

Hydroxylation induced surface stability of AnO₂ (An=U, Np Pu) from first-principles

Zsolt Rak, Rodney C. Ewing, Udo Becker

Department of Earth and Environmental Sciences, University of Michigan

Ann Arbor MI 48109

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Why study AnO₂ surfaces?

➤ technological importance:

- most common fuel forms used for the nuclear energy production
- the AnO₂ surface reactivity → fabrication of the fuel pellets, storage in pools or geologic disposal;
- surface-water interaction → corrosion, leaching of radionuclides

➤ fundamental scientific interest:

- presence of partially filled 5f orbitals – at the boundary between localized and itinerant behavior



Outline

➤ **Methodology**

- surface energy calculations
- f – electrons/DFT+ U method

➤ **Results**

- optimized surface geometry
- surface/adsorption energetics

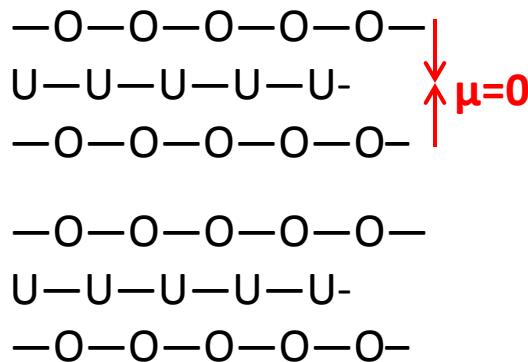
➤ **Conclusions**



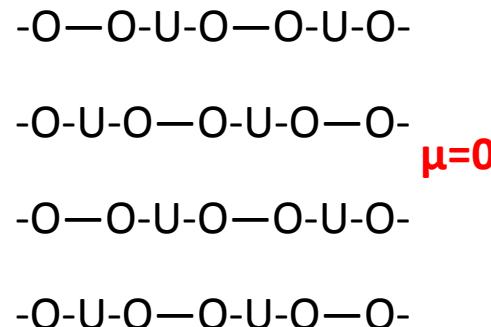
Computational parameters

- Projector Augmented Wave (PAW) method – implemented in VASP code
- Generalized Gradient Approximation (GGA – PBE)
- DFT+ U ; $U = 4.5$ eV, $J = 0.5$ eV for uranium
 $U = 4.0$ eV, $J = 0.5$ eV for neptunium and plutonium
- The (111), (110), and (100) surfaces of AnO_2 ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) are simulated by periodic slabs
- The Brillouin zones (BZ) sampling: (111), (110), and (100) slabs
 $6 \times 6 \times 1$, $6 \times 4 \times 1$, and $4 \times 4 \times 1$ k-points

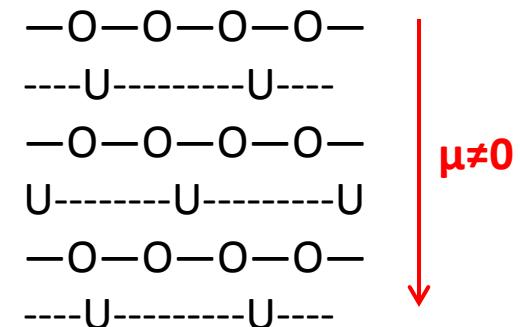
(111)



(110)



(100)

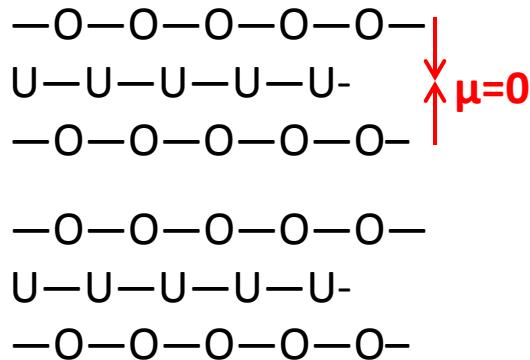




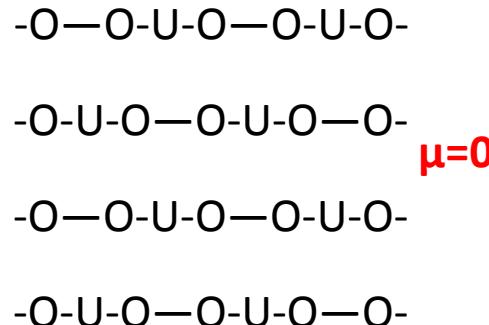
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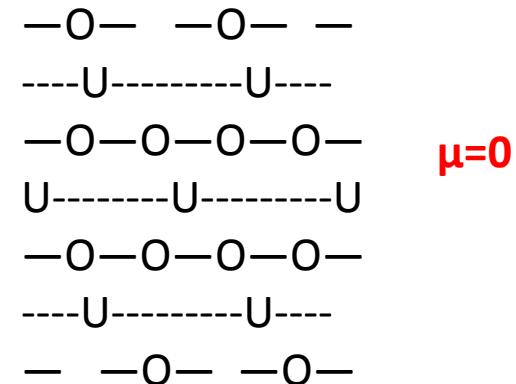
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(110)



(100)





Convergent surface energy

The surface energy can be calculated as:

$$\sigma(N) = \frac{1}{2} (E_{\text{slab}}^N - N E_{\text{bulk}})$$

- requires slab and bulk calculations
- diverges linearly with the slab thickness¹

Boettger:¹

$$E_{\text{bulk}} = E_{\text{slab}}^N - E_{\text{slab}}^{N-1}$$

Fiorentini and Methfessel:²

$$E_{\text{slab}}^N \approx 2\sigma + N E_{\text{bulk}}$$

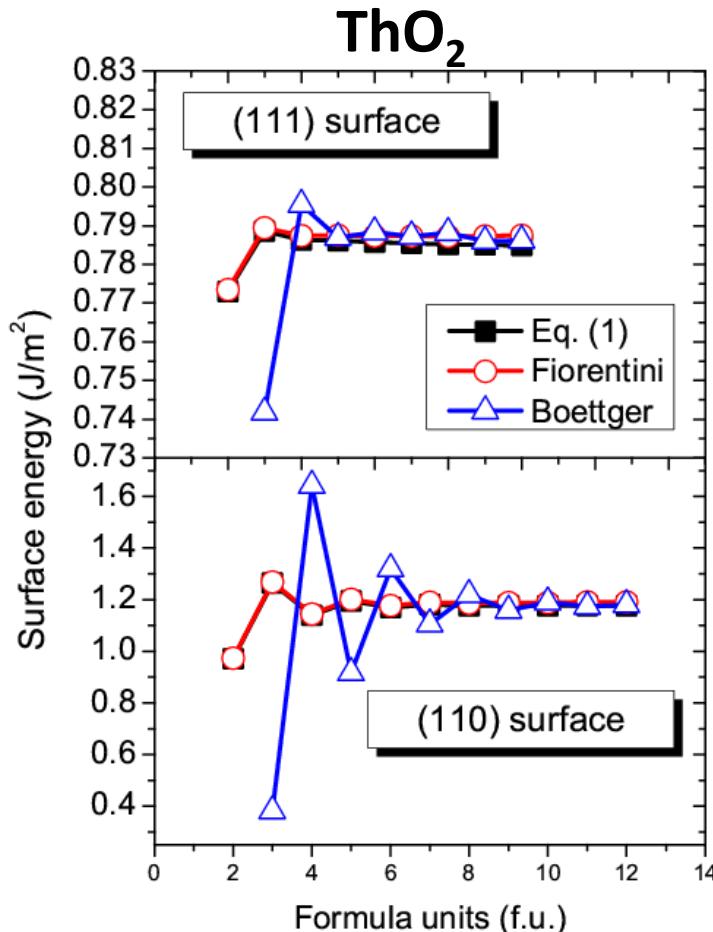
- }
- both methods eliminate the calculation on a separate bulk system, but require a series of slab calculations

¹ J. C. Boettger, Phys. Rev. B **49**, 16798 (1994).

² V. Fiorentini and M. Methfessel, J. Phys. Condens. Mat. **8**, 6525 (1996).



Convergent surface energy



- If the slab and bulk systems are calculated with the same high accuracy all three methods converge to the same surface energy

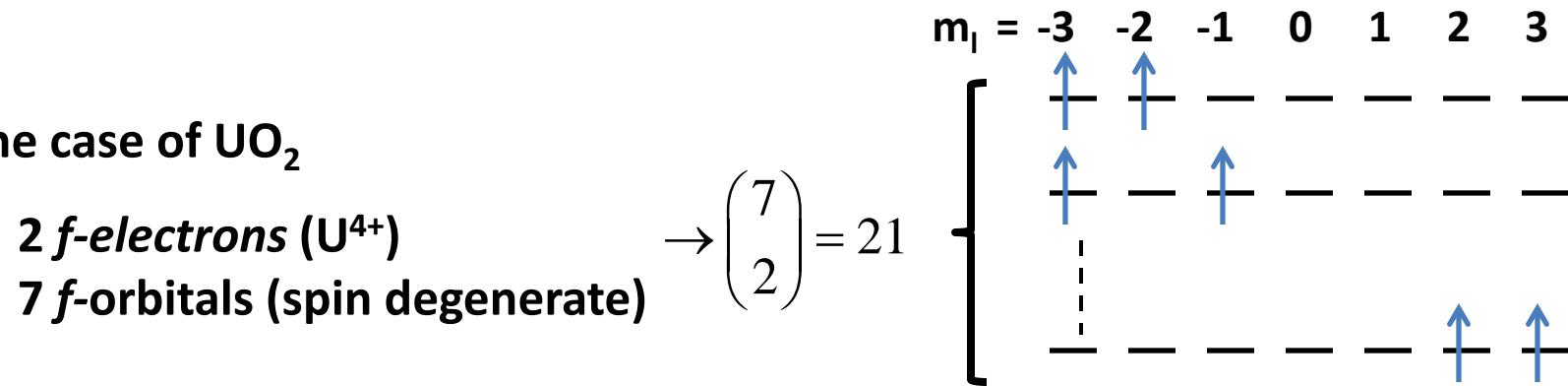
$$\sigma(N) = \frac{1}{2} (E_{\text{slab}}^N - N E_{\text{bulk}}) \quad (1)$$

- (1 × 1) slabs containing 6 f.u. are used to model the AnO₂ surfaces



5f – states of the actinides

- The orbital dependent Hamiltonian (DFT+U method) leads to multiple self-consistent solutions - “*metastable states*”



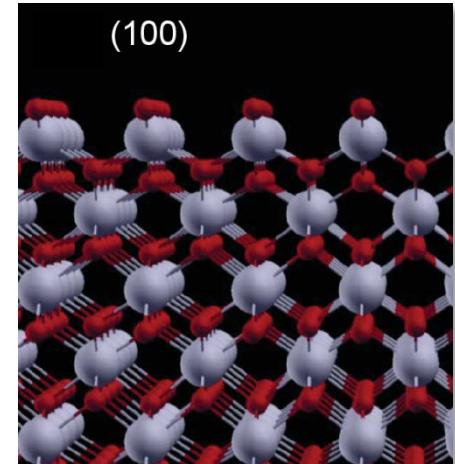
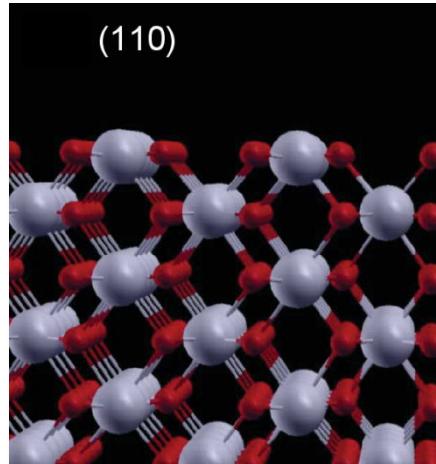
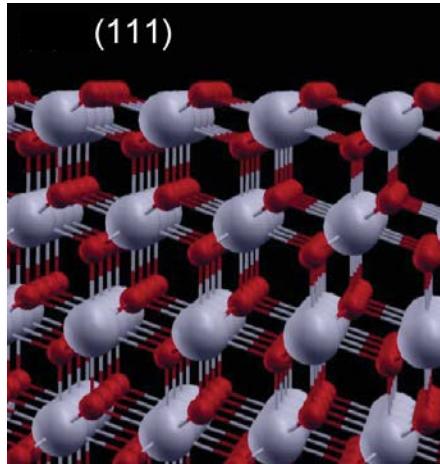
Methods that deal with the *metastability*

- ❖ **constrained density matrix method** – set up the initial orbital occupations and choose the lowest energy solution
- ❖ ***U*-ramping method** – start from $U=0$ and gradually increase U until integer band occupation³

³ B. Meredig, et al., Phys. Rev. B **82**, 195128 (2010).



Surface relaxation

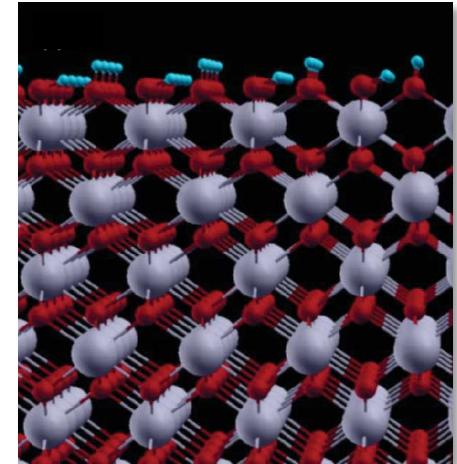
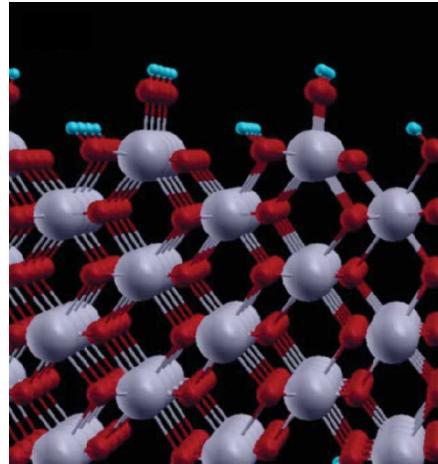
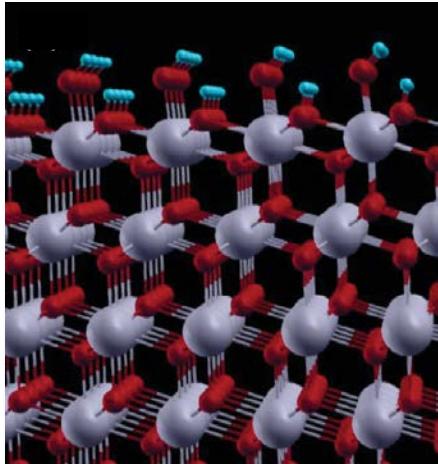


Relaxations of the outmost atomic layers of the AnO_2 ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) surfaces relative to the ideal bulk geometries

	(111)-dry		(111)-wet		(110)-dry		(110)-wet			(100)-dry		(100)-wet	
	O	An	O	An	O	An	O_{H}	O	An	O	An	O	An
UO_2	0.12	0.07	0.04	-0.01	0.05	0.18	-0.18	0.16	0	0.32	-0.02	0.12	0.03
NpO_2	0.06	0.03	0.09	0.05	0.05	0.18	-0.15	0.14	0.01	0.31	-0.02	0.08	0.02
PuO_2	0.08	0.04	0.05	0	0.03	0.16	-0.13	0.11	0	0.31	0	0.06	0.03



Surface relaxation



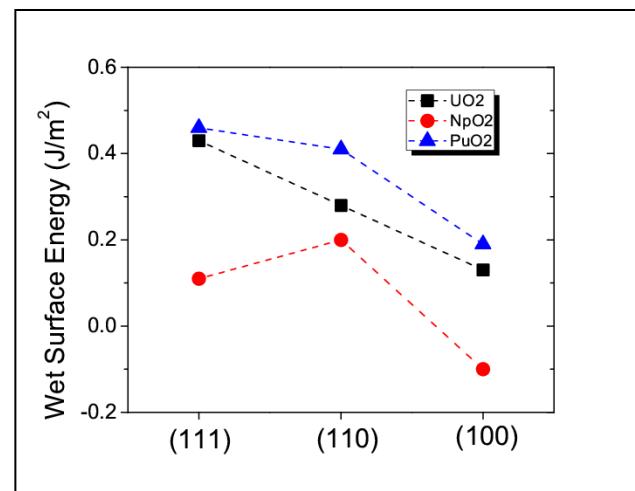
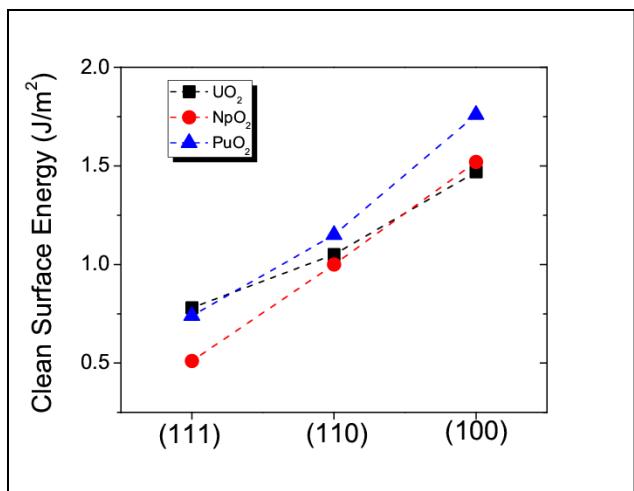
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Surface energies

	UO_2			NpO_2			PuO_2		
	(111)	(110)	(100)	(111)	(110)	(100)	(111)	(110)	(100)
Clean Surf. Energy	0.78	1.05	1.47	0.51	1.00	1.52	0.74	1.15	1.76
Ads. Energy	-0.35	-0.77	-1.34	-0.40	-0.80	-1.62	-0.28	-0.74	-1.57
Hydrox. Surf. Energy	0.43	0.28	0.13	0.11	0.20	-0.10	0.46	0.41	0.19





Conclusions

- The dry surface energies of AnO_2 ($\text{An}=\text{U, Np, Pu}$) reinforce the well-established trend observed in metal-dioxides with fluorite structure: $(111) < (110) < (100)$
- The relative stability of the dry surfaces is inversely correlated with the surface relaxations; the (111) surface is the most “bulk-like”
- dissociated water is adsorbed preferentially on the (100) surface for all AnO_2
- water adsorption changes the surface stability to : $(100) < (110) < (111)$.
this probably influences the morphology of the AnO_2 crystallites 

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allminerals.com





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