$ and comparing them to the pDOS calculated with sc-PBE0 and SCAN. These were calculated using the experimental structure with a udud spin distribution. The results for varying $U_{eff}$ and Fock-exchange in sc-PBE0 are shown in Figures S2 and S6 in the Supporting Information. A comparison of the pDOS obtained with $U_{eff} = 3.4$ eV and sc-PBE0 with $\alpha = 12.7\%$ for both phases is shown in Figures 5 and 6. With increasing $U_{eff}$, the conduction bands are shifted toward positive energies, as expected. Additionally, a vanadium-$d$-orbital separates from the unoccupied states and is shifted close to the Fermi energy. This localization occurs in both phases, leading to a small band gap in the R phase with $U_{eff} = 3.4$ eV as shown in Figure 5b. Further increase of $U_{eff}$ decreases the contribution of the localized $d$ orbital to the states near the Fermi level, leading to an equal contribution compared to the oxygen states.

The pDOS calculated with SCAN are shown in the Supporting Information Figures S3a and S3b. In the experimental structure, no band gap is predicted for the $M_1$ phase, different from the results of the optimized structures as listed in Table 5.

The pDOS calculated with sc-PBE0 likewise show a strong localization of one occupied vanadium-$d$-orbital at the Fermi energy in the $M_1$ phase. Different from PBE + U, this localization is not present in the pDOS of the R phase (Supporting Information Fig. S5). Additionally, in the pDOS calculated with the exchange fraction yielded for the monoclinic phase (Supporting Information Fig. S6), the localization of the $d$-orbital is much less pronounced compared to the results of PBE + U (Fig. 5a). This shows one of the flaws of the DFT + U method in describing different materials with the same value of $U_{eff}$. One reason of the distortion of the monoclinic phase could be the large similarities between the electronic states of the R and $M_1$ phase.

To further analyze the differences of the methods, crystal orbital Hamilton populations (COHP) were calculated. These are shown in the Supporting Information Figures S7–S9. The most significant difference in the COHP obtained with the three methods is the presence of oxygen–oxygen antibonding states near the Fermi energy, which are only found in the COHP calculated with PBE + U. No significant differences in the V–V bonding interaction were found, which would explain the observed behavior during structure optimization. It therefore remains the subject of future studies to further explore the reasons for the failure of GGA + U to calculate the structure of $M_1$ VO$_2$.

![Figure 4](wileyonlinelibrary.com)

**Table 2.** Magnetization of the V-atoms in $\mu_B$ and relative energies of the spin states (X) $\Delta E_{DM - X}$ in eV obtained with PBE + U, $U_{eff} = 3.4$ eV.

| Spin state | Magnetization | $\Delta E_{DM - X}$ |
|------------|---------------|---------------------|
| udud       | 1.01, 1.02, 1.01, 1.02 | 1.28                |
| uddu       | 1.01, 1.01, 1.01, 1.01 | 1.74                |
| uddu       | 1.01, 1.01, 1.01, 1.01 | 1.75                |
| fm         | 1.08, 1.08, 1.08, 1.08 | 1.38                |

| Spin state | Magnetization | $\Delta E_{DM - X}$ |
|------------|---------------|---------------------|
| (R)        |               |                     |
| fd         | 1.08, 1.08, 1.08, 1.08 | 2.02                |

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In the previous section, it was demonstrated that the PBE + U approach is not adequate to describe structural, electronic, and energetic properties of both VO₂ polymorphs. We therefore re-investigated hybrid methods as an alternative, in continuation of our previous work. [24] But instead of a semi-empirical approach using the amount of Fock exchange \( \alpha \) as an adjustable parameter, we employed a self-consistent hybrid functional using the static electronic dielectric constant \( \epsilon_\infty \) of the material [eq. (3)]. [48] The iterative procedure yielded two different \( \alpha \) values in the self-consistent functional PBE0 (sc-PBE0) [32] for both phases. \( \alpha = 0.0032\% \) was obtained for the rutile phase and \( \alpha = 12.7\% \) for the M1 phase. The value for the monoclinic phase is close to the value of 10% which was found using the semi-empirical approach. [24]

**Table 3.** Calculated band gaps in eV, and V–V distances in Å obtained with sc-PBE0, \( \alpha = 12.7\% \) (M1), 0.0032% (R); the relative phase stability \( \Delta E_{M1-R} \) (eV) is calculated with \( \alpha = 12.7\% \) for both phases.

| Spin states | Band gap | V–V distances | V–V distance | \( \Delta E_{M1-R} \) (eV) |
|-------------|----------|----------------|----------------|-----------------------------|
| dm          | 1.25     | 2.44, 3.23     |                | -0.25                       |
| udud        | 1.44     | 2.87, 3.16     |                | -0.19                       |
| uudd        | 1.38     | 2.80, 3.15     |                | -0.20                       |
| uddu        | 1.44     | 2.78, 3.13     |                | -0.19                       |
| fm          | 1.06     | 2.87, 3.15     |                | -0.11                       |
| Exp.        | 0.60 (Ref. [35]) | 2.65, 3.12 (Ref. [36]) | 0.0 (Ref. [35]) | 2.87 (Ref. [36]) | -0.044 (Ref. [23]), -0.008 (Ref. [17]) |

**Self-consistent hybrid functional sc-PBE0**

In the previous section, it was demonstrated that the PBE + U approach is not adequate to describe structural, electronic, and energetic properties of both VO₂ polymorphs. We therefore re-investigated hybrid methods as an alternative, in continuation of our previous work. [24] But instead of a semi-empirical approach using the amount of Fock exchange \( \alpha \) as an adjustable parameter, we employed a self-consistent hybrid functional using the static electronic dielectric constant \( \epsilon_\infty \) of the material [eq. (3)]. [48] The iterative procedure yielded two different \( \alpha \) values in the self-consistent functional PBE0 (sc-PBE0) [32] for both phases. \( \alpha = 0.0032\% \) was obtained for the rutile phase and \( \alpha = 12.7\% \) for the M1 phase. The value for the monoclinic phase is close to the value of 10%, which was found using the semi-empirical approach. [24]
The results for the band gaps, relative energies, and V–V distances are given in Table 3. The spin densities of the V atoms and the relative energies of the spin states are given in Table 4. As expected, sc-PBE0 with $\alpha = 0.0032\%$ gives a delocalization of the spin densities. The spin densities and the relative energies of the spin state with sc-PBE0 with $\alpha = 12.7\%$ are shown in Table S5 of the Supporting Information. A more detailed analysis of the structure parameters is provided in Table S3 of the Supporting Information.

The relative energies were calculated with $\alpha = 12.7\%$ for both phases. Interestingly, this large amount of exact exchange did not result in a band gap for the R phase. It is therefore possible to describe both phases with this fraction of exact exchange. In contrast to the PBE + U approach, the sc-PBE0 functional shows alternating V–V distances almost independent from the spin state in the optimized M1 structure. The bond alternation is overemphasized in the dm state and underemphasized in all afm and fm states. All relative energies have the correct sign. However, all relative energies are overestimated and stabilize the M1 phase. The relative energy $\Delta E_{\text{rel}} - \alpha = 12.7\%$ is considerably smaller than with PBE + U, 0.56–0.88 eV, with the most stable antiferromagnetic state corresponding to the uudd spin distribution.

The band gap of the M1 phase is overestimated (1.06–1.44 eV compared to 0.6 eV, Ref [35]). The deviations of the lattice parameters were also compared to the results of our previous work where the spin distribution uudd was used. Therefore, this configuration was used for comparison here. The deviations are shown in Figure S10 and S11 of the Supporting Information. The deviations of the lattice parameters of the monoclinic phase are in the same range as the standard and optimized hybrid functionals. For the R phase, the errors of sc-PBE0 are in the same range as with PBE, which is a large improvement compared to the unmodified hybrid functionals. The empirically varied range-separated hybrid functional HSE06 and SCAN show overall the smallest deviations from the experimental lattice parameters. Furthermore, the deviations of the atom positions are in the same range for all modified hybrid functionals. SCAN and PBE + U show the largest deviations of the atomic positions in the M1 phase.

**meta-GGA functional SCAN**

The meta-GGA functional SCAN was tested as an example of an accurate but computationally more efficient method, compared to the hybrid methods. It has been found to accurately describe structures and to yield the correct sign of the relative energy for VO$_2$ polymorphs.$^{[17]}$ Our results shown in Table 5 and Table 5 in the Supporting Information are in accordance with these studies. The magnetization of the V atoms and the relative energies of the spin states are given in Table 6. The relative phase stability is qualitatively correct but overestimated.

| Spin states | $\Delta E_{\text{rel}}$ | $\Delta E_{\text{EDM}}$ | $\Delta E_{\text{EM}}$ |
|-------------|----------------|----------------|----------------|
| uudd        | 0.32          | 2.47, 3.16      | 0.00           |
| udud        | 0.35          | 2.80, 3.07      | 0.00           |
| fm          | 0.00          | 2.73, 2.94      | 0.00           |

**Table 6. Magnetization of the V-atoms in $\mu_B$ and relative energies of the spin states (X) $\Delta E_{\text{EDM}} - X$ in eV obtained with SCAN.**

| Spin states | Magnetization | $\Delta E_{\text{rel}}$ | $\Delta E_{\text{EDM}}$ | $\Delta E_{\text{EM}}$ |
|-------------|---------------|----------------|----------------|----------------|
| uudd        | 0.76, −0.66, 0.76, −0.66 | 0.55          | 0.82, −1.07, 0.59, −1.07 | 0.27          |
| udud        | 0.92, 0.92, −0.92, −0.92 | 0.77          | 0.95, 0.95, −0.95, −0.95 | 0.42          |
| fd          | 1.10, 1.10, 1.10, 1.10 | 0.92          | 1.11, 1.11, 1.11, 1.11 | 0.85          |
resulting in an over-stabilization of the M1 phase. The relative phase stability obtained with SCAN is slightly larger than with sc-PBE0. Only the fm state—which is not the ground state—shows a small stabilization of the R phase by 0.01 eV. Additionally, a conducting state is yielded for the fm state of the M1 phase. The band gaps of the afm states of M1 are slightly smaller than the experimental value, except for the spin distribution uuud in the afm states, the alternation of the V–V distances is less pronounced compared to the sc-PBE0 results and much smaller than in experiment. The dm state on the other hand overestimates the alternation. The relative energy $\Delta E_{\text{afm}} - \Delta E_{\text{afm}}$ is smaller but similar to the results with sc-PBE0. The most stable afm state corresponds to the uuudd spin distribution.

The lattice parameters calculated with SCAN show the smallest deviation from experiment of all methods considered here (Supporting Information Table S4). The atom positions of the monoclinic phase show smaller deviations compared to the PBE + U method but are less accurate than sc-PBE0. Considering the computational efficiency of the functional SCAN compared to the self-consistent hybrid method and its accuracy in terms of lattice parameters and relative phase stability, it is the optimal method to describe VO$_2$.

**Conclusions**

We have analyzed the performance of the PBE + U approach to calculate structural, electronic, and energetic properties of the monoclinic and tetragonal polymorphs of vanadium dioxide. We found that the PBE + U method with standard values of the $U_{\text{eff}}$ parameter provides a strongly distorted structure of the monoclinic phase. The structure becomes similar to the rutile structure. It was also not possible to obtain the correct electronic ground state for both phases with the same $U_{\text{eff}}$ value. The experimentally observed relative phase stability could not be reproduced with PBE + U. We compared the electronic structure obtained with DFT + U method to the self-consistent hybrid method sc-PBE0 and the meta-GGA functional SCAN. We found that the localization of vanadium-d-states obtained with the DFT + U method occurs in both phases, which is not the case in the other methods.

Considering the computational effort of hybrid functionals, it is concluded that the functional SCAN represents the best compromise between computational cost and accuracy in terms of lattice parameters and relative phase stability for modeling VO$_2$.

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**Keywords:** computational chemistry – density functional theory – theoretical inorganic chemistry – vanadium dioxide – phase transitions – solid-state structures

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