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A Screened Hybrid DFT Study of Actinide Oxides, Nitrides, and Carbides

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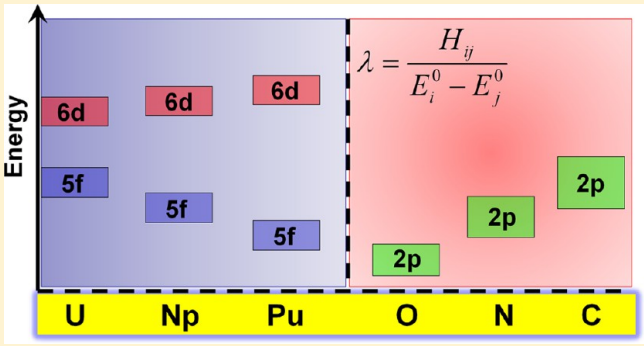
Supporting Information

ABSTRACT: A systematic study of the structural, electronic, and magnetic properties of actinide oxides, nitrides, and carbides (AnX_{1-2} with X = C, N, O) is performed using the Heyd−Scuseria−Ernzerhof (HSE) hybrid functional. Our computed results show that the screened hybrid HSE functional gives a good description of the electronic and structural properties of actinide dioxides (strongly correlated insulators) when compared with available experimental data. However, there are still some problems reproducing the electronic properties of actinide nitrides and carbides (strongly correlated metals). In addition, in order to compare with the results by HSE, the structures, electronic, and magnetic properties of these actinide compounds are also investigated in the PBE and PBE+U approximation. Interestingly, the density of states of UN obtained with PBE compares well with the experimental photoemission spectra, in contrast to the hybrid approximation. This is presumably related to the need of additional screening in the Hartree−Fock exchange term of the metallic phases.



1. INTRODUCTION

The actinide (U, Np, Pu) oxides, nitrides, and carbides are of both fundamental and applied interest. These actinide materials are members of a class of strongly correlated materials—while the early dioxides are Mott insulators, the later ones, beginning with Pu, are charge-transfer insulators. The mononitrides and carbides are generally metals; the nitrides (and perhaps the carbides) are strongly correlated. Technological interest in these materials stems from their use or potential use as advanced nuclear fuels. The actinide nitrides and carbides may be the ideal fuel candidates for certain generation IV reactors.[1] It is unfortunately true, however, that their physical and chemical complexity make them extremely challenging to characterize experimentally or theoretically. A number of basic properties associated with their electronic structure are still not known; this includes magnetic ordering and optical gaps.

The development of a first-principles predictive capability for strongly correlated materials (Mott insulators and correlated metals) is one of the grand challenges in electronic structure theory. Over the past decade significant progress has been made on the Mott insulator front. We have recently reviewed the predictions of DFT+U, self-interaction correction (SIC), dynamic mean field theory (DMFT), and the Heyd−Scuseria−Ernzerhof (HSE) screened hybrid density functional with respect to the properties of actinide dioxides[2,3] and U_3O_8 phases.[4] We find that HSE, in particular, provides a more balanced and overall quite satisfactory description of geometries, densities-of-states, and optical band gaps for these insulators. In this paper, we turn our attention to the metallic actinide compounds, exemplified by the strongly correlated metal UN. Previously unpublished results for the actinide monoxides are also reported here. We utilize the HSE functional[5] implemented in VASP (Vienna Ab-initio Simulation Package).[6] The details of the PAW potentials and plane-wave basis sets are as described previously.[2,4] The effect of spin−orbit coupling will be discussed in more detail in a subsequent publication, but we note that it had little effect on the properties reported here in the dioxide series.[2] The HSE parameters are universal, material independent, and reported in the original work.[7]

2. RESULTS AND DISCUSSIONS

2.1. Actinide Oxides, Rocksalt AnO (An = U, Np, and Pu). Table 1 summarizes the calculated relative energies for antiferromagnetic (AFM), ferromagnetic (FM), and nonmagnetic (NM) states; lattice constants (Å); magnetic moment (μ_B); and band gap (eV) of actinide monoxides using HSE.

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Table 1. Calculated Relative Energy (eV per AnO_2 or AnO, where An = U, Np, and Pu), Lattice Constants (Å), Magnetic Moment (μ_B), and Band Gap (eV) Using HSE

		magn state	$E_{rel.}$ (eV per AnO_2)	a_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnO_2	UO_2	AFM[a]	0.00	5.458	1.98	2.4
		FM	0.77	5.418		
		NM	1.72	5.326		
		expt		5.470[8]	1.8[9]	2.1[10]
	NpO_2	AFM[a]	0.00	5.412	3.00	2.6
		FM	−0.12	5.411		
		NM	1.41	5.400		
		expt		5.434[11]	0.4[12]	2.85[13]
	PuO_2	AFM[a]	0.00	5.383	4.00	2.4
		FM	0.15	5.378		
		NM	2.79	5.350		
		expt		5.398[14]	0.00[15]	2.80[13]
		magn state	$E_{rel.}$ (eV per AnO)	a_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnO	UO	AFM[a]	0.00	4.902	2.10	0.0
		FM	0.19	4.906		
		NM	1.19	4,782		
		expt		4.920[16]	–	–
	NpO	AFM[a]	0.00	4,867	3.50	0.0
		FM	0.00	4,867		
		NM	2.44	4.750		
		expt		5.010[17]		
	PuO	AFM[a]	0.00	4.927	4.00	0.0
		FM	0.16	5.004		
		NM	3.64	4.787		
		expt		4.960[18]	–	–

[a]A small tetragonal disorder with $a = b \neq c$ is found in AFM states.

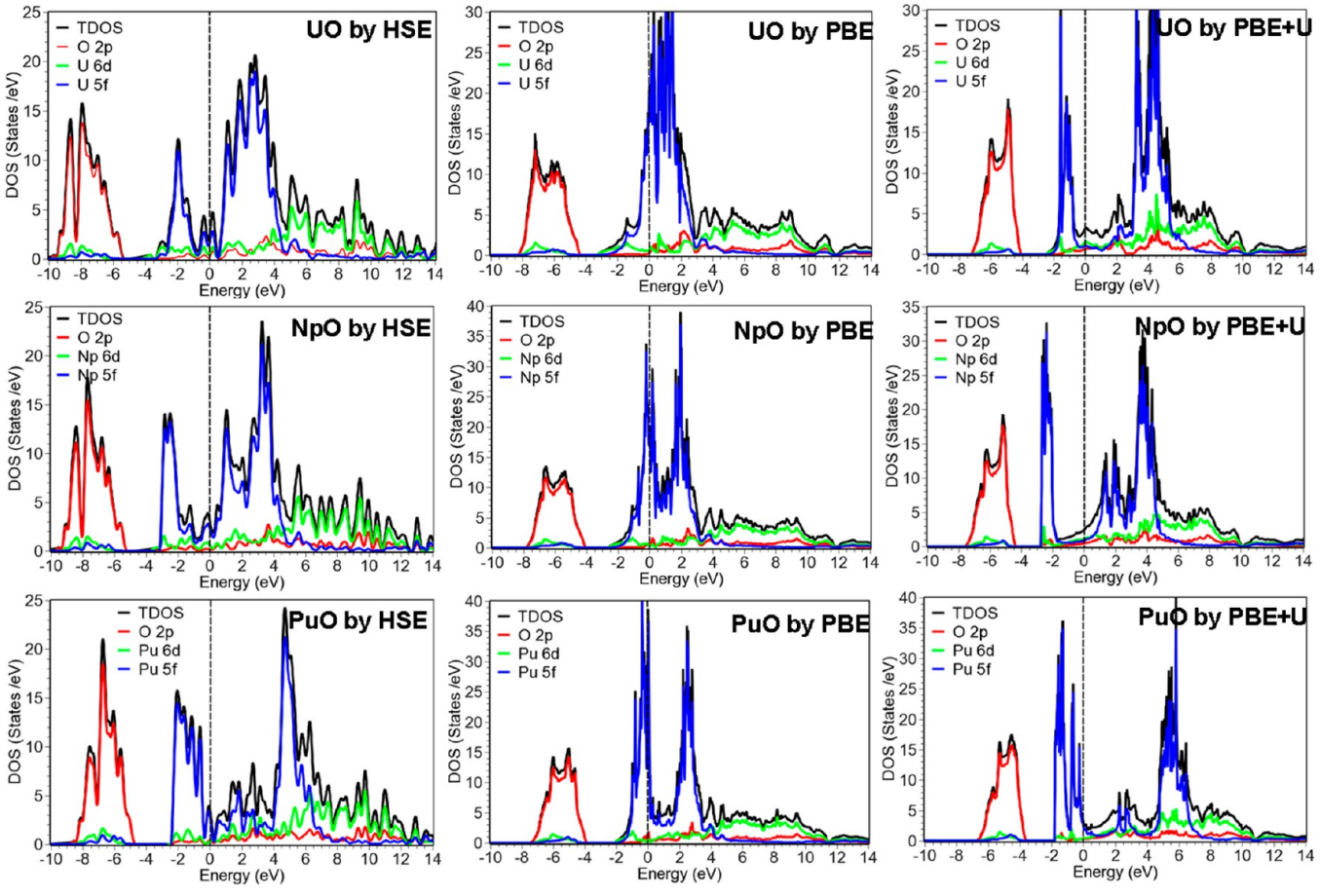

Figure 1. Calculated density of states of the corresponding most stable states AnO (An = U, Np, and Pu) obtained with HSE, PBE, and PBE+U (U_{eff} = 4 eV). Note that the highest occupied level is adjusted to zero.

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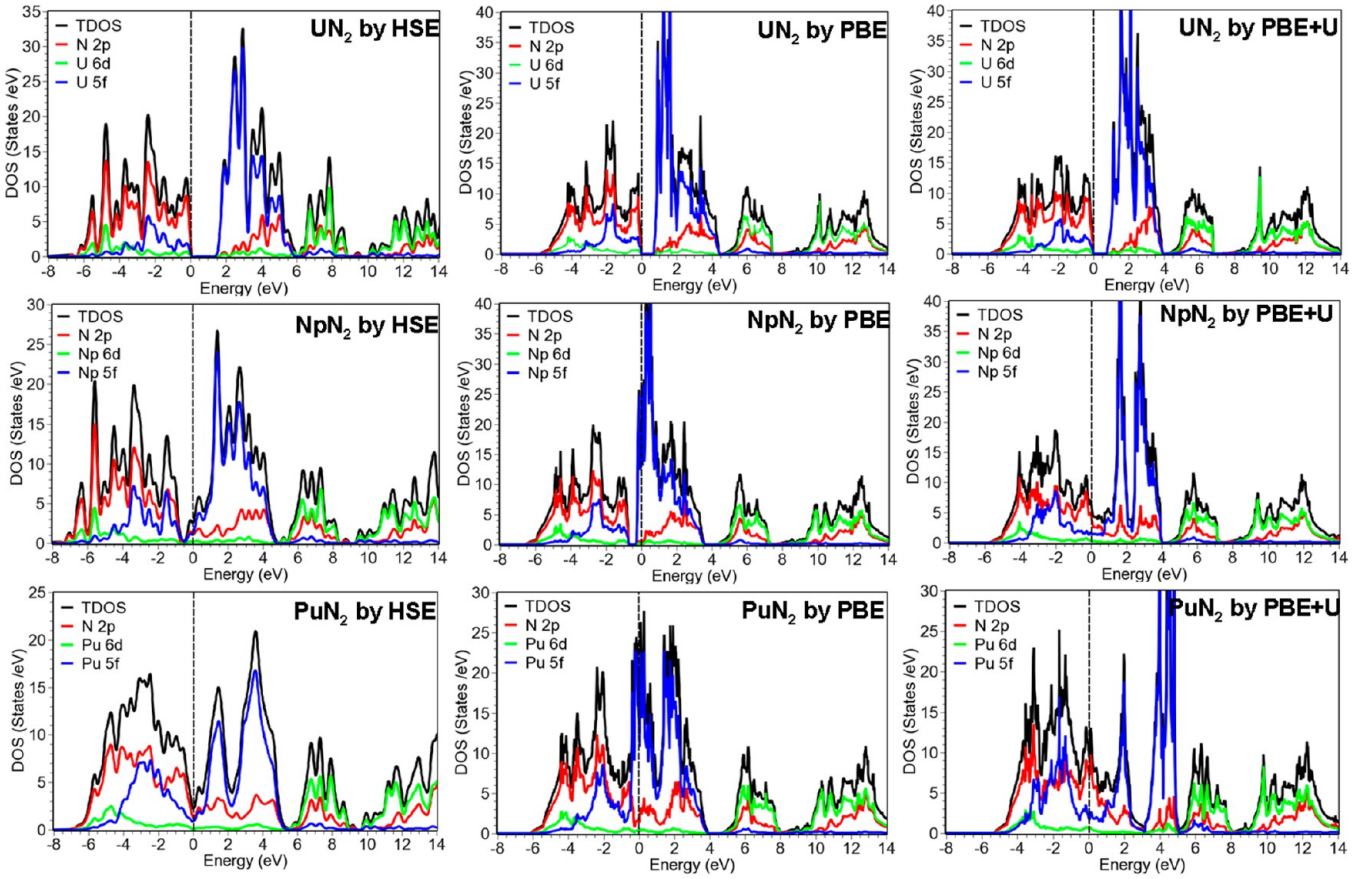

Figure 2. Calculated density of states of the corresponding most stable state of AnN_2 (An = U, Np, and Pu) obtained with HSE, PBE, and PBE+U (U_{eff} = 4 eV).

We also include for completeness our earlier results on the dioxides.[2] HSE finds the rocksalt AnO materials to be metallic, with AFM ordering along (100) (see the Supporting Information for details). The exception in the magnetic ordering occurs for NpO, where HSE finds no significant preference for the AFM over the FM state. Interestingly, the lattice constants of the three actinide monoxides obtained with HSE are underestimated when compared with experimental data, as shown in Table 1. The density of states computed with HSE (see Figure 1) for the three monoxides show a small density of An 5f states at the Fermi level, which is similar to the results obtained with PBE+U. However, this is in contrast to the results for the PBE generalized-gradient approximation, where sharp 5f peaks are seen at the Fermi energy in all three actinide monoxides. As is the case in the dioxides,[2] all three approximations separate the O 2p and U 5f quite distinctly in the uranium case, with the O 2p and An 5f densities merging in the later members.

2.2. Actinide Nitrides, Fluorite AnN_2, and Rocksalt AnN (An = U, Np, and Pu). Table 2 reports the relative energy, lattice parameter, magnetic moment, and band gap for actinide nitrides (AnN_2 and AnN) using the HSE functional. If one takes nitrogen as trivalent, the stoichiometry of AnN_2 implies An^{6+} and $2N^{3-}$, suggesting a $5f^0$ configuration for U, $5f^1$ for Np, and $5f^2$ for Pu. This expectation is reflected in the absence of a magnetic moment for UN_2 (Table 2). It is a band insulator, with an HSE predicted gap of 1.5 eV (Figure 2), consistent with a zero magnetic moment. PBE and PBE+U also predict UN_2 to be an insulator with a band gap of 0.8 eV.

The HSE lattice constant of UN_2 underestimates the experimental value by ca. 0.09 Å. A strong mixing between the N 2p and U 5f levels is apparent in the HSE DOS, implying a more covalent interaction than in the analogous dioxide (see Figure 2).

On the other hand, the Np and Pu dinitrides are predicted to be ferromagnetic metals. The moments on the metal sites can be used to infer a Np valence intermediate between 5+ and 6+ (f^2 and f^1), and a Pu valence near 5+ (f^3), with some 4+ (f^4) character. Again, HSE and PBE+U predict NpN and PuN to be poor metals, while PBE provides more density at the Fermi level, indicative of good metals.

HSE predicts UN to be a metallic AFM, ordered along (100), in agreement with experiment.[22] The calculated lattice constant (4.943 Å) is somewhat larger than the experimental data (4.890 Å), implying an underestimate of the delocalization (bandwidth), consistent with the observed overestimate of the magnetic moment by around 1.1 μ_B. Figure 3 shows the calculated density of states and band structure for UN, NpN, and PuN obtained with HSE, PBE, and PBE+U. Analyzing UN in more detail, the states near the Fermi level from HSE are mainly contributed from U 5f, and are well-separated from the N 2p/U 5f derived bands at higher binding energy. Interestingly, HSE significantly underestimates the DOS near the Fermi energy, in disagreement with photoemission, which sees a strong, narrow U 5f derived band at E_f.[23,24] The predictions from PBE+U are qualitatively similar to HSE (see Figure 3). On the other hand, the DOS at E_f from the semilocal PBE approximation is in good agreement with

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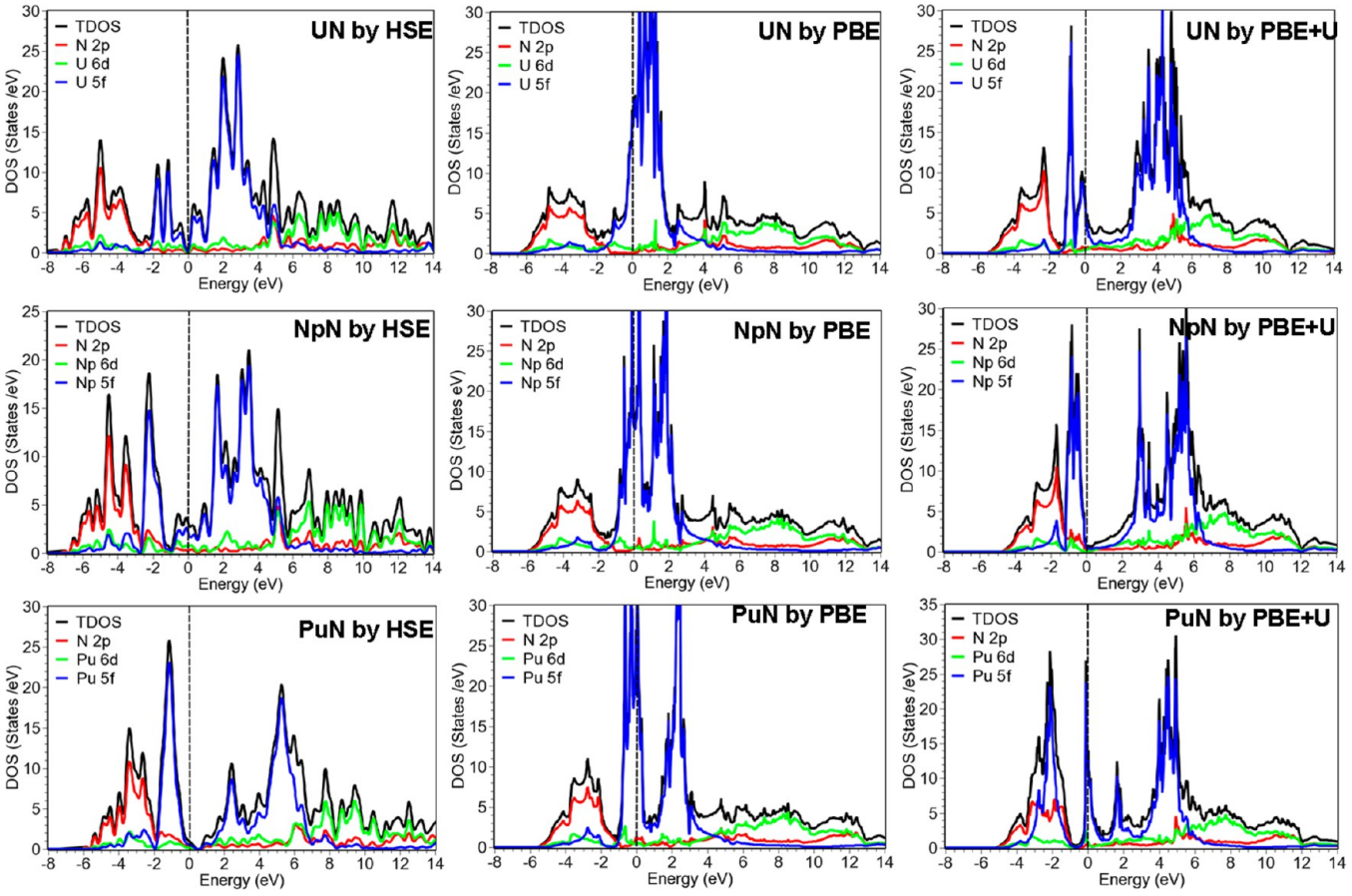

Figure 3. Calculated density of states of the corresponding most stable states of AnN (An = U, Np, and Pu) obtained with HSE, PBE, and PBE+U (U_{eff} = 4 eV).

experiment. The lattice constant is also improved (see the Supporting Information). Unfortunately, PBE incorrectly yields a ferromagnetic ground state.

We surmise that the origin of the issues with the screened hybrid HSE and the PBE+U approximations is associated with the increased screening expected in a metallic system compared with an insulator. There is presently no means to "dynamically" screen either the effective Hubbard U in PBE +U, or the screening length in HSE "on the fly". In HSE, the screening length ω is an adjustable parameter governing the extent of short-range interactions; the optimum value is approximately 0.2−0.3 Å^{-1}. In current calculations, ω is set up to its standard value of 0.207 Å^{-1}. As a numerical experiment, in order to test the sensitivity of our results on ω, we find that the density at the Fermi level increases with an increase of the screening parameter, suggesting that an approach in which the screening parameter is adjusted dynamically in response to the electronic structure would be very helpful for strongly correlated metals. Note that for ω = 0, HSE reproduces PBE0 (up to a slight deviation due to the parametrization of the PBE exchange hole). HSE reduces to the nonhybrid PBE functional for $\omega \rightarrow \infty$. A value of ω = 1 is effective in reproducing the experimental photoemission data (see the Supporting Information) We tentatively conclude that screened hybrid DFT is missing key physics in the correlated metal regime.

A number of other theoretical studies have addressed actinide mononitrides using approximations including GGA,[25−27] LSDA,[28] LDA+U,[29] SIC,[30] and DMFT.[31] The predicted lattice constants by these groups are all reasonably close to experiment

Table 2. Calculated Relative Energy (eV per AnN_2 or AnN, where An = U, Np, and Pu), Lattice Constants (Å), Magnetic Moment (μ_B), and Band Gap (eV) Using HSE

		magn state	$E_{rel.}$ (eV per AnN_2)	a_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnN_2	UN_2	AFM[a]	0.00	5.218	0.00	1.5
		FM	0.00	5.218		
		NM	0.00	5.218		
		expt		5.310[16]	–	–
	NpN_2	AFM[a]	0.00	5.187	1.59	0.0
		FM	−0.05	5.208	1.80	0.0
		NM	0.45	5.150		
		expt		–	–	–
	PuN_2	AFM[a]	0.00	5.234	3.02	0.0
		FM	−0.53	5.244	3.25	0.0
		NM	1.10	5.148		
		expt		–		
		magn state	$E_{rel.}$ (eV per AnN)	a_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnN	UN	AFM[a]	0.00	4.943	1.82	0.0
		FM	0.22	4.860		
		NM	0.67	4.795		
		expt		4.890[16]	0.75[19]	
	NpN	AFM[a]	0.00	4.906	3.17	0.0
		FM	−0.05	4.936	3.51	0.0
		NM	2.09	4.769		
		expt		4.899[20]		
	PuN	AFM[a]	0.00	4.978	4.80	0.0
		FM	0.04	5.013		
		NM	3.50	4.840		
		expt		4.905[21]		

[a]A small tetragonal disorder with $a = b \neq c$ is found in AFM states.

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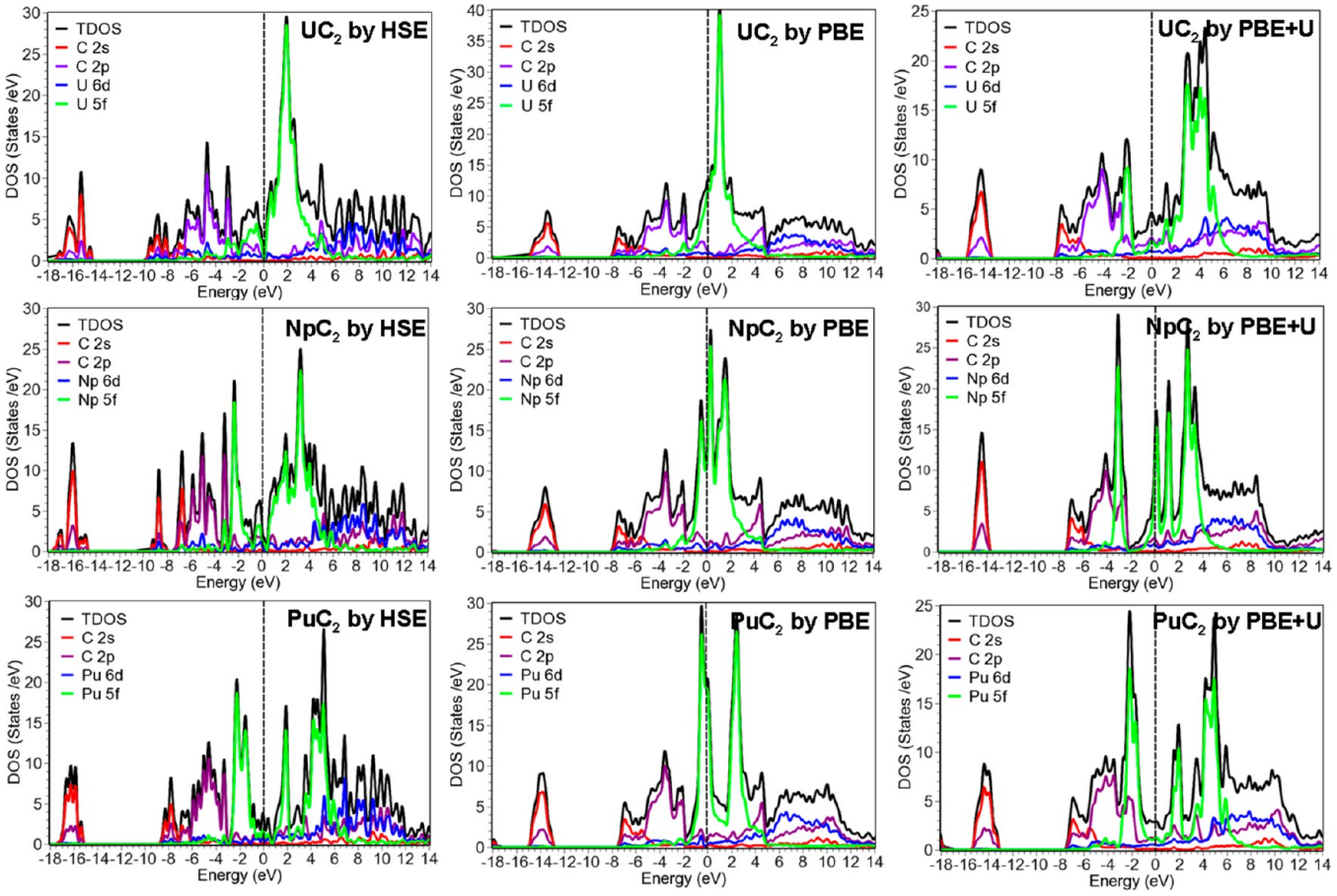

Figure 4. Calculated density of states of the corresponding most stable states of AnC_2 (An = U, Np, and Pu) obtained with HSE, PBE, and PBE+U (U_{eff} = 4 eV).

Table 3. Calculated Relative Energy (eV per AnC_2 or AnC, where An = U, Np, and Pu), Lattice Constants (Å), Magnetic Moment (μ_B), and Band Gap (eV) Using HSE

		magn state	$E_{rel.}$ (eV per AnC_2)	a_0/c_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnC_2	UC_2	AFM	0.00	3.515/5.913	1.00	0.0
		FM	0.18	3.457/5.893		
		NM	018	3.455/5.893		
		expt		3.524/5.999[16]	–	–
	NpC_2	AFM	0.00	3.626/6.085	3.16	0.0
		FM	0.02	3.635/6.078		
		NM	0.02	3.635/6.078		
		expt		–	–	–
	PuC_2	AFM	0.00	3.758/6.263	4.99	0.0
		FM	0.07	3.769/6.273		
		NM	3.33	3.499/5.916		
		expt		–	–	–
		magn state	$E_{rel.}$ (eV per AnC)	a_0 (Å)	μ (μ_B)	E_{gap} (eV)
AnC	UC	AFM[a]	0.00	5.055	1.40	0.0
		FM	0.05	4.996		
		NM	0.24	4.902		
		expt		4.961[16]	–	–
	NpC	AFM[a]	0.00	5.082	3.10	0.0
		FM	0.06	5.090		
		NM	1.89	4.890		
		expt		4.905[21]	–	–
	PuC	AFM[a]	0.00	5.115	4.35	0.0
		FM	0.12	5.043		
		NM	3.19	4.918		
		expt		4.897[17]	–	–

[a]A small tetragonal disorder with $a = b \neq c$ is found in AFM states.

(no lattice parameter from DMFT), as obtained in this work. Atta-Fynn and Ray[26] have shown that in full-potential GGA calculations there are no big differences on the structural and electronic properties with and without spin orbital coupling; their DOS is quite similar to those here reported with PBE. The electronic properties predicted for UN by SIC[30] and DMFT[31] are quite similar to the results from PBE in the current work

2.3. Actinide Carbides, CaC_2 Type AnC_2, and Rocksalt AnC (An = U, Np, and Pu). Table 3 summarizes the calculated relative energies for AFM, FM, and NM states; lattice constants (Å); magnetic moment (μ_B); and band gap (eV) of actinide carbides (CaC_2 type AnC_2 and rocksalt AnC) using HSE. A more detailed study on UC_2 phases has been published elsewhere.[32] HSE predicts all actinide carbides to be metallic. It is interesting to note that HSE underestimates the lattice constant in the *c* direction for UC_2, just as it did for UN_2. This is in contrast with the overestimates observed for the monoxides and mononitrides. In fact, it returns to form in the monocarbides, once again overestimating the bond lengths, presumably implying an overestimate of electron localization. The DOS at E_f is once again predicted to be rather small with HSE (see Figures 4 and 5), but greater in PBE, in agreement with the DMFT results.[31]

3. CONCLUSIONS

The structural, electronic, and magnetic properties of actinide oxides, nitrides, and carbides (AnX_{1-2} with X = C, N O) have

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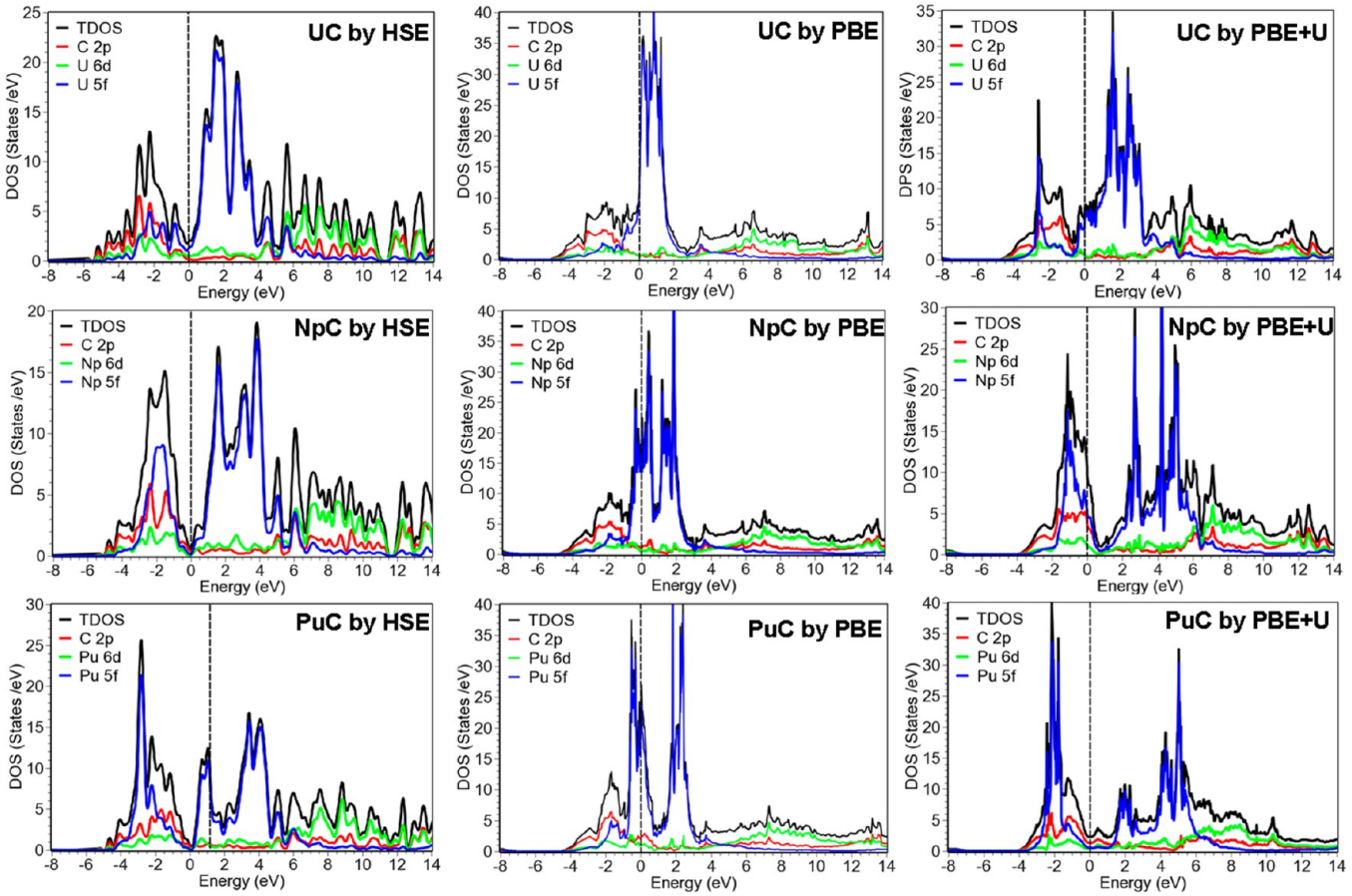

Figure 5. Calculated density of states of the corresponding most stable states of AnC (An = U, Np, and Pu) obtained with HSE, PBE, and PBE+U (U_{eff} = 4 eV).

been systematically investigated using the HSE, PBE, and PBE +U approximations. While the screened hybrid HSE functional seems clearly superior for the strongly correlated actinide dioxide insulators, its performance for the metallic nitrides and carbides is problematic, at least with respect to the densities-of-states. For properties other than magnetism, the semi-local PBE approximation gives an improved description of the properties, particularly the photoemission data. We conclude that a satisfactory approximation which smoothly interpolates from the limit of a simple metal to a strongly correlated Mott insulator remains a challenge in electronic structure theory.

■ ASSOCIATED CONTENT

Supporting Information

Section I, electronic properties of actinide oxides, nitrides, and carbides, a screened hybrid DFT study (HSE); section II, electronic properties of actinide oxides, nitrides and carbides, a PBE study; section III, electronic properties of actinide oxides, nitrides, and carbides, a PBE+U study; section IV, effect of screening length (ω) on the electronic and structural properties of UN. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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