The Interaction of Water with PuO_2 Surfaces

Joseph Wellington
UCL

DISTINCTIVE Meeting
12/11/2015
Lancaster University

PuO_2

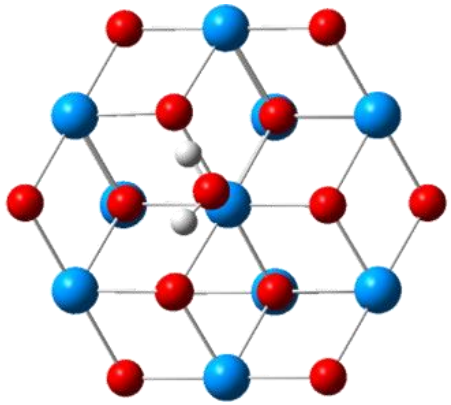
- The UK's stock of civil Pu is mainly stored as PuO_2 powder in multi layer cans
- Radiolytic decay causes the PuO_2 to heat and through various processes pressurisation occurs
- Study desorption of water from the PuO_2 surface and production of H_2 from adsorbed water

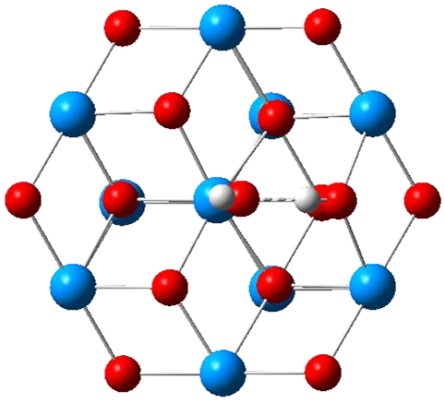
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Aims of the Project

- Investigate water adsorption on UO_2 surfaces
- To study the interaction of water on PuO_2 surfaces at the atomic level in terms of:
  - molecular vs. dissociative adsorption
  - different surface terminations
  - coverage dependence



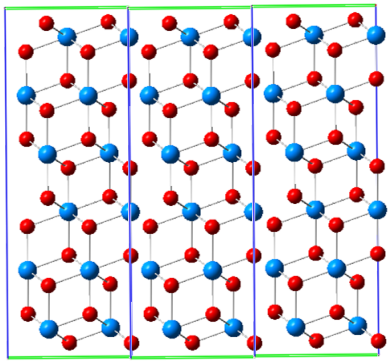


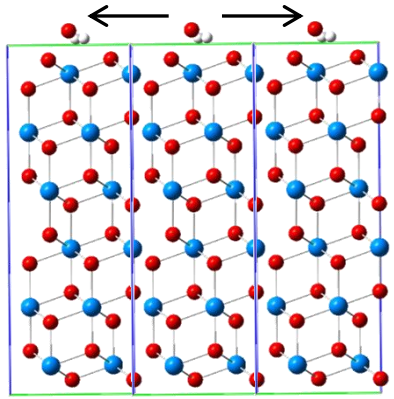
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Surface Calculations

- Periodic DFT usually used
- Create a repeated unit cell to represent the system
- Get interactions between adsorbates and their mirror images
- Time consuming to perform calculations with hybrid functionals
- Use a cluster based method



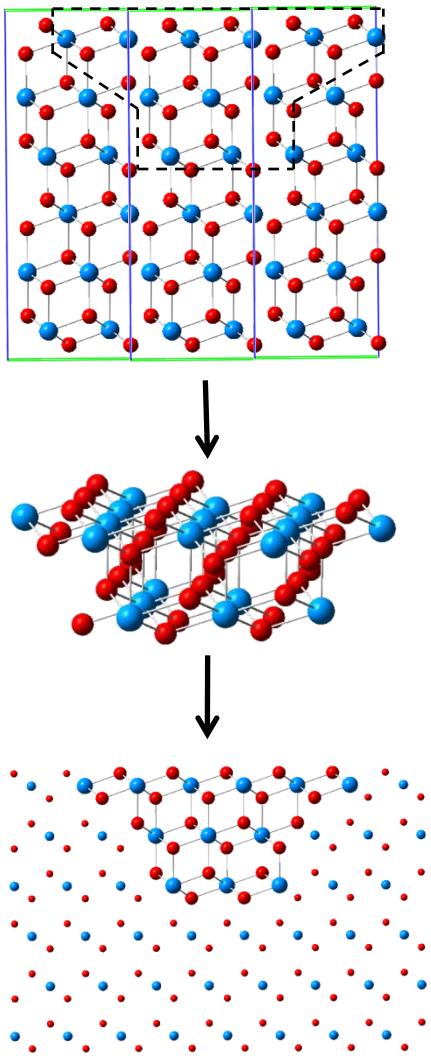


Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Cluster Method

- Using Periodic Electrostatic Embedded Cluster Method (PEECM)
- Implemented in TURBOMOLE
- Define a cluster to be treated quantum mechanically with DFT
- Embed the QM cluster in an array of point charges
- Points charges recreate long-range Coulombic interactions and reproduce the Madelung potential in the cluster

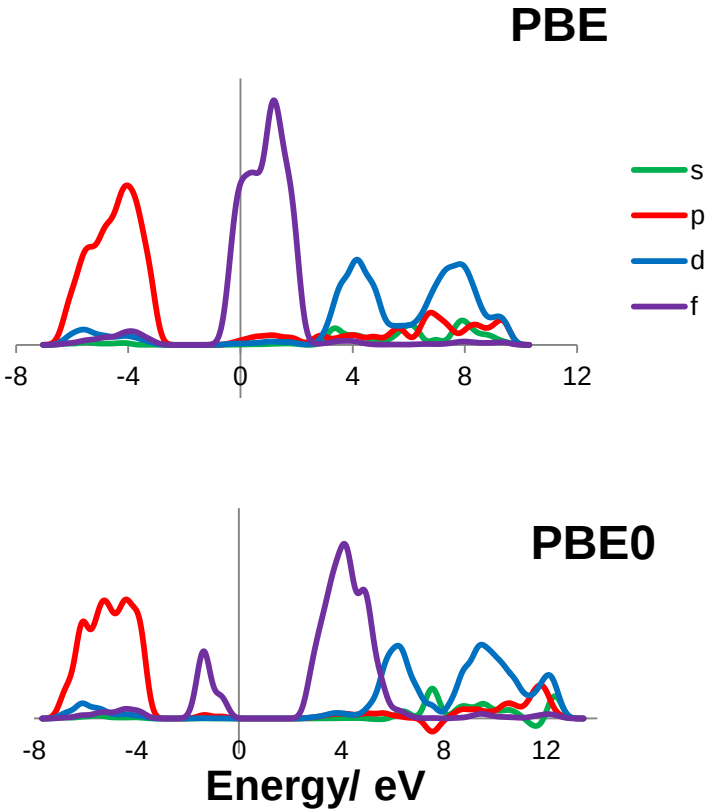


Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Electronic Structure Calculations

- Electronic structure of bulk UO_2 clusters calculated with PBE and PBE0 functional
- PBE predicts a metallic state with Fermi level in 5f band
- PBE0 predicts an insulating state



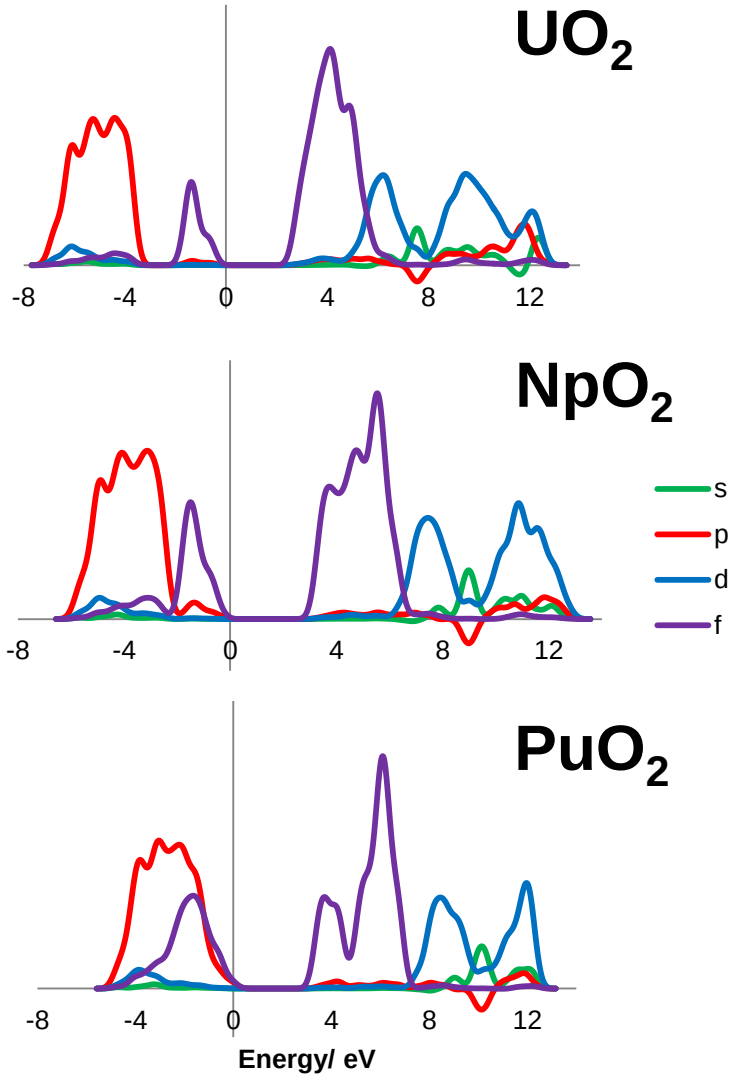
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Electronic Structure Calculations

- Electronic structure of bulk AnO_2 clusters calculated with PBE0 functional
- UO_2 and NpO_2 predicted to be Mott-Hubbard insulators
- PuO_2 predicted to be a charge transfer insulator

	UO_2	NpO_2	PuO_2
Band Gap (expt)/ eV	**2.1**	**2.80**	**2.85**
Calculated HOMO-LUMO gap/ eV	**3.2**	**3.6**	**3.3**

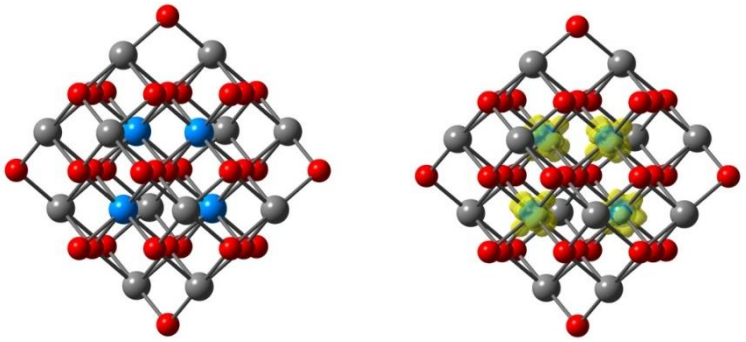


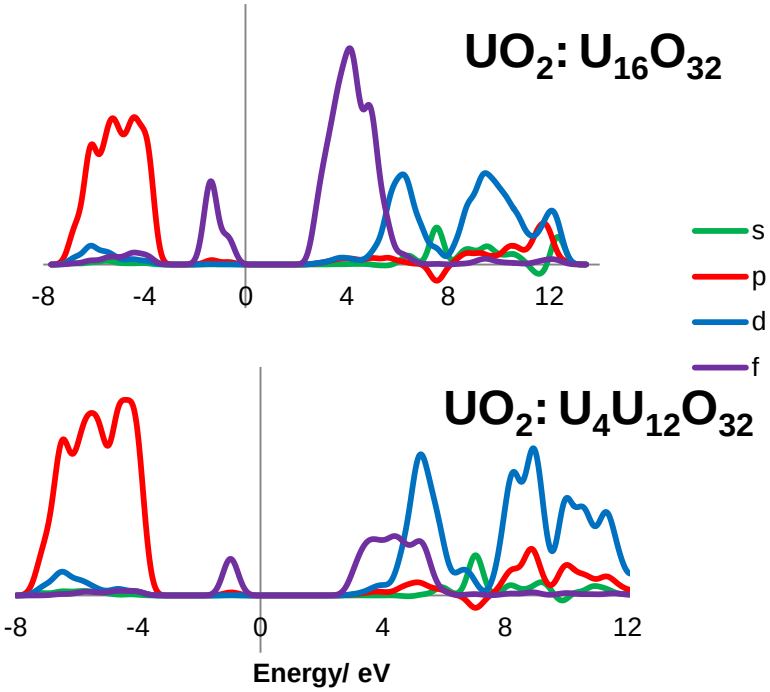
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

5f-in-core ECPs

- To save computational time some actinide ions use ECPs where the 5f electrons are in core
- Calculated electronic structure of a bulk $U_4U_{12}O_{32}$ cluster
- Spin density localised on 4 inner uranium ions
- Mott-Hubbard insulator predicted





Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Periodic Studies of Water Adsorption

- 2 periodic DFT + *U* papers out last year using LDA and PBE
- Calculated water adsorption on UO_2 (111) surface
- LDA predicts a higher binding energy by 0.4 - 0.5 eV

	Adsorption Energy/ eV													
	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m,1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
LDA + *U*[1]	**-1.10**	**-1.12**		**-1.23**				**-1.13**				**-1.19**		
PBE + *U*[2]	**-0.61**	**-0.68**								**-0.60**	**-0.60**	**-0.65**	**-0.53**	**-0.32**

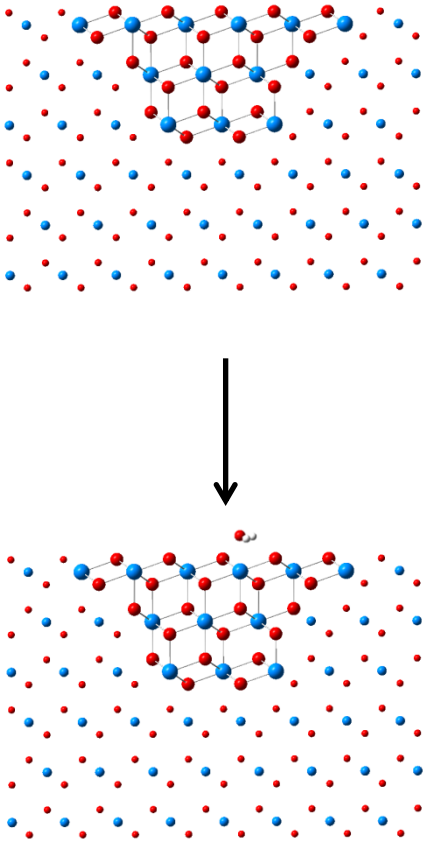
1) P. Maldonado, L. Z. Evins, and P. M. Oppeneer, *Journal of Physical Chemistry C*, 2014, **118**, 8491–8500
2) T. Bo, J. Lan, Y. Zhao, Y. Zhang, C. He, Z. Chai and W. Shi, *Journal of Nuclear Materials*, 2014, **454**, 446-454

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

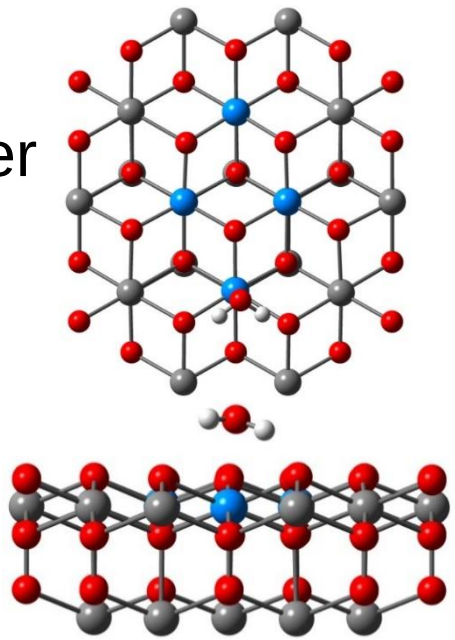
Adsorption Energy

- Optimise coordinates of inner atoms of the cluster
- Add water to the surface, optimise coordinates of water and inner atoms of cluster
- $E_{ads} = E(\text{Surface} + H_2O)_{optimized} - E(\text{Surface})_{optimized} - E(H_2O_{(g)})_{optimized}$



(111) Surface

- Calculated adsorption energies of 1 to 4 water molecules adsorbing on $U_4U_{15}O_{38}$ cluster
- Energies similar between molecular and dissociative adsorption
- Less than 0.2 eV between all the types of adsorption



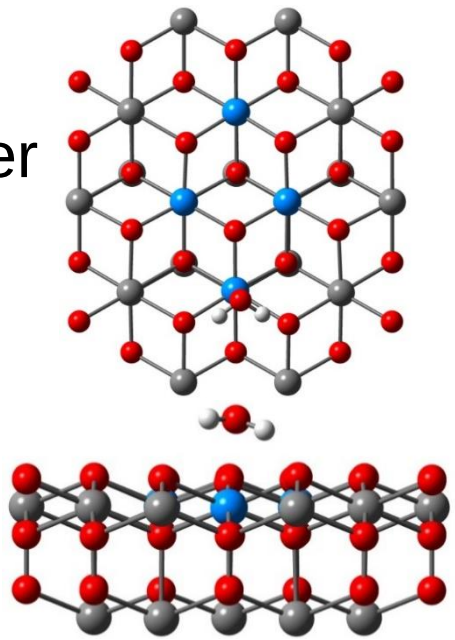
	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m,1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
Adsorption Energy (per molecule)/ eV	-1.04	-1.08	-	-1.19	-1.02	-1.07	-1.14	-1.12	-0.99	-	-1.17	-1.19	-1.09	-

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

(111) Surface

- Calculated adsorption energies of 1 to 4 water molecules adsorbing on $U_4U_{15}O_{38}$ cluster
- Energies similar between molecular and dissociative adsorption
- Less than 0.2 eV between all the types of adsorption



	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m, 1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
Adsorption Energy (per molecule)/ eV	-1.04	-1.08	-	-1.19	-1.02	-1.07	-1.14	-1.12	-0.99	-	-1.17	-1.19	-1.09	-
Periodic DFT[1]/ eV	-1.10	-1.12		-1.23				-1.13				-1.19		

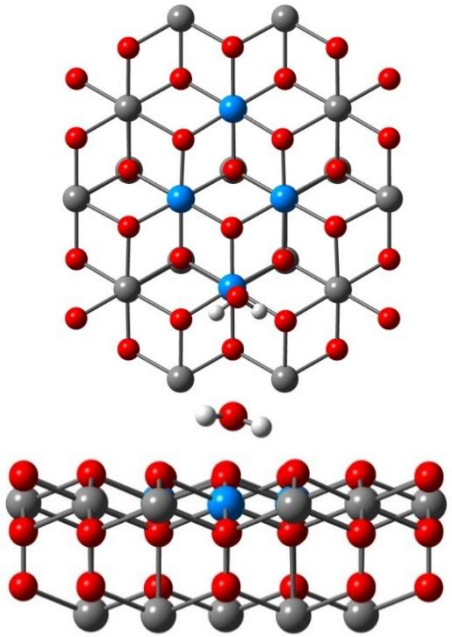
1) P. Maldonado, L. Z. Evins, and P. M. Oppeneer, *Journal of Physical Chemistry C*, 2014, **118**, 8491–8500

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

(111) Surface

- Similar energies for molecular adsorption between UO_2/PuO_2
- Larger adsorption energy on UO_2 for dissociation



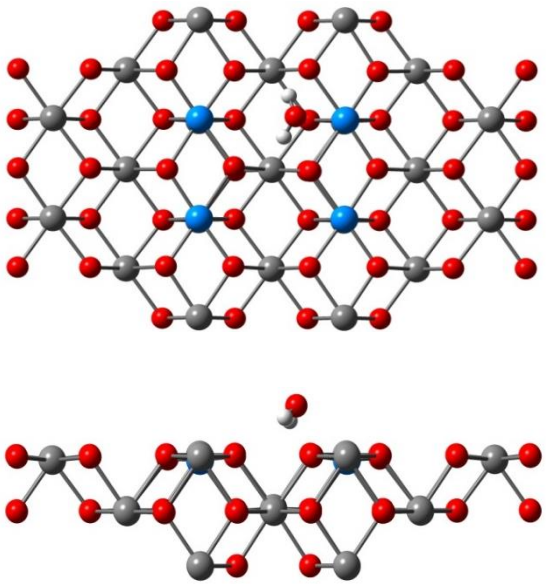
	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m,1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
UO_2	-1.04	-1.08	-	-1.19	-1.02	-1.07	-1.14	-1.12	-0.99	-	-1.17	-1.19	-1.09	-
PuO_2	-1.05	-0.99	-1.04	-1.12	-1.01	-1.04	-1.08	-1.06	-0.91	-1.09	-1.10	-1.09	-1.04	-0.89

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

(110) Surface

- Adsorption energy higher on (110) surface
- Larger difference between molecular and dissociative adsorption energy
- Similar dissociative adsorption energy on UO_2/PuO_2
- Molecular adsorption stronger on PuO_2



	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m,1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
UO_2	-1.46	-1.90	-1.50	-1.72	-1.89	-1.48	-1.61	-1.67	-1.81	-1.51	-1.55	-1.69	-1.73	-1.77
PuO_2	-1.61	-1.89	-1.65	-1.79	-1.91	-1.61	-1.70	-1.77	-1.79	-1.60	-1.68	-1.72	-1.74	-1.74

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Basis set dependence

- Increasing basis set size has a large impact on the adsorption energy
- Adsorption energy decreases

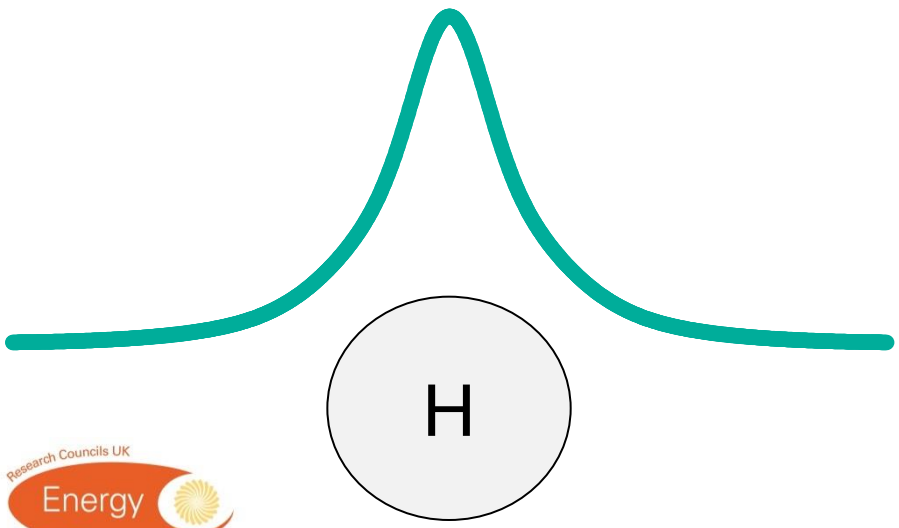
Basis Set	Adsorption Energy/ eV
Double zeta*	-1.08
Double zeta	-0.88
Triple zeta	-0.70
Quadruple zeta	-0.65

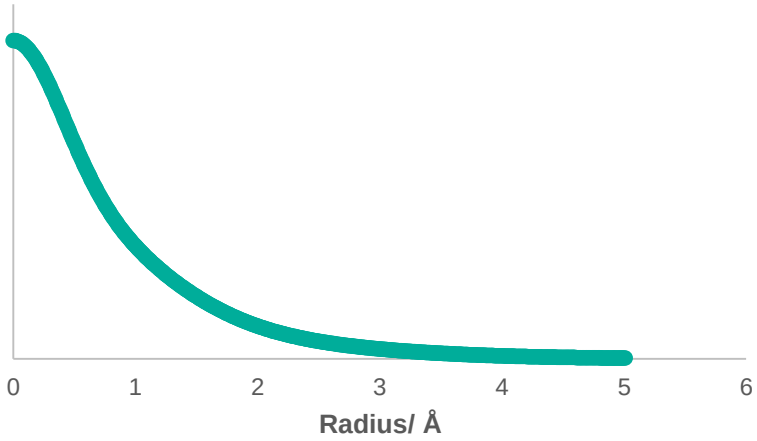
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Basis sets

- Mathematical representation of atomic orbitals (AO)
- A set of atom-centred basis functions
- Single zeta: One basis function for each AO
- Hydrogen: Only 1 basis function (1s)



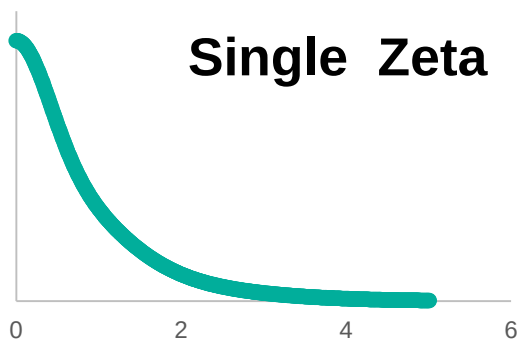


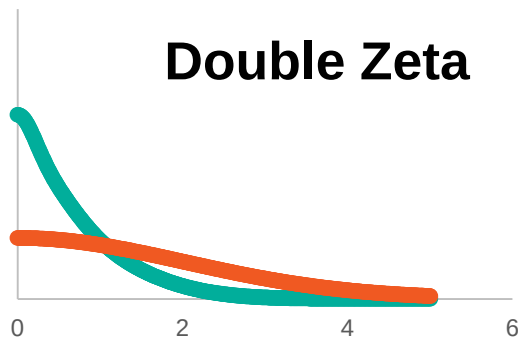
Basis sets

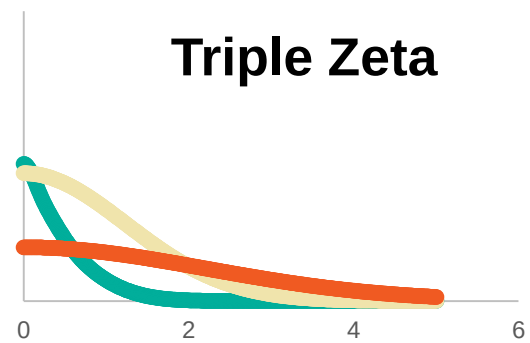
- For larger basis sets number of basis functions used increases

- So for H:
- Double zeta - 2 basis functions describe 1s orbital
- Triple zeta - 3 basis functions describe 1s orbital

- Only the radial dependence differs







Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Basis set dependence

- Increasing basis set size has a large impact on the adsorption energy
- Adsorption energy decreases
- Geometry affected little by basis set size
- <0.03 Å for U-O bond
- <3° for U-O-H bond

Basis Set	Adsorption Energy/ eV
Double zeta*	-1.08
Double zeta	-0.88
Triple zeta	-0.70
Quadruple zeta	-0.65

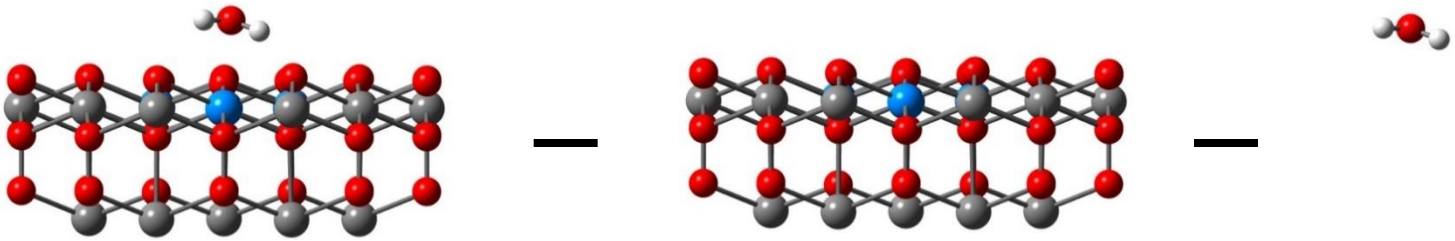
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Basis set superposition error

- When calculating adsorption energy:

$$E_{ads} = E(\text{Surface} + H_2O)_{optimized} - E(\text{Surface})_{optimized} - E(H_2O_{(g)})_{optimized}$$

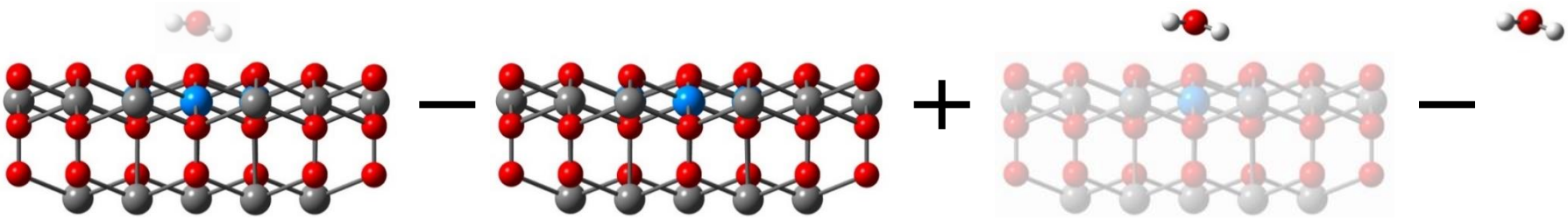


- When optimizing H_2O on the surface the H_2O atoms can use basis functions from the UO_2 surface, leading to an artificial increase in adsorption energy

Counterpoise Correction

- How we account for the BSSE

$BSSE_{(CP)} =$



$E_{ads(CP)} = E_{ads} - BSSE_{(CP)}$

BSSE

- Even single point QZVP calculation computationally expensive
- Basis set superposition error seen to have large impact on adsorption energy
- Use the counterpoise correction to account for this, gives energies close to QZVP energies and second periodic DFT study

	1 Water		2 Water			3 Water				4 Water				
	1m	1d	2m	1m,1d	2d	3m	2m,1d	1m,2d	3d	4m	3m,1d	2m,2d	1m,3d	4d
Double Zeta	**-1.04**	**-1.08**	**-**	**-1.19**	**-1.02**	**-1.07**	**-1.14**	**-1.12**	**-0.99**	**-**	**-1.17**	**-1.19**	**-1.09**	**-**
Quadruple Zeta	**-0.59**	**-0.60**	**-**	**-0.77**	**-0.65**	**-0.61**	**-0.69**	**-0.65**	**-0.57**	**-**	**-0.69**	**-0.70**	**-0.62**	**-**
Double Zeta + BSSE	**-0.66**	**-0.67**	**-**	**-0.78**	**-0.56**	**-0.64**			**-0.53**	**-**	**-0.71**	**-0.74**	**-0.68**	**-**
Periodic DFT[2]	**-0.61**	**-0.68**								**-0.60**	**-0.60**	**-0.65**	**-0.53**	**-0.32**

2) T. Bo, J. Lan, Y. Zhao, Y. Zhang, C. He, Z. Chai and W. Shi, *Journal of Nuclear Materials*, 2014, **454**, 446-454

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Dispersion Correction

- Dispersion corrections included with Grimme D3 parameters

- Adsorption energies increased:

- 0.17-0.20 eV for UO_2 (111)
- 0.23-0.28 eV for PuO_2 (111)

- No change in whether molecular or dissociative favourable

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Conclusions

- PBE0 functional predicts correct insulating states for AnO_2
- On (111) surface adsorption energies similar for molecular and dissociative
- On (110) surface dissociative adsorption favoured
- Large basis set dependence on adsorption energy but not geometry
- Good agreement with periodic DFT studies
- CP method can be used to account for BSSE

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Acknowledgements

- Prof. Nik Kaltsoyannis and Dr. Andrew Kerridge
- Scott Owens
  National Nuclear Laboratory
- Engineering and Physical Science Research Council
- M3S Centre for Doctoral Training