A Noncollinear Relativistic Computational Study of the Actinide Dioxides and their Interaction with Hydrogen

A Thesis Submitted for the Degree of Doctor of Engineering (Eng.D.) by:

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March 2018
Declaration

I, James Thomas Pegg, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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Abstract

The radiolytic decomposition of water and organic compounds (caused by the decay of actinide nuclei) results in the formation of hydrogen gas. The corrosion and oxidation of actinide metals is known to be catalysed by hydrogen; this has resulted in thermal excursions and the failure of containment vessels. The chemistry of the actinide dioxides (AnO$_2$, An = U, Np, Pu) is key to understanding corrosion mechanisms. To circumvent complex experimental issues, computational methods offer another mode of study. To investigate the complex electronic structure, one must consider: exchange-correlation influences, noncollinear magnetic behaviour, and relativistic contributions. The magnetic ground-state of the AnO$_2$ (An = U, Np, Pu) has been investigated. The diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states have been considered. To treat the on-site Coulomb repulsion of the actinide $f$-electrons, DFT+U and HSE06 calculations have been completed. A transverse 3k AFM state of UO$_2$ and NpO$_2$ coupled to $Pa\overline{3}$ (No. 205) crystal symmetry has been calculated; whereas, a longitudinal 3k AFM state of PuO$_2$ coupled to $Fm\overline{3}m$ (No. 225) crystal symmetry has been calculated. A noncollinear relativistic low-index AnO$_2$ (An = U, Np, Pu) PBEsol+U surface study has been conducted. The importance of relativistic influences and magnetic reorientation is highlighted. The electrostatic potential isosurfaces and scanning electron microscopy (SEM) images are shown. An octahedral Wulff AnO$_2$ crystal morphology has been identified. The interaction of hydrogen with low-index AnO$_2$ (An = U, Np, Pu) surfaces has been investigated by PBEsol+U. The density of states and Bader charges are included. A reduced actinide ion and OH group are formed by interaction of atomic H on all surfaces. The dissociation of molecular H$_2$ on the PuO$_2$ (011) and AnO$_2$ (001)$\alpha$ surfaces has been found, only.
Impact Statement

The microstructural evolution of nuclear fuels is an important field of research. The corrosion of actinide materials concerns nuclear industries. Incidents involving corrosion have resulted in: thermal excursions, the expansion of solids, and the formation of incondensable gases.

An oxide layer (that controls the reaction chemistry) is inexorably formed on actinide surfaces. The magnetic structure of the actinide dioxides (AnO$_2$) is key to the design of reliable computational models. A noncollinear relativistic computational study of magnetic order has been completed. The magnetic state is shown to influence the crystal symmetry and electronic structure. The identification of noncollinear 3k antiferromagnetic (AFM) AnO$_2$ ground-states impacts the computational treatment of the materials.

In collinear nonrelativistic surface models, the magnetic moments cannot be reorientated. A noncollinear relativistic model allows for the correct magnetic solution. The importance of magnetic reorientation on low-index AnO$_2$ surfaces has been highlighted. The electrostatic potential isosurface images can be used to interpret surface reactivity; whereas, scanning electron microscopy (SEM) images compliment experimental studies. The calculated crystal morphology impacts the design of nuclear fuels.

The interaction of hydrogen with low-index AnO$_2$ (An = U, Np, Pu) surfaces offers insight into the equilibration of the hydrogen-oxygen system. The information is useful for surface (oxygen, hydroxides and water) interaction studies. A considerable number of actinide compounds (hydrides, hydroxides, and halides) share the fluorite-type crystal structure. An investigation of these materials (from the described methods) can be completed.
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List of Publications

The following manuscripts for this thesis are in preparation.


Part I:
Introduction
Chapter 1:
Nuclear Engineering

1.1 Nuclear Fission

In nuclear engineering, fissile isotopes of uranium ($^{235}\text{U}$) and plutonium ($^{239}\text{Pu}$) are used as nuclear fuel; as a major by-product, neptunium ($^{237}\text{Np}$) is of considerable technological importance. The chemistry of the actinide (An = U, Np, Pu) elements concerns nuclear industries. Their behaviour influences the design of next-generation nuclear fuels, and the industrial reprocessing of nuclear materials. The radiolytic decomposition of water and organic compounds (caused by the decay of actinide nuclei) results in the formation of hydrogen gas. The corrosion and oxidation of actinide metals is known to be catalysed by hydrogen; this has resulted in thermal excursions and the failure of containment vessels. The interaction of hydrogen with actinide dioxides ($\text{AnO}_2$) by computational methods is the main objective of this study.

The actinide elements are imperative (due to their fissile and fertile character) to the nuclear fuel cycle. A nucleus is comprised of: the mass defect (a measure of the total binding energy), protons, and neutrons. A long-range repulsive (Coulomb) force (due to their positive charge) is created by the protons. To hold the nucleus together, the short-range strong nuclear force (that compensates for the electrostatic Coulomb repulsion) is introduced. The influence of the long-range repulsive Coulomb force is minimised by the neutrons; however, an instability in the nucleus can arise from an excess of neutrons. As the number of neutrons increases, the Pauli exclusion principle forces them into higher energetic states. The higher energetic states
are states inherently less stable. To minimise the energy, a nucleus radioactively (beta-decay or neutron emission) decays.

In a nucleus, a surface tension is created by the Coulomb force and the strong-nuclear force. A prolate spheroidal shape is adopted by the lanthanide and actinide nuclei to minimise the surface energy.\(^{(7)}\) A nucleus in an excited state oscillates; the oscillations decrease the repulsive Coulomb force and increase the surface tension. The competing surface and Coulomb forces form a potential energy barrier for nuclear fission. In the laws of quantum mechanics, there is a small finite probability of a nucleus decaying naturally. A nuclear reaction can be classified by: fission, fusion, or radioactive decay. In nuclear fission, a nucleus transmutes into lighter elemental fragments, emits neutrons and releases energy.

\[\text{Figure 1.1: The Liquid-Drop Model for Nuclear Fission.}\]

The induced fission of atomic nuclei by artificial means leads to the controlled release of nuclear energy.\(^{(8, 9)}\) The mechanism for induced nuclear fission involves the excitation of a nucleus. This can be achieved by electromagnetic radiation (photofission) or by particle capture (neutrons, protons, deuterons). As a charge neutral particle, a neutron is ideal candidate for inducing nuclear transformations.\(^{(10)}\) The liquid-drop model for nuclear fission offers an insight into the averaged behaviour of the nucleus (Figure 1.1).\(^{(11, 12)}\) A charged nucleus begins to vibrate and deforms on the adsorption of a neutron. If the activation energy for nuclear fission is breached, the deformation of the nucleus becomes irreversible and the absorption of
a neutron can induce a fission event. A fission event releases two daughter nuclei, neutrons and energy. (12) At rest the fragments are termed fission products. The excess energy of the fission fragments is lost by radioactive decay. An average of 2-3 neutrons are released in a fission event. These neutrons can be captured by other nuclei and induce more fission events that result in a chain reaction. A fissile isotope can be induced to fission by neutrons of any energy. (10) The fissile density of a material influences the rate of a nuclear reaction. Nuclear reactions can be controlled in a self-sustaining manner or result in an uncontrolled chain-reaction. The number of neutrons emitted increases the rate at which the reaction propagates, this is carefully controlled in commercial nuclear reactors.

The multiplication factor (k) defines the condition for a chain reaction; it is the ratio of fission events relative to the preceding generation. If k is less than 1, a nuclear chain reaction is unsustainable. If k is equal to 1, the material is described as a critical assembly. If k is greater than 1, the material is termed a supercritical assembly. In commercial fission reactors, nuclear energy is extracted by a controlled fission chain reaction. The value of k is moderated depending on the required energy levels. The choice of k reflects the gradual loss of fissile material and the build-up of neutron poisons, which impede the chain reaction. The reaction is controlled by neutron moderators designed to limit the number of thermal neutrons. Neutron moderators have a high neutron capture cross section; materials include, boron, cadmium and hafnium. Thermal energy is extracted by a coolant, coupled to a heat exchanger and used to generate steam. The steam drives a turbine generator to produce electrical energy.

In nuclear armaments, an uncontrolled fission chain reaction is used to generate nuclear energy; here greater k values are desirable. In other words, materials of a high fissile density. A metallic fissile core of enriched (a high-degree of fissile isotope) uranium or plutonium is used as the nuclear fuel. The corrosion of the metal by oxidation concerns nuclear stockpile storage and reliability. To reduce the risk of nuclear proliferation, nuclear cores can be recycled for commercial use. (13, 14) In spontaneous nuclear fission, a nucleus fissions by quantum tunnelling of the potential energy barrier. The mechanism does not involve any external influences. The spontaneous fission by nuclear decay is rare; however, can result in the premature detonation of nuclear devices. Thermal energy is released by the natural decay of radioactive materials. In radioisotope thermoelectric generators (RTG, RITEG), a voltage is formed by heating dissimilar electrical conductors (Seebeck effect) resulting in an electric current. As a long-term power source, RTGs have been used in cardiac pacemakers and deep-space probes. (15)
1.2 Reactor Fuel Types

In the general case, actinide nuclear fuels are metallic or an oxide derivative; however, nitride, carbide and molten salt fuels have been developed. (4, 16) The metals have a high fissile density (useful for nuclear armaments), are highly-reactive, and rapidly corrode by oxidation. The actinide oxides have a lower-fissile density (useful for commercial nuclear reactors), increased thermal stability (enables higher reactor operating temperatures) and hinder oxidative corrosion (although hypostoichiometric oxides and \( \text{AnO}_{2+x} \) are common). As the most stable oxide form, the actinide dioxide (AnO\(_2\)) with the fluorite crystal structure is commonly used.

In a fissile isotope, the critical energy for nuclear fission is less than the binding energy for the absorption of a neutron. (10, 17) A fission event can be induced by neutrons of any energy; this includes low-energy neutrons in thermal equilibrium with the environment. In a fertile material, a fission event will only occur with high-energy neutrons; however, fertile isotopes may be transmuted into fissile material. In commercial reactors, nuclear energy by fission chain reaction is extracted in a controlled manner. The adsorption of a neutron by a non-fissile isotope may not induce a fission event. For instance, neutron capture of fertile \( ^{238}\text{U} \) generates \( ^{239}\text{Pu} \) by \( \beta^- \)-emission. The \( \beta^- \)-emission is characterised by the release of an electron and an anti-neutrino (Equation 1.1).

\[
^{238}\text{U} + ^1\text{n} \rightarrow ^{239}\text{U} \rightarrow ^{239}\text{Np} \rightarrow ^{239}\text{Pu}
\]  

In contrast to fissile \( ^{235}\text{U} \), the \( ^{239}\text{Pu} \) isotope has a higher fissile cross-section. (18-20) This is a measure of the probability for a nucleus to interact with an incident neutron. The fission cross-section decreases with neutron energy. As a by-product of irradiated nuclear fuels, neptunium has seen use in detectors of high-energy neutrons. In a thermal reactor, a chain reaction is maintained by thermal (low-energy) neutrons in a controlled manner. Thermal nuclear fuels are comprised of fertile \( ^{238}\text{U} \) (97%) and fissile \( ^{235}\text{U} \) (3%) isotopes. In breeder reactors fast (high-energy) neutrons, rather than thermal neutrons, maintain the chain reaction by increasing the amount of fissile material. (17) A breeder reactor, relative to a thermal reactor, is more difficult and expensive to construct.
The design of mixed-oxide (MOX) fuels is of interest. These fuel blends offer a means of reducing excess nuclear material. In the defence industry, enriched $^{239}$Pu fuel is used for nuclear armaments. This can be blended with $^{235}$U to create MOX fuels for commercial use. MOX fuels can consist of independent phases or as a solid solution. A number of studies on thorium-MOX fuels have been completed. As a fertile material, a neutron source is needed as a driver component. This transmutes $^{232}$Th to $^{233}$U by beta-decay (Equation 1.2).

$$^{232}_{90}\text{Th} + ^1_0\text{n} \rightarrow ^{233}_{90}\text{Th} \rightarrow ^{233}_{91}\text{Pa} \rightarrow ^{233}_{92}\text{U} \tag{1.2}$$

A number of advantages for a thorium-MOX fuel cycle have been detailed: lower nuclear proliferation risk, reduced number of long-lived fissile components, a convenient means of transmuting high-level radioactive material. To reduce the risk of ecological contamination, thorium-MOX fuels are highly-insoluble and non-oxidisable.(22, 23)

### 1.3 Irradiated Fuel

The composition of nuclear fuels changes over their lifetimes. This influences thermal conductivity, corrosion mechanisms, and coolant interactions in case of failure.(24) The microstructural evolution of nuclear fuels involves complex multiphysics phenomena. In commercial nuclear reactors, the irradiated fuel is removed from the reactor in cycles; thereby maintaining a relatively even power distribution. At the end of each cycle, the oldest fuel is removed and fresh fuel is loaded.(25) The radioactive decay of the actinide elements releases thermal energy (although considerable, not commercially viable), the removed fuel is transferred to intermediate storage pools for cooling.

Intermediate storage ponds use a boric acid solution, coupled to a heat exchanger, to cool nuclear materials. To stop the formation of a critical assembly, a boric acid (a water soluble thermal neutron absorber) solution is introduced.(26) As the radiolysis of water and organic materials generates hydrogen gas, the environment in storage facilities is continuously monitored.(27) In the design of geological repositories, the radiation damage of containment vessels has to be considered. The radioactive nature of the actinide elements decreases over a
two-year to four-year period. After cooling, the nuclear fuel can be transferred to long-term dry storage. As a secondary concern, the evolution of hydrogen (caused by changes in temperature and pressure) introduces a risk of chemical explosion. In addition, actinide surfaces are an active template for catalytic reactions; anomalous corrosion rates have been recorded with hydrogen, oxygen, and water. (28-33) The failure of containment vessels, thermal excursions, and the dispersal of nuclear material by hydrogen-catalysed corrosion of nuclear fuel is an important issue. (34-36)

In the nuclear fuel cycle, a closed fuel loop (where all the material is recycled) is a key engineering objective. To reduce high-level radioactive material, elements can be transmuted into less-radioactive isotopes by nuclear reaction. (37) As a means of recycling fertile actinides, MOX fuels are an important field of research. The chemistry of the actinides is important to: the design of environmental contingencies in the case of accidental release, and the guardianship of nuclear materials in long-term storage. It is imperative that the chemistry of the actinides and their oxides is investigated.

1.4 Actinide Chemistry

The chemistry of actinide compounds is incredibly complex. (1) A number of unusual behaviours are shown. The list includes: very low-symmetry crystal structures, very low-melting temperatures, large anisotropic thermal-expansion coefficients, and intricate phase-diagrams. (38) The chemistry of actinide systems is key to the design of long-term storage facilities and next-generation nuclear fuels. (4) The actinide elements mark the filling of the 5f atomic subshell. (39) The electronic structure of the actinides controls their nonnuclear behaviour. This is influenced by electron relativistic motion and electron-electron correlations. (40-42)

An experimental study of actinide systems is incredibly challenging. The chemistry of the actinides is influenced by impurity phases, a number of factors influence the electronic structure. As highly-radioactive elements, self-irradiation damage to the crystal lattices in actinide systems is common. As a result of α-particle decay introducing an impurity phase, Frenkel defects are formed by the displacement of the fissioned nuclei into interstitial lattice sites. In addition, low-temperature measurements are complicated by thermal fluctuations from
the radioactive decay of atomic nuclei. To compensate for experimental issues, computational methods offer another mode of study. A computational investigation of actinide materials is nontrivial. For instance, a number of studies highlight the importance of relativity in heavy-fermion systems.(40-42) These investigations offer an insight into the unusual electronic structure of actinide materials.

An issue central to the study of actinide systems involves quantum phase transitions. A quantum-phase transition describes a sudden change to the ground-state wavefunction. A quantum-phase transition is characterised by a major change in material behaviour. The mechanism involves a negligible change in entropy. In addition, a material near a quantum-phase transition shows anomalous behaviour. This is known as quantum criticality.(43) The importance of quantum criticality is illustrated by investigations of: heavy-fermion materials, high-temperature superconductors and the magnetic behaviour of actinide materials.(44)

The electronic structure is influenced by relativistic contributions.(45, 46) The orbital angular momentum of an electron scales with the nuclear charge. As a result of special relativity, the effective mass of an electrons increases (Equation 1.3).

\[ m = m_0 \left( \sqrt{1 - \frac{v^2}{c^2}} \right)^{-1} \]  

Equation 1.3

The relativistic mass \( m \) of a particle is related to: the nonrelativistic mass \( m_0 \), invariant-mass), the velocity of a particle \( v \), and the speed of light \( c \).\( (47, 48) \) A contraction of the core \( s \)- and \( p \)-orbitals (caused by the increase in effective mass) results; the valence \( d \)- and \( f \)-orbitals (due to the increase in nucleonic shielding) become more diffuse.

A charged particle moving through space generates a magnetic field. This is true of an electron. The angular components of spin \( s \) and orbital moment \( l \) for an electron result in individual magnetic moments. The magnetic moments are coupled by the spin-orbit interaction (SOI); this abolishes conventional models of electron spin. The orientation of the individual magnetic moments determines if the SOI is energetically favourable or unfavourable (Figure 1.2).
As a function of angular velocity, the influence of the SOI increases with nuclear charge. In non-relativistic systems, the influence of SOI is negligible; however, in relativistic heavy-fermion systems, the importance of SOI is considerable. This impacts calculation of electronic structure. Note: the magnetic field created by the spin of the nucleus, relative to the magnetic field created spin of the electrons, is negligible.

The degree of electron itinerancy influences the physical-chemical nature of the actinide elements. Interacting wavefunctions in an infinite solid form in a continuous energy band. The bandwidth is proportional to the degree of orbital overlap. The completely in-phase (bonding) and completely out-of-phase (antibonding) Bloch wavefunctions define the energy range. In the isoelectric lanthanides series, the spatial extent of the 4f electrons is extremely limited. This prevents the 4f-electrons from participating in bonding interactions. As a result, the 4f-electrons are localised around specific lattice sites. In the actinides, the greater spatial extent of the 5f-electrons enables overlap with other actinide ions. The limited spatial extent of the 5f-orbitals results in a narrow band. In addition, the 5f, 6d and 7s-bands often hybridise due to comparable atomic energies. The degree of f-electron itineracy (delocalisation) is also influenced by orbital charge fluctuations. The formation of a small f-band means the electronic structure is influenced by small environmental changes. In the late-actinides, the overlap of the 5f-orbitals is insufficient to form an electronic band and the electrons become localised within their electronic potential energy wells.

The electronic structure of the actinides is complicated by the manifestation of metastable states and the juxtaposition of competing energy levels.(44) The interchangeability of the f-, d-, and p-configurations complicates the electronic structures. This is a result of competing $5f^n 6d^m 7s^2$ and $5f^{n-1} 6d^1 7s^2$ electronic configurations. The energy difference of the f- and d-levels increases
Part I: Introduction
Chapter 1: Nuclear Engineering

along the actinide series. In the late actinides, this stabilises the 5f^6 6d^0 7s^2 electronic configuration. The late actinides show relatively simple behaviour. If the 5f-electrons are itinerant (de-localised), the electrons are free to participate in bonding interactions. The characteristic nature of the material is reminiscent of transition metal complexes; multiple oxidations states, superconductivity. The electronic structure can often be inferred from simplistic band models. If the 5f-electrons are localised, the electrons do not participate in bonding interactions. The electrons of the light (early) actinides elements are itinerant (delocalised). The chemistry of the light actinides and transition metals are similar. The elements show greater chemical variation, higher oxidation states, and paramagnetic (PM) behaviour. The electrons of the heavy (late) actinide are highly localised. The chemistry of the heavy actinides and the lanthanides are comparable; the elements are relatively inert and have local magnetic moments. This includes a limited number of oxidation states, atomic electron behaviour, and local magnetic moments. An itinerant-localised 5f-electron transition is shown to occur with plutonium metal.

The electronic structure of plutonium is singularly complex; this is due to the juxtaposition of multiple electronic configurations. The metal is characterised by the quantum mechanical superposition of localised and itinerant electronic states.(46) In addition, the long-range ordered magnetic ground-state of plutonium metal is unresolved. The electrons can be localised or delocalised by small changes in the chemical environment. The metal is identified with phase instabilities and anomalous thermal expansions coefficients. As the metal solidifies it expands. An impressive number of allotropic forms are found within a narrow temperate range. The low-temperature α-phase crystallises in an intricate thirty-two atom body-centred unit cell. The density of the metal can change by twenty-five percent with minor incitement.(39) The electrical resistivity and specific heat capacity of the metal is unusually high at low-temperature. To circumvent the structural instability of the δ-phase, a few atomic percent of aluminium or gallium is added. This improves the malleability of the alloy.

The actinides are a class of highly-correlated materials for which conventional first-principle calculations fail. The complexity of actinides compounds is controlled by the degree of 5f-electrons localisation. A theoretical treatment of actinide systems has to consider: electron-correlation, magneto-elastic interactions, multipolar interactions, and relativistic influences.(45, 49, 50) As the crystal structure is coupled by SOI to the magnetic state, it is imperative to consider relativity when creating computational models. The complexity of
actinide systems has limited their study. This thesis uses computational methods to investigate the electronic structure of nuclear materials.

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Chapter 2: Corrosion of Nuclear Materials

2.1 Oxidation

The corrosion of actinide materials concerns nuclear industries. (1-7) Incidents involving corrosion have resulted in: thermal excursions, the expansion of solids, and the formation of incondensable gases. This has resulted in the failure of containment vessels, the dispersal of nuclear material, and has compromised the integrity of nuclear fuels. (8) In commercial nuclear reactors, metallic or oxide fuels are normally used; however, nitride, carbide, and molten salt fuels have been developed. (9) The actinide metals inexorably oxidize, under environmental conditions, to generate an oxide layer. (8, 10-14) The oxide layer influences the chemistry of the underlying actinide metal. This impacts the design of long-term storage facilities, and the industrial reprocessing of nuclear fuels. (1, 15-20) The corrosion and oxidation of the actinide metals are often treated as equivalent topics. (13) The actinide metals are highly-reactive. In oxygen environments, an unavoidable actinide dioxide ($\text{AnO}_2$) surface layer is formed by oxidation. As an active template for the equilibration of the hydrogen-oxygen system, the $\text{AnO}_2$ electronic structure influences corrosion mechanisms. (5, 17, 21, 22) The interpretation of corrosion mechanisms is complex and often inferred from studies with hydrogen, oxygen, and water. (5, 8) These involve the complex interplay of thermodynamic, kinetic, and catalytic factors. (13)

The chemistry of actinide systems is complicated by internal (radioactive decay) and external (chemical reaction) corrosion pathways. A number of factors influence the rate of corrosion:
environmental conditions, impurities, surface composition, extent of radiation damage. An experimental investigation of actinide materials is challenging, due to the inhomogeneity of samples, radiogenic issues, and international regulations. A number of factors influence the engineering characteristics of actinide-based materials. These include impurity content, temperature, and the method of fabrication. As a result of radioactive decay and complex temperature-pressure behaviour, single-phase samples are seldom isolated. The existence of an impurity phase influences the electronic structure considerably. This impacts the reliability of experimental data. To reduce the risk of nuclear proliferation, access to actinide materials is restricted. In addition, the actinides are highly-toxic and radioactive. This imposes limitations on laboratory methods and hinders experimental investigation. As the complexity of actinide materials has limited the number of investigations, an interpretation of corrosion mechanisms has come from a combination of experimental results.

The oxidative corrosion of the actinide metals each follow identical mechanisms (Figure 2.1). A ubiquitous oxide surface layer is retained, even if highly reducing (vacuum) conditions are enforced. This is confirmed by X-ray photoelectron spectroscopy (XPS) after repeated cycles of ultra-high vacuum ionic bombardment. The composition of the metal oxide layer is a function of oxygen partial pressure. The oxide surface controls the corrosion chemistry of actinide metals. The oxide layer hinders the diffusion of ions from the surface to the metal-oxide interface. The electronic properties of the gas-solid interface considerably influence the adsorption and dissociation of atoms throughout the solid phase. The rate of corrosion is

![Figure 2.1: A surface-based illustration of oxidative corrosion in actinide metals: a) molecular oxygen is adsorbed onto the metal surface, b) the adsorbed molecular oxygen dissociates into atomic oxygen and generates the actinide dioxide (AnO₂) layer. The rate of corrosion is limited by diffusion of oxygen from the surface to the metal-oxide interface. The period is characterised by parabolic growth, c) induced stresses at the metal-oxide interface result in the spallation of AnO₂ particles. The period is characterised by steady-state corrosion.](image-url)
influenced by surface energetics; this impacts the adsorption and dissociation of molecular species.

The actinide-oxygen phase diagram has been investigated by experimental methods. Intermediary characteristics are often shown by the neptunium-oxygen system. The corrosion of actinide metals is reliant on: the transport of electrons from the metal to the gas-solid interface, the dissociation of adsorbed reactants, and the diffusion of ionic species through the oxide layer. In the first instance, adsorbed O₂ dissociates on the metal surface (Equation 2.1). Adsorbed oxygen reacts to form an AnO₂ layer (Equation 2.2).

\[ \text{O}_2(\text{ads}) \rightarrow 2\text{O}^2-(\text{ads}) \]  \hspace{1cm} 2.1

\[ \text{An}(s) + 2\text{O}^2-(\text{ads}) \rightarrow \text{AnO}_2(s) + 2\text{e}^- \]  \hspace{1cm} 2.2

As the oxide surface layer is formed, the metal is passivated. Adsorbed oxygen on the surface dissociated to form O²⁻ anions. The rate of corrosion is limited by the diffusion of oxygen from the surface to the metal-oxide interface. At the metal-oxide interface, the oxidation of the metal induces stresses. The induced stresses transform nuclear material into dispersal particulate forms; this increases the risk of accidental release of nuclear material. In a one-dimensional model, the rate of a diffusion controlled reaction is determined by the flux (J) of the diffusing species (Equation 2.3).

\[ J = cD \frac{\partial c}{\partial \tau} \]  \hspace{1cm} 2.3

The rate of diffusion is dependent on; the proportionality constant (c), the temperature-dependent diffusion coefficient of oxygen (D), the reactant concentration gradient (C), and the depth of the coherent oxide layer (τ). The isothermal corrosion rate follows a paralinear relationship characteristic of a diffusion-controlled process. The initial parabolic region is defined by the rate of diffusion across a growing oxide surface layer. The linear behaviour results from equilibrium spallation of oxide material and continued oxidation of the metal. A
Part I: Introduction

Chapter 2: Corrosion of Nuclear Materials

diffusion-controlled mechanism of oxygen migration across the oxide layer to the metal-oxide interface fails to account for hydrogen-catalysed oxidation and pyrophoric behaviour. To limit unsolicited chemical reactions, nuclear materials are often stored in their oxide form. As a kinetically stable phase, the actinide dioxide (AnO$_2$) is normally used. This hinders further chemical reactivity. In oxygen rich environments, hyperoxides UO$_{2+x}$ (x < 0.20) and NpO$_{2+x}$ (x < 0.50) are formed (Equation 2.4). In contrast, the formation of the hyperoxide PuO$_{2+x}$ is not achieved by strong oxidants. These include ozone (O$_3$) and nitrogen dioxide (NO$_2$).

\[
\text{AnO}_2(s) + x\text{O}_2(g) \rightarrow \text{AnO}_{2+x}(s) \quad 2.4
\]

As an energetically less favourable oxidant, PuO$_{2+x}$ is formed by reaction with water, thereby illustrating the importance of thermodynamic and kinetic considerations. The mechanism by which water changes the chemical pathway is not yet understood. In extreme reducing environments, hypooxides (AnO$_{2-x}$) or sesquioxide (An$_2$O$_3$) are formed (Equation 2.5-2.7). These oxides are thermodynamically unstable and decompose; however, they are theorised to occur at the metal-oxide interface. In oxygen-rich environments, the AnO$_2$ is rapidly regenerated.

\[
\text{UO}_2(s) \rightarrow \text{UO}_{2-x}(s) + \text{O}_2(g) \quad 2.5
\]
\[
\text{NpO}_2(s) \rightarrow \text{UO}_{2-x}(s) + \text{O}_2(g) \quad 2.6
\]
\[
\text{PuO}_2(s) \rightarrow \text{Pu}_2\text{O}_3(s) + \text{O}_2(g) \quad 2.7
\]

The AnO$_2$ crystallise in the calcium fluoride (CaF$_2$) motif characterised by $Fm\overline{3}m$ (No. 225) crystal symmetry (Figure 2.2). The lattice is that of a face centred cubic (FCC) structure where oxygen occupies tetrahedral holes. In this structure, each actinide (An$^{4+}$) cation is coordinated with eight oxygen anions (O$^{2-}$) and each O$^{2-}$ is coordinated with four An$^{4+}$.
The lattice consists of eight-tetrahedral and four-octahedral interstitial sites. The eight tetrahedral sites are surrounded by four cations; whereas, the four octahedral sites are surrounded by six cations. The interstitial sites readily accommodate H\textsuperscript{+} and O\textsuperscript{2\textendash} ions; this increases anionic mobility. The fluorite crystal motif is adopted by numerous corrosion products. These include the actinide hydrides (AnH\textsubscript{x}) and the actinide hydroxides (AnOH). The actinide hydrides (AnH\textsubscript{2}) crystallise in the CaF\textsubscript{2} motif to form a solid AnH\textsubscript{x} (1.9 < x < 3.0) solution phase. The catalysed interaction of hydrogen with the AnO\textsubscript{2} offers a means by which interdicted nuclear materials can be converted into simple ingots.\textsuperscript{(31)} The AnOH is formed by the reaction of the actinide metals with liquid water. The charge balance of the ternary compound is achieved by the equal O\textsuperscript{2\textendash} and H\textsuperscript{+} occupation of tetrahedral interstitial sites. The inclusion of O\textsuperscript{2\textendash} ions in octahedral interstitial sites results in hyper-stoichiometric AnO\textsubscript{2+x} compounds.\textsuperscript{(8)} In contrast, the ordered removal of 25\% of the O\textsuperscript{2\textendash} anions in the PuO\textsubscript{2} system results in hypostoichiometric α-Pu\textsubscript{2}O\textsubscript{3} formed by reduction.

The diffusion of ions and solid-state reactivity is influenced by the crystal structure. The fluorite-type structures are characterised by a matrix of invariant, immobile actinide cations. In contrast, anionic species are considerably more mobile; here, variations in actinide oxidation states promote catalytic behaviour. In fluorite-type materials, ionic transport and exchange rates closely resemble that of superionic conductors. In this, superionic conductors\textsuperscript{(13)} are solids characterised by a rigid host lattice, light mobile ions, and high direct-current ionic conductivities. The isostructural lanthanide oxide, CeO\textsubscript{2}, exhibits a transition to a superionic regime at high-temperature.\textsuperscript{(32)} The impact of ionic mobility on corrosion mechanisms is relatively uncharted.
2.2 Hydroxylation

As a coolant for nuclear reactors, water is often encountered in the fuel cycle. (33) In addition, a number of facilities use a boric acid solution in intermediate storage ponds. The interaction of water with actinide materials remains an important issue. (17, 22, 34) The accidental release of radionuclides is a point of ecological concern. (35) The interaction of water with nuclear materials is key to assessing the environmental impact of actinide compounds.

The oxidation of the actinide metals is catalysed by the reaction with water. In standard conditions, the rate of corrosion of uranium (10) and plutonium, (12, 36) with water vapour is $10^2$-$10^4$ greater relative to an oxygen environment. This results in the formation of the AnO$_2$ and hydrogen gas (Equation 2.8).

$$\text{An}(s) + x\text{H}_2\text{O}(g) \rightarrow \text{AnO}_{2+x}(s) + x\text{H}_2(g) \quad 2.8$$

The mechanism works by increasing the oxygen concentration gradient through formation of the hyper-oxides and the diffusion O$^{2-}$ ions. Measurements of the lattice constant confirm the formation of UO$_{2+x}$ and PuO$_{2+x}$.(30, 37) The reaction is characterised by the formation of hydrogen gas. In sealed containers, gas of sufficient pressure results in explosions. In oxygen rich environments, a water-catalysed oxidation mechanism occurs (Equation 2.9-2.10).

$$\text{An}(s) + x\text{O}_2(g) \xrightarrow{\text{H}_2\text{O}} \text{AnO}_{2+x}(s) \quad 2.9$$

$$\text{AnO}_2(s) + x\text{H}_2\text{O}(\text{ads}) \rightarrow \text{AnO}_{2+x}(s) + x\text{H}(\text{ads}) \quad 2.10$$

Initially water molecules are adsorbed on the oxide surface. Adsorbed hydroxide and hydrogen ions are formed by the dissociation of water on the oxide surface. The result is an increase in the oxygen concentration gradient across the surface. By recombination on the metal-oxide surface, the adsorbed oxygen and hydrogen ions can regenerate adsorbed water (Equation 2.11).
The adsorbed water molecule forms the hyperoxide resulting in a catalytic cycle until the oxygen is depleted. In oxygen deficient environments the reaction of water with actinide metals results in the formation of actinide oxides and the release of hydrogen gas (Equation 2.12).

\[ 2H(ads) + O(ads) \rightarrow H_2O(ads) \]  

\[ 2H(ads) \rightarrow H_2(g) \]  

Isobaric oxidation rates with air and water vapour are identical at high temperature.\(^{(8, 13, 36)}\) A water-independent kinetic regime for U at 250-500 °C and Pu at 110-200 °C has been identified.

### 2.3 Hydrogenation

The actinide metal-hydrogen system is extraordinarily complex.\(^{(38, 39)}\) The role of anionic and cationic hydrogen corrosion has been considered.\(^{(40)}\) As intermediates for the formation of nitrides and powdered metals, the actinide hydrides (AnH\(_x\), 2.0 ≤ x ≤ 3.0) are important to nuclear industries.\(^{(41)}\) As a result of the relative small size and chemical valence, hydrogen is capable of occupying a number of interstitial sites. Although the composition changes from cubic dihydrides to hexagonal trihydrides, initial tests show identical formation mechanism.\(^{(42, 43)}\) The magnetic character of a material is influenced by the extent of hydrogen corrosion. The cubic dihydrides are metallic and order magnetically below 40 K; whereas, the hexagonal trihydrides are semi-conductors and do not order magnetically above 4 K.\(^{(43)}\)

A hydrogen-oxygen mixture is formed by the radiolytic decomposition of water.\(^{(11)}\) This impacts fuel fabrication, reactor operation, and long-term storage of nuclear material. The oxidative corrosion of the metal is catalysed by the hydrogen gas; though the mechanism is not fully understood (Figure 2.3). In addition, AnO\(_2\) surfaces provides an active template for the equilibration of the oxygen-hydrogen system. The formation of non-condensable gases and
dimensional changes within the solid have led to the failure of containment vessels.\(^{(8)}\) It is important to investigate how hydrogen interacts with oxide surfaces due to the catalytic formation of water and its role in corrosion mechanisms.

![Figure 2.3: A surface-based illustration of actinide hydride-catalysed oxidation: a) molecular hydrogen is adsorbed and dissociates on the actinide dioxide (AnO\(_2\)) surface. The H\(^+\) anions diffuse through the actinide dioxide (AnO\(_{2+x}\)) layer. At the metal-oxide interface, the metal reacts with H\(^+\) anions to form the actinide hydride (AnH\(_x\)), b) molecular oxygen adsorbs, dissociates and diffuses across the AnO\(_{2+x}\) layer. At the oxide-hydride interface, AnH\(_x\) reacts with the O\(^2\) anions to generate more AnO\(_{2+x}\) and H\(^+\) anions. The H\(^+\) anions diffuse to the metal-hydride interface, react and regenerate the AnH\(_x\) layer.](image)

The interaction of hydrogen with the metal dioxide is relevant to the corrosion of the mechanisms and the stability of oxide fuels. Incidents involving hydride-catalysis have resulted in the rupture of containment vessels.\(^{(14)}\) A number of mechanisms incorporate the diffusion of hydrogen (H or H\(^+\)) or hydrogen-containing species (H\(_2\)O or OH\(^-\)) from the oxide surface layer to the metal oxide interface.

The interaction of hydrogen with actinide oxide interfaces is limited to a few publications.\(^{(5, 8, 40, 44, 45)}\) The hydrogen-oxygen system is thermodynamically unstable relative to water. The actinide and oxide surfaces offer an active substrate for the equilibration of the hydrogen-oxygen system. The metal-oxide surface is ever-present; unless extreme reducing environmental conditions are enforced. Initially, hydrogen is adsorbed and dissociated on the metal-oxide surface. A metal hydride is formed at the metal-oxide interface by the reaction of the metal with diffused hydrogen ions. The reaction of hydrogen and oxygen on the AnO\(_2\) surface forms a considerable amount of water (Equation 2.13-2.15).

\[
H_2(g) \rightarrow 2H(ads) \quad \text{Equation 2.13}
\]
The rate of metal-hydride corrosion is temperature-independent. The dissociated hydrogen atoms diffuse from the surface to the metal-oxide interface. An actinide hydride (AnH$_x$) layer is formed by reaction at the metal-oxide interface (Equation 2.16). (8)

\[
\text{An(s) + H}_2\text{(g) \rightarrow AnH}_x\text{(s)}
\]

The composition of the AnH$_x$ is influenced by hydrogen partial pressure. The reaction is limited by dissociation of hydrogen on the metal-oxide surface. In contrast to oxidation, metal-hydride corrosion is not diffusion-controlled, is $\sim 10^{11}$ times faster, and initiates at a limited number of nucleation sites. The intermediate metal-hydride is known to catalyse oxidation of the metal at the hydride-oxide interface (Equation 2.17-2.18). Note: information on the reaction of hydrogen with neptunium compounds is limited.

\[
\text{UH}_x\text{(s) + O}^2^- \rightarrow \text{UO}_2\text{(s) + xH}^- \]

\[
2\text{PuH}_x\text{(s) + 3O}^2^- \rightarrow \text{Pu}_2\text{O}_3 + \text{xH}^-\text{(ads)}
\]

The hydride ions react (after diffusing across the oxide-hydride interface) at the metal-hydride interface. The reaction is characterised by pyrophoric behaviour and an increase in the rate of corrosion. In hydrogen-oxygen environments, the oxidation of the metal is catalysed by the formation of water on the oxide surface (Equation 2.19-2.20).

\[
\text{AnO}_2\text{(s) + xO}_2\text{(g) \rightarrow AnO}_{2+x}\text{(s)}
\]
\[ \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H(ads)} + 2\text{O(ads)} \]  

The reaction incorporates the dissociative adsorption on the AnO$_2$ surface of H$_2$ and O$_2$ molecules and is impacted by surface energetics.\(^{(13)}\) In sealed containment vessels, the reaction is characterised by an O$_2$ partial-pressure decrease. This has resulted in the implosion (by pressure decrease) or rupture (by increase of solid volume) of sealed containment vessels. An investigation of hydrogen with AnO$_2$ surfaces is key to understanding corrosion mechanisms.

### 2.4 Thesis Outline

A relativistic noncollinear computational study of the actinide dioxides (AnO$_2$) and their interaction with hydrogen has been conducted. The corrosion of actinide materials concerns nuclear industries. This impacts the design of long-term storage facilities and next-generation nuclear fuels. An experimental investigation of actinide materials is incredibly complex, due to radiogenic concerns, international regulations, and sample inhomogeneity. To circumvent experimental issues, computational methods offer another means of investigation.

In Part I: Introduction. The reader is introduced to the nuclear fuel cycle and the corrosion of actinide materials. In Chapter 1, an overview of basic nuclear fission theory and the nuclear fuel cycle is described. The interaction of nuclear materials with the environment and the design of MOX fuels remains a key issue. In Chapter 2, the complex chemistry of actinide materials in relation to corrosion mechanism is described. The actinides corrode by oxidation to from a AnO$_2$ barrier which controls the reaction chemistry. Of the oxides forms, the metal dioxide is the most stable and the most prevalent in the nuclear industry. The electronic structure of the AnO$_2$ are important for understanding corrosion mechanisms. The radiolysis of water and organic material generates hydrogen gas which impacts the chemical behaviour of nuclear materials.\(^{(11)}\) The rate of oxidative corrosion is increased by the presence of hydrogen. The interaction of hydrogen with AnO$_2$ surfaces is key to develop a mechanistic understanding of corrosion mechanisms. The synthesis, isolation, toxicology, radioactivity and governance of nuclear materials has limited the experimental study of the actinide elements and their oxides.
In Part II: Computational Methodology. A commentary on first-principle methods and their implementation is offered. In Chapter 3, quantum mechanical methods and Hartree-Fock (HF) theory are introduced. In Chapter 4, planewave Density Functional Theory (DFT) is described. The implementation of theory is detailed and a number of commercial codes are reviewed.

In Part III: Results & Discussions. The calculation of the crystal structure, the design of surface models and their interaction with hydrogen is detailed. In Chapter 5, noncollinear relativistic calculations of the AnO₂ materials have been completed. The first systematic study of magnetic order in the AnO₂ along with a systematic analysis of DFT constraints is detailed. The study considers the importance of spin-orbit interactions, noncollinear magnetic behaviour and exchange-correlation influences. The results of which are contrasted against high-accuracy hybrid (HSE06) calculations. In Chapter 6, the low-index surfaces of the AnO₂ are calculated where noncollinear magnetism and spin-orbit contributions to the surface energetics are considered. The AnO₂ crystal surfaces have yet to be fully resolved by experimental and theoretical methods. This is the first instance whereby such a rigorous computational methodology is employed. In doing so, numerous deficiencies in previous models have been pointed out. These mainly pertain to how the magnetic moments on the actinide ions are aligned relative to the surface plane. In addition, the numerous reconstructions of the dipolar (001) surface is investigated. In Chapter 7, the interaction of hydrogen with AnO₂ surface has been calculated where the electronic structure and enthalpy of adsorption is reported. This is the first comprehensive study of hydrogen interaction on AnO₂ surfaces considering noncollinear magnetism.

In Part IV: Epilogue. In Chapter 8, the results of this thesis are concluded. In Chapter 9, further research is recommended.

2.5 Bibliography

Part I: Introduction

Chapter 2: Corrosion of Nuclear Materials


Part II:

Computational Methodology
Chapter 3:
Quantum Chemistry Methods

3.1 The Schrödinger Equation

In quantum mechanics the position of a particle (instead of discrete coordinates) is described by a probability distribution function. In the wave-matter physics interpretation, a wavefunction (Ψ(r)) describes the position and motion of a particle. In each instance, the electromagnetic force is considered only; the gravitational force, the strong nuclear force, and the weak nuclear force are ignored (Equation 3.1-3.3).

\[ \hat{H}\Psi(r) = E\Psi(r) \]

\[ \hat{H} = -\sum_{i=1}^{n} \frac{\nabla_i^2}{2} - \sum_{A=1}^{N} \frac{\nabla_A^2}{2M_A} - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N-1} \sum_{B=A+1}^{N} \frac{Z_A Z_B}{r_{AB}} \]

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]

The non-relativistic Hamiltonian (\(\hat{H}\)) operator is comprised of multiple terms: the kinetic energy of the electrons (1st term), the kinetic energy of the nuclei (2nd term), the electron-nuclei
interaction (3\textsuperscript{rd} term), the electron-electron interaction (4\textsuperscript{th} term) and the nuclei-nuclei interaction (5\textsuperscript{th} term).

As an initial simplification to the Schrödinger equation, the Born-Oppenheimer approximation considers the nuclei to have infinite mass. (3) Any change in nuclear position instantly influences the electrons. The nuclear and electronic wavefunctions can therefore be treated as individual components. (4) The nuclei can be described by classical mechanics; whereas, the electrons display quantum effects. (3) A constant electrostatic potential is generated by the nuclei frozen in position. The electrons are at their energy minima and move in an effective potential field generated by a fixed nuclear configuration. The ground-state energy of a system is described as a function of the nuclear coordinates. The kinetic energy of the nuclei can therefore be ignored; however, the nuclei-nuclei and nuclei-electron interactions must be considered. The ground-state total electronic energy ($E_e$) is calculated from the electronic wavefunction ($\Psi_e$) (Equation 3.4-3.5):

\[ \hat{H}_e \Psi_e (r) = E_e \Psi_e (r) \]

\[ \hat{H}_e = -\sum_{i=1}^{n} \left( \frac{\nabla_i^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}} \]

The electronic Hamiltonian ($\hat{H}_e$) is a function of; the kinetic energy of the electrons (1\textsuperscript{st} term), the nuclei-electron interaction (2\textsuperscript{nd} term), and the electron-electron interaction (3\textsuperscript{rd} term). As a limitation of the Born-Oppenheimer approximation, the method can fail if the correlation of electronic-ionic motion is important or when dealing with extremely light particles. In these circumstances, the time-dependent Schrödinger equation offers a more exacting method.

In the general case, an exact solution to the Schrödinger equation can only be found for one-electron systems. (5, 6) The kinetic energy of the electrons and the nuclei-nuclei interaction, relative to the electron-electron interaction, is trivial to calculate mathematically. The electron-electron interaction, due to quantum entanglement (the many-body problem), cannot be solved by conventional mathematics. (7) Numerically iterative methods must be applied.
3.2 The Hartree Model

A result of the quantum entanglement of electronic states (known as the many body problem), conventional mathematical methods are unable to resolve the electron-electron interaction. Iterative numerical methods are needed. (7) In the absence of the electron-electron interaction (one-electron system), an exact numerical solution can be calculated. A system of non-interacting electrons forms the basis of the Hartree model (a one-electron Hamiltonian is obtained if electron-electron interactions are ignored). (8) A numerically solvable series of spin-orbital which satisfy the one-electron Hamiltonian is obtained by ignoring the electron-electron interaction (Equation 3.6-3.7).

\[
\hat{H}_e = \sum_{i} \hat{h}(i) \tag{3.6}
\]

\[
\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A} \frac{Z_A}{r_{iA}} \tag{3.7}
\]

The motion of an electron is described by the one-electron (\(\hat{h}(i)\)) operator (in a potential field created by the nuclei). A series of spin-orbitals (\(\chi_i(r_i)\)) involving the one-electron Hamiltonian (ignoring the electron-electron interaction) are described (Equation 3.8).(9)

\[
\hat{h}(i)\chi_i(r_i) = \varepsilon_i\chi_i(r_i) \tag{3.8}
\]

The terms in the parentheses describe the; Fock operator (\(\hat{h}\)) electron (i), one-electron wavefunction (\(\chi_n(r_n)\)), and energy (\(\varepsilon\)). The Fock operator describes the; kinetic energy of the electrons, the nuclei-electron interaction, the averaged electron-electron interactions. The product of the one-electron wavefunctions result in the Hartree product with corresponding total energy (Equation 3.9-3.10).
\[ \Psi_H = \prod_n \chi_n(r_n) \]  

3.9

\[ E_H = \sum_n \epsilon_n = \int \chi_n^*(r_n) \hat{H} \chi_n(r_n) \]  

3.10

The independent electron model can be modified to consider electron-electron interactions. It is assumed that the electrons move in an averaged potential field (created by all the other electrons and the nuclei of the system). An averaged potential field forms the basis of the Hartree Self-Consistent Field (SCF) model. As the average potential field and wavefunction are commensurate, a numerically iterative method follows from an initial trial wavefunction. The ground and excited-states of a system can then be calculated.

3.3 The Pauli Antisymmetric Principle

As an independent electron model (Hartree model), the Pauli antisymmetric principle is ignored. The sign of the wavefunction must be inverted from an exchange operation on two identical fermions (identical quantum mechanical particles cannot be distinguished) (Equation 3.11-3.12).

\[ \psi(..., \chi_i(r_i), \chi_j(r_j), ...) \neq \psi(..., \chi_i(r_j), \chi_j(r_i), ...) \]  

3.11

\[ \psi(..., \chi_i(r_i), \chi_j(r_j), ...) = -\psi(..., \chi_i(r_j), \chi_j(r_i), ...) \]  

3.12

To correct this issue, a Slater determinant is introduced. It is impossible for more than one electron to occupy the same spin-orbital (Equation 3.13).
The introduction of an anti-symmetric wavefunction (composed of a single Slater determinant) forms the basis of Hartree-Fock (HF) theory. As the double occupation of a spin-orbital is forbidden, the Pauli exclusion principle is built into the wavefunction. The one-electron energy is calculated from the Coulomb ($U$, electrostatic repulsion of the electrons) and exchange ($J$, antisymmetric wavefunction) terms (Equation 3.14-3.16).

\[
\hat{\mathbf{h}} + \sum_{i \neq j} U_{ij} - \sum_{i \neq j} J_{ij} \chi = \varepsilon \chi \quad 3.14
\]

\[
U_{ij} = \int \int \chi_i(r_1)\chi^*_i(r_2) \frac{1}{r_{12}} \chi_j(r_1)\chi^*_j(r_2) \, dr_1 \, dr_2 \quad 3.15
\]

\[
J_{ij} = \int \int \chi_i(r_1)\chi^*_i(r_2) \frac{1}{r_{12}} \chi_j(r_1)\chi^*_j(r_2) \, dr_1 \, dr_2 \quad 3.16
\]

The one-electron Hamiltonian ($\hat{\mathbf{h}}$) is indicated by the term in the parentheses. As a computationally complex negative term, the exchange integral reduces the total energy of the system. To find a solution for the wavefunction, a numerically iterative procedure follows employing the variation principle. To computationally reduce the energy, a convergence threshold is used. As an approximate form of the wavefunction is used in the HF method; instantaneous correlations are generally ignored and the electrons are treated by a mean-field potential. The electron-electron interaction is treated as an average effect (by a single Slater determinate), and electron-correlation is ignored.
3.4 The Orthonormality Condition

A n-dimensional structure is described by a linear combination of basis vectors. A wavefunction (wavevector) is a function of a basis vector. A condition of the basis wavefunctions is that they satisfy orthonormality condition, the scalar or inner product of wavevectors must be zero (Equation 3.17).

\[ (\varepsilon_i - \varepsilon_j) \int \chi_i^*(r_i)\chi_j(r_j)dr = 0 \]

3.17

The probability of finding a particle between a and b is given by the Born probability density amplitude (Equation 3.18). As a result of the probability density amplitude interpretation, the orthonormality condition for finding the wavefunction over infinity must be one (Equation 3.19). As a condition for orthonormality, the Kronecker delta describes the condition of the individual wavefunctions (Equation 3.20).

\[ \int_{a}^{b} |\chi(r)|^2 dr = P[a \leq R \leq b] \]

3.18

\[ \int_{-\infty}^{\infty} |\chi(r)|^2 dr = 1 \]

3.19

\[ \int \chi_i^*(r_i)\chi_j(r_j)dr = \delta_{ij} \]

3.20

The terms in the parentheses describes the; Kronecker delta (\(\delta_{ij}\)), the complex conjugate wavefunction (\(\chi_i^*(r_i)\)) and the wavefunction (\(\chi_j(r_j)\)). As a mathematical construct, the Hermitian nature of the Hamiltonian matrix ensures that the eigenvalues are real.
3.5 The Roothann-Hall Matrix

By a linear combination of mathematical functions, the solutions to the Schrödinger equation form a complete basis set of functions (Equation 3.21).

\[ \Psi_i = \sum_\mu C^i_\mu \phi_\mu \]  

The terms in the parentheses describe the; spatial molecular orbital (\(\Psi_i\)), the spatial atomic orbital (\(\phi_\mu\)), and the atomic-molecular orbital coefficient (\(C^i_\mu\)). To solve the Hartree-Fock equations, a Roothann-Hall matrix of equations is used to calculate the atomic-molecular orbital coefficient (Equation 3.22).

\[ Fc = Sc\varepsilon \]  

The terms in the parentheses describe the; one-electron Fock matrix (\(F\)), the matrix of overlap integrals (\(S\)), the matrix of atomic-molecular orbital coefficients (\(c\)), and the diagonal matrix of eigenvalues (\(\varepsilon\)).

3.6 The Variational Theorem

An implicit limitation of the HF modal is that the correlation energy cannot be calculated as the ground-state wavefunction is unknown; however, the electrostatic repulsion Coulomb exchange energy is calculated exactly. The correlation energy is defined as dynamical or non-dynamical. The dynamical correlation energy is the probability of finding the position of an electron in relation to another. In highly-localised systems, the dynamical correlation energy results in a considerable error. The non-dynamical correlation energy relates to the unequal population of degenerate states.
As a consideration to the Schrödinger equation, the variational method offers a means by which the ground-state of a system can be calculated by an arbitrary wavefunction (Equation 3.23).

$$\Psi_T \geq \Psi_0$$

The energy calculated from a trial wavefunction ($\Psi_T$), relative to the energy calculated from the ground-state wavefunction ($\Psi_0$), is either greater than or equal to. The correlation energy is the difference between the HF wavefunction and the ground-state wavefunction. The energy of the wavefunction can be calculated by an iterative method, thus obtaining more realistic solution to the ground-state.

In terms of computation, the wavefunction is derived from a complex $3n$-dimensional object; whereby, the number of electrons (n) is denoted by the term in the parentheses. Importantly, all-electron wavefunction methods are: computationally expensive, neglect electron exchange, and only considers electron correlation. The electron correlation energy can be partially recovered in post-HF methods. These include Møller–Plesset (MP) perturbation,(13, 14) configuration interaction (CI),(15) or coupled cluster (CC) methods.(16-18) These methods are computationally intractable for the study of actinide systems. A mean of calculating the correlation energy, density functional theory (DFT) considers the total energy of a system as a function of the electron density.

3.7 Bibliography

Chapter 4:
Density Functional Theory

4.1 Density Functional Theory: Principles

4.1.1 Hohenberg-Kohn & Kohn-Sham

The many-body Hartree-Fock (HF) wavefunction is a complex 3n-dimensional (n is the number of electrons in the system). As a computationally intuitive 3-dimensional object, the electron density complexity does not scale with electron count. In density functional theory (DFT), the energy is a functional (a function of a function) of the electron density (n(r)).

The electron density is a function of position (r). The basis of DFT is described by the Hohenberg-Kohn (HK)(2) and Kohn-Sham (KS)(3) theorems. In the Hohenberg-Kohn theorem, the total energy of a system is described by a functional of the electron density. In addition, the ground-state electron density is described by a universal density functional. The total DFT energy (E) is described by kinetic energy ($T_e$), nuclear-electron ($E_{Ne}$), and electron-electron ($E_{ee}$) interactions (Equation 4.1-4.2).

\[
E[n(r)] = T_e[n(r)] + E_{Ne}[n(r)] + E_{ee}[n(r)] 
\]

\[
E[n(r)] = F[n(r)] + \int n(r)V_{ext}(r) \, dr 
\]
As a revision of the total energy, the system is described by: the Hohenberg-Kohn functional (F[n(r)]) and an external potential (V_{ext}). The nature of the Hohenberg-Kohn functional is unknown and considers electron exchange-correlation contributions. The external potential is derived from the electron density.

The reintroduction of the wavefunction enables the calculation of the total energy (Kohn-Sham theorem); where, a non-interacting and fully interacting system of electrons are considered to be equal (Equation 4.3).

\[ n(r) = \sum |\chi_{KS}(r)|^2 \quad 4.3 \]

The total energy is described by the: non-interacting electron kinetic energy, nuclei-electron interaction, Coulomb interaction, and exchange-correlation interaction (Equation 4.4-4.7).

\[ \begin{align*}
E_{\text{DFT}}[n(r)] &= T_S[n(r)] + E_{Ne}[n(r)] + J[n(r)] + E_{xc}[n(r)] \quad 4.4 \\
E_{\text{DFT}}[n(r)] &= F[n(r)] + E_{Ne}[n(r)] \quad 4.5 \\
F[n(r)] &= T_S[n(r)] + J[n(r)] + E_{xc}[n(r)] \quad 4.6 \\
T[n(r)] &= T_S[n(r)] + T_C[n(r)] \quad 4.7
\end{align*} \]

The Hohenberg-Kohn functional (in the Kohn-Sham theorem) is calculated from: a system of non-interacting electrons, the classical Coulomb interaction, and the exchange-correlation energy. The exchange-correlation energy is the non-classical part of the electron-electron interaction. As a result, DFT considers both electron exchange and correlation within the formalism. The total electron kinetic energy is the sum of the non-interacting electron kinetic energy and a correction to the electron kinetic energy. The non-interacting electron kinetic energy, the nucleus-electron interaction, and the Coulomb interaction are then written in terms of the wavefunction (Equation 4.8-4.10).
\[ T_S[n(r)] = -\frac{1}{2} \sum_i^N \int \chi_i |\nabla^2 | \chi_i \]  

\[ J[n(r)] = \frac{1}{2} \sum_i^N \sum_j^N \int |\chi_i|^2 \frac{1}{r_{12}} |\chi_j|^2 \, dr_1 \, dr_2 \]  

\[ E_{Ne}[n(r)] = -\sum_i^n \int \sum_A^M \frac{Z_A}{r_{iA}} |\chi_i|^2 \, dr_i \]  

As an impediment to calculating the KS equations for total energy, the nature of the exchange-correlation functional is unknown and must be estimated (Equation 4.11-4.12).

\[ E_{XC}[n(r)] = T[n(r)] - T_S[n(r)] + E_{ee}[n(r)] - J[n(r)] \]  

\[ E_{XC}[n(r)] = T_C[n(r)] + E_{NC}[n(r)] \]  

The electron-electron interaction energy is a function of the classical Hartree energy and the non-classical part of the electron-electron interaction (Equation 4.13).

\[ E_{ee}[n(r)] = -\frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} + E_{NC}[n(r)] \]  

The terms in the parentheses describe the; electron-electron interaction total energy \( (E_{ee}[n(r)]) \), and the non-classical part of the electron-electron interaction \( (E_{NC}[n(r)]) \). The non-classical electron-electron interaction term is analogous to the exchange-correlation term in HF theory.

The energy as a function of electron density can be expressed by the Schrödinger equation for one-electron orbitals (Equation 4.14).
\[
\left[-\frac{1}{2} \nabla^2 + \left( \hat{h}_{\text{ext}}(r) + \hat{h}_H(r) + \hat{h}_{\text{xc}}(n(r)) \right) \right] \chi_i(r) = \varepsilon_i \chi_i(r)
\]

The one-electron Hamiltonian consists of: the kinetic energy of the electrons, the external potential \( \hat{h}_{\text{ext}} \), the Hartree (mean-field) potential \( \hat{h}_H \), and exchange-correlation \( \hat{h}_{\text{xc}} \) terms. By employing an iterative numerical method with the variation principle, identical to that of the Hartree-Fock method, the ground-state of a system can be resolved. Iterative methods are numerous and include the: conjugate-gradient algorithm (CGA), blocked-Davidson (DAV), and residual minimization method direct inversion in iterative subspace (RMM-DIIS) algorithms.\(^{(5)}\)

### 4.1.2 Exchange-Correlation Functionals

The nature of the exchange-correlation functional (a central issue in DFT) is unknown. To offer an approximated from, the exchange and correlation terms are described as individual components. These relate to the electron density (Equation 4.15-4.16).

\[
E_{\text{xc}}[n(r)] = E_x[n(r)] + E_c[n(r)]
\]

\[
E_{\text{xc}}[n(r)] = \int \varepsilon_x[n(r)] n(r) \, dr + \int \varepsilon_c[n(r)] n(r) \, dr
\]

The terms in the parentheses describe the: total exchange energy \( E_x[n(r)] \), total correlation energy \( E_c[n(r)] \), one-electron exchange energy \( \varepsilon_x \), and one-electron correlation energy \( \varepsilon_c \). The exchange-correlation functionals are often calculated from perturbation series expansion or in-depth quantum-Monte-Carlo simulations from a uniform electron gas model. In a hypothetical uniform electron gas model, an infinite number of electrons are contained within a neutral continuum. The concept is analogous to the behaviour of valence electrons in an ideal metal.
To estimate the exchange-correlation energy term, the local (spin) density approximation (L(S)DA) functional is derived from a uniform electron gas model. The functional is based on the idea that the electron density of a real system varies smoothly in space. If one assumes the exchange-correlation functional to be local, a numerical form may be determined from many-body calculations (Equation 4.17).

$$E_{\text{XC}}^{\text{LDA}}[n(r)] = \int n(r) \varepsilon_{\text{XC}}(n) \, dr$$  \hspace{1cm} (4.17)

The total exchange-correlation LDA energy ($E_{\text{XC}}^{\text{LDA}}[n(r)]$) is derived from the local electron density ($n(r)$) by the local exchange-correlation ($\varepsilon_{\text{XC}}n(r)$) term. The Dirac expression gives the exchange energy for a uniform electron gas (Equation 4.18).

$$\varepsilon_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} [n(r)]^{1/3}$$  \hspace{1cm} (4.18)

As no expression exists for the correlation term ($\varepsilon_c$), the correlation energy is derived from Ceperley-Alder (CA) or Vosko, Wilk, Nusair (VWN) interpolation formula of Monte Carlo data. A number of limitations of LDA (due to the functionals over-binding nature) have been identified: underestimation of bond lengths, overestimation of atomisation energies, overestimation of ionisation energies. The generalised gradient approximation (GGA) (by considering the local density and the gradient density) offers an improvement (Equation 4.19).

$$E_{\text{XC}}^{\text{GGA}}[n(r)] = \int n(r) \varepsilon_{\text{XC}}(n, \nabla n) \, dr$$  \hspace{1cm} (4.19)

The terms in the parentheses described the: total exchange-correlation GGA energy ($E_{\text{XC}}^{\text{GGA}}[n(r)]$), local electron density ($n(r)$), and local gradient for the exchange-correlation
energy ($\varepsilon_{\text{XC}}(n, \nabla n)$). To calculate the exchange-correlation energy in terms of the local gradient of electron density, a number of non-empirical functionals have been developed: Perdew-Burke-Ernzerhof (PBE), Armiento-Mattsson (AM05), revised Perdew-Burke-Ernzerhof for solids (PBEsol). These functionals often fail to describe highly-correlated systems.

The inability to deal with highly-correlated systems (as with the HF model) is a major limitation of DFT. The exchange energy in HF theory is calculated exactly and the correlation energy is ignored; whereas, the exchange and correlation energy in DFT are approximated only. As a more computationally intensive method, hybrid functionals incorporate HF exchange energy into the DFT formalism (Equation 4.20).

$$E_{\text{XC}}^{\text{Hybrid}} = E_{\text{XC}}^{\text{GGA}} + a(E_{\text{X}}^{\text{HF}} - E_{\text{X}}^{\text{GGA}})$$  \hspace{1cm} (4.20)

The total exchange-correlation energy ($E_{\text{XC}}^{\text{Hybrid}}$) is calculated from: the exchange-correlation GGA energy ($E_{\text{XC}}^{\text{GGA}}$), ratio of exchange (a), exchange HF energy ($E_{\text{X}}^{\text{HF}}$), and exchange GGA energy ($E_{\text{X}}^{\text{GGA}}$). As a means of reducing the computational cost of hybrid calculations, the Heyd–Scuseria–Ernzerhof (HSE) method (a = 0.25) is reduced to short-range (SR) and long-range (LR) components (Equation 4.21).

$$E_{\text{XC}}^{\text{HSE}} = (a)E_{\text{X}}^{\text{HF,SR}}(\mu) + (1-a)E_{\text{X}}^{\text{PBE,SR}}(\mu) + E_{\text{X}}^{\text{PBE,LR}}(\mu) + E_{\text{C}}^{\text{PBE}}$$  \hspace{1cm} (4.21)

The adjustable screening ($\mu$) modifier in the HSE06 functional is 0.207 Å$^{-1}$. The long-range HF and long-range PBE terms are assumed to be equal and cancel.
4.1.3 The DFT+U Method

The nature of highly-correlated materials (heavy-fermion materials) is often incorrectly described by DFT: electronic structure, magnetic moments, equilibrium crystal structure. The over-delocalization of electronic states causes the band-gaps to be underestimated. A full account of the multi-determinant nature of the N-electron wave function and of the many-body terms of the electronic interactions is needed. As hybrid functionals are limited by their computationally intense nature, the DFT+U method offers a tractable means of investigation. To treat the double-occupation of bands (a result of the self-interaction error, SIE), an empirical Hubbard model correction is introduced (Equation 4.22-4.23).

\[
E_{\text{tot}}(n, \hat{n}) = E_{\text{DFT}}(n) + E_{\text{HF}}(\hat{n}) - E_{\text{dc}}(\hat{n}) \quad 4.22
\]

\[
E_{\text{dc}}(\hat{n}) = \frac{U}{2} \hat{n}_{\text{tot}}(\hat{n}_{\text{tot}} - 1) - \frac{1}{2} \sum_{\sigma} \hat{n}_{\text{tot}}^{\sigma}(\hat{n}_{\text{tot}}^{\sigma} - 1) \quad 4.23
\]

The terms in the parentheses indicate the: total energy \((E_{\text{tot}}(n, \hat{n}))\), DFT energy \((E_{\text{DFT}}(n))\), Hartree-Fock energy \((E_{\text{HF}}(\hat{n}))\), double counting energy \((E_{\text{dc}})\), main quantum number \((n)\), and spin index \((\sigma)\). The method forces the on-site matrix to be idempotent, and an integer occupational ground-state result. To compensated for the on-site Coulomb repulsion of the electrons, an energetic penalty for non-integer orbital occupation is implemented. The contraction of the orbitals (by the artificial Coulombic potential) impacts bonding (overlap) interactions.

In the rotationally invariant Liechtenstein et al(22) formalism, for the double-counting energy term, the Coulomb \((U)\) and exchange \((J)\) modifiers are treated as independent variables.(22) In the simplified Dudarev et al DFT+U formalism, an effective \((U_{\text{eff}} = U - J)\) modifier is derived by combination of \(U\) and \(J\) terms. In this case, the Dudarev et al(23) formalism and Liechtenstein et al(22) formalism when \(J = 0.00 \text{ eV}\) are equivalent.(24) As the total energy of a system is controlled by the \(U\) and \(J\) modifiers, it is meaningless to compare energies derived from different values.
4.2 Density Functional Theory: Implementation

4.2.1 Periodic Boundary Conditions

A planewave basis set is ideal for solid-state calculations. This represents a complete departure from localised atom centred functions. The ground-state wavefunction of a Bravais lattice can be calculated by applying Bloch wave theorem and Born-von Karman periodic boundary conditions. This reduces the computational cost of modelling a periodic system. In condensed matter physics, a Bravais lattice is a periodic system described by an infinite array of discrete points (Figure 4.1).

![Figure 4.1: A visual representation of a periodic cell. In this representation, the conventional unit cell has been expanded five times in all dimensions. In practice, the conventional unit cell is repeated an infinite number of times.](image)

An n-dimensional structure can be described by a linear combination of basis vectors. As a key condition, the contents of a Bravais lattice are unchanged by a translational lattice vector. If the basis vectors are orthonormal, the scalar or inner product is zero. As a limitation to the periodic boundary model, the system is considered to be infinite and defect free. If one wishes to consider defects within their system, a suitably large supercell must be constructed to minimise the interaction of periodic defect images.
4.2.2 Bloch Wave Theorem

In mathematics and solid-state physics, the first Brillouin zone is represented by an irreducible primitive unit cell in reciprocal k-space (momentum space). A set of discrete translation operations generate a periodic lattice. The importance of the first Brillouin zone relates to the Bloch wave description of a periodic medium. In the Bloch wave description, the first Brillouin zone completely characterizes the nature of a periodic system. (25) The eigenvalues of the Hamiltonian in the first Brillouin zone all take unique values. The ground-state energy of a system is described by the Bloch theorem of planewaves if Born-von Karman periodic boundary conditions are applied. (26) A particle moving in a periodic potential can be written in terms of the periodicity of the system (Equation 4.24-4.25).

\[ \psi_k(r) = e^{ikr}u_k(r) \]  \hspace{1cm} 4.24
\[ \psi_k(r) = e^{ipr/\hbar}u_k(r) \]  \hspace{1cm} 4.25

The terms in the parentheses describe the; wavefunction (\(\psi\)), position vector (\(r\)), periodic function of the crystal (\(u\)), wavevector of the crystal (\(k\)), and wave momentum (\(p\)). The wavevector of the crystal describes the phase relationship of the periodic wavefunction. The idea of k-space is used to describe the momentum vector of the electrons. As a consequence, the Bloch wavefunctions denotes the energy eigenstate of an electron.

4.2.3 Band Structure & K-Points

A continuous low-energy (in-phase, bonding) to high-energy (out-of-phase, anti-bonding) band is formed by an infinite periodic solid. The phase relationship of the wavefunction in adjacent cells is described by its k-vector (k-point or wavevector); therefore, an infinite number of k-points (and energy levels) fully describe a periodic system. To truncate the planewave expansion, a cut-off energy is used. As a smooth wavefunction is modelled at k-point close together, a finite number of k-points are used in condensed matter physics. The number of filled bands as a functional of the k-points changes in a metal (this is not the case for an insulator
which have a band gap. As the electron occupancies of the bands changes in metals, a large number of k-points are needed. An insulator (comprised of fully occupied or fully unoccupied bands) can be modelled by a small number of k-points.

The number of k-points in the irreducible Brillouin zone (IBZ) and the precision of the mesh are (usually) directly proportional; however, not to the number of divisions. An increase in unit cell size corresponds to an inversely proportional decreases in the number of k-point needed for a calculation (a characteristic of reciprocal space.) A greater number of phase combinations in a large unit cell are allowed; therefore, the phase dependence with adjacent cells is less important (as the distances involved are larger). A finely distributed k-point mesh is often used to sample reciprocal space. The complexity of the mesh influences the computational cost of a system. If the numerical integration k-point grid is converged to a defined threshold, the impact on material characteristics is minimal. A high-number of k-points is needed for metallic systems and small unit cells; whereas, a small-number of k-points is enough for non-metallic systems and large unit cells. It is imperative to converge the cut-off energy and k-point mesh in planewave DFT calculations. The distribution of k-points is classified by regular or special grids. If the grid is regular the k-points are equally spaced; if the grid is special the k-points are irregularly dispersed. The integration of reciprocal space by an equally spaced regular grid includes: the Monkhorst-Pack method or a Γ-centred k-point mesh. The inclusion of the reciprocal origin (Γ-point, in a Γ-centred k-point mesh) corresponds to completely in-phase interactions. The high-symmetry Γ-point often contains important information; however, it can increase the computational cost of the system. A Γ-centred k-mesh with tetrahedron Blöchl correction method (for calculations of semiconductors and insulators) is recommended. The tetrahedron method with Blöchl corrections does not require any empirical parameters; however, it is invariant with respect to partial electron occupancies which manifests as a deviation in calculated forces.

4.2.4 Effective Core Potentials

A result of the orthonormality condition with respect to the core electrons, a valence wavefunction oscillates rapidly when proximal to the nucleus. To model rapid oscillations, a large number of high-kinetic energy planewaves are needed. This increases the computational cost of the calculation. An effective core potential (pseudopotential) models the interaction of
the valence wavefunction. The core electrons are eliminated from the calculation and a smooth valence wavefunction is obtained. As a result of a smooth valence wavefunction, a lower planewave cut-off energy can be used to reduce the cost of the calculation. An effective core potential is calculated from: numerical Hartree-Fock, relativistic Dirac-Hartree-Fock, or DFT calculations. The valence orbitals are replaced by a set of node-less pseudo-orbitals that are designed to correctly model their outer region. The nodal structure of the core region is neglected. The inner electrons are modelled by a core potential; this core potential can include relativistic contributions.\(^{(27, 28)}\)

The projector augmented-wave (PAW) Blöchl method employs an all-electron linear augmented planewave methodology, in which the core electrons are frozen while the valence electrons are allowed to relax. The core electrons are represented by localised basis sets derived by all-electron relativistic calculations. The number of planewaves is reduced by the frozen core approximation. In contrast to norm-conserving and ultra-soft pseudopotentials, PAW pseudopotentials offer a more computational tractable method by which characteristics that involve core-electron states can be calculated.

### 4.2.5 Ionic Relaxation

The ionic coordinates of a system (as influenced by crystal environment) impact the electronic structure. The juxtaposition of \(p\)-, \(d\)- and \(f\)-levels and the radial extent of the orbitals (in actinide-based systems) result in highly-complex electronic structures. To calculate the electronic structure, it is imperative to converge the equilibrium geometry. As the nature of the true exchange-correlation functional is unknown, numerous functionals approximate the energy of a system and equilibrium geometry. The potential energy wells for the equilibrium geometry are approximated. This impacts calculation of the equilibrium bond lengths. The potential energy surface must be converged irrespective of experimental information.

An iterative geometry-optimization sub-routine, the Hellmann-Feynman theorem calculates the ionic forces directly from the wavefunction.\(^{(29)}\) An ionic-relaxation algorithm finds the equilibrium structure from the ionic forces. These algorithms include the quasi-Newtonian and conjugate-gradient methods. The quasi-Newtonian algorithm offers an efficient means of relaxing ions; however, it can fail if the initial positions are extremely inaccurate. In the
conjugate-gradient algorithm, the total energy is reduced by an iterative quadratic model of the ionic forces. This results in a converged potential energy surface. An energetic minimum is reached when the ionic forces are nil. An acceptable threshold is introduced with respect to the convergence criteria. An incomplete planewave basis set introduces a Pulay error (Pulay stress), the result of changes to the reciprocal lattice volume. The diagonal components of the stress tensor are incorrect (often nearly isotropic), and for a finite planewave basis set results in an underestimation of the equilibrium volume. A high cut-off planewave energy can minimise the Pulay error.

4.2.6 Relativistic Contributions

To include relativistic effects central to heavy-fermion modelling, the computational expensive four-component Dirac equation can be used. A relativistic effective core potential (that incorporates the contraction of the s- and p-orbitals, and expansion of the d- and f-electrons) simplifies the planewave expansion. To couple the magnetisation direction to the crystal lattice, the spin-orbit (SOI) interaction can be included. A point charge generates a magnetic field under motion. The spin (s) and orbital (l) angular momentum of an electron result in individual magnetic moments. The total spin-orbit (j) angular momentum is obtained by vector addition. The relativistic inflation of the p-orbitals is counteracted by the SOI; whereas the d- and f-orbitals become more diffuse. As a result of the intense computational cost, the SOI is often ignored in heavy fermion materials. The inclusion of SOI enables the investigation of noncollinear magnetic structures.

4.2.7 Noncollinear Magnetism

The all-electron projector augmented-wave (PAW) method for noncollinear magnetic structures is based on a generalised local-spin-density theory. The method allows for the self-consistent simultaneous relaxation of atomic and magnetic structures. As a generalisation of the Vanderbilt-type ultrasoft-pseudopotential (USPP) and linear-augmented-plane-wave (LAPW) methods, the PAW formalism for noncollinear magnetism has been discussed in detail.
An all-electron wavefunction ($\Psi_n^{\alpha}$) (derived by means of a pseudo-wavefunction ($\tilde{\Psi}_n^{\alpha}$) linear transformation) is used in the PAW method. The noncollinear magnetic pseudo-wave function consists of $2N$ eigenspinors (where $N$ is the total number of eigenvalues) expanded in planewave reciprocal space (Equation 4.26-4.27).

\[
|\Psi_n^{\alpha}\rangle = |\tilde{\Psi}_n^{\alpha}\rangle + \sum_i (|\chi_i\rangle - |\tilde{\chi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi}_n^{\alpha}\rangle 
\]

\[
\langle r | \tilde{\Psi}_n^{\alpha}\rangle = \frac{1}{\Omega_r^{1/2}} \sum_k C_{nk}^\alpha (r)e^{ikr} 
\]

The terms in the parentheses describe: the volume of the Wigner-Seitz cell ($\Omega$), on-site density matrices ($n$), atomic index ($i$), reference energy index ($k$), projector functions ($\tilde{p}_i$). The all-electron partial waves ($\chi_i$) are obtained from a nonmagnetic reference atom. The pseudo partial waves ($|\tilde{\chi}_i\rangle$) outside of a core radius are considered to be equivalent. A continuous vector variable of position ($r$) is used in the PAW method to treat noncollinear magnetic structures.

### 4.2.8 Computational Codes

A number of computational codes are able to model solid-state materials, where one must consider: functionality, implementation, and license. Of the computational codes; Crystal(39) (limited choice of effective core potentials), Quantum Espresso(40) (non-existent actinide basis set library), and CP2k(41) (reduced functionality) are unsuitable. A complete basis set library and improved functionality is offered by the Vienna Ab-initio Simulation Package (VASP)(42-44), imperative for the study of actinide materials.

### 4.3 Bibliography

Part II: Computational Methodology

Chapter 4: Density Functional Theory

Part III:

Results & Discussions
Chapter 5: Condensed Matter Physics

5.1 Introduction

An investigation of the actinide dioxide (AnO$_2$) magnetic ground-state is incredibly challenging. (1) An accurate description of the underlying physics (including the magnetic ground-state) is key to the design of reliable computational models. The magnetic ground-state impacts the calculation of: phonon frequencies, thermodynamic properties, and excited electronic states. (2-4) The influence of magnetism on the electronic structure has been investigated. A computationally tractable method has been designed, from which more complicated systems can be based.

![Crystal Structure of AnO$_2$](image)

Figure 5.1: The crystal structure of the AnO$_2$ with: left) Fm$ar{3}$m (No. 225) right) Pa$ar{3}$ (No. 205) crystal symmetry. The colours in the parentheses indicate the An$^{4+}$ (blue) and O$^{2-}$ (red) ions. Note, in Pa$ar{3}$ symmetry, the displacement of the O$^{2-}$ ions is exaggerated.
In environmental conditions the AnO$_2$ share the calcium fluoride (CaF$_2$) crystal structure with \textit{Fm\textbar 3m} (No. 225) cubic symmetry.\textsuperscript{(5, 6)} In this structure, the An$^{4+}$ cations occupy octahedral (4a) sites, whereas the O$^{2-}$ anions occupy tetrahedral (8c) sites. In addition, low-temperature measurements of uranium dioxide (UO$_2$) have indicated the \textit{Pa\textbar 3} (No. 205) crystal symmetry. In this structure, there is no distortion of the An$^{4+}$ ions or of the overall cubic environment, but there is an internal distortion of the O$^{2-}$ ions within the cubic lattice (Figure 5.1).

![Figure 5.2: The one-electron interpretation of the AnO$_2$ cubic electric crystal-field. Note: this is only valid for the one-electron case.](image)

To characterise the nature of condensed matter systems, it is imperative to identify coupled and competing magnetic interactions.\textsuperscript{(7)} The magnetic structure of the AnO$_2$ is often inferred by the one-electron crystal electric field (Figure 5.2). In the one-electron crystal-field (CF) model, the 5f-electrons are highly localised due to the insulating nature of the materials. The orbitals do not hybridise and the crystal-field is influenced by the electrostatic potential. The influence of the SOI is initially considered, whereby $j = 7/2$ and $j = 5/2$ electronic levels are formed. The degeneracy of the levels are further broken by the crystal-field as a second-order perturbation. The interpretation of the magnetic structure by CF theory is only valid for the one-electron case.\textsuperscript{(8, 9)} In reality the magnetic structure of the AnO$_2$ is complicated by nontrivial: super-exchange, magnetoelastic, electron-phonon, multipolar spin-lattice interactions, and noncollinear contributions.\textsuperscript{(2, 8-10)} The type of magnetism can be classified into; paramagnetic (PM), diamagnetic (DM), ferromagnetic (FM), anti-ferromagnetic (AFM), and ferrimagnetic (FI) behaviour.
In non-ordered DM materials, as all electrons are paired, no magnetic moments are associated with the individual ions and as a result the net magnetic moment of the crystal is zero as well. The only magnetic response is a weak repulsion in an applied magnetic field.

A magnetic moment is formed by an odd number of electrons. At low-temperature, magnetic moments may couple (ordered magnetic, OM) in a periodic arrangement. If the magnetic moments are aligned in one dimension, the material is FM and has a net crystal moment. The direction of the magnetic moment may vary, resulting in FM (111), (011), or (001) states in the crystal. If the magnetic moments are opposed, the material is AFM and no net magnetic moment exists. The implications of noncollinearity in the DM and FM states are irrelevant. In the propagation vector formalism, contributions can be combined from a number of symmetry-related wavevectors. These are termed multi-k structures. In the following, 1k (one wave-vector), 2k (two independent wave-vectors), or 3k (three independent wave-vectors) structures have been considered (Figure 5.3). The magnetic domain (longitudinal or transverse) is defined by the order of moments. A phase transition at the Curie temperature is FM; whereas, a phase transition at the Néel temperature is AFM.

If the opposing magnetic moments on the ions are unequal, the material is FI and the crystal has a net magnetic moment. If the magnetic moments are decoupled, the material is PM and there is no ordered distribution. The net magnetic moment of the crystal (by law of averages)
remains zero. An ion with a magnetic moment is also termed PM in isolation. A low-temperature FI (as the magnetic moment of the An$^{4+}$ ions are equal) or PM (an excited state only formed by thermal excitations) state has not been considered.

The manifestation of metastable states and the juxtaposition of energy levels makes the determination of the magnetic ground-state challenging. The crystal structure is coupled by SOI(13) to the magnetic state. In the high-temperature PM state, the $Fm\overline{3}m$ (No. 255) crystal structure is stabilized by the intrinsic magnetic disorder. At low-temperature, due to an imbalance of magnetic forces, the ordered FM and AFM configurations can result in a crystallographic distortion. The nature of the crystallographic distortion and its exact relation to the magnetic state is unknown. The extent of the disruption is dependent upon the magnitude of the magnetic forces within the crystal.

Low-temperature measurements of the AnO$_2$ magnetic ground-state are extremely challenging, due to thermal energy generated by the radioactive decay of the actinide nuclei.(14) In addition, actinide compounds are highly sensitive to chemical impurities and environmental conditions.(15-21) This is due to the radial extent of the elements’ $f$-orbitals. For instance, the band structure is sensitive to the degree of $f$-orbital overlap, which is highly influenced by the interatomic lattice spacing. In addition, international safeguards governing the handling of and access to nuclear materials have hindered experimental investigation.(22) These regulations are designed to limit the risk of nuclear proliferation through access restriction. Additional impediments to experimental research on actinide compounds arise from the health and safety hazards associated with radiogenic materials.(23) To circumvent these issues, computational methods offer another mode of study.

A computational investigation of AnO$_2$ systems is also incredibly complicated, due to the treatment of exchange-correlation, relativistic influences, and complex magnetic structures. An incorrect electronic structure (for highly correlated $f$-electron systems) is calculated by conventional DFT(24, 25) methods.(26, 27) To calculate highly correlated materials, numerous methods offer a correction to the self-interaction error. These include the self-interaction correction (SIC) method,(28) modified density functional theory (DFT+U),(24, 25, 29-31) dynamic mean field theory (DMFT),(32) the Korringa–Kohn–Rostoker Green function (KKR-GF),(33-35) and hybrid density functionals.(36-38) In condensed matter physics, the DFT+U method offers a computational tractable means of study. The on-site Coulomb repulsion of the $f$-electrons is treated in DFT+U by tuneable U and J modifiers. The ground-state characteristics
of f-electron compounds can be captured by DFT+U when SOI are included.\(^{(39)}\) In comparison, a computationally tractable (though highly expensive) and thorough hybrid functional method can also be used. The computationally intense nature of DMFT+U (which can incorrectly calculate the early AnO\(_2\) as charge-transfer insulators) has been highlighted by numerous authors.\(^{(1, 40-42)}\)

The computational expense of AnO\(_2\) systems has limited their investigation. The majority are restricted to discussions of collinear 1k magnetism.\(^{(3, 4, 26, 27, 38, 43-53)}\) The low-temperature AnO\(_2\) show noncollinear 3k AFM or PM behaviour;\(^{(22, 54-61)}\) A low-temperature ordered magnetic state can result in a crystallographic distortion.\(^{(2, 10, 62, 63)}\) A transverse 3k AFM order (in UO\(_2\)) results in \(P\bar{a}3\) symmetry; whereas, a longitudinal 3k AFM order (in neptunium dioxide, NpO\(_2\)) or DM order (in plutonium dioxide, PuO\(_2\)) retains \(Fm\bar{3}m\) symmetry. As the crystal structure is coupled by SOI to the magnetic state, it is imperative to incorporate relativistic influences when creating computational models. Although a limited number of investigations fully consider noncollinear relativistic contributions.\(^{(27, 40, 46, 51-53, 62, 64, 65)}\)

The magnetic structure of AnO\(_2\) is key to the design of quantum mechanical models. The exact nature of the magnetic ground-state is uncertain. A fully relativistic noncollinear investigation of magnetic order has been conducted for the first time. To study the complex electronic structure by computational methods one must consider: exchange-correlation influences, relativistic contributions, and noncollinear magnetic behaviour. The noncollinear interactions that have been studied are illustrated (Figure 5.3). The relative energetics of the magnetic states have been calculated and contrasted against other systems. To design a computational model from which further properties can be extrapolated, the performance of numerous exchange-correlation DFT functionals has been evaluated.

### 5.1.1 Literature Review

The magnetic ground-state of UO\(_2\) impacts the design of computational models. The magnetic ground-state of the U\(^{4+}\) ion is a \(^3H_4\) (\(\Gamma_5\) triplet) multiplet (from the Russel-Saunders (low-spin) coupling scheme).\(^{(8, 9, 64)}\) Low-temperature measurements of \((U_{1-x}Th_x)O_2\) confirm a \(\Gamma_5\) triplet magnetic ground-state.\(^{(66)}\) A discontinuous first-order phase transition at the Néel temperature.
(T_N = 30.8 K) has been established by: magnetic susceptibility (a measure of a materials response in an applied field), heat capacity, and neutron diffraction measurements. Initial neutron diffraction measurements identified: a collinear 1k AFM ground-state, and a homogeneous lattice distortion. An internal distortion of the O^2- ions by the Jahn-Teller theorem has been considered; however, no evidence for a reduction in the external cubic crystal symmetry has been found. As a result of the internal O^2- distortion, a noncollinear 2k AFM ground-state was latter inferred.

An internal crystallographic Pα3̅ (No. 205) distortion (indicative of transverse 3k AFM order) has been confirmed by: low-temperature neutron diffraction, and X-ray diffraction measurements. The displacement of the O^2- ions is 0.014 Å. In a number of experimental studies, a transverse 3k AFM ground-state has been inferred from: inelastic neutron scattering (INS), resonant X-ray scattering (RXS), and nuclear magnetic resonance (NMR) measurements. By minimising quadrupolar and exchange terms, antiferroquadrupolar ordering with Pα3̅ (No. 205) crystal symmetry is favoured. An ordered effective U⁴⁺ magnetic moment of 1.74 μ_B/U⁴⁺ ion by neutron diffraction measurements has been established. To computationally model UO_2 condensed matter physics, a transverse 1k AFM state with Fm3̅m (No. 225) cubic symmetry is often used. The model contradicts experimental measurements; a transverse 3k AFM ground-state with Pα3̅ (No. 205) cubic symmetry has been confirmed. In terms of the electronic structure, the f-f Mott-Hubbard insulating character of UO_2 with a band-gap of 2.00-2.50 eV has been established by: optical adsorption, X-ray adsorption (XAS), X-ray photoemission (XPS), bremsstrahlung isochromatic spectroscopy (BIS), resonant photoemission spectroscopy (RPES), and inverse photoemission spectroscopy (IPES). The magnetic ground-state of NpO_2 is highly-complex. In crystal-field theory, the Np⁴⁺ ion results in the 4^I9/2 (Γ_8 quartet) configuration. Indeed, the tetravalent f^3 nature of the Np⁴⁺ ion has been confirmed by Mossbauer isomer shift spectroscopy. At low-temperature, a first-order AFM phase transition at T = 25.4 K has been indicated by magnetic susceptibility and specific heat capacity measurements. In addition, a longitudinal 3k AFM ground-state coupled to Fm3̅m (No. 225) crystal symmetry has been inferred from resonant X-ray scattering (10 K < T < 17 K) and 17O NMR measurements (T = 17 K).
an external distortion of the cubic cell further indicates non-collinear 3k AFM behaviour. (61) In contrast, low-temperature Mossbauer (T = 1.5 K) (98) and neutron diffraction measurements (12 K < T < 30 K) (101) have failed to identify a magnetic moment. The upper limit for the magnetic moment set by muon spin rotation measurements (0.3 K < T < 25.4 K) is 0.06-0.15 μB/Np⁴⁺ ion. (2, 102) whereas the upper limit for the magnetic moment set by Mössbauer spectroscopy is 0.01 μB/Np⁴⁺ ion. (98) The absence of a measurable local magnetic moment is inconsistent with the idea of magnetic order and the nature of the small-moment AFM state is unresolved. (2) As a Kramers ion, i.e. an ion with an uneven number of valence electrons, the ground Np⁴⁺ state should order magnetically in the absence of interactions that break time-reversal symmetry conditions. A mechanism by which the magnetic moment of the Np⁴⁺ ion can be suppressed is AFM super-exchange. (2) which is the coupling between moment-bearing cations via nominally DM anions. (103, 104)

The inhomogeneous nature of NpO₂ samples has hindered experimental investigation. (61, 105) For instance, the extreme difficulty in manufacturing large single-crystal samples impacts the search for low-temperature crystallographic distortions. (61, 106) In the past, the detection threshold of neutron diffraction measurements has been limited to 0.02-0.03 Å. (2) By comparison, crystallographic distortions of isostructural UO₂ are of the order of 0.01-0.02 Å. (10) In a search for low-temperature anharmonic effects in NpO₂ by neutron diffraction (12 K < T < 30 K) (101) and in an independent RXS (9 K < T < 25 K) study, (61) no evidence of a dynamical distortion of the O²⁻ ions has been found. However, Mossbauer spectroscopy of NpO₂ has indicated an internal O²⁻ ion distortion inferred by the small broadening of spectroscopic lines. (98) In addition, inelastic neutron scattering (INS) studies (107, 108) indicate an internal O²⁻ ion distortion of 0.02 Å, which is reminiscent of the internal O²⁻ ion distortion in UO₂. The internal O²⁻ ion distortion may result in Pa3̅ (No. 205) crystal symmetry that is indicative of transverse 3k AFM behaviour, although this has yet to be experimentally confirmed.

The upper-limit of the magnetic moment (0.01-0.10 μB/Np⁴⁺ ion) indicates that NpO₂ is a small-moment system. (61, 98) To our knowledge, small moments have only been identified in heavy-fermion metals (109-111) and has yet to be identified in insulators. In this regard, computational investigations of plutonium dioxide (PuO₂) have inferred the possibility of an unconfirmed small-moment insulating magnetic ground-state. (112) A number of DFT calculations have indicated an AFM ground-state, which contrasts with the DM state established by experimental
methods. (113-116) The magnetic ground-state of NpO₂ remains unresolved. The mechanisms behind the intriguing electronic states are not yet fully understood.

The low-temperature magnetic structure of PuO₂ remains an enigmatic issue. (2) A controversy exists between experimental and theoretical methods. In the Russell-Saunders coupling scheme, under the cubic crystal-field, the degeneracy of the $^5I_4$ multiplet is split into ascending $\Gamma_1 (1)$, $\Gamma_4 (3)$, $\Gamma_3 (2)$, and $\Gamma_5 (3)$ crystal-field levels (the number in the parentheses denotes the degeneracy). (64, 65, 113) The calculated singlet $\Gamma_1$ ground-state to triplet $\Gamma_4$ excited state transition is 123 meV as measured by neutron inelastic scattering. (117) The crystal-field model is technically only valid for the one-electron case; nevertheless, the DM state inferred by experiment is often justified by crystal-field theory. (22, 114-117) A number of computational investigation conflict with experimental result. In addition, a FM or an AFM ground-state has been calculated. (3, 4, 26, 27, 38, 43-53) The magnetic ground-state impacts the basic models of reactivity, the design of surface models, and the interaction of adsorbents by influencing the electronic structure. Noncollinear contributions to PuO₂ magnetic order have remained uninvestigated.

A low-temperature characterisation of the PuO₂ magnetic ground-state is highly challenging. This is due to nucleonic radioactive decay, (118) the toxicity of the metals, (119) and the inhomogeneity of samples. (22) A singlet $\Gamma_1$ DM ground-state (in accordance with the one-electron crystal-field model) has been inferred by: magnetic susceptibility ($T = 4$ K), (115) INS ($T > 30$ K), (114, 117) and NMR ($T > 4$ K) (22, 116) measurements. Although a number of inconsistences in the literature have been recorded, (10) The temperature-independent magnetic susceptibility of PuO₂ ($5.4 \times 10^{-4}$ cm³·mol⁻¹) indicates a singlet $\Gamma_1$ DM ground-state; (2) whereas, the temperature-dependent magnetic susceptibility of Th$_{1-x}$Pu$_x$O₂ ($-1.1 \times 10^{-3}$ cm³·mol⁻¹) illustrates a magnetic response that is inconsistent with earlier results. (120) In addition, INS measurements of PuO₂ show a singlet $\Gamma_1$ to triplet $\Gamma_4$ transition of 123 meV; this corresponds to a temperature-dependent magnetic susceptibility of $\sim 1 \times 10^{-3}$ cm³·mol⁻¹ when $T > 400$ K.

The magnetic coupling of proximal cations by intermediary DM anions is described by magnetic superexchange. (103, 104) The full width at half maximum (FWHM) INS peak of 25 meV is indicative of AFM superexchange. (2, 113) The magnetic susceptibility measurements of U$_{1-x}$Pu$_x$O₂ also indicates AFM superexchange with high concentrations of plutonium. (121) Low-temperature $^{17}$O NMR measurements of PuO₂ result in an apparent DM state at 6 K. Low-temperature measurements of U$_{1-x}$Pu$_x$O₂ indicate a Néel temperature of under 5 K for when x
It is conceivable that lower temperatures may result magnetic ground-state that are unknown. A number of experimental measurements on PuO$_2$ report $Fm\bar{3}m$ (No. 225) crystal symmetry. A study of low-temperature ($T < 30.8$ K) lattice anomalies (reminiscent of transverse 3k AFM behaviour in UO$_2$ with $Pa\bar{3}$ (No. 205) crystal symmetry) remains uninvestigated. As a key computational consideration, the SOI (which couples the lattice structure to the magnetic state) is fully considered in this study.

In contrast to experimental measurements, computational studies have calculated order magnetic ground-states. To justify the computational result, inherent DFT approximation have been used. A number of studies have focused on the DM ground-state solution. Those investigations that do report on an ordered magnetic ground-state limit themselves to discussion of collinear 1k magnetism. Of these studies, due to the high computational cost, few incorporate SOI into their calculations. This is absolutely necessary and critically important for the treatment of the actinide elements. The high nuclear charge causes the electrons in the inner $s$- and $p$-orbitals to contract. The consequent increase in nuclear shielding causes the outer $d$- and $f$-orbitals to become more diffuse. This influences the degree of orbital overlap and impacts interatomic bonding interactions. In addition to general complications associated with highly correlated systems, the magnetic ground-state of the AnO$_2$ are influenced by superexchange, multipolar and noncollinear interactions.

In another study, by correcting the exchange-correlation errors common to DFT, the complete active space (CAS) wavefunction method calculates a DM ground-state. A limitation of the embedded cluster method, however, is that the quantum cluster may not be sufficiently large enough to capture the superexchange interactions in PuO$_2$, and therefore the findings are incomplete. In addition, the ground-state electronic structure and crystal-field levels of PuO$_2$ have been calculated by DFT in terms of the total energy difference. The total energy of the crystal-field states are calculated by the Clebsch-Gordon method from a standard model of rare-earth elements and as a function of their single-electron components. The calculated ground $\Gamma_1$ state-excited $\Gamma_4$ state transition of 99 meV compares with the measured INS result of 123 meV.
5.2 Computational Methodology

5.2.1 Calculation Details

A noncollinear relativistic computational study of the AnO$_2$ magnetic structure by the Vienna Ab-initio Simulation Package (VASP) code has been conducted.(28, 32, 125) The code employs relativistic effective core potentials (ECPs), the frozen-core projector-augmented wave (PAW) method(37, 126) and a planewave basis set. The cut-off energy of the planewave basis set is 500 eV. The following explicit electrons for each atomic species are considered: uranium (6$s^2$, 7$s^2$, 6$p^6$, 6$d^5$ 5$f^2$), neptunium (6$s^2$, 7$s^2$, 6$p^6$, 6$d^5$ 5$f^3$), plutonium (6$s^2$, 7$s^2$, 6$p^6$, 6$d^2$ 5$f^4$) and oxygen (2$s^2$, 2$p^4$). The ion-electron interaction considers spin-orbit interactions (SOI)(13) and noncollinear magnetic wave vectors. Ionic forces are evaluated via the Hellmann-Feynman theorem(127) and conjugate gradient algorithm.(128) The space group has been evaluated to 10$^{-5}$ Å based on a symmetry analysis of the unit cell.

As a computationally intensive method, the hybrid (HSE06) functional has been employed. The integration over the Brillouin zone has been completed by the conventional Gaussian method with a Γ-centred 4·4·4 k-point mesh.(129, 130) The iteration threshold for electronic and ionic convergence is 1x10$^{-6}$ eV and 1x10$^{-2}$ eV Å$^{-1}$, respectively.

![Figure 5.4: The total energy of the AnO$_2$ as a function of: a) the cut-off energy, b) the k-point grid. The cut-off energy has been calculated with a 5·5·5 k-point grid; whereas the k-point grid has been calculated with a cut-off energy of 500 eV. The UO$_2$ (Red), NpO$_2$ (Blue) and PuO$_2$ are indicated by the couleurs in the parentheses. The experimental UO$_2$ (transverse 3k AFM, $U = 3.35$ eV, $J = 0.00$ eV), NpO$_2$ (longitudinal 3k AFM, $U = 5.00$ eV, $J = 0.75$ eV), and PuO$_2$ (DM, $U = 6.35$ eV, $J = 0.00$ eV) states and theoretical UO$_2$ (transverse 1k AFM, $U = 3.50$ eV, $J = 0.00$ eV), NpO$_2$ (transverse 3k AFM, $U = 4.25$ eV, $J = 0.00$ eV) and PuO$_2$ (longitudinal 3k AFM, $U = 6.00$ eV, $J = 0.00$ eV) states are indicated in the parentheses.]
An f-electrons. The correction of the electron self-interaction error (SIE) implicit in DFT calculations, is treated by the rotationally invariant Liechtenstein et al(30) formalism. In the rotationally invariant Liechtenstein et al(30) formalism, the on-site Coulombic (U) and exchange (J) modifiers are treated as independent variables. The constraints are applied to the f-orbitals of the actinides. The integration over the Brillouin zone has been completed by the Blöchl tetrahedron method with a \(\Gamma\)-centred 5·5·5 k-point mesh. The iteration threshold for electronic and ionic convergence is 1×10^{-8} eV and 1×10^{-3} eV·Å^{-1}, respectively. A converge cut-off energy and k-point mesh PBEsol+U test (for the experimental and theoretical magnetic ground-states) has been completed (Figure 5.4).

In the optical absorbance calculations, the k-point mesh is 15·15·15. In the band structure calculations, the \(Fmmm\) (No. 69) (Γ→Y→X→Z→Γ→L), \(Pa\bar{3}\) (No. 205) (Γ→M→R→X→Γ→R) and \(Fm\bar{3}m\) (Γ→L→W→X→Γ) k-point pathway is defined in the parentheses. The exchange-correlation energy is evaluated with: the local density approximation (LDA), Perdew-Burke-Ernzerhof (PBE), the Armiento-Mattsson (AM05), and the revised Perdew-Burke-Ernzerhof for solids (PBEsol) functionals.

### 5.2.2 Magnetic Structure

The manifestation of metastable states and the juxtaposition of energy levels makes the determination of the magnetic ground-state challenging. The magnetic structure of the AnO\(_2\) have been calculated from a number of configuration (Table 5.1)

#### Table 5.1: The wavevectors for the ordered magnetic states.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ferromagnetic</th>
<th>Antiferromagnetic</th>
<th>(Transverse Domain)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(001)</td>
<td>(011)</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>(000)</td>
<td>(100)</td>
<td>(010)</td>
</tr>
<tr>
<td></td>
<td>(010)</td>
<td>(001)</td>
<td>(100)</td>
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<td></td>
<td>(001)</td>
<td>(010)</td>
<td>(001)</td>
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<tr>
<td></td>
<td>(010)</td>
<td>(001)</td>
<td>(100)</td>
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<tr>
<td></td>
<td>(100)</td>
<td>(001)</td>
<td>(010)</td>
</tr>
<tr>
<td></td>
<td>(100)</td>
<td>(001)</td>
<td>(100)</td>
</tr>
<tr>
<td></td>
<td>(010)</td>
<td>(001)</td>
<td>(010)</td>
</tr>
</tbody>
</table>
The magnetic wavevectors are directed along the main axes of the crystal unit cell. By implementing the Pythagorean theorem, final magnetic moment of each ion is calculated (Equation 5.1).

\[
||\mu||^2 = \sum_{k=1}^{3} ||\mu_k||^2
\]

The magnitude of the vector (\(\mu\)) is calculated from its orthogonal (\(\mu_k\)) components. To access the noncollinear 2-3k AFM states, SOI one must be considered.

5.3 Results & Discussions

5.3.1 Uranium Dioxide

5.3.1.1 Magnetic Structure

The electronic and crystallographic nature of UO₂ is influenced by the magnetic state. An energetically degenerate transverse 1-2k AFM HSE06 ground-state has been calculated (Table 5.2). The initial DM HSE06 state is unstable. A metastable, highly-energetic, and weakly FM configuration (0.85 \(\mu\)B/U ion) has been identified. A comparatively insignificant low-index FM and AFM state (1.42-1.53 \(\mu\)B/U ion) energy difference has been found. In relation to the experimental transverse 3k AFM ground-state, the FM (001), FM (111), longitudinal 1k AFM, and transverse 1-2k AFM states are marginally lower in energy by -0.01 eV·formula unit⁻¹.

A band-gap of 2.42-2.57 eV (for the low-index FM states) and 2.82-3.02 eV (for the AFM states) has been calculated. This is considerably higher than current experimental measurements. In contrast with experimental studies indicating \(P\alpha\overline{3}\) crystal symmetry, an actinide \(Fmmm\) (No. 69) or \(Pbca\) (No.61) crystallographic distortion for the transverse 1-2k AFM states has been found.(60) It is noted that the transverse 1k AFM state is consistent with experimental static and low-frequency dynamical magnetic measurements.(2) To isolate the magnetic ground-state, the relative energetics of competing magnetic phases have been
calculated with PBEsol+U, where the magnitude of the U influences the relative energetics of the magnetic states (Figure 5.5). In contrast with hybrid HSE06 calculations, the PBEsol+U DM state is stable. As a physically unrealistic system, the DM state is considerably higher in energy. In these calculations the metallic FM (111) ground-state, calculated by PBEsol (U = 0 eV), is inconsistent with the experimental data.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Relative Energy (eV)</th>
<th>Band-gap (eV)</th>
<th>Magnetic Moment (μB/U ion)</th>
<th>Lattice Volume (Å³)</th>
<th>Space Group (Number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic</td>
<td>0.659</td>
<td>1.75</td>
<td>0.85</td>
<td>161.70</td>
<td>Fm̅m (No. 225)</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>0.010</td>
<td>2.42</td>
<td>1.53</td>
<td>162.78</td>
<td>4/mmm (No. 139)</td>
</tr>
<tr>
<td>(011)</td>
<td>0.026</td>
<td>2.62</td>
<td>1.45</td>
<td>162.81</td>
<td>4/mmm (No. 71)</td>
</tr>
<tr>
<td>(111)</td>
<td>0.012</td>
<td>2.57</td>
<td>1.44</td>
<td>162.60</td>
<td>3/m (No. 166)</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.006</td>
<td>2.79</td>
<td>1.51</td>
<td>162.63</td>
<td>4/mmm (No. 139)</td>
</tr>
<tr>
<td>2k</td>
<td>0.019</td>
<td>2.88</td>
<td>1.43</td>
<td>162.48</td>
<td>4/mmm (No. 139)</td>
</tr>
<tr>
<td>3k</td>
<td>0.023</td>
<td>2.82</td>
<td>1.42</td>
<td>162.47</td>
<td>Fm̅m (No. 225)</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.000</td>
<td>3.02</td>
<td>1.49</td>
<td>162.53</td>
<td>Pmmm (No. 69)</td>
</tr>
<tr>
<td>2k</td>
<td>0.000</td>
<td>3.02</td>
<td>1.49</td>
<td>162.55</td>
<td>Pbcn (No. 61)</td>
</tr>
<tr>
<td>3k</td>
<td>0.014</td>
<td>2.99</td>
<td>1.43</td>
<td>162.57</td>
<td>Pa3 (No. 205)</td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
<td>2.00-2.50(58,138)</td>
<td>1.74(58,59,70)</td>
<td>163.85(58,70)</td>
<td>Pa3 (No. 205\textsuperscript{pin})</td>
</tr>
</tbody>
</table>

A metallic conductor is calculated for UO\textsubscript{2} when U = 0 eV (illustrating the failure of DFT to account for the highly localised character of the 5f electrons). The insulating nature of UO\textsubscript{2} (described by experiment) has been calculated for U = 3-4 eV. The introduction of the U modifier results in an AFM ground-state immediately. The exact nature of the AFM ground-state is influenced by the U constraint. A degenerate longitudinal 2-3k AFM and transverse 1-3k AFM ground-state is formed when U = 1-7 eV.

The low-temperature crystal structure of UO\textsubscript{2} shows Pa\textsuperscript{3} crystal symmetry indicated by neutron scattering and X-ray diffraction measurements.\textsuperscript{(60)} In these calculations, transverse 3k AFM Pa\textsuperscript{3} crystal symmetry has been identified. This is consistent with experimental information.\textsuperscript{(55, 60, 73, 78)} In addition, transverse 1k AFM with Fmmm (No. 69) orthorhombic symmetry has been identified; whereas, longitudinal 1k AFM state with I4/mmm (No. 139) tetragonal symmetry has been identified. The collinear 1k AFM states (an invalid interpretation of the low-temperature magnetic structure) influence the calculation of the material. This impacts: surface structure, crystal morphologies, and catalytic activity. The
The magnetic moment of UO$_2$ is 1.74 μB/U ion, reported by neutron diffraction measurements. In these calculations, the magnetic moment of UO$_2$ is underestimated by DFT+U and the hybrid HSE06 functional with the closest approximation obtained by the FM (111) states. In terms of the lattice volume, no discernible change is detected between the ordered magnetic states, but the lattice volume is considerably lower in the DM state.

Figure 5.5: The relative ground-state energies, band-gaps, and effective magnetic moments against the Coulomb modifier (U) for diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states of UO$_2$, calculated with PBEsol+U. The antiferromagnetic transverse (T) and longitudinal (L) domains are additionally represented. The k-prefix denotes the number of independent wave vectors: upper row) the calculated energy of magnetic states relative to the transverse 3k antiferromagnetic ground-state; middle row) the direct band-gap; lower row) the effective $U^{4+}$ magnetic moment. The DM (yellow), FM (Red), longitudinal AFM (Green) and transverse AFM (Blue) states are denoted by the colours in the parentheses.
5.3.1.2 DFT+U Constraints

A number of DFT functionals modelling the UO$_2$ system has been investigated. These include the transverse 3k AFM (experimental) and transverse 1k AFM (theoretical) states (Figure 5.6). Identical trends are observed for the magnetic states. The insulating nature of UO$_2$ is calculated when $U = 3.00$-$4.00$ eV for all functionals. In this range, only AM05/PBEsol emulate the experimental lattice constant. In contrast, the lattice constant is calculated by PBE when $U = 2$ eV and LDA when $U = 6$ eV. This gives a poor representation of the electronic structure. In addition, the magnetic U$^{4+}$ moment is underestimated by all functionals. In the calculation of the magnetic moment, the PBE functional offers the closest comparison with the experimental data. In general, the choice of PBEsol is validated for the reproduction of the band-gap, lattice constant and magnetic moment.

![Graphs showing DFT+U performance](image)

*Figure 5.6: The performance of DFT+U functionals in UO$_2$ for: upper row) transverse 3k AFM order, lower row) transverse 3k AFM order. The performance of the DFT+U functional is characterised against the: left column) band-gap, middle column) lattice constant, right column) effective magnetic U$^{4+}$ moment. Results are generated from the transverse 3k AFM ground-state.*
The influence of J on the PBEsol functional for the UO₂ system has been investigated for the: transverse 3k AFM (experimental) and transverse 1k AFM (theoretical) states (Figure 5.7). As with the assessment of functional performance, changes to the magnetic structure offer no important changes. The introduction of J has minimal impact on the band-gap and the lattice constant. In contrast, the introduction of J detrimentally reduces the effective magnetic U⁴⁺ moment. It is therefore favourable to omit J from further calculations.

![Figure 5.7: The influence of exchange (J) on PBEsol+U calculations of UO₂: upper row) transverse 3k AFM order, lower row) transverse 3k AFM order. The performance of the DFT+U functional is characterised against the: left column) band-gap, middle column) lattice constant, right column) effective magnetic U⁴⁺ moment. Results are generated from the transverse 3k AFM ground-state.](image)

### 5.3.1.3 DFT+U Electronic Structure

The electronic structure of the UO₂ system is modelled by the PBEsol functional (Figure 5.8). The transverse 3k AFM (U = 3.35 eV, J = 0.00 eV) and transverse 1k AFM (U = 3.50, J = 0.00 eV) states are modelled by the terms in the parentheses. The modifiers are consistent with past investigations. In contrast, a constrained random phase approximation (cRPA) model of the
collinear 1k AFM state calculated $U = 5.70 \text{ eV}$ and $J = 0.40 \text{ eV}$ modifiers. In respect to past DFT+U investigations, these values are considerably higher.

Figure 5.8: The electronic structure of UO$_2$ calculated by PBEsol for the: upper) experimental transverse 3k AFM state ($U = 5.00 \text{ eV}, J = 0.75 \text{ eV}$); lower) theoretical transverse 1k AFM state ($U = 4.25 \text{ eV}, J = 0.00 \text{ eV}$). In the band structure, the valence bands are coloured blue; whereas, the conduction bands are coloured orange. In the density of states, the colours in the parentheses indicate the $Uf$- (blue), $Ud$- (green) and O$p$- (red) states.

The optical absorbance, band structure and density of states has been calculated. The fundamental (ideal) band-gap (the difference between the ionisation potential and the electron affinity, the valence band maximum (VBM) to conduction band minimum (CBM) transition) and optical band-gap (electronic transitions are restricted by orbital symmetry) are influenced by the magnetic state. An objective experimental PM band-gap is therefore not directly comparable. A considerable range of materials illustrate how the band-gaps can differ: In$_2$O$_3$, AgCuS, PbO$_2$, Tl$_2$O$_3$ and SrCu$_2$O$_2$. In the density of states (DoS) for both magnetic structures, the valence band maximum (VBM) and conduction band minimum (CBM) are mainly comprised of uranium $f$-states. The U $d$-states are considerably higher in energy and the impact on bonding interactions should be minor. This electronic
structure indicates that UO$_2$ is a Mott-Hubbard insulator, consistent with experimental information.

The band structure of UO$_2$ with the transverse 1k AFM ground-state results in an indirect band-gap of 2.27 eV from $\Gamma$ (VBM) to $\Gamma$-Y (CBM). In contrast, the calculated optical absorption spectra shows a band-gap of 2.49 eV and the direct band-gap and optical band-gap thus differ by 0.22 eV, although they are not strictly directly comparable. The direct band-gap defines the VBM-CBM energy difference, whereas, the optical band-gap defines the minimum allowed transition as controlled by symmetry rules. Nevertheless, the calculated band-gap and bulk modulus are in good agreement with experimental information (Table 5.3).

Table 5.3: The direct band-gap (eV), optical band-gap (eV), lattice constant (Å), bulk modulus (GPa) and magnetic moment ($\mu$/U ion) for the transverse 1k antiferromagnetic (T-1k AFM) and transverse antiferromagnetic (T-3k AFM) states of UO$_2$.

<table>
<thead>
<tr>
<th>DFT+U</th>
<th>Band-gap (eV)</th>
<th>Lattice Constant (Å)</th>
<th>Bulk Modulus (GPa)</th>
<th>Magnetic Pu$^{4+}$ Moment ($\mu$/ion$^{-1}$)</th>
<th>Crystal Symmetry</th>
<th>Magnetic State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$ (eV)</td>
<td>$J$ (eV)</td>
<td>Ideal</td>
<td>Optical</td>
<td>210</td>
<td>1.42</td>
<td>$Fmmmm$ (69)</td>
</tr>
<tr>
<td>3.50</td>
<td>0.00</td>
<td>2.77</td>
<td>2.49</td>
<td>5.476</td>
<td>210</td>
<td>1.35</td>
</tr>
<tr>
<td>3.35</td>
<td>0.00</td>
<td>2.06</td>
<td>2.20</td>
<td>5.474</td>
<td>210</td>
<td>1.74</td>
</tr>
</tbody>
</table>

The band structure of UO$_2$ for the transverse 3k AFM state results in an indirect $\Gamma$ (VBM) to R (CBM) band-gap of 2.06 eV. A band-gap of 2.20 eV is calculated from the optical absorbance. This results in a 0.14 eV difference between the direct and optical band-gaps; however, both are in good agreement with experimental information. Finally, the calculated bulk modulus of 210 GPa is in excellent agreement with experimental data.

5.3.2 Neptunium Dioxide

5.3.2.1 Magnetic Structure

In this part for NpO$_2$, the relative energetics for each magnetic state, the band-gap, the Np$^{4+}$ magnetic moment, and the crystal structure have been calculated. Note, however, that due to the $f^6$ nature of the Np$^{4+}$ Kramers ion, the DM configuration is physically unrealistic. In these hybrid functional HSE06 calculations, the transverse 3k AFM state is only 0.002 eV · formula unit$^{-1}$ higher in energy than the FM (111) ground-state (Table 5.4). The transverse 3k AFM state results in $P\overline{4}$3 (No. 205) crystal symmetry, which satisfies observations of non-collinear
magnetic behaviour and the inferred internal crystallographic distortion; however, the magnetic moment is anomalously high and does not fit the picture of a small-moment AFM state. As with UO$_2$ and PuO$_2$, the magnetic structure of NpO$_2$ is coupled by SOI to the crystal symmetry. The low-temperature crystal structure of NpO$_2$ is unresolved, thus far $Pa\overline{3}$ (No. 205) and $Pn\overline{3}m$ (No 224) structures have been inferred by RXS measurements.(147)

Table 5.4: The Relative Energy (eV), Band-gap (eV), Magnetic Moment (μB/Np ion), Lattice Volume (Å$^3$) and Space Group (number) for each NpO$_2$ Magnetic Configuration, Calculated by the HSE06 Functional. The Energetics of the Magnetic Configurations are Calculated Relative to the Ferromagnetic (111) Ground-state.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Relative Energy (eV)</th>
<th>Band-gap (eV)</th>
<th>Magnetic Moment (μB/Np ion)</th>
<th>Lattice Volume (Å$^3$)</th>
<th>Space Group (Number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetic</td>
<td>(001) 0.081</td>
<td>2.65</td>
<td>2.63</td>
<td>158.74</td>
<td>$I/mmm$ (No. 139)</td>
</tr>
<tr>
<td></td>
<td>(011) 0.017</td>
<td>2.65</td>
<td>2.63</td>
<td>158.85</td>
<td>$Immm$ (No. 71)</td>
</tr>
<tr>
<td></td>
<td>(111) 0.000</td>
<td>2.42</td>
<td>2.67</td>
<td>158.82</td>
<td>$R\overline{3}m$ (No. 166)</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td>1k 0.079</td>
<td>2.65</td>
<td>2.60</td>
<td>158.78</td>
<td>$I/mmm$ (No. 139)</td>
</tr>
<tr>
<td></td>
<td>2k 0.083</td>
<td>3.14</td>
<td>2.52</td>
<td>158.69</td>
<td>$I/mmm$ (No. 139)</td>
</tr>
<tr>
<td></td>
<td>3k 0.004</td>
<td>2.88</td>
<td>2.64</td>
<td>158.69</td>
<td>$Pn\overline{3}m$ (No. 225)</td>
</tr>
<tr>
<td>Transverse</td>
<td>1k 0.064</td>
<td>3.26</td>
<td>2.55</td>
<td>158.74</td>
<td>$Pmmn$ (No. 69)</td>
</tr>
<tr>
<td></td>
<td>2k 0.001</td>
<td>3.20</td>
<td>2.64</td>
<td>158.79</td>
<td>$Pbcn$ (No. 61)</td>
</tr>
<tr>
<td></td>
<td>3k 0.002</td>
<td>3.20</td>
<td>2.64</td>
<td>158.71</td>
<td>$Pa\overline{3}$ (No. 205)</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>2.85-3.10$^{148, 149}$</td>
<td>$\pm 0.01-0.10^{91, 90}$</td>
<td>159.84$^{61}$</td>
<td>$Pm\overline{3}m$ (No. 225)$^{62}$, $Pa\overline{3}$ (No. 205)$^{107, 108}$</td>
</tr>
</tbody>
</table>

The magnetic ground-state has also been investigated by the PBEsol+U functional (Figure 5.9). The trigonal distortion of the unit cell for the PBEsol FM (111) $R\overline{3}m$ (No. 166) ground-state is inconsistent with current experimental data. A number of experimental investigations have indicated an AFM ground-state, although the nature of the magnetic moment has thus far not been determined. No evidence of a trigonal crystallographic distortion has been reported, but non-collinear 3k AFM behaviour has been identified, where the domain is unresolved.$^{(56, 61, 108, 147, 150)}$ In these calculations, only the non-collinear 3k AFM states result in cubic symmetry. The transverse 3k AFM state is marginally lower in energy than the longitudinal 3k AFM state, with the external cubic symmetry retained in both cases.

The electronic structure of NpO$_2$ is influenced by the magnetic state. The band-gap, as measured by optical absorbance of NpO$_2$ epitaxial thin films, is 2.85 eV.$^{(148)}$ In these calculations, the correct insulating nature of NpO$_2$ is reproduced when $U = 4-6$ eV for all magnetic states. In this range, the relative energy differences between the longitudinal 3k AFM, transverse 2-3K AFM, and the FM (111) states are minimal.
Figure 5.9: The relative ground-state energies, band-gaps, and effective magnetic moments against the Coulomb modifier (U) for diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states of NpO$_2$, calculated with PBEsol+U. The antiferromagnetic transverse (T) and longitudinal (L) domains are additionally represented. The $k$-prefix denotes the number of independent wave vectors: upper row) the calculated energy of magnetic states relative to the transverse 3$k$ antiferromagnetic ground-state; middle row) the direct band-gap; lower row) the effective Np$^{4+}$ magnetic moment. The FM (Red), longitudinal AFM (Green) and transverse AFM (Blue) states are denoted by the colours in the parentheses.

The longitudinal 3$k$ AFM state results in $Fm\bar{3}m$ (No. 225) symmetry, which is supported by RXS measurements. In contrast, the transverse 3$k$ AFM state results in $Pa\bar{3}$ (No. 205) symmetry, characterised by an internal O$^{2-}$ distortion of 0.011 Å. The distortion is equal to that implied by Mossbauer spectroscopy(98) and INS(107, 108) measurements. In theory, the non-collinear AFM domain can be established by its crystalline environment, but the distortion
cannot be confirmed as this is below the instrument resolution. In terms of the lattice volume, no discernible change between different magnetic states is observed.

As mentioned above, the magnetic moment of the Np ions is unresolved. Experimentally, the NpO$_2$ system appears to be a small-moment system, but this picture cannot be confirmed by first-principle methods. The magnetic moment in the FM states decreases from 2.77 $\mu_B$/Np ion$^{-1}$ to 2.68 $\mu_B$/Np ion$^{-1}$ when U ranges from 0-7 eV, whereas in AFM states, it increases from 2.35 $\mu_B$/Np ion$^{-1}$ to 2.71 $\mu_B$/Np ion$^{-1}$ for the same values of U = 0-7 eV. Although the calculated magnetic moment is considerably greater than the low-temperature measurement, it is consistent with that of the high-temperature PM state.

5.3.2.2 DFT+U Constraints

![Graphs showing band-gap, lattice constant, and magnetic moment for NpO$_2$]

Figure 5.10: In neptunium dioxide (NpO$_2$), the performance of the functionals measured against the: a) band-gap, b) lattice constant, c) effective magnetic Np$^{4+}$ moment. Results are generated from the longitudinal 3k AFM (experimental) and transverse 3k AFM (theoretical) ground-states.
The noncollinear AFM states are supported by experimental data. These are used to evaluate the performance of the DFT functionals (Figure 5.10). The performance of the functionals follows identical trends regardless of the magnetic state. In terms of the band-gap, as with UO\textsubscript{2} and PuO\textsubscript{2}, the choice of functional is inconsequential. The lattice constant is calculated by the terms in the parentheses for the LDA (U = 7.00 eV), PBE (U = 0.00 eV), AM05 (U = 3.00-4.00 eV) and PBEsol (U = 3.00-4.00 eV) functionals. In contrast with experimental information, the magnetic moment of the Np ion continues to be overestimated; however, LDA offers a minor improvement. In general, PBEsol offers the best calculation of the band-gap and lattice constant.

To investigate the influence of J on the system, the noncollinear 3k AFM states of NpO\textsubscript{2} are used (Figure 5.11). The calculations are performed with the PBEsol functional. The introduction of J to the NpO\textsubscript{2} system offers only a minor change to the band-gap and lattice constant. As a means of controlling the electronic structure, the introduction of J reduces the magnetic moment of the Np\textsuperscript{4+} ions in-line with experimental information. In terms of
computation, the introduction of greater U values increases the anisotropic nature of the f-
states.\textsuperscript{(64)} The introduction of J influences noncollinear magnetic systems.\textsuperscript{(151)} In the absence of J, DFT+U and HSE06 results are highly comparable. It is therefore favourable to reproduce the experimental properties by the minimum U modifier possible. This involves either the complete or partial removal of J from the system.

5.3.2.3 DFT+U Electronic Structure

No experimental information on NpO$_2$ exists to support a FM (111) ground-state. The consensus is that NpO$_2$ possesses an AFM ground-state.\textsuperscript{(61, 101, 108, 150, 152)} The electronic structure of the longitudinal 3k AFM (U = 5.00 eV, J = 0.75 eV) transverse 3k AFM (U = 4.25 eV, J = 0.00 eV) state has been calculated by the PBEsol functional (Figure 5.12).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_5.12.png}
\caption{The electronic structure of NpO$_2$ calculated by PBEsol for the: upper) experimental longitudinal 3k AFM state (U = 5.00 eV, J = 0.75 eV); lower) theoretical transverse 3k AFM state (U = 4.25 eV, J = 0.00 eV). In the band structure, the valence bands are coloured blue; whereas, the conduction bands are coloured orange. In the density of states, the colours in the parentheses indicate the Np f- (blue), Np d- (green) and O p- (red) states.}
\end{figure}
The results are consistent with experimental observations of noncollinear magnetic behaviour and the conservation of external cubic symmetry. The longitudinal 3k AFM state retains the \( Fm\bar{3}m \) crystal symmetry.\(^{(62, 64)} \) The transverse 3k AFM state results in \( Pa\bar{3} \) (No. 205) crystal symmetry with an internal \( O^2^- \) distortion of 0.011 Å. This distortion is identical to observations of \( Pa\bar{3} \) crystal symmetry in \( UO_2 \).\(^{(60)} \)

### Table 5.5: The direct band-gap (eV), optical band-gap (eV), lattice constant (Å), bulk modulus (GPa) and magnetic moment (\( \mu_B/\text{Np ion} \)) for the longitudinal 3k antiferromagnetic (L-3k AFM) and transverse antiferromagnetic (T-3k AFM) states of \( \text{NpO}_2 \)

<table>
<thead>
<tr>
<th>DFT+U</th>
<th>Band-gap (eV)</th>
<th>Lattice Constant (Å)</th>
<th>Bulk Modulus (GPa)</th>
<th>Magnetic Pu(^{4+}) Moment (( \mu_B/\text{ion} ))</th>
<th>Crystal Symmetry</th>
<th>Magnetic State</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (eV)</td>
<td>J (eV)</td>
<td>Ideal</td>
<td>Optical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>0.75</td>
<td>3.08</td>
<td>3.11</td>
<td>5.448</td>
<td>214</td>
<td>1.87</td>
</tr>
<tr>
<td>4.25</td>
<td>0.00</td>
<td>2.79</td>
<td>2.81</td>
<td>5.442</td>
<td>215</td>
<td>2.70</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.85-3.10(^{(14,140)})</td>
<td>5.427(^{(61)})</td>
<td>200(^{(5)})</td>
<td>-0.01-0.10(^{(61,98)})</td>
<td>( Fm\bar{3}m ) (225), ( Pa\bar{3} ) (205)</td>
</tr>
</tbody>
</table>

In contrast with previous investigations, the longitudinal 3k AFM state predominately results in a charge-transfer insulator.\(^{(62)} \) The charge-transfer characteristics are likely due to the absence of an \( J \) modifier that otherwise serves to reduce the effective \( \text{Np}^{4+} \) magnetic moment.\(^{(62)} \)

In the transverse 3k AFM (theoretical) state, the VMB is formed equally of oxygen \( p \)-states and neptunium \( f \)-states, indicating that \( \text{NpO}_2 \) shares both Mott and charge-transfer characteristics. In both instances, the Np \( d \)-states have no significant role in chemical bonding interactions.

The band structure of the transverse 3k AFM state reveals a direct R-centred band-gap of 2.79 eV, which compares with a calculated optical absorbance of 2.81 eV. The calculated bulk modulus of \( \text{NpO}_2 \) for the longitudinal 3k AFM state is 214 GPa, whereas the bulk modulus for the transverse 3k AFM state is 215 GPa (Table 5.5). The introduction of the \( J \) modifier reduces the magnetic moment in-line with experimental information. To calculate the band-gap, larger \( U \) values need to be introduced. The anisotropic nature of the \( f \)-states is increased by the \( U \) modifier.\(^{(64)} \) This is known to influence magnetostriction, piezomagnetic response, magnetoelectric response, and exchange bias coupling related to spin canting.\(^{(151)} \) In contrast, calculations of the magnetic moment, by PBEsol+U and HSE06, are comparable when \( J \) is ignored. Therefore, the introduction of \( J \) increases the divergence of the PBEsol+U and HSE06 results. As from a computational outlook, and given the inconsistencies noted with the experimental measurements, the absence of \( J \) is beneficial. As charge-transfer and Mott-insulating characteristics are observed, \( \text{NpO}_2 \) offers a transition point in the \( \text{AnO}_2 \) series.
Part III: Results & Discussions
Chapter 5: Condensed Matter Physics

5.3.3 Plutonium Dioxide

5.3.3.1 Magnetic Structure

In the current study, the magnetic structure of PuO$_2$ has been investigated by first-principle methods. The magnetic state clearly influences: relative energetics, band structure, magnetic moment, and crystal symmetry (Table 5.6). In hybrid HSE06 and PBEsol+U calculations, the DM state of PuO$_2$ is the highest energy magnetic configuration. In each instance, a longitudinal 3k AFM ground-state with $Fm\overline{3}m$ cubic symmetry has been calculated. The ordered FM and AFM states are ~1.00 eV·formula unit$^{-1}$ lower in energy. The finding inconsistent with current experimental information.(22, 114-117)

Table 5.6: The Relative Energy (eV), Band-gap (eV), Magnetic Moment ($\mu$/Pu$^{4+}$ ion), Lattice Volume (Å$^3$) and Space Group (number) for each PuO$_2$ Magnetic Configuration, Calculated by the HSE06 Functional. The Energetics of the Magnetic Configurations are Calculated Relative to the Longitudinal 3k Antiferromagnetic Ground-state.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Relative Energy (eV)</th>
<th>Band-gap (eV)</th>
<th>Magnetic Moment ($\mu$/U ion)</th>
<th>Lattice Volume (Å$^3$)</th>
<th>Space Group (Number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic</td>
<td>1.069</td>
<td>2.92</td>
<td>0.00</td>
<td>155.37</td>
<td>$Fm\overline{3}m$ (No. 225)</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>0.074</td>
<td>1.91</td>
<td>3.66</td>
<td>155.88</td>
<td>$I\overline{4}mnm$ (No. 139)</td>
</tr>
<tr>
<td>(011)</td>
<td>0.037</td>
<td>1.79</td>
<td>3.68</td>
<td>156.03</td>
<td>$Immm$ (No. 71)</td>
</tr>
<tr>
<td>(111)</td>
<td>0.027</td>
<td>1.68</td>
<td>3.68</td>
<td>155.99</td>
<td>$R\overline{3}m$ (No. 166)</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.058</td>
<td>2.83</td>
<td>3.63</td>
<td>155.69</td>
<td>$I\overline{4}mnm$ (No. 139)</td>
</tr>
<tr>
<td>2k</td>
<td>0.011</td>
<td>3.05</td>
<td>3.65</td>
<td>155.65</td>
<td>$I\overline{4}mnm$ (No. 139)</td>
</tr>
<tr>
<td>3k</td>
<td>0.000</td>
<td>3.04</td>
<td>3.65</td>
<td>155.65</td>
<td>$Fm\overline{3}m$ (No. 225)</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.062</td>
<td>2.50</td>
<td>3.64</td>
<td>155.64</td>
<td>$Fmmm$ (No. 69)</td>
</tr>
<tr>
<td>2k</td>
<td>0.020</td>
<td>2.93</td>
<td>3.66</td>
<td>155.73</td>
<td>$P\bar{6}ca$ (No. 61)</td>
</tr>
<tr>
<td>3k</td>
<td>0.009</td>
<td>2.68</td>
<td>3.66</td>
<td>155.72</td>
<td>$Pa\overline{3}$ (No. 205)</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>-</td>
<td>2.80(148)</td>
<td>0.00(122)</td>
<td>157.25(122) $Fm\overline{3}m$ (225)$^{a, 122, 153}$</td>
</tr>
</tbody>
</table>

PBEsol calculates a degenerate metallic FM (111), (011), (001) ground-state; however, the metallic ground-state is inconsistent with the known insulating nature (Figure 5.13). The result highlights the failure of conventional DFT methods with highly-correlated systems. In all instances, an energetically unfavourable metastable DM state (relative to the ordered magnetic states) has been calculated.

Investigations of surface reactivity and bonding often rely on interpretations of the electronic structure. The experimental band-gap of 2.80 eV is reported by optical absorbance measurements of epitaxial thin films.(148) In these calculations, the electronic structure is shown to be influenced by the magnetic state. A metallic FM ground-state is calculated by
PBEsol; thus, PBEsol fails due to the highly correlated nature of the Pu 5f-electrons. It is evident that one must correct for the exchange-correlation interaction. The band-gap is only replicated by the AFM and DM states when U = 5-7 eV. In particular, the band-gap of the experimental DM state and longitudinal 3k AFM ground-state is reproduced when U = 6.35 eV and U = 6.00 eV, respectively. In contrast, when calculating the band-gap for the FM states, at every value of U, the band-gap is underestimated relative to experimental values.

![Graphs showing relative energies, band-gaps, and effective magnetic moments against the Coulomb modifier (U) for diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states of PuO₂, calculated with PBEsol+U. The antiferromagnetic transverse (T) and longitudinal (L) domains are additionally represented. The k-prefix denotes the number of independent wave vectors: upper row) the calculated energy of magnetic states relative to the transverse 3k antiferromagnetic ground-state; middle row) the direct band-gap; lower row) the effective Pu⁴⁺ magnetic moment. The DM (yellow), FM (Red), longitudinal AFM (Green) and transverse AFM (Blue) states are denoted by the colours in the parentheses.](image-url)
In experimental studies, the absence of an effective magnetic moment indicates DM order.\textsuperscript{(22, 114-117)} In this study, the effective magnetic Pu moment of the ordered FM and AFM states is reported. In the FM states, the effective magnetic moment decreases from 3.85-3.75 μ_B/Pu ion in the U = 0-2 eV range. This then increases from 3.75 μ_B/Pu ion to 3.83 μ_B/Pu ion when U = 3-7 eV. In contrast, the effective magnetic moment of the AFM states continually increases from 3.55 μ_B/Pu ion to 3.80 μ_B/Pu ion over the range of U = 0-7 eV. One notes, when U = 6 eV, the effective magnetic moment converges at 3.80 μ_B/Pu ion for all magnetic states. The electronic structure of the longitudinal 3k AFM ground-state is calculated when U = 6 eV. This corresponds to an effective magnetic moment of 3.80 μ_B/Pu ion.

The magnetic structure is coupled by SOI to the crystal symmetry. High-temperature measurements of PuO\textsubscript{2} report \textit{Fm\overline{3}m} crystal symmetry.\textsuperscript{(5, 122)} This is synonymous with calculations of DM and longitudinal 3k AFM order. In these calculations, the collinear 1k AFM states results in: orthorhombic \textit{Fmmm} (No. 69) or tetrahedral \textit{I4/mmm} (No. 139) crystallographic distortions.\textsuperscript{(3, 4, 26, 27, 38, 43-53, 154)} The crystal structure of the collinear 1k AFM states (used by past studies) is inconsistent therefore with experimental results. In addition, a transverse 3k AFM state results in \textit{Pa\overline{3}} crystal symmetry (observed by UO\textsubscript{2} and AmO\textsubscript{2} investigations).\textsuperscript{(60, 62)}

The low-temperature structure of PuO\textsubscript{2} (not necessarily indicative of DM order) is experimentally characterised by the absence of a lattice distortion and a magnetic moment. The ambient PM state, experimental DM ground-state, and theoretical longitudinal 3k AFM ground-state retain \textit{Fm\overline{3}m} crystal symmetry. If a phase transition occurs then it is not first-order and cannot be characterised by a change in space group. The absence of any change in crystal structure between PM, DM, and the longitudinal 3k AFM states is thought to have helped the ground-state elude detection.

A complete analysis can be conducted by comparing other \textit{f}-electron materials. The results are rationalised by considering magnetic anomalies in NpO\textsubscript{2} URu\textsubscript{2}Si\textsubscript{2}, UPt\textsubscript{3}, and UPd\textsubscript{3}.\textsuperscript{(2)} In the absence of an ordered moment and of noticeable lattice anomalies, a phase-transition could be driven by an ordered parameter no longer invariant under time-reversal symmetry.\textsuperscript{(2)} The interaction leading to a phase-transition would have to arise from a purely electronic mechanism, as phonons may only carry interactions between time-reversal-invariant multipoles. A magnetic multipole (for which Kramers' theorem would no longer apply) by AFM superexchange is a candidate for an ordered mechanism.\textsuperscript{(2, 10, 155)} As an indication of
superexchange, the magnetic susceptibility measurements PuO₂ and Th₁₋ₓPuₓO₂ are inconsistent.\(^{(115, 120, 121)}\) The interaction of the Pu⁴⁺ ions in Th₁₋ₓPuₓO₂ is reduced by dilution; the superexchange mean-field weakens and the magnetic susceptibility increases.\(^{(2)}\) In addition, anomalies in the INS measurements of PuO₂ have been attributed to Jahn-Teller distortions and superexchange interactions.\(^{(114, 117)}\) A superexchange interaction is theorised to occur in NpO₂ by comparison, where a magnetic octupole has been established.\(^{(150, 152, 155-158)}\)

In another interpretation, PuO₂ may be a small-moment system. This is observed in other actinide materials where the AFM response of URu₂Si₂ \(T_N = 17.5\) K, UPt₃ \(T_N = 5\) K and UPd₃ \(T_N = 4.5\) K is 0.02-0.03 μB/U ion⁻¹.\(^{(2)}\) Indeed, a small-moment magnetic state has been theorised for NpO₂ where muon spin rotation measurements of the magnetic moment is 0.06-0.15 μB/Np ion.\(^{(2, 102)}\) The nature of small-moment systems in unclear.\(^{(2)}\) The moment of a system may be reduced by competing magnetic interactions. In the localised PuO₂ \(f\)-electron system, the interaction may be Rudermann, Kittel, Kasuya, Yoshida (RKKY) or Kondo in nature.\(^{(2, 10)}\) If a small-moment in the PuO₂ system exists, quantifying the magnetic ground-state becomes a considerable challenge. The calculated magnetic moment of the longitudinal 3k AFM ground-state is ~3.65 μB/ Pu⁴⁺ ion. Note: a number of computation studies show that DFT methods overestimate small-moment actinide materials.\(^{(109-111, 159)}\) Lastly, it is conceivable that PuO₂ undergoes a second low-temperature phase transition. This is known to occur in other actinide compounds. For instance, the specific heat capacity of UPt₃ has two distinct anomalies at \(T_C1 = 0.49\) K and \(T_C2 = 0.44\) K indicative of changing magnetic order.

### 5.3.3.2 DFT+U Constraints

The performance of the DFT functionals on the PuO₂ system has been investigated. The experimental DM state and theoretical longitudinal 3k AFM states are considered. The results are contrasted for the; band-gap, lattice volume and magnetic moment (Figure 5.14). The magnetic moment of Pu⁴⁺ ions in the DM state is nil and not considered. As with the calculations of UO₂ and NpO₂, the magnetic state has no impact on functional performance. As a generalisation, the AM05 and PBEsol functional offer the best correlation with respect to the band-gap and lattice volume. The magnetic moment of the Pu⁴⁺ ion in the longitudinal 3k
AFM state is 3.38-3.86 $\mu_B$/Pu ion. The small-moment magnetic state of PuO$_2$ cannot be replicated by the DFT method.

![Graphs showing band-gap, lattice constant, and magnetic moment against U (eV)](image)

*Figure 5.14: In plutonium dioxide (PuO$_2$), the performance of the functionals measured against the: a) band-gap, b) lattice constant, c) effective magnetic Pu$^{4+}$ moment. Results are generated for the diamagnetic (1st row) and the longitudinal 3k AFM (2nd row) states.*

The influence of the J on the PuO$_2$ system has been investigated (Figure 5.15). The experimental DM state and theoretical longitudinal 3k AFM states are considered. The results are contrasted for the; band-gap, lattice volume and magnetic moment. The magnetic moment of Pu$^{4+}$ ions in the DM state is nil and not considered. The influence of the J modifier on the DM PuO$_2$ system reduces the calculated band-gap. In addition, the effect on the lattice volume is negligible. As such, it is advantageous to neglect J from calculations of the DM state. The influence of the J modifier on the longitudinal 3k AFM PuO$_2$ system is negligible for calculations of the band-gap and lattice volume; however, the magnetic moment of the Pu$^{4+}$ is reduced considerably. This offers a potential means by which a small-moment state may be obtained.
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Figure 5.15: In plutonium dioxide (PuO$_2$), the influence of exchange on the: a) band-gap, b) lattice constant, c) effective magnetic Pu$^{4+}$ moment. Results are generated from the transverse 3k AFM ground-state.

5.3.3.3 DFT+U Electronic Structure

The electronic structure of PuO$_2$ has been calculated for the DM (experimental) and longitudinal 3k AFM (theoretical) ground-state (Figure 5.16). The noncollinear magnetic ground-state of UO$_2$, NpO$_2$ (established by experimental means) and PuO$_2$ (herein calculated) are highly-comparable. In each instance, the experimental lattice constant is marginally overestimated.(118, 122, 160, 161) A charge-transfer insulator is calculated for both magnetic configurations. An electronic transition occurs between the CBM Pu $f$- and VBM O $p$-states. The valence band and condition band are primarily formed of Pu $f$- and O $p$-states, respectively. This contradicts the Mott-insulating nature as calculated by the fully relativistic linear combinations of Gaussian-type orbitals–fitting function (LCGTO-FF) method.(52)
Figure 5.16: The electronic structure of PuO$_2$ calculated by PBEsol for the: upper) experimental DM state ($U = 6.35 \text{ eV}, J = 0.00 \text{ eV}$); lower) theoretical longitudinal 3k AFM state ($U = 6.00 \text{ eV}, J = 0.00 \text{ eV}$). In the band structure, the valence bands are coloured blue; whereas, the conduction bands are coloured orange. In the density of states, the colours in the parentheses indicate the Pu f- (blue), Pu d- (green) and O p- (red) states.

Table 5.7: The direct band-gap (eV), optical band-gap (eV), lattice constant (Å), bulk modulus (GPa) and magnetic moment ($\mu_B$/Pu ion) for the diamagnetic (DM) and longitudinal 3k antiferromagnetic (L-3k AFM) state of PuO$_2$.

<table>
<thead>
<tr>
<th>DFT+U</th>
<th>Band-gap (eV)</th>
<th>Lattice Constant (Å)</th>
<th>Bulk Modulus (GPa)</th>
<th>Magnetic Pu$^{4+}$ Moment ($\mu_B$·ion$^{-1}$)</th>
<th>Crystal Symmetry</th>
<th>Magnetic State</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (eV)</td>
<td>J (eV)</td>
<td>Ideal Optical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.35</td>
<td>0.00</td>
<td>2.81 2.82</td>
<td>5.411</td>
<td>217</td>
<td>0.00</td>
<td>$\overline{Fm\bar{3}m}$ (225)</td>
</tr>
<tr>
<td>6.00</td>
<td>0.00</td>
<td>2.80 2.97</td>
<td>5.415</td>
<td>215</td>
<td>3.80</td>
<td>$\overline{Fm\bar{3}m}$ (225)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>- 2.80$^{(160)}$</td>
<td>-5.398$^{(122)}$</td>
<td>178-379$^{(5, 153)}$</td>
<td>0.00</td>
<td>$\overline{Fm\bar{3}m}$ (225)</td>
</tr>
</tbody>
</table>

The optical band-gap and effective Pu$^{4+}$ magnetic moment of the experimental DM and theoretical longitudinal 3k AFM ground-states has been calculated by PBEsol (Table 5.7). In the DM state, a $\Gamma$ centred direct band-gap of 2.81 eV is calculated; whereas, an optical band-gap of 2.82 eV is calculated. In the longitudinal 3k AFM state, an indirect X-$\Gamma$ (VBM) to X-$\Gamma$ (CBM) band-gap of 2.80 eV is calculated; whereas an optical band-gap of 2.97 is calculated. The degeneracy of the bands in the longitudinal 3k AFM ground-state is perturbed by the presence of magnetic order. This is a key finding made possible only when SOI and non-
collinear contributions are included. The calculated bulk modulus of PuO$_2$ in the DM (217 GPa) and longitudinal 3k AFM state (215 GPa) are additionally reported. This considerably narrows the 178-379 GPa experimental range.

5.4 Conclusions

In this chapter, the magnetic structure of the AnO$_2$ has been investigated by first-principle methods. As highly-correlated and heavy-fermion systems, the electronic structure of the AnO$_2$ is notoriously difficult to calculate. It is imperative to consider relativistic contributions (as the crystal structure is coupled by SOI to the magnetic state) when creating computational models. The performance of the DFT functionals and the influence of J on the system has been evaluated. To study the magnetic ground-state in fluorite-type materials, a computational method has been designed by the author. The results show that the crystal symmetry is strongly influenced by the magnetic environment. For instance, the experimental cubic environment is only preserved by non-collinear 3k AFM states. The longitudinal 3k AFM states results in $Fm\bar{3}m$ (No. 225) crystal symmetry; whereas, the transverse 3k AFM states results in $Pa\bar{3}$ (No. 205) crystal symmetry, with a distortion of the O$^2-$ ions of 0.01-0.02 Å. The collinear 1k AFM states (used in past studies) calculate an incorrect crystal structure. A tetragonal $I4/mmm$ (No. 139) (longitudinal 1k AFM) or orthorhombic $Fmmm$ (No. 69) (transverse 1k AFM) crystallographic distortion results. This impacts the design of surface models, the determination of surface energetics, and the interaction of adsorbents. Lastly, the identity of the magnetic ground-state may be inferred by the crystal structure.

In these calculations, the transverse 1k AFM ground-state of UO$_2$ is consistent with both static and low-frequency measurements of spin-wave excitations.(2) This in contrast to the transverse 3k AFM state linked to $Pa\bar{3}$ (No. 205) crystal symmetry established by inelastic neutron scattering (INS),(78) resonant X-ray scattering (RXS) and nuclear magnetic resonance (NMR)(55) measurements.(55, 78) All ordered magnetic states are in close energetic proximity. The influence of entropy on the dynamic stability of the ordered magnetic states remains unknown. The insulating nature of NpO$_2$ is calculated by PBEsol when U = 4-6 eV for all magnetic configurations. In this study, due to the limitations of DFT, the existence of a small-moment system cannot be confirmed.(109, 110) A FM (111) ground-state with $R\bar{3}m$ (No. 166) has been calculated; the result contradicts resonant X-ray scattering(74) and $^{17}$O
NMR measurements.(56) In contrast, the transverse 3k AFM state with $Pa\overline{3}$ (No. 205) crystal symmetry is only 0.001 eV higher in energy. This magnetic structure has been linked to experimental measurements.(61, 101, 108, 150, 152) The influence of entropy on the low-temperature magnetic state is unknown and is believed to impact the magnetic ground-state. In addition, due to computational expense, the implication of phonon activity on dynamic stability has yet to be studied. A small-moment longitudinal 3k AFM ground-state of $\text{PuO}_2$ has been indicated by DFT and HSE06 results. This is analogous to $\text{NpO}_2$; however, DFT methods are unsuitable for magnetic moment calculations. The calculated metastable DM state (in contrast with the calculated longitudinal 3k AFM ground-state) is inconsistent with current experimental information. A longitudinal 3k AFM ground-state with $Fm\overline{3}m$ crystal symmetry has been calculated. The fact this magnetic ground-state has not been experimentally observed may be explained by three possibilities. First, $\text{PuO}_2$ may be a small-moment material for which current experimental resolution is insufficient to identify an ordered magnetic state. Second, an AFM-DM phase transition may occur outside of the temperature range studied. Third, superexchange of $\text{Pu}$ ions results in a hidden magnetic phase transition. To resolve this enigmatic issue additional experimental measurements are needed: low-temperature specific heat capacity, muon spin relaxation.

An excellent interpretation of the band-gap and lattice constant is offered by the PBEsol functional. The ideal DFT+U constraints for $\text{UO}_2$ ($U = 3.35$ eV, $J = 0.00$ eV), $\text{NpO}_2$ ($U = 4.25$ eV, $J = 0.00$ eV), $\text{PuO}_2$ ($U = 6.00$ eV, $J = 0.00$ eV) are indicated in the parentheses. These have been applied to the theoretical magnetic ground-state. A transverse 3k AFM state is calculated for $\text{UO}_2$ and $\text{NpO}_2$ with $Pa\overline{3}$ crystal symmetry; whereas, a longitudinal 3k AFM state is calculated for $\text{PuO}_2$ with $Fm\overline{3}m$ crystal symmetry. The influence of the magnetic structure on its crystal structure may be of relevance to other actinide compounds as well. This will be the topic of future research.

5.5 Bibliography

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Chapter 6: The Design of Surface Models

6.1 Introduction

In commercial nuclear reactors, metallic or oxide fuels are normally used; however, nitride, carbide, and molten salt fuels have been developed.\(^1\) The actinide metals inexorably oxidize (under environmental conditions) to generate an oxide layer.\(^2\) The oxide layer influences the chemistry of the underlying actinide metal. This impacts the design of long-term storage facilities, and the industrial reprocessing of nuclear fuels.\(^8\) The surface chemistry of the actinide dioxides \((\text{AnO}_2, \text{An} = \text{U}, \text{Np}, \text{Pu})\) is key to understanding corrosion mechanisms.\(^2\) To reduce the risk of nuclear proliferation and assists in nuclear decommissioning, the controlled oxidation of actinide materials offers a means of converting classified nuclear material to simple ingots.\(^7\) The interaction of hydrogen, oxygen and water with the \(\text{AnO}_2\) has been shown to catalyse corrosion and impact surface composition.\(^17\) The surface energetics of the \(\text{AnO}_2\) impact (in terms of fuel fabrication) fuel sintering and particle morphology.\(^18\) The inhomogenic and radioactive nature of \(\text{AnO}_2\) systems has hindered experimental measurements.\(^8, 19, 20\) A limited number of experimental \(\text{AnO}_2\) surface studies have been completed.\(^8, 12, 19-25\) As the oxide product is the only one formed under environmental conditions, the corrosion and oxidation of actinide materials are often treated as equivalent topics. To investigate the surface chemistry of the \(\text{AnO}_2\), computational methods offer insight into the electronic structure.
The rate of corrosion of actinide metals by oxidation is limited by the AnO$_2$ surface layer which hinders the diffusion of O$^{2-}$ ions from the surface to the metal-oxide interface. As such, under standard conditions, the rate determining step is the diffusion of O$^{2-}$ ions as confirmed by kinetic data.\(^\text{(2-7, 15, 26, 27)}\) This diffusion-controlled model only applies for temperatures below 773 K. The mechanism, however, fails to account for the pyrophoric phenomena and other anomalous kinetic behaviour. For instance, it is known that the corrosion of actinide metals is catalysed by hydrogen and water vapor.\(^\text{(2-7, 15, 28)}\) An interpretation of corrosion mechanisms has come from a combination of results studying reactions with hydrogen, oxygen and water vapor.\(^\text{(5)}\) The radiolysis of water into its individual constituents is theorized to accelerate the corrosion of actinide metals and generate pressure within sealed containers.\(^\text{(2-7, 15)}\) In atmospheres containing hydrogen and oxygen, the catalytic formation of water by the adsorbed species enhances the corrosion of the metal. In oxygen deficient environments, the reaction of water with actinide metals result in the formation of actinide oxides and the release of hydrogen gas.\(^\text{(2-7, 15)}\) It is clear that actinide oxide surfaces provide an active substrate for the equilibration of the hydrogen-oxygen system.\(^\text{(13)}\) Investigating corrosion mechanisms is imperative for the control of nuclear materials.\(^\text{(13)}\) Assessing the low-index AnO$_2$ surfaces is therefore imperative. The electronic structure of the AnO$_2$ surface layer greatly influences adsorption and dissociation mechanisms. To properly study corrosion and oxygen diffusion, the electronic structure must be calculated correctly.

An experimental characterisation of the AnO$_2$ magnetic ground-state is highly complex. This is due to nucleonic radioactive decay,\(^\text{(29)}\) the toxicity of the metals,\(^\text{(30)}\) and the inhomogeneity of samples.\(^\text{(31)}\) Information from experimental sources on AnO$_2$ surfaces energies is relatively absent from the literature.\(^\text{(8, 12, 19-25)}\) As a means to compensate for experimental issues (thermal energy released by the decay of actinide nuclei), the magnetic ground-state can be studied by computational methods. Although a computational investigation of AnO$_2$ materials is also incredibly challenging. The importance of including spin-orbit interactions (SOI, although computationally intensive) has been highlighted in numerous investigations.\(^\text{(20)}\) In conventional density functional theory (DFT), the strong on-site Coulomb repulsion of the actinide $f$-electrons is underestimated. To investigate the complex electronic structure by computational methods, one must consider: exchange-correlation influences, relativistic contributions, and noncollinear magnetic behaviour. A number of methods to calculated highly-correlated systems have been developed: the self-interaction correction (SIC) method,\(^\text{(32)}\) modified density functional theory (DFT+U),\(^\text{(33-37)}\) dynamic mean field theory
As a computationally tractable method, DFT+U offers means of study in which the electronic structure can be computed. In the Liechtenstein DFT+U formalism, independent Coulomb (U) and exchange (J) terms treat the on-site Coulomb repulsion of the An f-electrons. The values are derived from computational methods or empirical analysis.

The impact of noncollinear magnetic behaviour on the low-index AnO$_2$ surfaces has remained unexplored. The importance of magnetic vector reorientation and inclusion of SOI (as the electronic structure is influenced by magnetic order) has been highlighted. The impact of oxygen ion reconstruction on the inherently unstable dipolar (001) surface stability is considered. A number of characteristics have been calculated: scanning tunnelling microscopy (STM) images, electrostatic potential isosurfaces, crystal morphology.

### 6.1.1 Literature Review

The low-temperature crystal structure of the AnO$_2$ is coupled by SOI to the magnetic ground-state. A myriad of experimental investigations on the AnO$_2$ confirm their fluorite-type cubic nature; however, the internal structure and space group remains controversial. The crystal structure and antiferromagnetic (AFM) ground-state of the AnO$_2$ has been inferred by experimental and first-principle methods. An experimental noncollinear AFM ground-state for UO$_2$ and NpO$_2$ has been identified; the calculate DFT ferromagnetic (FM 111) ground-state has been ignored. In this investigation, the transverse 3k AFM state of UO$_2$ and NpO$_2$ is coupled to $P_{a\overline{3}}$ (No. 205) crystal symmetry; whereas, the longitudinal 3k AFM state of PuO$_2$ is coupled to $Fm\overline{3}m$ (No. 225) crystal symmetry (Figure 6.1).

The surface structure of UO$_2$ has been the most extensively studied; investigations on NpO$_2$ and PuO$_2$ surfaces are uncommon. The surface energetics are impacted by: sample homogeneity, defect chemistry, and environmental conditions. To highlight the experimental complexity and sensitivity of these materials to environmental conditions, low-energy electron diffraction (LEED) measurements of the UO$_2$ (111) surface indicate 16 individual patterns.
As a result of complex surface reactivity, experimental investigations of AnO$_2$ (001) surfaces are complicated. To eliminate the dipole moment of AnO$_2$ (001) surface, a reconstruction removes the inherent instability. A scanning tunnelling microscopy (STM) study has confirmed the UO$_2$ (001)r surface reconstruction; however, a number of different crystallographic forms (with competing energetics) have been identified.\(^{(52)}\) In addition, low-voltage scanning electron microscopy (SEM) measurements of UO$_2$ single-crystals (formed at 400 MPa and 1973 K) have been conducted.\(^{(53)}\) A truncated octahedral Wulff crystal morphology (surface energy $\gamma_{(001)}/\gamma_{(111)}$ ratio 1.42) has been identified. A controversy has arisen in terms of the surface energy $\gamma_{(001)}/\gamma_{(111)}$ ratio (where surface energy is $\gamma$) (Equation 6.1).

$$\text{Surface Energy Ratio} = \frac{\gamma_{(001)}}{\gamma_{(111)}}$$  

An ideal surface energy $\gamma_{(001)}/\gamma_{(111)}$ ratio of 1.42 for UO$_2$ result in a truncated octahedron. In all other AnO$_2$ investigations, a conventional octahedron has been calculated.\(^{(25, 54)}\) In terms of experimental complications, the morphology can be influenced by: environmental conditions and synthetic method.\(^{(55)}\) As the surface structure changes fuel behaviour, it is important to study the crystal morphology and characteristics.

The empirical nature of the interatomic potentials has limited the study of AnO$_2$ surfaces by computational means. The inability of interatomic potential methods to reliably discriminate between structures has been shown.\(^{(56)}\) In contrast and as an improvement, quantum
mechanical (QM) methods offer information on the electronic structure. The surface energies calculated by QM methods, relative to interatomic potentials, are generally considerably higher.\(^{(18)}\)

![Figure 6.2: The surface magnetism of a two-dimensional material. The direction of the magnetic moments for the respective surfaces are shown for the first two layers of the bulk crystal structure. The highlighted (01) (green) and (11) (blue) surfaces correctly emulate the magnetic structure in the bulk crystal. In contrast, the (11) (red) surface illustrates an incorrect depiction where the magnetic moments are aligned orthogonal to the surface.](image)

The computational modelling of magnetic order in AnO\(_2\) surfaces has historically been linear: FM or collinear 1k AFM order. To reduce the computational cost of the systems and improve tractability, calculations are often completed in the absence of SOI.\(^{(10, 28, 45, 57)}\) In this manner, the magnetic moments are directed orthogonal to the surface plane. If not corrected, the orientation of the magnetic field is also directed orthogonal to the surface plane because the principle axis differs between the surface. Consequently, the electronic, magnetic, and crystal structures differ between the bulk crystal structure and individual surfaces. If the magnetic vectors are not reorientated, the energetics and structural relaxations derived by this approach are incomplete.\(^{(43, 44)}\) This is particularly concerning when calculating the surface energy as this is derived from the bulk structure. To compensate, one must reorientate the crystal structure or the magnetic vectors relative to the surface.
A major limitation of scalar calculations is the inability to orientate the magnetic moments relative to the direction of the surface. Therefore, the magnetic structure of the AnO$_2$ (111), (011) surfaces are often approximated. This leads to notable inconsistencies within the electronic structure. The magnetic structure is commonly defined by the principle axis. The principle axis of the AnO$_2$ (111), (011) surface differs from that of the bulk crystal. Therefore, the final magnetic, electronic and crystal structures are inequivalent. It is not the case for the AnO$_2$ (001) surface which shares the same axes. To illustrate, in two-dimensional material, consider the first two layers of a collinear 1k AFM material (Figure 6.2).

The (01) surface and the crystal share the same principle axis; therefore, the magnetic structures are directly related. In the (11) surface, the principle axis differs from that of the crystal which results in an unrelated magnetic and electronic structure. It is therefore critical to orientate the magnetic vectors to emulate the initial crystal structure. As stated, the magnetic ground-state is coupled by SOI to the crystal structure.\cite{45} Investigation of magnetic order in the AnO$_2$ with SOI\cite{45} show that collinear 1k AFM configurations cause a reduction in cubic crystal symmetry. This is characterised by a tetragonal $I4/mmm$ (No. 139, longitudinal 1k AFM) or orthorhombic $Fmmm$ (No. 69, transverse 1k AFM) distortion of the unit cell. The distortion is inconsistent with the AnO$_2$ cubic crystal symmetry by experimental measurements, impacting: surface structure, energy, and reactivity. In terms of surface structure investigation, collinear 1k magnetic order can be considered unsuitable. In contrast, the experimental cubic crystal $Fm\bar{3}m$ (No. 225, longitudinal 3k AFM) or $P\bar{a}\bar{3}$ (No. 205, transverse 3k AFM) environment is retained by noncollinear magnetic order. Note: a first-principle transverse 1k AFM (UO$_2$) and FM (NpO$_2$) ground-state has been calculated. As a result of collinear 1k AFM order with SOI\cite{45} the impact of a crystallographic distortion on surface energetics remains uninvestigated.

The surface energetics of the AnO$_2$ have been investigated by DFT methods, often ignoring SOI and employing collinear 1k AFM order. These calculations have failed to modify the magnetic vectors, and thus the findings are incomplete. Indeed, only a few calculations on UO$_2$\cite{8} and PuO$_2$\cite{20} have considered relativistic contributions to the total energy. Initially the importance of SOI in UO$_2$ appeared to be negligible; the study is often cited in support of studies that neglect the influence of SOI\cite{8, 20, 45}. In contrast, the importance of SOI concerning the calculation of PuO$_2$ (111) surface energies has been highlighted by hybrid DFT.\cite{20} A preference for an AFM state where the surface energy is 0.70-0.80 J·m$^{-2}$ has been indicated.
6.2 Computational Methodology

6.2.1 Calculation Details

A noncollinear relativistic computational study of AnO₂ low-index surfaces by the Vienna *Ab-initio* Simulation Package (VASP) code has been conducted.(32, 38, 58) employing a planewave basis set, relativistic effective core potentials (ECPs) and the frozen-core projector-augmented wave (PAW) method. The cut-off energy of the planewave basis set is 500 eV. The uranium (6s², 7s², 6p⁶, 6d⁶ 5f⁵), neptunium (6s², 7s², 6p⁶, 6d⁶ 5f³), plutonium (6s², 7s², 6p⁶, 6d⁶ 5f⁴) and oxygen (2s², 2p⁴) valence electrons are implicitly considered. The integration over the Brillouin zone has been performed using the Blöchl tetrahedron method.(59) The influence of noncollinear magnetic wave-vectors and SOI(45) are considered. The magnetic ground-state for the low-index AnO₂ surfaces has been identified. A transverse 3k AFM ground-state results in *Pa̅3* (No. 205) crystal symmetry (UO₂ and NpO₂); whereas, a longitudinal 3k AFM ground-state results in *Fm̅3m* (No. 225) crystal symmetry (PuO₂).(42-44)

The on-site Coulomb repulsion of the An 5f electrons is treated by the Liechtenstein *et al* DFT+U(35-37) formalism.(36) In the Liechtenstein *et al* formalism, the Coulomb (U) and exchange (J) modifiers are treated as independent variables.(36) The Coulomb modifier for each ion is written in the parentheses: uranium (U = 3.35 eV), neptunium (U = 4.25 eV) and plutonium (U = 6.00 eV). The influence of J on noncollinear magnetic materials has been investigated.(42-44, 60) The introduction of J increased the anisotropic nature of the f-states.(61) It is therefore not considered in this study; the J modifier is kept at a constant value of 0.00 eV.(42) In addition, when J = 0.00 eV the Dudarev *et al*(35) formalism and Liechtenstein *et al*(36) formalism are equivalent.(60) The selected conditions offer an accurate representation of the electronic structure. The integration of the Brillouin zone is performed with a Γ-centred k-point grid.(62) The exchange-correlation energy is evaluated by the revised Perdew-Burke-Ernzerhof for solids (PBEsol) functional.(33, 34, 63) The iteration threshold for electronic and ionic convergence is 1x10⁻⁵ eV and 1x10⁻² eV·Å⁻¹, respectively.

As a measure of surface stability, the surface energy (γ, surface energy per unit area) is minimised by ionic relaxations. All ions are relaxed while the dimensions of the unit cell are fixed. The conjugate gradient method is employed in the relaxation of the ions. The surface energy can be calculated relative to the crystalline solid (Equation 6.2):
\[ y = \frac{E_{\text{System}}^{\text{Total}}(N) - N \cdot E_{\text{Solid}}^{\text{Total}}}{2A} \]

The terms in the equation describe: the number of formula units (N), the surface system total energy (\(E_{\text{System}}^{\text{Total}}(N)\)), the formula unit total energy (\(E_{\text{Solid}}^{\text{Total}}\)), the surface area (A). As the number of monolayers and the total energy of the system are commensurate, one can derive the total energy per formula unit from the convergence threshold.

### 6.2.2 Low-Index Models

The low-index AnO₂ (111), (011), (001) surfaces are generated by the METADISE code (Figure 6.3). (64) The ionically relaxed crystal structure as an initial template has been used. A vacuum gap of 20 Å isolates the surfaces from their periodic image. The nonpolar (111) surfaces are comprised of repeat O-An-O unit layers. In the (111) surface, the individual monolayers are charged; however, the surface is characterised by the absence of a dipole moment perpendicular to the surface. In contrast, the (011) surface is comprised of nonpolar and charge neutral planes.

The polar (001) surface (formed of dipolar An-O layers) is inherently unstable. (18, 52, 65) Increasing the number of monolayers causes the electrostatic energy to diverge. (66, 67) To avoid the formation of an electrostatic dipole, a dipolar surface undergoes a reconstruction. As environmental conditions influence surface reconstruction, numerous configurations are possible. (56) To remove the dipolar component of the (001) surface, half of the oxygen anions are transposed to actinide cationic surface. An oxygen terminated surface with half-filled oxygen vacancies is created (Figure 6.4). The result is a non-polar reconstructed (001) r surface. The reconstructed (001)α or (001)β surface in a (1·1) unit cell can be formed. As a hybridisation of these forms, the reconstructed (001)αβ surface in a (1·2) unit cell has been modelled. The relative stability of these surface configurations has been calculated.

The crystal and electronic structure of AnO₂ is highly-dependent on the magnetic state. It is imperative to correctly reorientate the magnetic vectors with respect to the surface plane. A
number of studies forgo this crucial transformation; consequently, the energy of the bulk and the surface are often incompatible.

A considerable error is introduced if the reorientation of magnetic vectors is ignored. This is evidenced by changes in the total energy. As a result the magnetic vectors are reorientated relative to the surface plane. In these calculations, the noncollinear 3k AFM states of the AnO$_2$ is maintained with cubic crystal symmetry. Hence, the reduction of cubic symmetry associated with collinear 1k AFM states is avoided. (43, 44)
Figure 6.5: The surface energy is converged with respect to the k-point grid for each surface: a) uranium dioxide, b) neptunium dioxide, c) plutonium dioxide. The colours in the parentheses indicate the (111) (Green), (011) (Blue), (001)α (Red) and (001)β (Yellow) surfaces. In these calculations, the (111), (001)α, (001)β surfaces are formed of 15 monolayers; whereas the (011) surface is formed of 9 monolayers.

The surface energy is converged with respect to the k-point grid to under 0.05 J·m$^{-2}$ (Figure 6.5). The (111) surface is calculated from a 5·5·1 Γ-centred k-point grid recommended for hexagonal structures, whereas the (011), (001) surfaces are calculated from a 4·4·1 Γ-centred k-point grid. (65) To minimize potential aliasing errors the initial crystal structure (from which the surfaces are derived) are calculated with either a 4·4·4 and a 5·5·5 Γ-centred k-point grid. Lastly, the (001)αβ surface is calculated form a 4·2·1 Γ-centred k-point.

6.2.3 The HIVE Code

In the scanning tunnelling microscopy (STM) HIVE code,(68, 69) the Tersoff-Hamann model is considered (the tunnelling-current is equivalent to the local density of states). (70) A point source at a constant height of 2.5 Å and a Fermi energy sample bias of -2.50 eV is used. Topographies calculated by HIVE include: copper,(71) germanium,(68, 69) gold,(72) iron oxide,(73) thorium dioxide.(54)

6.2.4 Wulff Reconstruction

The equilibrium crystal morphology (according to the Gibbs thermodynamic principle), is influenced by total surface energy of the medium interface. An equilibrium crystal morphology (that minimises $\Delta G_i$) has been calculated (Equation 6.3).
\[ \Delta G_i = \sum_j \gamma_j A_j \]

The terms in the parentheses describe: the total crystal-medium interface free energy (\( \Delta G_i \)), the surface Gibbs free energy (\( \gamma_j \)), the surface area (\( A_j \)).

6.3 Results & Discussion

6.3.1 Model Constraints

6.3.1.1 Surface Energetics

The energy of the low-index surfaces has been calculated as a function of the number of monolayers (Figure 6.6). The ions are fully relaxed while keeping the dimensions of the unit cell fixed. The surface energy is converged to within 0.01 J·m\(^{-2}\) when 12 or more monolayers are used. The surface energy increases across the (111) < (011) < (001)\( \alpha \) < (001)\( \beta \) series, as is typical of structured fluorite-type materials (Table 6.1).\(^{(54, 66)}\)

![Figure 6.6](image)

*Figure 6.6: The surface energy (J·m\(^{-2}\)) as converged with respect to the number of monolayers (N) employed for (left) uranium dioxide, (middle) neptunium dioxide, and (right) plutonium dioxide. The symbols in the parentheses indicate the (111) (blue circle), (011) (green triangle), (001)\( \alpha \) (red square) and (001)\( \beta \) (yellow diamond) surfaces.*

The energy difference of the (001)\( \alpha \) and (001)\( \beta \) surface for UO\(_2\) (0.08 J·m\(^{-2}\)), NpO\(_2\) (0.06 J·m\(^{-2}\)) and PuO\(_2\) (0.19 J·m\(^{-2}\)) is indicated by the parentheses. If one uses a (1·1) unit cell model, the (001)\( \alpha \) surface relative to the (001)\( \beta \) surface is energetically favourable. An independent investigation on UO\(_2\) with interatomic potentials confirms the result.\(^{(56)}\) In this study, the
surface energies are considerably higher when contrasted against past DFT-based investigations. In contrast, interatomic potential models and relativistic hybrid calculations of UO₂ result in even higher surface energies.

Interatomic potentials models of UO₂ have calculated surface (001) reconstructions of lower energy. The configurations were formed with a (2·2) unit cell. In the reconstruction of the (001) surface, only the (001)α and (001)β configurations can be generated in a (1·1) unit cell. In this study, the surface energy of the (001)αβ configuration in a (1·2) unit cell has been calculated using 15 monolayers. The surface energy, relative to the (001)α and (001)β configurations, is considerably lower in energy. This implies a limitation of the DFT (1·1) unit cell model; however, other possible configurations in even larger cells are more stable. As the size of the cell increases the computational cost of the system, a full relativistic systematic DFT study is computationally currently intractable.

### 6.3.1.2 Ionic Relaxation

To enable a quantitative analysis of structural relaxations between layers, the surfaces are characterised by the change of interlayer spacing (Figure 6.7-Figure 6.8). The degree of interlayer relaxation (Δd_{interlayer}) is calculated from a full ionic relaxation (Equation 6.4).

\[
\Delta d_{\text{interlayer}} = (d_{i,i+1}\text{relaxed}) - d_{\text{unrelaxed}}
\]

The averaged interlayer separation of ions in the relaxed \((d_{i,i+1}\text{relaxed})\) and unrelaxed \((d_{\text{unrelaxed}})\) surface is defined by the terms in the parentheses. The interlayer relaxation is reminiscent of studies of isostructural CeO₂ for the (111) and (011) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>(111)</th>
<th>(011)</th>
<th>(001)α</th>
<th>(001)β</th>
<th>(001)αβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>0.85</td>
<td>1.23</td>
<td>1.75</td>
<td>1.83</td>
<td>1.69</td>
</tr>
<tr>
<td>NpO₂</td>
<td>0.90</td>
<td>1.28</td>
<td>1.86</td>
<td>1.92</td>
<td>1.80</td>
</tr>
<tr>
<td>PuO₂</td>
<td>0.92</td>
<td>1.35</td>
<td>1.96</td>
<td>2.13</td>
<td>1.85</td>
</tr>
</tbody>
</table>
Figure 6.7: The interlayer An-An relaxation for: a) (111), b) (011), c) (001)α, d) (001)β surfaces. The interlayer spacing index (i) is indicated in the parentheses.

Figure 6.8: The interlayer O-O relaxation for: a) (111), b) (011), c) (001)α, d) (001)β surfaces. The interlayer spacing index (i) is indicated in the parentheses.
Figure 6.9: The ionic relaxation of the low-index AnO$_2$ (001) reconstructed surfaces. The transverse (001)$\beta$ surface is representative of transverse 3k AFM behaviour for UO$_2$ and NpO$_2$, whereas the longitudinal (001)$\beta$ surface is representative of longitudinal 3k AFM behaviour in PuO$_2$. The hybridised (001)$\alpha$$\beta$ surface is calculated regardless of magnetic order for the AnO$_2$. The oxygen (red) and actinide (blue) ions are indicated by the colours in the parentheses.

In the context of An-An relaxation, the (111) surface is marginally distorted. The major difference is confined to the oxygen separation in the second interlayer space. The (011) surface undergoes the greatest overall interlayer relaxation. The first surface layer experiences a marked contraction. In this regard, the first An layer contracts significantly more than the first O layer. The contraction of the first layer is countered by a slight expansion of An ions in the second layer. The bulk structure is perfectly converged by the fifth layer. The terminal O ions, in the (001)$\alpha$ and (001)$\beta$ surface, undergo a significant contraction; the remainder of the structure is relatively unaffected. In general, the interlayer relaxation is confined to the first 5 Å. The results are mirrored by studies on CeO$_2$ and ThO$_2$.\(^{(54)}\) It is therefore advised that, for investigations of surface reactivity, one uses a 10 Å thick slab as a minimum. To reduce the computational cost of the system, a smaller number of monolayers can be used.

In the context of interlayer O-O relaxation, the distortion of the surface is primarily confined to the first three to four monolayers. In general, for AnO$_2$ surfaces, the degree of ionic relaxation is identical. The exception is the PuO$_2$ (001)$\beta$ surface. In the PuO$_2$ (001)$\beta$ surface, relative to the UO$_2$ and NpO$_2$ (001)$\beta$ surfaces, the relaxation of the oxygen ions is significantly less. In the AnO$_2$ (001)$\tau$ surfaces, the UO$_2$ and NpO$_2$ (001)$\beta$ surfaces undergo the greatest
surface relaxation; whereas in PuO$_2$, the (001)$\alpha$ surface undergoes the greatest surface relaxation. This is a result of magnetic order and the relaxation in the xy-plane.

A notable structural distortion, of the AnO$_2$ (111), (011), (001)$\alpha$ surfaces, has not been found in the xy-plane; a potential result of noncollinear 3k AFM order. This keeps $\text{Pa}\bar{3}$ (No. 205) or $\text{Fm\bar{3}m}$ (No. 225) cubic symmetry.\(\text{43, 44}\) In contrast, the oxygen ions in the UO$_2$ and NpO$_2$ (001)$\beta$ configuration are shifted from their initial positions by the use of transverse 3k AFM ordering (Figure 6.9). This distortion is not observed in the corresponding PuO$_2$ surface in which the ions are relatively fixed; however, a minor distortion of the surface Pu ions is observed. This is a consequence of using transverse 3k AFM or longitudinal 3k AFM behaviour. By comparison, the oxygen ions in the (001)$\alpha\beta$ configuration are relatively static. Instead the actinide ions are shifted minimally towards the terminal oxygen ions.

### 6.3.2 Surface Properties

#### 6.3.2.1 Electronic Structure

The electronic structure of the AnO$_2$ surfaces has been calculated (Figure 6.10). The covalent nature AnO$_2$, as a consequence of An $f$- and O $p$-mixing, is seen to increase along the series.

![Figure 6.10: The calculated density of states for the low-index AnO$_2$ (111), (011), (001)$\alpha$ surfaces; (left) UO$_2$, (centre) NpO$_2$, (right) PuO$_2$. The colours in the parentheses indicate the actinide $f$ (blue), actinide $d$ (green) and oxygen $p$ (red) bands. The Fermi level is set at 0 eV.](image-url)
The Mott-Hubbard insulating nature of UO$_2$ is characterised by transitions primarily occurring across the An\textit{f}-bands. In contrast to relativistic hybrid DFT calculations of UO$_2$, the calculated band-gaps for the low-index surfaces are considerably greater.\cite{14} The charge-transfer insulating nature of PuO$_2$ is characterised by transitions primarily between the valence Pu\textit{f}-band and conduction O\textit{p}-band. In NpO$_2$, both Mott insulating and charge-transfer characteristics are shown on the surface. The electronic structure of each surface differs negligibly for identical compounds.

<table>
<thead>
<tr>
<th></th>
<th>(111)</th>
<th>(011)</th>
<th>(001)$_\alpha$</th>
<th>(001)$_\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$ Electron Affinity (eV)</td>
<td>2.44</td>
<td>1.45</td>
<td>3.69</td>
<td>2.93</td>
</tr>
<tr>
<td>Ionization Potential (eV)</td>
<td>4.54</td>
<td>3.51</td>
<td>5.75</td>
<td>5.00</td>
</tr>
<tr>
<td>Band-gap (eV)</td>
<td>2.11</td>
<td>1.96</td>
<td>2.01</td>
<td>2.15</td>
</tr>
<tr>
<td>Surface Energy (J.m$^{-2}$)</td>
<td>0.85</td>
<td>1.23</td>
<td>1.75</td>
<td>1.83</td>
</tr>
<tr>
<td>NpO$_2$ Electron Affinity (eV)</td>
<td>3.11</td>
<td>2.11</td>
<td>4.33</td>
<td>3.45</td>
</tr>
<tr>
<td>Ionization Potential (eV)</td>
<td>5.98</td>
<td>4.89</td>
<td>7.11</td>
<td>6.23</td>
</tr>
<tr>
<td>Band-gap (eV)</td>
<td>2.64</td>
<td>2.47</td>
<td>2.14</td>
<td>2.50</td>
</tr>
<tr>
<td>Surface Energy (J.m$^{-2}$)</td>
<td>0.90</td>
<td>1.28</td>
<td>1.86</td>
<td>1.92</td>
</tr>
<tr>
<td>PuO$_2$ Electron Affinity (eV)</td>
<td>3.60</td>
<td>1.74</td>
<td>4.89</td>
<td>4.65</td>
</tr>
<tr>
<td>Ionization Potential (eV)</td>
<td>6.45</td>
<td>4.53</td>
<td>7.67</td>
<td>7.44</td>
</tr>
<tr>
<td>Band-gap (eV)</td>
<td>2.58</td>
<td>2.12</td>
<td>1.84</td>
<td>2.03</td>
</tr>
<tr>
<td>Surface Energy (J.m$^{-2}$)</td>
<td>0.92</td>
<td>1.35</td>
<td>1.96</td>
<td>2.13</td>
</tr>
</tbody>
</table>

The electron affinity (a measure of the electron absorption energy) and ionisation potential (a measure of the electron reduction energy from the valence orbital) has been calculated (Table 6.2). The electron affinity and the ionization potential of the (011) < (111) < (001)$_\beta$ < (001)$_\alpha$ surfaces increases along the series. The results can be confirmed by experimental measurements: X-ray photoelectron spectroscopy (XPS), Kelvin probe microscopy measurements.

6.3.2.2 Scanning Tunnelling Microscopy

Indistinguishable STM AnO$_2$ (111), (011), (001)$_\alpha$ images have been calculated (Figure 6.11). The terminal O$^{2-}$ ions are observed in white; whereas, the An$^{4+}$ ions considerably darker. In the (111) surface, the O$^{2-}$ ions result in a hexagonal structure. In the (011) surface, a series of darker channels are observed in one direction. In the (001)$_\alpha$ surface, the alignment of the O$^{2-}$ ions results in a diamond pattern.
Figure 6.11: Low-Index Scanning Tunnelling Microscopy (STM) Images. The AnO₂ (111), (011), (001)α are indistinguishable. The transverse (001)β surface is found for UO₂ and NpO₂; whereas, the longitudinal (001)β surface is found for PuO₂. The terminal O²⁻ ions are observed in white; the An⁴⁺ ions in dark grey.

The magnetic state (longitudinal or transverse) of the (001)β surface can be used to differentiate between compounds. In the transverse 3k AFM state for UO₂ and NpO₂, the O²⁻ channels oscillate continuously; whereas, in the longitudinal 3k AFM state for PuO₂, the O²⁻ channels are perfectly linear. In other words, the structures can be differentiated by the transverse 3k AFM state of UO₂ and NpO₂ or by the longitudinal 3k AFM state of PuO₂. The resulting images are analogous to experimental STM studies of AnO₂ surfaces. The STM images offer a predictive guide in the absence of experimental data. The information is relevant for differentiating (001)α and (001)β surfaces. In a STM experiment, ionic positions are influenced by perturbations of the electric field caused by the probe. The calculated resolution is considerably greater compared to that of an experimental study.

6.3.2.3 Electrostatic Potential Isosurface

The electrostatic potential isosurface has been calculated (Figure 6.12). The colours indicate regions of high (red) and low (blue) charge density.
An interesting region of high-charge density associated with an An ion (highlighted in light-blue) on the (111) surface has been identified. The area is expected to have different reaction chemistry compared to the remaining An ions, potentially a site of catalytic activity. In general, regions of high charge density are localized near the oxygen ions. As a consequence of the surface ionic relaxation in the xy-plane, the UO$_2$ and NpO$_2$ (transverse 3k AFM order) (001)$\beta$ surface differs from that of the PuO$_2$ (longitudinal 3k AFM order) (001)$\beta$ surface. The magnetic structure clearly impacts the surfaces chemistry and the surfaces are expected to have different chemical activities.

### 6.3.2.4 Crystal Morphology

A high-temperature truncated octahedral UO$_2$ Wulff crystal morphology (consistent with fluorite-type crystal structures) has been identified by low-voltage SEM images.(53, 55, 79) A low-temperature octahedral AnO$_2$ Wulff morphology (noncollinear 3k AFM order at 0 K) has been calculated by PBEsol+U (connected to the low-index (111), (011), (001)$\alpha\beta$ surface
energetics) (Figure 6.13). As a result of their relative instability, the energy of the (001)α and (001)β surfaces have been ignored. In addition, the energetic influence of higher-index surfaces are considered negligible. In the octahedral crystal morphology, the (111) surface dominates the surface. Note: symmetry constraints hinder (011) facet formation. In comparison with computational studies of AnO₂ surfaces, an octahedral AnO₂ Wulff morphology is consistent with other investigations.(25, 54, 56) As an important computational consideration, the crystal structure is coupled by SOI to the magnetic state. At high-temperature the AnO₂ show paramagnetic order (PM); this impacts the surface energetics and crystal structure. The formation of a truncated octahedral Wulff crystal morphology is a potential consequence. A truncated octahedral structure can only be formed under certain energetic conditions (Equation 6.5).(53)

$$Y_{(001)} < \sqrt[3]{Y_{(111)}}$$

6.5

A number of lower-energy surface configurations, in a (2·2) unit cell, have been calculated by UO₂ (001) surface interatomic potential models; however, the energy is not sufficiently low enough to result in a truncated octahedron.(56)

![Figure 6.13: The AnO₂ Wulff reconstruction. The crystal structure is formed of (111) facets.](image)

In the calculation of (001) surface configurational energetics, the major limitation is the size of the unit cell. There is a possibility that larger cells may result in a configuration of sufficiently low enough energy to result in a truncated octahedron. In this study, the (001)α or (001)β
configuration is used in (1·1) unit cell. Additional configurations are possible in larger supercells. One of these surfaces may possess sufficiently low energy to reduce the surface energy $\gamma_{(001)}/\gamma_{(111)}$ ratio. A systematic investigation of the (2·2) surface is currently computationally unfeasible because of the large number of configurations that must be explored.

In another scenario, the experimental sensitivity of UO$_2$ resulted in a crystal morphology influenced by environmental conditions. It is known that the interaction of oxygen with the AnO$_2$ surfaces influences the composition range of the solid and the formation of superficial structures.(17) An oxygen-rich environment (300 K) can result in a truncated octahedron; this is indicated by DFT+U studies.(80) In addition, interatomic potentials indicate that the AnO$_2$ (001) surface energy is reduced by hydroxylation.(11, 18) This results in a truncated octahedron. An octahedral morphology at thermodynamic equilibrium is also calculated by interatomic potentials; however, these studies concluded that the truncated morphology is the result of kinetic limitations.(81) A number of experimental investigations have shown that the surfaces energies are temperature-dependent.(49, 82)

### 6.4 Conclusions

A noncollinear relativistic low-index AnO$_2$ (An = U, Np, Pu) PBEsol+U surface study has been conducted. A computationally tractable method for the inclusion of magnetic order in the AnO$_2$ has been implemented. A limited number of investigations fully consider relativistic influence.(19, 20, 42, 61, 83-86) The importance of spin-orbit interactions (SOI)(45) for treatment of the actinide elements has been highlighted. The noncollinear magnetic ground-state of the AnO$_2$ is maintained by reorientation of magnetic vectors relative to the surface index. In collinear nonrelativistic surface models, the magnetic moments cannot be reoriented. The use of noncollinear relativistic methods is key to the design of reliable computational models. A computationally tractable method to model the low-index AnO$_2$ surfaces with improved energetics has been constructed. The importance of magnetic vector reorientation has been realised for the first time.

The interlayer relaxation of the (111), (011) and (001)$_\alpha$ surfaces is confined to the first 5 Å. To illustrate the importance of noncollinear magnetic behaviour and relativistic contributions,
compared to scalar DFT studies, the surface energies calculated herein are considerably higher.\(^\text{(10, 28)}\) As is common to fluorite-type structures, the energy of the \((001)\beta < (001)\alpha < (011) < (111)\) surfaces decreases along the series. The calculated octahedral Wulff morphology is completely dominated by \((111)\) facets. This is consistent with theoretical calculations of fluorite-type structures; however, is inconsistent with current experimental information.

### 6.5 Bibliography

Part III: Results & Discussions

Chapter 6: The Design of Surface Models

Chapter 7: Interaction of Hydrogen with Actinide Dioxide Surfaces

7.1 Introduction

The corrosion of actinide materials concerns nuclear industries.\(^1\) The radiolysis of organic compounds and other sources generate hydrogen, known to catalyse the corrosion of the actinide metals.\(^6\) Incidents involving corrosion have resulted in: thermal excursions, the expansion of solids, and the formation of incondensable gases. This has resulted in the failure of containment vessels, and the dispersal of nuclear material.\(^8\) As an imperative to the design of long-term storage facilities, the interaction of hydrogen with nuclear materials must be investigated.\(^9\)

The corrosion and oxidation of the actinide metals are often treated as equivalent topics.\(^10\) The actinide metals are highly-reactive. An unavoidable actinide dioxide (AnO\(_2\)) surface layer is formed by oxidation. This oxide layer then controls the corrosion chemistry of the metal. As an active template for the equilibration of the hydrogen-oxygen system, the AnO\(_2\) electronic structure impacts corrosion mechanisms.\(^5, 11-13\) The interpretation of corrosion mechanism is complex and inferred from studies with hydrogen, oxygen and water.\(^5, 8\) These involve the complex interplay of thermodynamic, kinetic, and catalytic factors.\(^10\) A diffusion-
controlled mechanism of oxygen migration across the oxide layer to the metal-oxide interface fails to account for hydrogen-catalysed oxidation and pyrophoric behaviour.

The interaction of hydrogen with the AnO$_2$ (An = U, Np, Pu) is critical to the long-term storage of nuclear material.(5) After burnt nuclear fuel is removed from commercial reactors, it is transferred to intermediate storage pools for cooling. At this point the thermal energy generated by the radioactive decay of the actinide nuclides is too great for long-term storage. As a soluble thermal neutron absorber, the formation of a super-critical assembly is hindered by a boric acid solution. This boric acid solution surrounds the fuel assembly. The radiolysis of water by the decay of the actinide nuclides forms hydrogen gas. To limit the build-up of hydrogen gas in storage facilities, the environment is monitored and often well ventilated. The evolution of hydrogen gas, once transferred to long-term dry storage, can occur from changes in pressure and temperature. This presents an explosive risk. It is critical to investigate the interaction of hydrogen with the AnO$_2$ surfaces. This also offers insight into the catalytic behaviour of water with actinide materials.

The influence of hydrogen on AnO$_2$ corrosion chemistry is unclear. Mechanisms for water-catalysed corrosion often incorporate the diffusion of hydrogen (H or H$^+$) or hydrogen-containing species (H$_2$O or OH) across the oxide surface layer to the metal oxide interface.(14) The mechanism includes the formation of hyperoxides (AnO$_{2+x}$) increasing the oxygen concentration gradient, this facilitates the migration of O$^{2-}$ ions to the metal-oxide interface.

7.1.1 Literature Review

The interaction of hydrogen with AnO$_2$ surfaces is experimentally difficult to study. The rate of corrosion is influenced by the extent of radiation damage, environmental conditions and surface energetics. A limited number of experimental AnO$_2$ surface investigations have been published.(5-8, 10, 15-19) To compensate for these issues, computational methods offer another means of investigation. Theoretical investigations on the AnO$_2$ are nontrivial. The actinides are highly-correlated f-electron systems for which conventional methods fail. To calculate highly-correlated systems, a number of methods have been developed. These include the self-interaction correction (SIC) method,(20) modified density functional theory
(DFT+U), (21-25) dynamic mean field theory (DMFT), (26) and hybrid density functionals. (27-29) Of these methods, DFT+U offers a tractable means of investigation.

A fluorite-type structural motif is adopted by the AnO$_2$ under standard conditions. At low-temperature, the AnO$_2$ show noncollinear 3k antiferromagnetic (AFM) behaviour. The transverse 3k AFM state of UO$_2$ and NpO$_2$ results in $P$4$\overline{3}$ crystal symmetry; whereas the longitudinal 3k AFM state of PuO$_2$ results in $Fm\overline{3}m$ crystal symmetry. (30-32) In each case, the external cubic symmetry is retained. In contrast, collinear 1k AFM states cause a reduction of cubic crystal symmetry and are not considered. (31, 32)

A computational investigation of AnO$_2$ systems is incredibly complicated. This has limited theoretical investigations on surface interactions. Of these investigations, few fully consider relativistic influences. (33-36) In addition, only one considers noncollinear magnetic behaviour. (36) The corrosion chemistry of the AnO$_2$ (111) surface is controlled by the electronic structure. As an imperative to obtaining the correct corrosion chemistry, the electronic structure of the AnO$_2$ surface must be calculated correctly. The importance of noncollinear magnetic behaviour and spin-orbit interactions (SOI) on the electronic structure has been highlighted by numerous investigations. (30-32, 34, 36) The electronic structure of the AnO$_2$ surface controls hydrogen interactions. This is influenced by relativistic interactions and magnetic order. A number of studies on the AnO$_2$ confirm noncollinear 3k AFM behaviour. (30-32, 36) A transverse 3k AFM state (UO$_2$, NpO$_2$) and a longitudinal 3k AFM state (PuO$_2$) has been calculated for the AnO$_2$ in the parentheses. (31, 32) As the inclusion of relativistic influences are computationally expensive, scaler collinear calculations are often used to evaluate the electronic structure. The interaction of hydrogen has only been studied on the PuO$_2$ (011) surface by DFT+U. (37, 38) The study indicates that atomic H is chemisorbed with an energy of -5.15 eV; whereas, molecular H$_2$ is weakly physisorbed with a dissociation energy of 0.48 eV. As noncollinear magnetic behaviour and SOI were not considered, the findings are incomplete.

The interaction of hydrogen with the low-index AnO$_2$ (111), (011), (001)$\alpha$ surfaces has been investigated by DFT+U. The first fully relativistic investigation has been conducted; here, noncollinear 3k AFM order and SOI contributions have been incorporated. As the surface offers a nonuniform interface, numerous inequivalent adsorption sites are investigated.
7.2 Computational Methodology

7.2.1 Calculation Details

A noncollinear relativistic computational study of the interaction of hydrogen with AnO$_2$ low-index surfaces by the Vienna *Ab-initio* Simulation Package (VASP) code has been conducted.\(^{(20, 26, 39)}\) A planewave basis set, relativistic effective core potentials (ECPs) and the frozen-core projector-augmented wave (PAW) method are used.\(^{(28, 40)}\) The cut-off energy of the planewave basis set is 500 eV. The hydrogen (1s$^1$), oxygen (2s$^2$, 2p$^4$), uranium (6s$^2$, 7s$^2$, 6p$^6$, 6d$^2$ 5f$^5$), neptunium (6s$^2$, 7s$^2$, 6p$^6$, 6d$^2$ 5f$^3$), and plutonium (6s$^2$, 7s$^2$, 6p$^6$, 6d$^2$ 5f$^4$) valence electrons are implicitly considered. The integration over the Brillouin zone has been performed using the Blöchl tetrahedron method.\(^{(41)}\) Noncollinear magnetic wave-vectors and SOI are considered. The on-site Coulomb repulsion of the An 5f electrons is treated by the Liechtenstein *et al* formalism, in which the Coulomb (U) and exchange (J) modifiers are treated as independent variables.\(^{(21-25)}\) The exchange-correlation energy is evaluated by the revised Perdew-Burke-Ernzerhof for solids (PBEsol) functional.\(^{(42)}\) The iteration threshold for electronic and ionic convergence is 1x10$^{-5}$ eV and 1x10$^{-2}$ eV·Å$^{-1}$, respectively.

![Figure 7.1: The low-index AnO$_2$ (111), (011), (001)α surfaces. The An$^{4+}$ (blue) and O$^{2-}$ (red) ions are indicated by the colours in the parentheses. Ionic sites are differentiated, either as superior (s) or inferior (i), by their position relative to the plane of the surface. The surface plane bisects the O$_{(0)}$ ions illustrated by the dashed black line.](image)

An ionically relaxed bulk cell is used to construct the AnO$_2$ (111), (011), (001) surfaces from the METADISE code (Figure 7.1).\(^{(43)}\) As a polar system, the (001) surface is physically...
unrealistic. (44-46) The dipolar component can be eliminated by a surface reconstruction. A nonpolar surface is built by transposing half of the \( O^2- \) ions from the oxygen terminated surface to the actinide terminated surface. The rearrangement of the \( O^2- \) ions results in numerous distinct structural configurations. (36, 47, 48) A number of studies show that in a (1·1) unit cell, the (001)\( \alpha \) surface is the most stable reconstruction. (36, 47) In this study the (001)\( \alpha \) reconstruction (where the \( O^2- \) ions are arranged by rows in the xy-plane) is used to investigate the interaction of hydrogen.

The number of monolayers in the low-index AnO\(_2\) (111) (15 monolayers), (011) (7 monolayers) (001)\( \alpha \) (15 monolayers) surface are indicated in the parentheses. The vacuum gap for each surface is 20 Å. A transverse 3k AFM state for UO\(_2\) (\( U = 3.35 \) eV, \( J = 0.00 \) eV) and NpO\(_2\) (\( U = 4.25 \) eV, \( J = 0.00 \) eV) model is used; whereas, a longitudinal 3k AFM for PuO\(_2\) (\( U = 6.00 \) eV, \( J = 0.00 \) eV) model is used. (31, 32, 36) All ions are fully relaxed with the conjugant gradient algorithm as implemented by VASP. The threshold for electronic and ionic convergence is \( 1 \times 10^{-5} \) eV and \( 1 \times 10^{-2} \) eV·Å\(^{-1} \), respectively. The integration of the Brillouin zone, for the AnO\(_2\) (111) surfaces, is calculated with a \( \Gamma \)-centred k-point grid and a 5·5·1 k-point grid suitable for hexagonal constructs. (49) The integration of the Brillouin zone, for the AnO\(_2\) (011), (001)\( \alpha \) surfaces, is calculated with a \( \Gamma \)-centred k-point grid and a 4·4·1 k-point grid suitable for hexagonal constructs.

### 7.2.2 Inequivalent Positions

The adsorption of atomic H and molecular H\(_2\) on the low-index AnO\(_2\) surfaces has been calculated (Figure 7.2–Figure 7.4). To confirm a global minimum at the low-energy high-symmetry lattice adsorption sites (magnetic inequivalence is assumed to be negligible), a small non-symmetric perturbation has been introduced. The inequivalent oxygen sites are differentiated, either as superior (\( S \)) or inferior (\( I \)), by their position relative to the plane of the surface. The plane of the surface is defined as that which extends across the \( O(S)^{2-} \) ions. Though the transverse 3k AFM structure of UO\(_2\) and NpO\(_2\) results in an internal \( Pa\bar{3} \) crystallographic distortion; the distortion is only 0.014-0.016 Å in magnitude. (31) This is assumed to be negligible relative to the relaxation of the surface ions. (36) For molecular H\(_2\), the orientation is further considered. In this study, molecular H\(_2\) is placed orthogonal to the plane of the surface or parallel along the direction of a bond. In each configuration, hydrogen is situated at a
minimum of 1 Å above the plane of the surface. To avoid the formation of a polar surface, hydrogen is adsorbed on both sides of the surface with inverse symmetry.

The inequivalent sites of interest on the AnO₂ (111) surface include; three atomic (An, O₁(S), O₁(I)) positions, three (An-O₁(S), An-O₁(I), O₁(S)-O₁(I)) bridges and one interstitial (I) site. The surface affords 19 inequivalent H₂ configurations of interest. The inequivalent sites of interest on the AnO₂ (011) surface include; four atomic (An₁(S), An₁(I), O₁(S), O₁(I)) positions, four (An₁(S)-O₁(S), An₁(S)-O₁(I), An₁(I)-O₁(S), An₁(I)-O₁(I)) bridges and three interstitial (I₁(A), I₁(B), I₁(C)) sites. As a result of the orientation of molecular H₂, twenty-eight configurations are investigated. The inequivalent sites of interest on the AnO₂ (011) surface include; four atomic (An₁(S), An₁(I), O₁(S), O₁(I)) positions, four (An₁(S)-O₁(S), An₁(S)-O₁(I), An₁(I)-O₁(S), An₁(I)-O₁(I)) bridges and one interstitial (I) site. The surface affords 23 inequivalent H₂ configurations of interest.

The hydrogen adsorption energy (E_{ads}) is calculated from a full ionic relaxation of the unit cell. The hydrogen adsorption energy is a function of: the total energy of the solid with adsorbate (E_{solid+adsorbate}), the energy of the adsorbate (E_{adsorbate}) and the clean (no adsorbent) total solid energy (E_{solid}) (Equation 7.1).

![Figure 7.2](image_url)

*Figure 7.2: The initial inequivalent configurations of the atomic and molecular hydrogen on the AnO₂ (111) surface. The An⁴⁺ (blue) and O⁻ (red) ions are indicated by the colours in the parentheses. The individual hydrogen positions are shown in grey. The minimum distance of the hydrogen atoms from above the plane of the surface is 1 Å. The hydrogen molecule is considered with either orthogonal (v) or parallel (n) orientations relative to the surface plane.*
Figure 7.3: The initial inequivalent configurations of the atomic and molecular hydrogen on the AnO$_2$ (011) surface. The An$^{4+}$ (blue) and O$^{2-}$ (red) ions are indicated by the colours in the parentheses. The individual hydrogen positions are shown in grey. The minimum distance of the hydrogen atoms from above the plane of the surface is 1 Å. The hydrogen molecule is considered with either orthogonal (v) or parallel (n) orientations relative to the surface plane.

Figure 7.4: The initial inequivalent configurations of the atomic and molecular hydrogen on the AnO$_2$ (001)$_\alpha$ surface. The An$^{4+}$ (blue) and O$^{2-}$ (red) ions are indicated by the colours in the parentheses. The individual hydrogen positions are shown in grey. The minimum distance of the hydrogen atoms from above the plane of the surface is 1 Å. The hydrogen molecule is considered with either orthogonal (v) or parallel (n) orientations relative to the surface plane.
\[ E_{\text{ads}} = E_{\text{solid+adsorbate}} - (E_{\text{solid}} + E_{\text{adsorbate}}) \] 7.1

\( E_{\text{adsorbate}} \) has been calculated by PBEsol from an isolated \( \text{H}_2 \) molecule in a 10 Å\(^3\) cubic cell. Integration of the Brillion zone is completed with a 2·2·2 \( \Gamma \)-centred k-point mesh. The H-H bond length (\( r_{\text{H-H}} \)) of 0.758 Å (experimental value is 0.740 Å) has been calculated by PBEsol.\(^{(50)}\) A negative adsorption energy corresponds to exothermic mechanism; whereas, a positive adsorption energy corresponds to an endothermic mechanism.

The dissociation energy of molecular \( \text{H}_2 \) (\( E_{\text{ds}} = 4.478 \text{ eV} \)) has been measured by fluorescence-excitation spectroscopy.\(^{(51, 52)}\) An error of 0.152 eV is introduced by PBEsol (\( E_{\text{ds}} = 4.630 \text{ eV} \), this impacts adsorption energetics). The error is an order of magnitude less that the chemisorption energetics and therefore relatively insignificant; however, the error is considerable when considering physisorption energetics.

### 7.2.3 Bader Charge Distribution

![Figure 7.5: The inequivalent actinide (An\(_a\)-An\(_d\)) and oxygen (O\(_a\)-O\(_b\)) ions for the low-index AnO\(_2\) (111), (011), (001)\(_{\alpha}\) surfaces are indicated by the parentheses.](image)

The inequivalent actinide (An\(_a\)-An\(_d\)) and oxygen (O\(_a\)-O\(_b\)) ions for the low-index AnO\(_2\) (111), (011), (001)\(_{\alpha}\) surfaces are indicated by the parentheses.
The Henkleman et al\(^{(53-55)}\) code is used to calculate the Bader charge distribution of the low-index AnO\(_2\) (111), (011), (001)\(\alpha\) surface (Figure 7.5). The inequivalent actinide (An(a)-An(d)) and oxygen (O(e)-O(l)) ions for each surface are labelled (Figure 7.5). As an inherent issue common to DFT-based methods, the Bader charges of the ions is often underestimated.\(^{(57)}\)

### 7.3 Results & Discussion

#### 7.3.1 Uranium Dioxide

##### 7.3.1.1 The (111) Surface

The adsorption of atomic H on the UO\(_2\) (111) surfaces (in the a-bH\(_{\text{(111)}}\) configurations) is endothermic (Figure 7.6). The importance of endothermic chemisorption mechanisms has been established for hydrogenation and oxidation mechanisms.\(^{(58)}\) The energy of adsorption of the aH\(_{\text{(111)}}\) site, relative to the bH\(_{\text{(111)}}\) site, is 0.73 eV higher. In the high-energy aH\(_{\text{(111)}}\) configuration, atomic H is located above an U ion. The minimum U-H (2.001 Å) and O-H (2.589 Å) distances are shown in the parentheses. As the electronic structure of the surface is unperturbed by the adsorption of atomic H, the absence of defect states or hybrid H\(s\)- and O\(p\)-states indicates physisorption. In the low-energy bH\(_{\text{(111)}}\) configuration, the interaction results in an unusual endothermic adsorption mechanism. The O-H bond distance of 0.975 Å is indicative of a hydroxyl (OH) group. The formation of an OH group is confirmed by the hybridisation of H\(s\)- and O\(p\)-states at -9 eV to -8 eV and the Bader charge of the H (0.61 eV) ion (Table 7.1). This indicates a protonic H state. In addition, the reduction of an uranium ion, as a result of atomic H adsorption, is indicated by the formation of the U\(f\)-defect in the bandgap. The reduction of the U (d) ion from (2.55 eV) to (2.19 eV) is confirmed in the Bader charge distribution. As the U (a-c) ions are closer in proximity to the H\(^+\) ion, the reduction of the U (d) ion is unusual in terms of electrostatics.

The adsorption of molecular H\(_2\) on the UO\(_2\) (111) surface results in six distinct a-eH\(_2\)\(_{\text{(111)}}\) configurations (Figure 7.7). As with NpO\(_2\) and PuO\(_2\), the dissociation of molecular H\(_2\) on the (111) surface is not observed; though potential dissociation mechanisms are considered. In each instance, molecular H\(_2\) is adsorbed in the -0.01 eV to -0.10 eV energy range. In the a-bH\(_2\)\(_{\text{(111)}}\) configurations, molecular H\(_2\) is located proximal to the U ion. In the aH\(_2\)\(_{\text{(111)}}\)
configuration, the H ions occupy chemically equivalent positions with a potential electrostatic attraction to the nearby O(S) ions resulting in a slight off-centring from the U ion. In theory, the dissociation of the molecule H$_2$ may occur by increasing the H-H separation as each H moves uniformly along separate U-O(S) bonds. In the lowest-energy bH$_2$(111) configuration, characterised by an adsorption energy of -0.10 eV, the dissociation of molecular H$_2$ does not occur. In the Bader charge distribution, the charge of the UO$_2$ (111) surface and the H ions is unaffected.

![Image](image.png)

**Figure 7.6:** The adsorption sites of atomic H on the UO$_2$ (111) surface. The U$^{4+}$ (blue), O$^-$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is indicated. The density of states of the a-bH$_2$(111) configurations for the UO$_2$ (111) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.

In the cH$_2$(111) configuration molecular H$_2$ is located directly above an O(S) ion, offering another possibility for molecular H$_2$ dissociation whereby one H ion initially forms an OH group. This then proceeds by the formation of second OH group involving the remaining H ion. In the high-energy dH$_2$(111) configuration, molecular H$_2$ is located above an O(I) ion orthogonal to the plane of the surface. Given the relatively high energetics of this configuration, it is unlikely to play any role in the dissociation of the H$_2$ molecule. In the eH$_2$(111) configuration, molecular H$_2$ is proximal to the O(I) ion and directed towards the neighbouring O(S) ion, which is suggestive of
the electrostatic attraction of hydrogen to the O(S) ion as a prelude to dissociation. The electronic structure for molecular H$_2$ adsorption on the UO$_2$ (111) surface, as indicated by the DoS, has been calculated for the a-eH$_2$(111) configurations. The absence of defect states or hybrid H s- and O p-states, in the a-eH$_2$(111) configurations, indicates that molecular H$_2$ is physisorbed. The magnitude of the electrostatic interaction is indicated by the position of the H s-band.

![Image of adsorption sites and density of states](image)

**Figure 7.7:** The adsorption sites of molecular H$_2$ on the UO$_2$ (111) surface. The $U^{4+}$ (blue), $O^{2-}$ (red) and $H$ (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{ads}$) is indicated. The density of states of the a-eH$_2$(111) configurations for the UO$_2$ (111) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.

The dissociation of molecular H$_2$ is not observed on the UO$_2$ (111) surface (although there is clear evidence of atomic H chemisorption). The adsorption energies, DoS, and optimized geometries, indicate molecular H$_2$ is physisorbed onto the (111) surface. This is likely due to a large energetic barrier for the dissociation pathways relative to the energetically favourable (-0.1 eV to -0.01 eV) physisorption based on van der Waals interactions. A series of climbing
Nudged Elastic Band (cNEB) calculation can confirm the diagnosis. As of the unusual charge distribution in the atomic aH(111) configuration, the absence of dissociation may be a limitation of a (1·1) unit cell model. In contrast, a (2·2) unit cell offers the option of distributing the charge imparted by the adsorption of a H ion over a larger surface area. One notes that the distribution of charge and the separation of hydrogen ions over a great surface would introduce a significant energetic barrier for dissociation. As a limitation of this model, a full systematic study of a (2·2) unit cell is computationally unfeasible at this time.

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### 7.3.1.2 The (011) Surface

The interaction of atomic H on the UO$_2$ (011) surface is endothermic in nature. As a result, the a-dH$_{\text{(111)}}$ configurations are formed (Figure 7.8). This is identical to the reaction of atomic H on the UO$_2$ (111) surface which also results in an endothermic adsorption mechanism. In the aH$_{\text{(011)}}$ configuration, characterised by an adsorption energy of 1.13 eV, atomic H is located at 2.044 Å from the U(S) ion; whereas, in the bH$_{\text{(011)}}$ configurations, characterised by an adsorption energy of 1.45 eV, atomic H is located at 2.092 Å from the U(S) ion. Of interest, in the cH$_{\text{(011)}}$ configuration, atomic H is location within the IC interstitial channel. This offers a means by which H ions diffuse through the oxide layer. The minimum U(I)-H, O(S)-H and O(I)-H distances are 2.250 Å, 2.317 Å and 2.258 Å respectively.

The formation of the U f-defect state proximal to the conduction band minimum (CBM) and absence of hybrid H s- and O p-states, in the high-energy a-cH$_{\text{(011)}}$ configurations, is indicative of the oxidation of the U$^{4+}$ ion to the U$^{5+}$ ion and the existence of a hydride group, confirmed by the Bader charge distribution. In the past, a hydride induced corrosion mechanism has been proposed for actinide compounds.(6, 14, 16, 59) As the a-cH$_{\text{(011)}}$ configurations are
energetically unfavourable, a hydride induced corrosion mechanism by the UO$_2$ (011) surface is improbable.

Figure 7.8: The adsorption sites of atomic H on the UO$_2$ (011) surface. The U$^{4+}$ (blue), O$^2-$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{ads}$) is additionally indicated. The density of states of the a-dH$_{(011)}$ configurations for the UO$_2$ (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.

In the a-cH$_{(011)}$ configurations, the H s-band is located proximal to the valence band maximum (VBM) indicates physisorption; whereas, for the dH$_{(001)}$ configuration, the H s-band is located at -9 eV to -8 eV which indicates chemisorption. In the low-energy dH$_{(011)}$ configuration, the H atom is positioned along the U$_{(i)}$-O$_{(S)}$ bond. The minimum U$_{(i)}$-H and O$_{(S)}$-H distance is 2.644 Å and 0.995 Å, respectively. In this, the O$_{(S)}$-H bond is reminiscent of an OH group. In addition, there is a considerable distortion of the surface structure, in which the U$_{(S)}$-O$_{(S)}$ bond increases from 2.313 Å to 2.446 Å. The formation of the U f-defect in the band-gap and presence of hybrid H s- and O p-states confirms the reduction of the U$^{4+}$ ion to the U$^{3+}$ ion and the existence of the OH group, respectively. A protonic state and the reduction of the U (b) ion is confirmed by the Bader charge analysis.
Figure 7.9: The adsorption sites of molecular $H_2$ on the $UO_2$ (011) surface. The $U^{4+}$ (green), $O^{2-}$ (red) and $H$ (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{ads}$) is additionally indicated. The density of states of the a-$H_2$(011) configurations for the $UO_2$ (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.
The interaction of molecular H\(_2\) on the UO\(_2\) (011) surface results in 12 distinct a-IH\(_2\)(011) configurations (Figure 7.9). In each instance, molecular H\(_2\) is physisorbed in the -0.05 eV to -0.11 eV energy range. In the a-ch\(_2\)(011) configurations, characterised by an adsorption energy of -0.08 eV to -0.07 eV, molecular H\(_2\) located above the U\(_{5}\) ion with no discernible effect on the electronic structure of the UO\(_2\) (011) surface. The electronic structure for molecular H\(_2\) adsorption on the UO\(_2\) (011) surface, as indicated by the DoS, has been calculated for the for the a-hH\(_2\)(111) configurations. The absence of defect states or of hybrid H s- and O p-states, in the high-energy a-IH\(_2\)(111) configurations, indicates that molecular H\(_2\) is physisorbed. The magnitude of the electrostatic interaction is indicated by the position of the H s-band. In the low-energy iH\(_2\)(011) configuration, the Bader charge indicates that the H\(_2\) molecular is partially polarised by 0.04 eV (Table 7.2). This is unusual as the H ions occupy ionically equivalated lattice positions. The polarisation may be due to the magnetisation of the U ions causing a minor chemical inequivalence or due to errors inherent to these calculations. As with the interaction of molecular H\(_2\) on the UO\(_2\) (111) surface, the dissociation of molecular H\(_2\) is not observed on the UO\(_2\) (011) surface. As an OH group is formed with atomic H, it is curious that the dissociation of molecular H\(_2\) does not occur. This is potentially the result of an endothermic adsorption mechanism or steric hindrances preventing the formation of a second chemically equivalent OH group.

### Table 7.2: The Bader charge distribution (eV) of the UO\(_2\) (011) surface for each configuration.

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7.3.1.3 The (001)α Surface

The interaction of atomic H interaction on the UO$_2$ (001)α surface has been calculated. This results in the aH$_{(001)\alpha}$ configuration. The configuration is characterised by an endothermic adsorption energy of 0.46 eV (Figure 7.10). This is the only stable configuration. The H ion is located within the O vacancy generated by the reconstruction of the polar (001) surface. The minimum U$_{(S)}$-H (2.125 Å) and O$_{(S)}$-H (2.781 Å) O$_{(I)}$-H (2.420 Å) bond distances are indicated in the parentheses. The electronic structure for atomic H adsorption on the UO$_2$ (001)α surface, as indicated by the DoS, has been calculated for the aH$_{(001)\alpha}$ configuration. The formation of the U f-defect state near to the CBM and absence of hybrid H s- and O p-states, in the aH$_{(001)\alpha}$ configuration, confirms the oxidation of the U ion and the existence of a hydride group. The Bader charge of the H ion (-0.45 eV) confirms the formation of a hydride ion. This is accompanied by the oxidation of the U (a) ion and equal reduction of the O (g-h) ions (Table 7.3).

![Image of adsorption sites of atomic H on the UO$_2$ (001)α surface](image)

Figure 7.10: The adsorption sites of atomic H on the UO$_2$ (001)α surface. The U$^{4+}$ (blue), O$^{2-}$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the aH$_{(001)\alpha}$ configuration for the UO$_2$ (001)α surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.

The interaction of molecular H$_2$ with the UO$_2$ (001)α surface generates six distinct a-fH$_{2(001)\alpha}$ configurations (Figure 7.11). The sites are characterised by an exothermic adsorption in the -
0.06 eV to -0.26 eV energy range. In these calculations, the dissociation of molecular H\(_2\) is not observed. In the aH\(_2\) configuration, molecular H\(_2\) is located above a U\(_S\) ion; whereas, in the bH\(_2\) configuration, molecular H\(_2\) is located above a U\(_I\) ion. In each instance, molecular H\(_2\) is orientated towards the neighbouring O\(_S\) ions, which indicates an electrostatic interaction. In the c-dH\(_2\) configurations, molecular H\(_2\) is located near to the U\(_I\) ion. In these configurations, molecular H\(_2\) is offset in the vertical plane and directed towards an O\(_S\) ion. Though the configurations are structurally similar, a difference of 0.02 eV is calculated.

Figure 7.11: The adsorption sites of molecular H\(_2\) on the UO\(_2\) \((001)\)α surface. The U\(^{4+}\) (blue), O\(^{2-}\) (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E\(_{ads}\)) is additionally indicated. The density of states of the a-fH\(_2\) configurations for the UO\(_2\) \((001)\)α surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.

In the eH\(_2\) configuration, molecular H\(_2\) is located orthogonal to an O\(_S\) ion. The electronic structure is unusual. The formation of the U f-defect state in the band-gap and the absence of hybrid H s- and O p-states, in the high-energy eH\(_2\) configuration, indicates that oxidation of the U\(^{4+}\) ion to the U\(^{5+}\) ion occurs and the advocates the existence of a hydride group. Indeed, the Bader charge distribution indicates the polarisation of the molecular H\(_2\); however, molecular H\(_2\) dissociation does not occur.
In the low-energy fH$_2$(001)$_a$ configuration, molecular H$_2$ is located within the O(S) defect formed by the reconstruction of the UO$_2$ (001) surface. The configuration is considerably more stable compared to other adsorption sites. This indicates a potential pathway by which molecular H$_2$ can be transported by diffusion across an oxide surface layer. In the Bader charge distribution, molecular H$_2$ is partially oxidised and the neighbouring An (c) and An (d) ions are partially reduced. The electrostatic interaction is epitomised by the location of the H s-band at -7 eV.

<table>
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<th>O</th>
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<tr>
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</table>

The interaction of atomic H on the low-index UO$_2$ (111), (011) (001)$_a$ surfaces indicate an endothermic adsorption mechanism, characterised by the formation of a hydride ion and oxidation of an U ion. In contrast, the interaction of molecular H$_2$ is characterised by an exothermic mechanism. No evidence of molecular H$_2$ dissociation is observed.

7.3.2 Neptunium Dioxide

7.3.2.1 The (111) Surface

A result of the interaction of atomic H$_2$ on the NpO$_2$ (111) surface, the aH$_{(111)}$ configuration is characterised by an exothermic adsorption energy of -0.10 eV (Figure 7.12). In contrast to atomic H adsorption on UO$_2$ and PuO$_2$ (111) surfaces, no other configurations have been found. An exothermic adsorption energy of -0.10 eV is calculated for the NpO$_2$ aH$_{(111)}$ configuration. This contrasts against the endothermic adsorption energy of 0.82 eV for the UO$_2$ bH$_{(111)}$ configuration. The configurations are structurally nearly identical. Atomic H is adsorbed directly above an O(S) ion. The OH group is characterised by an OH bond length of 0.975 Å. In conjunction with the formation of an OH group, a H protonic state is confirmed by the Bader charge distribution (Table 7.4).
The formation of an OH group is confirmed by the hybridisation of the H s- and O p-states at -8 eV. The Bader charge analysis shows the reduction of the Np (d) ion. The reduction of the Np (d) ion is confirmed by the Np f-defect located within the band-gap. The defect state reduces the band-gap of NpO$_2$ to 0.16 eV and shows Mott-Hubbard characteristics. As a result of the experimental complexity of NpO$_2$, measurements of the band-gap vary from 0.40-3.10 eV.(60-62)

In comparison, the interaction of molecular H$_2$ on the NpO$_2$ (111) surface generates five distinct a-eH$_2$(111) configurations (Figure 7.13). The aH$_2$(111) site, relative to the bH$_2$(111) site, is 0.006 eV lower in energy. As with UO$_2$ and PuO$_2$, the dissociation of molecular H$_2$ on the (111) surface is not observed. The electronic structure indicates that molecular H$_2$ is physisorbed in each instance. In the low-energy aH$_2$(111) configuration, characterised by an adsorption energy of -0.10 eV, molecular H$_2$ is located proximal to the Np ion. The adsorption of molecular H$_2$, relative to atomic H, is thermodynamically unstable.
Part III: Results & Discussions  Chapter 7: Interaction of Hydrogen with Actinide Dioxide Surfaces

Figure 7.13: The adsorption sites of molecular \( \text{H}_2 \) on the NpO\(_2\) (111) surface. The Np\(^{4+}\) (blue), O\(^{2-}\) (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (\( E_{\text{ads}} \)) is additionally indicated. The density of states of the a-e\( \text{H}_2\)(111) configurations for the NpO\(_2\) (111) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.

Table 7.4: The Bader Charge Distribution (eV) of the NpO\(_2\) (111) Surface for each Configuration.

| Ion | H  | H  | Np | a  | b  | c  | d  | O  | e  | f  | g  | h  | i  | j  | k  | l  |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Clean Surface | - | - | 2.51 | 2.51 | 2.51 | -1.25 | -1.25 | -1.25 | -1.25 | -1.25 | -1.25 | -1.25 |
| Atomic Interaction | 0.57 | 2.48 | 2.10 | 2.48 | 2.48 | -1.27 | -1.27 | -1.27 | -1.26 | -1.26 | -1.28 | -1.26 |
| Molecular Interaction | a 0.02 -0.01 2.52 2.52 2.51 2.51 -1.25 -1.25 -1.24 -1.25 -1.25 -1.25 | b -0.04 0.04 2.25 2.53 2.48 2.48 -1.25 -1.25 -1.25 -1.25 -1.25 -1.25 | c 0.03 -0.03 2.51 2.53 2.51 2.51 -1.25 -1.25 -1.24 -1.25 -1.25 -1.25 | d -0.04 0.04 2.51 2.52 2.49 2.49 -1.24 -1.25 -1.24 -1.25 -1.25 -1.25 | e 0.01 -0.01 2.51 2.53 2.50 2.50 -1.25 -1.25 -1.24 -1.25 -1.25 -1.25 |

It is unusual that the molecular \( \text{H}_2 \) dissociation is not observed. Again, by analysis of the Bader charge distribution of the atomic aH\(_{111}\) state, a limitation of the \((1\cdot1)\) unit cell model employed is the inability to partition the electron density over a larger surface area. In addition, a large
energetic barrier, introduced from the need to spread the negative charge over a greater distance, possibly hinders the formation of two OH groups. As such, even if molecular H\textsubscript{2} dissociates, recombination is highly probable. Given the surface areas involved in the distribution of charges, kinetic factors likely control the dissociation of molecular H\textsubscript{2} on the NpO\textsubscript{2} (111) surface. The dissociation mechanism may proceed by elongation of the H-H bond as each H ion moves towards an O(S) ion.

7.3.2.2 The (011) Surface

The interaction of hydrogen on the NpO\textsubscript{2} (011) surface has been investigated. The interaction of atomic H on the NpO\textsubscript{2} (011) surface generates 2 distinct a-bH_{(111)} configurations (Figure 7.14). The aH_{(011)} configuration, characterised by an endothermic adsorption energy of 1.86 eV; whereas, the bH_{(011)} configuration, characterised by an exothermic adsorption energy of -0.47 eV. The aH_{(011)} configuration forms a minor hybrid H s- and Np f-defect state in the bandgap. This implies the oxidation of Np\textsuperscript{4+} to Np\textsuperscript{5+} resulting in the formation of a hydride species. The Np-H bond length is 2.129 Å.

![Figure 7.14: The adsorption sites of atomic H on the NpO\textsubscript{2} (011) surface. The Np\textsuperscript{4+} (blue), O\textsuperscript{2-} (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E_{ads}) is additionally indicated. The density of states of the a-bH_{(011)} configurations for the NpO\textsubscript{2} (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.](image)
Figure 7.15: The adsorption sites of molecular $H_2$ on the NpO$_2$ (011) surface. The Np$^{4+}$ (blue), O$^2-$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the a-j$H_2$(011) configurations for the NpO$_2$ (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.
Table 7.5: The Bader charge distribution (eV) of the NpO$_2$ (011) surface for each configuration.

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In the bH$_{(011)}$ site, the H ion is bound to an O$_{(5)}$ ion resulting in the formation of an OH group with an O-H bond length of 0.997 Å. The result is confirmed by the Bader charge of the H ion of 0.64 eV indicating a protic state (Table 7.5). The reduction of the nearby Np (b) ion is caused by imparting a negative charge. The OH group can be inferred from the of hybrid H s- and O p-states at -8 eV to -7 eV. Additionally, the reduction of the Np$^{4+}$ ion to the Np$^{3+}$ ion is indicated by the Np f-defect in the band-gap. The formation of the Np f-defect results in Mott-Hubbard characteristics, an instance whereby environmental conditions influence the electronic structure considerably. In the literature, epitaxial absorbance measurements of NpO$_2$ thin films report a band-gap of 2.85 eV.(60) whereas, electrical resistivity measurements of NpO$_2$ report a band-gap of 0.4 eV.(61) The difference between the two measurements might be attributed to the method of sample preparation. The inhomogeneity of samples is a major obstacle for accurate experimental measurements of the band structure.

The interaction of molecular H$_2$ on the NpO$_2$ (011) surface generates 10 distinct a-jH$_{(111)}$ configurations characterised by an adsorption energy of -0.10 eV to -0.06 eV (Figure 7.15). The dissociation of molecular H$_2$ on the NpO$_2$ (011) surface has not observed in these calculations. In the a-bH$_{2(011)}$ configurations, molecular H$_2$ is located proximal to the Np$_{(5)}$ ion; whereas, in the c-dH$_{2(011)}$ configurations, molecular H$_2$ is located proximal to the Np$_{(4)}$ ion. The stability of the a-bH$_{2(011)}$ configurations, relative to the c-dH$_{2(011)}$ configurations, is accentuated by the H s-band in the DoS. In the more stable f-hH$_{2(011)}$ configurations, molecular H$_2$ is located proximal to the O$_{(4)}$ ion. In the i-jH$_{2(011)}$ configurations, molecular H$_2$ occupies interstitial positions.
In the low-energy molecular fH$_{2011}$ configuration, as stated, the dissociation of molecular H$_2$ is not observed. This is confirmed by the Bader charge distribution of the NpO$_2$ (011) surface that is relatively uninfluenced. In addition, the H$_2$ species is polarised and results in a total Bader charge difference 0.01 eV (Table 7.5). In the atomic bH$_{(011)}$ configuration, it is noted that atomic H binds to form an OH group. It is therefore curious, that despite this activity, the dissociation of the molecular H$_2$ is not observed, likely due to steric hindrances preventing the formation of a second chemically equivalent OH group.

7.3.2.3 The (001)\(\alpha\) Surface

The interaction of atomic H on the NpO$_2$ (001)\(\alpha\) surface has been investigated (Figure 7.16). This results in distinct a-cH$_{2(001)\alpha}$ configurations. The a-bH$_{(001)\alpha}$ configurations, characterised by an adsorption energy of -0.83 eV to -0.82 eV, result in the formation of an OH group. The low-energy aH$_{(001)\alpha}$ configuration, relative to the bH$_{(001)\alpha}$ configuration, is 0.01 eV lower in energy. The O-H bond length of 0.974 Å is indicative of the OH group. The electronic structure, as indicated by the DoS, indicates an O \(p\)-defect state in the band-gap. This results in a narrowing of the band-gap to 1.47 eV and results in Mott-Hubbard characteristics.

Figure 7.16: The adsorption sites of atomic H on the NpO$_2$ (001)\(\alpha\) surface. The Np$^{4+}$ (blue), O$^{2-}$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the a-cH$_{(001)\alpha}$ configurations for the NpO$_2$ (001)\(\alpha\) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.
The formation of the OH group is confirmed by the Bader charge of the H ion (0.63 eV) indicating a protonic state. The imparted charge from the H ion causes the Np (a) ion and O (e-f) ions to be reduced. In contrast, in the bH(001)α configuration, the H ion generates a minor distortion of the NpO₂ (001)α surface. The electronic structure of the bH(001)α configuration, relative to the aH(001)α configuration, is almost identical. The O-H bond distance is 0.974 Å. In the cH(001)α configuration, characterised by an adsorption energy of 1.42 eV, atomic H is located within the O(S) defect site formed by the reconstruction of the NpO₂ (001) surface. The configuration is structurally identical to the UO₂ aH(001)α configuration. The reduction of a Np ion indicated by the Np f-defect at the CBM is indicative of the formation of a hydride ion, confirmed by the Bader charge distribution.

Figure 7.17: The adsorption sites of molecular H₂ on the NpO₂ (001)α surface. The Np⁴⁺ (blue), O²⁻ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E_ads) is additionally indicated. The density of states of the a,fH₂(001)α configurations for the NpO₂ (001)α surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.

The interaction of molecular H₂ on the NpO₂ (001)α surface generates six distinct a,fH₁₁₁ configurations (Figure 7.17). In the a,dH₂(001)α configurations, the dissociation of molecular H₂ does not occur. The energy of adsorption is exothermic in the -0.07 eV to -0.23 eV range. In
the aH$_2$(001)$_{\alpha}$ configuration, molecular H$_2$ is adsorbed above the Np$_{(S)}$ ion; whereas, in the bH$_2$(001)$_{\alpha}$ configuration, molecular H$_2$ is adsorbed above the Np$_{(I)}$ ion. In both instances, molecular H$_2$ is directed along the O$_{(S)}$ path, which indicates an electrostatic interaction. In the cH$_2$(001)$_{\alpha}$ configuration, molecular H$_2$ is adsorbed directly above the O$_{(S)}$ ion with no indication of dissociation. In the dH$_2$(001)$_{\alpha}$ configuration, molecular H$_2$ is physisorbed proximal and above the O vacancy formed by the reconstruction of the (001) surface. The configuration, relative to other physisorbed sites, is considerably more stable.

In the e-fH$_2$(001)$_{\alpha}$ configurations, the dissociation of molecular H$_2$ is observed. The energy of adsorption is exothermic in the -0.96 eV to -1.01 eV energy range. The individual H ions are chemisorbed by O$_{(S)}$ ions as indicated by the H s-band located at ~8 eV in the density of states. The eH$_2$(001)$_{\alpha}$ configuration, relative to the fH$_2$(001)$_{\alpha}$ configuration, is 0.05 eV higher in energy. In the eH$_2$(001)$_{\alpha}$ configuration, the OH groups are chemically equivalent. The O-H bond length is 0.972 Å and results in a minimal distortion of the surface. In contrast, the OH groups in the fH$_2$(001)$_{\alpha}$ configuration, with an O-H bond length of 0.974-0.990 Å, are chemically inequivalent and result in a considerable distortion of the O$_{(S)}$ surface ions. The protonic nature of the H ions is shown in the Bader charge distribution indicating chemisorption (Table 7.6). In both instances, the Np (c-d) and O ions are reduced. The formation of the OH groups is confirmed by the hybrid H s- and O p-states. The formation of the Np f-defect near the CBM indicates the reduction of the Np ions. The defect results in either a metallic or semi-metallic ground-state highlighting the sensitivity of NpO$_2$ to environmental conditions. For instance, the band-gap, as measured by electrical conduction, is 0.40 eV; (61) whereas, the band-gap, as measured by optical absorbance spectroscopy, is 2.85 eV. (60) In terms of mechanism, the dissociation of molecular H$_2$ is likely to initiate from the physisorbed dH$_2$(001)$_{\alpha}$ site. A cNEB calculation would confirm the mechanism. A cNEB search is unfortunately impracticable at this time, due to the computationally intensive nature of these calculation.

The interaction of atomic H on the low-index NpO$_2$ (111), (011) (001)$_{\alpha}$ surfaces indicates an exothermic adsorption mechanism. No evidence of molecular H$_2$ dissociation is found on the (111) surface. The dissociation of molecular H$_2$ is only observed on the (011) and (001)$_{\alpha}$ surfaces, resulting in the formation of an OH group. In regards to the chemistry of the low-index AnO$_2$ surfaces, the NpO$_2$ offers an intermediary state for the adsorption of hydrogen. The formation of a hydride species is only observed in UO$_2$ and NpO$_2$; whereas, the formation of an OH group is only observed in NpO$_2$ and PuO$_2$.
Table 7.6: The Bader Charge Distribution (eV) of the NpO$_2$ (001)$\alpha$ Surface for each Configuration.

| Ion | H $^x$ | | Np $^a$ | | O $^e$ | | a | | b | | c | | d | | e | | f | | g | | h |
|-----|-------|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| a   | 0.63  | -                | 2.52  | 2.51  | 2.07  | 2.41  | -1.28 | -1.28 | -1.22 | -1.34 |
| b   | 0.60  | -                | 2.53  | 2.53  | 2.07  | 2.40  | -1.28 | -1.28 | -1.22 | -1.30 |
| c   | -0.39 | -                | 2.52  | 2.51  | 2.46  | 2.53  | -1.24 | -1.25 | -1.07 | -1.08 |
| a   | 0.01  | 0.00             | 2.53  | 2.53  | 2.43  | 2.44  | -1.27 | -1.27 | -1.19 | -1.18 |
| b   | -0.01 | 0.02             | 2.51  | 2.51  | 2.44  | 2.44  | -1.27 | -1.27 | -1.18 | -1.19 |
| c   | -0.06 | 0.06             | 2.51  | 2.53  | 2.44  | 2.43  | -1.27 | -1.27 | -1.18 | -1.18 |
| d   | 0.03  | -0.01            | 2.52  | 2.52  | 2.43  | 2.43  | -1.27 | -1.26 | -1.19 | -1.19 |
| e   | 0.58  | 0.57             | 2.50  | 2.26  | 2.07  | 2.32  | -1.28 | -1.28 | -1.31 | -1.32 |
| f   | 0.61  | 0.60             | 2.52  | 2.11  | 2.41  | 2.05  | -1.26 | -1.27 | -1.33 | -1.32 |

7.3.3 Plutonium Dioxide

7.3.3.1 The (111) Surface

The interaction of hydrogen with the PuO$_2$ (111) surface results in a-bH$_{(111)}$ configurations (Figure 7.18). The aH$_{(111)}$ configuration is characterised by an endothermic adsorption energy of 2.18 eV; whereas, the bH$_{(111)}$ configuration is characterised by an exothermic adsorption energy of -1.25 eV. In the aH$_{(111)}$ configuration, the atomic H is positioned directly above a Pu ion. After a full ionic relaxation, the minimum Pu-H (2.403 Å) and O-H distance (2.754 Å) distances are indicated in the parentheses. The configuration shares structural similarities with the UO$_2$ aH$_{(111)}$ configuration; although the endothermic energy of adsorption is considerably greater. In reference to the UO$_2$ bH$_{(111)}$ site and the NpO$_2$ aH$_{(111)}$ configurations, the PuO$_2$ bH$_{(111)}$ configuration is reasonably identical in terms of structural configuration. The energy of absorption decreases from 0.82 eV to -1.25 eV along the AnO$_2$ (An = U, Np, Pu) series. This offers an indication of the increasing reactivity of the AnO$_2$ (111) surface. In the bH$_{(111)}$ site, the H atom is bonded to an O$_{(S)}$ atom to form an OH group; where, the O-H bond distance of 0.976 Å is consistent with that of an OH group. The adsorption energy is -1.25 eV indicating an exothermic chemisorption mechanism. At the O$_{(S)}$ site the neighbouring oxygen ions are drawn inwards, this causes in a slight structural deformation. The formation of the OH group is confirmed by the H ion Bader charge of 0.58 eV (Table 7.7). In each instance the electronic structure of the PuO$_2$ (111) surface is relatively uninfluenced and indicates molecular H$_2$ physisorption. As there is clear evidence of atomic H chemisorption on the PuO$_2$ (111) surface, it is surprising that the dissociation of molecular H$_2$ is not observed. A large energetic barrier is thought to influence the adsorption mechanism; though cNEB calculations would markedly confirm this image. Indeed, given the unusual charge distribution in the aH(111) configuration, the result may be a limitation of a (1·1) unit cell. In contrast, a (2·2) unit cell offers the option
of distributing the charge imparted by the adsorption of a H ion over a large surface area. This indicates a protonic state. In addition, the Pu (d) ion is reduced; whereas, the O ions are only partially oxidised.

The instability of the aH\textsubscript{(111)} configuration is highlighted by the H s-defect state located within the band-gap. In the bH\textsubscript{(111)} configuration, the number of Pu f-states in the valence band increases; whereas, the number of Pu f-states in the conduction band decreases. This indicates that, due to the interaction of hydrogen, high-energy Pu f-states are shifted to lower energy levels. The reduction of the formal Pu\textsuperscript{4+} (2.47 eV) ion to Pu\textsuperscript{3+} (2.08 eV) ion by hydrogen is confirmed by the Bader charge. Additionally, the hybridisation of the H s- and O p-states at 6 eV is indicative of the formation of an OH group.

Figure 7.18: The adsorption sites of atomic H on the PuO\textsubscript{2} (111) surface. The Pu\textsuperscript{4+} (blue), O\textsuperscript{2−} (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E\textsubscript{ads}) is additionally indicated. The density of states of the a-bH\textsubscript{(111)} configurations for the PuO\textsubscript{2} (111) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.

In comparison, the interaction of molecular H\textsubscript{2} on the PuO\textsubscript{2} (111) surface results in four distinct a-dH\textsubscript{2(111)} configurations (Figure 7.19). As with the UO\textsubscript{2} (111) and NpO\textsubscript{2} (111) surfaces, the dissociation of the molecular H\textsubscript{2} on the PuO\textsubscript{2} (111) surface is not observed. In each instance, the physisorption of molecular H\textsubscript{2} is in an energy range of -0.01 eV to -0.08 eV. The aH\textsubscript{2(111)}
site, relative to the bH\textsubscript{2}(111) site, is marginally higher in energy by 0.003 eV. In both instances, molecular H\textsubscript{2} is positioned proximal to a Pu ion. In the cH\textsubscript{2}(111) site, molecular H\textsubscript{2} is located above an O\textsubscript{(S)} ion with an adsorption energy of -0.03 eV. The configuration potentially acts as an intermediary position for the dissociation of H\textsubscript{2} and the formation of the OH group. This is seen in the atomic aH\textsubscript{4}(111) site; however, as stated this has not been observed in these calculations. In addition, the dH\textsubscript{2}(111) site is reminiscent of the cH\textsubscript{2}(111) site, though molecular H\textsubscript{2} is now located above the O\textsubscript{(I)} ion. The lowest-energy bH\textsubscript{2}(111) site is characterised by an adsorption energy of -0.08 eV. A physisorption mechanism is confirmed by the Bader charge distribution (Table 7.7). The disruption to the surface is negligibly influenced and the hydrogen ions remain effectively charge neutral.

Figure 7.19: The adsorption sites of molecular H\textsubscript{2} on the PuO\textsubscript{2} (111) surface. The Pu\textsuperscript{4+} (blue), O\textsuperscript{2−} (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E\textsubscript{Ads}) is additionally indicated. The density of states of the a-dH\textsubscript{2}(111) configurations for the PuO\textsubscript{2} (111) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.
In each instance the electronic structure of the PuO$_2$ (111) surface is relatively uninfluenced and indicates molecular H$_2$ physisorption. As there is clear evidence of atomic H chemisorption on the PuO$_2$ (111) surface, it is surprising that the dissociation of molecular H$_2$ is not observed. A large energetic barrier is thought to influence the adsorption mechanism; though cNEB calculations would markedly confirm this image. Indeed, given the unusual charge distribution in the aH$_{(111)}$ configuration, the result may be a limitation of a (1·1) unit cell. In contrast, a (2·2) unit cell offers the option of distributing the charge imparted by the adsorption of a H ion over a large surface area.

### Table 7.7: The Bader Charge Distribution (eV) of the PuO$_2$ (111) Surface for each Configuration.

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</tr>
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<td>2.45</td>
</tr>
</tbody>
</table>

7.3.3.2 The (011) Surface

As a result of the interaction of atomic H$_2$ on the PuO$_2$ (011) surface, the aH$_{(111)}$ configuration is characterised by an exothermic adsorption energy of -1.71 eV (Figure 7.20). In contrast to atomic H adsorption on UO$_2$ and PuO$_2$ (011) surfaces, no other configurations have been found. This is likely an artefact of the considerable stability of the adsorption site. In the aH$_{(111)}$ configuration, the H ion is directly bonded to an O(S) ion. The O-H bond length of 1.00 Å is reminiscent of an OH group. In addition, the Bader charge distribution indicates that atomic H exists in a protonic state (Table 7.8). This results in a reduction of the Pu (a) ion; whereas, the charge of the O ions is only partially increased.

The formation of the OH group results in a strong distortion of the PuO$_2$ (011) surface. The Pu$_{(S)}$-O$_{(S)}$ (2.30 Å to 2.44 Å) and Pu$_{(I)}$-O$_{(S)}$ (2.23 Å to 2.24 Å) bond length is shown to increase. In contrast to past investigations, the chemisorption energy of the H ion is considerably lower.(37) A single adsorption site is found in these calculations; compared to multiple sites previously indicated. The electrostatic repulsion of the Pu$_{(S)}$ ion potentially forces the aH$_{(011)}$
configuration. If the H ion was bound and located above the interstitial channel, then the electrostatic repulsion generated by the Pu_{(S)} ion would be greater than that of the Pu_{(I)} ion. The number of Pu \( f \)-states in the valence band increases; whereas, the number of Pu \( f \)-states in the conduction band decreases. This indicates that, due to the interaction of hydrogen, high-energy Pu \( f \)-states are shifted to lower energy levels. Additionally, the band located at -7 eV to -6 eV is comprised of H \( s \)- and O \( p \)-states, confirms the formation of the OH group.

![Figure 7.20: The adsorption sites of atomic H on the PuO\(_2\) (011) surface. The Pu\(^{4+}\) (blue), O\(^2-\) (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (\( E_{\text{ads}} \)) is additionally indicated. The density of states of the aH\(_{(011)}\) configuration for the PuO\(_2\) (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide \( f \)- (blue), actinide \( d \)- (green) and oxygen \( p \)- (red) and hydrogen \( s \)- (yellow) bands. Note, the hydrogen \( s \)-band has been magnified by a factor of 40 for clarity.](image)

The interaction of molecular \( \text{H}_2 \) on the PuO\(_2\) (011) surface results in thirteen distinct a-mH\(_{2(011)}\) configurations (Figure 7.21). A physisorption energy of -0.04 eV to -0.13 eV defines the a-mH\(_{2(011)}\) configurations (confirmed by the electronic structure). In the c-dH\(_{2(011)}\) configurations (adsorption energy of -0.13 eV), molecular \( \text{H}_2 \) is located orthogonal to surface and proximal to the Pu\(_{(I)}\) ion. As a potential prelude to dissociation of molecular \( \text{H}_2 \) (due atomic aH\(_{(011)}\) configuration resemblance), molecular \( \text{H}_2 \) is proximal to the O\(_{(S)}\) ions in the i-jH\(_{2(011)}\) configurations (physisorption energy of -0.10 eV to -0.11 eV). It is of interest that molecular \( \text{H}_2 \) does not dissociate from this configuration. A high-energetic barrier due to by steric forces could be hinder molecular dissociation. In addition, the k-lH\(_{2(001)}\) configuration offers another unreactive site located between O ions.
Figure 7.21: The adsorption sites of molecular $\text{H}_2$ on the $\text{PuO}_2$ (011) surface. The $\text{Pu}^{4+}$ (blue), $\text{O}^2-$ (red) and $\text{H}$ (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the a-m$\text{H}_2$(011) configurations for the $\text{PuO}_2$ (011) surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.
In the low-energy mH$_2$(011) configuration, molecule H$_2$ dissociates with a chemisorption energy of -2.57 eV to form chemically inequivalent OH groups. The OH group formed by the H (x) ion is structurally identical to the atomic aH$_{(011)}$ configuration. In contrast the OH group formed by the H (y) ion is bound orthogonally to the plane of the surface. In the mH$_2$(011) configuration, it is conceivable that the H (x) ion binds first followed by the H (y) ion, supported by the fact that the aH$_{(011)}$ configuration is the only one found with atom H adsorption. In the formation of the second OH group, steric forces force the H (y) ion to bind orthogonal to the surface. The Bader charge of the H (x) is 0.64 eV; whereas, the Bader charge of the H (y) ion is 0.56 eV. This shows that the H ions are chemisorbed through the formation of the OH groups. In the mH$_2$(011) configuration, the number of Pu f-states in the valence band increases; whereas, the number of Pu f-states in the conduction band decreases. This indicates that, due to the interaction of hydrogen, high-energy Pu f-states are shifted to lower energy levels. In addition, the bands located at -7 eV to -6 eV, comprised of H s- and O p-states, confirms the formation of the chemically inequivalent OH group.

**7.3.3.3 The (001)α Surface**

The interaction of hydrogen on the PuO$_2$ (001)α surface has been investigated. The interaction of atomic hydrogen on the PuO$_2$ (001)α surface generates two distinct a-bH$_{(001)\alpha}$ configurations (Figure 7.22). The aH$_{(001)\alpha}$ configuration, relative to the bH$_{(001)\alpha}$ configuration, is marginally lower in energy by 0.01 eV. In each instance, the O-H bond distance of 0.974 Å is indicative
of the OH group. The formation of the OH group is confirmed by the Bader charge distribution and the density of states. In conjunction with the formation of a proton, the neighbouring Pu(S) ion and the O(S) ion are reduced. In the bH(001)α site, the formation of an OH group is accompanied by a considerable structural distortion whereby the bound O(S) ions are shifted from their initial positions occurs. The reduction of the Pu ion is shown in the electronic structure. The number of Pu f-states in the valence band increases; whereas, the number of Pu f-states in the conduction band decreases. This indicates that, due to the interaction of hydrogen, high-energy Pu f-states are shifted to lower energy levels. In addition, the band located at -6 eV, comprised of hybrid H s- and O p-states, confirms the formation of the OH group.

Figure 7.22: The adsorption sites of atomic H on the PuO₂(001)α surface. The Pu⁴⁺ (blue), O²⁻ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption (E_ads) is additionally indicated. The density of states of the a-bH(001)α configurations for the PuO₂(001)α surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 40 for clarity.

The interaction of molecular H₂ on the PuO₂(001)α surface generates six distinct a-fH₂(001)α configurations (Figure 7.23). In the a-cH₂(001)α configurations, characterised by an adsorption energy of -0.27 eV to -0.04 eV, the dissociation of molecular H₂ is not observed. In the aH₂(001)α configuration, molecular H₂ is adsorbed at the Pu(S) site; whereas, in the bH₂(001)α configuration, molecular H₂ is adsorbed at the Pu(I) site. In both instances, molecular H₂ is orientated towards the O(S) ions from which an electrostatic interaction is inferred. The cH₂(001)α configuration (adsorption energy of -0.27 eV) is the most stable of the physisorbed states. In the described
configuration, molecular H$_2$ is located in the O vacancy (formed by the reconstruction of surface).

In the d-fH$_2$(001)$_{\alpha}$ configurations, characterised by an adsorption energy of -3.64 eV to 0.26 eV, the dissociation of molecular H$_2$ is observed resulting in the formation of OH groups. The dH$_2$(001)$_{\alpha}$ configuration, characterised by an adsorption energy of 0.26 eV, is highly unusual. The H$_2$ molecule has dissociated to form an OH species; however, the remaining H atom appears to be directly adsorbed above the OH group. The dH$_2$(001)$_{\alpha}$ configuration thus appears to be an intermediary step in either the recombination or dissociation of the H$_2$ molecule. The eH$_2$(001)$_{\alpha}$ configuration, relative to the fH$_2$(001)$_{\alpha}$ configuration, is marginally lower in energy by 0.008 eV.

In the eH$_2$(001)$_{\alpha}$ configuration, which results in chemically inequivalent OH groups, the structural distortion of the O$_{(S)}$ ions is considerable. By contrast, in the low-energy fH$_2$(001)$_{\alpha}$ configuration, the distortion of the O$_{(S)}$ ions is minor. The structural distortion is reminiscent of Np eH$_2$(001)$_{\alpha}$ configuration that results in chemically equivalent OH groups.

![Image of adsorption sites of molecular H$_2$ on the PuO$_2$ (001)$_{\alpha}$ surface. The Pu$^{4+}$ (blue), O$^-$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the a-fH$_2$(001)$_{\alpha}$ configurations for the PuO$_2$ (001)$_{\alpha}$ surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.]

Figure 7.23: The adsorption sites of molecular H$_2$ on the PuO$_2$ (001)$_{\alpha}$ surface. The Pu$^{4+}$ (blue), O$^-$ (red) and H (grey) ions are indicated by the colours in the parentheses. The energy of adsorption ($E_{\text{ads}}$) is additionally indicated. The density of states of the a-fH$_2$(001)$_{\alpha}$ configurations for the PuO$_2$ (001)$_{\alpha}$ surface is shown. The total density of states is coloured black. The colours in the parentheses indicate the actinide f- (blue), actinide d- (green) and oxygen p- (red) and hydrogen s- (yellow) bands. Note, the hydrogen s-band has been magnified by a factor of 10 for clarity.
The formation of identical protonic states is confirmed by the Bader charge of the H ion (0.60 eV) (Table 7.9). The electronic structure of the PuO\(_2\) (001)\(\alpha\) surface for the a-cH\(_2\)(001)\(\alpha\) configurations, indicating a physisorption mechanism, is relatively uninfluenced. In the cH\(_2\)(001)\(\alpha\) configuration, the OH group is identified by the H \(s\)- and O \(p\)-band located at -6 eV. In addition, a H \(s\)-defect state is identified at -3 eV indicative of the H-H bond. In the e-fH\(_2\)(001)\(\alpha\) configurations, due to the formation of the OH group, a greater number of high-energy Pu \(f\)-states migrate from the conduction band and into the valence band. In the eH\(_2\)(001)\(\alpha\) configuration, the \(s\)- and \(p\)-bands at -7 eV to -5 eV confirm the formation of two chemically inequivalent OH groups; whereas, in the eH\(_2\)(001)\(\alpha\) configuration, the \(s\)- and \(p\)-bands at -7 eV confirms the formation of chemically equivalent OH groups.

Table 7.9: The Bader Charge Distribution (eV) of the PuO\(_2\) (001)\(\alpha\) Surface for each Configuration.

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<th>Ion</th>
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</table>

In total, an investigation of hydrogen interaction with low-index PuO\(_2\) surfaces has been conducted. The interaction of atomic H on the low-index PuO\(_2\) (111), (011) (001)\(\alpha\) surfaces indicate an exothermic adsorption mechanism. No evidence of molecular H\(_2\) dissociation is found on the (111) surface. The dissociation of molecular H\(_2\) and the formation of an OH group is found for the (011) and (001)\(\alpha\) surfaces only.

7.4 Conclusions

The interaction of atomic H and molecular H\(_2\) on the low-index AnO\(_2\) (An = U, Np, Pu) surfaces has been investigated by PBEsol+U. The influence of noncollinear 3k AFM behaviour and SOI has been considered. Intermediary characteristics are shown by the NpO\(_2\) system for the adsorption of hydrogen. The interaction of hydrogen with the low-index AnO\(_2\) (111), (011), (001)\(\alpha\) surfaces can be understood in term of; the formation of a hydride ion by oxidation of
an actinide ion, the formation of an OH group by reduction of an actinide ion, or molecular adsorption where molecular H₂ does not dissociate. These individual mechanisms can be identified by their influence on the electronic structure. The absence of defect states or of hybrid H s- and O p-states indicates molecular H₂ physisorption. The magnitude of the electrostatic interaction is indicated by the position of the H s-band. The formation of An f-defect state near the CBM and absence of hybrid H s- and O p-states indicates the oxidation of the An⁴⁺ ion to the An⁵⁺ ion and the existence of a hydride group. In contrast, the formation of an An f-defect in the band-gap and presence of hybrid H s- and O p-states in the valence band confirms the reduction of the An⁴⁺ ion to the An³⁺ ion and the existence of the OH group, respectively.

The interaction of atomic H with the AnO₂ (111) surfaces results in the formation of an OH group and the reduction of an An ion. The energy of atomic H adsorption for UO₂ (-0.82 eV), NpO₂ (-0.10 eV) and PuO₂ (-1.25 eV) for the lowest-energy configurations is shown in the parentheses. A clear shift from an endothermic to an exothermic mechanism is identified. The formation of an OH group is confirmed by the DoS and the Bader charge distribution. The material structure of the low-energy UO₂ bH₁₁₁, NpO₂ aH₁₁₁, and PuO₂ bH₁₁₁ configurations is effectively identical. The dissociation of molecular H₂ on the AnO₂ (111) surface is not observed. Instead, molecular H₂ is weakly physisorbed. As the formation of the OH group is thermodynamically feasible, the dissociation of molecular H₂ might be hindered by kinetic factors. These observations can be explained in terms of the Bader charge distribution. In the formation of an OH group, the An ion furthest from the adsorption site is reduced. As a key limitation of a (1·1) unit cell model, the formation of a second OH group is prevented by the Bader charge distribution. To incorporate the reduction of another An ion furthest away from the OH group, a second unit cell must be included within the model. To calculate the dissociation energy of hydrogen, cNEB calculations should be performed. At present, a fully relativistic cNEB investigation is computationally intractable. The interaction of atomic H on the AnO₂ (011) surface results in the formation of an OH group with the O(S) ion. In addition, the bound H ion is located above the neighbouring An(I) ion. No evidence of molecular H₂ dissociation is found with the UO₂ (011) and NpO₂ (011) surface. A large steric barrier for the dissociation of molecular H₂ might be responsible. Molecular H₂ dissociation is only observed for the PuO₂ on the (011) surface. This result is the formation of two chemically inequivalent OH groups. No evidence of OH formation or molecular H₂ dissociation has been observed on the UO₂ (001)a surface. As a result of the initial surface reconstruction, atomic H and molecular H₂ are incorporated into the oxygen vacancy. As evidence for a hydride-catalysed corrosion
mechanism in the case of atomic H adsorption, the Bader charge distribution indicates the formation of a hydride ion. The adsorption of hydrogen on the NpO$_2$ (001)$\alpha$ and PuO$_2$ (001)$\alpha$ surface results in the formation of an OH group.

7.5 Bibliography


Part IV:
Epilogue
Chapter 8:
Thesis Conclusions

The main aim of this thesis has been to study the interaction of hydrogen with low-index actinide dioxide (AnO₂) surfaces by computational methods. As the crystal structure is coupled by spin-orbit interaction (SOI) to the magnetic state, it is imperative to consider relativity when creating computational models. A fully relativistic noncollinear investigation of magnetic order has been conducted for the first time. The construction of accurate surface models demanded an intense investigation of the magnetic ground-state. The influence of the magnetic state on crystal symmetry is highlighted. The identification of a longitudinal 3k antiferromagnetic (AFM) ground-state in PuO₂ is a key finding. The first systematic analysis of DFT functionals for AnO₂ modelling has been reported. This thesis offers the first study of AnO₂ surfaces incorporating noncollinear and relativistic influences. Lastly, the first comprehensive study of hydrogen interaction with the low-index AnO₂ surface has been conducted. The investigation involved an exhaustive search of all adsorption sites.

In the nuclear fuel cycle, the AnO₂ play an important role as fissile materials. An experimental study of actinide systems is highly challenging. This is due to their toxic, inhomogenic and radiogenic nature. To circumvent experimental issues, computational methods offer another mode of investigation. To investigate the complex electronic structure by computational methods, one must consider: exchange-correlation influences, relativistic contributions, and noncollinear magnetic behaviour. The magnetic ground-state of the AnO₂ is key to the design of computational models. The actinides are highly-correlated f-electron systems for which conventional methods fail. To calculate highly correlated materials, a number of methods offer
a correction to the self-interaction error. The electronic structure of the AnO$_2$ is calculated by DFT+U and hybrid functionals. The importance of noncollinear magnetic order and relativistic influences are highlighted. A transverse 3k AFM state with $Pa\overline{3}$ symmetry is calculated for UO$_2$ and NpO$_2$; whereas, a longitudinal 3k AFM state with $Fm\overline{3}m$ symmetry is calculated for PuO$_2$. The performance of a number of DFT functionals has been tested. An excellent comparison with known experimental data is obtained with PBEsol. This is used to calculate the band structure, density of states, and optical absorbance.

The surface energetics of the low-index AnO$_2$ (An = U, Np, Pu) surfaces has been calculated by PBEsol+U. This study considers the importance of SOI and noncollinear magnetic behaviour. The importance of the magnetic domain orientation relative to the plane of the surface is highlighted. In addition, for the reconstructed (001) surface, the configuration of the terminal oxygen ions has been explored. In this, the (001)$\alpha$ configuration, relative to the (001)$\beta$, is lower in energy; however, the hybridised (001)$\alpha\beta$ configuration is lower still. The overall surface order of (111) < (011) < (001)$\alpha\beta$ < (001)$\alpha$ < (001)$\beta$ is conveyed in terms of increasing energy. This is common with fluorite-type materials. The ionic relaxation of each surface is shown to be confined to the first three monolayers. The electrostatic potential isosurface (EPI) and scanning tunnelling microscopy (STM) images have been calculated. By considering the energetics of the low-index AnO$_2$ surfaces, an octahedral Wulff crystal morphology has been calculated.

The interaction of hydrogen with low-index AnO$_2$ surfaces has been calculated by PBEsol+U. The adsorption of atomic H results in the formation of an OH group for all surfaces. The reaction becomes increasingly more exothermic along the actinide series. No evidence of molecular H$_2$ dissociation on the (111) surface is found. This might be a limitation of a (1·1) unit cell model. Evidence of molecular H$_2$ dissociation on the (011) surface is only found with PuO$_2$, which results in the formation of chemically inequivalent OH groups. In contrast, the dissociation of molecular H$_2$ on the AnO$_2$ (001)$\alpha$ surfaces results in chemically equivalent OH groups in each instance. To investigate dissociation mechanisms further, a series of climbing nudged elastic band (cNEB) calculations are recommended.
Chapter 9: Further Investigations

The chemistry of the actinide materials concerns nuclear industries. The microstructural evolution of nuclear fuels is an important field of research. The electronic structure of nuclear fuels is influenced by impurity phases, influencing the design of next-generation nuclear fuels and the industrial reprocessing of nuclear materials. In commercial nuclear industries, metal oxide fuels are commonly used. The oxide phase limits further oxidation of the metal and enables higher operating temperatures. To investigate the magnetic structure of the AnO$_2$ further experimental and computational calculations will be needed. In neptunium dioxide (NpO$_2$), a ferromagnetic (FM) (111) ground-state has been calculated. This contradicts experimental information. The influence of entropy on the low-temperature magnetic state is unknown, and phonon activity on low-temperature dynamic stability has yet to be studied.

As a means of recycling nuclear material, the design of mixed-oxide (MOX) fuels is of interest. To transmute highly-radioactive elements, MOX fuels offer a path towards a closed-fuel cycle. MOX fuels can be comprised of individual phases or as solid solutions. A number of uranium-plutonium MOX fuels have been studied; however, thorium-based MOX fuels offer a number of advantages. In addition, americium and curium MOX fuels formed by neutron capture are in development. To form the basis of computational models, the magnetic ground-state of these compounds must be resolved. This can be achieved by hybrid (HSE06) calculations. As a computationally more tractable means of investigation, DFT+U calculations can be used to study surface interactions.
In regard to the design of surface models for fluorite-type materials, the dipolar component of (001) surfaces has to be removed by a reconstruction. The nature of the surface reconstruction has yet to be identified. This impacts surface energetics, particle morphology and reaction chemistry. A systematic investigation of surface energetics in a (2·2) unit cell or greater is needed. This is a logical extension of (1·1) surface reconstruction conducted on fluorite-type systems.

The interaction of oxygen and water with low-index AnO\textsubscript{2} surface influences corrosion mechanisms. A considerable number of actinide compounds (hydrides, hydroxides, and halides) share the fluorite-type crystal structure. The reaction chemistry can be investigated by the methods detailed. The cubic dihydrides are metallic; whereas, the hexagonal trihydrides are semi-conductors. The nature of their magnetic ground-states and the influence of hydrogen content remains unknown.
Index
Notation & Symbols

In the general case, equations are written in terms of atomic units.

\[ \alpha \] Alpha Radiation
\[ \beta^- \] Beta Radiation
\[ \gamma \] Gamma Radiation, Lorentz Factor or Surface Energy
\[ \varepsilon \] Eigenvalue Diagonal Matrix
\[ \sigma \] Spin Index
\[ \Gamma \] Gamma Point, Origin
\[ \hat{h} \] One-electron Hamiltonian Operator
\[ \hat{H} \] Hamiltonian Operator
\[ \chi \] One-electron Wavefunction
\[ \Psi \] Multi-electron Wavefunction

AFM Antiferromagnetic
AM05 Armiento-Mattsson DFT functional
AnO\(_2\) Actinide Dioxide
B Bulk Modulus
c Proportionality Constant
C Diffusion Constant
CBM Conduction Band Minimum
DM Diamagnetic
DMFT Dynamic Mean Field Theory
DFT Density Functional Theory
DFT+U Hubbard Corrected Density Functional Theory
DoS Density of States
E Energy
F One-electron Fock Matrix
FI Ferrimagnetic
FM Ferromagnetic
FWHM Full Width at Half Maximum
<table>
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<th>Notation &amp; Symbols</th>
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<td>Generalised Gradient Approximation</td>
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<tr>
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<td>Heyd Scuseria Ernzerhof hybrid DFT functional</td>
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<td>Inelastic Neutron Scattering</td>
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<td>k</td>
<td>Wave Vector</td>
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<td>Local Density Approximation</td>
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<td>Low-Energy Electron Diffraction</td>
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<tr>
<td>m</td>
<td>Mass</td>
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<tr>
<td>M</td>
<td>Simple Cubic M Point, Centre of an Edge</td>
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<tr>
<td>MOX</td>
<td>Mixed-oxide</td>
</tr>
<tr>
<td>n</td>
<td>Electron Density or Main Quantum Number</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>PAW</td>
<td>Projector Augmented Wave</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof DFT functional</td>
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<td>PBESol</td>
<td>Perdew-Burke-Ernzerhof revised for solids DFT functional</td>
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<td>Self-Interaction Correction</td>
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<td>Scanning Electron Microscopy</td>
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<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package</td>
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<td>Valence Band Minimum</td>
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<tr>
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<td>Simple Cubic X Point, Centre of a Face</td>
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