DFT + U Study of Uranium Dioxide and Plutonium Dioxide with Occupation Matrix Control

Jia-Li Chen and Nikolas Kaltsoyannis*

Cite This: J. Phys. Chem. C 2022, 126, 11426−11435

ABSTRACT: DFT + U with occupation matrix control (OMC) is applied to study computationally bulk UO₂ and PuO₂, the latter for the first time. Using the PBESol functional in conjunction with OMC locates AFM and NM ground states for UO₂ and PuO₂, respectively, in agreement with experimental findings. By simulating the lattice parameter, magnetic moment, band gap, and densities of states, U = 4.0 eV is recommended for AFM UO₂, yielding data close to experiments for all considered properties. U = 4.5 and 4.0 eV are recommended for NM and AFM PuO₂, respectively, though much larger U values (c. 10 eV) are required to yield the most recently reported PuO₂ band gap. For both oxides, several excited states have similar properties to the ground state, reinforcing the need to employ OMC wherever possible.

INTRODUCTION

In the actinide series of elements, many of the chemical and physical properties display a turning point at plutonium. This includes the change from the more covalent early actinides to the more ionic mid and later elements, and the extensive range of oxidation states exhibited by the early elements diminishes significantly after Pu.¹ The actinide dioxides, which are the subject of this work, change from Mott−Hubbard insulators to charge transfer insulators at PuO₂.²−⁴ UO₂ and NpO₂ have antiferromagnetic (AFM) ground states ⁵−⁷ while a non-magnetic (NM) ground state is found for PuO₂.⁸,⁹ As PuO₂ is a product of the recycling of spent UO₂ nuclear fuel, detailed understanding of PuO₂ is clearly essential not just at a fundamental level but also to inform its safe current and long-term storage.

Due to the high radioactivity of PuO₂, experiments are very challenging, and hence theoretical simulations play a particularly valuable role in its study. Density functional theory (DFT) with a Hubbard U correction is widely used⁴,¹⁰,¹¹ as it gives reasonable predictions at the lowest computational costs. However, the ability of the DFT + U approach to correctly identify the NM magnetic ground state of PuO₂ remains an issue. The NM ground state has been established by various experiments over a wide temperature range (4−1000 K), including by inelastic neutron scattering and nuclear magnetic resonance.⁶,⁹,¹²−¹⁴ By contrast, previous DFT + U simulations have predicted an AFM ground state for PuO₂,¹¹,¹⁵,¹⁶ although this does not match with experiments, many of the other calculated properties of AFM PuO₂ do agree quite well. There are also some other theoretical works that adopt the experimentally indicated NM state.⁵,¹⁷,¹⁸ The inconsistency between experiments and DFT + U simulation over the correct magnetic ground state of PuO₂ requires further study.

The majority of actinide compounds are open-shell and frequently feature several unpaired electrons in the seven valence 5f orbitals. There are typically many different ways in which the actinide f orbitals may be populated, and use of the Hubbard U parameter in DFT calculations can lead to the location of excited states arising from those electronic configurations.¹⁹,²⁰ It is unclear whether the previous computational reports of an AFM ground state for PuO₂ arise from a fundamental inability of DFT + U to locate the correct ground state or if they have become trapped in higher energy states. To address this question, we here consider all possible filling patterns of the 4 electrons in the 7 5f orbitals of Pu(IV), using the occupation matrix control (OMC) approach.²¹ To the best of our knowledge, there is no such work so far. Wang and Konashi considered all possible occupation matrices (OMs) for AFM Pu (5f⁵) in PuO₂,²² though not Pu (5f⁴) in which we are interested, and found that there are low-lying excited states. Dorado et al. considered all possible OMs for the 2 electrons in the 7 5f orbitals of AFM UO₂,²³ finding that the highest energy OM state is about 3.5 eV above the lowest one.
In this work, we first consider all possible OMs for AFM, FM, and NM UO2. Although previous DFT + U simulations agree with experiments over the AFM ground state for UO2,^24 it is worth considering all possible OMs for FM and NM as well as AFM to be sure of the correct computed ground state for UO2 and UO2 provides a good test of the DFT + U with the OMC method as there are more data available on UO2. We then consider all possible OMs for AFM, FM, and NM PuO2, in order to establish the correct theoretical ground state. Through exploration of the effect of the choice of Hubbard U on a range of computed properties (lattice parameter, band gap, magnetic moment, and density of states), we also aim to provide recommendations as to the best values of U to employ in DFT + U + OMC studies of UO2 and PuO2.

### COMPUTATIONAL DETAILS

All calculations were performed using density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP), version 5.4.1.25–28 The generalized gradient approximation functional of Perdew, Burke, and Ernzerhof, revised for solids (PBEsol), was used,^29 with a Hubbard U correction for the 5f electrons.30 A wide range of U values (0.0–7.0 eV) was considered to establish the most suitable values for the simulation of UO2 and PuO2 bulk (Figure 1a). Plane wave basis sets and projector augmented wave pseudopotentials were used to describe the ions.31 Plane wave cutoff energy and k mesh sizes were tested for UO2 bulk with the lattice parameter fixed at 5.470 Å (the experimental values are 5.470–5.473 Å).32–34 Figure 1b shows that a plane wave cutoff energy of 500 eV and gamma-centered 5 × 5 × 5 Monkhorst–Pack grid for the Brillouin zone are sufficient.35 Therefore, a 650 eV (1.3 × 500 eV) cutoff energy (to weaken the influence of Pulay stress) and gamma-centered 5 × 5 × 5 Monkhorst–Pack grid were used for all calculations in this work. The iteration threshold for electronic and ionic convergence was set to 1 × 10−5 and 1 × 10−2 eV, respectively.

Antiferromagnetic (AFM), ferromagnetic (FM), and nonmagnetic (NM) states were considered with 1 k colinear ordering (along the c direction, Figure 1a) for both UO2 and PuO2. 1 k colinear ordering was chosen over 3 k non-colinear ordering because, although AnO2 exhibit non-colinear magnetic behavior,^36 in which the magnetic moments of the ions have contributions in more than one direction, 1 k ordering is much more computationally tractable than 2 k or 3 k ordering. Furthermore, most previous computational work also uses 1 k ordering, so even using it facilitates more direct comparison, and we here in part aim to find a theoretical approach that gives accurate simulation of UO2 and PuO2 at manageable computational cost. As the 1 k colinear ordering is used, we have only Type G magnetic arrangements (along the c direction). U/Pu labeled 1 and 2 in Figure 1a are set to spin up and 3 and 4 are set to spin down for all AFM calculations in this work.

Occupation matrix control (OMC), developed by Dorado et al.,^33,37 and incorporated into VASP by Allen and Watson,^21 was used to explore all possible OMs. Only the diagonal elements were set to non-zero values for initial OMs:

\[
\begin{pmatrix}
0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.0 & 0.0 & n & 0.0 & 0.0 & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & n & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0
\end{pmatrix}
\]

where n is either 0.0 or 1.0. U and Pu in their dioxide bulk have 2 and 4 5f electrons, respectively; these are unpaired in the FM and AFM states and paired in the NM state. Therefore, we studied C21 = 21 OMs for FM and AFM UO2, C21 = 7 OMs for NM UO2, C17 = 35 OMs for FM and AFM PuO2, and C17 = 21 OMs for NM PuO2; all OMs are listed in the Supporting Information (Tables S1 and S2). Although some of the electronic configurations defined by the OMs are degenerate, we decided to follow the approach of Dorado et al., who used DFT + U + OMC to investigate bulk UO2,^33 and study all the OMs as the imposition of U can decrease the degeneracy of the f orbitals. The initially imposed OMs remain unchanged during the self-consistent field calculations.

All of the data presented in the main text were obtained with the PBEsol functional. We also performed all the calculations using the PBE functional and found that PBEsol predicts better lattice parameters. The PBE data are collected in Figures S5–S9 and Table S3 in the Supporting Information.

### RESULTS AND DISCUSSION

Uranium Dioxide (UO2). We now explore the energies of the AFM, FM, and NM states of UO2 with the OMs as described in the Computational Details. As the Hubbard U has an influence on the localization and energy of the f orbitals, a wide range of U values is considered. The pure PBEsol method (U = 0.0 eV) predicts the same energy for all solutions of AFM, FM and NM UO2 (Figure 2). Furthermore, checking the magnetic moment on each U atom indicates that all AFM and NM states optimize to FM states. Introduction of a non-

---

**Figure 1.** (a) UO2/PuO2 bulk, gray and red spheres represent U/Pu and O, respectively. (b) Energy against cutoff energy (U = 4.0 eV and k points = 5) and energy against k point (U = 4.0 eV and cutoff energy = 500 eV) for UO2 with a lattice parameter of 5.470 Å.
As noted above, pure DFT and low $U$ values (<2.0 eV) predict an FM ground state, regardless of the initially chosen magnetic state; the energies obtained with $U \geq 2.0$ eV are compared for AFM, FM, and NM states in Figure 3. As shown in Figure 3b, an NM ground state is found for UO$_2$ with $2.0 \leq U < 3.0$ eV; when $U \geq 3.0$ eV, the AFM ground state appears. Previous experiments have confirmed that the ground state of UO$_2$ is AFM, so the chosen $U$ value should be not smaller than 3.0 eV to give reasonable prediction. As the ground state is predicted differently with low and high $U$ values, we suggest caution when employing the $U$-ramping method, in which $U$ is scanned from zero to the desired value in small steps, while reading the previous step’s result.

We did not find any distortion of cubic UO$_2$ bulk, i.e., 1 k AFM UO$_2$ keeps the $Fm-3m$ crystal symmetry. The lattice parameter gradually increases with the $U$ value, and 3 eV $\leq U \leq 4$ eV yields lattice parameters close to the experimental values (Figure 4a). The magnetic moment on the U ions also increases with increasing $U$ (Figure 4b); imposing $U$ on the f orbitals leads to more localized f electrons. AFM and FM UO$_2$ simulations slightly overestimate the magnetic moment on U ions, but the differences are small, and AFM UO$_2$ is predicted to have a magnetic moment closer to the experimental value.38

The band gap of UO$_2$ increases with $U$ in a similar way for the AFM, FM, and NM states. Across the range of $U$ studied, NM UO$_2$ has the largest band gap and FM UO$_2$ has the smallest band gap, with the band gap of AFM UO$_2$ being slightly lower than for NM. Figure 4c suggests that 4.0 eV $\leq U \leq 5.0$ eV gives good agreement with experiments for the band gap of AFM UO$_2$.39,40

As well as the band gap, the density of states (DOS) is an important electronic property against which to evaluate the simulation. As AFM is the experimentally and theoretically reported ground state, only the DOS of AFM UO$_2$ is discussed here. We plot the DOS for AFM UO$_2$ with $U$ values ranging from 2.0 to 7.0 eV in steps of 1.0 eV (Figure 5). We are mainly interested in three bands in the DOS: the valence band, the conduction band, and the second band below the Fermi level. Increasing the Hubbard $U$ localizes and stabilizes the f electrons. The valence band, which is mainly U 5f, moves downward in the DOS. This increases the band gap, and the gap between the valence band and the second band (which is mainly of O 2p character) reduces, such that the two bands become mixed at high $U$ (6.0 and 7.0 eV). As the Fermi level is fixed at 0.0 eV, the conduction band and the second band under the Fermi level move upward with increasing $U$ value.

X-ray absorption data indicate that the valence band is mainly U 5f,41 so we can exclude $U \geq 6.0$ eV. Previous experiments also show that the second peak under the Fermi level consists of O 2p states at around $-4.0$ eV,41,42 so we can also exclude $U = 5.0$ eV. Though $U = 2.0$ eV predicts a reasonable position for the second peak under the Fermi level, the band gap is much smaller than the experimental value and it predicts an NM ground state. Therefore, 2.0 eV $< U < 5.0$ eV is the preferred range to obtain reasonable DOS for UO$_2$ bulk simulation.

Overall, we find that 3.0 eV $\leq U \leq 5.0$ eV gives the best balance of agreement with experimental data over a range of properties, with the best value being 4.0 eV. Some properties of AFM UO$_2$ calculated with the PBESol $+ U$ ($U = 4.0$ eV) + OMC method are summarized and compared with experimental values in Table 1.
Plutonium Dioxide. We now explore AFM, FM, and NM PuO$_2$ calculated with the OMs described in the Computational Details, with the PBESol + $U$ ($U = 0.0$−$7.0$ eV) method. The energies of these states are summarized in Figure S1. As for UO$_2$, $U$ values ≥$2.0$ eV predict the same solution as the most stable: for AFM and FM, the most stable solution has the four
unpaired electrons occupying the $f_{\text{−}3}, f_{\text{−}1}, f_1$, and $f_3$ orbitals (the 31st OM in Table S2), while for the NM states, the most stable solution has two pairs of electrons in the $f_1$ and $f_3$ orbitals (the 20th OM in Table S2). In the following discussion, we focus on the most stable AFM, FM, and NM solutions and refer to them as the AFM, FM, and NM states for simplicity.

Properties of the AFM, FM, and NM states are compared in Figure 6. When $U \geq 2.0$ eV, an NM ground state is found, in agreement with previous experiments in the temperature range 4−1000 K.8,14 However, the energy difference between AFM and NM is small (Figure 6b), increasing from $U = 2.0$ to 4.0 eV and then decreasing again, with the largest difference of $-0.18$ eV. Previous DFT + U simulations have found an AFM ground state for PuO$_2$, although given the small energy differences with NM states, it may be that DFT + U simulation of PuO$_2$ without OMC can become trapped in an AFM state.

Similar to UO$_2$, PuO$_2$ bulk remains face-centered cubic after optimization and the optimized lattice parameter increases with the $U$ value (Figure 6c), with $4.0 \leq U \leq 5.0$ eV giving values close to experiments for AFM and NM.34,43−46 These states have similar lattice parameters for a given $U$, while a much larger lattice parameter is predicted for FM PuO$_2$ with

| AFM UO$_2$ | NM PuO$_2$ | AFM PuO$_2$ |
|-------------|-------------|-------------|
| exp. | cal. | exp. | cal. | cal. |
| lattice parameter (Å) | | | | | |
| 5.470 | 5.473 | 5.393 | 5.394 | 5.390 |
| magnetic moment ($\mu_B$) | 1.74 | 1.88 | 0 | 0 | 3.72 |
| band gap (eV) | 2.0−2.5 | 2.0 | 1.8−4.1 | 1.56 | 0.9 |

Data obtained with PBESol + $U$ + OMC ($U = 4.0$ eV for AFM UO$_2$ and AFM PuO$_2$, 4.5 eV for NM PuO$_2$). The equivalent PBE data can be found in Table S3.

Figure 6. As a function of $U$, the (a) energies of AFM, FM, and NM PuO$_2$, (b) energy difference between AFM and NM PuO$_2$ ($E_{\text{NM}} - E_{\text{AFM}}$), (c) lattice parameter of AFM, FM, and NM PuO$_2$, experimental values from refs 34, 43, 46, and (d) band gap of AFM, FM, and NM PuO$_2$, experimental values from refs 38, 47. Inset to panel (d) shows the band gap of NM PuO$_2$ calculated with $U = 5$−11 eV.
the same $U$ value. This is by contrast to UO$_2$, where although the largest lattice parameter was also obtained for the FM state, it is close to the AFM and NM lattice parameters for a given $U$ value (Figure 4a). This may well be reminiscent of previous work on the paramagnetic to ferromagnetic transition of La(Fe,Si)$_{1-x}$)$_{3}$, where a larger volume change is observed for $x = 0.88$ (where Fe has a larger magnetic moment) than for $x = 0.86$ (where Fe has a smaller magnetic moment); as Pu$^{4+}$ has a larger magnetic moment than U$^{4+}$, the difference between the lattice parameter of FM and AFM/NM for PuO$_2$ is larger than for UO$_2$.

PuO$_2$ is found to be nonmagnetic by experiment, and hence the magnetic moment of Pu should be zero, and experiments indeed find only a very small nuclear magnetic moment for Pu$^{4+}$ (about 0.15 $\mu_B$), which may arise from coupling between the singlet $\Gamma_1$ ground state and (an) excited state(s). The excited state could be solely the triplet $\Gamma_4$ state, at an energy of about 0.120 eV, or two or more states in the energy region 0.110–0.140 eV, but spectral resolution is insufficient to be certain. We here find that AFM PuO$_2$ is higher in energy than NM PuO$_2$ by less than 0.18 eV, so ground-state PuO$_2$ could have a small contribution from the AFM state; high-resolution neutron spectroscopy would be helpful here. The Pu magnetic moments of AFM and FM PuO$_2$ against the $U$ value are given in Figure S2; due to more localized f states with increasing $U$ value, the magnetic moment of Pu increases with $U$.

Pure PBEsol and PBEsol + $U$ with a small $U$ value ($< 3.0$ eV) predict PuO$_2$ to be metallic; with increasing $U$, PuO$_2$ becomes a semiconductor with a band gap that increases with $U$. As with UO$_2$, NM PuO$_2$ has the largest band gap, and FM has the smallest. 5.0 $\leq U \leq$10.0 eV are needed to give band gaps in the range of the experimental data (1.8 eV–4.1 eV), see inset to Figure 6d.

We now examine the DOS of the NM PuO$_2$ ground state (Figure 7). As with UO$_2$, we are interested in the conduction and valence bands as well as the second band under the Fermi level. Different from UO$_2$, there is a mix of p and f states in both the valence band and the second band under the Fermi level, although similar to the DOS of UO$_2$, increasing $U$ leads to the downward movement of the valence band while upward movement of the conduction band and second band under the Fermi level is observed in Figure 7. Downward movement of the valence band results in a larger band gap and more complicated interaction between the valence band and the second band under the Fermi level. When $U < 4.0$ eV, the valence band moves downward and approaches the second band, but there is a clear boundary to the position of the valence band (f state-dominated and at around $-2$ to 0 eV) and the second band (p state-dominated and at around $-7$ to $-2$ eV). When $U \geq 4.0$ eV, the origin of the second band and valence band are merged; a new valence band (at around $-4$ to 0 eV) and a new second band under the Fermi level (p state-dominated and at around $-7$ to $-4$ eV; though it is connected with the valence band, we name it as the second band under the Fermi level to distinguish it from the abovementioned new valence band) are observed. The new valence band has a similar contribution from the p and f states. When $U \geq 5.0$ eV, O p states gradually dominate the valence.

The valence band of PuO$_2$ is a mixed f and p character, with a higher contribution of the former, so $U \geq 5.0$ eV values are not good choices as they predict a higher (or equal) contribution of p states than f states for the valence band. Previous X-ray photoelectron spectra have shown that the valence band is split into a mainly Pu 5f-contributed state (at higher energy) and a mainly O 2p-contributed state (at lower energy), which is also supported by previous theoretical simulations. Previous UPS studies showed that the contribution of Pu 5f states is centered at around 2 eV below the Fermi level, in agreement with XPS data. UPS also shows that the O 2p band, which covers a wider range below the Fermi level, extends to $-10$ eV, while it ends at around $-8$ eV from UPS data.

The center of the Pu 5f states moves downward with increasing $U$; for NM PuO$_2$ simulated with $U = 2.0$ eV, the 5f states are centered at around $-1.5$ eV, at around $-2.0$ eV with $U = 4.0$ eV, matching the experiment well, and at around $-2.5$ eV with $U = 5.0$ eV, which is also reasonable. The O 2p states end at around $-7$ eV for NM PuO$_2$ with $U = 2.0$ eV, which is the closest value to experimental data (about $-8$ eV), as the second band moves upward with increasing $U$, ending at around $-6$ eV for NM PuO$_2$, with $U = 5.0$ eV. In general, 4.0 eV $\leq U < 5.0$ eV gives reasonable prediction for the position of the Pu 5f states in the valence band (Figure 7). We have also...
studied NM PuO$_2$ bulk with $U = 4.5$ eV; the DOS is given in Figure 8, which meets the experimentally reported features well, such as the composition and center of the valence band. Previous works also suggest that there is a peak of the O p state character on the left shoulder of the valence band, a feature which can be seen in our DOS for NM PuO$_2$ simulated with $U = 4.0$ and 4.5 eV. Overall, 4.0 eV $\leq U \leq$ 4.5 eV is good for NM PuO$_2$ bulk simulation with $U = 4.5$ eV being the best, as this value predicts a larger band gap than $U = 4.0$ eV.

We also studied the DOS of AFM PuO$_2$ as it is the most studied state of PuO$_2$ and may have a contribution to the ground state. The DOS of AFM PuO$_2$ (Figure 9) is similar to those of NM PuO$_2$, with some minor differences. The DOS of AFM PuO$_2$ shown here is also similar to previous theoretical simulations. Therefore, although most previous DFT + $U$ works without OMC study the AFM state of PuO$_2$, they still obtain results similar to experiments, i.e., AFM PuO$_2$ is a good approximation to NM PuO$_2$ in the simulation of certain properties. To obtain good DOS for AFM PuO$_2$, the $U$ value should be smaller than 5 eV as $U \geq 5.0$ eV predicts an O 2p state-dominated valence band. The DOS of PuO$_2$ calculated with $U = 4.5$ eV is given in Figure S3 and predicts almost the same contribution of p and f states to the valence band, so $U \leq$ 4.5 eV is needed to predict an f state-dominated valence band, while $U < 3.0$ eV predicts AFM PuO$_2$ as metallic. Overall, for AFM PuO$_2$, 4.0 eV $\leq U \leq$ 4.5 eV with $U = 4.0$ eV is the best as it predicts more reasonable DOS.

In summary, first, to obtain an NM ground state for PuO$_2$, the chosen $U$ value must be larger than 2 eV; second, to obtain reasonable lattice parameters, 4.0 eV $\leq U \leq$ 5.0 eV is suggested; third, 5.0 eV $\leq U \leq$ 10.0 eV is needed to reproduce the range of experimentally reported band gaps; fourth, to give reasonable DOS, 4.0 eV $\leq U \leq$ 5.0 eV is suggested. Hence, no single $U$ value can simultaneously reproduce the band gap and the other three pieces of experimental data. $U = 10.0$ predicts a band gap of 4.10 eV, which is the latest experimental datum, but it also predicts totally wrong DOS (Figure S4). Overall, therefore, we suggest 4.0 eV $\leq U \leq$ 5.0 eV with 4.5 and 4.0 eV being the best values for the simulation of NM and AFM PuO$_2$ bulk, respectively. Some properties of NM and AFM PuO$_2$ calculated with PBESol + $U$ (4.5/4.0 eV) + OMC are listed in Table 1.

### Dependence of Energy, Lattice Parameter, and Band Gap on the Occupation Matrix

With the ground state OMs and the effect of the Hubbard $U$ on the properties of those ground states in hand for both UO$_2$ and PuO$_2$, we here provide an insight into how the solutions calculated from different initial OMs affect the energy, lattice parameter, and band gap. Table 2 presents these data for the solutions arising from the different initial OMs of AFM UO$_2$ and NM PuO$_2$, using $U$ values of 4.0 and 4.5 eV, respectively. We find the same OM for ground-state AFM UO$_2$ as does previous work, and the energy range spanned by the solutions is about 9 eV. This is significantly larger than in the previous study, where the highest energy solution is only 3.45 eV higher than the ground state, although we note that previous workers report some non-converged states, which have the same OMs as the high-energy solutions (Table 2, in red) we find here. These high-energy solutions have a slightly larger lattice parameter ($\sim$5.53 Å) than the ground state (5.479 Å) and much smaller band gaps ($\sim$1.0 eV vs 1.99 eV). We expect that, due to their high energy, optimizations without initial OMC have a good chance of avoiding these solutions.

There are 6 medium-energy solutions of AFM UO$_2$ with relative energies of c. 1 to 3 eV (Table 2, in orange) and a further 8 low-energy solutions with relative energies of $<$1 eV
In this work, we have studied bulk UO$_2$ and PuO$_2$ with PBESol $+$ $U$ (0−7 eV) $+$ OMC. By calculating the energies of all possible solutions with different initially imposed OMs of 1 k AFM, FM and NM UO$_2$ and PuO$_2$, PBESol $+$ $U$ + OMC simulation predicts AFM and NM ground states for UO$_2$ and PuO$_2$, respectively. Our UO$_2$ ground state is in agreement with previous experimental results and theoretical simulations. For PuO$_2$, we show for the first time that PBESol $+$ $U$ + OMC correctly reproduces the experimentally reported NM ground state. We have also considered a wide range of $U$ in order to find the best value for theoretical simulation. The lattice parameter, magnetic moment, band gap, and density of states have been simulated. $U$ = 4.0 eV is recommended for AFM UO$_2$, as this gives data close to experiments for all considered properties. For NM and AFM PuO$_2$, we recommend $U$ = 4.5 and 4.0 eV, respectively, though note that extremely large $U$ values (c. 10 eV) are required to yield the most recently reported PuO$_2$ band gap. Exploration of the energies, lattice parameters, and band gaps of AFM UO$_2$ and NM PuO$_2$ calculated with PBESol $+$ $U$ (4.0 and 4.5 eV, respectively) + OMC reveals that several excited states have similar properties to the ground state and hence it is very hard to distinguish them from the ground state in the absence of OMC.

### ASSOCIATED CONTENT

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03804.

Occupation matrices of U and Pu 5f orbitals for AFM, FM, and NM UO$_2$ and PuO$_2$; energies of AFM, FM, and NM PuO$_2$; magnetic moment of Pu in AFM and FM PuO$_2$; DOS of AFM PuO$_2$ calculated with PBESol $+$ $U$ (4.5 eV) + OMC; DOS of NM PuO$_2$ calculated with PBESol $+$ $U$ (10.0 eV) + OMC; PBE $+$ $U$ + OMC results for UO$_2$ and PuO$_2$ (PDF)

### AUTHOR INFORMATION

**Corresponding Author**
Nikolas Kaltsoyannis — Department of Chemistry, School of Natural Sciences, University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0003-0293-5742; Email: nikolas.kaltsoyannis@manchester.ac.uk

**Author**
Jia-Li Chen — Department of Chemistry, School of Natural Sciences, University of Manchester, Manchester M13 9PL, United Kingdom

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03804

**Notes**
The authors declare no competing financial interest.

The data underlying this study are openly available at https://data.mendeley.com/datasets/zrcv3yw9sn/1.

---

### Table 2. Occupation Matrix (OM, Details in Tables S1 and S2), Relative Energy (E, eV), Lattice Parameter (L, Å), and Band Gap (G, eV) of Each Solution of AFM UO$_2$ and NM PuO$_2$ Calculated with PBESol $+$ $U$ (4.0 eV and 4.5 eV, Respectively)

| OM  | UO$_2$          |   |   | PuO$_2$          |   |   |
|-----|-----------------|---|---|-----------------|---|---|
|     | E   | L   | G   | E   | L   | G   |
| [0000100] | 0.00 | 5.479 | 1.99 | [0000020] | 0.00 | 5.393 | 1.56 |
| [0010000] | 0.05 | 5.479 | 2.47 | [0000020] | 0.17 | 5.395 | 2.20 |
| [1000100] | 0.13 | 5.481 | 1.93 | [2000000] | 0.26 | 5.397 | 2.12 |
| [0001000] | 0.29 | 5.479 | 0.00 | [2000000] | 0.56 | 5.403 | 1.54 |
| [1010000] | 0.29 | 5.485 | 1.82 | [0000020] | 1.02 | 5.412 | 1.51 |
| [00000100] | 0.52 | 5.483 | 1.94 | [0000020] | 1.63 | 5.399 | 2.61 |
| [10000100] | 0.58 | 5.493 | 1.79 | [2000000] | 1.80 | 5.397 | 2.11 |
| [00000001] | 0.71 | 5.483 | 2.44 | [2000000] | 3.12 | 5.398 | 2.22 |
| [10000001] | 0.97 | 5.490 | 1.89 | [2000000] | 3.53 | 5.405 | 2.13 |
| [00110000] | 1.18 | 5.485 | 1.94 | [0000020] | 4.25 | 5.402 | 1.49 |
| [10010000] | 1.33 | 5.483 | 1.91 | [0200000] | 4.43 | 5.407 | 1.48 |
| [00011000] | 1.80 | 5.483 | 2.52 | [0000020] | 8.67 | 5.397 | 2.60 |
| [10100000] | 2.10 | 5.488 | 2.23 | [0200000] | 9.03 | 5.405 | 2.59 |
| [00010100] | 2.51 | 5.483 | 1.95 | [0200000] | 10.27 | 5.405 | 1.47 |
| [10010100] | 2.79 | 5.491 | 1.91 | [2000000] | 10.46 | 5.410 | 1.46 |
| [01001000] | 7.93 | 5.517 | 0.74 | [0200000] | 25.64 | 5.440 | 0.89 |
| [00100100] | 7.94 | 5.519 | 0.78 | [0200000] | 25.65 | 5.444 | 0.89 |
| [11000000] | 8.05 | 5.520 | 0.75 | [2000000] | 25.97 | 5.446 | 0.72 |
| [10100000] | 8.10 | 5.522 | 0.79 | [2000000] | 26.02 | 5.452 | 0.77 |
| [01001000] | 9.33 | 5.523 | 0.66 | [0200000] | 31.57 | 5.444 | 0.65 |
| [01010000] | 9.46 | 5.526 | 0.80 | [0200000] | 31.86 | 5.460 | 0.76 |

*Low-, medium- and high-energy solutions are in given blue, orange, and red, respectively.*
ACKNOWLEDGMENTS

We acknowledge financial support from the EPSRC (EP/T013842/1) and are grateful to The University of Manchester for access to its Computational Shared Facility and associated support services. We also thank the HEC Materials Chemistry Consortium, which is funded by the EPSRC (EP/L000202, EP/R029431), for access to ARCHER2, the UK’s National Supercomputing Service (https://www.archer2.ac.uk).

REFERENCES

(1) Konings, R. J. M.; Beneš, O.; Kovács, A.; Manara, D.; Sedmidubský, D.; Gorokhov, L.; Iorish, V. S.; Youngman, V.; Shenyavskaya, E.; Osina, E. The thermodynamic properties of the f-elements and their compounds. Part 2. The lanthanide and actinide oxides. J. Phys. Chem. Ref. Data 2014, 43, No. 013101.

(2) Chen, J.-L.; Kaltsoyannis, N. Computational study of the bulk and surface properties of minor actinide dioxide MANO2 (MAN = Np, Am, and Cm); Water adsorption on stoichiometric and reduced {111}, {110}, and {100} surfaces. J. Phys. Chem. C 2019, 123, 15540–15550.

(3) Chen, J.-L.; Kaltsoyannis, N. Hybrid functional/embedded cluster study of uranium and actinide (actinide = Np, Pu, Am or Cm) mixed oxides bulk and {110} surfaces. J. Nucl. Mater. 2022, 560, 153490.

(4) Pegg, J. T.; Aparicio-Angles, X.; Storr, M.; de Leeuw, N. H. DFT +U study of the structures and properties of the actinide dioxide. J. Nucl. Mater. 2017, 492, 269–278.

(5) Kern, S.; Loong, C.-K.; Lander, G. H. Crystal-field transitions in f-electron oxides. Phys. Rev. B 1985, 32, 3051.

(6) Osborn, R.; Taylor, A. D.; Bowden, Z. A.; Hackett, M. A.; Hayes, W.; Hutchings, M. T.; Amoretti, G.; Caciuffo, R.; Blaise, A.; Fournier, J. M. High-resolution neutron spectroscopy of crystal-field excitations in uranium dioxide. J. Phys. C: Solid State Phys. 1988, 21, L931.

(7) Kern, S.; Morris, J.; Loong, C. K.; Goodman, G. L.; Lander, G. H.; Cort, B. Neutron inelastic experiments on actinide dioxide: Search for crystal-field levels in NpO2. J. Appl. Phys. 1983, 53, 3598–3600.

(8) Raphael, G.; Lallement, R. Susceptibilité magnétique de PuO2. Solid State Commun. 1968, 6, 383–385.

(9) Kern, S.; Loong, C. K.; Goodman, G. L.; Cort, B.; Lander, G. H. Crystal-field spectroscopy of PuO2: further complications in actinide dioxide. J. Phys.: Condens. Matter 1990, 2, 1933–1940.

(10) Chen, J.-L.; Kaltsoyannis, N. Computational study of plutonium–Americium mixed oxides (PuO2-xAmO2-xO2); Water adsorption on {111}, {110}, and {100} surfaces. J. Phys. Chem. C 2020, 124, 6646–6658.

(11) Sun, B.; Zhang, P.; Zhao, X.-G. First-principles local density approximation + U and generalized gradient approximation + U study of plutonium oxides. J. Chem. Phys. 2008, 128, No. 084705.

(12) Kern, S.; Robinson, R. A.; Nakotte, H.; Lander, G. H.; Cort, B.; Watson, P.; Vígil, F. A. Crystal-field transition in PuO2. Phys. Rev. B 1999, 59, 104.

(13) Tokunaga, Y.; Sakai, H.; Fujimoto, T.; Kambe, S.; Walstedt, R.; Ikushima, K.; Yasuoka, H.; Aoki, D.; Homma, Y.; Haga, Y.; Matsuda, T. D.; Ikeda, S.; Yamamoto, E.; Nakamura, A.; Shiokawa, Y.; Nakajima, K.; Arai, Y.; Onuki, Y. NMR studies of actinide dioxide. J. Alloys Compd. 2007, 444–445, 241–245.

(14) Yasuoka, H.; Koutroulakis, G.; Chudo, H.; Richardson, S.; Veirs, D. K.; Smith, A. I.; Bauer, E. D.; Thompson, J. D.; Jarvinen, G. D.; Clark, D. L. Observation of 239Pu nuclear magnetic resonance. Science 2012, 336, 901–904.

(15) Zhang, P.; Wang, B.-T.; Zhao, X.-G. Ground-state properties and high-pressure behavior of plutonium dioxide: Density functional theory calculations. Phys. Rev. B 2010, 82, No. 144110.

(16) Jomard, G.; Amadon, B.; Bottin, F.; Torrent, M. Structural, thermodynamic, and electronic properties of plutonium oxides from first principles. Phys. Rev. B 2008, 78, No. 075125.
(39) Meek, T. T.; Von Roedern, B.; Clem, P. G.; Hanrahan, R., Jr.
Some optical properties of intrinsic and doped UO₂ thin films. Mater.
Lett. 2005, 59, 1085–1088.

(40) Schoenes, J. Optical properties and electronic structure of UO₂.
J. Appl. Phys. 1978, 49, 1463–1465.

(41) Yu, S.-W.; Tobin, J. G.; Crowhurst, J. C.; Sharma, S.; Dewhurst, J. K.; Olalde-Velasco, P.; Yang, W. L.; Siekhaus, W. J. f-f origin of the
insulating state in uranium dioxide: X-ray absorption experiments and
first-principles calculations. Phys. Rev. B 2011, 83, No. 165102.

(42) Teterin, Y. A.; Popel, A. J.; Maslakov, K. I.; Teterin, A. Y.;
Ivanov, K. E.; Kalmykov, S. N.; Springell, R.; Scott, T. B.; Farman, I.
XPS study of ion irradiated and unirradiated UO₂ thin films. Inorg.
Chem. 2016, 55, 8059–8070.

(43) Haschke, J. M.; Allen, T. H.; Morales, L. A. Reaction of plutonium
dioxide with water: formation and properties of PuO₂₋ₓ.
Science 2000, 287, 285–287.

(44) Noe, M.; Fuger, J. Self-radiation effects on the lattice parameter
of ²³⁹PuO₂. Inorg. Nucl. Chem. Lett. 1974, 10, 7–19.

(45) Yamashita, T.; Muto, H.; Tsuji, T.; Nakamura, Y. Thermal
expansion of neptunium—plutonium mixed oxides. J. Alloys Compd.
1998, 271, 404–407.

(46) Roussel, P.; Graham, K. S.; Hernandez, S. C.; Joyce, J. J.;
Nelson, A. J.; Sykes, R.; Venhaus, T.; White, K. Electronic and optical
properties of plutonium metal and oxides from Reflection Electron
Energy Loss Spectroscopy. Appl. Surf. Sci. 2021, 553, No. 149559.

(47) Fujita, A.; Akamatsu, Y.; Fukamichi, K. Itinerant electron
metamagnetic transition in La (FeₓSi₁₋ₓ)₁₃ intermetallic compounds.
J. Appl. Phys. 1999, 85, 4756–4758.

(48) McCleskey, M. T.; Bauer, E.; Jia, Q.; Burrell, A. K.; Scott, B. L.;
Conradson, S. D.; Mueller, A.; Roy, L.; Wen, X.; Scuseria, G. E.;
Martin, R. L. Optical band gap of NpO₂ and PuO₂ from optical
absorbance of epitaxial films. J. Appl. Phys. 2013, 113, No. 013515.

(49) McNeilly, C. The electrical properties of plutonium oxides. J.
Nucl. Mater. 1964, 11, 53–58.

(50) Courteix, D.; Chayrouse, J.; Heintz, L.; Baptist, R. XPS study of
plutonium oxides. Solid State Commun. 1981, 39, 209–213.

(51) Gouder, T.; Seibert, A.; Havela, L.; Rebizant, J. Search for
higher oxides of Pu: A photoemission study. Surf. Sci. 2007, 601,
L77–L80.

(52) Seibert, A.; Gouder, T.; Huber, F. Interaction of PuO₂ thin
films with water. Radiochim. Acta 2010, 98, 647–657.