First-principles Hubbard $U$ and Hund’s $J$ corrected approximate density-functional theory predicts an accurate fundamental gap in rutile and anatase TiO$_2$

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Titanium dioxide (TiO$_2$) presents a long-standing challenge for approximate Kohn-Sham density-functional theory (KS-DFT), as well as to its Hubbard-corrected extension, DFT+$U$. We find that a previously proposed extension of first-principles DFT+$U$ to incorporate a Hund’s $J$ correction, termed DFT+$U$+$J$, in combination with parameters calculated using a recently proposed linear-response theory, predicts fundamental band-gaps accurate to well within the experimental uncertainty in rutile and anatase TiO$_2$. Our approach builds upon established findings that Hubbard correction to both titanium 3$d$ and oxygen 2$p$ subspaces in TiO$_2$, symbolically giving DFT+$U^{d,p}$, is necessary to achieve acceptable band-gaps using DFT+$U$. This requirement remains when the first-principles Hund’s $J$ is included. We also find that the calculated gap depends on the correlated subspace definition even when using subspace-specific first-principles $U$ and $J$ parameters. Using the simplest reasonable correlated subspace definition and underlying functional, the local density approximation, we show that high accuracy results from using a relatively uncomplicated form of the DFT+$U$+$J$ functional. For closed-shell systems such as TiO$_2$, we describe how various DFT+$U$+$J$ functionals reduce to DFT+$U$ with suitably modified parameters, so that reliable band gaps can be calculated for rutile and anatase with no modifications to a conventional DFT+$U$ code.

I. INTRODUCTION

Titanium dioxide (TiO$_2$) has been widely used for several decades in diverse industrial applications such as pigmention and coating due to its non-toxicity, low-cost production and thermal stability. TiO$_2$ came under particularly intense scrutiny with the ground-breaking work of Fujishima and Honda, who demonstrated water splitting in TiO$_2$ photo-chemical cells in the ultra-violet (UV) spectral range in 1972. Indeed, since then, TiO$_2$-based structures have been engineered for diverse opto-electronic applications such as photo-catalysts, photovoltaics, sensors, and for energy and environmental applications. In nature, TiO$_2$ has three common polymorphs: rutile, anatase, and brookite. TiO$_2$-rutile and TiO$_2$-anatase are more common in industrial applications, as brookite is less stable and difficult to synthesize in large volumes. The electronic structures of pristine TiO$_2$-rutile and TiO$_2$-anatase have been extensively studied experimentally, and the most reliable data currently available shows that TiO$_2$-rutile and TiO$_2$-anatase have fundamental (electronic, not optical) band gaps of 3.03 eV and 3.47 eV, respectively.

First-principles simulations can provide valuable insights into the electronic structures and processes at play in TiO$_2$-based systems, offering clues for the engineering of these systems for desired applications. This requires the accurate description of their electronic structures in the region of their band edges, naturally, and this must necessarily be done by means of computationally feasible and scalable methods if disordered structures and diverse dopants are to be assessed in any detail. There exist numerous acceptably reliable approaches, such as quantum chemistry methods, hybrid-functional methods, and many-body perturbation methods, however these methods are too computationally high-demand for routine application to defective and disordered systems.

Density-functional theory (DFT), specifically Kohn-Sham DFT (KS-DFT) using (semi-)local density exchange-correlation functionals offers a computationally feasible framework to study the electronic structures of spatially complex TiO$_2$-based systems. In the present work, with that challenge in mind, we use a linear-scaling implementation of DFT, the Order-N Electronic Total Energy Package (ONETEP). However, it is well-known that semi-local KS-DFT is unable to capture the approximate magnitude of the band-gap of TiO$_2$, a common observation among transition-metal oxides (TMOs) generally, and so it requires, at the very least, some corrective measures for reliable use.

In this article, we revisit the computationally efficient approach of applying Hubbard-model inspired corrections to approximate KS-DFT, namely DFT+$U$ which is technically a generalized Kohn-Sham method, in terms of its capability of accurately describing the fundamental electronic band gap of TiO$_2$ polymorphs. We find that unlike-spin Hund’s $J$ correction, specifically introduced in the pioneering work of Ref. 41, is the key ingredient that enables the band gaps of TiO$_2$ to be accurately described with this method. A corrective functional is only as good as its parameters, and here we use the recently-proposed minimum-tracking linear-response formalism of Ref. 42 for calculating them. Encouragingly for practical use, moreover, we find that for closed-shell (non-spin-polarized) systems such as pristine TiO$_2$ and other TMOs towards the edges of the periodic table $d$-block, no modification to a standard DFT+$U$ code is needed to include Hund’s $J$ corrections.

No differently to what has been found in previous works and as an inevitable consequence of the O 2$p$ character of the valence-band edge, in order to achieve significantly improved results using DFT+$U$, we need to...
apply corrective potentials to oxygen 2p orbitals on the same footing as to titanium 3d orbitals. The addition of Hund’s J does not change this fact, and irrespective of whether J is included we denote this two-species correction as DFT+U^d,p, short for DFT+U^d+U^p, following the literature. Unlike prior works on TiO_2, in which one or both of U^d and U^p was found to require empirical tuning for good results, in this work we only use first-principles calculated U and J parameters (specifically, using the minimum-tracking linear-response method^{42,45}), for both the Ti 3d and O 2p sub-spaces.

When the unlike-spin Hund’s J term is included (using a particularly simple form of DFT+U+J, in agreement with the detailed analysis of Ref. 41) we predict a generalised Kohn-Sham band-gap of a better quality to that which hybrid functionals or G_0W_0 gives, for both polymorphs, when gauged against reported experimental findings (recent, high-quality ones in the case of anatase, where it seems to be more challenging to measure). We note in passing that both functional classes, DFT+U and hybrids, are differentiable in terms of the density-matrix and have a non-local potential, and so their generalised Kohn-Sham gaps include exchange-correlation derivative discontinuities^{48} and are directly comparable to experiment. Promisingly for future TiO_2 simulation, and as the central conclusion of this work, we find that the same first-principles DFT+U^d,p+J^d,p method predicts the experimental fundamental gap to within the uncertainty of the experiment, for both polymorphs.

II. METHODOLOGY

Perhaps the most well-known systematic error exhibited by conventional approximate functionals in KS-DFT is the self-interaction error (SIE)^{49–53}, and its many-body generalization, the delocalization error^{54–60}. SIE arises due to spurious self-repulsion of electronic density in the KS-DFT formalism and it also persists, albeit often to a lesser extent, within generalized Kohn-Sham schemes. While the origins of SIE are well understood, it is hard to avoid it in the construction of closed-form approximate functionals. SIE leads to the well-known significant, even drastic underestimation of fundamental band gaps of TMOs in particular^{28–30}, and TiO_2-rutile and TiO_2-anatase are no exception in this regard^{61}. Less well understood is the generalization of SIE to account for the spin degree of freedom, which is not necessarily less relevant in closed-shell systems where the spin happens to evaluate to zero. In this section, we outline in detail our methodology for computing and incorporating parameters, the Hubbard U^d,p for density-related error and Hund’s J^d,p for spin-related error, to correct a very low-cost density functional for the specific case of TiO_2.

A. DFT+U+J functionals and their simplification for closed-shell systems

DFT+U is routinely applied to correct for SIE, particularly for the spurious delocalization of electronic states associated with transition-metal 3d orbitals. The DFT+U total energy is given by

\[ E_{\text{DFT+U}} = E_{\text{DFT}} + E_U, \]

where the rotationally-invariant form of \( E_U \) for a given SIE-prone subspace^{26,36,62}, particularly if we take its relatively recent DFT+U+J form of Ref. 41, is given by

\[ E_U[\{n^\sigma\}] = \frac{1}{2} \sum_{\sigma} \sum_{m,m'} \left\{ U \left[ n^\sigma_{m'm} - n^\sigma_{m'm} n^\sigma_{m'm} \right] \right\} + \frac{J}{4} \sum_{m,m'} \left[ n^\sigma_{m'm} n^\sigma_{m'm} - 2J \left| \delta^\sigma_{\text{min}} \right| \right]. \]

Here, \( \sigma \) is a spin index, \( \sigma_{\text{min}} \) is the corresponding opposite spin, \( \sigma_{\text{min}} \) is the index of the minority-population spin channel for the subspace at hand, \( n_{m'm'} \) is the subspace-projected KS density-matrix, the Hubbard U is (in this work at least) interpreted as the subspace-and-spin-averaged net Hartree-plus-exchange-correlation interaction. Hund’s J is its spin-splitting counterpart. We will presently detail what, precisely, is meant by spin-averaging and spin-splitting in this context.

The choice of appropriate form of DFT+U(+J) energy functional depends on various factors such as the system under consideration, the limitations and robustness of approaches to determine the Hubbard U and Hund’s J parameters, and underlying approximate density functional. For instance, it was argued in Ref. 41 that term (IV), which we dub the ‘minority spin term’, is best not to include, as it arises due to the double-counting correction of a type of two-particle density-matrix interaction that is unlikely to be very much present in the underlying density functional. Our numerical results will support this analysis. It was furthermore found to lead to numerical instabilities, and we have also noted this effect in our own calculations. Our tentative explanation of this instability is that, when the net spin of a site is weak, the potential arising due to this term can switch over discretely from one spin channel to the other. The simplest functional form is achieved, of course, by neglecting the explicit correction of exchange and effectively by setting \( J = 0 \). If a value for \( J \) is available, then so is the Dudarev functional^{31}, which includes only like-spin correction terms (the terms (I) and (II)) via an effective parameter, \( U_{\text{eff}} = U - J \) resulting symbolically in DFT+U_{\text{eff}}.

Inspired by the Dudarev model, we note and primarily use in this work the fact that the full DFT+U+J functional of Eq. (2) may be applied to closed-shell systems,
without approximation, using an unmodified DFT+U code with no \( J \) implementation. For this, we rearrange Eq. (2) and introduce an additional parameter, \( \alpha \), which is exactly that \( \alpha \) which is available and used to calculate the Hubbard \( U \) in many standard DFT+U codes\(^{38}\). Here, it captures the inclusion minor spin term (term IV), when re-writing Eq. (2) as

\[
E_U = \sum_{\sigma, m, m'} \left\{ \frac{U_{\text{full}}}{2} [n_{m m'}^\sigma \delta_{m' m} - n_{m m'}^\sigma n_{m m'}^\sigma] + \alpha n_{m m'}^\sigma \delta_{m' m} \right\},
\]

(3)

where \( U_{\text{full}} = U - 2J \). Three viable scenarios for \( \alpha \) are tested in this study, representing different interpretation of the minority spin (term IV):

1. The most natural treatment of (term IV) for closed-shell systems, that suggested in Ref. \( 41 \), is to interpret \( \sigma_{\text{min}} = \sigma \), such that \( \delta^{\sigma \sigma_{\text{min}}} = 1 \). This requires us to set \( \alpha = -J/2 \).

2. A modification of the latter, intended to avoid a discontinuity in the total energy at the onset of non-zero spin polarization (it doesn’t avoid such a discontinuity in the potential), is to “share” the minority spin term between the two spins, setting \( \delta^{\sigma \sigma_{\text{min}}} = 1/2 \) for closed-shell systems. This leads to \( \alpha = 0 \) and the resulting Hubbard functional is simply a Dudarev functional with \( U_{\text{full}} = U - 2J \).

3. In the last case, the minority spin term is neglected, as it was argued best to do in its originating Ref. \( 41 \), by setting \( \delta^{\sigma \sigma_{\text{min}}} = 0 \). For closed-shell systems, DFT+U+J is then recovered by DFT+U code with parameters \( U_{\text{full}} \) and \( \alpha = J/2 \).

B. DFT+U on 2p and 3d orbitals: DFT+U\(^{d,p}\)

In principle, SIE is harboured by all subshells and cannot be partitioned out between them, however, it is commonly more dominant in 3d subshells due to their spatially localized nature. Hence, in titanium-compromising systems, the Hubbard correction in DFT+U is conventionally applied to the Ti 3d subshell only. The Hubbard \( U \) parameters used for the 3d orbitals of Ti atom have ranged over \( \sim 2.5 - 10 \text{ eV}^{63} \), and have most commonly been determined by tuning to some observed quantity\(^{64–70}\). Even when overlooking our serious concerns regarding the the robustness and conceptual validity of \( U \) values calibration to observable quantities, particularly when those are not ground-state observables, a practical problem arises for DFT+U due to the location of Ti on the extreme left of the transition-metal block. It is well known that Hubbard \( U \) correction to the 3d-orbitals alone is not very effective for opening the band gap of TiO\(_2\), which saturates even with unreasonably large \( U \) values, as the dominant 2p-states at the valence band-edge remain barely affected. Moreover, when actually plotted, the 2p pseudo-orbitals of O atoms are are slightly more localized than their Ti 3d counterparts, and so it is not at all unreasonable, quite the contrary, to calculate (or at least tune, where calculation is not possible) Hubbard \( U \) and even Hund’s \( J \) parameters for O 2p. Indeed, it has been demonstrated in several prior works that applying the Hubbard \( U \) correction simultaneously on the 3d orbitals of Ti and the 2p orbitals of O atoms, symbolically giving DFT+U\(^{d,p}\), readily addresses the aforementioned gap saturation problem and provides a more accurate description of the band structure around the Fermi level\(^{43–46}\). We follow this procedure here as standard, presenting DFT+U\(^{d}\) (no O 2p correction) results only for the sake of illustration and completeness.

C. The minimum-tracking linear-response approach for first-principles Hubbard \( U \) and Hund’s \( J \) parameters

The results of DFT+U\(^{d,p}\) are only as good as its input Hubbard \( U \) and Hund’s \( J \) parameters. Finite-difference linear-response theory provides a practical, widely available first-principles method for calculating these\(^{37,38,41}\). It has been found that linear-response tends to give Hubbard \( U \) parameters for closed-shell systems that are too high for practical use, and this is usually deemed to be an erroneous overestimation\(^{42,71–73}\). The present work provides hints that these values may be correct after all, but that Hund’s \( J \) effectively reduces them and so the latter is (counter-intuitively, perhaps) more important to include in closed-shell systems. If a system has zero spin polarization, the systematic error in the approximate functional related to the spin degree of freedom may still be large. In this work, we employed the recently-introduced minimum-tracking variant\(^{47}\) of linear-response as implemented in the ONETEP code\(^{74}\), and in particular, its spin-specific extension introduced in Ref. \( 42 \). The ‘scaled 2 \times 2’ method was used here to evaluate the Hubbard \( U \), Hund’s \( J \), and effective Hubbard \( U \) parameters (\( U_{\text{eff}} = U - J \) and \( U_{\text{full}} = U - 2J \)) for the Ti 3d and O 2p subshells of pristine TiO\(_2\)-rutile and TiO\(_2\)-anatase using

\[
U = \frac{1}{2} \frac{\lambda_U (f^{\uparrow \uparrow} + f^{\downarrow \downarrow}) + f^{\uparrow \downarrow} + f^{\downarrow \uparrow}}{\lambda_U + 1}
\]

(4)

and

\[
J = -\frac{1}{2} \frac{\lambda_J (f^{\uparrow \downarrow} - f^{\downarrow \uparrow}) + f^{\uparrow \downarrow} - f^{\downarrow \uparrow}}{\lambda_J - 1},
\]

(5)

where

\[
\lambda_U = \frac{\chi^{\uparrow \uparrow} + \chi^{\downarrow \downarrow}}{\chi^{\uparrow \downarrow} + \chi^{\downarrow \uparrow}}, \quad \text{and} \quad \lambda_J = \frac{\chi^{\uparrow \downarrow} - \chi^{\downarrow \uparrow}}{\chi^{\uparrow \uparrow} - \chi^{\downarrow \downarrow}},
\]

(6)

and where the projected interacting response matrices are given by \( \chi^{\sigma \sigma'} = d n^\sigma/dv_{\text{ext}}^{\sigma'} \). The spin-dependent interaction strengths \( f^{\sigma \sigma'} \) are calculated by solving \( 2 \times 2 \)
matrix equation given by
\[
f = \left[ \frac{\delta v_{\text{KS}}}{\delta v_{\text{ext}}} - 1 \right] \left( \frac{\delta n}{\delta v_{\text{ext}}} \right)^{-1}, \tag{7}
\]
for which matrix entities are obtained by linear fitting to small changes of the subspace occupancies $\delta n$ and subspace-averaged Kohn-Sham potentials $\delta v_{\text{KS}}$ with respect to incrementally varying uniform perturbing potentials $\delta v_{\text{ext}}$ on the targeted subspaces. These definitions are equivalent to a particular choice of perturbation in the more physically transparent but perturbation-independent expressions
\[
U = \frac{d(v_{\text{Hxc}}^\uparrow + v_{\text{Hxc}}^\downarrow)}{2d(n^\uparrow + n^\downarrow)} \quad \text{and} \quad J = -\frac{d(v_{\text{Hxc}}^\uparrow - v_{\text{Hxc}}^\downarrow)}{2d(n^\uparrow - n^\downarrow)}, \tag{8}
\]
where the factor $1/2$ signifies averaging (or halving the of splitting between) the subspace averaged Hartree-Fock-plus-exchange-correlation potentials, $v_{\text{Hxc}}$ Eqs. 8 can be taken as definition of minimum-tracking linear response, and if using them separately it is natural to use $\delta v_{\text{ext}} = \delta \sigma$ for $U$ and $\delta v_{\text{ext}} = \delta J$ for $J$.

The scaling factors become $\lambda_U = 1$ and $\lambda_J = -1$ for spin-unpolarized systems such as the pristine TiO$_2$-rutile and TiO$_2$-anatase. This reflects the vanishing linear coupling between subspace occupancy and magnetization in such systems. As a result, the ‘scaled $2 \times 2$’ method reduces to the ‘simple $2 \times 2$’ method\textsuperscript{42}, which can be summarized as $U = (f^{\sigma \sigma} + f^{\sigma \sigma})/2, \ J = (f^{\sigma \sigma} - f^{\sigma \sigma})/2$ (this gives a Dudarev $U_{\text{eff}} = f^{\sigma \sigma}$, which is reasonable for a like-spin-only corrective functional). In fact, time-reversal symmetry can be readily exploited for closed-shell systems, where it is sufficient to perturb one spin channel only, filling in half of the matrix elements by symmetry, e.g. $\chi^{\uparrow \downarrow} = \chi^{\downarrow \uparrow}$. This feature of the $2 \times 2$ approach enabled the simultaneous calculation of $U$ and $J$ in this work, from a single group of self-consistent calculations perturbing one spin channel only by finite-differences. The response coupling Ti 3$d$ and O 2$p$ subspaces is not included in these calculations, as to include such entries in the response matrices would necessitate corresponding terms in the corrective functional, which would complicate our analysis focused on Hund’s $J$.

### D. Computational details

Initial crystallographic information for TiO$_2$-rutile and TiO$_2$-anatase were adopted from Refs. 75 and 76. Norm-conserving LDA pseudo-potentials were produced using the pseudo-potential generator OPIUM\textsuperscript{77}. A Ti$^{3+}$ configuration was chosen following transferability testing. Full geometry relaxation were performed with variable cell parameters at a high plane-wave cut-off energy $E_{\text{cut}}$ (75 Ha) and automatically generated $3 \times 3 \times 5$ (TiO$_2$-rutile) and $5 \times 5 \times 3$ (conventional-cell TiO$_2$-anatase) Monkhorst-Pack Brillouin zone sampling grids using the Quantum Espresso (QE) code\textsuperscript{78,79}. The converged cell parameters were used to construct unfolded super-cells with 270 and 900 atoms, respectively, in order to emulate the same Brillouin zone sampling with real-valued Kohn-Sham orbitals within the ONETEP code. This is a linear-scaling implementation of approximate KS-DFT using two nested optimization loops for the density kernel and a minimal set of non-orthogonal generalized Wannier functions (NGWFs)\textsuperscript{26,27}.

An under-pinning basis of $3^1 5^2 = 75$ psinc functions in all directions for TiO$_2$-rutile (corresponding to the effective kinetic energy cut-offs of $\sim 1776$ eV, $\sim 1776$ eV, and $\sim 1552$ eV), and $3^1 7^2 = 75$ in the x- and y-directions and $3^1 7^2 = 147$ in z-direction for TiO$_2$-anatase (corresponding to $\sim 945$ eV, $\sim 945$ eV, and $\sim 1578$ eV respectively), provided a error of $\leq 1$ meV in the total energy per atom. A total of 13 variationally optimized NGWFs initially centred on Ti atoms, to complete the second and third periods up to Kr, and a total 4 NGWFs variationally optimized NGWFs initially centred on O atoms to complete the period up to Ar, were used. A converged, common NGWF cutoff radius of 12 $a_0$ was used for both species, with the same total energy tolerance. A second set of NGWFs, with the number and cutoff radii, where then added and variationally optimised, following Ref. 80, in order to reproduce the Kohn-Sham states around the conduction-band minimum. For energies much above the conduction-band edges, the conduction band parts of the LDOS plots in Figs 1-3 are qualitatively but not necessarily quantitatively reliable.

A discrete perturbation strength grid, $\delta \Lambda^\uparrow = \{0, \pm 0.01, \pm 0.10, \pm 0.50, \pm 1.00\}$ eV (without restarts in order to remove any risk of premature convergence declaration and hence under-estimated response) was used to calculate the Hubbard $U$ and Hund’s $J$ parameters. This was applied to a single spin channel only, following the $2 \times 2$ procedure of Ref. 42. A nice, smooth response was obtained for all matrix elements for both species, Ti 3$d$ and O 2$p$, and for both crystal structures.

### III. RESULTS AND DISCUSSION

We first present the calculated Hubbard $U$ and Hund’s $J$ parameters for pristine, closed-shell TiO$_2$-rutile and TiO$_2$-anatase. As a preliminary test, LDA-appropriate parameters were calculated for TiO$_2$-rutile with two different definitions of the DFT+$U$ target subspace for Ti 3$d$ orbitals. Specifically, both neutral and 3+ (still non-spin-polarized) atomic DFT calculations\textsuperscript{81} were separately performed to generate pseudo-atomic orbitals to define the 3$d$ subspace, and also to build the initial density and NGWF guesses. An OPIUM\textsuperscript{77} norm-conserving pseudo-potential with a 3+ reference state was used for Ti, while a charge-neutral atomic configuration was used for O (OPIUM pseudo-potential generation, DFT+$U$ definition, and initial density and NGWF guess generation) throughout. The resulting Hubbard $U$ and Hund’s $J$ pa-
The relationship between the Kohn-Sham gap and the fundamental gap is thereby not only assured in principle, but the derivative discontinuity gives, in practice, the opportunity for direct comparability to the experimental insulating gap. Shown in Table III is the band gap of TiO$_2$-rutile calculated using LDA and first-principles DFT+$U$, DFT+$U_{\text{eff}}$, DFT+$U_{\text{full}}$ with different $\alpha$ values, and explicit DFT+$U$+$J$ (minority spin term (IV) neglected), both when applied only to the Ti 3$d$ sub-shell and when applied also to the O 2$p$ sub-shell.

Experimental, first-principles, semi-empirical hybrid, GW results, and several previous DFT+$U$ results from the literature are also shown in Table III, for comparison. The experimental direct gap quoted$^{12,13}$ is based on absorption, photoemission, and resonant-Raman scattering data, and is expected to be very reliable due to the relatively small exciton binding and phonon coupling effects in rutile$^{11}$, and moreover in light of its good agreement with available inverse photoemission data.$^{82}$

The LDA yields a Kohn-Sham band gap of 1.96 eV, much lower than the experimental band gap of 3.03 eV, as expected given its absence of a derivative discontinuity. Regardless of the Hund’s $J$ incorporation scheme used, and as is generally attested in the literature on calculations with $J = 0$ eV, first-principles DFT+$U$ applied to Ti 3$d$ states only performs poorly and here predicts a band gap of 2.17–2.24 eV. The inadequacy of the conventional DFT+$U$ subspace definition can be explained by comparing the very different valence and the conduction band edges characters seen in all of the local density of states plots shown in Fig. 1, and additionally motivated by recalling the very similar degree of spatial localization of Ti 3$d$ and O 2$p$ atomic orbitals. The valence (conduction) band edge is left almost perfectly unaffected by applying the Hubbard correction only to the Ti 3$d$ (O 2$p$) sub-shell, regardless of any reasonable Hubbard $U$ parameter (hence, unreasonable values have been tested in the prior literature). In qualitative agreement with that, we observe that the impact of the method on the band-gap increases substantially as soon as correction is also applied to the oxygen 2$p$ subshell, within DFT+$U^{d,p}$ (as we show in detail in Table III).

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
LDA rutile & Ti$^0$ conf. & Ti$^{3+}$ conf. \\
\hline
 & Ti & O & Ti & O \\
\hline
$U$ & 3.56 & 8.57 & 5.59 & 8.57 \\
$J$ & 0.29 & 0.92 & 0.38 & 0.89 \\
$U_{\text{eff}} = U - J$ & 3.27 & 7.66 & 5.20 & 7.68 \\
$U_{\text{full}} = U - 2J$ & 2.98 & 6.74 & 4.82 & 6.80 \\
\hline
\end{tabular}
\caption{First-principles LDA-appropriate Hubbard $U$ and Hund’s $J$ parameters calculated using the minimum-tracking linear-response method$^{47,74}$, both for the Ti 3$d$ and O 2$p$ subspaces of TiO$_2$-rutile. The Ti 3$d$ parameters depend significantly on the pseudo-atomic solver charge configuration used to construct the corresponding DFT+$U$ subspace, with 3$^+$ providing a significantly more localised subspace and consequently higher parameters. Shown also are the effective Hubbard $U$ parameter of the Dudarev model ($U_{\text{eff}}$) and that which reproduces the DFT+$U$+$J$ functional (with minority term IV) for closed-shell systems ($U_{\text{full}}$).}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|}
\hline
LDA anatase & Ti & O \\
\hline
$U$ & 3.57 & 8.56 \\
$J$ & 0.29 & 0.91 \\
$U_{\text{eff}} = U - J$ & 3.28 & 7.66 \\
$U_{\text{full}} = U - 2J$ & 3.00 & 6.75 \\
\hline
\end{tabular}
\caption{First-principles LDA-appropriate Hubbard $U$ and Hund’s $J$ parameters calculated using the minimum-tracking linear-response method$^{47,74}$, both for the Ti 3$d$ and O 2$p$ subspaces of TiO$_2$-anatase. Only the neutral pseudo-atomic solver configuration Ti$^0$ is used here. Shown also are the effective Hubbard $U$ parameter of the Dudarev model ($U_{\text{eff}}$) and that which reproduces the DFT+$U$+$J$ functional (with minority term IV) for closed-shell systems ($U_{\text{full}}$).}
\end{table}
The fundamental gap (in eV) of TiO$_2$-rutile calculated within DFT(LDA), DFT$+U$ with Hund’s $J$ neglected, when treated within the Dudarev model ($U_{\text{eff}}$), and when treated in a manner which fully reproduces DFT$+U$+$J$ using only DFT$+U$ code for closed-shell systems ($U_{\text{full}}$), both when treated with ($\alpha = -J/2$) and without ($\alpha = J/2$) its minority-spin (term IV). DFT$+U^d$ and DFT$+U^{d,p}$ results are separately shown, using parameters calculated from first principles using the minimum-tracking linear-response method, using only the neutral pseudo-atomic solver configuration TiO$^\beta$. Prior experimental, first-principles local, semi-local, semi-empirical hybrid, perturbative $G_0W_0$, empirical and first-principles SCF linear-response (Ref. 88) and ACBN0 (Ref. 89) DFT$+U$ values are provided for convenient comparison. Our central results are highlighted in bold. 

| TiO$_2$-rutile $E_{\text{gap}}$ | DFT (LDA) | $U^d$ | $U^{d,p}$ |
|---------------------------------|-----------|-------|-----------|
| DFT$+U$                         | 1.96      | 2.24  | 3.59      |
| DFT$+U_{\text{eff}} = U - J$   | 2.21      | 3.38  |           |
| DFT$+U_{\text{full}} = U - 2J$, $\alpha = -J/2$ | 2.17 | 3.32 |           |
| DFT$+U_{\text{full}} = U - 2J$, $\alpha = J/2$ | 2.18 | 3.18 |           |
| DFT$+U_{\text{full}} = U - 2J$, $\alpha = J/2$ | 2.20 | **3.04** |           |
| DFT$+U^d$ (no minority spin term) | 2.20 | **3.04** |           |

### Experiment$^{12,13}$
- LDA$^{46}$: 1.79
- PBE$^{19}$: 1.88
- PBE$^{83}$: 1.86
- PBE$^{84}$: 1.77
- HSE06$^{85}$: 3.3
- HSE06$^{19}$: 3.39
- HSE06 ($\alpha = 0.2$)$^{84}$: 3.05
- sX Hybrid$^{83}$: 3.1
- LDA+$G_0W_0$$^{18}$: 3.34
- PBE+$G_0W_0$$^{19}$: 3.46
- HSE+$G_0W_0$$^{19}$: 3.73
- DFT$+U$ ($U=7.5$ eV)$^{86}$: 2.83
- DFT$+U$ ($U=10$ eV)$^{87}$: 2.97
- DFT$+U^d$ ($U = 3.25$ eV)$^{86}$: 2.01
- DFT$+U^{d,p}$ ($U^d = 3.25$ eV, $U^p = 10.65$ eV)$^{88}$: 3.67
- DFT$+U^{d,p}$ ($U^d = 3.25$ eV, $U^p = 5.0$ eV)$^{88}$: 2.69
- DFT$+U^{d,p}$ ($U^d = 0.15$ eV, $U^p = 7.34$ eV)$^{89}$: 2.83

**TABLE III.** The fundamental band gap (in eV) of TiO$_2$-rutile calculated within DFT(LDA), DFT$+U$ with Hund’s $J$ neglected, when treated within the Dudarev model ($U_{\text{eff}}$), and when treated in a manner which fully reproduces DFT$+U$+$J$ using only DFT$+U$ code for closed-shell systems ($U_{\text{full}}$), both when treated with ($\alpha = -J/2$) and without ($\alpha = J/2$) its minority-spin (term IV). DFT$+U^d$ and DFT$+U^{d,p}$ results are separately shown, using parameters calculated from first principles using the minimum-tracking linear-response method, using only the neutral pseudo-atomic solver configuration TiO$^\beta$. Prior experimental, first-principles local, semi-local, semi-empirical hybrid, perturbative $G_0W_0$, empirical and first-principles SCF linear-response (Ref. 88) and ACBN0 (Ref. 89) DFT$+U$ values are provided for convenient comparison. Our central results are highlighted in bold.

Focusing on our own first-principles DFT$+U^{d,p}$ results and comparing with experiment, we find that when the correction for energy-magnetization curvature is neglected (letting $J = 0$ eV), the band gap is overestimated by $\sim 0.56$ eV with respect to the experimental gap. The important point here is that, even though the system harbours no magnetism in its ground-state, this does not imply that the error in the approximate energy functional related to the magnetic degree of freedom vanishes. When including this effect only in the like-spin term, (using Dudarev’s $U_{\text{eff}} = U - J$) this overestimation reduces to $\sim 0.35$ eV, and when also applying the unlike-spin term (using $U_{\text{full}} = U - 2J$ and $\alpha = -J/2$, which is equivalent to DFT$+U$+$J$ including its standard minority spin term (IV), for closed-shell systems such as this one), the overestimation reduces further to $\sim 0.29$ eV.

However, when we apply DFT$+U$+$J$ in its simplest form, i.e., neglecting the minority spin term (IV) of Eq. (2) (in practice using $U_{\text{full}} = U - 2J$ and $\alpha = J/2$), the gap underestimation vanishes to within the expected error in the experiment (using the zero-temperature extrapolation of the direct fundamental gap provided in Ref. 12) and the theoretical methodology. We note that the zero-point phonon correction is held to be very small in rutile, unlike in anatase. As shown in Table III, we also carried out DFT$+U$+$J$ calculations using explicit+$J$ code, with the same results to a high precision, as predicted. We note, in passing, that the deduction in the calculated gap due to the omission of the minority spin term, of $\sim 0.29$ eV, is very close to $(J^p - J^d)/2 \sim 0.31$ eV, as might be predicted by considering the different characters of the band edges and the change in the potentials acting upon them.

These fundamental gap changes are reflected in the local density of states (LDOS) plots shown in Fig. 1. Here, we see the successive effects of first turning on $+U^{d,p}$ correction, and then by moderating it using $J$ per Dudarev’s $U_{\text{eff}} = U - J$ prescription, which mostly brings the valence band back up in energy in this case. Moving ultimately to DFT$+U^{d,p}_{\text{full}}$, $\alpha = J/2$ (which means $\alpha^d = J^d/2$, etc., and which gives identical results to DFT$+U^{d,p} + J^{d,p}$ by construction), we see a further closing of the gap and upward shift both in the valence and conduction bands. Interestingly, we obtain an extremely similar valence-band DoS from the Dudarev prescription and DFT$+U^{d,p}_{\text{full}}$, $\alpha = -J/2$, i.e. DFT$+U^{d,p} + J^{d,p}$ with the minority spin term intact. This reflects the almost-cancellation of the potentials due to terms (III) and (IV) in Eq. (2), for a subspace near full occupancy.

### B. The effects of the pseudo-atomic solver configuration for generating the DFT$+U$ subspace for Ti 3d

Before moving on to anatase, we return to check the effect of varying the charge configuration for Ti used in the pseudo-atomic solver$^{81}$, which constructs the set of the pseudo-atomic orbitals defining the 3d subspace of Ti. The neutral configuration is perhaps a natural choice, giving a relatively smooth, diffuse subspace (hence, e.g., less pressure on the plane-wave convergence) and, more importantly, since it does not rely on any prior chemical intuition. We also investigated the
FIG. 1. The total and local generalized Kohn-Sham density of states (LDOS) of pristine TiO₂-rutile calculated within DFT(LDA), DFT+U with Hund’s J neglected, when treated within the Dudarev model (U_{dev}), and when treated in a matter which fully reproduces DFT+U+J using only DFT+U code for closed-shell systems (U_{full}), both when treated with (α = -J/2) and without (α = J/2) its minority-spin (term IV). The spectrum is partitioned on a per-species basis using Mulliken analysis based on the variationally optimized NGWFs. DFT+U_{d,p} results only are shown, using parameters calculated from first principles using the minimum-tracking linear-response method, using only the Ti^0 pseudo-atomic solver configuration, and a Gaussian broadening of 0.1 eV. In order to show the separate effects of the corrective functionals tested on the valence and conduction bands, each panel uses the mid-gap energy of the DFT(LDA) calculation for 0 eV.

3+ atomic charge configuration, as a slightly more “informed” spatially localized subspace test case. Given the LDA-appropriate U and J parameters already calculated for each of the two subspace types, in this sub-section we performed the matching DFT+U, DFT+U_{eff}, and various DFT+U+J band-gap calculations, both within DFT+U and DFT+U_{d,p}. We also performed the “cross” calculations in the case of α = 0, i.e., where we used the 3+ subspace parameters for correcting the neutral subspace, and vice-versa, in order to illustrate the separate effects of over-localizing the projectors.

The results of these tests are shown in Table IV. We find that first-principles calculation of the Hubbard U and Hund’s J parameters does not compensate for the arbitrariness of the subspace choice, for Ti 3d. Instead, it reinforces this arbitrariness as far as the fundamental
gap is concerned in this system. Table IV reveals that this trend holds irrespective of whether correction is also applied to O 2p orbitals, denoted DFT+Ud,p, or indeed whether we are using DFT+U, DFT+Ueff, or DFT+Ufull. As previously discussed, the increase in spatial localization of the 3d subspace, when we move from a neutral to a 3+ configuration, increases the corresponding calculated U and J parameters. This, of course, increases the predicted gap, when those parameters are applied to either subspace type. Moreover, the table reveals that, for either fixed set of parameters, the increase in subspace localization also tends to open the gap, in this system, in fact by roughly the same amount. The net increase in the gap in going from neutral to 3+ from first-principles is approximately due, half-and-half, to the increase in parameters and increase in localization of the projection, working together.

On the basis of these results, we can envisage that both the first-principles LDA-appropriate U and J parameters, and the fundamental gap for a fixed reasonable set of parameters, will attain maxima for some reasonable (though not generally the same) value of the pseudo-atomic configuration charge. A tentative step towards plotting observables as functions of a DFT+U subspace localization quantifier was presented in Ref. 90. We do not necessarily expect that this projector arbitrariness reinforcement effect will arise transition-metal oxides generally, particularly since projector arbitrariness cancellation has previously been observed in molecular FeO+ using a self-consistently evaluated Hubbard U parameter.91. This issue in DFT+U clearly warrants further investigation on diverse systems using various approaches, such as parameter or projector self-consistency. Pragmatically, we have found in our minimum-tracking linear-response calculations to date that using the simplest, neutral pseudo-atomic configuration (irrespective of the prior pseudopotential generator reference state, which is a somewhat different, technical matter related the transferability in norm-conserving pseudopotentials) for constructing the DFT+U projections works well relative to more localised charged configurations. We note, in passing that there is a small discrepancy in the gap from 3+ subspace explicit DFT+U+J and the DFT+U-code appropriate equivalent form with α = J/2, reflecting that calculations with more localised subspaces are harder to converge, aside from giving less favourable results.

### C. The first-principles band gap of pristine TiO2-anatase

A similar procedure was followed for pristine TiO2-anatase as that which we have outlined for TiO2-rutile, except that only the neutral atomic configuration of Ti was used in the pseudo-atomic solver, in view of our previously discussed findings. As reflected in the calculated U and J parameters of Tables I and II, the electronic structures of the two polymorphs are rather similar, and again the valence (conduction) band edge is dominated by O 2p (Ti 3d) character in TiO2-anatase, necessitating DFT+Ud,p for successful gap correction. Shown in Table V is the fundamental band gap of TiO2-anatase calculated using LDA and first-principles DFT+U, DFT+Ueff, DFT+Ufull, and DFT+U+J (minority spin term (IV) included, spin-averaged, and neglected), both when applied only to the Ti 3d sub-shell and when applied also to the O 2p sub-shell. The corresponding NGWF-partitioned Mulliken LDOS plots are show in in Fig. 3. We anticipate a slight overestimation in our calculated gap values for TiO2-anatase, due to our necessarily finite effective sampling of the Brillouin zone. The band gap of anatase is of a moderately indirect character and, in practice, we cannot precisely sample it valence band maximum (most studies hold the fundamental gap of rutile to be direct at Γ, on the other hand, which we do sample). Again, experimental, first-principles, semi-empirical hybrid, many-body perturbation theory, and several previous DFT+U results from the literature are shown for comparison.

While anatase has been thoroughly studied using optical techniques, our focus here is on the fundamen-
Table V. The band gap (in eV) of TiO₂-anatase calculated within DFT(LDA), DFT+U with Hund’s J neglected, when treated within the Dudarev model \( (U_{\text{eff}}) \), and when treated in a matter which fully reproduces DFT+U+J using only DFT+U code for closed-shell systems \( (U_{\text{full}}) \), both when treated with \( (\alpha = -J/2) \) and without \( (\alpha = J/2) \) its minority-spin (term IV). DFT+\( U_d \) and DFT+\( U_{d,p} \) results are separately shown, using parameters calculated from first principles using the minimum-tracking linear-response method, using only the neutral pseudo-atomic solver configuration \( \text{Ti}_0 \). Experimental, first-principles semi-local, semi-empirical hybrid, perturbative \( G_0W_0 \), empirical and first-principles SCF linear-response DFT+U (Ref. 88) values from the literature are provided for convenient comparison. Our central results are highlighted in bold.

|          | DFT (LDA) | DFT+U | DFT+\( U_{\text{full}} \) | DFT+\( U_{\text{full}} \), \( \alpha = J/2 \) | DFT+\( U_{\text{full}} \), \( \alpha = -J/2 \) |
|----------|-----------|-------|----------------|----------------|----------------|
| Experiment \(^{11}\) | 3.47 | 1.94 | | | |
| PBE \(^{19}\) | 1.94 | 3.60 | | | |
| HSE06 \(^{19,85}\) | 3.56 | 3.61 | | | |
| LDA+\( G_0W_0 \) \(^{18}\) | 4.05 | 3.73 | | | |
| PBE+\( G_0W_0 \) \(^{11}\) | 3.27 | 2.43 | | | |
| PBE+\( G_0W_0 \) \(^{19}\) | 3.27 | 2.43 | | | |
| HSE+\( G_0W_0 \) \(^{19}\) | 3.27 | 2.43 | | | |
| DFT+\( U_{d} \) \( (U = 7.5 \text{ eV}) \) \(^{86}\) | 3.27 | 2.43 | | | |
| DFT+\( U_{d,p} \) \( (U = 3.23 \text{ eV}, U^p = 10.59 \text{ eV}) \) \(^{88}\) | 4.24 | | | | |
| DFT+\( U_{d,p} \) \( (U = 3.23 \text{ eV}, U^p = 5.0 \text{ eV}) \) \(^{88}\) | 3.23 | | | | |

The LDA gives a Kohn-Sham band gap of 2.21 eV, substantially underestimating the experimental electronic gap of 3.47 eV. DFT+\( U_d \) is ineffective at opening the gap as is in TiO₂-rutile, given the LDA-appropriate calculated first-principles \( U \) and \( J \) parameters. DFT+\( U_{d,p} \) opens the gap very efficiently and, closely mirroring what
we found for TiO$_2$-rutile, both DFT+$U$ with $J$ neglected and Dudarev’s DFT+$U_{eff}$ cause the gap to be overestimated. Similarly, again, first-principles DFT+$U$+$J$ including O 2$p$ correction gives decent agreement with the experimental gap, overestimating it by 0.03 eV (0.34 eV) when the minority spin term is neglected (included). Interestingly, both the HSE06 and DFT+$G_0W_0$ approximations seem to better recover the anatase gap than the rutile one, based on the available literature. DFT+$U_{\text{full}}$, $\alpha = J/2$ (which is to say, technically, first-principles DFT+$U^{d,p}+J^{d,p}$ with the minority spin term neglected, which doesn’t require an explicit Hund’s $J$ implementation for closed-shell systems) seems to be very competitive with respect to both methods as far as both the fundamental gap and computational complexity are concerned. The key ingredient for TiO$_2$ in this sort of method, aside from the established message that the O 2$p$ subspace needs to be treated on the same footing as the Ti 3$d$ one, is evidently to correct both for the usual charge-related ($U$) and spin-related ($J$) systematic errors in the approximate functional. Indeed, more generally it has been shown in Ref. 42, by using the $2 \times 2$ formalism to analyse the linear-response approach for Hubbard $U$ parameter calculation, that the non-neglect of Hund’s $J$ is advisable even on abstract consistency grounds. We judge that our results are, overall, very encouraging for the continued, very widespread use of DFT+$U$ and its extensions for studying TiO$_2$, and that they serve as a counter-example to the concept that such methods are fundamentally limited in their applicability to high-spin systems. It remains for a future study to establish whether TiO$_2$ is a special case for the Ref. 74 and Ref. 90 combination, or whether it is as successful for oxides, particularly closed-shell oxides, more generally. What has hampered closed-shell applications to date, as highlighted in Ref. 94, have been available Hubbard $U$ values, calculated or otherwise, that are too high for practical use. Our results demonstrate that Hund’s $J$, which is subtracted from $U$ once in the Dudarev formalism, and effectively twice in DFT+$U$+$J$ for closed-shell systems, yielding $U_{\text{full}} = U - 2J$, may be the key ingredient to moderating the $U$. The first-principles $U$ values in common circulation for Ti 3$d$ orbitals in TiO$_2$, in the range of approximately 3 – 4 eV depending on the projector choice, are perhaps fine after all. Meanwhile, our directly calculated, relatively high-seeing-at-first $U$ values for O 2$p$ orbitals in TiO$_2$ (which are more localised than Ti 3$d$ ones, when plotted) sit among the few previously reported calculated values for TiO$_2$ in the literature$^{68,89}$. Our results are consistent with the prescriptions detailed in Ref. 41 and Ref. 42, for the use and calculation of $U$ and $J$ parameters, respectively, simply being correct. The contribution of the explicit unlike-spin $J$ correction (term (III) in Eq. (2)) to the potential subspace matrix elements for spin $\sigma$, is given by $V_{\sigma m \sigma n}^{m \sigma} = J_{\sigma m \sigma n}$. It seems that this is a very good approximation, given that there are $J$ parameters involved for two different subspace types and the net result is very accurate, of benefit to the approximate generalized Kohn-Sham potential. Our results strongly support the conclusions of Ref. 41 that the minority spin term (IV) of Eq. (2), which arises only due to the double-counting correction of a unlike-spin interaction that unlikely to be well described in the underlying functional in the first place, should be neglected. Equivalently, they support the conclusion that the fully localized limit double-counting term of Refs. 95 and 96 is sufficient at this level of theory, at least as far as the potential is concerned. The DFT+$U$+$J$ gap is just one aspect of the potential, of course, and its correctness cannot be used to judge whether the double-counting in the total energy is correct, for example. In previous works, we have pointed out cases where the standard DFT+$U$ potential fails due to non-satisfaction of Koopmans’ condition$^{97}$, or due to inadequate projection onto the states adjacent to the band edges$^{98}$, neither of which effects are expected to be alleviated particularly by the incorporation of Hund’s $J$. On a similar cautionary note, it is worth emphasising that our first-principle calculations of $U$ and $J$ in TiO$_2$ were made simpler by the vanishing occupancy-magnetization coupling in closed-shell systems, by which we mean that $d\left(n^\uparrow + n^\downarrow\right)/d\alpha = 0$ and $d\left(n^\uparrow - n^\downarrow\right)/d\alpha$. In this case, the elegant formulae of of Eq. (8) become un-
ambiguous with respect to the spin-polarization of the perturbing potential. In our current view, these two formulas are essentially the correct ones for $U$ and $J$, neglecting self-consistency over parameters. As a result, without approximation and very conveniently, we were able to perturb one spin only and obtain $U$ and $J$ simultaneously. A disadvantage of this decoupling, however, is that we cannot judge on the basis of the present calculations between the merits of the “scaled 2×2” and “simple 2×2” procedures of Ref. 42, since they become identical. Overall, there is without doubt much further calculations between the merits of the “scaled 2×2” and “simple 2×2” procedures of Ref. 42, since they become identical.

We acknowledge the support of Trinity College Dublin School of Physics, of Science Foundation Ireland (SFI) through The Advanced Materials and Bioengineering Research Centre (AMBER, grant 12/RC/2278 and 12/RC/2278_P2), and of the European Regional Development Fund (ERDF). We also acknowledge the DJEI/DES/SFI/HEA Irish Centre for High-End Computing (ICHEC) for the provision of computational facilities and support. We further acknowledge Trinity Centre for High Performance Computing and Science Foundation Ireland, for the maintenance and funding, respectively, of the Boyle (Cuimhne upgrade) cluster on which further calculations were performed.

V. ACKNOWLEDGEMENTS

We acknowledge the support of Trinity College Dublin School of Physics, of Science Foundation Ireland (SFI) through The Advanced Materials and Bioengineering Research Centre (AMBER, grant 12/RC/2278 and 12/RC/2278_P2), and of the European Regional Development Fund (ERDF). We also acknowledge the DJEI/DES/SFI/HEA Irish Centre for High-End Computing (ICHEC) for the provision of computational facilities and support. We further acknowledge Trinity Centre for High Performance Computing and Science Foundation Ireland, for the maintenance and funding, respectively, of the Boyle (Cuimhne upgrade) cluster on which further calculations were performed.

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