Effect of spin-orbit coupling on the actinide dioxides AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{and Am}$): A screened hybrid density functional study

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We present a systematic comparison of the lattice structures, electronic density of states, and band gaps of actinide dioxides, AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{and Am}$) predicted by the Heyd-Scuseria-Ernzerhof screened hybrid density functional (HSE) with the self-consistent inclusion of spin-orbit coupling (SOC). The computed HSE lattice constants and band gaps of AnO_2 are in consistently good agreement with the available experimental data across the series, and differ little from earlier HSE results without SOC. ThO_2 is a simple band insulator (f^0), while PaO_2 , UO_2 , and NpO_2 are predicted to be Mott insulators. The remainders (PuO_2 and AmO_2) show considerable $\text{O}2p/\text{An}5f$ mixing and are classified as charge-transfer insulators. We also compare our results for UO_2 , NpO_2 , and PuO_2 with the PBE+U, self interaction correction (SIC), and dynamic mean-field theory (DMFT) many-body approximations. [<http://dx.doi.org/10.1063/1.4757615>]

I. INTRODUCTION

The actinide oxides have been extensively studied in the context of the nuclear fuel cycle. They are also of fundamental interest as members of the class of strongly correlated materials – the Mott insulators – and a number of many-body approximations have been applied to their electronic structure.¹ We have previously reported the predictions of screened hybrid density functional theory across this series, and in particular have commented on the unexpected appearance of covalent mixing as one progress to the right in the series.² In the present contribution, we consider the effect of spin-orbit-coupling (SOC) on these results, and compare our results for the geometric structure, density of states (DOS), and band gaps with experiment and other theoretical approximations.

II. COMPUTATIONAL DETAILS

The results in this paper are based on plane wave expansions using the computer program VASP (Vienna *Ab-initio* Simulation Package).³ The energy cutoff for the plane-wave basis was set to 500 eV. Scalar relativistic effects are included with the PAW-PBE potentials^{4,5} available in the distributed code. The Brillouin zone was sampled by Monkhorst-Pack meshes of $5 \times 5 \times 5$ grid for hybrid density functional

(HSE) calculations. This grid was tested at single points by expansion to $6 \times 6 \times 6$. No significant differences were found. For the band structure calculations, 59 k-points were used. Convergence of the electronic degrees of freedom was met when the total energy change and the band structure energy change between two steps were both smaller than 1×10^{-5} . We relax all structural parameters (atomic position, lattice constants) using a conjugate-gradient algorithm until the Hellmann-Feynman forces are less than 0.01 eV/Å. Spin-orbit coupling has been implemented in VASP by Kresse and Lebacqz.⁶ The non-spherical contributions⁷ from the gradient corrections inside the PAW spheres are considered in current calculations.

III. RESULTS AND DISCUSSIONS

A. Crystal structure of AnO_2

Figure 1 shows the well-known fcc CaF_2 fluorite structure, in which the actinide dioxides AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{and Am}$) appear with eight-coordinated An and four-coordinated O. If one takes oxygen as divalent, the stoichiometry implies An^{4+} and 2O^{2-} . UO_2 is known to order antiferromagnetically, assuming the AFM-I spin motif as marked in Figure 1 by black arrows. The other members of the series have more complex magnetic ordering motifs that are beyond the scope of the present work. We focus here on the properties of the ferromagnetic (FM) and AFM-I states.

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FIG. 1. The fluorite crystal structure exhibited by AnO_2 , where $\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, and Am . O atoms = red balls, An atoms = green balls. The black arrows illustrate the (100) AFM ordering.

B. Calculated parameters of AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, and Am)

Table I reports the relative energies, lattice constants, magnetic moments (AFM), and band gaps (AFM) for AFM and FM states of the AnO_2 series with HSE and HSE+SOC. One can see that there are no large changes in the properties associated with inclusion of SOC. The HSE generally predicts AFM ordered AnO_2 to be more favorable than the corresponding FM states.

The SOC generally decreases the splitting between AFM and ferromagnetic states. In PaO_2 , PuO_2 , and AmO_2 this leads to very small Heisenberg couplings – of the order of 10–50 meV. The lone exception is NpO_2 , where inclusion of SOC changes the predicted ground state from ferromagnetic to AFM-I. The calculated band gaps and lattice constants (from HSE and HSE+SOC) are in good agreement with the

corresponding experimental values, as shown in Table I and Figure 2. We note that the band gaps in Table I were extracted from a numerical tabulation of the gap vs. k point. These values are slightly different from those inferred from the DOS plots. We were advised by the VASP team that the direct examination of the numerical data is preferred.

The values for the unpaired spin density on the metal site follow that expected from the formal valences very closely, and are affected very little by SOC (see supplementary material³³). The calculated magnetic moment for U ($1.95 \mu_B$) in the dioxide agrees well with the experimental value of 1.8–2.0 μ_B ⁸ (see Table I). However, the corresponding magnetic moments on the metal in NpO_2 and PuO_2 of 2.92 and 3.91 μ_B , respectively, differ significantly from their corresponding experimental observation, 0.4 μ_B ⁹ or something similarly small^{10,11} for Np and no moment for Pu.¹² The discrepancy in the former likely stems from the complex magnetic ordering issues, and the absence of a moment in the latter from atomic multiplet effects difficult to address within density functional theory (DFT). The magnetic ground states involve a competition between states differing very little in energy, and remain a significant challenge for theory.

There is an additional point worth making here. We sometimes see significant differences in the computed band gaps depending on whether we are studying the antiferromagnetic or ferromagnetic phase. For example, the band gap for UO_2 in the AFM phase is ~ 2.4 eV, while it becomes 2.2 eV in the ferromagnetic phase. The experimental result is 2.1 eV. Most of the measurements of the optical gap are made above the Néel temperature, and so it is not clear which of our theoretical values should be compared with experiment. The closed-shell, nonmagnetic, electronic state lies much higher in energy than the Néel temperature, and is surely not the appropriate state with which to compare. Presumably, the experimental paramagnet is most similar to the underlying AFM

TABLE I. Calculated relative energies for AFM and FM AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, and Am) from HSE and HSE+SOC, respectively, as well the calculated AFM gap and magnetic moment.

		$E_{\text{rel.}}$ (eV)		a_0 (Å)		$\mu(\mu_B)$	Gap (eV) VASP	Gap (eV) Gaussian ²
		AFM	FM	AFM	FM	AFM	AFM	AFM
ThO ₂	HSE	0.00	0.00	5.586	5.586	0.00	6.0	6.1
	HSE+SOC	0.00	0.00	5.580	5.580	0.00	5.8	6.1
	Expt.			5.602 (Ref. 13)		0.00	5.75 (Ref. 13)	
PaO ₂	HSE	0.00	0.25	5.501	5.483	0.94	1.2	1.1
	HSE+SOC	0.00	0.02	5.499	5.494	0.95	1.5	1.2
	Expt.			5.505 (Ref. 14)		...	...	
UO ₂	HSE	0.00	0.19	5.458	5.418	1.98	2.4	2.8
	HSE+SOC	0.00	0.10	5.457	5.457	1.95	2.4	2.7
	Expt.			5.470 (Ref. 15)		1.8 ~ 2.0 (Ref. 8)	2.10 (Ref. 16)	
NpO ₂	HSE	0.00	−0.12	5.412	5.411	3.00	2.4	3.0
	HSE+SOC	0.00	0.15	5.418	5.418	2.92	2.4	3.0
	Expt.			5.434 (Ref. 17)		~0.4	2.85 (Ref. 18)	
PuO ₂	HSE	0.00	0.15	5.383	5.378	4.00	2.4	2.6
	HSE+SOC	0.00	0.01	5.379	5.373	3.91	2.6	2.6
	Expt.			5.398 (Ref. 19)		0.00 (Ref. 12)	2.80 (Ref. 18)	
AmO ₂	HSE	0.00	0.23	5.375	5.362	4.99	1.5	1.5
	HSE+SOC	0.00	0.05	5.357	5.355	4.96	1.5	1.5
	Expt.			5.376 (Ref. 20)		...	1.30 (Ref. 21)

FIG. 2. Left: The computed gap (HSE) versus the experimental gap of AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, and Am). The dashed line has a slope of unity. Note the circle for PaO_2 represents only a computed value, as we are not aware of an experimental result. Right: The computed lattice constant (HSE) versus the experimental lattice parameter for the AnO_2 series.

result with disordered moments, and so that is what we have reported here. In principle, we should do a calculation on a unit cell large enough to simulate the disordered paramagnetic phase, but that is presently beyond our capabilities. Finally, we note that the band gaps quoted in Table I for NpO_2 and PuO_2 , 2.85 eV and 2.8 eV¹⁸ differ significantly from those in the earlier literature, 0.4 eV²² for NpO_2 and 1.8 eV²³ for PuO_2 . The previous literature values were inferred from optical conductivity measurements, whereas the more recent measurements utilized direct optical absorption on single crystal quality thin films. The band gaps from our calculations, even those published earlier which did not include SOC, are in good agreement with these new measurements.

The values in Figure 2 were obtained from VASP with a plane-wave basis set, the PAW treatment of the relativistic core, and a spin-orbit correction. We have also computed these properties with the *Gaussian* suite of electronic structure codes using a basis set of Gaussian orbitals and the relativistic effective core potentials described previously,² in conjunction with the SOC methodology described by Peralta *et al.*²⁴ It is gratifying that the results agree fairly well between the two approaches (Table I). The largest discrepancy occurs for NpO_2 , where the gaps differ by some 0.6 eV. The origin of this discrepancy is unknown, but may arise from the differing basis sets, representations of the relativistic core, and manner in which the spin-orbit coupling is approximated. We are investigating these issues now.

C. Calculated density of states of AnO_2 from HSE and HSE+SOC

The DOS of the AFM-I phase of AnO_2 from HSE+SOC shown in Figure 3 are similar to those from HSE (see supplementary material). We can see that among these oxides, PaO_2 , UO_2 , and NpO_2 are Mott insulators, with the gap associated with an $\text{An}5f$ to $\text{An}5f$ transition. At PuO_2 the $5f$ band becomes nearly degenerate with the $\text{O}2p$ band, which is reflected in the distinctly mixed $\text{An}5f$ - $\text{O}2p$ character of the valence band as shown in the partial DOS in Figure 3. The conduction band

remains nearly pure $\text{An}5f$, and so we associate PuO_2 through AmO_2 as ligand-to-metal charge-transfer (LMCT) insulators ($\text{O}2p$ to $\text{An}5f$). These classifications are in agreement with the earlier work in a localized basis set.² The appearance of significant $\text{An}5f$ / $\text{O}2p$ mixing arises from the increasing stabilization of the $\text{An}5f$ band due to incomplete shielding of the nuclear charge as one proceeds across the actinide series. The $\text{An}5f$ band becomes nearly degenerate with the $\text{O}2p$ band in the region of Pu , and results in a near degeneracy mixing (see Scheme 1), as commented on previously.^{2,25} In our previous work,² the spin density on the metal was observed to increase incrementally in early members of the An series in just the way expected from formal f -orbital occupations based upon An^{4+} ions; at Cm , however, evidence of an intermediate valence ($\text{Cm}^{3+}/\text{Cm}^{4+}$) emerged. This is also true of the present results with spin-orbit coupling. A discussion of the results for CmO_2 is deferred to a subsequent paper. Additional information (on the spin density and integrations of f states) for all the actinide dioxides is given in the supplementary material.

SCHEME 1. Schematic of the atomic orbital energy levels for $\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{Am}$, and the $\text{O}2p$ band. The $5f$ orbital energy decreases steadily across the row, becoming nearly degenerate with the $\text{O}2p$ band beginning with Pu . This leads to a metal-ligand mixing proportional to a Hamiltonian matrix element between the $\text{An}5f$ and the $\text{O}2p$ orbitals divided by the orbital energy difference. Although the matrix element decreases steadily across the row as the actinide $5f$ orbital contracts, it is offset by the energy denominator which becomes small for the later member of the row, leading to significant mixing and predictions of covalency in the calculations.

FIG. 3. The calculated density of states of AFM AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu},$ and Am) from the HSE approximation with spin-orbital coupling. The magnitudes of the gap in these figures are slightly from those in Table II.

D. Comparing the lattice constants and band gaps to other approximations

Other approximations have been applied to these actinide materials, including a number of DFT+ U studies.²⁶ They are generally capable of giving a reasonable band gap, given a judicious choice for the empirical parameter U , but we have found that the U which reproduces the band gap often yields significant errors in other metrics such as the lattice constant. We have performed PBE+ U calculations on the series, with a $U_{\text{eff.}}$ ($=U - J$) for all actinides set to 4 eV. As shown in Table II, the lattice constants of UO_2 , NpO_2 , and PuO_2 calculated by PBE+ U are much longer than the corresponding experimental value. PBE+ U predicts ThO_2 as a charge-transfer insulator with a band gap of 4.7 eV, smaller than the experimental gap by 1 eV, while the insulating oxides PaO_2 and AmO_2 are predicted to be metallic.

Most recently Yin *et al.*²⁷ have applied dynamic mean-field theory (DMFT) to UO_2 , NpO_2 , and PuO_2 . In contrast to their earlier DMFT work²⁸ in which the most important parameter in the theory, the on-site repulsion U , was determined empirically, they have now determined U “*ab initio*”.

The consequence of this is that while the early work described UO_2 as a Mott insulator, the most recent work finds it to be a charge-transfer insulator, and the ground state to be Zhang-Rice singlet in nature. This conclusion is in contradiction with photoemission results, which show $5f$ character at the Fermi energy, as well as a recent comprehensive x-ray absorption study by Yu *et al.*^{29,30} and femtosecond pump-probe studies³¹ which firmly establish UO_2 as a Mott-Hubbard insulator. Femtosecond pump-probe studies have also followed ultrafast hopping dynamics of $5f$ electrons in UO_2 . The major difference between the two studies is the much larger value for U (6 eV)²⁷ determined “*ab initio*” versus the earlier empirical value of 3 eV.²⁸ The result is similar to what is seen in LDA+ U studies where a value for U that is too large pushes the f states too far down into the $\text{O}2p$ based levels. This is likely the cause of the problem here.

Petit *et al.*³² have studied actinide monoxides, sesquioxides and dioxides ($\text{An} = \text{U} \dots \text{Cf}$) using the silicon integrated circuit (SIC) approximation. The dioxides, with the exception of UO_2 , are generally found to be insulating. Interestingly, the most stable configuration for UO_2 is found to be a

TABLE II. Comparison of various approximations for the lattice constant ($\text{\AA}$), band gap (eV), and insulator classification for AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, and Am), as well as experiment.

		Band gap (eV)	Latt. Const. ($\text{\AA}$)	Classification
ThO_2	HSE (VASP) ^a	5.8	5.580	Charge-transfer
	HSE (Gaussian) (Ref. 2)	6.2	5.595	Charge-transfer
	PBE+U ^a	4.7	5.671	Charge-transfer
	Expt.	5.75 (Ref. 13)	5.602 (Ref. 13)	...
PaO_2	HSE (VASP) ^a	1.5	5.499	Mott-Hubbard
	HSE (Gaussian) (Ref. 2)	1.4	5.518	Mott-Hubbard
	PBE+U ^a	0.0	5.544	...
	Expt.	...	5.505 (Ref. 14)	...
UO_2	HSE (VASP) ^a	2.4	5.458	Mott-Hubbard
	HSE (Gaussian) (Ref. 2)	2.6	5.463	Mott-Hubbard
	PBE+U ^a	2.3	5.568	Mott-Hubbard
	SIC (Ref. 32)	0.0 ^b	5.400	...
	DMFT (Ref. 27)	2.5	...	Charge-transfer
	Expt.	2.1 (Ref. 16)	5.470 (Ref. 15)	Mott-Hubbard (Refs. 29–31)
NpO_2	HSE (VASP) ^a	2.4	5.412	Mott-Hubbard
	HSE (Gaussian) (Ref. 2)	2.8	5.430	Mott-Hubbard
	PBE+U ^a	2.6	5.498	Charge-transfer
	SIC (Ref. 32)	2.3	5.460	Charge-transfer
	DMFT (Ref. 27)	...	...	...
	Expt.	2.85 (Ref. 18)	5.434 (Ref. 17)	...
PuO_2	HSE (VASP) ^a	2.6	5.383	Charge-transfer
	HSE (Gaussian) (Ref. 2)	2.8	5.396	Charge-transfer
	PBE+U ^a	1.6	5.465	Charge-transfer
	SIC (Ref. 32)	1.2	5.440	Charge-transfer
	DMFT (Ref. 27)	~3.5	...	Charge-transfer
	Expt.	2.80 (Ref. 18)	5.398 (Ref. 19)	...
AmO_2	HSE (VASP) ^a	1.5	5.357	Charge-transfer
	HSE (Gaussian) (Ref. 2)	1.6	5.369	Charge-transfer
	PBE+U ^a	0.0	5.425	...
	SIC (Ref. 32)	0.8	5.420	Charge-transfer
	Expt.	1.3 (Ref. 21)	5.376 (Ref. 20)	...

^aCurrent work; $U_{\text{eff}} = 4.0$ eV in PBE+U calculations.^bThe SIC finds an insulating state with a gap of 2.6 eV (a charge-transfer insulator), only 100 meV higher than this metallic ground state.

$\text{U(V)}, f^1$, species, which is metallic. They point out that the $\text{U(IV)}, f^2$, state lies only 100 meV higher in energy, and it is gapped by 2.6 eV, in good agreement with the HSE results. The gap, however, is charge transfer in nature, as was the case for the DMFT results. The ground states of NpO_2 and PuO_2 are found to be tetravalent with the SIC. It is interesting that

the $\text{An}5f/\text{O}2p$ orbital mixing with SIC decreases with increasing Z ; an intuitively appealing result, but in contrast to the hybrid DFT predictions.

For completeness, the dielectric functions and optical spectrum of UO_2 , NpO_2 , and PuO_2 predicted by HSE and PBE+U approaches are given in the supplementary material.

FIG. 4. Left: Correlation of experimental gap for AnO_2 with computed gap from various approximations. Right: Correlation of experimental lattice constant with computed lattice constant from various approximations. We were unable to find lattice constants reported with DMFT.

In general, both approaches are in qualitative agreement with experiment.

IV. CONCLUSIONS

We conclude that the HSE functional gives a reasonably faithful reproduction of the band gaps and lattice constants for these actinide dioxides when compared with available experimental data (Figure 2). A similar plot of lattice constants and band gaps of various approximations with experiment is given in Figure 4. With a judicious choice of the parameter U , the DFT+ U approximations appear to be capable of yielding reasonable band gaps. This occurs at the expense of other important properties such as the lattice constant and the density of states. In addition to the magnitude of the band gap, these approximations differ in their assignments of the origin. HSE and PBE+ U correctly describe UO_2 as a Mott insulator, while the SIC and the most recent DMFT approximations incorrectly predict the early members of this series to be charge-transfer insulators.

In conclusion, HSE performs quite well for this series of Mott insulators. It is particularly encouraging that unlike the DFT+ U and practical implementations of DMFT, *it does not require the introduction of material specific parameters*. Problems remaining to be addressed include multiplet effects, and the proper treatment of the complex magnetic properties of these oxides.

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³³See supplementary material at <http://dx.doi.org/10.1063/1.4757615> for (1) Calculated density of states from HSE; (2) Calculated band structure of AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$ and Am) from HSE+SOC; (3) Spin density and integrations of f states for AnO_2 ($\text{An}=\text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{Am}$); (4) TDOS of FM NpO_2 by HSE and PBE+ U ; and (5) Calculated dielectric function and optical spectrum of UO_2 , NpO_2 , and PuO_2 .