

Embedded Cluster Calculations of Water Adsorption on the UO₂ (111) Surface – 16503

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ABSTRACT

The adsorption of water on the (111) surface of UO₂ has been investigated with density functional theory calculations using the periodic electrostatic embedded cluster method. In particular, the adsorptions of a single water molecule, molecularly and dissociatively, as well as two water molecules, one molecularly and one dissociatively, have been studied. A strong dependence of the adsorption energy on basis set is found, and good agreement with energies calculated from previous theoretical studies using different methods is obtained.

INTRODUCTION

Both UO₂ and PuO₂ are relevant to the nuclear power industry, and the adsorptions of water on PuO₂ are of particular concern for its safe medium- and long-term storage. We are developing a computational method to study these adsorptions; however, uranium dioxide has been studied both experimentally[1]–[3] and theoretically[4]–[9] in much greater detail than plutonium dioxide[10]–[14]. Therefore results obtained on UO₂ can provide a benchmark when building a methodology aimed at studying PuO₂. When investigating such problems computationally, density functional theory (DFT) with periodic boundary conditions (PBC) - where a unit cell representing a portion of the system is repeated infinitely in two or three dimensions - is most commonly used. Two recent studies[7], [8] have probed water adsorption on UO₂ surfaces using this method, employing the local density approximation (LDA)[7] and the generalized gradient approximation (GGA) PBE[8] exchange-correlation functionals in the DFT+*U* formalism. However, with PBC DFT, when considering a surface with low coverage or one where water does not adsorb uniformly, large unit cells must be used. With an increase in unit cell size the computational time required is greatly increased. In addition, the use of hybrid exchange-correlation functionals, which are well-known in molecular quantum chemistry to provide good descriptions of electronic structure, can make the calculations prohibitively expensive. We are therefore developing an alternative approach to investigating water adsorption on actinide dioxide surfaces, based on the periodic electrostatic embedded cluster method (PEECM). This allows us to use many of the techniques and analysis tools of molecular quantum chemistry, including hybrid DFT. It is the aim of this study to compare the use of the PEECM with PBC DFT studies of water adsorption on the UO₂ (111) surface, in order to validate its applicability for future studies of PuO₂.

COMPUTATIONAL DETAILS

All calculations were performed with the TURBOMOLE 6.5 program[15]. The PBE0[16] (hybrid-GGA) exchange-correlation functional was used for all calculations. The self-consistent field convergence was set to 1×10^{-6} whilst geometry optimizations were performed with convergence criteria of 1×10^{-6} a.u. for the total energy and 1×10^{-3} a.u. for the maximum norm of the cartesian energy gradient.

For geometry optimizations the def-SV(P) basis sets[17][18] contained in the TURBOMOLE library were used for all oxygen and hydrogen atoms and uranium atoms that used the small-core pseudopotential (PP) (see below), and the double-zeta MWB-AVDZ basis set[19] was used for uranium atoms using the large-core PP, noted from now on as the SV(P) basis set. Single point calculations were performed with larger basis sets at geometries obtained with the SV(P) basis set; SVP calculations with def-SVP[17][18] and MWB-AVDZ basis sets, TZVP calculations with def-TZVP[18][20] and MWB-AVTZ[19] and QZVP calculations with def-QZVP[18][21] and MWB-AVOZ[19] basis sets.

PPs were used for the uranium ions in the quantum mechanically treated cluster; small-core (60 electron) def-PPs from the TURBOMOLE library[22][23] or, where stated, large-core PPs[19] incorporating the 5f electrons, corresponding to an 80 electron core - these are electrons with principal quantum number 5 or lower. These 5f-in-core PPs have been parameterized specifically for tetravalent states. When the 5f-in-core PPs are used the clusters are written as $U_xU_yO_{2(x+y)}$ where x refers to the number of uranium ions with explicit 5f electrons and y to the number of uranium ions described by 5f-in-core PPs.

All calculations were performed using the PEECM[24]. In this approach, the system is split into three regions; an inner explicit cluster region, which is treated quantum mechanically as described above, the outer embedding region, consisting of point charges, and an intermediate region, consisting of negative point charges and PPs (Fig. 1). The infinite outer embedding region recreates the Madelung potential of the bulk system; formal charges were used for the ions in this region, +4 for uranium ions and -2 for oxygen ions. The PPs used in the intermediate region were the Ce CRENBL PPs[25], employed in order to avoid overpolarization of the electron density in the explicit cluster, whilst -2 charges again represented the oxygen ions. The Ce CRENBL PP, which corresponds to a +4 charge when used without any basis functions, was used since no uranium PPs corresponding to a +4 charge were available. However, the 8-coordinate Ce(IV) ionic radius, 0.97 Å, is similar to that of U(IV), 1.00 Å.[26]

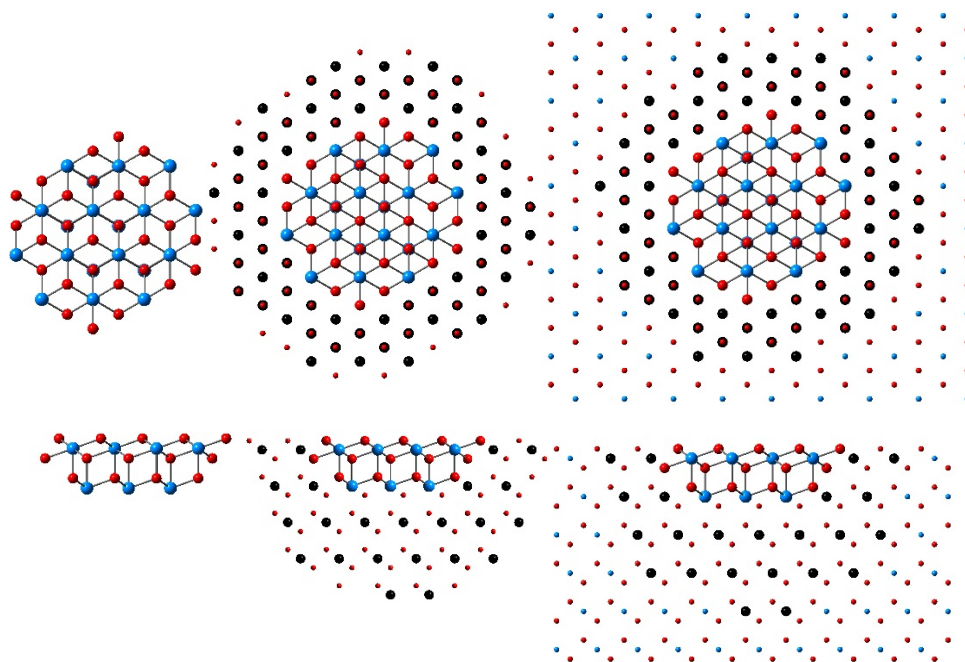


Fig. 1. The quantum mechanical cluster embedded in the intermediate and outer regions. Large blue spheres represent explicit uranium ions, large red explicit oxygen, large black, PPs of the intermediate region, small blue uranium point charges, and small red oxygen point charges.

As lattice parameters cannot be optimized within the PEECM, the experimental lattice parameter for UO_2 was used, $a = 5.470 \text{ \AA}$ [27].

The uranium ions are coupled ferromagnetically in which there are 2 unpaired electrons per uranium.

For geometry optimizations the geometry of the clean surface cluster was optimized, with only the positions of the ions in the cluster coordinated only to other quantum mechanical ions being optimized. When performing adsorption calculations, the coordinates of the water molecules were additionally allowed to relax. Adsorption energies were calculated using the following equation, with each species being optimized as described above:

$$E_{\text{ads}} = E_{\text{surface}+\text{H}_2\text{O (optimized)}} - E_{\text{surface(optimized)}} - E_{\text{H}_2\text{O(optimized)}} \quad (\text{Eq. 1})$$

RESULTS

The geometries of different configurations of water adsorbing on the $\text{U}_4\text{U}_{15}\text{O}_{38}$ cluster of the (111) surface (Figure 2) were optimized with the SV(P) basis set. The configurations considered are where one water adsorbs either molecularly, referred to from now on as (1m), or dissociatively (1d), as well as where two water molecules adsorb, one molecularly and one dissociatively (1m,1d).

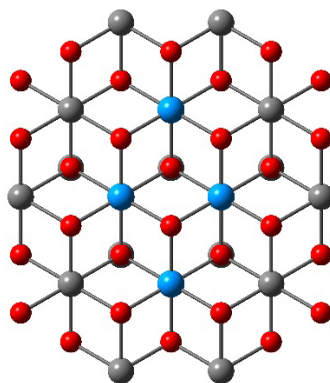


Fig. 2. $U_4U_{15}O_{38}$ cluster viewed perpendicular to the surface. Oxygen atoms are shown in red and uranium atoms in blue and grey. Grey spheres represent uranium atoms treated with 5f-in-core PPs. Embedding ions not shown.

(1m) adsorption occurs with the oxygen atom of water adsorbing above a uranium ion and the two hydrogen atoms pointing towards two of the UO_2 surface oxygen atoms (Figure 3, left). The $U-O_{\text{water}}$ distance is 2.57 Å, in between values recently calculated with periodic DFT of 2.48 Å[7] and 2.60 Å[8], whilst the $H-O_{\text{surf}}$ distance is 1.76 Å, close to one of the values calculated at 1.72 Å[7] but further away from the other of 1.61 Å[8]. All these studies, however, show a short $H-O_{\text{surf}}$ distance, indicative of a hydrogen bond. The second $H-O_{\text{surf}}$ distance is longer at 1.99 Å.

(1d) adsorption of water forms two hydroxyl groups on the surface: a hydroxide, formed from a hydrogen of the water molecule binding to a surface oxygen, which will be referred to as the surface hydroxide, and a second in which an OH group of water adsorbs above a uranium ion, which will be referred to as the adsorbed hydroxide (Figure 3, middle). The hydrogen of the surface hydroxyl points towards the oxygen of the adsorbed hydroxyl, with a distance of 1.58 Å; hence there is a hydrogen bond between the two OH species. This value lies between the two values calculated in recent studies of 1.45 Å[7] and 1.66 Å[8]. The $U-O_{\text{adsorbedOH}}$ distance is 2.21 Å and agrees very well with recent theoretical studies which both calculated a distance of 2.23 Å[7], [8].

For (1m,1d) the two individual water molecules adsorb in a similar way to the individual (1m) and (1d) cases, however a hydrogen bond forms between the two adsorbates (Figure 3, right). The hydrogen bond between the water molecule and the adsorbed hydroxyl has a distance of 1.81 Å, which is good agreement with the $PBE+U$ study[8] which found hydrogen bonds between adsorbates of 1.71 to 1.80 Å (the $LDA+U$ study did not report bond lengths where more than one water molecule was being adsorbed).

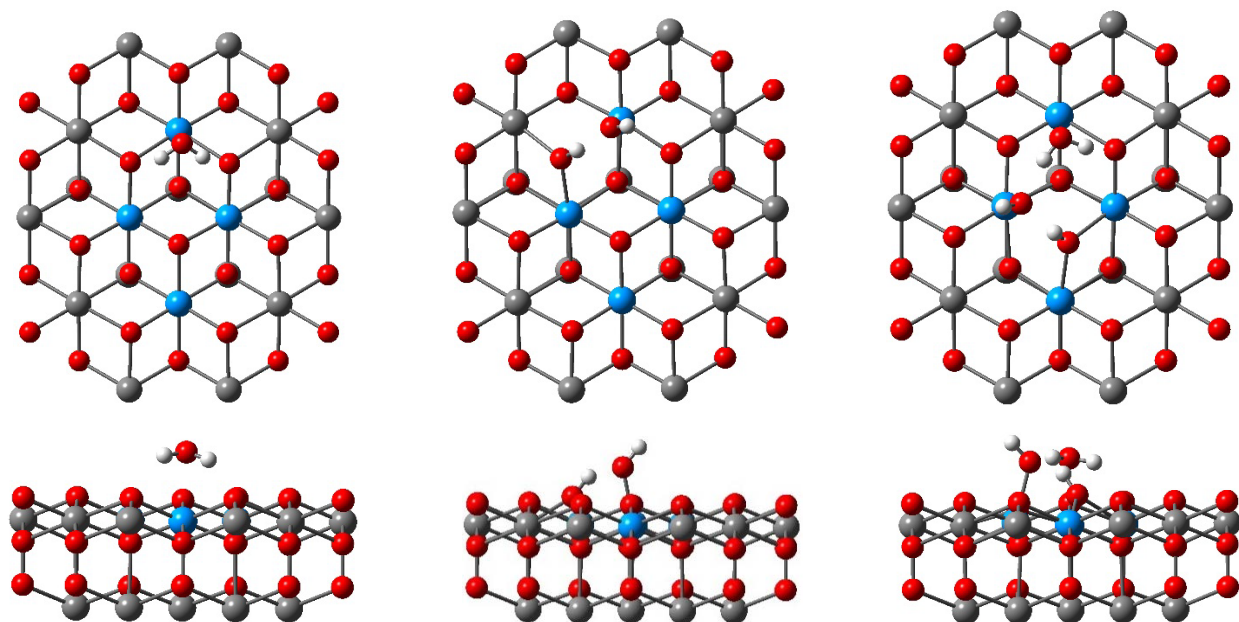


Fig. 3. $U_4U_{15}O_{38}$ cluster viewed perpendicular (top row) and parallel (bottom row) to the surface, with (1m) left, (1d) middle and (1m,1d) right. Oxygen atoms are shown in red, hydrogen atoms in white and uranium atoms in blue and grey. Grey spheres represent uranium atoms treated with 5f-in-core PPs. Embedding ions not shown.

The size of the basis set can often have an effect on the adsorption energy, with more sophisticated (larger) basis sets providing in principle better energies. To test this for our method we performed single point energy calculations of the three types of adsorption shown in Figure 3 with increasing basis set size at their SV(P) optimized geometries; the results are collected in TABLE I.

TABLE I. Energies of (1m), (1d) and (1m,1d) adsorption configurations of water on the $U_4U_{15}O_{38}$ cluster calculated at the SV(P) optimized geometry with increasing basis set size. Adsorption energy shown is per water molecule.

Basis Set	Adsorption energies/ eV		
	(1m)	(1d)	(1m,1d)
SV(P)	-1.04	-1.08	-1.19
SVP	-0.95	-0.88	-1.09
TZVP	-0.62	-0.70	-0.82
QZVP	-0.46	-0.65	-0.69

It can be seen from TABLE I that the adsorption energy has a clear dependence on the size of the basis set used. As the size of the basis set increases the adsorption

energy decreases, with a difference of up to 0.58 eV between the SV(P) and QZVP basis sets. In addition the adsorption energy does not converge with respect to basis set size, even when the QZVP basis set is used. We take the adsorption energies obtained with the QZVP basis set to be our best estimate. It should be noted that although the TURBOMOLE basis set library provides valence basis sets for the actinides from the SV(P) level up to QZVP, in fact the same basis, the QZVP, is used at each level. Hence only the oxygen and hydrogen basis sets change from the SV(P) calculations to the QZVP, and thus the decreasing adsorption energies in TABLE 1 are obtained from increasingly well balanced basis sets.

Recent theoretical studies using PBC DFT calculated adsorption energies for (1m) of -1.10 eV[7] and -0.60 to -0.61 eV (dependent on unit cell size)[8], whilst (1d) adsorption was calculated to be stronger at -1.12 eV[7] and -0.68 to -0.77 eV[8]. The (1m,1d) adsorption was calculated with adsorption energies of -1.23 eV[7] and -0.65 to -0.76 eV[8]. Our energies obtained with the smallest basis set (SV(P)) are in good agreement with those of the LDA+*U* study[7] whilst our energies obtained with the highest-quality QZVP basis set are closer to those from the PBE+*U* study[8]. The LDA exchange-correlation functional is known often to overestimate binding energies, and indeed the results of the previous LDA study are in close agreement with our adsorption energy calculated with the lowest-quality basis set.

The effect of basis set size on the adsorption geometries was also explored. As calculations with the larger basis sets are very expensive it was hoped that, as we have done when producing the data in TABLE I, geometry optimizations could be performed with the SV(P) basis set, with subsequent single point energy calculations performed at a higher quality basis set. The change in adsorption energy when optimizing the geometry with the SVP and TZVP basis sets is shown in TABLE II, given as the difference between single point calculations on the SV(P) optimized structures with the higher basis set and the higher basis set optimized structure with the higher basis set. Geometry optimizations with the QZVP basis set are prohibitively expensive and were not performed.

TABLE II. Change in adsorption energy as a function of basis set for water on the $U_4U_{15}O_{38}$ cluster representation of the (111) surface of UO_2 . Adsorption energy shown is per water molecule.

Basis Sets	Adsorption Energy/ eV		
	(1m)	(1d)	(1m,1d)
SVP	-0.04	-0.10	-0.03
TZVP	-0.03	-0.01	-0.02

The change in adsorption energy when the geometries are re-optimized at the higher basis set are small, and the differences are smaller for the TZVP than the SVP basis set.

The changes in geometric parameters when optimizing the geometry with the SVP and TZVP basis sets, compared to the SV(P), are shown in TABLE III for the U-O_{water} bond lengths and TABLE IV for the bond angles.

TABLE III. Change in U-O_{water} bond lengths (Å) as a function of basis set for water on the U₄U₁₅O₃₈ cluster representation of the (111) surface of UO₂.

Basis sets	(1m)	(1d)	(1m,1d)	
SVP	0.009	-0.013	-0.009	0.043
TZVP	0.030	-0.016	0.000	-0.024

TABLE IV. Change in bond angles (°) as a function of basis set for water on the U₄U₁₅O₃₈ cluster representation of the (111) surface of UO₂.

Basis sets	(1m)	(1d)	(1m,1d)	
	<H-O-H	<U-O-H	<H-O-H	<U-O-H
SVP	-1.63	2.96	-1.783	-0.975
TZVP	-0.83	2.99	-0.656	1.749

Clearly, the changes in the bond lengths and bond angles are modest when optimizing the structure with a higher basis set.

CONCLUSIONS

We have calculated the adsorption geometries and energies of water molecules on a cluster representation of the UO₂ (111) surface. Increasing the size of the basis set has a significant effect on the adsorption energies but a much more modest effect on the adsorption geometries. We therefore conclude that the small SV(P) basis set can be used for geometry optimizations of these systems, followed by single point energy calculations with the higher-quality QZVP basis set in order to obtain reliable adsorption energies. We are now employing this approach to the study of water adsorption on other low index UO₂ surfaces, as well as those of PuO₂.

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REFERENCES

- 1 S. D. Senanayake and H. Idriss, "Water reactions over stoichiometric and reduced UO₂ (111) single crystal surfaces," *Surf. Sci.*, vol. 563, no. 1–3, pp. 135–144, Aug. 2004.
- 2 S. D. Senanayake, G. I. N. Waterhouse, A. S. Y. Chan, T. E. Madey, D. R. Mullins, and H. Idriss, "The reactions of water vapour on the surfaces of stoichiometric and reduced uranium dioxide: A high resolution XPS study," *Catal. Today*, vol. 120, no. 2, pp. 151–157, Feb. 2007.
- 3 S. D. Senanayake, R. Rousseau, D. Colegrave, and H. Idriss, "The reaction of water on polycrystalline UO₂: Pathways to surface and bulk oxidation," *J. Nucl. Mater.*, vol. 342, no. 1–3, pp. 179–187, Jun. 2005.
- 4 Z. Rák, R. C. Ewing, and U. Becker, "Hydroxylation-induced surface stability of AnO₂ (An=U, Np, Pu) from first-principles," *Surf. Sci.*, vol. 608, pp. 180–187, Feb. 2013.
- 5 F. N. Skomurski, L. C. Shuller, R. C. Ewing, and U. Becker, "Corrosion of UO₂ and ThO₂: A quantum-mechanical investigation," *J. Nucl. Mater.*, vol. 375, no. 3, pp. 290–310, Apr. 2008.
- 6 P. F. Weck, E. Kim, C. F. Jové-Colón, and D. C. Sassani, "On the role of strong electron correlations in the surface properties and chemistry of uranium dioxide," *Dalt. Trans.*, vol. 42, no. 13, pp. 4570–8, Apr. 2013.
- 7 P. Maldonado, L. Z. Evins, and P. M. Oppeneer, "Ab Initio Atomistic Thermodynamics of Water Reacting with Uranium Dioxide Surfaces," *J. Phys. Chem. C*, vol. 118, no. 16, pp. 8491–8500, 2014.
- 8 T. Bo, J.-H. Lan, Y.-L. Zhao, Y.-J. Zhang, C.-H. He, Z.-F. Chai, and W.-Q. Shi, "First-principles study of water adsorption and dissociation on the UO₂ (111), (110) and (100) surfaces," *J. Nucl. Mater.*, vol. 454, no. 1–3, pp. 446–454, Nov. 2014.
- 9 J. C. Boettger and A. K. Ray, "Fully relativistic density functional calculations on hydroxylated actinide oxide surfaces," *Int. J. Quantum Chem.*, vol. 90, no. 4–5, pp. 1470–1477, Oct. 2002.
- 10 J. M. Haschke and T. E. Ricketts, "Adsorption of water on plutonium dioxide," *J. Alloys Compd.*, vol. 252, no. 1–2, pp. 148–156, May 1997.
- 11 J. L. Stakebake, "Thermal desorption study of the surface interactions between water and plutonium dioxide," *J. Phys. Chem.*, vol. 77, no. 5, pp. 581–586, Mar. 1973.

- 12 M. Paffett, D. Kelly, S. Joyce, J. Morris, and K. Veirs, "A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces," *J. Nucl. Mater.*, vol. 322, no. 1, pp. 45–56, Oct. 2003.
- 13 G. Jomard, F. Bottin, and G. Geneste, "Water adsorption and dissociation on the PuO₂ (110) surface," *J. Nucl. Mater.*, vol. 451, no. 1–3, pp. 28–34, Aug. 2014.
- 14 X. Wu and A. Ray, "Density-functional study of water adsorption on the PuO₂ (110) surface," *Phys. Rev. B*, vol. 65, no. 8, p. 085403, Jan. 2002.
- 15 R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, "Electronic structure calculations on workstation computers: The program system Turbomole," *Chem. Phys. Lett.*, vol. 162, no. 3, pp. 165–169, Oct. 1989.
- 16 J. P. Perdew, M. Ernzerhof, and K. Burke, "Rationale for mixing exact exchange with density functional approximations," *J. Chem. Phys.*, vol. 105, no. 22, p. 9982, 1996.
- 17 A. Schäfer, H. Horn, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets for atoms Li to Kr," *J. Chem. Phys.*, vol. 97, no. 4, p. 2571, 1992.
- 18 K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, "Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials," *Theor. Chem. Acc.*, vol. 97, no. 1–4, pp. 119–124, 1997.
- 19 A. Moritz, X. Cao, and M. Dolg, "Quasirelativistic energy-consistent 5f-in-core pseudopotentials for divalent and tetravalent actinide elements," *Theor. Chem. Acc.*, vol. 118, no. 5–6, pp. 845–854, Jun. 2007.
- 20 A. Schäfer, C. Huber, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.*, vol. 100, no. 8, p. 5829, 1994.
- 21 F. Weigend, F. Furche, and R. Ahlrichs, "Gaussian basis sets of quadruple zeta valence quality for atoms H–Kr," *J. Chem. Phys.*, vol. 119, no. 24, p. 12753, 2003.
- 22 W. Küchle, M. Dolg, H. Stoll, and H. Preuss, "Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide," *J. Chem. Phys.*, vol. 100, no. 10, p. 7535, 1994.
- 23 X. Cao, M. Dolg, and H. Stoll, "Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials," *J. Chem. Phys.*, vol. 118, no. 2, p. 487, 2003.

- 24 A. M. Burow, M. Sierka, J. Döbler, and J. Sauer, "Point defects in CaF₂ and CeO₂ investigated by the periodic electrostatic embedded cluster method," *J. Chem. Phys.*, vol. 130, no. 2009, pp. 0–11, May 2009.
- 25 R. B. Ross, S. Gayen, and W. C. Ermler, "Ab initio relativistic effective potentials with spin-orbit operators. V. Ce through Lu," *J. Chem. Phys.*, vol. 100, no. 11, p. 8145, 1994.
- 26 R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallogr. Sect. A*, vol. 32, no. 5, pp. 751–767, Sep. 1976.
- 27 J. Schoenes, "Optical properties and electronic structure of UO₂," *J. Appl. Phys.*, vol. 49, no. 3, p. 1463, 1978.