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Unraveling the Highest Oxidation States of Actinides in Solid-State Compounds with Particular Focus on Plutonium

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Calculation method for physical oxidation state (OS_p)

Notably, the widely used OS is formal OS (denoted as OS_f) based on the concept of Lewis electron pairs, which is a somewhat unphysical concept and usually invalid within a non-innocent ligand. Especially, in the solid-state compounds containing *f*-block elements, the assignment of OS_f is not always straightforward. An alternative physical OS (denoted as OS_p) based on a projection approach from molecular orbital to atomic orbital, straightly determines the OS_p in various solid-state compounds by counting the rest of the An valence electrons. Herein, we use this successful approach to calculate the OS_p of actinide ions in their solid-state compounds to elucidate some trends of OS and chemical bonding. Special attention is paid on the determination of the highest OS_p of Pu, the most representative and important actinide element. The results show that the highest OS_p of Pu solid ion is Pu^V in the compounds PuO_2F and $PuOF_4$. Our work is the first attempt to rigorously calculate the OS_p of solid-state actinide materials and the methods can be extended to investigate the oxidation state of more complicated solid-state actinide compounds.

Here we take Pu-O bond as an example to illustrate the determination of physical oxidation state (OS_p) of Pu ions. The basic bonding behavior of Pu-O bond is showed in Fig. S1.

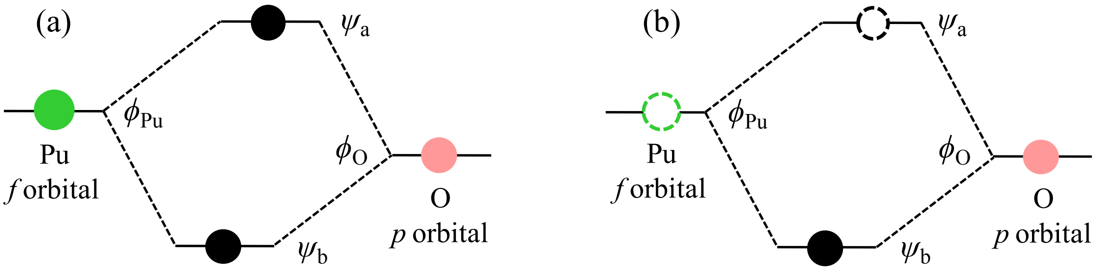

Fig. S1 Schematic of the basic Pu-O bonding behavior. (a) Occupied Pu *f* and O *p* orbitals form fully occupied bonding and antibonding orbitals; (b) An empty Pu *f* orbital and an occupied O *p* orbital form an occupied bonding orbital and an empty antibonding orbital. Solid and open circles denote occupied and unoccupied orbitals, respectively.

Bonding ψ_b and antibonding ψ_a orbitals can be represented by the Gram-Schmidt procedure:

$$\psi_b = \alpha\phi_{Pu} + \beta\phi_O, \tag{1}$$

$$\psi_a = \beta^*\phi_{Pu} - \alpha^*\phi_O, \tag{2}$$

where the coefficients α and β satisfy the normalization criterion, $|\alpha|^2 + |\beta|^2 = 1$.The occupation number of an *f* orbital can be derived via the projection of all occupied orbitals onto the atomic *f* orbital. In the case that contains one occupied Pu *f* orbital and one occupied O *p* orbital, as shown in Fig. S1(a), the occupation number η always equals to 1, because the orbital projection satisfies the following relationship:

$$\eta = \langle\psi_b|\phi_{Pu}\rangle\langle\phi_{Pu}|\psi_b\rangle + \langle\psi_a|\phi_{Pu}\rangle\langle\phi_{Pu}|\psi_a\rangle = |\alpha|^2 + |\beta|^2 = 1. \tag{3}$$

In the case that contains one unoccupied Pu f orbital and one occupied O p orbital (Fig. S1(b)), the same projection procedure on the f orbital yields an occupation number smaller than 1; that is:

$$\eta = <\psi_{b}|\phi_{Pu}><\phi_{Pu}|\psi_{b}> = |\alpha|^2 < 1. \quad (4)$$

We can calculate the occupation number of one Pu f orbital via the above procedure. For the whole Pu 5f orbitals, we define a 7 × 7 occupation matrix ($n^{I\sigma}_{mm'}$) by projecting the first-principles Kohn-Sham orbital (ψ^{σ}_{kv}) of the system onto the 7 local f orbitals (ϕ^{I}_{m}) of Pu:

$$n^{I\sigma}_{mm'} = \sum_{k,v} f^{\sigma}_{kv} <\psi^{\sigma}_{kv}|\phi^{I,\sigma}_{m}><\phi^{I,\sigma}_{m'}|\psi^{\sigma}_{kv}>, \quad (5)$$

where m and m' denote the 7 orthonormal f orbitals, k, v and σ label Bloch wave vector, energy band index and spin index, and f^{σ}_{kv} is Fermi-Dirac occupation number as the input of first-principles calculation. Under the framework of DFT + U method, $n^{I\sigma}_{mm'}$ is the direct output, and the occupation number of each f orbital (σ, m) is obtained by diagonalizing the occupation matrix. By counting the number of fully occupied f orbitals and comparing with the ground-state electronic configuration of Pu, we can determine the actual number of f electrons to be assigned to Pu and to determine the oxidation state unambiguously. The calculated occupation number of 5f orbitals of Pu ion in PuO_2 is 4, or four 5f electrons do not participate into bonding with oxygen; as a result, we assign a robust Pu^{IV} ion irrespective of the possible valence configurations $5f^{6-x}6d^{x}7s^{2}$ ($0 \leq x \leq 1$) of isolated Pu atom because delocalized 6d and 7s electrons completely participate into bonding. It is worth pointing out that the method regarding the definition of occupation matrix and occupation number is insensitive to the choice of the orthonormal f orbitals and the first-principles techniques.

Results and discussion

In solid state, PuO_2 (Pu^{IV}) had long been considered the highest composition binary oxides; the further oxidizing of PuO_2 in normal chemical conditions was unsuccessful. It is naturally conceivable that more electronegative F might oxidize PuO_2 to higher *OS* of Pu ion. In fact, fluorides and oxyfluorides are the two main targets for the search of the highest *OS* of TMs and lanthanides. Pu-F binary compounds such as PuF_5 and PuF_6 are highly volatile and their solid state forms might preserve only under some extreme conditions. Furthermore, similar to the solution state, strong alkaline conditions pave the way for the formation of higher *OS* of Pu solid ions. Solid-state Na (or other alkali metals)-Pu-O ternary compounds are experimentally prepared and characterized. However, these ternary compounds are not optimal choice for the highest OS_p of Pu solid ions, primarily because the completely ionized Na that locates in the cavity and shows solution-like feature would donate their valence electrons to PuO_6 moiety, similar to the typical charge-back donation complexes in which even the OS_f of central metal atoms are elusive, let alone OS_p. For the above reasons, Pu oxyfluorides are the ideal choices for searching for the highest OS_p of Pu solid ions. Simultaneously, we consider the hypothetical models of PuO_2 with 1−4 octahedral interstitial site (OIS) F atoms for the investigation of gradual change of OS_p; the scenario is reasonable because the incorporation of OIS F atoms could be viewed as the rudimental process of $PuO_2 + F_2$ reactions.

The calculation of OS_p using the theoretical approach established in Quantum-ESPRESSO package, which was successfully used in the determination of OS_p of TMs. We firstly calculate the OS_p of Mn in its intricate binary oxides and the experimentally known highest binary metal oxides OsO_4 and RuO_4 to demonstrate the validity of the approach transplanted to VASP package. The calculated OS_p of Mn ions in MnO, Mn_3O_4, Mn_2O_3, MnO_2 and Mn_2O_7, of Os in OsO_4, and of Ru in RuO_4, agree well with the assigned OS_f in terms of ionic approximation. In addition, this approach is physically capable of resolving the mixed *OS* in Mn_3O_4─one third of Mn^{II} and two thirds of Mn^{III}. Based on these validating results, we extend the approach to actinide solid-state compounds. The only difference lies in that a 7 × 7 5*f*-orbital occupation matrix (instead of 5 × 5*d*-orbital occupation matrix for TMs) by projecting the first-principles eigenfunction of the compound onto the 7 atomic 5*f*-orbitals of the An ions. After diagonalizing the occupation matrix, the 5*f*-orbitals occupation can be obtained from the eigenvalues. Thus, OS_p can be inferred by counting the number of 5*f*-orbitals with full occupancy (close to 1). In Table 1, we list the occupation numbers of 5*f*-oritals and OS_p of some Pu and U compounds selected for searching for the highest OS_p of Pu and U, considering that 5*f* electrons in Pu and U typically feature localization and delocalization, respectively. The calculation method for OS_p and the occupation number results of Pu and other actinides in some selected compounds are included in the followed tables.

The results of OS_p of Pu ions in some compounds not included in the article are listed in Table S1.

Table S1 Calculated spin-up and spin-down 5*f*-orbital occupation numbers and OS_p of Pu ions. The occupation numbers for full occupancy are marked with bold. The numbers in the parenthesis denote the fraction of metal ion with the OS_p.

Compounds	Spin	Occupation number of 5*f* orbitals							OS_p
Pu_4O_8F	Up	0.12	0.05	0.04	0.03	0.02	0.02	0.02	IV(¾)
	Down	0.08	0.10	0.23	**1.00**	**1.00**	**1.00**	**1.00**	
	Up	0.21	0.09	0.09	0.10	0.04	0.04	0.04	V(¼)
	Down	0.27	0.24	0.22	0.36	**1.00**	**1.00**	**1.00**	
$Pu_4O_8F_2$	Up	0.05	0.02	0.02	0.02	0.05	0.01	0.1	IV(½)
	Down	0.11	0.10	0.22	**1.00**	**1.00**	**1.00**	**1.00**	
	Up	0.03	0.08	0.09	0.04	0.08	0.03	0.20	V(½)
	Down	0.24	0.22	0.28	0.37	**1.00**	**1.00**	**1.00**	
$Pu_4O_8F_3$	Up	0.01	0.01	0.03	0.04	0.09	0.04	0.01	IV(¼)
	Down	0.10	0.10	0.23	**1.00**	**1.00**	**1.00**	**1.00**	
	Up	0.08	0.05	0.07	0.03	0.03	0.02	0.16	V(¾)
	Down	0.23	0.20	0.40	0.37	**1.00**	**1.00**	**1.00**	
$Pu_4O_8F_4$	Up	0.06	0.02	0.02	0.06	0.15	0.06	0.02	V
	Down	0.30	0.30	0.22	0.39	**1.00**	**1.00**	**1.00**	
PuF_5	Up	0.47	0.14	0.12	0.19	**1.00**	**1.00**	**1.00**	V
	Down	0.20	0.08	0.06	0.04	0.03	0.05	0.11	
PuF_6	Up	**1.00**	**1.00**	0.15	0.15	0.47	0.47	0.47	VI
	Down	0.28	0.09	0.08	0.00	0.09	0.28	0.28	
PuH_3	Up	0.02	0.02	0.00	0.00	0.03	0.02	0.00	III
	Down	0.07	0.06	**0.98**	**0.98**	**1.00**	**1.00**	**0.98**	
Pu_4O_9	Up	0.03	0.02	0.11	0.06	0.04	0.02	0.02	IV(¾)
	Down	0.08	0.21	0.15	**1.00**	**1.00**	**1.00**	**1.00**	
	Up	0.21	0.08	0.08	0.08	0.04	0.04	0.04	V(¼)
	Down	0.37	0.25	0.30	0.27	**1.00**	**1.00**	**1.00**	
PuB_{12}	Up	0.30	0.32	0.32	**0.99**	**0.97**	**0.97**	**0.97**	IV
	Down	0.00	0.03	0.03	0.04	0.02	0.02	0.02	
PuC_2	Up	0.05	0.61	0.61	**0.93**	**0.97**	**0.97**	**0.97**	IV
	Down	0.02	0.01	0.01	0.01	0.00	0.00	0.00	
PuN	Up	0.05	0.06	**0.97**	**0.97**	**0.98**	**0.99**	**0.99**	III
	Down	0.00	0.01	0.01	0.01	0.03	0.03	0.03	

The quantity of charge of each atom in the actinide compounds is listed in Table S2. Here, some Pu and U compounds in which Pu and U have high OS_f are selected. In addition, we list the results of $Am_4O_8F_4$ and $Cm_4O_8F_4$ to illustrate that even multiple F atoms cannot oxidize Am and Cm into higher OS_p. For Pu(U)-O-F systems, with the increasing concentration of F, the quantity of charge gain for O and F decreases. With comparison to their dioxides, we propose that the charge gain of F could be viewed as from O atom. In fact, the bonding strength of pure Pu(U)-F bonds is rather weak, as can be inferred by the charge transfer in PuF_6 and UF_6.

Table S2 Quantity of charge of each atom in some selected actinide compounds.

Compounds	Quantity of charge (|e|)				
	An	O	F	Na	B
PuO_2	+2.42	-1.21			
PuO_2F	+2.77	-1.01	-0.75		
PuO_2F_2	+3.00	-0.77	-0.73		
$PuOF_4$	+2.97	-0.57	-0.60		
PuF_6	+3.00		-0.50		
Na_4PuO_5	+2.52	-1.30		+0.99	
Na_5PuO_6	+2.60	-1.26		+0.99	
PuB_{12}	+1.62				-0.135
UO_2	+2.50	-1.25			
UO_2F	+3.05	-1.15	-0.75		
UO_2F_2	+3.14	-0.82	-0.75		
UOF_4	+3.27	-0.75	-0.63		
UF_6	+3.30		-0.55		
Na_4UO_5	+2.90	-1.37		+0.99	
UB_{12}	+1.90				-0.158
AmO_2	+2.32	-1.16			
$Am_4O_8F_4$	+2.42	-0.89	-0.64		
CmO_2	+2.28	-1.14			
$Cm_4O_8F_4$	+2.29	-0.83	-0.63		

We test Hubbard parameter U value on the OS_p of Pu. Some analogues of U and Np compounds are selected for comparison. We choose the U values from 4 eV to 8 eV. From the available papers on the DFT + U calculations of actinide materials, we find that $U = 4$ eV is widely used and $U = 8$ eV could be viewed as the extreme value for actinide 5*f* electrons. The results are listed in Table S3. Here, we just give the OS_p results at $U = 4$ eV and 8 eV. We find that the OS_p of actinide ions in most compounds are not changed with the increase in U values, despite that the occupation numbers may increase. The significant changes on the OS_p of Pu happen on the Na-Pu-O ternary compounds. When U values increase from 4 eV to 8 eV, the OS_p of Pu decrease from VI to V in Na_4PuO_5, and from VII to IV in Na_5PuO_6. Note that the U and Np analogues do not occur the changes of OS_p. The results indicate that the rather weak Pu-O bonds exist in the ternary compounds, and the OS_p of Pu^{VI} and Pu^{VII} could be regarded as unstable chemical states.

Table S3 Calculated spin-up and spin-down 5*f*-orbital occupation numbers and OS_p of U and Pu ions with different Hubbard parameter *U*. The occupation numbers for full occupancy are marked with bold.

Compounds	*U* (eV)	Spin	Occupation number of 5*f* orbitals							OS_p
PuO_2	4	Up	0.23	0.08	0.08	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.13	0.05	0.04	0.05	0.03	0.03	0.03	
	8	Up	0.19	0.05	0.05	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.10	0.03	0.03	0.03	0.02	0.02	0.02	
UO_2	4	Up	**0.99**	**0.99**	0.14	0.04	0.03	0.03	0.03	IV
		Down	0.11	0.03	0.02	0.02	0.03	0.03	0.03	
	8	Up	**1.00**	**1.00**	0.10	0.03	0.02	0.02	0.02	IV
		Down	0.08	0.02	0.02	0.02	0.02	0.02	0.02	
Na_5PuO_6	4	Up	0.60	0.20	0.18	**0.99**	0.20	0.60	0.66	VII
		Down	0.37	0.13	0.12	0.46	0.37	0.00	0.13	
	8	Up	0.10	0.10	0.09	**0.93**	**1.00**	**0.95**	**0.94**	IV
		Down	0.15	0.05	0.05	0.18	0.15	0.00	0.05	
Na_5NpO_6	4	Up	0.44	0.16	0.15	0.00	0.51	0.43	0.16	VII
		Down	0.44	0.16	0.15	0.00	0.51	0.43	0.16	
	8	Up	0.65	0.59	0.26	0.07	0.09	0.09	0.00	VII
		Down	0.66	0.64	0.29	0.08	0.09	0.10	0.00	
Na_4PuO_5	4	Up	0.15	**1.00**	0.64	0.64	**0.99**	0.19	0.25	VI
		Down	0.33	0.33	0.06	0.07	0.00	0.10	0.14	
	8	Up	0.06	0.09	0.71	0.70	**1.00**	**1.00**	**1.00**	V
		Down	0.10	0.10	0.02	0.02	0.00	0.03	0.05	
Na_4UO_5	4	Up	0.39	0.09	0.39	0.00	0.12	0.09	0.16	VI
		Down	0.39	0.09	0.39	0.00	0.12	0.09	0.16	
	8	Up	0.40	0.06	0.40	0.00	0.06	0.09	0.12	VI
		Down	0.40	0.06	0.40	0.00	0.06	0.09	0.12	
PuO_2F	4	Up	0.12	0.14	0.33	0.62	**1.00**	**1.00**	**1.00**	V
		Down	0.20	0.03	0.04	0.04	0.06	0.07	0.08	
	8	Up	0.77	0.78	**1.00**	**1.00**	**1.00**	0.06	0.04	V
		Down	0.09	0.09	0.02	0.02	0.05	0.03	0.00	
$PuOF_4$	4	Up	**0.81**	**1.00**	**0.99**	0.35	0.15	0.16	0.31	V
		Down	0.70	0.23	0.20	0.03	0.01	0.09	0.09	
	8	Up	**0.96**	**1.00**	**1.00**	0.33	0.11	0.12	0.24	V
		Down	0.74	0.18	0.02	0.01	0.15	0.08	0.08	

We test magnetic order on the OS_p of Pu. From the published results and our calculation results on PuO_2 and other actinide dioxides, we find that the total energy of nonmagnetic (NM) state is always higher that of ferromagnetic state (FM) or anti-ferromagnetic(AFM)state, and the total energy of AFM state is generally slightly lower than that of FM state. Table S4 list the OS_p of Pu in PuO_2 in both FM and AFM states. For comparison, we also give the OS_p of U in UO_2 in both magnetic states. Clearly, the magnetic state has insignificant effect on the OS_p of Pu and U. We test the spin-orbit coupling (SOC) on the OS_p of Pu. The results of OS_p of Pu and U in the dioxides are also listed in Table S4. We find that the OS_p are not changed with the inclusion of SOC despite that the occupation numbers slightly decrease. In addition, we test exchange-correlation potentials (LDA, GGA-PW91 and GGA-PBE) on the OS_p of Pu and U in their dioxides, and find that potentials have insignificant effect on the OS_p of Pu and U in their dioxides.

Table S4 The tests of magnetic order, spin-orbit coupling and exchange-correlation potentials on the OS_p of Pu and U in their dioxides. The occupation numbers for full occupancy are marked with bold.

Compounds	Test	Spin	Occupation number of 5*f* orbitals							OS_p
PuO_2	AFM	Up	0.23	0.08	0.08	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.13	0.05	0.04	0.05	0.03	0.03	0.03	
	FM	Up	0.22	0.10	0.10	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.13	0.05	0.04	0.04	0.03	0.03	0.03	
UO_2	AFM	Up	**0.99**	**0.99**	0.14	0.04	0.03	0.03	0.03	IV
		Down	0.11	0.03	0.02	0.02	0.03	0.03	0.03	
	FM	Up	**1.00**	**1.00**	0.12	0.03	0.05	0.04	0.04	IV
		Down	0.10	0.04	0.04	0.03	0.02	0.02	0.02	
PuO_2	SOC		**1.00**	**1.00**	**1.00**	**0.99**	0.18	0.32	0.10	IV
			0.23	0.18	0.14	0.10	0.08	0.00	0.00	
UO_2	SOC		**0.92**	**0.82**	0.33	0.22	0.41	0.30	0.21	IV
			0.14	0.10	0.08	0.03	0.03	0.03	0.03	
PuO_2	LDA	Up	0.24	0.08	0.08	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.15	0.05	0.05	0.05	0.03	0.03	0.03	
	PW91	Up	0.24	0.08	0.08	**1.00**	**1.00**	**1.00**	**1.00**	IV
		Down	0.13	0.05	0.05	0.04	0.03	0.03	0.03	
UO_2	LDA	Up	**0.99**	**0.99**	0.15	0.05	0.03	0.03	0.03	IV
		Down	0.13	0.03	0.03	0.03	0.03	0.04	0.04	
	PW91	Up	**0.99**	**0.99**	0.14	0.04	0.03	0.03	0.03	IV
		Down	0.11	0.02	0.02	0.03	0.03	0.03	0.03	