Noncollinear Relativistic DFT+U Calculations of Actinide Dioxide Surfaces (Supporting Information)

James T. Pegg,[1,2*] Ashley E. Shields,[3] Mark T. Storr,[2] David O. Scanlon,[1,4,5] and Nora H. de Leeuw.[1,6]

[1] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom.

[2] Atomic Weapons Establishment (AWE) Plc, Aldermaston, Reading, RG7 4PR, UK.

[3] Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, Tennessee 37831, USA

[4] Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom.

[5] Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK

[6] Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff, CF1D 3AT, United Kingdom.

Corresponding Author James T. Pegg: uccajtp@ucl.ac.uk

Supporting Information

Monolayer Surface Energetics.

The energy of the low-index surfaces has been calculated as function of the number of formula units (**Figure S1**).

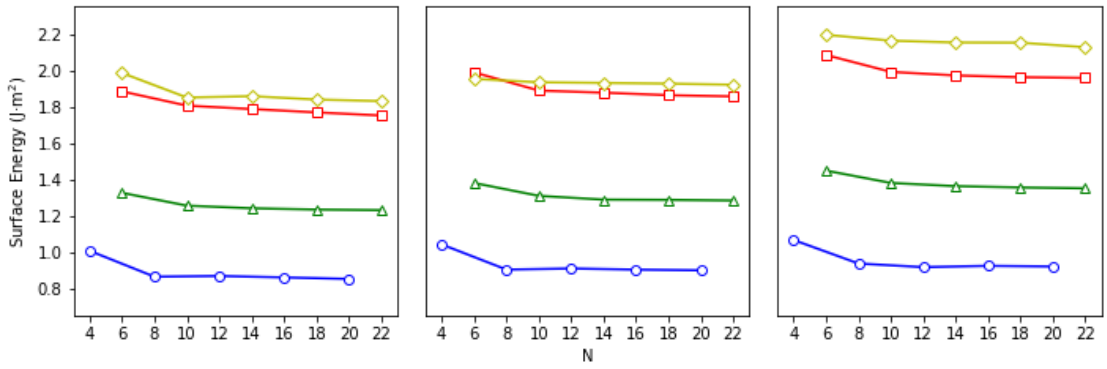

Figure S1: *Convergence of the surface energies (J m^{-2}) with respect to the number of formula units (N) employed: (left) uranium dioxide, (middle) neptunium dioxide, and (right) plutonium dioxide. The symbols in the parentheses indicate the (111) (blue circle), (011) (green triangle), (001)α (red square) and (001)β (yellow diamond) surfaces.*

Fixed Unit Cell Dimensions

Table S1: *The fixed unit cell dimensions for the AnO_2 (111) surface. Note: the z-dimension varies depending on the number of monolayers.*

Surface	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
(111)	7.742	0.000	0.000	7.697	0.000	0.000	7.651	0.000	0.000
	3.871	6.705	0.000	3.849	6.666	0.000	3.826	6.626	0.000
	0.000	0.000	35.803	0.000	0.000	35.712	0.000	0.000	35.618
(011)	5.474	0.000	0.000	5.442	0.000	0.000	5.410	0.000	0.000
	0.000	7.742	0.000	0.000	7.697	0.000	0.000	7.651	0.000
	0.000	0.000	39.398	0.000	0.000	39.282	0.000	0.000	39.128
(001)	5.474	0.000	0.000	5.442	0.000	0.000	5.410	0.000	0.000
	0.000	5.474	0.000	0.000	5.442	0.000	0.000	5.410	0.000
	0.000	0.000	50.077	0.000	0.000	49.904	0.000	0.000	49.756

Initial Magnetic Structure

The initial periodic magnetic vectors of the low-index AnO_2 (111), (011), (001)r surfaces are given with respect to the plane of the surface (**Tables S2-S4**). A transverse 3k AFM sate for UO_2 and NpO_2 is used; whereas, a longitudinal 3k AFM state for PuO_2 is used.

Table S2: *The initial periodic arrangement of magnetic vectors for the AnO_2 (111) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A, E, I, M, Q	-0.45	-0.64	1.10	-0.90	-1.27	2.21	-1.26	-1.79	-3.10
B, F, J, N, R	-0.45	-0.64	-1.10	2.70	0.00	0.00	-1.26	3.58	0.00
C, G, K, O, S	-0.45	1.27	0.00	-0.90	-1.27	-2.21	-1.26	-1.79	3.10
D, H, L, P, T	1.35	0.00	0.00	-0.90	2.55	0.00	3.79	0.00	0.00

Table S3: *The initial periodic arrangement of magnetic vectors for the AnO_2 (011) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A, E, I, M, Q, U	0.00	-1.17	0.68	0.00	-2.34	1.35	-3.28	0.00	1.90
B, F, J, N, R, V	-1.17	0.00	-0.68	-2.34	0.00	-1.35	3.28	0.00	1.90
C, G, K, O, S	0.00	1.17	0.68	0.00	2.34	1.35	0.00	3.28	-1.90
D, H, L, P, T	1.17	0.00	-0.68	2.34	0.00	-1.35	0.00	-3.28	-1.90

Table S4: *The initial periodic arrangement of magnetic vectors for the AnO_2 (001)r surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A, E, I, M, Q, U	-0.78	-0.78	0.78	1.56	1.56	1.56	2.19	-2.19	-2.19
B, F, J, N, R, V	0.78	0.78	0.78	-1.56	-1.56	1.56	2.19	2.19	2.19
C, G, K, O, S	-0.78	0.78	-0.78	1.56	-1.56	-1.56	-2.19	-2.19	2.19
D, H, L, P, T	0.78	-0.78	-0.78	-1.56	1.56	-1.56	-2.19	2.19	-2.19

Structural Ionic Relaxation

The fully relaxed output geometry of the AnO_2 (111), (011), (001)α surfaces has been recorded (**Tables S5-S7**).

Table S5: *The relaxed ionic direct coordinates for the AnO_2 (111) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	0.667	0.666	0.023	0.667	0.666	0.023	0.667	0.667	0.022
B	0.667	0.167	0.023	0.167	0.166	0.023	0.667	0.166	0.022
C	0.167	0.666	0.023	0.666	0.167	0.023	0.166	0.667	0.022
D	0.167	0.167	0.023	0.167	0.666	0.023	0.166	0.167	0.022
E	0.333	0.333	0.111	0.333	0.333	0.110	0.333	0.333	0.109
F	0.333	0.834	0.111	0.833	0.833	0.110	0.333	0.833	0.109
G	0.833	0.333	0.111	0.333	0.834	0.110	0.834	0.333	0.109
H	0.833	0.833	0.111	0.833	0.333	0.110	0.833	0.833	0.109
I	0.000	1.000	0.199	0.000	0.000	0.199	0.000	0.000	0.197
J	0.000	0.500	0.199	0.500	0.500	0.199	1.000	0.500	0.197
K	0.500	1.000	0.199	1.000	0.500	0.199	0.500	0.000	0.197
L	0.500	0.500	0.199	0.500	0.000	0.199	0.500	0.500	0.197
M	0.667	0.667	0.288	0.667	0.667	0.287	0.667	0.667	0.285
N	0.667	0.166	0.288	0.167	0.167	0.287	0.667	0.167	0.285
O	0.167	0.667	0.288	0.667	0.166	0.287	0.166	0.667	0.285
P	0.167	0.167	0.288	0.167	0.667	0.287	0.167	0.167	0.285
Q	0.333	0.334	0.376	0.333	0.334	0.375	0.333	0.333	0.372
R	0.333	0.833	0.376	0.833	0.834	0.375	0.333	0.834	0.372
S	0.833	0.334	0.376	0.334	0.833	0.375	0.834	0.333	0.372
T	0.833	0.833	0.376	0.833	0.334	0.375	0.834	0.833	0.373

Table S6: *The relaxed ionic direct coordinates for the AnO_2 (011) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	0.500	0.750	0.005	0.000	0.500	0.004	0.500	0.750	0.004
B	0.500	0.250	0.005	0.000	0.999	0.004	0.500	0.250	0.004
C	0.000	0.000	0.047	0.500	0.750	0.047	0.000	0.000	0.046
D	0.000	0.500	0.047	0.500	0.250	0.047	0.000	0.500	0.046
E	0.501	0.250	0.100	0.000	0.000	0.099	0.501	0.250	0.098
F	0.500	0.750	0.100	0.000	0.500	0.099	0.499	0.750	0.098
G	0.001	0.500	0.148	0.500	0.250	0.147	0.000	0.500	0.146
H	0.001	0.000	0.148	0.500	0.750	0.147	0.000	0.000	0.146
I	0.500	0.750	0.197	0.000	0.500	0.196	0.500	0.750	0.196
J	0.500	0.250	0.197	0.000	0.000	0.196	0.500	0.250	0.196
K	0.000	0.000	0.246	0.500	0.750	0.245	0.000	1.000	0.244
L	0.000	0.500	0.246	0.500	0.250	0.245	0.000	0.500	0.244
M	0.500	0.250	0.295	0.000	0.000	0.294	0.500	0.250	0.293
N	0.500	0.750	0.295	0.000	0.500	0.294	0.500	0.750	0.293
O	-0.001	0.500	0.345	0.500	0.250	0.344	0.000	0.500	0.343
P	-0.001	0.000	0.345	0.500	0.750	0.344	0.000	0.000	0.343
Q	0.499	0.750	0.393	0.000	0.500	0.392	0.499	0.750	0.391
R	0.500	0.250	0.393	0.000	0.000	0.392	0.501	0.250	0.391
S	0.000	0.000	0.445	0.500	0.750	0.444	0.000	0.000	0.443
T	0.000	0.500	0.445	0.500	0.250	0.444	0.000	0.500	0.443
U	0.500	0.250	0.488	0.000	0.000	0.486	0.500	0.250	0.485
V	0.500	0.750	0.488	0.000	0.501	0.486	0.500	0.750	0.485

Table S7: *The relaxed ionic direct coordinates for the AnO_2 (001)α surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	0.997	0.997	0.026	0.002	0.988	0.026	1.000	1.000	0.026
B	0.497	0.497	0.026	0.502	0.488	0.026	0.500	0.500	0.026
C	0.495	0.994	0.081	0.501	0.988	0.081	0.500	1.000	0.081
D	0.995	0.494	0.081	0.002	0.488	0.081	1.000	0.500	0.081
E	0.996	0.991	0.136	0.002	0.989	0.136	0.000	0.000	0.136
F	0.497	0.492	0.136	0.502	0.489	0.136	0.500	0.500	0.136
G	0.500	0.992	0.191	0.501	0.993	0.190	0.500	1.000	0.190
H	0.999	0.492	0.191	0.001	0.493	0.190	1.000	0.500	0.190
I	0.001	0.995	0.246	0.000	0.997	0.245	0.000	0.000	0.245
J	0.501	0.495	0.246	0.500	0.497	0.245	0.500	0.500	0.245
K	0.500	0.000	0.300	0.498	0.003	0.300	0.500	0.000	0.299
L	0.000	0.500	0.300	0.998	0.503	0.300	0.000	0.500	0.299
M	0.999	0.005	0.355	0.998	0.008	0.354	1.000	1.000	0.353
N	0.499	0.505	0.355	0.498	0.508	0.354	0.500	0.500	0.353
O	0.500	0.008	0.410	0.499	0.009	0.409	0.500	0.000	0.408
P	0.001	0.508	0.410	0.999	0.509	0.409	0.000	0.500	0.408
Q	0.004	0.009	0.464	0.999	0.009	0.463	1.000	1.000	0.462
R	0.503	0.508	0.464	0.499	0.509	0.463	0.500	0.500	0.462
S	0.505	0.006	0.519	0.500	0.009	0.518	0.500	0.000	0.517
T	0.005	0.506	0.519	1.000	0.509	0.518	0.000	0.500	0.517
U	0.003	0.003	0.574	0.999	0.008	0.573	0.000	0.000	0.572
V	0.503	0.503	0.574	0.499	0.508	0.573	0.500	0.500	0.572

Magnetic Deviation

The magnetic deviation in the low-index AnO_2 (111), (011), (001)α surfaces is given for each actinide ion (**Tables S8-S10**).

Table S8: *The deviation of the magnetic vectors for the AnO_2 (111) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	0.43	0.30	0.28	0.40	-0.47	-0.19	0.32	-0.06	-0.11
B	0.44	-0.58	0.39	-2.07	-2.64	0.03	0.32	0.13	-0.01
C	0.41	0.01	0.61	0.28	0.01	-0.11	0.32	-0.07	0.11
D	-1.33	1.27	0.64	0.27	0.09	-0.08	-0.08	0.37	-0.74
E	-0.68	0.26	-0.42	-0.17	0.04	-0.06	-0.04	0.00	0.01
F	-0.74	0.31	0.51	0.00	-0.02	0.00	-0.04	-0.01	0.01
G	0.42	-0.03	-0.57	-0.06	0.01	0.03	-0.03	0.00	-0.01
H	-0.05	-0.38	0.03	-0.10	-0.04	0.01	0.01	0.00	0.00
I	-0.19	0.09	-0.04	0.03	-0.01	0.00	0.00	0.00	0.00
J	0.78	-0.47	0.35	0.00	-0.02	0.00	0.00	0.00	0.00
K	-0.50	-0.29	0.03	0.04	0.00	-0.01	0.00	0.00	0.00
L	-0.29	0.39	-0.75	0.05	0.01	-0.02	0.01	0.00	0.00
M	-0.68	0.26	-0.42	-0.17	0.04	-0.06	-0.04	0.00	0.01
N	-0.73	0.32	0.51	0.00	-0.02	0.00	-0.04	-0.01	0.01
O	0.42	-0.03	-0.57	-0.06	0.01	0.03	-0.03	0.00	-0.01
P	-0.05	-0.38	0.03	-0.10	-0.04	0.00	0.01	0.00	0.00
Q	0.43	0.30	0.28	0.40	-0.47	-0.19	0.32	-0.06	-0.11
R	0.44	-0.58	0.39	-2.07	-2.64	0.03	0.32	0.13	-0.01
S	0.41	0.01	0.61	0.28	0.01	-0.11	0.32	-0.07	0.11
T	-1.33	1.27	0.64	0.27	0.08	-0.07	-0.08	0.37	-0.73

Table S9: *The deviation of the magnetic vectors for the AnO_2 (011) surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	-0.02	0.10	0.37	0.00	-0.38	-1.27	0.16	0.00	0.32
B	1.15	1.08	-0.35	2.36	2.72	1.27	-0.16	0.00	0.32
C	-0.87	-1.18	0.41	0.01	-0.29	0.39	0.00	-0.07	-0.14
D	0.21	0.00	0.48	-0.16	0.01	-0.25	0.00	0.07	-0.14
E	0.01	-0.20	-0.61	0.00	0.12	0.18	0.13	0.00	0.22
F	0.74	0.61	-0.48	0.20	0.07	-0.29	-0.13	0.00	0.22
G	-0.17	0.14	-0.35	-0.02	-0.15	0.22	0.00	-0.18	-0.29
H	0.20	-0.05	0.71	-0.12	-0.01	-0.19	0.00	0.18	-0.29
I	0.13	-0.19	-0.63	0.02	0.14	0.21	0.17	0.00	0.27
J	0.13	0.42	-0.10	0.16	0.02	-0.24	-0.17	0.00	0.27
K	-0.14	0.17	-0.47	-0.03	-0.13	0.20	0.00	-0.18	-0.30
L	0.19	-0.17	0.73	-0.14	-0.03	-0.21	0.00	0.18	-0.29
M	0.13	-0.19	-0.63	0.02	0.14	0.21	0.17	0.00	0.27
N	0.13	0.42	-0.10	0.16	0.02	-0.24	-0.17	0.00	0.27
O	-0.17	0.14	-0.35	-0.02	-0.15	0.22	0.00	-0.18	-0.30
P	0.20	-0.05	0.71	-0.12	-0.01	-0.19	0.00	0.18	-0.29
Q	0.01	-0.20	-0.61	0.00	0.12	0.18	0.13	0.00	0.23
R	0.74	0.61	-0.48	0.20	0.07	-0.29	-0.13	0.00	0.23
S	-0.87	-1.18	0.41	0.01	-0.29	0.39	0.00	-0.07	-0.14
T	0.21	0.00	0.48	-0.16	0.01	-0.25	0.00	0.07	-0.14
U	-0.02	0.11	0.37	0.00	-0.38	-1.27	0.16	0.00	0.32
V	1.15	1.08	-0.35	2.36	2.73	1.27	-0.16	0.00	0.32

Table S10: *The deviation of the magnetic vectors for the AnO_2 (001)α surface.*

Actinide Ion	Uranium Dioxide			Neptunium Dioxide			Plutonium Dioxide		
	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis	z-Axis	y-Axis	x-Axis
A	0.80	-0.26	0.29	-1.48	-3.47	0.35	1.64	2.17	2.21
B	-0.77	-1.82	0.28	1.63	-0.35	0.35	1.64	-2.17	-2.21
C	0.79	0.21	1.77	-0.06	-0.04	-0.01	-0.13	0.07	-0.07
D	-0.80	-0.22	-0.20	0.11	0.05	3.18	-0.14	-0.07	0.07
E	0.01	-0.01	0.02	0.04	-0.02	-0.03	0.02	0.01	0.01
F	0.14	0.11	-1.26	0.13	-0.05	0.07	0.02	-0.01	-0.01
G	-0.25	0.11	0.84	-0.01	-0.03	0.02	0.00	0.00	0.00
H	0.09	0.01	0.07	-0.05	0.01	0.07	0.00	0.00	0.00
I	0.65	-0.13	0.24	-0.03	-0.02	0.04	0.00	0.00	0.00
J	0.12	-0.67	0.25	0.09	-0.03	0.05	0.00	0.00	0.00
K	0.40	0.17	-0.11	0.00	-0.03	0.04	0.00	0.00	0.00
L	-0.51	-0.19	-0.16	-0.04	0.01	0.06	0.00	0.00	0.00
M	0.65	-0.13	0.24	-0.03	0.01	0.00	0.00	0.00	0.00
N	0.12	-0.67	0.25	0.04	-0.01	0.02	0.00	0.00	0.00
O	-0.25	0.11	0.84	-0.05	-0.02	-0.02	0.00	0.00	0.00
P	0.09	0.01	0.08	-0.02	0.00	0.03	0.00	0.00	0.00
Q	0.01	0.00	0.02	0.05	0.00	-0.07	0.02	0.01	0.01
R	0.14	0.11	-1.26	0.11	-0.04	0.05	0.02	-0.01	-0.01
S	0.79	0.21	1.77	-0.06	-0.04	-0.01	-0.14	0.07	-0.07
T	-0.81	-0.22	-0.20	0.10	0.04	3.18	-0.13	-0.07	0.07
U	0.80	-0.26	0.28	-1.57	-3.47	0.35	1.64	2.17	2.21
V	-0.77	-1.82	0.28	1.54	-0.35	0.35	1.64	-2.17	-2.21