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On the Multi-Reference Nature of Plutonium Oxides: PuO_2^{2+}, PuO_2, PuO_3 and $PuO_2(OH)_2$

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Supporting Information

1 XYZ Coordinates in Angstroms

1.1 linear PuO_2

Pu	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	1.814000000000
O	0.000000000000	0.000000000000	−1.814000000000

1.2 linear PuO_2^{2+}

Pu	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	1.711000000000
O	0.000000000000	0.000000000000	−1.711000000000

1.3 bent PuO_2^{2+}

Pu	0.000000000000	0.000000000000	0.000000000000
O	−0.118952247373	0.000000000000	1.762991594661
O	−0.118952247373	0.000000000000	−1.762991594661

1.4 PuO_3

Pu	0.000000000000	0.000000000000	0.000000000000
O	1.934000000000	0.000000000000	0.000000000000
O	−0.118952247373	0.000000000000	1.762991594661
O	−0.118952247373	0.000000000000	−1.762991594661

1.5 $PuO_2(OH)_2$

Pu	0.000000000000	0.000000000000	1.000000000000
O	1.743451431370	0.000000000000	0.926500976503
O	−1.743451431370	0.000000000000	0.926500976503
O	0.000000000000	1.692384295153	2.243316290217
O	0.000000000000	−1.692384295153	2.243316290217
H	0.779782242822	2.098494984571	2.631304385035
H	−0.779782242822	−2.098494984571	2.631304385035

2 DMRG convergence and occupation numbers

Table S1: Ground state energies of all investigated plutonium oxides. The convergence of DMRG calculations with respect to the number of renormalized system states (indicated in brackets) is summarized. The number of block states was kept fixed for $m = 256$ and $m = 512$, while the DBSS procedure was used for larger m. [1024]: $m_{\text{min}} = 512$, $m_{\text{init}} = m_{\text{max}} = 1024$, the threshold for the quantum information loss was set to 10^{-5}. [2048]: $m_{\text{min}} = 512$, $m_{\text{init}} = 1024$, $m_{\text{max}} = 2048$, the threshold for the quantum information loss was set to 10^{-5}.

	E/Hartree				
Molecule	PuO_2	PuO_2^{2+} (linear)	PuO_2^{2+} (bent)	PuO_3	$PuO_2(OH)_2$
DMRG					
FV-CAS					
[256]	–	–	–	–	−852.858 6
[512]	−701.966 0	−701.224 8	−701.256 0	−776.642 0	−852.862 5
[1024]	−701.967 1	−701.226 4	−701.258 8	−776.642 4	−852.864 4
[2048]	−701.967 3	−701.227 1	−701.260 3	−776.642 6	−852.865 5
optCAS					
[256]	–	–	–	−776.611 5	−852.815 7
[512]	−701.925 8	−701.202 3	−701.179 9	−776.611 5	−852.816 9
[1024]	−701.925 9	−701.202 6	−701.180 2	–	−852.817 4

Table S2: Occupation numbers of each active space orbital with index i for the converged DMRG wavefunctions and investigated plutonium oxides. The orbitals i are ordered as mentioned in the main manuscript.

PuO_2				PuO_2^{2+} (linear)				PuO_2^{2+} (bent)				PuO_3				$PuO_2(OH)_2$			
FV-CAS		optCAS		FV-CAS		optCAS		FV-CAS		optCAS		FV-CAS		optCAS		FV-CAS		optCAS	
i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}	i	n_{occ}
1	2.00	1	0.02	1	2.00	1	1.97	1	2.00	1	1.89	1	2.00	1	2.00	1	2.00	1	1.97
2	2.00	2	1.99	2	2.00	2	0.00	2	1.99	2	1.96	2	2.00	2	1.98	2	2.00	2	1.98
3	1.99	3	1.98	3	1.98	3	1.91	3	1.99	3	0.50	3	2.00	3	0.24	3	2.00	3	2.00
4	0.02	4	0.99	4	0.00	4	0.50	4	1.89	4	0.12	4	2.00	4	0.00	4	2.00	4	1.99
5	0.00	5	0.07	5	0.00	5	0.10	5	1.95	5	1.89	5	1.99	5	1.98	5	2.00	5	0.47
6	0.00	6	1.99	6	0.00	6	1.91	6	0.50	6	0.12	6	2.00	6	1.99	6	1.99	6	0.54
7	1.99	7	1.98	7	1.99	7	0.50	7	0.13	7	0.50	7	1.98	7	0.78	7	1.97	7	0.00
8	1.98	8	0.99	8	1.91	8	0.10	8	0.01	8	1.90	8	0.22	8	0.00	8	1.98	8	0.00
9	0.99	9	0.07	9	0.49	9	1.92	9	0.01	9	1.96	9	0.00	9	0.02	9	1.99	9	0.02
10	0.07	10	1.93	10	0.10	10	0.51	10	0.00	10	0.51	10	0.01	10	1.98	10	1.99	10	0.02
11	1.99	11	0.95	11	1.99	11	0.09	11	1.99	11	0.13	11	0.01	11	1.97	11	0.47	11	1.97
12	1.98	12	0.07	12	1.91	12	1.96	12	1.89	12	0.03	12	1.99	12	0.26	12	0.55	12	1.98
13	0.99	13	1.99	13	0.52	13	0.03	13	0.50	13	1.95	13	1.98	13	0.01	13	0.01	13	1.97
14	0.07	14	0.02	14	0.10	14	1.96	14	0.13	14	0.51	14	1.99	14	0.78	14	0.00	14	2.00
15	0.01	15	1.99	15	0.01	15	0.03	15	0.01	15	0.03	15	0.81			15	0.03	15	2.00
16	2.00	16	0.02	16	1.99	16	0.51	16	0.00			16	0.01			16	0.03	16	0.56
17	1.99	17	0.96	17	1.99			17	1.99			17	0.03			17	0.00	17	0.45
18	1.93			18	1.91			18	1.99			18	2.00			18	0.00	18	0.00
19	0.96			19	0.50			19	1.89			19	2.00			19	2.00	19	0.01
20	0.07			20	0.08			20	1.95			20	1.99			20	2.00	20	0.01
21	1.99			21	1.96			21	0.51			21	1.97			21	2.00	21	0.02
22	0.02			22	0.03			22	0.13			22	1.96			22	1.99	22	0.04
23	1.99			23	1.96			23	0.04			23	0.25			23	1.99		
24	0.02			24	0.03			24	1.95			24	0.01			24	1.96		
25	0.96			25	0.52			25	0.51			25	2.00			25	1.97		
								26	0.04			26	0.81			26	1.96		
																27	1.99		
																28	1.99		
																29	0.58		
																30	0.44		
																31	0.00		
																32	0.02		
																33	0.01		
																34	0.03		
																35	0.05		

Table S3: DMRG orbital ordering used in all calculations.

Molecule	FV-CAS
PuO_2	$2a_g$ $5a_g$ $6a_g$ $3a_g$ $1a_g$ $5b_{1u}$ $3b_{1u}$ $2b_{3u}$ $2b_{2u}$ $4b_{3u}$ $4b_{2u}$ $1a_u$ $4b_{1u}$ $2b_{1u}$ $1b_{3g}$ $1b_{2g}$ $2b_{3g}$ $2b_{2g}$ $1b_{1u}$ $3b_{2u}$ $3b_{3u}$ $4a_g$ $1b_{2u}$ $1b_{3u}$ $1b_{1g}$
PuO_2^{2+} (linear)	$1b_{1g}$ $1b_{1u}$ $3b_{2u}$ $3b_{3u}$ $1a_u$ $4b_{1u}$ $2b_{2g}$ $2b_{3g}$ $1b_{2g}$ $1b_{3g}$ $2b_{1u}$ $2b_{2u}$ $4b_{2u}$ $2b_{3u}$ $4b_{3u}$ $1b_{2u}$ $1b_{3u}$ $3b_{1u}$ $5b_{1u}$ $5a_g$ $2a_g$ $3a_g$ $4a_g$ $1a_g$ $6a_g$
PuO_2^{2+} (bent)	$1a_1$ $9a_1$ $5b_1$ $8a_1$ $2a_1$ $3a_1$ $1b_1$ $2b_2$ $10a_1$ $6a_1$ $3b_1$ $5b_2$ $2a_2$ $5a_1$ $3b_2$ $6b_2$ $3a_2$ $7a_1$ $4a_1$ $7b_2$ $4b_1$ $2b_1$ $4b_2$ $1a_2$ $1b_2$ $6b_1$
PuO_3	$1b_2$ $1a_2$ $5b_1$ $11a_1$ $3b_2$ $2b_2$ $2b_1$ $5a_1$ $3b_1$ $6a_1$ $6b_1$ $7b_2$ $4b_2$ $9a_1$ $5b_2$ $10a_1$ $7a_1$ $1b_1$ $6b_2$ $4b_1$ $2a_2$ $8a_1$ $4a_1$ $2a_1$ $1a_1$ $3a_1$
$PuO_2(OH)_2$	$1a$ $2a$ $3a$ $4a$ $5a$ $6a$ $9a$ $10a$ $15a$ $7a$ $11a$ $12a$ $16a$ $8a$ $13a$ $14a$ $17a$ $18a$ $4b$ $10b$ $9b$ $5b$ $7b$ $8b$ $6b$ $11b$ $12b$ $17b$ $16b$ $14b$ $15b$ $13b$ $1b$ $2b$ $3b$
Molecule	optCAS
PuO_2	$3b_{3u}$ $3b_{2u}$ $1a_u$ $4b_{1u}$ $4b_{3u}$ $4b_{2u}$ $2b_{2u}$ $2b_{3u}$ $5b_{1u}$ $3b_{1u}$ $1b_{3g}$ $2b_{3g}$ $2b_{2g}$ $1b_{2g}$ $1b_{3u}$ $1b_{2u}$ $4a_g$
PuO_2^{2+} (linear)	$3b_{3u}$ $3b_{2u}$ $4b_{1u}$ $1a_u$ $2b_{2u}$ $2b_{3u}$ $4b_{2u}$ $4b_{3u}$ $3b_{1u}$ $2b_{3g}$ $2b_{2g}$ $1b_{3g}$ $1b_{2g}$ $5b_{1u}$ $3a_g$ $4a_g$
PuO_2^{2+} (bent)	$4b_1$ $6a_1$ $2a_2$ $5b_2$ $3b_2$ $6b_2$ $2b_1$ $4a_1$ $3b_1$ $7a_1$ $5a_1$ $1a_2$ $4b_2$ $3a_2$ $7b_2$
PuO_3	$5b_1$ $7b_2$ $3b_1$ $4b_2$ $2b_1$ $5b_2$ $6b_1$ $7a_1$ $6b_2$ $4b_1$ $2a_2$ $8a_1$ $6a_1$ $9a_1$
$PuO_2(OH)_2$	$9a$ $10a$ $16a$ $17b$ $14b$ $16b$ $6b$ $8a$ $7a$ $12a$ $11a$ $12b$ $11b$ $8b$ $15a$ $7b$ $15b$ $9b$ $13a$ $10b$ $13b$ $14a$