Quantum Mechanical Studies of the Early Actinide Compounds

by

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Submitted in partial fulfilment of the requirements for the degree

PhilosophiaeDoctor (PhD)

in the Department of Physics

Faculty of Natural and Agricultural Sciences

University of Pretoria

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February 17, 2014
UNIVERSITY OF PRETORIA

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Abstract

This study involves the investigation of the early actinide systems using ab initio techniques based on density functional theory (DFT). It was motivated by: (i) the incomplete description of these systems using conventional DFT because they are strongly correlated, (ii) the usefulness of these systems in nuclear energy generation, (iii) the complexity that arises in experimentally studying these systems due to their inherent radioactive nature and (iv) their limited availability.

The results obtained from this study are divided into two broad sections. The first comprises chapters 3 and 4 while the second comprises chapters 5 and 6. Thorium based compounds are studied in chapters 3 and 4. In the first section, the Hubbard $U$ parameter is not necessary to accurately describe the electronic, elastic and mechanical properties of these systems. In the second, the inclusion of the Hubbard $U$ parameter is shown to be paramount for the accurate description of most compounds considered.

Chapter 3 presents the electronic, structural and bonding character of thorium based nitrides. We obtained the result that $\text{Th}_2\text{N}_2\text{NH}$, which is crystallographically equivalent to metallic $\text{Th}_2\text{N}_3$, is insulating. Chapter 4 demonstrates that the formation of a meta-stable thorium-titanium based alloy is plausible and also further information on bonding, electronic and elastic properties of the determined meta-stable alloy is provided. This has provided important new knowledge about these bulk systems.

In Chapter 5 the DFT + $U$ based study on Pa and its oxides is presented. The electronic, structural and bonding character of these systems was studied. We found that $\text{PaO}_2$ is a Mott-Hubbard insulator with an indirect band gap of 3.48 eV within the generalized gradient approximation GGA + $U$. Chapter 6 discusses various actinide nitrides. We explored the electronic properties, elastic properties, lattice dynamics and the energetics of the various compounds using GGA + $U$. Also, we
investigated the effect of the Hubbard $U$ parameter and magnetic configuration on these systems.

The use of the DFT + $U$ based method provides a rapid way to study strongly correlated systems, while other methods such as Hybrid functional, GW, DMFT+DFT, etc. are highly intensive, computationally speaking. Finally, the results obtained with the inclusion of this ad hoc parameter give a very good description of these systems.
I would like to dedicate this thesis to my family for all they have done, provided and put up with to help me achieve this extraordinary milestone in my life.
Acknowledgements

I would like to acknowledge the University of Pretoria for funding, members of the computational and theoretical physics group at the department of Physics for useful discussions, my supervisor for his guidance, and my friends and loved ones for their general support. Lastly, I am grateful to my family for their unwavering support and prayers.
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Acronyms

AE all-electron. 21, 23

BOA Born-Oppenheimer Approximation. 8, 30

BZ Brillouin zone. 19, 24, 25

DFT Density Functional Theory. 2, 4, 5, 7, 11, 13, 20, 39, 45, 119, 120

DFT+U DFT plus the Hubbard $U$ Correction. 5, 7, 34, 119–122

FFT fast Fourier transform. 17

GGA Generalized Gradient Approximation. 3, 4, 16, 17, 32

GGA+U GGA plus the Hubbard $U$ Correction. 4

HF Hartree-Fock approximation. 9–11

KS Kohn-Sham. 13–15, 17–19, 24, 27, 34

LDA+U LDA plus the Hubbard $U$ Correction. 4, 34–36, 38, 39

LSDA Local Spin Density Approximation. 4, 15–17, 32, 35

MP Methfessel-Paxton. 25, 26

OPW Orthogonalized Plane Wave. 20, 22

PAW projector augmented wave. 21–23, 39
PBE Perdew-Burke-Ernzerhof. 3, 4

SCF Self-Consistent Field. 18

XC exchange-correlation. 14–17, 32
Chapter 1

Introduction

1.1 Actinide systems

The actinides can be divided into two sub-series: the early (Th-Pu) and the late (Am-Lr).\[^1\]
This is based on their position in the series and the different characteristics exhibited. The early actinides comprise the elements Thorium (Th 90), Protactinium (Pa 91), Uranium (U 92), Neptunium (Np 93) and Plutonium (Pu 94).

One of the major aspects of the importance of actinide compounds are their potential application in advanced fuel materials for fast breeder reactors. In particular, actinide nitrides are considered important as a source for nuclear fuel material in the proposed Generation IV nuclear power plants (future fast neutron fission reactors).\[^2;3;4;5;6;7;8;9;10\] Also, actinide compounds find a use as target materials to transmute plutonium and minor actinides in fast reactor cores and in accelerator driven systems. The high density of the nitride fuel creates more excess neutrons and has a higher potential to transmute the long-lived fission products. If one considers the breeding ratio, appropriate thermophysical properties, high thermal conductivity, high melting point and fuel density, chemical compatibility with the Na coolant, and reprocessing feasibility, actinide nitrides appear to be a compromise between oxide and metal fuels.

The understanding of the early actinide compounds from both scientific and technological points of view is a very complex and challenging area of research.\[^11;12;13;14;15;16;17\] The theoretical description of the early actinide compounds presents a considerable challenge due to the onset of 5f-electron localization phenomena. They contain a partially filled 5f-orbital that is spatially localized around the nucleus. The large number of electrons per atom in these strongly correlated compounds leads to various exotic properties such as half-metallicity,
metal-insulator transition, Mott insulators, high-Tc, heavy Fermion materials, etc. Noteworthy is a parabolic decrease of the volume as a function of the atomic number, which shows a similar trend to that of the transition metals. For the early actinides, this behavior is attributed to the nature of electron-electron interactions in the 5f compounds. However, for the transition metals, this behavior is attributed to the 3d electrons. Hence, the actinides are sometimes referred to as a form of the 5f transition series.[18]

The crossover of localization/delocalization influences the phase diagram of actinide compounds immensely. This can be seen in the difference between the electronic and magnetic properties of Uranium and Berkelium compounds.[19] The f-electron contribution to the chemical bonding character can be greatly influenced by a minimal change in the external or chemical pressure of the system. This results in a wide array of characteristics for the alloys and compounds of a given actinide element. It was suggested by Hill[11] that the actinide-actinide bond distance determines the extent of magnetic order through the control of the f-f overlap in actinide compounds. Various studies have shown that actinide compounds do not necessarily follow the systematics based solely on f-band formation. The f-d and f-p hybridizations are equally important in describing the electronic and magnetic properties of these compounds.

Electronic correlation, which is not considered in traditional density functional approximations or Hartree-Fock theory, treats the systems as non-interacting entities, which is the essential feature that defines these systems. To give a qualitative description of the early actinides (particularly Pa to Pu), going beyond standard Density Functional Theory (DFT) or Hartree-Fock theory, is consequently essential. Several methods such as the DFT + $U$, SIC, GW, etc. as well as simplified model Hamiltonians (e.g. Hubbard-like models) have been proposed to account for these.

This study focuses on the actinide compounds formed by these elements with nitrogen, oxygen and titanium.

1.2 Aims and objectives

This study is divided into two parts. The first comprises chapters 3 and 4, which focus on the Thorium based compounds. This part shows that such compounds do not need inclusion of the Hubbard $U$ parameter for a proper description of these systems, in spite of their being early actinides. In the second section, which comprises chapters 5 and 6, the importance of the Hubbard $U$ parameter is underscored for the proper description of these systems.
1.2.1 Thorium based alloys

The first part of this study demonstrates that the structural, elastic, and mechanical properties and the formation energy of the actinide compounds without the 5f electrons can be accurately determined without the inclusion of the Hubbard $U$ parameter. This part is divided into two chapters.

Firstly, using a DFT approach within the Perdew-Burke-Ernzerhof (PBE) Generalized Gradient Approximation (GGA) [GGA (PBE)] implemented in the VASP codes, we investigate the structural, elastic and electronic properties of Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$(NH). The calculated structural properties of the nitrides are in good agreement with experimental data. We observed that all the Th-N based compounds considered are energetically favorable and elastically stable. We found that Th$_3$N$_4$ is semiconducting with a band gap of 1.59 eV, which compares well with the experimental band gap of 1.7 eV, while Th$_2$N$_3$ is metallic. Th$_2$N$_2$(NH), which is crystallographically equivalent to Th$_2$N$_3$ is insulating with a band gap of 2.12 eV. This is due to the -(NH) group that results in the shifting of the energy bands consequently opening up a gap at the Fermi-level. We observe that all the investigated Th-N based compounds are predominantly ionic.[25]

Secondly, using a quantum chemical method, we investigate the dearth of ordered alloys involving thorium and titanium. Based on the fact that both these elements are known to alloy very readily with various other elements, for example with oxygen, nitrogen and carbon current experimental data suggests that Th and Ti do not alloy very readily with each other. This study explored the possibility of the formation of a stoichiometry compound involving these elements by considering a variety of ordered alloys of ThTi based compounds. By probing the energetics, electronic, phonon and elastic properties of these systems, we confirm the scarcity of ordered alloys involving Th and Ti, since for a variety of reasons many of the systems that we considered were found to be unfavorable. However, our investigations resulted in one plausible ordered structure: We propose ThTi$_3$ in the Cr$_3$Si structure as a metastable ordered alloy.[26]

1.2.2 Effect of Hubbard $U$ parameter

The second part of this study highlights the importance of the Hubbard $U$ parameter for the proper determination of the structural, elastic, and mechanical properties and energetics of formation for the various actinide compounds with 5f electrons. This part is divided into two chapters.
Firstly, the electronic structure and properties of protactinium and its oxides (PaO and PaO₂) were studied within the framework of the Local Spin Density Approximation (LSDA), GGA (PBE), LDA plus the Hubbard $U$ Correction (LDA+U) and GGA plus the Hubbard $U$ Correction (GGA+U) implementations of DFT. The dependence of selected observables of these materials on the effective $U$ parameter has been investigated in detail. The examined properties include lattice constants, bulk moduli, effect of charge density distributions, the hybridization of the $5f$ orbital and the energy of formation for PaO and PaO₂. The LSDA yields better agreement with experiments for the bulk modulus than the GGA for Pa, while GGA results in better lattice parameters. We observed that PaO is metallic while PaO₂ is a Mott-Hubbard insulator\cite{27} (materials that should conduct electricity under conventional band theories, but are insulators when measured). This is consistent with observations for the other actinide oxides.\cite{28} We discovered that GGA and LSDA incorrectly give metallic behavior for PaO₂. The GGA+U calculated indirect band gap of 3.48 eV reported for PaO₂ is a prediction and should stimulate further studies of this material.\cite{29} Other oxides involving uranium, neptunium and plutonium were not explored because they have been studied previously within the DFT+ $U$ approach.\cite{30;31;32;33;9}

Secondly, we present a detailed comparative study of the electronic and mechanical properties of the early actinide mononitrides and dinitrides within the framework of the GGA (PBE) and GGA+U implementations of DFT with the inclusion of spin-orbit coupling. The dependence of selected observables of these materials on the effective $U$-parameter is investigated in detail. The properties include the lattice constant, bulk modulus, charge density distribution, hybridization of the atomic orbitals, energy of formation and the lattice dynamics. The inclusion of the Hubbard $U$ parameter results in a proper description of the $5f$ electrons, and is subsequently used in the determination of the structural and electronic properties of these compounds. The mononitrides and dinitrides of the early actinides are metallic except for UN₂, which is a semiconductor. These actinide nitrides are non-magnetic with the exception of UN, NpN, PuN, NpN₂ and PuN₂: these are magnetic systems with orbital-dependent magnetic moments oriented in the $z$-axis. We observed that ThN₂ is elastically unstable to isotropic pressure. We discovered that UN₂ is thermodynamically unstable, but may be stabilized by N vacancy formation.\cite{34;6;10}
1.3 Thesis structure

The structure of the thesis is described below:

- Chapter 1 presents a brief and general introduction. Some properties of the actinide compounds and the motivation behind the studies are highlighted. In-depth introductions and further motivations behind these studies are presented in the subsequent sections on individual systems considered.

- In Chapter 2, the theoretical formulation used to develop and implement DFT as a practical tool in the study of many-body systems is presented. Also, a brief overview on the need for an additional parameter, the onsite Hubbard correction term $U$ for certain systems, is given. Methods and algorithms implemented to make the calculation practical for large systems are presented. Furthermore, the basic theory on the elasticity and lattice dynamics needed to ascertain structural strength and stability is covered.

- Chapter 3 presents the studies on the various stoichiometries of Th-Ti based compounds. A detailed study on Th-Ti based alloys is carried out to evaluate their stability and feasibility.

- In Chapter 4 the studies on the Th-N based compounds are presented. We explored the electronic properties, elastic properties and the energetics of the various compounds.

- Chapter 5 presents the studies on Pa and its oxides. We explored the electronic properties, elastic properties, lattice dynamics and the energetics of the various compounds. Also, we investigated the effect of the Hubbard $U$ parameter and magnetic configuration on these systems.

- Chapter 6 contains the studies on various actinide nitrides. We explored the electronic properties, elastic properties, lattice dynamics and the energetics of the various compounds. In addition, we investigated the effect of the Hubbard $U$ parameter and magnetic configuration on these systems.

- In Chapter 7, a the general conclusion is drawn.

In the next chapter, the theoretical framework is introduced, with emphasis placed on DFT and DFT plus the Hubbard $U$ Correction (DFT+U).
Chapter 2

Theoretical Framework

First, the methodology used in the study of physical and electronic properties of real materials is introduced. This involves determining the solution of the Schrödinger equation using \textit{ab initio} based methods. In this study, total energy of any given system, which is a many body problem, is obtained using DFT. DFT using quantum mechanical based concepts, which relies on the notion that the physical properties (equilibrium lattice constants, bulk moduli, phonons, piezoelectric constants, phase transition pressures and temperature, etc.) and the electronic properties (band structure, density of states, valence charge density distribution, etc.) of any given system can be accurately determined provided the charge density and ionic framework is known. Subsequently, the algorithms implemented within the broad theory of DFT for the determination of the total energy is presented. Next, the theory behind the calculation of the elastic properties and the lattice dynamics are provided. Lastly, we discuss the basic background of DFT+U approximation, which is relevant in capturing the physics of strongly correlated systems.

2.1 Many-Body Problem

Any given material can be described as a quantum mechanical system that is composed of atoms and consists of a positive core (referred to as the ion) surrounded by a cloud of electrons. Neglecting relativistic effects, this quantum mechanical system is described by solving the many-body fully-interacting Schrödinger equation:\cite{note135}
\[ \hat{H}\Psi = E\Psi \]

\[ \left[ \hat{T}_I + \hat{T}_e + \hat{V}_{II} + \hat{V}_{ee} + \hat{V}_{eI} \right] \Psi(|r_i, \sigma_i|) = E\Psi(|r_i, \sigma_i|) \]

where $\Psi$ is the many-body wavefunction dependent on both the ionic and electronic degrees of freedom ($R_\alpha$ and $r_i, \sigma_i$).

The ionic (I) and electronic (e) kinetic energy terms are given below as:

\[ \hat{T}_I = \sum_{\alpha=1}^{N} -\frac{\hbar^2}{2M_\alpha} \nabla^2_\alpha \]

(2.2)

\[ \hat{T}_e = \sum_{i=1}^{n} -\frac{\hbar^2}{2m_i} \nabla^2_i \]

(2.3)

The potential energy terms describing the various interactions are given by:

\[ \hat{V}_{II} = \frac{1}{2} \sum_{\alpha \neq \beta} e^2 Z_\alpha Z_\beta \frac{1}{|R_\alpha - R_\beta|} \]

(2.4)

where $\hat{V}_{II}$ is the potential energy due to ion-ion interactions

\[ \hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} e^2 \frac{1}{|r_i - r_j|} \]

(2.5)

where $\hat{V}_{ee}$ is the potential energy due to electron-electron interactions, and

\[ \hat{V}_{eI} = -\sum_{\alpha=1}^{N} \sum_{i=1}^{n} e^2 Z_\alpha \frac{1}{|R_\alpha - r_i|} \]

(2.6)

where $\hat{V}_{eI}$ is the potential energy due to electron-ion interactions.

To solve equation 2.1, the ionic and electronic degree of freedom is partially decoupled using the concept of Born-Oppenheimer Approximation (BOA), which is also referred to as the adiabatic approximation. This approximation assumes that the faster moving electrons become the stationary ground state for a given instantaneous configuration of the slowly varying nuclei, which arises due to the massive mass difference between the electrons and nuclei, and hence, results in the simplification of the many-body problem. The many-body wavefunction is a product of electronic and ionic wavefunctions with the electronic Schrödinger equation given by:
The electronic wavefunction has a parametric dependence on the fixed ionic configuration but not on their velocities

\[ \Psi((R_\alpha), (\mathbf{r}_i, \sigma_i)) = \Psi_f((R_\alpha)) \Psi_e((\mathbf{r}_i, \sigma_i); (R_\alpha)). \]  

Therefore, the electronic energy obtained is an effective interaction potential that varies with the ionic configurations in the ionic Schrödinger equation given by:

\[ [\hat{T}_f + \hat{V}_I + E_e(R_\alpha)] \Psi_f(R_\alpha) = E_f \Psi_f(R_\alpha). \]  

It is now imperative to find the ground state wavefunction that minimizes the following Hamiltonian for the electronic system

\[ [\hat{T}_e + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}}] \Psi(\mathbf{r}_i, \sigma_i) = E \Psi(\mathbf{r}_i, \sigma_i) \]  

where \( V_{ee} = V_{\text{int}} \) is the potential from electron-electron interaction, \( V_{ei} = V_{\text{ext}} \) is the potential from electron-ions interaction and \( n(r) \) is the electronic density.

The major challenge in solving the electronic Schrödinger equation is that of determining the electron-electron interaction potential. Various approaches have been formulated that incorporate this interaction to make the problem more manageable. The Hartree-Fock approximation (HF)\(^\text{[37,38]}\) is the simplest approach, which accounts for the anti-symmetric nature of many-electron wavefunction called Pauli correlation by using a Slater determinant\(^\text{[39]}\) that minimizes the Hamiltonian of a fully interacting system.\(^\text{[40]}\)

\[ \Psi_e((\mathbf{r}_i, \sigma_i)) = \Phi = \frac{1}{\sqrt{N}} \begin{pmatrix} \Phi_1(\mathbf{r}_1, \sigma_1) & \Phi_2(\mathbf{r}_1, \sigma_1) & \Phi_3(\mathbf{r}_1, \sigma_1) & \ldots & \Phi_1(\mathbf{r}_N, \sigma_N) \\ \Phi_1(\mathbf{r}_2, \sigma_2) & \Phi_2(\mathbf{r}_2, \sigma_2) & \Phi_3(\mathbf{r}_2, \sigma_2) & \ldots & \Phi_N(\mathbf{r}_2, \sigma_2) \\ \Phi_1(\mathbf{r}_3, \sigma_3) & \Phi_2(\mathbf{r}_3, \sigma_3) & \Phi_3(\mathbf{r}_3, \sigma_3) & \ldots & \Phi_N(\mathbf{r}_3, \sigma_3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Phi_1(\mathbf{r}_N, \sigma_N) & \ldots & \ldots & \ldots & \Phi_N(\mathbf{r}_N, \sigma_N) \end{pmatrix} \]  

\[ \Phi_i(\mathbf{r}_j, \sigma_j) = \Psi^\eta_i(\mathbf{r}_j) \sigma_i(\sigma_j) \]
where each single particle spin-orbital $\Phi_i(r_j, \sigma_j)$ can be decoupled into its position $\Psi_i(r_j)$ and spin variable $\alpha_i(\sigma_j)$ components.

The expectation value of the many-body electronic Schrödinger equation (spin independent) of equation 2.7 using the wavefunction (equation 2.11) in Hartree atomic units (where $\hbar = m_e = e = 4\pi/\epsilon_0 = 1$) is given by:\(^{[60]}\)

$$E_{HF} = \langle \Phi \mid \hat{H} \mid \Phi \rangle = \sum_{i,\sigma} \int d^3r \Psi_i^\sigma(r) \left[ -\frac{1}{2} \nabla^2 + V_{el} \right] \Psi_i^\sigma(r) + E_H$$

$$+ \frac{1}{2} \sum_{i,j,\sigma_1,\sigma_2} \int d^3r d^3r' \Psi_i^{\sigma_1}(r) \Psi_j^{\sigma_2}(r) \Psi_j^{\sigma_1}(r') \frac{1}{|r-r'|} \Psi_i^{\sigma_2}(r') \Psi_i^{\sigma_1}(r)$$

$$- \frac{1}{2} \sum_{i,j,\sigma} \int d^3r d^3r' \Psi_i^{\sigma}(r) \Psi_j^{\sigma}(r') \frac{1}{|r-r'|} \Psi_j^{\sigma}(r') \Psi_i^{\sigma}(r).$$

The first term in equation 2.12 is the single-body expectation value, the second term describes the classical interaction between the nuclei, the third term gives the direct exchange interactions and the fourth term accounts for the exchange interactions among electrons. The fictitious self-interactions in the direct and exchange terms also known as the self-interaction terms are included but cancel each other out. Including these interactions and summing over all orbitals results in the electron density, while the direct term is the Hartree energy given by:

$$E_H = \frac{1}{2} \int d^3r d^3r' \frac{n(r) n(r')}{|r-r'|}$$

where the classical charge density of the self-interacting energy with density $n(r)$ is used to treat $E_H$.

The exchange energy term comprises of two effects: from the self-term and Pauli exclusion. This effects must be deducted to cancel out the spurious self-term included in the direct Coulomb Hartree energy. The exchange energy leads to lowering of the energy as a result of each electron interacting with its positive exchange hole. This is the difference between the total energy of the interacting many-body system of density $n(r)$ and the HF system with anti-symmetric uncorrelated electrons given below as:
\[ E_x = E - E_{HF} = [\langle \hat{V}_{\text{int}} \rangle - E_H]_{HF}. \] (2.14)

The minimization of equation 2.12 with respect to all the degrees of freedom using the many-body wavefunction in the form of equation 2.11 gives the single-electron HF equations as presented below

\[
\begin{align*}
\left[ -\frac{1}{2} \nabla^2 + V_e(r) + V_H(r) + V_{x}(r) \right] \psi_{\sigma}^{\sigma}(r) &= \epsilon_{\sigma}^{\sigma} \psi_{\sigma}^{\sigma}(r) \\
V_{H}(r) &= \sum_{j,\sigma} \int d^3 r' \psi_{\sigma}^{*}(r') \frac{1}{|r-r'|} = \int d^3 r' \frac{n(r')}{|r-r'|} \\
V_{x}(r) &= -\sum_{j} \int d^3 r' \left( \psi_{\sigma}^{*}(r') \psi_{\sigma}^{\sigma}(r') \frac{1}{|r-r'|} \right) \frac{\psi_{\sigma}^{*}(r') \psi_{\sigma}^{\sigma}(r')}{\psi_{\sigma}^{*}(r') \psi_{\sigma}^{\sigma}(r')}.
\end{align*}
\] (2.15)

The Hartree potential \( V_H \) accounts for the electric fields of the other electrons and they act as a smooth background electron density \( n(r) \) to the single electron. The exchange potential \( V_x \) incorporates the Pauli exclusion principle for all the electrons and eliminates the self-interaction terms in \( V_H \).

The solution to the many-body problem using HF is intractable except for very small systems and specialized cases. Another way to solve the many-body problem, which is currently the most popular method, entails changing from \( N \) internal degrees of freedom to a single quantity: the ground state electron density using Density Functional Theory (DFT). Note that, DFT is an exact formalism and Hartree-Fock approach is forever an approximation.

### 2.2 Density Functional Theory

The two theorems by Hohenberg and Kohn\(^{[41]}\) in 1964 laid the foundation for DFT and can be stated (as presented Richard Martin’s book\(^{[40]}\)) as follows:

**Theorem 1** For any system of interacting particles in an external potential \( V_{ext}(r) \), the potential \( V_{ext}(r) \) is determined uniquely, except for a constant, by the ground state particle density \( n_0(r) \).

**Corollary I:** Since the Hamiltonian is thus fully determined, except for a constant shift of the energy, it follows that the many-body wavefunctions for all states (ground and excited) are
determined. *Therefore all properties of the system are completely determined given only the ground stated density* \( n_0(r) \).

**Theorem 2** A universal functional for the energy \( E[n] \) in terms of the density \( n(r) \) can be defined, valid for any external potential \( V_{ext}(r) \). For any particular \( V_{ext}(r) \), the exact ground state energy of the system is the global minimum value of this functional, and the density \( n(r) \) that minimizes the functional is the exact ground state density \( n_0(r) \).

**Corollary II:** The functional \( E[n] \) alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means.

Using a *reductio ad absurdum* Theorem 1 is proved as follows:

Given two different \( V_{ext}^{(1)}(r) \), \( V_{ext}^{(2)}(r) \) with the same ground state density \( n_0(r) \) but different Hamiltonians \( \hat{H}^{(1)} \) and \( \hat{H}^{(2)} \) and ground state wavefunction \( \Psi^{(1)} \) and \( \Psi^{(2)} \), it follows using the Rayleigh Ritz variational principle, that:

\[
E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \tag{2.16}
\]

Hence

\[
E^{(1)} < \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle < E^{(2)} + \int d^3r [V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)] n_0(r). \tag{2.17}
\]

Similarly, considering \( E^{(2)} \) results in

\[
E^{(2)} < \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | \hat{H}^{(2)} - \hat{H}^{(1)} | \Psi^{(1)} \rangle < E^{(1)} + \int d^3r [V_{ext}^{(2)}(r) - V_{ext}^{(1)}(r)] n_0(r). \tag{2.18}
\]

Addition of equation 2.17 and equation 2.18 results in the contradictory inequality

\[
E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}, \tag{2.19}
\]

hence the same ground state density cannot yield two external potentials that differ by more than a constant. Therefore the external potential \( V_{ext}(r) \) is uniquely determined to within a constant by the ground state density \( n_0(r) \), for a system of interacting particles.
Provided the functional of the density is properly defined, theorem 2 is proved as follows

\[
E_{HK}[n] = T[n] + E_{\text{int}}[n] + \int d^3 r \, V_{\text{ext}} n(r) + E_{II}
\]

\[
\equiv F_{HK}[n] + \int d^3 r \, V_{\text{ext}} n(r) + E_{II}
\]

where \( F_{HK}[n] = T[n] + E_{\text{int}}[n] \) represents all internal energies, kinetic and potential energy; while \( E_{II} \) represents the interaction energy of the nuclei.

For a system having a ground state density \( n^{(1)}(r) \) with wavefunction \( \Psi^{(1)} \), which corresponds to an external potential \( V^{(1)} \), and a different density \( n^{(2)}(r) \), which corresponds to a wavefunction \( \Psi^{(2)} \), then

\[
E^{(1)} = E[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle
\]

\[
E^{(2)} = E[n^{(2)}] = \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle > E^{(1)}
\]

Therefore the evaluated ground state density \( n^{(1)}(r) \) is indeed a global minimum of the Hohenberg-Kohn energy functional. Also, the exact ground state density and energy can be obtained by minimizing the total energy of a given system with respect to changes in the density function \( n(r) \) provided the functional \( F_{HK}[n] \) is known.

The brilliance of DFT is finding the solution to the density \( n(r) \) in 3-dimension that minimizes the functional \( E[n(r)] \) rather than the solution of the N-body problem in equation 2.7. In the current form of equation 2.20, the solution is intractable and general properties of the system cannot be deduced from the density since the exact form of the universal energy functional is unknown.[40]

### 2.3 Kohn-Sham equations

Kohn and Sham[42] in 1965 transformed the problem of the fully interacting system to a non-interacting auxiliary system which has the same ground state density, leading to the practicality of DFT.

This electronic ground state density is defined as

\[
n(r) = \sum_{\sigma} n^{\sigma}(r) = \sum_{\sigma} \sum_{i} |\Psi_{i}^{\sigma}(r)|^2,
\]
where $\sigma = \uparrow$ or $\downarrow$ spin for all Kohn-Sham (KS) electron orbitals $\Psi^\sigma_i(r)$.

The energy functional for the auxiliary system has the form \[^{43}\]

$$E_{KS}[n] = T_s[n] + E_H[n] + \int d^3 r \, V_{ext}(r) \, n(r) + E_{xc}[n]$$

with $T_s[n] = \sum_{\sigma} \sum_i \langle \Psi^\sigma_i | \hat{T} | \Psi^\sigma_i \rangle$

$$E_H = \frac{1}{2} \int d^3 r \, d^3 r' \, \frac{n(r)n(r')}{|r-r'|}$$

where the Hartree energy is as presented in equation 2.13.

The auxiliary KS energy functional has the same ground state energy as the fully interacting energy functional, which is solvable. The exchange-correlation (XC) energy $E_{xc}$ contains all the difficult many-body terms missing and some corrections related to the kinetic energy, going from a fully interacting system to the auxiliary KS non-interacting system, allowing the KS equation to be an exact formulation. \[^{40}\]

$$E_{xc}[n] = E[n] - E_H[n]$$

Using the KS variational equation, \[^{40}\]

$$\frac{\delta E_{KS}}{\delta \Psi^\sigma_{i}^*(r)} = \frac{\delta T_s}{\delta \Psi^\sigma_{i}^*(r)} + \left[ \frac{\delta E_{ext}}{\delta n^\sigma(r)} + \frac{\delta E_H}{\delta n^\sigma(r)} + \frac{\delta E_{xc}}{\delta n^\sigma(r)} \right] \frac{\delta n^\sigma(r)}{\delta \Psi^\sigma_{i}^*(r)} = 0$$

(2.25)

depending on the constraints of orbital orthonormalization

$$\langle \Psi^\sigma_i | \Psi^\sigma_j \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}.$$ 

(2.26)

This results in the KS equations
\[
\begin{align*}
\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}} + V_H + V_{\text{xc}}^\sigma \right] \psi_i^\sigma &= \epsilon_i^\sigma \psi_i^\sigma \\
V_{\text{ext}}(r) &= \frac{\delta E_{\text{ext}}}{\delta n^\sigma(r)} \\
V_H(r) &= \frac{\delta E_H}{\delta n^\sigma(r)} = \int d^3r' \frac{n(r)}{|r - r'|} \\
V_{\text{xc}}^\sigma(r) &= \frac{\delta E_{\text{xc}}}{\delta n^\sigma(r)}
\end{align*}
\] (2.27)

The crucial term in the KS approach is the XC energy. The exact form of the XC is unknown, with the exception of the free electron gas. Therefore, there is a need for approximations to carry out practical calculations.

### 2.3.1 Local Spin Density Approximation

The first approximation to account for the \( E_{\text{xc}} \) is the LSDA. In this approximation, the general inhomogeneous electronic system is considered as a local homogeneous electron gas. The XC energy density at each point \( r \) is the same as homogenous electron gas with the same density.

\[
\begin{align*}
E_{\text{LSDA}}^{\text{xc}}[n^\uparrow, n^\downarrow] &= \int d^3r \, n(r) \, \epsilon_{\text{xc}}^{\text{hom}}(n^\uparrow(r), n^\downarrow(r)) \\
&= \int d^3r \, n(r) \left( \epsilon_x^{\text{hom}}(n^\uparrow(r), n^\downarrow(r)) + \epsilon_c^{\text{hom}}(n^\uparrow(r), n^\downarrow(r)) \right)
\end{align*}
\] (2.28)

The formulation of LSDA can be in terms of \( n^\uparrow \) and \( n^\downarrow \), or \( n(r) \) and the fractional spin polarization parameter \( \xi(r) \)

\[
\xi = \frac{n^\uparrow - n^\downarrow}{n}.
\] (2.29)

\( E_{\text{LSDA}}^{\text{xc}} \) is generated using highly accurate results from the Quantum Monte-Carlo simulation established by Ceperley and Alder and parameterized by Perdew and Zunger that has a simple analytical form.
The LSDA potential undergoes an asymptotic decay having an exponential form, whereas the true XC potential decays in a Coulombic manner much slower. This leads to various deficiencies in the LSDA potential such as: (i) Inability to support a Rydberg series and to bind with high energy states. A consequence of that is very high HOMO energy, which gives inaccurate ionization potential based on Koopman’s theorem. (ii) Also, erroneous predication of species as being unstable as a result of poor description of electron-rich species such as anions because often these do not bind to an additional electron.\[40\]

In spite of the above-mentioned drawbacks, LSDA has proven to be successful,\[46;40\] even though it relies on the assumption that the electron density is slowly varying. The reasons are that the XC hole obeys all the sum rules and does not require a detailed shape for the hole. Also, there is error cancellation in the exchange and correlation energy. The success of LSDA has led to its extensive use and the motivation for improved XC functionals (like the GGA).

### 2.3.2 Generalized Gradient Approximation

The GGA tries to remedy the deficiency of the LSDA, by taking into account the gradient of the electron density. This involves inclusion of the subsequent term in the derivative expansion of the electron density,

\[
E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3r \, \epsilon_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|, \ldots)
\]

\[= \int d^3r \, \epsilon_{xc}^{hom}(n) F_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|, \ldots)
\]

where \(\epsilon_{xc}^{hom}\) gives the exchange energy of the unpolarized gas and \(F_{xc}\) is a dimensionless quantity.

Symbolically GGA is presented as follows:

\[
E_{xc}^{GGA} = E_{xc}^{GGA}(n(r), \nabla n(r))
\]

where \(\nabla n(r)\) is the gradient of the density as a function of position.

GGA offers significant improvement in the treatment of molecules compared to LSDA. It leads to improvement in the total energies, atomization energies, energy barriers and structural
energy differences. However, GGA tends to expand and soften bonds, sometimes overcorrecting the LSDA prediction. Generally, GGA is more suitable for inhomogeneity in density than LSDA.\cite{47} Among the numerous available GGA XC functionals there are three widely used forms of the these: Beck (B88) \cite{48}, Perdew and Wang (PW91)\cite{49} and Perdew, Burke, and Enzerhof (PBE)\cite{47}. Moreover, various forms of PBE (revPBE, PBEsol\cite{50}, rPBE, etc.) have been developed to deal with different kinds of systems (surfaces, closed packed systems, defects, etc).

2.4 Algorithms used in the implementation of the Kohn-Sham equation

The various algorithms implemented in practice to obtain the converged total energy of any given system are presented. These algorithms solve the KS equations employing different techniques like:

1. Using localized atomic orbitals to study atom-like features typically used in chemistry.

2. Using the augmented plane wave (APW), Green’s functions Korringa-Kohn-Rostoker (KKR)\cite{51,52} and the muffin-tin orbital (MTO) methods, etc., which implements the atomic sphere methods.

3. Using the plane wave grid approach that implements fast Fourier transform (FFT) to determine the solution of the KS equations.

The plane wave grid approach as implemented in the VASP code is used in this study.

2.4.1 Plane wave formalism

In practice, crystalline solids have a finite number of atoms and a very large number of electrons. Based on the periodicity of the system, the large number of one-electron wavefunctions is reduced to approximately half the electron number in the unit cell of the crystal by application of Bloch’s theorem.\cite{53} For any periodic system, the KS potential is a periodic function given as:

\[ V_{KS}(r + R) = V_{KS}(r); \forall R \in \text{Bravias Lattice}. \] (2.32)
Figure 2.1: Schematic representation of the Self-Consistent Field (SCF) procedure to solve the KS equations. [54]
Applying the Bloch theorem shows that the wavefunction of an electron in a periodic potential is a product of the plane wave $e^{ik \cdot r}$ and the cell periodic function $u_i(r)$:

$$u_i(r) = \sum_G c_{i,G} e^{G \cdot r}$$

$$\psi_i(r) = e^{ik \cdot r} u_i(r) = \sum_G c_{i,k+G} e^{ik+G \cdot r}$$

(2.33)

Where, the electronic wavefunction is the sum of the plane waves at each $k$-point within the first Brillouin zone (BZ) and $c_{i,k+G}$ are the coefficients of the planes waves. Substituting equation 2.33 into equation 2.23 allows the KS equations to be expressed in the reciprocal space:

$$
\sum_{G'} \left( \frac{\hbar^2}{2m} |k + G'|^2 \delta_{GG'} + V_{ion}(G - G') + V_H(G - G') + V_w(G - G') \right) c_{i,k+G'} = \epsilon_i c_{i,k+G'}.
$$

(2.34)

Therefore, using Bloch’s theorem, the infinite solution of equation 2.23 can be determined, where the electronic wavefunction is represented as an expansion of plane waves that involves the convergence of a single parameter, the energy cut-off $E_{cut}$ (which originates from the kinetic energy term). The kinetic energy term is diagonal, and the various potentials in equation 2.23 are described in terms of their Fourier transforms. The use of fast Fourier transforms allows for translation between real and reciprocal space, significantly improving the efficiency of plane waves calculations. In equation 2.34, the kinetic energy term is the diagonal components and the potentials are given in terms of their Fourier components.

For practical calculation, we define the kinetic energy cut-off as shown in equation 2.35, which limits the maximum length of the $G$ vectors leading to a finite Hamiltonian matrix.

$$E_{cut} = \frac{\hbar^2}{2m} |k + G|^2.$$  

(2.35)

The truncation of the plane waves expansion that results in the kinetic energy term being less than the cut-off energy might introduce errors in the computed total energy of some systems. Hence, an increase in the $E_{cut}$ would lead to reduction of the error in the total energy.

The flowchart in Fig. 2.1 summarizes the KS equations derived in section 2.3 and expanded in equation 2.34. This shows how an actual calculation can be performed to determine the
ground state energy, forces, stresses, etc. A numerical procedure is implemented in DFT codes to successively update the $n$ and $V_{\text{eff}}$ until self-consistency is achieved.

### 2.4.2 Pseudopotential

In the pseudopotential approximation, the numerous plane waves in the tightly bound core electrons are replaced with an effective potential acting on the valence electrons.\[55;56;57;58;59\]. This approach was developed largely from the Orthogonalized Plane Wave (OPW) method introduced by Herring,\[60\] where the expansion of the valence wavefunctions in a set of plane waves is orthogonalized to all of the core wavefunctions. The orthogonality of the wavefunctions is because they are eigenstates of a Hermitian operator. It effectively reduces the computational time required for convergence of the total energy of the system.

In Fig. 2.2, the pseudo wavefunction oscillates less than the original wavefunction; hence, needs fewer plane waves to describe compared to the original plane wavefunctions. The pseudo wavefunction is applicable to a large number of systems, which is a smooth function within the core region.\[61\]

Several methods exist for pseudopotentials generation; therefore they are not unique. However, they must satisfy the following criteria:

1. The pseudo wavefunctions and the atomic wavefunctions must produce the same core charge (both should agree beyond a chosen core radius $R_c$).
2. The pseudo-electron and the atomic eigenvalues must be the same for a chosen atomic reference configuration.
3. Logarithmic derivatives of the two wavefunctions at $R_c$ must be norm-conserving (should agree).
4. The integrated charge inside the $R_c$ must be norm-conserving.
5. The first energy derivative of the logarithmic derivatives must agree at $R_c$ for both wavefunctions.

As a result of points 1 and 2, the pseudo atom and the ionic core will yield the same scattering properties while a smooth pseudo-electron wavefunction is guaranteed from point 3. From point 4, the correct charge inside the core is guaranteed, and point 5 guarantees an adequate description of an ion in a quantum system for a given pseudopotential. The choice of the $R_{\text{cut}}$
Figure 2.2: Schematic representation of the pseudopotential method, where the all-electron (solid lines) and pseudo-electron (dashed lines) potentials and their corresponding wave functions. They both agree at the designated radius $r_{\text{cut}}$.

Ensures adequate description of the wavefunction close to the atom but large enough to give smooth wavefunctions.

Various pseudopotentials have been developed such as: the norm-conserving pseudopotential (the norm of each pseudo-wavefunction is identical to the all-electron (AE) wavefunction outside the cutoff radius), the ultrasoft pseudopotential (reducing the basis-set size by relaxing the constraint imposed by the norm-conserving), etc. A closely related technique is the projector augmented wave (PAW) method (this leads to greater computational efficiency, which takes into account concepts from the pseudopotential and linear augmented-plane-wave methods).
2.4.3 Projector augmented wave method

The PAW\textsuperscript{[62;63;64]} method reformulates the OPW method, leading to marked improvement in the norm conserving\textsuperscript{[65]} and ultrasoft\textsuperscript{[66]} pseudopotential methods. This approach is adaptable to modern methods for total energy, force, and stress calculations leading to high computational efficiency and accuracy. However, complexity can arise in its implementation. This approach maintains the full core wavefunctions and uses the pseudopotential operators.

The PAW method maps the physical all electron (AE) valence wavefunctions $\psi^v_j(r)$ onto a smooth pseudo wavefunctions $\tilde{\psi}^v_i(r)$, which is similar to the OPW and the augmented plane wave (APW) formulation.\textsuperscript{[40]} Also, a linear combination of $\psi^v_i = \tau \tilde{\psi}^v_i$ links the set of all-electron valence functions to their smooth pseudo wavefunction. The transformation is taken to be unity $\tau = 1$ except when a sphere is centered on the nucleus, $\tau = 1 + \tau_0$. In PAW formulation, the Dirac notation is adopted. The expansion of the smooth wavefunction within the sphere (superscript $v$ and subscript $i, j$ are neglected for simplicity) is given as

$$|\tilde{\psi}\rangle = \sum_m c_m |\tilde{\psi}_m\rangle$$  \hspace{1cm} (2.36)

and the corresponding all electron wavefunction

$$|\psi\rangle = \sum_m c_m |\psi_m\rangle.$$  \hspace{1cm} (2.37)

The full wavefunction in all space is given as

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_m c_m (|\psi_m\rangle - |\tilde{\psi}_m\rangle).$$  \hspace{1cm} (2.38)

The coefficients $c_m$ represent the projection in each sphere, for a linear transformation $\tau$

$$c_m = \langle \tilde{p}_m | \tilde{\psi} \rangle.$$  \hspace{1cm} (2.39)

Provided that for some set of the projection operators $\tilde{p}$ the biorthogonality condition is satisfied,\textsuperscript{[40]}

$$\langle \tilde{p}_m | \tilde{\psi}'_{m'} \rangle = \delta_{mm'}.$$  \hspace{1cm} (2.40)

it follows that one-center expansion
\[
\sum_m |\tilde{\psi}_m \rangle \langle \tilde{\psi}_m |
onumber
\]
\[= \tilde{\psi}_m \langle \tilde{\psi}_m | (2.41)\]
of the smooth function is unchanged.

The transformation operator \(\tau\) unlike the pseudopotential involves the full AE wavefunction

\[
\tau = 1 + \sum_m |\psi_m \rangle - |\tilde{\psi}_m \rangle \langle \tilde{\psi}_m |. \tag{2.42}\]

The PAW equations can be written in the form of equation 2.42. The variation of the parameters leads to more response from the smooth wavefunction compared to the AE wavefunction. Therefore the expectation value of the smooth function is given as follows\(^4\)

\[
\tilde{\mathcal{A}} = \tau^\dagger \hat{\mathcal{A}} \tau = \hat{\mathcal{A}} + \sum_{m,m'} \langle \psi_m | \hat{\mathcal{A}} | \psi_{m'} \rangle \langle \tilde{\psi}_{m'} | \tilde{\psi}_m \rangle \langle \tilde{\psi}_m | \tilde{\psi}_{m'} \rangle \langle \tilde{\psi}_{m'} | \tilde{\psi}_m \rangle. \tag{2.43}\]

The charge density and total energy of a given system can be evaluated from the operator in equation 2.43. The density is divided into the smooth charge density \(\tilde{n}(r)\) evaluated on a regular Fourier grid and the outer centre charge densities \(n^1(r)\) and \(\tilde{n}^1(r)\) evaluated in the angular momentum on the radial grid, given by:

\[
n(r) = \tilde{n}(r) + n^1(r) - \tilde{n}^1(r). \tag{2.44}\]

The smooth and outer charge density components can be expressed in terms of the eigenstates labeled \(i\) with occupation \(f_i\), where

\[
\tilde{n}(r) = \sum_i f_i |\tilde{\psi}_i(r)|^2, \tag{2.45}\]

\[
n^1(r) = \sum_i f_i \sum_{mm'} \langle \psi_i | \tilde{\psi}_m \rangle \tilde{\psi}_m^* (r) \tilde{\psi}_{m'} (r) \langle \tilde{\psi}_{m'} | \tilde{\psi}_i \rangle, \tag{2.46}\]

and the last term given as

\[
\tilde{n}^1(r) = \sum_i f_i \sum_{mm'} \langle \psi_i | \tilde{\psi}_m \rangle \tilde{\psi}_m^* (r) \tilde{\psi}_{m'} (r) \langle \tilde{\psi}_{m'} | \tilde{\psi}_i \rangle, \tag{2.47}\]
where the outer centre charge densities $n_1(r)$ and $\tilde{n}_1(r)$ are localized around each atom and the integrals evaluated in the spherical coordinates. The VASP\cite{vasp} code in this thesis implements this method, along with other codes such as ABINIT,\cite{abinit} Quantum Espresso,\cite{qm} etc.

### 2.4.4 Brillouin zone integration

The total energy for a given system can be determined if the KS eigenvalues are known. The eigenvalues are self-consistent solutions of the $\mathbf{k}$-dependent Hamiltonian.\cite{ks} The first BZ can be mapped out by a continuous set of $\mathbf{k}$-points throughout the reciprocal space. To carry out a numerical calculation for the total energy, the integral over the first BZ is converted into a summation over discrete points in $\mathbf{k}$-space. The $\mathbf{k}$-points represent the position in the first BZ where the electronic states are calculated in a solid system. The choice of the $\mathbf{k}$-points should maximize accuracy and minimize the number of $\mathbf{k}$-points set because for each new $\mathbf{k}$-point a self-consistent KS calculation will be carried out. Errors in the self-consistent calculation can be minimized by using a dense set of $\mathbf{k}$-points in the BZ (metallic systems need more $\mathbf{k}$-points because of difficulty in calculating the Fermi surface).

#### 2.4.4.1 Linear tetrahedron method

Lehmann\cite{lehmann} developed the linear tetrahedron method, which is largely used to evaluate integrals in the BZ. This was further improved by Bloch et al.\cite{bloch} In this approach, the irreducible wedge of the BZ is divided into equal volume tetrahedra, with the matrix element and the energy eigenvalues evaluated at each vertex.

In this study, this method is used for the BZ integration due to its simplicity. But some problems might arise due to the negligence of the second-order band information leading to difficulties in band crossing and bad representation of the van Hove singularities.\cite{vhs}

#### 2.4.4.2 Special $\mathbf{k}$-points

In this study, the special $\mathbf{k}$-points are used to determine the choice of points needed to sample the BZ. They are well suited for the plane wave representation of the Hamiltonian and lead to simple and accurate calculations. This approach uses the "mean value point" developed by Baldereschi\cite{baldereschi} that integrates a function averaged over the entire BZ, which was extended by Chadi\cite{chadi}, while later a more systematic approach was devised by Monkhorst and Pack\cite{mp,monkhorst}:

$$F(r) = \frac{\Omega}{2\pi^3} \int_{BZ} f(k) d^3 k$$

(2.49)
where $\Omega$ is the volume of the unit cell, $f(k)$ is the Fourier transformation of $F(r)$ and the function provides a complete representation of the lattice symmetry. The Fourier transform is given in terms of $A_m(k)$:

$$f(k) = f_0 + \sum_{m=1} A_m(k)$$ \hspace{1cm} (2.50)

where the transformation expression $A_m(k) = \sum e^{ik.r}$ and $m$ is any given integer. $A_m(k)$ is a real function and is associated with any given shell of the lattice. Using this scheme, the integral in equation 2.49 yields an approximate value that is exact when $A_m(k) = 0$.

The Monkhorst and Pack generated set of points using this scheme provides an unbiased approach for choosing the set of $k$-points required to sample the BZ in fractional co-ordinates. Monkhorst and Pack-points are also referred to as $k$-mesh. They present the generated points in a rectangular grid ($k_x, k_y, k_z$). Larger $k$-mesh leads to finer and more accurate sampling but uses up increased computational time. The $k$-mesh is determined by the crystal lattice (simple cubic, body centered cubic, face centered cubic, etc.), and therefore takes advantage of the space group symmetry operations to reduce computed points by determining equivalent points.

$A_m(k)$ in equation 2.50 is satisfied by the choice points for the lattice vectors (represented by the infinite set of nearest-neighbor shells).

### 2.4.4.3 Fermi level smearing

The basic difference between an insulator and a metal is the presence of a band gap which is determined by the location of the Fermi level in the systems. In terms of BZ integration,\cite{78} insulators play a smooth function with the density of state easily going to zero, while metals have unoccupied states close to the Fermi level; hence the necessity to smear the bands to obtain a smooth integrated function which is more tractable. There are various kinds of smearing schemes, such as, Methfessel-Paxton (MP), Gaussian, Fermi-Dirac and Marzari-Vanderbilt smearing.\cite{78} The MP smearing is used in this study because of the systems investigated and its simplicity.

The MP smearing scheme expands the delta-function in the form of Hermite functions (which are the product of Hermite polynomials and Gaussians) then integrates it.

$$\delta(x) \approx D_N = \sum_{n} A_n H_{2n} e^{-x^2}$$ \hspace{1cm} (2.51)
where \( A_n \) are suitable coefficients. They use Hermite polynomials of even order only since the delta function is even. The delta function is obtained by integrating \( D_N \) in the following way

\[
\delta(x) \approx S_N = 1 - \int_{-\infty}^{x} D_N(t) dt
\]  

(2.52)

Using recursion properties of Hermite functions, we arrive at

\[
S_N = S_0 x + \sum_{n}^{N} A_n H_{2n-1} e^{-x^2}
\]

(2.53)

where \( S_0 \) corresponds to the Fermi-Dirac smearing whereas the other terms serve to correct errors introduced. MP smearing results in good zero temperature energies using large smearing widths, but has a downside, which is the presence of negative occupation values that might be problematic in visualizing the density of states. The proposed Marzari-Vanderbilt approach addresses the negative occupancies by estimating the delta-function with a Gaussian multiplied by a first order polynomial term.

### 2.4.5 Atomic relaxations

To study the atoms in different coordination, a self-consistent total energy calculation is required. The forces acting on the atoms needs to be determined in order to update the atomic positions (geometric optimization) and then determine the dynamic evolution of the system. These forces can be obtained using the Hellmann-Feynman theorem.

#### 2.4.5.1 Hellmann-Feynman theorem

The Hellmann-Feynman theorem\(^{[79;80]}\) (also referred to as the force theorem)\(^{[40]}\) proposes that the force on the atoms is given by\(^{[40]}\)

\[
F_I = \frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_I} = -\left( \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | H | \psi_i \rangle + \frac{\partial E_{\text{ion}}}{\partial \mathbf{R}_I} \right),
\]

(2.54)

where \( \mathbf{R}_I \) represents the atomic positions. If the wavefunction \( \psi_i \) is an eigenstate of a given Hamiltonian \( H \), then

\[
\frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | H | \psi_i \rangle = \langle \psi_i | \frac{\partial H}{\partial \mathbf{R}_I} | \psi_i \rangle.
\]

(2.55)
Based on the fact that the energy is an extremal with respect to all feasible changes of the wavefunction at the true ground state solution (using equation 2.55), the force will be

\[
F_I = -\{\langle \psi_i | \frac{\partial}{\partial R_I} H | \psi_i \rangle + \frac{\partial E_{\text{ion}}}{\partial R_I} \}.
\]  

(2.56)

From equation 2.56, the partial derivative of the KS energy functional with respect to the atomic positions gives the force on the atoms provided each wavefunction \( \psi_i \) is an eigenstate of \( H \). However, to avoid incurring errors that arise from the use of unconverted wavefunctions, the Hellmann-Feynman theorem should only be implemented once the wavefunctions are close to self-consistency because the force (unlike the energy) is not a variational quantity.

In equation 2.54, an additional term called the *Pulay force* can arise from taking the partial derivative of the basis set with respect to their atomic positions. Using a plane-waves basis, the *Pulay force* vanishes because the derivate reduces to zero, which is one of the numerous advantages of this basis set compared to any other localized basis set approach.

The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm,\[^{[81]}\] also known as the *quasi-Newton* or the *variable metric* method, implements the Hellmann-Feynman theorem for the convergence of the total energy with respect to the atomic positions. This approach is based on the fact that the energy surface around the minimum is quadratic, and therefore, can be determined from the second derivative of the energy, which is a Hessian matrix. But the Hessian matrix is unknown, so an approximation is made, using a progressive improvement of the trial matrix as the atoms move. The BFGS method is used in this study because it leads to a rapid convergence of the total energy.

### 2.5 Elastic Properties

The elastic constants characterize the elastic behavior of a given material. They describe its reaction to an applied stress. The relationship between stress and strain is not trivial in a general anisotropic material. Stress and strain comprise three tensile and shear components respectively, resulting in six components in total. The stiffness tensor of elasticity subscripts obey the added condition that\[^{[82]}\] \( ijk l = klij \), since the strain tensor is symmetric.

Theoretically and experimentally the knowledge of elastic constants leads to the understanding of the elastic properties of any given system. The elastic constants of a given crystal can be determined by using a strain matrix "\( \varepsilon \)" to shift the Bravais lattice vector \( \mathbf{R} = a,b,c \),

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leading to the deformation of the unit cell, therefore, changing the unstrained Bravais lattice vector to $\mathbf{R}' = a', b', c'$

$$
\mathbf{R}' = \mathbf{R} \begin{pmatrix} 1 + e_{xx} & \frac{1}{2} e_{xy} & \frac{1}{2} e_{yx} \\ \frac{1}{2} e_{yx} & 1 + e_{yy} & \frac{1}{2} e_{yz} \\ \frac{1}{2} e_{xy} & \frac{1}{2} e_{yz} & 1 + e_{zz} \end{pmatrix}.
$$

(2.57)

The total energy of the crystal changes in accordance with the deformation equation\cite{78}

$$
E_{tot} = E_0 + \frac{1}{2} V_0 C_{ij} e_i e_j
$$

(2.58)

where $E_0$ is the total energy of the undisturbed lattice, $V_0$ is the equilibrium volume of the undisturbed cell and the $C_{ij}$ are the elements of the elastic constant matrix. Based on the symmetry of the unit cell, the stiffness tensor (elastic constants) contains a maximum of 21 unique elements\cite{78} as shown in Table 2.1.

**Table 2.1:** Number of unique elastic constants for unit cells of different symmetry

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Elastic constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>21</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>13</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>9</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>6 or 7</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>6 or 7</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>5</td>
</tr>
<tr>
<td>Cubic</td>
<td>3</td>
</tr>
</tbody>
</table>

A detailed description of the symmetry of stress, strain and elastic constants is furnished by Nye.\cite{83} The *ab initio* elastic constants are determined by carefully choosing the applied deformation (strain) and the resulting stress. This method is less computationally intensive because structural optimization is not required.

\footnote{This table was copied from the Medea manual\cite{78}}
As stated earlier, from the elastic constants, the elastic properties of all crystal classes can be determined. The bulk modulus of a given material is the ratio of the change in pressure to the fractional volume compression.

The bulk modulus (upper bound) from the Voigt approach:

$$K_{Voigt} = \frac{1}{9} (c_{11} + c_{22} + c_{33}) + \frac{2}{9} (c_{12} + c_{23} + c_{13}) \quad (2.59)$$

The shear modulus (upper bound) from the Voigt approach:

$$G_{Voigt} = \frac{1}{15} (c_{11} + c_{22} + c_{33}) - \frac{1}{15} (c_{12} + c_{23} + c_{31}) + \frac{1}{5} (c_{44} + c_{55} + c_{66}) \quad (2.60)$$

Given that $S_{ijkl}$ is the compliance matrix (i.e. the inverse matrix to $C$), the bulk modulus (lower bound) from the Reuss approach:

$$\frac{1}{K_{Reuss}} = (s_{11} + s_{22} + s_{33}) + 2 (s_{12} + s_{23} + s_{13}) \quad (2.61)$$

The shear modulus (lower bound) from the Reuss approach:

$$15/G_{Reuss} = 4 (s_{11} + s_{22} + s_{33}) - 4 (s_{12} + s_{23} - s_{13}) + 3 (s_{44} + s_{55}) + s_{66} \quad (2.62)$$

In real (polycrystalline) materials, the stiffness matrix takes into account orientational disorder. This can be estimated if the system is assumed to be made up of crystallites rather than grain boundaries.\textsuperscript{[84]} Using that approach, Hill proposed that the true modulus is an arithmetic mean of two extremes, which are the Voigt (lower bounds) and Reuss (upper bounds) moduli.\textsuperscript{[85]}

$$G_{Hill} = \frac{1}{2} \left[ G_{Voigt} + G_{Reuss} \right] \quad (2.63)$$

$$K_{Hill} = \frac{1}{2} \left[ K_{Voigt} + K_{Reuss} \right]$$

where $G$ and $K$ are the shear and bulk moduli respectively.

Subsequently, the Poisson’s ratio ($\alpha$) and Young’s modulus ($Y$) can be determined from $G$ and $K$

$$\alpha = \frac{1}{2} \left[ \frac{K - \frac{2}{3}G}{K + \frac{1}{3}G} \right] \quad (2.64)$$

$$Y = \frac{9K}{1 + \frac{4}{3}G}$$
Correspondingly, the Debye temperature which measures the hardness or stiffness of a material is proportioned to the mean sound velocity, and is given as

\[ \theta_D = \frac{h}{k_B} \left( \frac{6\pi q}{V_0} \right)^{1/3} v_m, \]  

(2.65)

where \( h/k_B \) have the usual definition as in quantum mechanics, \( q \) is the number of atoms in the system, and \( V_0 \) is the equilibrium volume of the unit cell. And, the mean \( v_m \) sound velocity is given by

\[ v_m = \left( \frac{1}{3} \left( \frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right)^{-1/3}, \]  

(2.66)

where the transverse \( v_s \) and longitudinal \( v_l \) sound velocity are defined by

\[ v_s = \sqrt{G/\rho} \]  

(2.67)

\[ v_l = \sqrt{\left( K + \frac{4}{3} G \right)/\rho} \]

(2.67)

with \( \rho \) as the density.

### 2.6 Lattice Dynamics

From BOA, the dependence of electronic energies on the motion of the nuclei is neglected. Therefore, the equations of motion for the ions are determined by the total energy \( E(R) \) of the system, which has a parametric dependence on the fixed positions of the ions’ \( R \).[40]

To give a complete quantum description of the ions from the Schrödinger equation is very difficult[86] but treating the ions classically, reduces the problem to that of a coupled classical equation of motion for each ionic position \( \mathbf{R}_I(t) \)

\[ M_I \frac{\partial^2 \mathbf{R}_I}{\partial t^2} = \mathbf{F}_I(R) = \frac{\partial}{\partial R} E(R), \]  

(2.68)

where \( \mathbf{R}_I \) are the coordinates and \( M_I \) is the mass of the ions I, \( R \equiv \{ \mathbf{R}_I \} \) shows the set of all ionic coordinates, and \( E(R) \) is the ground state total energy, which is also referred to as the Born-Oppenheimer energy surface.

The energy is expanded in terms of the powers of displacements and external perturbation for stable solid systems at average temperature. At equilibrium position \( \{ \mathbf{R}^0 \} = \mathbf{R}^0 \), the zero-force on each ion is

\[ \mathbf{F}_I(R^0) = 0. \]  

(2.69)
At the quantum-zero point motion, the higher power of displacements gives the thermal vibrations and response to perturbations,\(^{[40]}\)

\[
C_{I, \alpha; J, \beta} = \frac{\partial^2 E(R)}{\partial R_I, \alpha \partial R_J, \beta}, C_{I, \alpha; J, \beta; K, \gamma} = \frac{\partial^2 E(R)}{\partial R_I, \alpha \partial R_J, \beta \partial R_K, \gamma}, \ldots. \tag{2.70}
\]

where \(\alpha, \beta, \ldots\) represent Cartesian components.

Using the harmonic approximation\(^{[87]}\), the displacements describe the vibrational modes at frequency \(\omega\)

\[
u_I(t) = R_I(t) - R^0_I \equiv \text{u}_I e^{i\omega t}. \tag{2.71}\]

Then, for a given \(I\), equation 2.68 becomes

\[-\omega^2 M_I \text{u}_I = - \sum_{J} C_{I, \alpha; J, \beta} \text{u}_J. \tag{2.72}\]

The classical equation provides the complete solution for all vibrational states, which is the set of independent oscillators having individual vibrational frequency \(\omega\)

\[\text{det} \left| \frac{1}{\sqrt{M_I M_J}} C_{I, \alpha; J, \beta} - \omega^2 \right| = 0. \tag{2.73}\]

where the dependence upon the masses \(M_I, M_J\) is given in a symmetric form.

Since the atomic displacement eigenvectors in a crystal obey the Bloch theorem (equation 2.33) the vibrations are grouped by \(k\) with the displacements \(\text{u}_s(T_n) = R_s(T_n) - R^0_s(T_n)\) of atom \(s = 1, S\) in the cell \(T_n\) given by

\[\text{u}_s(T_n) = e^{i\text{k}\cdot T_n} \text{u}_s(k). \tag{2.74}\]

Putting equation 2.74 into equation 2.73 results in the decoupling of the equations at different \(k\), with frequencies \(\omega_{ik}, i = 1, 3S\) called dispersion curves, which are solutions of the \(3S \times 3S\) determinants equation

\[\text{det} \left| \frac{1}{\sqrt{M_s M_{s'}}} C_{s, \alpha, \beta; s', \alpha'}(k) - \omega_{ik}^2 \right| = 0, \tag{2.75}\]

where the reduced force constant matrix for wave vector \(k\) is presented as

\[C_{s, \alpha, \beta; s', \alpha'}(k) = \sum_{T_n} e^{i\text{k}\cdot T_n} \frac{\partial^2 E(R)}{\partial R_{s, \alpha}(0) \partial R_{s', \alpha'}(T_n)} = \frac{\partial^2 E(R)}{\partial \text{u}_{s, \alpha}(k) \partial \text{u}_{s', \alpha'}}(k). \tag{2.76}\]
Quantization can be easily included as usual for the harmonic oscillators because the vibrations are independent: phonons are the quantized states of each oscillator with energy $\hbar \omega_{ik}$.

To calculate the phonons \textit{ab initio}, three approaches have been developed: (i) the direct method which hinges on calculating the total energy changes or forces for atoms displaced slightly from their equilibrium position, \cite{59} (ii) using a perturbative expansion of atoms around their equilibrium position for analytical calculation of the force constant matrix, \cite{88} (iii) the Fourier transform of the atomic velocity autocorrelation function calculated from a molecular dynamics trajectory. \cite{78;89}

The major challenge for the third approach is equilibrating at reasonable simulating times; the second approach requires specialized codes and significant implementation efforts, while the first approach requires no specialized codes but makes use of a supercell for a small unit cell. The first approach is used in this thesis to determine the phonon frequencies, and an adequate interaction range is used to ensure accuracy.

2.7 DFT+U

LSDA/GGA XC functionals fail in properly describing the electronic structure and the conduction properties for highly localized and strongly interacting systems such as: in transition metal oxides and rare-earth metal compounds. They tend to over-delocalize electrons, and hence do not properly account for the onsite Coulomb repulsion. Self-interaction is a problem because the electrons can see their own potential. Also, the solution from LSDA/GGA is mean-field, hence the absence of correlation among the electrons. Some correlation phenomena exhibited by the $d$ and $f$ compounds include metal-insulator transitions, Mott insulators, heavy Fermion behavior, high-temperature superconductivity, etc. GGA functionals can lead to slight improvement over LSDA in some cases for the physical properties of non homogeneous systems, such as transition metal compounds and rare-earth metal compounds, mainly in description of there binding energies, magnetic and structural properties, e.g. UO$_2$, NiO, MnO, etc. \cite{33;90;91} For most strongly correlated systems LSDA (or GGA) gives a reasonable description of the crystal structure and magnetic properties, but fails dramatically in the description of the conduction properties, while sometimes resulting in totally wrong structural properties ($\delta$-Pu). \cite{18}

The poor description of the electronic structure of correlated systems can be analyzed from a simple band structure calculation for a given system (such as a simple metal). If the band structure is calculated for the valence states with a stepwise increase in interatomic distances,
the width of energy bands around the Fermi level will diminish, leading to an insulating system at infinite interatomic distance. This leads to extremely localized charge density distribution around the atoms which hinders conduction of states around and crossing the Fermi level.\textsuperscript{[92,93]}

To solve this paradoxical situation, the Hamiltonian of the many-body electron system is presented in terms of second quantization\textsuperscript{[94,95]},

\[
\hat{H} = \hat{H}_0 + \hat{V}_{ee}
\]
\[
\hat{H}_0 = \int d^3 r \hat{a}_\sigma^\dagger(r) \left[ \frac{\hat{p}^2}{2m} + V_{ext}(r) \right] a_\sigma(r)
\]

\[
\hat{V}_{ee} = \frac{1}{2} \int d^3 r d^3 r' V_{ee}(r - r') a_\sigma^\dagger(r) a_{\sigma'}^\dagger(r') a_{\sigma'}(r') a_\sigma(r)
\]

where the localized basis states are:

\[
a_\sigma(r) = \sum_i \psi_{R_i}(r) a_{i\sigma} \quad a_\sigma^\dagger(r) = \sum_i \psi_{R_i}^\dagger(r) a_{i\sigma}^\dagger.
\]

The Hamiltonian of the electronic system is:

\[
\hat{H} = \sum_{i'i'} a_{i\sigma}^\dagger t_{i'i'} a_{i'\sigma'} + \sum_{i'i'j'f} U_{i'i'j'f} a_{i\sigma}^\dagger a_{i'\sigma'}^\dagger a_{j'\sigma'} a_{j\sigma}
\]

\[
t_{i'i'} = \int d^3 r \psi_{R_i}^\dagger(r) \left[ \frac{\hat{p}^2}{2m} + V(r) \right] \psi_{R_i}(r)
\]

\[
U_{i'i'j'f} = \frac{1}{2} \int d^3 r d^3 r' \psi_{R_i}^\dagger(r) \psi_{R_i}(r) V(r - r') \psi_{R_{i'}}^\dagger(r') \psi_{R_{i'}}(r').
\]

The subsequent equation gives the ’simplified Hubbard model’. The $U_{i'i'j'f}$ matrix elements are largest when $i = j$ and $i' = j'$

\[
\hat{H} = \sum_{i'i'} a_{i\sigma}^\dagger t_{i'i'} a_{i'\sigma'} + \sum_{i'i'} U_{i'i'j'f} a_{i\sigma}^\dagger a_{i'\sigma'}^\dagger a_{j'\sigma'} a_{j\sigma}.
\]

If only $i = i'$ is most important then $\sigma \neq \sigma'$, and the Hamiltonian, becomes,

\[
\hat{H} = \sum_{i'i'} a_{i\sigma}^\dagger t_{i'i'} a_{i'\sigma'} + U \sum_i a_{i\sigma}^\dagger a_{i\sigma}^\dagger a_{i\sigma} a_{i\sigma}
\]

\[
= \sum_{i'i'} a_{i\sigma}^\dagger t_{i'i'} a_{i'\sigma'} + U \sum_i a_{i\sigma}^\dagger a_{i\sigma}^\dagger a_{i\sigma} a_{i\sigma}
\]

\[
= \sum_{i'i'} a_{i\sigma}^\dagger t_{i'i'} a_{i'\sigma'} + U \sum_i \hat{h}_{i'i'} \hat{n}_{i'\sigma}.
\]
The Hubbard model in a more concise form is

\[ \hat{H}_0 = -t \sum_{\langle ij \rangle} a_i^\dagger \sigma a_j \sigma + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \]  

(2.82)

From equation 2.82, the total energy is minimized by two competing factors: the kinetic term and the Coulomb term. In simple metals, electron-electron scattering is weak with particles spending vanishingly small amount of time in the ionic regions, whereas in the strongly correlated systems (typically systems with partially filled \( d \) or \( f \) orbitals), the electron-electron scattering has a strong Coulomb repulsion due to the relatively large amount of time the electrons spend within the ionic regions. If the kinetic energy is dominant (in simple metals besides the nuclei attractions), the total energy is minimized by delocalization of the Bloch states resulting in metallic behavior. On the other hand, if the Coulomb term is dominant (in systems with partially filled \( d \) or \( f \) orbitals), the total energy is minimized by the localized states which are linear combinations of all \( k \)-states (Wannier states); hence the systems become insulating (Mott-Hubbard type).\(^{[93]}\)

Therefore, band structure analysis gives an improper description of a correlated system. This is because it uses the KS DFT that is a one-body problem to account for a many-body problem. Also, the exchange correlation as previously stated is made primary for homogenous electron gas, and hence does not properly describe correlated systems. Therefore, theoretical treatment of correlated systems is carried out using model Hamiltonians (explicitly taking into account the behavior of the system in regimes with different competing factors) or the introduction of an additional parameter using hints from many-body formalism in first principle DFT calculation to account for onsite Coulomb repulsion, referred to as the DFT+U.\(^{[95;23;24;96;29]}\)

The DFT+U method (henceforth referred to as LDA+U) takes into account the orbital dependence of the Coulomb and exchange interactions which is absent in the LDA. The main notion is to divide the electrons into two subsystems: \(^{[92;93]}\)

- localized states (\( d \) or \( f \)) which accounts for the onsite Coulomb interaction term in a model Hamiltonian

\[ \sum_{\nu' \nu} U_{\nu' \nu} a_{\nu \sigma}^\dagger a_{\nu' \sigma}^\dagger a_{\nu' \sigma'} a_{\nu \sigma'} \implies \frac{U}{2} \sum_{i \neq j} n_i n_j. \]  

(2.83)

- delocalized states (\( s \) or \( d \)) which can be described by the orbital-independent one-electron potential.
The new energy functional which is the generalized LDA+U is given as

$$E^{LDA+U}[n] = E^{LDA}[n] + E^U[n^U] - E^{dc}[n^U]$$  \hspace{1cm} (2.84)

where $E^U[n^U]$ is the Hubbard term and $E^{dc}[n^U]$ is the “double counting” term, which removes the energy contribution of orbitals already present in the LSDA functional included in the Hubbard term. The double counting term is a mean-field value of the Hubbard term in line with DFT representation. Hence $E^{dc}[n^U]$ is $UN(N-1)/2$, where $N = \sum n_i$.

Therefore, the $E^{LDA+U}[n]$ functional is

$$E^{LDA+U}[n] = E^{LDA}[n] + \frac{U}{2} \sum_{i \neq j} n_in_j - UN\left(\frac{N-1}{2}\right).$$  \hspace{1cm} (2.85)

The orbital eigenvalues or energies $\epsilon_i$ are obtained by taking the derivative of equation 2.85 with respect to the occupation number of that orbital $n_i$:

$$\epsilon_i = \frac{\partial E^{LDA+U}}{\partial n_i} = \epsilon^{LDA}_i + U \sum_{j \neq i} n_j - \frac{U(N-1)}{2} - UN + \frac{U}{2}$$

\hspace{1cm} (2.86)

$$= \epsilon^{LDA}_i + U(N - n_i) - UN + \frac{U}{2}$$

$$= \epsilon^{LDA}_i + U(\frac{1}{2} - n_i).$$

For the occupied orbital ($n_i = 1$), the LSDA orbital energy is shifted by $-U/2$ and for the unoccupied orbitals ($n_i = 0$) by $+U/2$, as presented in equation 2.86. A similar expression is obtained for the LDA+U potential which is $V_i(\mathbf{r}) = V_{LDA}(\mathbf{r}) + U(\frac{1}{2} - n_i)$. The $V_i(\mathbf{r})$ formulation makes the Hubbard potential repulsive for less than a half filled orbital and attractive for more than a half filled orbital, encouraging localization on a particular site. This results in upper and lower Hubbard bands with the energy difference being equivalent to the Coulomb parameter $U$. This will qualitatively yield the correct physics of Mott-Hubbard insulators. But, in order to obtain a quantitively accurate computational scheme, the direct and exchange Coulomb interaction inside a partially filled $d$ or $f$ orbital needs to be accounted for.

### 2.7.1 Rotationally-invariant formulation

The LDA+U formulation in equation 2.86 depends on the choice of the localized basis set because the atomic orbital is not rotationally invariant. Liechtenstein et al.\cite{21} introduced a
formulation of LDA+U independent of the choice of basis set, where Hubbard on-site correlation functional $E^U$ and the mean field double counting term $E^{dc}$ have a generic expression obtained from the HF method to solve the orbital dependency. The $E^U$ term is evaluated starting from equation 2.79, where the indices $i, i', j, j'$ represents the different $m$ orbitals of a given $I$ subspace.\cite{21}

$$E^U[[n]] = \sum_{I,m'n''m'''} U_{mm''m'} a^\dagger_{m\sigma} a^\dagger_{m'\sigma'} a_{m''\sigma'} a_{m'\sigma'} \quad (2.87)$$

The matrix element associated with $U$ is:

$$U_{mm''m'} = \frac{1}{2} \int d^3r d^3r' \psi^*_m(r) \psi_{m'}(r) V(r - r') \psi^*_{m''}(r') \psi_{m'''}(r') \quad (2.88)$$

If $\sigma \neq \sigma'$, we obtain

$$a^\dagger_{m\sigma} a^\dagger_{m'\sigma'} a_{m''\sigma'} a_{m'\sigma} = a^\dagger_{m\sigma} a_{m'\sigma'} a^\dagger_{m''\sigma'} a_{m'\sigma} = n^\sigma_{m} n^{-\sigma}_{m'} m'' m' \quad (2.89)$$

and if $\sigma = \sigma'$, there are two possibilities:

$$a^\dagger_{m\sigma} a^\dagger_{m'\sigma} a_{m''\sigma'} a_{m'\sigma} = a^\dagger_{m\sigma} a_{m'\sigma} a^\dagger_{m''\sigma} a_{m'\sigma} = n^\sigma_{m} n^{\sigma}_{m'} m'' m' \quad (2.90)$$

Putting together the Hubbard $E^U$ term gives:

$$\hat{E}^U[[n]] = \frac{1}{2} \sum_{|m\rangle,\sigma} \{ \langle m, m' | V_{ee} | m'' m''' \rangle n^{\sigma}_{mm'} n^{-\sigma}_{m'm''} \
 + (\langle m, m' | V_{ee} | m'' m''' \rangle - \langle m, m' | V_{ee} | m' m''' \rangle) n^\sigma_{mm'} n^{-\sigma}_{m'm''} \} \quad (2.91)$$

where $V_{ee}$ accounts for the screened Coulomb electron-electron interactions. The $E^{dc}$ term accounts for double counting but in the absence of orbital polarizations equation 2.84 gives the original $E^{LSDA}$. The double counting term is given by

$$E^{dc}[[n]] = \frac{1}{2} UN(1 - N^\dagger - N^\dagger + N^\dagger(N^\dagger - 1)) \quad (2.92)$$
where $N = N^\uparrow + N^\downarrow$, $U$ and $J$ are screened Coulomb and exchange terms. The expression in equation 2.92 is referred to as the full localized limit (FLL). Czyzyk and Sawatzky proposed another approach called around mean field expression for the $E^{dc}$ term which is slightly different compared to the FLL.

In equations 2.91 and 2.92, the invariance stems from transformation of the interaction parameters as quadruplets of localized wave functions and the functional’s dependence on the trace of the occupation matrices respectively. While the $V_{ee}$ integral accounts for the Coulomb electron-electron interaction of the localized basis (e.g. $d$ or $f$), we can compute these quantities from the expansion of the Coulomb potential $\left(2/|r - r'|\right)$ in terms of spherical harmonics:

$$\langle m, m'|V_{ee}|m', m''\rangle = \int d^3rd^3r' R^*_m(r)Y^*_{lm}(r)Y^*_{lm'}(r)V(r - r')R^*_{m'}(r')Y^*_{lm''}(r') V(r - r')$$

and $V(r - r')$ is

$$V(r - r') = \frac{1}{\epsilon(r - r')} = \frac{1}{\epsilon} \sum_{l=0}^{\infty} \frac{4\pi}{2l + 1} \frac{r_1^l}{r_1^{l+1}} \sum_{m=-l}^{l} Y_{lm}(r)Y^*_{lm}(r').$$

Then

$$\langle m, m'|V_{ee}|m', m''\rangle = \sum_k a_k(m, m', m', m'') F^k$$

where $0 \leq k \leq 2l$ ($l$ is the angular moment of the localized manifold; $-l \leq m \leq l$) and the $a_k$ factors can be obtained as products of Clebsh-Gordan coefficients:

$$a_k(m, m', m', m'') = \frac{4\pi}{2k + 1} \sum_{q=-k}^{k} \langle l_m|Y_{kq}|l_m'\rangle\langle l_m'|Y_{kq}'|l_m''\rangle.$$
\[ U = \frac{1}{(2l + 1)^2} \sum_{m,m'} \langle m, m' | V_{ee} | m, m' \rangle = F^0 \]

\[ J = \frac{1}{(2l)(2l + 1)} \sum_{m,m'} \langle m, m' | V_{ee} | m, m' \rangle = \frac{F^2 + F^4}{14}. \]

where \( m \) and \( m' \) account for electronic orbitals with the identical \( l \). For systems with \( f \) electrons, \( J \) can be expressed as \( J = (286F^2 + 195F^4 + 250F^6)/6435 \), which includes \( F^6 \).

### 2.7.2 A simplifier formulation

The most complete formulation of the LDA+U scheme is given in section 2.7.1 that is based on the multi-band Hubbard model. A simpler expression of the \( E_U \) has been formulated by Dudarev et al.\(^{[99]} \) where only the lower order Slater integrals \( F^0 \) are retained and \( F^2 = F^4 = J = 0 \). This implies neglecting the non-sphericity of the electronic interactions \( a_0(m, m', m'', m''') = \delta_{m,m'} \delta_{m'', m'''} \), along with the coupling difference between the parallel spin and anti-parallel spin electrons (captured by \( J \) the exchange interaction). The energy functional can be obtained from recalculation of equations 2.91 and 2.92 from which we derive:\(^{[92;93]}\)

\[ E_U [\{ n^{l}_{mm'} \}] = E_{Hub} [\{ n^{l}_{mm'} \}] - E_{dc} [\{ n^{l}_{mm'} \}] 
= \sum_{l} \frac{U^{l}}{2} \left[ (n')^2 - \sum_{\sigma} Tr [(n^{\sigma})^2] \right] - \sum_{l} \frac{U^{l}}{2} n^{l} (n^{l} - 1) \]

\[ = \sum_{l,\sigma} \frac{U^{l}}{2} Tr \left[ (n^{\sigma}) (1 - n^{\sigma}) \right]. \]  

(2.98)

The rotational invariance obtained in equations 2.91 and 2.92 is preserved in the simplified functional given in equation 2.98. This is because the “+U” functional depends on the trace of the occupation matrices and its products but the formal resemblance to the Hartree-Fock energy functional is missing. Therefore, only the \( U^l \) interaction parameter is necessary to account for the corrective functional. The simplified version of the Hubbard correction has been used in numerous studies and proved to be successful with similar results to the fully rotational invariant Hubbard correction. In some cases the Hund’s rule coupling \( J \) is essential to determine the correct ground state of the system, for example in systems characterized by non-collinear magnetization, correlation effects in multi-band metals and heavy Fermion systems. For a detailed
discussion on the theoretical formulation of LDA+U, strengths, limitations and comparison with other corrective techniques see Reference 93. \([93]\)

2.8 Software code

All calculations in this study were done within the framework of DFT as implemented in the VASP codes. The Paw method was used for the non-magnetic, spin-polarized and spin-orbit calculations. Elastic constants were obtained using the method of least-squares fit as implemented in the VASP/MedeA-MT module. Phonon dispersions were obtained using the direct method as implemented in the VASP/MedeA-PHONON module.

This concludes the overview of the theoretical framework. The next chapter presents the results of the \textit{ab initio} studies on Th-N based alloys.
Chapter 3

_Ab initio_ studies of Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$(NH)

This section to be submitted for publication as[^25] "Obodo, K. O., and Chetty, N. (2013). _Ab initio_ studies of Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$(NH)."
Ab initio studies of Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$(NH)

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Abstract

Using density functional theory within the Perdew-Burke-Ernzerhof generalized gradient approximation [GGA (PBE)] implemented in the VASP codes, we investigate the structural, elastic and electronic properties of Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$(NH). The calculated structural properties of these thorium-based nitrides are in good agreement with experimental data. We observe that all the Th-N based compounds that we considered are energetically favorable and elastically stable. We find that Th$_3$N$_4$ is semiconducting with a band gap of 1.59 eV, which compares well with the experimental band gap of 1.7 eV and we find Th$_2$N$_3$ to be metallic. Th$_2$N$_3$(NH), which is crystallographically equivalent to Th$_2$N$_3$, is insulating with a band gap of 2.12 eV. This is due to the -(NH) group that effects a shifting of the energy bands that results in the opening of a gap at the Fermi-level. The Th-N based compounds that we considered are predominantly ionic.

Keywords: A. Thorium nitride; C. Density functional theory; D. Electronic and structural properties

1. Introduction

Thorium-nitride (Th-N) based compounds are of great interest in the field of physics, chemistry and material science because of their properties such as high melting points, high density, high thermal conductivity, low creep rate, good corrosion resistance, etc. [5] For instance, these materials are used in nuclear reactor systems, in the breeder reactors where it is incorporated into the mixed actinide nitride fuels and in subcritical accelerator driven systems.

There have been several theoretical studies using first principles approaches and experimental studies of thorium mononitride. [6, 7, 8, 9, 10] To the best of our knowledge, a detailed theoretical analysis of the following Th-N based compounds within density functional theory (DFT) approach is absent: Th$_2$N$_2$(NH), Th$_2$N$_3$ and Th$_3$N$_4$. The Th$_2$N$_2$(NH) compound is known to be isomorphous to Th$_2$N$_3$ (also referred to as a sesquinitride). [11] Th$_2$N$_2$(NH) and Th$_2$N$_3$ crystallizes in the La$_2$O$_3$-type hexagonal structure with space group $P3m1$, whereas Th$_3$N$_4$ belongs to the $R-3m$ space group. We have shown in our previous studies that standard density functional approximation without the inclusion of Hubbard $U$ parameter gives an accurate description of the electronic, structural and elastic properties of thorium based systems. [5, 12]
Recently, Silva et al. [11] experimentally synthesized Th$_2$N$_2$(NH) by heating ThNF and LiNH$_2$. These workers characterized Th$_2$N$_2$(NH) using x-ray diffraction (XRD), and the Rietveld analysis to determine the crystal structure along with DFT approach to elucidate the crystal chemistry. Also, from Fourier transform infrared spectroscopy (FTIR) and high-resolution transmission electron microscopic (HRTEM) images, they confirm the presence of -NH group due to the lattice fringe disruptions observed in nanoparticle areas of the nitride species.

In this letter, we use ab initio techniques to determine the structural, elastic, and electronic properties and the energy of formation for Th$_2$N$_2$(NH), Th$_2$N$_3$ and Th$_3$N$_4$. Subsequently, by analysing the valence charge density distribution, we examine the compounds to investigate their bonding character. These systems are found to be non-magnetic (NM). The inclusion of spin-polarization (SP) or spin-orbit coupling (SOC) did not result in any changes to the structural, elastic and electronic properties. Hence, all the results presented are for the non-magnetic (NM) case.

2. Theory

We perform ab initio calculations on the Th-N based compounds using density functional theory [13] as implemented in the VASP code. [14] We use the Perdew-Burke-Ernzerhof (PBE) [15] exchange-correlation functional for the generalized gradient approximation (GGA). A kinetic energy cutoff of 550 eV is chosen to ensure adequately converged total energies for the compounds under consideration. A k-point spacing of 0.2 Å for the Monkhorst-Pack [16] grid is used to sample the Brillouin zone (BZ), and a Methfessel-Paxton smearing [17] width of 0.2 eV is used to integrate the bands at the Fermi level. The density of states function (DOS) is calculated using the tetrahedron integration method with Bl"ochl corrections. [18]

A method using the least-squares fit, [19] as implemented in the MedeA-MT module, is used to obtain the elastic constants. This method uses the tetrahedron method for the Brillouin zone integrations. The elastic properties are calculated from the Hill value, which is a geometric mean of the Voigt and Reuss values. The Hill values are used in the estimation of longitudinal ($v_l$), shear ($v_s$) and mean ($v_m$) sound velocities, and the Debye temperatures. [20]

The energy of formation for each compound is computed by taking the difference between the total energy of the Th-N based compounds and the sum of the energies of its constituents in their respective bulk elemental forms, and nitrogen in its diatomic gaseous form.

3. Results and Discussion

The crystal structures for Th$_2$N$_3$, Th$_2$N$_2$(NH) and Th$_3$N$_4$ are presented in Fig. 1. The experimentally determined structures are fully optimized geometrically using highly converged parameters. A full description of the structural parameters for Th$_2$N$_3$, Th$_2$N$_2$(NH) and Th$_3$N$_4$ is given in Ref 11, 21, 2.

In Table 1, we present the calculated lattice parameters ($a_0$ and c), c/$a_0$, and the energy of formation for Th$_2$N$_2$(NH), Th$_2$N$_3$ and Th$_3$N$_4$. The calculated lattice parameters compare well with the given experimental data. The calculated bond distances for Th-N(1) and Th-N(2) are 2.922 Å and 2.373 Å respectively for Th$_2$N$_2$(NH). This result is in good agreement with the XRD measurement [11] where the bond distances for Th-N(1) and Th-N(2) are 2.696 Å and 2.34 Å respectively.

The energy of formation for the Th-N based compounds considered is negative as presented in Table 3. This implies that the formation of these compounds is energetically favorable with
Figure 1: (Color online) The optimized structures for (a) Th$_2$N$_3$ (b) Th$_2$N$_2$(NH) (c) Th$_3$N$_4$; where the blue atoms represents Th atoms, the purple atoms represents N atoms and the brown atoms represents the oxygen atoms.

respects to the elements in their standard state. We find that Th$_3$N$_4$ is the most energetically favorable nitride among those compounds considered.

Table 1: The calculated and experimental [21, 22] lattice constants, a (Å) and c (Å), c/a and the energy of formation (eV) per formula unit for the Th-N based compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>a</th>
<th>c</th>
<th>c/a</th>
<th>E$_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th$_3$N$_4$</td>
<td>GGA</td>
<td>3.882</td>
<td>27.452</td>
<td>7.072</td>
<td>-11.380</td>
</tr>
<tr>
<td></td>
<td>Exp</td>
<td>3.873</td>
<td>27.385</td>
<td>7.072</td>
<td>-</td>
</tr>
<tr>
<td>Th$_2$N$_3$</td>
<td>GGA</td>
<td>3.913</td>
<td>6.161</td>
<td>1.575</td>
<td>-6.890</td>
</tr>
<tr>
<td></td>
<td>Exp</td>
<td>3.875</td>
<td>6.175</td>
<td>1.594</td>
<td>-</td>
</tr>
<tr>
<td>Th$_2$N$_2$(NH)</td>
<td>GGA</td>
<td>4.021</td>
<td>6.165</td>
<td>1.533</td>
<td>-5.254</td>
</tr>
<tr>
<td></td>
<td>Exp</td>
<td>3.886</td>
<td>6.185</td>
<td>1.592</td>
<td>-</td>
</tr>
</tbody>
</table>

The elastic properties of thorium-nitride based systems considered are calculated for the NM phase. The elastic constants ($c_{ij}$) obtained are shown in Table 2. The elastic stability is related to sum rules. Therefore, negative elastic constants does not necessary signify elastic instability.

Table 3 shows the calculated elastic properties of various ordered alloys of Th-N based compounds in the NM phase. They are elastically stable with positive bulk, shear and Young’s
Table 2: Elastic constants Cijs (values in GPa).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>c_{11}</th>
<th>c_{12}</th>
<th>c_{13}</th>
<th>c_{14}</th>
<th>c_{33}</th>
<th>c_{44}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th_3N_4</td>
<td>275.94</td>
<td>163.80</td>
<td>89.30</td>
<td>31.68</td>
<td>170.77</td>
<td>79.15</td>
</tr>
<tr>
<td>Th_2N_3</td>
<td>237.67</td>
<td>143.77</td>
<td>96.15</td>
<td>31.73</td>
<td>196.55</td>
<td>73.26</td>
</tr>
<tr>
<td>Th_2N_2(NH)</td>
<td>223.39</td>
<td>157.18</td>
<td>82.32</td>
<td>-18.94</td>
<td>109.24</td>
<td>92.50</td>
</tr>
</tbody>
</table>

moduli, positive shear velocity (obtained from the shear sound velocity) and positive longitudinal velocity (obtained from the longitudinal sound velocity). [23] The calculated bulk modulus for Th_3N_4, Th_2N_3 and Th_2N_2(NH) are 147.92 GPa, 147.10 GPa and 121.51 GPa respectively. The mean velocity \( v_{mn} \) calculated from shear (transverse) velocity \( v_s \) and longitudinal velocity \( v_l \) is used to determine the Debye temperature. The Debye temperature \( \theta_D \) for the Th-N based nitrides is calculated to determine the stiffness of the system. The \( \theta_D \) for the Th_3N_4 is highest at 311.6 K, which indicates that Th_3N_4 is stiffer compared to the other compounds considered.

Table 3: The bulk, shear and Young’s moduli (Hill values in GPa), acoustic velocities \((m s^{-1})\), and Debye temperature (K)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>B</th>
<th>Shear</th>
<th>Young’s</th>
<th>( v_s )</th>
<th>( v_l )</th>
<th>( v_{mn} )</th>
<th>( \theta_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th_3N_4</td>
<td>147.92</td>
<td>60.54</td>
<td>159.73</td>
<td>2406</td>
<td>4677</td>
<td>2695</td>
<td>311.6</td>
</tr>
<tr>
<td>Th_2N_3</td>
<td>147.10</td>
<td>52.34</td>
<td>140.07</td>
<td>2256</td>
<td>4593</td>
<td>2533</td>
<td>297.2</td>
</tr>
<tr>
<td>Th_2N_2(NH)</td>
<td>121.51</td>
<td>44.64</td>
<td>118.94</td>
<td>2140</td>
<td>4309</td>
<td>2401</td>
<td>293.9</td>
</tr>
</tbody>
</table>

In Fig. 2, we present the computed total density of states (DOS) for the Th-N based compounds, together with projections on the thorium \( p, d, f \), and nitrogen \( 2p \) states. Figure 2a and 2c show that Th_3N_4 and Th_2N_2(NH) are insulating with a band gap of 1.59 eV and 2.12 eV respectively. The top of the valence band for Th_3N_4 and Th_2N_2(NH) is determined mainly by the N-2p states. The bottom of the conduction band shows significant hybridization of the thorium \( d \) and \( f \) states with the nitrogen \( 2p \) states in Th_2N_2(NH) compound. For Th_3N_4, the bottom of the conduction band is determined mainly by the hybridization of the thorium \( d \) and \( f \) states. Gouder et al. [3], experimentally obtained a band gap of about 1.7 eV for Th_3N_4 using photoelectron spectroscopy studies. This agrees well with our theoretically predicted band gap. On the other hand, Figure 2b shows that Th_2N_3 is metallic. This metallicity is determined mainly by the N-2p states. The insulating properties of Th_2N_2(NH), which is crystallographically similar to metallic Th_2N_3 is attributed to the shifting of the valence band due to the presence of the -(NH) group. It is worth noting that these Th-N based compounds all show significant hybridization of the thorium \( p, d \) and \( f \) states with the nitrogen \( 2p \) states.

In order to elucidate the bonding characteristic for all the compounds considered, we present their valence charge density distribution plots in Figure 3. The charge density distribution is computed in the (110) plane. The scale in Figure 3 is such that blue is devoid of electrons and red has a high concentration of electrons. In general, we observe charge accumulation around N and charge depletion around the Th atoms. This suggests that there is charge transfer from thorium to nitrogen, indicating that the Th-N chemical bonds are primarily ionic in character. This is expected since the N atom is more electronegative than the metal actinide atom. Moreover, we observe in Figure 3 a slight charge accumulation between the atomic spheres compared to the rest of the interstitial regions.
Figure 2: (Color online) The total and projected densities of states (DOS) for (a) Th$_2$N$_2$(NH) (b) Th$_2$N$_3$ (c) Th$_3$N$_4$ within the description of the GGA. The Fermi energy level is set at zero and is represented using dashed line.

Of note in Figure 3a is the distortion in the charge density due to the presence of the -(NH) group that has resulted in a bean-shaped charge distribution compared to Figure 3b. This charge density bridge is attributed to the covalent bonding by this group to the ionic parent structure. [24, 10, 12]

4. Conclusions

In conclusion, the DFT technique has been used to study the structural, elastic and electronic properties of Th-N based compounds. This work is motivated by the physics of the thorium nitrides and the usefulness of various Th-N based compounds in the generation of energy. The inclusion of SP and SOC results in no significant change in the calculated properties of these compounds. We determined that Th-N based compounds are energetically and elastically stable. We observed that Th$_3$N$_4$ is the most energetically stable nitride. We found that Th$_2$N$_3$ and Th$_2$N$_2$NH are insulating, while Th$_2$N$_3$ is metallic. The insulating character of Th$_2$N$_2$(NH) is attributed to covalent bonding of the -(NH) group to the otherwise ionic parent system. Generally, the calculated DOS show significant thorium $d$ and $f$ states hybridization with the nitrogen $2p$ in the Th-N based compounds.

Acknowledgment

The authors gratefully acknowledge financial support from the University of Pretoria. We thank Dr. Walter Meyer and Dr. Jannie Pretorius for assistance with the computational resources. KO gratefully acknowledges support of Dr. Molepo Mahlaga, Obodo T. Joshua and the members...
Figure 3: (Color online) Valence charge density distribution plots for (a) Th$_2$N$_2$(NH) (b) Th$_2$N$_3$ (c) Th$_3$N$_4$ computed in the (110) plane. Charge density distribution for the atoms are labeled accordingly, and the scale is presented.

of the Theoretical and Computational Solid State Physics Research Group at the University of Pretoria for useful discussions.

References


The next chapter presents results for the theoretical studies of thorium titanium alloys. This is motivated by the technological and scientific importance of thorium alloys and titanium alloys as demonstrated by their wide applications and vast scientific publications. Using DFT, the possibility of obtaining an ordered alloy of ThTi based system is investigated. The stability for the systems investigated is validated using arguments based on the bonding characters, enthalpy of formation, charge density distribution, electron localization function, elastic and lattice dynamic properties.
Chapter 4

A theoretical study of thorium titanium-based alloys

A theoretical study of thorium titanium-based alloys

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Abstract

Using theoretical quantum chemical methods, we investigate the dearth of ordered alloys involving thorium and titanium. Whereas both these elements are known to alloy very readily with various other elements, for example with oxygen, current experimental data suggests that Th and Ti do not alloy very readily with each other. In this work, we consider a variety of ordered alloys at varying stoichiometries involving these elements within the framework of density functional theory using the generalized gradient approximation for the exchange and correlation functional. By probing the energetics, electronic, phonon and elastic properties of these systems, we confirm the scarcity of ordered alloys involving Th and Ti, since for a variety of reasons many of the systems that we considered were found to be unfavorable. However, our investigations resulted in one plausible ordered structure: We propose ThTi\textsubscript{3} in the Cr\textsubscript{3}Si structure as a metastable ordered alloy.

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I. INTRODUCTION

Thorium, a heavy metal, combined with various elements such as boron, carbon, nitrogen and oxygen has been studied both theoretically\textsuperscript{1–3} and experimentally\textsuperscript{4–6} in relation\textsuperscript{2} to a range of physical, chemical, electronic, and thermophysical properties, often exhibiting high density, good thermal conductivity and good mechanical properties. The applications of Th-based alloys are wide-ranging. These include uses in nuclear reactors and in the aerospace industry because of its good corrosion resistant properties and high melting points. Th binary systems exist in various ordered alloys such thorium monocarbide (ThC),\textsuperscript{7} mononitride (ThN)\textsuperscript{8} and monoxide ThO.\textsuperscript{9} ThO crystallizes in the rock salt structure, while ThO\textsubscript{2} crystallizes in the fluorite structure. ThB\textsubscript{4}\textsuperscript{10} and ThB\textsubscript{6} exist in the ThB\textsubscript{4} and CaB\textsubscript{6} structures.

Titanium, a relatively light metal is strong, has excellent corrosion resistant properties and a high melting point. Given its relatively small atomic size, Ti can be easily impregnated into materials without radically altering the host crystal structure. Therefore, Ti is a versatile element for alloying and modifying the properties - especially the strength properties - of materials. Applications range from additives in paints to metals for aerospace and industry. In this way, Ti is useful for engineering the properties of materials. Ti-based oxides are very well known, for example TiO\textsubscript{2} exists in the equilibrium rutile, and the metastable anatase and brookite structures, and the high pressure monclinic and orthorhombic forms. Ti also combines very readily with other metals, such as Pt in a variety of crystallographic forms and stoichiometries.

It would seem, then, that ordered alloys involving Th and Ti should form readily when in fact this is not the case. Experimental evidence by Carlson \textit{et al.}\textsuperscript{11} dating back to 1956 still appears to be the only authoritative view on this subject, although similar results were found by Pedersen \textit{et al.} in 1980.\textsuperscript{12} Carlson \textit{et al.} discovered that Th-Ti forms a simple eutectic at 1190°C and at 12 wt % Ti, with no intermediate phases. Pedersen \textit{et al.} found the eutectic composition to be 13.26 wt % Ti. The solid phases at the eutectic are $\alpha$-Th (cubic) and $\beta$-Ti (hexagonal). Carlson \textit{et al.} concluded that solid solubilities at room temperatures are negligible. They argued that since the atomic radii of Th and Ti differ by about 22%, and because the Hume-Rothery rules for alloying suggest that extensive solid solubility should not occur between metals differing in size by more than 15%, the dearth of compounds (ordered or not) should not be surprising. Furthermore, they argued that since there is a marginal difference in the electronegativity of these two elements (the electronegativities are 1.3 for Th and 1.5 for Ti), compound phases should not form readily.
Since the authoritative experimental work done on these systems is more than fifty years old, and given the technological interest in both Th and Ti, and the potential scientific and technological interest in alloys involving these elements, we have investigated these alloy systems using modern theoretical quantum chemical methods, which over the past two decades has proven to be an excellent tool to study such systems for a variety of material properties.

In the next section we present a brief description of our theoretical and computational methodology. In Section III, we present analysis on various ordered alloys of Th-Ti based systems with the aim of investigating their stability. In Section IV, an in-depth analysis of the bonding and electronic character of our proposed stable alloy is presented. Finally, we present our conclusions in Section V.

II. METHODOLOGY

All calculations were performed using density functional theory\cite{13} as implemented in the VASP code.\cite{14} We used the PBE\cite{15} and PBEsol exchange-correlation functional\cite{16} for the generalized gradient approximation (GGA). A kinetic energy cutoff of 500 eV was chosen to ensure adequately converged total energies for the alloy systems under consideration. A Monkhorst-Pack\cite{17} grid of 12×12×12 was used to sample the Brillouin zone (BZ) and Methfessel-Paxton smearing\cite{18} with a width of 0.2 eV was used to integrate the bands to the Fermi level. The total energy, electronic band structure and density of states (DOS) were calculated using the tetrahedron integration method with Blöchl corrections.\cite{19}

We tested our calculations with so-called Hubbard-U corrections of 1 eV for the onsite correlation energy, which for Th could in principle be important since it is an actinide. Our investigations showed that the differences in a range of results involving the physical structure, the electronic structure and the energetics over the conventional GGA approach were negligible. This, in hindsight, is not surprising since Th has a closed f-shell of electrons with no highly localized orbital. All results subsequently presented have not included the Hubbard correction.

A method using the least-squares fit,\cite{20} as implemented in the MedeA-MT module, was used to obtain the elastic constants. This method uses the tetrahedron method for the Brillouin zone integrations. The elastic properties are calculated from the Hill value which is a geometric mean of the Voigt and Reuss values. The eigenvalues of the stiffness matrix gives an indication of the mechanical stability of the systems under consideration. The Hill values were used in the
estimation of longitudinal, shear and mean sound velocities, and the Debye temperatures. The phonon dispersion curves and lattice dynamics were determined using linear response theory as implemented in the MedeA-PHONON package.

The heat of formation for each system was calculated by taking the difference between the total energy of the alloy unit cell and the sum of the energies of its constituents in their respective bulk elemental forms. The heat of formation of the system is strongly dependent on the spin-orbit coupling (SOC) due to the presence of relativistic effects in this heavy atomic systems.

Lu et al. used the same method based on the elastic, valence charge density distribution and phonon dynamics to study ThN, which has been experimentally synthesized with an experimental lattice constant of 5.154 Å and bulk modulus of 175 GPa. This validates the approach used in this study. Therefore, we applied our methods to studies of pristine cubic Th and hexagonal Ti, and alloys of these elements in the Cr\textsubscript{3}Si, Cu\textsubscript{3}Au, Al\textsubscript{3}Ti, CsCl, CuAu, CuPt, and NiAs crystal forms. For the off-50:50 compounds we considered both the alloy and its dual alloy, e.g. both Th\textsubscript{3}Ti and ThTi\textsubscript{3} in the Cr\textsubscript{3}Si structure.

### III. INVESTIGATION OF STABILITY

The calculated elastic properties, phonon dispersion and heat of formation for thorium-titanium alloys is used to determine the elastically, dynamically and energetically stable alloys of Th-Ti based systems.

The GGA (PBEsol) exchange correlation functional is an improved functional that takes into account the interactions present in closely packed structures. Hence, it is largely used in this investigation to understand the properties of Th, Ti and Th-Ti based alloys. The results obtained using the GGA (PBEsol and PBE) for Th and Ti shows that the PBE exchange-correlation functional gives a slightly improved description of the lattice constants for Th and Ti. But, there is no fundamental difference in the description of the electronic properties of Th-Ti based alloys except in the heat of formation were the PBEsol gives consistently lower heat of formation compared to the PBE functional. Hence the results presented for the elastic properties, the electronic properties and the phonon dispersion considers the non-magnetic (NM) structure of Th-Ti based alloys using PBEsol. However, the heat of formation is strongly dependent on the exchange correlation functional along with the presence of relativistic effects. Therefore, these issues are taken into account only for the proposed stable alloy.
The calculated lattice parameter using GGA (PBEsol) with the NM structure for Th (face centered cubic structure) is 4.95 Å, and Ti (hexagonal close pack structure) are $a$ of 2.90 Å and $c$ of 4.59 Å. The inclusion of SOC leads to a slight change in the lattice parameters of these systems. The calculated equilibrium lattice constants ($a_0$) for Th, Ti and Th-Ti based alloys is given in Table I for the NM cases. The lattice constants for Th-Ti based alloys in the NM phase shows there is an increase in the lattice constant with increase in Th concentration. This is expected because the Th atom is larger compared to Ti atom.

**TABLE I.** Lattice constant $a_0$ (Å), $c$ (Å) and heat of formation (eV) of Th-Ti based alloys in various crystal structure using PBEsol in the non-magnetic phase

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$c$ (Å)</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>4.95</td>
<td>4.95</td>
<td>–</td>
</tr>
<tr>
<td>ThTi$_3$ (Cr$_3$Si)</td>
<td>5.32</td>
<td>5.32</td>
<td>0.740</td>
</tr>
<tr>
<td>ThTi$_3$ (Cu$_3$Au)</td>
<td>4.28</td>
<td>4.28</td>
<td>0.683</td>
</tr>
<tr>
<td>ThTi$_3$ (Al$_3$Ti)</td>
<td>4.11</td>
<td>9.19</td>
<td>0.685</td>
</tr>
<tr>
<td>ThTi (CsCl)</td>
<td>3.60</td>
<td>3.60</td>
<td>0.433</td>
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<tr>
<td>ThTi (CuAu)</td>
<td>3.21</td>
<td>4.62</td>
<td>0.585</td>
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<tr>
<td>ThTi (CuPt)</td>
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<td>15.54</td>
<td>0.773</td>
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<tr>
<td>ThTi (NiAs)</td>
<td>4.40</td>
<td>6.29</td>
<td>4.196</td>
</tr>
<tr>
<td>Th$_3$Ti (Cr$_3$Si)</td>
<td>6.05</td>
<td>6.05</td>
<td>2.514</td>
</tr>
<tr>
<td>Th$_3$Ti (Cu$_3$Au)</td>
<td>4.78</td>
<td>4.78</td>
<td>0.930</td>
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<tr>
<td>Th$_3$Ti (Al$_3$Ti)</td>
<td>4.60</td>
<td>10.27</td>
<td>0.336</td>
</tr>
<tr>
<td>Ti</td>
<td>2.90</td>
<td>4.59</td>
<td>–</td>
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</tbody>
</table>

The possibility of a magnetic ground state in Th-Ti based alloys is examined. For this purpose, the spin-polarized (SP) calculations, assuming an initial ferromagnetic ground state are carried out for the Th-Ti based alloys. We found that the ground state of all the Th-Ti based alloys considered is NM, without any localized atomic magnetic moments. The NM and SP calculations yield similar lattice parameters and lead to NM ground state structures for both PBE and PBEsol functionals. Subsequently, the inclusion of relativistic effects leads to a slight (insignificant) change in the lattice constant and a (significant) change in the heat of formation compared to the NM and SP cases for both GGA (PBE and PBEsol) functionals.
A. Elastic properties

The elastic properties of various ordered alloys of Th-Ti based systems are calculated for the NM phase. The elastic constants ($c_{ij}$) obtained are shown in Table II. The criteria for elastic stability are: positive elastic constants, positive bulk, shear and Young’s moduli, positive shear velocity (obtained from the shear sound velocity), positive longitudinal velocity (obtained from the longitudinal sound velocity). The systems that satisfy these criteria are elastically stable. However, this does not imply that such a system is dynamically stable. The negative elastic constant values for Th-Ti based alloy (in CuPt and NiAs structures) shows that these structures might be unstable because stability is related to sum rules.

<table>
<thead>
<tr>
<th>TABLE II. Elastic constants $C_{ij}$’s (values in GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
</tr>
<tr>
<td>Th</td>
</tr>
<tr>
<td>ThTi$_3$ (Cr$_3$Si)</td>
</tr>
<tr>
<td>ThTi$_3$ (Cu$_3$Au)</td>
</tr>
<tr>
<td>ThTi$_3$ (Al$_3$Ti)</td>
</tr>
<tr>
<td>ThTi (CsCl)</td>
</tr>
<tr>
<td>ThTi (CuAu)</td>
</tr>
<tr>
<td>ThTi (CuPt)</td>
</tr>
<tr>
<td>ThTi (NiAs)</td>
</tr>
<tr>
<td>Th$_3$Ti (Cr$_3$Si)</td>
</tr>
<tr>
<td>Th$_3$Ti (Cu$_3$Au)</td>
</tr>
<tr>
<td>Th$_3$Ti (Al$_3$Ti)</td>
</tr>
<tr>
<td>Ti</td>
</tr>
</tbody>
</table>

In Table III, we present the calculated bulk modulus of the various Th-Ti based alloys. The calculated bulk modulus for Ti, Th and ThTi$_3$ (in Cr$_3$Si structure) are 118.48 GPa, 58.21 GPa and 100.98 GPa respectively. Other alloys of Th-Ti based systems have lower bulk modulus compared to ThTi$_3$ (in Cr$_3$Si structure). ThTi$_3$ (in Al$_3$Ti structure) has the largest magnitude of shear modulus and Young’s modulus compared to the other alloys. The mean velocity calculated from shear (transverse) velocity and longitudinal velocity is used to determine the Debye temperature. The
Debye temperature ($\theta_D$) gives an indication of the stiffness of the material. ThTi$_3$ (Al$_3$Ti), Ti, ThTi$_3$ (in Cr$_3$Si structure) has $\theta_D$ of 445.0 K, 426.1 K, 346.7 K respectively. This shows that the alloying of Th with Ti leads to considerable improvement in the mechanical properties of Th metal.

TABLE III. The bulk, shear and Young’s moduli (Hill values in GPa), acoustic velocities ($ms^{-1}$), and Debye temperature (K)

<table>
<thead>
<tr>
<th></th>
<th>$B_H$</th>
<th>$G_H$</th>
<th>$Y_H$</th>
<th>$\nu_s$</th>
<th>$\nu_l$</th>
<th>$\nu_m$</th>
<th>$\Theta_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>58.21</td>
<td>24.94</td>
<td>64.72</td>
<td>1401</td>
<td>2684</td>
<td>1568</td>
<td>149.7</td>
</tr>
<tr>
<td>ThTi$_3$ (Cr$_3$Si)</td>
<td>100.9</td>
<td>64.65</td>
<td>159.8</td>
<td>2798</td>
<td>4760</td>
<td>3101</td>
<td>346.7</td>
</tr>
<tr>
<td>ThTi$_3$ (Cu$_3$Au)</td>
<td>92.70</td>
<td>31.38</td>
<td>84.58</td>
<td>1986</td>
<td>4112</td>
<td>2232</td>
<td>246.5</td>
</tr>
<tr>
<td>ThTi$_3$ (Al$_3$Ti)</td>
<td>89.80</td>
<td>108.7</td>
<td>207.7</td>
<td>3697</td>
<td>5432</td>
<td>4030</td>
<td>445.0</td>
</tr>
<tr>
<td>ThTi (CsCl)</td>
<td>79.82</td>
<td>12.19</td>
<td>34.79</td>
<td>1106</td>
<td>3106</td>
<td>1257</td>
<td>131.0</td>
</tr>
<tr>
<td>ThTi (CuAu)</td>
<td>77.45</td>
<td>24.81</td>
<td>67.16</td>
<td>1592</td>
<td>3360</td>
<td>1791</td>
<td>185.5</td>
</tr>
<tr>
<td>ThTi (CuPt)</td>
<td>73.19</td>
<td>-52.86</td>
<td>-430.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ThTi (NiAs)</td>
<td>-484.0</td>
<td>929.3</td>
<td>39630</td>
<td>15670</td>
<td>14130</td>
<td>15090</td>
<td>1138</td>
</tr>
<tr>
<td>Th$_3$Ti (Cr$_3$Si)</td>
<td>66.17</td>
<td>29.52</td>
<td>77.07</td>
<td>1626</td>
<td>3073</td>
<td>1817</td>
<td>178.9</td>
</tr>
<tr>
<td>Th$_3$Ti (Cu$_3$Au)</td>
<td>69.55</td>
<td>30.37</td>
<td>79.41</td>
<td>1638</td>
<td>3118</td>
<td>1832</td>
<td>181.1</td>
</tr>
<tr>
<td>Th$_3$Ti (Al$_3$Ti)</td>
<td>64.84</td>
<td>31.24</td>
<td>80.63</td>
<td>1657</td>
<td>3060</td>
<td>1849</td>
<td>183.2</td>
</tr>
<tr>
<td>Ti</td>
<td>118.5</td>
<td>51.44</td>
<td>134.1</td>
<td>3257</td>
<td>6223</td>
<td>3643</td>
<td>426.1</td>
</tr>
</tbody>
</table>

B. Phonon dispersion

The phonon frequency of crystalline structures is one of the basic aspects when considering the phase stability, phase transformations, and the thermodynamics of these materials. The absence of imaginary (negative frequencies in the figures) frequencies in phonon dispersion curve and the phonon density of states give an indication that the structure is dynamically stable or vice versa. The phonon frequency for various Th-Ti based alloys in the NM phase using PBEsol is presented in Fig. 1. The use of PBE or PBEsol exchange correlation functional does not lead to a change in the lattice dynamics of these alloys. In Fig. 1a, 1b and 1c, the phonon plots of Th, Ti and ThTi$_3$ (in Cr$_3$Si structure) are shown respectively. They possess no imaginary phonon frequencies mode. Hence, they are structurally and thermodynamically stable. While, the other structures considered
have various degree of instabilities due to the presence of imaginary frequencies. The phonon
frequencies for the unstable structures are presented for completeness.

FIG. 1. Phonon dispersion and phonon density of state (DOS) plots for Th, Ti and Th-Ti based alloys in
various ordered crystalline structures
ThTi\textsubscript{3} (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures) have the same ratio of atoms as ThTi\textsubscript{3} (in Cr\textsubscript{3}Si structure). It is interesting to note that ThTi\textsubscript{3} (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures) is stable at the $\Gamma$-point but possess few imaginary frequencies. This implies that the structure might transform to another structure or undergo pressure-induced stabilization. Therefore, these ordered structures with imaginary frequencies do not exist.

Isotropic pressure was applied to ThTi\textsubscript{3} (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures) with the aim of stabilizing or transforming these structures to its stable form. These structures did not undergo any structural stabilization or phase transformation with change in pressure. This can be attributed to the size of the unit cell and the actual number of atoms.

In the same line, isotropic pressure is applied to the dual alloys of ThTi\textsubscript{3} (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures) which is Th\textsubscript{3}Ti (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures). The phonon dispersion is evaluated to determine its stability. Pressure induced stabilization of these structures occurred for Th\textsubscript{3}Ti (in Cu\textsubscript{3}Au and in Al\textsubscript{3}Ti structures) respectively. For Th\textsubscript{3}Ti alloy (in Cu\textsubscript{3}Au structure), a pressure of about 324.7 GPa is applied to the dynamically unstable structure to achieve a stable structure. Also Th\textsubscript{3}Ti alloy (in Al\textsubscript{3}Ti structure), a pressure of about -3.574 GPa was applied to the dynamically unstable structure to achieve a stable structure. The energies of formation of these pressure stabilized structures are positive and higher than that of ThTi\textsubscript{3} alloy (in Cr\textsubscript{3}Si structure). Therefore, Th-Ti based alloys is most likely to be found as ThTi\textsubscript{3} (in Cr\textsubscript{3}Si structure) rather than the pressure stabilized structures.

The phonon dispersion of ThTi\textsubscript{3} alloy (in Cr\textsubscript{3}Si structure) has a splitting at $\Gamma$-point between the LO-TO, owing to the fact that Th atom is heavier than Ti atom. The low lying frequency modes are governed by the dynamics of heavy Th atoms, whereas the higher frequencies are governed by the dynamics of lighter Ti atoms.

C. Heat of formation

The Gibbs free energy of the various alloys is calculated. These calculations are performed at zero temperature and zero pressure, hence the Gibbs free energy reduces to the heat of formation, $\Delta H$. The calculated heat of formation of the various alloys is investigated to determine its relative stability. Th and Ti metal are used as the reference systems to obtain the heat of formation for the alloys as described in the methodology. This is because they are the basic constituent of the alloy. The heat of formation for all the structures are presented in Table I for the NM phase with PBEsol.
pseudopotential. The structure with the lowest heat of formation for the investigated Th-Ti based alloys using the PBEsol (with NM) is ThTi (in CsCl structure). This structure is highly elastically and dynamically unstable.

<table>
<thead>
<tr>
<th>$a_0$ (Å)</th>
<th>functional</th>
<th>method</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.409</td>
<td>PBE</td>
<td>SOC</td>
<td>0.851</td>
</tr>
<tr>
<td>5.406</td>
<td>PBE</td>
<td>SP</td>
<td>1.003</td>
</tr>
<tr>
<td>5.406</td>
<td>PBE</td>
<td>NM</td>
<td>1.014</td>
</tr>
<tr>
<td>5.322</td>
<td>PBEsol</td>
<td>SOC</td>
<td>0.591</td>
</tr>
<tr>
<td>5.325</td>
<td>PBEsol</td>
<td>SP</td>
<td>0.727</td>
</tr>
<tr>
<td>5.325</td>
<td>PBEsol</td>
<td>NM</td>
<td>0.740</td>
</tr>
</tbody>
</table>

To accurately determine the total energy and the heat of formation for the stable alloys the inclusion of SOC is essential for these alloys. We calculated the heat of formation for ThTi$_3$ alloy (in Cr$_3$Si structure) using the PBEsol functional with SOC to be 0.591 eV as listed in Table IV. Our calculated heat of formation for the system using PBEsol with SOC is less than NM and SP methods. In addition, using PBE functional with NM, SP and SOC method this results in a greater heat of formation compared to PBEsol with SOC. Generally, the inclusion of SOC leads to an effective lowering of the heat of formation in the structure for both GGA (PBE and PBEsol) functional.

The positive heat of formation of our system implies that the system will not occur spontaneously rather will require a positive energy input to create this alloy. The low value obtained for the heat of formation gives an indication that the formation of a metastable ordered alloy of Th and Ti is possible.

IV. THE PROPOSED METASTABLE ALLOY

The band structure, density of states, valence charge density distribution and electron localization function (ELF)$^{25-27}$ for the metastable system under consideration are presented to analyze
the electronic properties and bonding character.

The metastable alloy obtained from our investigation is ThTi$_3$ alloy (in Cr$_3$Si structure) as shown in Fig. 2. The alloy has the $Pm-\bar{3}n$ space group (with group number 223). And the Th atoms in the unit cell are located in the (0.0, 0.0, 0.0) and (0.5, 0.5, 0.5) positions. The Ti atoms are located in the (0.5, 0.25, 0) and (0.5, 0.75, 0).

![FIG. 2. The Structure of ThTi$_3$ in Cr$_3$Si where the white atoms represents Th atoms and the black atoms represents Ti atoms.](image)

In Table IV, we present the GGA (PBE and PBEsol) results of the lattice parameter of the proposed metastable alloy. The difference in the lattice parameter obtained using PBE and PBEsol for the metastable system is about 1.6%. It should be mentioned here that ThTi$_3$ alloy (in Cr$_3$Si structure) irrespective of the initial magnetic configuration gives a NM ground state as previously stated for all Th-Ti based alloys. This is corroborated by the insignificant difference in the lattice parameters between the NM, SP and SOC phase of the structure.

A. Band structure and partial density of states

In Fig. 3, we present the calculated band structures for Th, Ti and ThTi$_3$ (in Cr$_3$Si structure) along the high symmetry lines of BZ, and this evidently shows that they are all metallic structures. Th and Ti metals are comprised of two groups of bands with a huge difference of about 200% between the Th and Ti valence bands. This difference in the valence bands suggests difficulty in bonding between these two metals. It is no surprise then that only one plausible structure is obtained from our investigation.

The band structure of ThTi$_3$ (in Cr$_3$Si structure) consists of three isolated groups of valence bands with a slight energy dispersion $E(k)$, which is typical of crystals with a relatively low degree
FIG. 3. The band structure for Th, Ti and ThTi$_3$ alloy (in Cr$_3$Si structure) with the Fermi energy level set (dashed line) at zero.

The lowest group of band is from the Th $s$-orbital and is located around -38 eV. The following bands in Fig. 3c are from the Th $p$-orbital and are located around -21 eV and -15 eV with a slight contribution from the Ti $p$-orbital in later bands. These bands have a quasi-core character. The broadest occupied band is in the range of -5.5 eV to 1.5 eV.

The PDOS for the metastable alloy is presented to highlight the effect of orbital hybridization around the Fermi level. The Th ($d$ and $f$)-orbitals and the Ti ($p$ and $d$)-orbitals are presented in PDOS for ThTi$_3$ (in Cr$_3$Si structure) in Fig 4. The most dominant contribution at the Fermi level is from the Ti $d$-orbital while, the Th ($d$ and $f$)-orbitals provide almost equal contribution of states. The effect Ti $p$-orbital is marginal in determining the metallicity of ThTi$_3$ (in Cr$_3$Si structure). Looking at the contribution from Th, the dominant state in the conduction band is the Th $f$-orbital and in the valence band is the Th $d$-orbital. The system is very sensitive to the concentration of Ti atoms due to its overall contribution in determining the metallicity of the alloy. Hence, the configuration and concentration of Ti atoms will overall determine the electronic nature of this alloy.

B. Valence charge density

The computed valence charge density for ThTi$_3$ alloy (in Cr$_3$Si structure) is presented to elucidate the bonding character. Fig. 5 shows the computed charge density distribution plot for ThTi$_3$ alloy (in Cr$_3$Si structure) in the (100) plane. The valence charge density is indicated by the color scale on the side (blue is devoid of electrons and red has a high concentration of electrons). The valence charge densities plotted pertains to the valence states only summed over both spin direc-
FIG. 4. (Color online) The partial density of states (PDOS) for ThTi$_3$ (in Cr$_3$Si structure). The DOS are calculated at the optimized geometry for the given density functional and magnetic ordering. The Fermi energy level is set at zero and is represented using dashed line.

FIG. 5. (Color online) The valence charge density distribution for ThTi$_3$ (in Cr$_3$Si structure). The color pattern of the calculated valence charge density in the (001) plane, where the Th atom is depicted by the black balls and the Ti atoms by white balls. The color pattern of the valence charge density (scale: no electrons are represented as deep blue (0.0) and large concentration of electrons is represented as deep red (0.8); scale for remaining frames in increasing order of intensity: light blue, green, yellow, orange).

It is clearly seen that ThTi$_3$ alloy (in Cr$_3$Si structure) is metallic, characterized by a nearly spherical charge density distribution around the Th and Ti ions with very high concentration of...
valence charge and an appreciable charge density in all the interstitial regions. Hence, in $\mathbf{k}$-space, appreciable band overlap exists between Th and Ti ions. Compared to the charge density in the rest of the interstitial region relatively high charge density bridges are present between the atomic spheres. This indicates ionization in the bridge sites suggestive of the presence of covalency.

In order to ascertain the presence of covalency in all of the bridge sites, we calculated the distribution of the ELF.

C. Electron localization function for ThTi$_3$ (in Cr$_3$Si structure)

The ELF for the ground state bonding configuration of ThTi$_3$ alloy in (Cr$_3$Si structure) is evaluated to gain further insight into its bonding character and nature. ELF is given as $[1 + (D/D_h)^2]^{-1}$, $D$ is $\tau - t_W$ represents an excess of the local kinetic energy due to the Pauli principle. Where $\tau = \frac{1}{2} \sum |\nabla \varphi_i|^2$ is the Kohn-Sham local kinetic energy, $\varphi_i$ are the Kohn-Sham orbitals, and $t_W$ is the value of $\tau$ in the absence of the Pauli principle ($\sim |\nabla \rho|^2/\rho$ and $\rho$ being the charge density). $D_h$ being $D$ for the corresponding uniform electron gas ($\sim \rho^{5/3}$). The spatial organization of ELF provides a basis for a proper classification of bonds$^{27,29}$. Based on this definition ELF takes values ranging from 0 and 1, where 1 represents perfect localization. The Th metal has more valence and core electrons than the Ti metal. They both exhibit similar features such as the large concentration of electrons around the atoms and an appreciable density of electrons away from the atoms (non-directional), which is consistent with metallic bonding. In Fig. 6 the ELF is shown for the same plane as considered above for the valence charge-density distribution. Both picture are quite similar, with almost spherical shapes of the ELF around the Th atoms and a lower localization of the electrons on Ti atoms. Remarkably, the concentration of electrons between the Th and Ti bridges has a region of electron depletion compared to the Ti and Ti bridges. This observation gives an insight that the slight covalent character observed is from Ti atoms, which has a shared-electron pair. Hence, this particular crystal structure with more number of Ti atoms is stable compared to the corresponding structure (Th$_3$Ti alloy in (Cr$_3$Si structure) with more Th atoms.

Based on these observations, the ThTi$_3$ alloy in (Cr$_3$Si structure) is predominantly metallic.
FIG. 6. (Color online) The electron localization function for ThTi$_3$ (in Cr$_3$Si structure). The color pattern of the calculated electron charge density in the (001) plane, where the Th atom is depicted by the black balls and the Ti atoms by white balls. The color pattern of the ELF (scale: no electrons are represented as deep blue (0.0) and large concentration of electrons is represented as deep red (0.1); scale for remaining frames in increasing order of intensity: light blue, green, yellow, orange).

V. CONCLUSIONS

This work is motivated by the usefulness of various alloys of Th and Ti, hence the search for the possibility of ordered alloys involving Th and Ti. We considered a number of different structures and stoichiometries involving these elements. A predicted metastable structure was established using arguments based on elastic constants, phonon frequencies, electron localization function, valence charge density, band structure, density of states and heat of formation.

The calculated phonon frequencies and elastic constants shows that ThTi$_3$ (in Cr$_3$Si structure) is dynamically stable at zero Kelvin and zero pressure as indicated by their positive values. This system using PBESol with the inclusion of SOC is energetically more favorable and gives an appropriate description with a heat of formation of 0.591 eV compared with to the other methods. Though stabilization of some systems where achieved via pressure, the heat of formation of these systems are less favorable compared to ThTi$_3$ (in Cr$_3$Si structure). We propose ThTi$_3$ (in Cr$_3$Si structure) as a plausible metastable ordered alloy of Th-Ti based systems.

This should stimulate experimental efforts to synthesize this material.
ACKNOWLEDGMENTS

We are grateful to the University of Pretoria for financial support. We thank Dr. Walter Meyer and Dr. Jannie Pretorius for assistance with the computational resources. Also we acknowledge Prof Richard Martin for assistance and the members of Theoretical and Computational Solid State Research Group at the University of Pretoria for useful discussions.

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This concludes the studies on actinide compounds with out the inclusion of the Hubbard $U$ parameter. The next chapter explores the significance of the Hubbard $U$ parameter in the proper description of actinide system. A case study of Pa and its oxides is presented.
Chapter 5

First principles LDA + $U$ and GGA + $U$ study of protactinium and protactinium oxides: dependence on the effective $U$ parameter

First principles LDA + $U$ and GGA + $U$ study of protactinium and protactinium oxides: dependence on the effective $U$ parameter

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(Dated: July 27, 2013)

Abstract

The electronic structure and properties of protactinium and its oxides (PaO and PaO$_2$) have been studied within the framework of the LDA, GGA(PBE), LDA + $U$ and GGA(PBE) + $U$ implementations of density functional theory. The dependence of selected observables of these materials on the effective $U$ parameter has been investigated in detail. The examined properties include lattice constants, bulk moduli, effect of charge density distributions, the hybridization of the 5f orbital and the energy of formation for PaO and PaO$_2$. The LDA gives better agreement with experiment for the bulk modulus than the GGA for the Pa but GGA give better structural properties. We obtained that PaO is metallic and PaO$_2$ is a Mott-Hubbard insulator. This is consistent with observations for the other actinide oxides. We discover that GGA and LDA incorrectly give metallic behavior for PaO$_2$. The GGA(PBE) + $U$ calculated indirect band gap of 3.48 eV reported for PaO$_2$ is a prediction and should stimulate further studies of this material.

PACS numbers: 61.48.Gh, 68.35.bg, 73.22.Pr
I. INTRODUCTION

Protactinium is the first element in the actinide series with a 5f electron. In some systems (PaO₂, UO₂, NpO₂, PuO₂), the presence of 5f electrons leads to an improper description of the electronic and the structural properties by DFT. Several approaches have been developed to overcome these shortcomings of DFT such as the self-interaction correction (SIC), DFT hybrid approach, DFT + U, GW etc. The DFT + U (LDA + U and GGA + U) approach has been shown to effectively correct many of the deficiencies observed by this class of materials with regards to the band gap. This approach introduces an on-site Hubbard U and the Hund’s J. Dudarev et al. combined these two terms in the rotationally invariant formalism to a single term $U_{\text{eff}}=U-J$, referred to as the simplified LSDA + U. The introduction of this adhoc parameter leads to a significant improvement in the description of some 5f systems where DFT fails but the choice of the value of this parameter is debatable. The $U_{\text{eff}}$ parameter can be obtained: (i) from constrained LDA approach, (ii) from constrained RPA, (iii) from a self-consistent approach, and (iv) from fitting the parameter to experimental observables.

Pa and its oxide are used in scintillators for detecting X-rays, for radioactive dating (determination of ancient artifact), in cathode ray tubes with bright green fluorescence, as high temperature dielectrics for ceramic capacitors, in nuclear weapons (used as support in nuclear chain reactions), etc. These materials have downsides which has limited its study, namely (i) the high toxicity and radioactive nature and (ii) the limited availability. These materials are mainly found as a by-product in nuclear reactions. Furthermore, these materials are (iii) strongly correlated, giving rise to failures by conventional DFT methods.

The understanding of the electronic and structural properties is paramount to harness and control these materials optimally. The elements in the 5f series with localized electrons possess greater atomic volumes and symmetrical structures compared to those with itinerant electrons. Hence, Pa exists in the bct, fcc and orthorhombic ($\alpha$-U) phase at standard temperature and pressure (STP), high temperature and high pressure respectively. Pa metal possesses itinerant 5f electrons with characteristic properties such as superconducting and high vaporization.

There has been significant interest in the understanding of Pa metal, due to its unique behavior as the first element with a 5f electron. The effect of pressure induced phase transitions has been explored theoretically and experimentally. Haire et al. experimentally showed that Pa metal undergoes a pressure induced structural phase transition at 77 GPa from the bct structure (space...
group $I4/mmm$) to an orthorhombic, $\alpha$-U structure (space group $Cmcm$) with $\sim$ 30% atomic volume reduction and no subsequent phase transition. This was predicted by theoretical studies,\cite{16,22} which attribute this to the increase in $5f$ electron participation in the bonding.

The studies of protactinium oxides (PaO and PaO$_2$) have been limited to the mode of synthesis and purification for the production of Pa metal.\cite{15} Prodan $et\ al.$\cite{23} used the density functional hybrid approach to study actinide dioxides and obtained a band gap of 1.4 eV for PaO$_2$. To the best of our knowledge, no further studies have been performed to shed more light on the electronic structure of PaO$_2$. Hence, a proper description of the electronic and structural properties of these oxides within the DFT and DFT $+ U$ methods is appropriate to understand the physics of these materials.

A systematic first principles study of the dependence of the effective Hubbard-$U$ parameter on LDA $+ U$ and GGA $+ U$ functionals in Pa and its oxides is lacking. In this work, the DFT methodology is applied to calculate the electronic and structural properties of Pa metal. Using a semi-empirical fit, we then optimize the Hubbard $U$ parameter to give a proper description of PaO and PaO$_2$. The structural and electronic properties of these oxide materials are determined to investigate the role played by the $5f$ electrons.

In Section II, a brief description of the theoretical and computational methodologies is presented. In Section III, the results and discussions for Pa and its oxides are presented, followed by the conclusions in Section IV.

II. THEORY AND COMPUTATIONAL DETAILS

All calculations were performed using density functional theory\cite{24} as implemented in the VASP code.\cite{25} The electron wave functions were described using the projector augmented wave (PAW) method of Blöchl in the implementation of Kresse and Joubert.\cite{26} The LDA\cite{27} and PBE\cite{28} form of the GGA exchange-correlation potentials were used together with their LDA $+ U$ and GGA $+ U$ variants. An adequately converged kinetic energy cutoff of 500 eV, 500 eV, 550 eV was chosen to ensure fully converged total energies for Pa, PaO and PaO$_2$ respectively. A spacing of $k$-points of 0.2/Å fine mesh for the Monkhorst-Pack\cite{29} grid is used to sample the Brillouin zone, and Methfessel-Paxton smearing\cite{30} with a width of 0.2 eV was used to integrate the bands at the Fermi level. The total energy, electronic band structure and density of states (DOS) were calculated using the tetrahedron integration method with Blöchl corrections.

Subsequently, we introduce the Hubbard $U$ parameter for the onsite interaction strength. The
$U$ parameter was computed by optimizing the lattice parameter with respect to $U$. This resulted in differences for a range of results involving the physical structure, the electronic structure and the energetics within the GGA and LDA schemes for the oxides. Results presented in this work uses LSDA, GGA, LSDA + $U$ and GGA + $U$ for the oxides but without the $U$ parameter for Pa atom.

**TABLE I**: Partial 5\textit{f} occupation for Pa, PaO and PaO$_2$ systems using GGA with SOC.

<table>
<thead>
<tr>
<th>System</th>
<th>$U$</th>
<th>5\textit{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa</td>
<td>0</td>
<td>1.327</td>
</tr>
<tr>
<td>PaO</td>
<td>2.5</td>
<td>1.228</td>
</tr>
<tr>
<td>PaO$_2$</td>
<td>2</td>
<td>1.414</td>
</tr>
</tbody>
</table>

A method using the least-squares fit,$^3$ as implemented in the MedeA-MT module, was used to obtain the elastic constants. This uses the tetrahedron method for the Brillouin zone integrations. The elastic properties were calculated from the Hill values which are a geometric mean of the Voigt and Reuss values. The eigenvalues of the stiffness matrix gives an indication of the mechanical stability of the systems under consideration, which is used to obtain the elastic constants. The Hill values$^2$ were used in the estimation of longitudinal, shear and mean sound velocities, and the Debye temperatures.$^3$

The energy of formation for each structure was calculated by taking the difference between the total energy of the compound ($\text{PaO}_n$) and the energies of its constituents in their corresponding bulk forms:

$$\Delta H_f = E_{\text{tot}}(\text{PaO}_n) - N_{\text{Pa}} E_{\text{bulk}}^{\text{(Pa)}} - N_{\text{O}} E_{\text{bulk}}^{\text{(O)}},$$  \hspace{1cm} (1)

where $n$ is either 1 or 2, $N_{\text{Pa}}$ and $N_{\text{O}}$ are the number of Pa atoms and O atoms in the $\text{PaO}_n$ compound respectively, $E_{\text{bulk}}^{\text{(Pa)}}$ is the energy per Pa atom in the bct phase, and $E_{\text{bulk}}^{\text{(O)}}$ is the energy per O atom in the oxygen molecule.

The phonon calculations were done using the general direct approach of lattice dynamics as implemented in the MedeA-PHONON package.$^4$
III. RESULTS AND DISCUSSION

A. Preamble

We carried out self consistent calculations to determine the ground states of Pa and its oxides using spin-polarized (SP) and spin-orbit coupling (SOC) within the DFT $+\ U$ approach. The inclusion of the effective Hubbard $U$ is excluded for Pa metal because DFT gives a reasonable description of the metal. Pa element is a heavy metal with an atomic number of 91, hence relativistic effects are important. In order to account for the relativistic effects in these systems, the inclusion of SOC is important. In this study, we have shown that in order to obtain the correct properties of PaO$_2$, the effect of SOC has to be taken into account.

The $U$ parameter in this study is optimized with respect to the lattice constant. The $U$ parameter obtained is used to calculate the structural and electronic properties of the systems. This gives a qualitatively and quantitatively better description of the properties of PaO and PaO$_2$.

The $U$ parameter accounts for the onsite Coulomb interaction which leads to the localization of the 5$f$ electrons in these systems. In contrast, the standard DFT fails to account for the localization of the electrons, but leads to the delocalization which is a consequence of the Pauli-exclusion principle. The localization of the 5$f$ orbitals leads to a non-magnetic (NM) insulating ground state for PaO$_2$ but does not change PaO from metallic to insulating.

In order to obtain the correct ground state for PaO$_2$ for a given $U$ parameter, we lifted the symmetry constraints in the calculations of the electronic and the structural properties allowing the systems to evolve and explore all of phase space, i.e. all stable and metastable phases, including magnetic phases. This has an effect of significantly increasing the computational time as all k-points in the Brillouin zone are treated independently, i.e. the special k-point set is not reduced by symmetry.

Gryaznov et al.,$^{35}$ studied UN, UO$_2$ and PuO$_2$ with the inclusion of SOC and showed that to correctly describe these systems the lifting of symmetry constraints is absolutely essential. There have been various methodologies proposed by different authors on how to achieve the true ground state within the DFT $+\ U$ formalism including SOC, such as monitoring the occupation matrix,$^{36}$ ramping the Hubbard $U$ parameter,$^{37}$ etc. In this study, the symmetry constraints are lifted and the correct ground state is obtained for PaO$_2$ within the SOC scheme for all the values of $U$ considered. In our work, the symmetry constraints are lifted and the correct ground state is obtained for PaO$_2$.
within the SOC. However, the SP does not yield the correct ground state because relativistic effects are unaccounted for.

B. Crystal structures

Fig. 1 shows the conventional unit cells of Pa, PaO and PaO$_2$.

Pa has three crystallographic forms which are (i) the body centered tetragonal structure (bct) at STP which transforms to (ii) the face centered cubic structure (fcc) at elevated temperature, and which undergoes a pressure-induced structural transformation to the (iii) $\alpha$-Uranium structure. The Pa (bct) phase is presented in Fig. 1a.

In Fig. 1b, we present the PaO system which crystallizes in the NaCl structure.

PaO$_2$ contains antiferromagnetically (AFM) ordered Pa atoms with an underlying fluorite structure that leads to a double tetragonal unit cell (with $c = \sqrt{a}$) when the magnetic ordering is taken into account. The AFM ordered structure is shown in Fig. 1c, where the magnetic ordering is in the z-axis.

![Crystal structures](image)

FIG. 1: (Color online) The crystallographic unit cells of (a) Pa, (b) PaO (c) PaO$_2$. Blue spheres depict Pa and the red spheres depict the oxygen atoms. The black arrows illustrate the AFM ordering in the z-axis.
C. Structural properties

As indicated earlier, Pa has been observed to exist in various different phases. The STP phase which is the bct structure has experimental lattice parameters of \( a_0 = 3.925 \text{ Å} \) and \( c = 3.238 \text{ Å} \).\(^{21}\) LDA is known to underestimate the lattice parameter while GGA generally overestimates the lattice parameter. However, in the early actinides lattice constants obtained using the GGA are found to be better corroborated with experiment compared with the LDA.\(^{38}\) In Table II, we show our calculated values of the lattice parameters obtained using the GGA and the LDA within the SOC and the SP schemes. Upon complete optimization, the system evolves to a NM ground state consistent with experiment. The lattice parameter, density and volume obtained within the GGA approximation are more comparable to experiment than LDA. As far as the structural properties are concerned, the extension of our methodology to include the Hubbard \( U \) parameter is not necessary in the case of metallic Pa.

In Fig. 2, we present the calculated lattice parameter of PaO as a function of the \( U \) parameter, where the dotted line indicates the experimental value of \( a_0 \). The variation of the lattice parameter is a monotonically increasing function with respect to the \( U \) parameter within the SOC and SP scheme. At \( U = 2.5 \text{ eV} \), the GGA + \( U \) (SOC and SP scheme) yields the experimental lattice parameter for PaO. The corresponding result using the LDA + \( U \) (SOC and SP scheme) significantly underestimates the lattice parameter. Increasing \( U \) to a value of 5.5 eV still does not give a sufficiently accurate result for the lattice parameter within the LDA + \( U \) scheme. This shows that the use of the \( U \) parameter is better suited within GGA than LDA in the present case. Since a value for \( U \) that is too large pushes the \( f \) orbitals too far down into the \( O2p \) based levels.\(^{39}\) At \( U = 0 \text{ eV} \), PaO (within SOC scheme) results in a magnetic ground state. This system evolves with the increase of the \( U \) parameter to a NM metallic ground state. This observation is similar to the SP case for the GGA + \( U \). LDA + \( U \) gives a NM metallic ground state at all values of the \( U \) parameter.

The PaO\(_2\) structure is fully geometrically optimized using the SP and SP + SOC (hence forth referred to as SOC) within the DFT + \( U \). The inclusion of SOC in the fluorite structure of PaO\(_2\) without SP does not transform the structure to the AFM ordered state similar to UO\(_2\). Rather, the inclusion of SP does yield structures which are AFM ordered leading to the symmetry breaking for the PaO\(_2\). For consistency, the structure used in the study is the tetragonally distorted structure obtained when the PaO\(_2\) is in the AFM ordered state. In Fig. 3, the calculated lattice parameter as a function of the \( U \) parameter is presented where the dotted line indicates the experimental value.
FIG. 2: (Color online) The change in the lattice parameters is plotted within the description of DFT + $U$ (GGA, LDA) approximations for PaO. The $U$ - parameter results in a significant change in the structural parameters.

The variation of the lattice parameter is a monotonically increasing function with respect to the $U$ parameter within the SOC and SP schemes. Fig. 3a and 3b shows the variation of $a_0$ and $c_0$ respectively as a function of the $U$ parameter. For $U = 4.0$ eV, the LDA + $U$ with SOC yields a reasonable lattice parameter (5.501 Å) which is approximately equal to the experimental value (5.509 Å), compared to the LDA + $U$ with SP, which grossly underestimates lattice parameter. On the other hand, for $U = 2.0$ eV, the GGA + $U$ with SOC gives a slightly higher (about 0.8 %) lattice parameter for PaO$_2$ and only slightly underestimates (about −1.01 %) the lattice parameter using the SP scheme. With this value for $U$ we go on to evaluate all further properties of interest for this PaO$_2$.

Our conclusions for PaO$_2$ about the accuracy of GGA over LDA within the DFT + $U$ schemes are similar to those for PaO.

D. Elastic properties

We find Pa to be elastically stable due to the absence of negative elastic constants. In Table II, we present the theoretical and experimental bulk modulus for Pa. There are discrepancies between previously reported theoretical$^{38}$ and experimental$^{40,41}$ values for the bulk modulus of Pa. In these previous studies, the value of the experimental bulk modulus obtained was found to be high compared to the theoretical value. These discrepancies were suggested to result from (i) the presence of a small amount of hard martensitic phase not detectable using X-rays and/or (ii) the presence of...
FIG. 3: (Color online) The change in the lattice parameters is plotted within the description of DFT + $U$ (GGA, LDA) approximations for PaO$_2$. It shows that the $U$-parameter leads to a change in the structural parameters.

The elastic properties of PaO using GGA and GGA + $U$ (SOC scheme) is presented in Table III. The elastic constants obtained for PaO are all positive definite, hence PaO is elastically stable. But
the value of the $c_{44}$ elastic constant for PaO within GGA and GGA + $U$ using the SOC approach is very low compared to the other elastic constants. We calculated the elastic constants for NM and SP cases. The $c_{44}$ elastic constant obtained using NM and SP is also very low compared to the other elastic constants. This is an indication that the material will readily yield to shear stresses. The Debye temperature ($\Theta_D$) is calculated to determine the stiffness of the system. The $\Theta_D$ for PaO is 275.4 K.

TABLE III: Elastic constants, bulk and shear in GPa, Debye temperature in K for PaO. PaO results presented are for the SOC case and the U parameter is 2.5 eV.

<table>
<thead>
<tr>
<th>Type of Calculation</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{44}$</th>
<th>$c_{54}$</th>
<th>$c_{66}$</th>
<th>$\Theta_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>348.61</td>
<td>106.75</td>
<td>9.08</td>
<td>187.37</td>
<td>34.11</td>
<td>216.5</td>
</tr>
<tr>
<td>GGA + $U$</td>
<td>363.98</td>
<td>92.19</td>
<td>27.57</td>
<td>182.79</td>
<td>55.69</td>
<td>275.4</td>
</tr>
</tbody>
</table>

The elastic constants obtained for PaO$_2$ are all positive definite. Hence, the PaO$_2$ structure is elastically stable within GGA and GGA + $U$ as presented in Table IV. The elastic properties obtained using GGA are less than those using LDA. This is also consistent with the GGA + $U$ and LDA + $U$. This is expected because the value of the lattice parameter is higher within the GGA than those obtained using the LDA. The Debye temperature for PaO$_2$ is 409.5 K. This material is stiff and suggestive of covalent and ionic character. We conclude that PaO$_2$ is significantly stiffer compared to PaO. The bonding character is fully analyzed in the next subsection.

TABLE IV: Elastic constants, bulk modulus and shear modulus in GPa, Debye temperature in K for PaO$_2$. The PaO$_2$ results presented corresponds to the SOC and $U = 2.0$ eV

<table>
<thead>
<tr>
<th>Type of Calculation</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{13}$</th>
<th>$c_{33}$</th>
<th>$c_{44}$</th>
<th>$c_{66}$</th>
<th>$\Theta_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>316.96</td>
<td>156.15</td>
<td>103.69</td>
<td>369.93</td>
<td>80.34</td>
<td>132.98</td>
<td>192.32</td>
</tr>
<tr>
<td>GGA + $U$</td>
<td>297.93</td>
<td>141.76</td>
<td>99.41</td>
<td>343.81</td>
<td>73.11</td>
<td>123.83</td>
<td>180.09</td>
</tr>
</tbody>
</table>

E. Valence charge densities of PaO and PaO$_2$

The computed valence charge density using the GGA + $U$ optimized structures (SOC scheme) is presented to elucidate the bonding characteristics and crystal structures of PaO and PaO$_2$. The
computed charge density distribution plot for PaO and PaO$_2$ is in the (100) plane. The electron density is indicated by the color scale on the side (blue is devoid of electrons and red indicates a high concentration of electrons). The charge densities plotted pertain to the valence states only, summed over both spin directions.

In the PaO crystal structure, the Pa$^{2+}$ ion is almost devoid of valence electrons and the cloud of electrons around O$^{6+}$ ion is almost the full eight electrons needed to give O$^{2-}$ (conventional oxygen is lacking two electrons). The valence charge density for PaO is calculated at $U = 2.5$ eV, which is determined to be the optimum $U$ parameter for this structure. In Fig 4, it is clearly seen that PaO is characterized by a high spherical charge density distribution around the Pa and O ions and a low charge density in the interstitial region. Compared to the charge density in the interstitial region, relatively high density bridges are present between the atomic spheres. These bridges are an indication of weak covalent bonding between Pa and O atoms due to hybridization of oxygen 2$p$ states with partially occupied Pa $f$ and $d$ states. Therefore, PaO is strongly ionic and weakly covalently bonded.

FIG. 4: (Color online) The color pattern of the calculated valence charge density distribution for PaO in the (100) plane, where the blue spheres depict Pa atoms and the red spheres depict the O atoms.

In the AFM PaO$_2$ crystal structure, the valence charge density is calculated at $U = 2.0$ eV, which is determined to be the optimum $U$ parameter for this structure. In Fig. 5, it is clearly seen that PaO$_2$ is characterized by high spherical charge density distribution around the Pa and O ions.
with a low charge density in the interstitial region. Compared to the charge density in the rest of the interstitial region there is a low presence of charge density bridges present between the atomic spheres. These bridges are an indication of weak covalent bonding between Pa and O atoms due to hybridization of oxygen 2\(p\) states with partially occupied Pa \(f\) and \(d\) states. The charge density around the Pa atom in PaO\(_2\) structure is low compared to the PaO structure. This is an indication of stronger ionic character in AFM PaO\(_2\) and weak covalent character compared to PaO system. Therefore, PaO\(_2\) is predominantly ionic with significant insulating behavior.

![Diagram of calculated valence charge density distribution](image)

**FIG. 5:** (Color online) The color pattern of the calculated valence charge density distribution for PaO\(_2\) in the (001) plane, where the blue spheres depict Pa atoms and the red spheres depict the O atoms. The color scale: deep blue color represents low valence charge while the red color represents high concentration valence charge.

Also, in Table I, the \(f\) occupation for PaO\(_2\) compared to PaO gives credence to the notion that PaO\(_2\) is more ionic.

**F. Band structure and density of states**

The computed band structure and density of states (DOS) presented below is within GGA + \(U\). The result obtained using LDA + \(U\) (with a large value of \(U\)) gives qualitatively similar results to GGA + \(U\).

In Fig. 6, we present the band structure and density of states of Pa metal calculated using GGA within the SOC scheme. The band structure and DOS clearly shows that Pa is metallic. The metallicity is largely determined by the Pa-\(f\) electrons and a slight contribution from Pa-\(d\) electrons, while the Pa-\(s\) and Pa-\(p\) electrons contribute to the deep lying states.
Fig. 6 shows the band structure of PaO$_2$ with an indirect band gap of 3.48 eV which is calculated using GGA + $U$ within the SOC scheme at $U = 2.0$ eV. The LDA + $U$ within the SOC scheme at $U = 2.0$ eV underestimates the band gap, while the SP scheme within the DFT + $U$ results in a metallic system. The valence band maximum for PaO$_2$ using GGA + $U$ within the SOC scheme at $U = 2.0$ eV is located in between the Z-point (0.0 0.0 0.5) and the A-point (0.5 0.5 0.5). While, the conduction band minimum is located at the R-point (0.0 0.5 0.5). In Table V, the effect of tuning the $U$ parameter on the band gap is tabulated. Increasing the $U$ parameter leads to opening of the band gap at $U = 2.0$ eV. Subsequently, increasing the $U$ parameter leads to a decrease in the band gap, which is accompanied by a change in the position of the conduction band minimum and valence band maximum.

The DOS for the PaO system using GGA + $U$ is presented in Fig. 8. We find that PaO using various exchange correlation functionals (GGA and LDA) and inclusion of the $U$ parameter is a metallic system. The states around the Fermi level is dominated by the 5$f$-electrons, which effectively determine the metallicity of the PaO system as shown in Fig. 8. The partial density of states as a function of change in the effective $U$ parameter for the SOC and SP schemes provides an insight on the hybridization and magnetic nature of the system. In the SOC scheme, the PaO system undergoes hybridization and evolves from a magnetic ground state at $U = 0$ eV with total magnetization of 0.47 $\mu_B$ to a NM metallic ground state as a function of $U$. In the SP scheme, the PaO system undergoes hybridization and evolves from a magnetic ground state at $U = 0$ eV with total magnetization of 0.51 $\mu_B$ to a NM metallic ground state as a function of the $U$. This is consistent with its neighboring oxides ThO and UO. This observation for PaO with respect to its neighboring oxides ThO and UO.
TABLE V: The optimum U parameter as a function of band gap (null band gap indicates a metal) for PaO$_2$. Where Z (0.0 0.0 0.5), A (0.5 0.5 0.5), R(0.0 0.5 0.5), X (0.0 0.5 0.0), and Γ (0.0 0.0 0.0)

<table>
<thead>
<tr>
<th>U</th>
<th>Band gap</th>
<th>Position of Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Valence Band</td>
</tr>
<tr>
<td>0.0</td>
<td>0.00</td>
<td>−</td>
</tr>
<tr>
<td>1.0</td>
<td>0.00</td>
<td>−</td>
</tr>
<tr>
<td>2.0</td>
<td>3.48</td>
<td>in between Z and A</td>
</tr>
<tr>
<td>2.5</td>
<td>3.40</td>
<td>in between Z and A</td>
</tr>
<tr>
<td>3.0</td>
<td>3.30</td>
<td>in between Z and A</td>
</tr>
<tr>
<td>4.0</td>
<td>3.01</td>
<td>in between Z and A</td>
</tr>
<tr>
<td>5.0</td>
<td>2.72</td>
<td>in between Z and A</td>
</tr>
<tr>
<td>5.5</td>
<td>2.55</td>
<td>in between Z and A</td>
</tr>
</tbody>
</table>

GGA is consistent with LDA, hence the figures and data on LDA are not presented.

The electronic structure of the early actinides dioxides (AO$_2$, where A=Th, Pa, U, Np) all show insulating character. The ground state of UO$_2$ and NpO$_2$ show varying degrees of magnetism.

FIG. 7: (Color online) The calculated band structure plot of PaO$_2$ using DFT + U (U = 2.0 eV) in the full Brillouin zone with an AFM structure. The system contains two unique Pa atoms due to the spin configuration and the O atoms are same.
Figure 9. The total and projected densities of states (DOS) for the spin polarized and spin–orbit coupling of PaO within the descriptions of the GGA and GGA
+ U approximations. All the DOS are calculated at the optimized geometry for the given density functional and magnetic ordering. The Fermi energy level is set at zero and is represented using dashed line. It contains one Pa atom and the O atoms are same.

(a) SOC
U =
0.
(b) SP
U =
0.
(c) SOC
U =
1.
(d) SP
U =
1.
(e) SOC
U =
2.
(f) SP
U =
2.

Table 5.
The calculated energy of formation (eV) for PaO and PaO2 using LDA + U and GGA + U within the SOC and SP scheme.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ueff</th>
<th>LDA (SOC)</th>
<th>LDA (SP)</th>
<th>GGA (SOC)</th>
<th>GGA (SP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PaO</td>
<td>2.5</td>
<td>6.19</td>
<td>3.89</td>
<td>5.43</td>
<td>3.19</td>
</tr>
<tr>
<td>PaO2</td>
<td>2.0</td>
<td>12.60</td>
<td>10.30</td>
<td>11.62</td>
<td>8.93</td>
</tr>
</tbody>
</table>

FIG. 8: (Color online) The total and projected densities of states (DOS) for the spin polarized and spin-orbit coupling of PaO within the descriptions of GGA and GGA + U approximations. All the DOS are calculated at the optimized geometry for the given density functional and magnetic ordering. The Fermi energy level is set at zero and is represented using dashed line. It contains one Pa atom and the O atoms are same.
while ThO$_2$ is NM. These characteristics of U and Np are attributed to the partially occupied 5f electrons, which favors itinerancy for the early actinides. The PaO$_2$ system within the standard LDA and GGA approach (with SP or/and SOC scheme) is a metallic NM ground state. The inclusion of the Hubbard $U$ parameter leads to band gap opening for the system using the SOC scheme (for GGA and LDA). Because the SOC splits the orbitals, thus allowing for a $U$ induced orbital polarization that opens a gap. However, the $U$ parameter does not lead to band gap opening using the SP scheme due to the negligence of relativistic effects. In the SOC and SP schemes, the coupling between the Pa (5f and 6d) electrons and the O (2p) electrons is important as presented in Fig. 9.

As mentioned in the preamble, PaO$_2$ is a difficult system to study computationally due to the subtle nature of the electron correlation for this system. The DOS for an energy cutoff of 400 eV and 550 eV is shown in Fig. 10 and 9 to buttress this point. The lattice parameter of PaO$_2$ is fully converged as a function of the energy cutoff at 500 eV. Hence, a less converged energy cutoff (400 eV) and a fully converged energy cutoff (550 eV) are used to show the sensitivity of the $U$ parameter. At an energy cutoff of 400 eV, tuning the $U$ parameter leads to significant change in the band gap from 0.3 eV at $U = 3.0$ eV to 1.37 eV at $U = 5.5$ eV. At an energy cutoff of 550 eV, the converged $U = 2$ eV results in a band gap of 3.48 eV. Further tuning of the $U$ parameter leads to a decrease in the band gap, which is shown in Table V. The band gap obtained for $U = 5.5$ eV at an energy cutoff of 400 eV is consistent with the study by Prodan et al. and recently by Wen et al.\textsuperscript{39} using the HSE hybrid exchange-correlation functional. Using $U = 2.0$ eV at a converged energy cutoff of 550 eV, the band gap obtained is 3.48 eV. This value is intermediate to that of ThO$_2$ (6.2 eV) and UO$_2$ (2.0 eV) which is consistent with the trend because it shows the onset of 5f electron occupation. The Pa 5f electrons determine the conduction band maximum and play a significant role in the electronic properties of these systems. The Pa f electrons are localized and result in insulating behavior. This corroborates other results where the crystal structure and the volume of actinides exhibit different bonding configurations.\textsuperscript{17}

G. Energy of formation of PaO and PaO$_2$

The energy of formation for the oxides is calculated using equation 1. The total energy of the constituent elements is deducted from the total energy for the system (PaO or PaO$_2$). In Table VI, we present the energy of formation for the oxides using the LDA + $U$ and GGA + $U$ within the
FIG. 9: (Color online) The total and projected densities of states (DOS) for the SP and SP + SOC of PaO$_2$ in the AFM ordered phase within the descriptions of GGA and GGA + $U$ approximations at an energy cutoff of 550 eV. All the DOS are calculated at the optimized geometry for the given density functional and magnetic ordering. The Fermi energy level is set at zero and is represented by the dashed line. It contains two unique Pa atoms (label Pa$_1$ and Pa$_2$) due to the spin configuration and the O atoms are same.
SOC and SP schemes. The calculated energy of formation for PaO and PaO$_2$ using SOC is lower than that obtained with SP within the DFT + $U$ (LDA and GGA). This implies that the SOC case is more energetically favorable than the SP case. The formation for PaO and PaO$_2$ is exothermic. This indicates that metallic Pa will oxidize in the presence of oxygen. The energy of formation of PaO$_2$ is lower than that of the PaO. The implication is that PaO readily oxidizes in the presence of oxygen to form the more energetically favorable di-oxide. Our theoretical results is in line with experimental observation, that the oxides are more favorable than the parent metal and that PaO$_2$ is more stable than PaO in the presence of oxygen.$^{15}$

TABLE VI: The calculated Energy of formation (eV) for PaO and PaO$_2$ using LDA + $U$ and GGA + $U$ within the SOC and SP scheme.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$U_{eff}$</th>
<th>LDA(SOC)</th>
<th>LDA(SP)</th>
<th>GGA(SOC)</th>
<th>GGA(SP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PaO</td>
<td>2.5</td>
<td>−6.19</td>
<td>−3.89</td>
<td>−5.43</td>
<td>−3.19</td>
</tr>
<tr>
<td>PaO$_2$</td>
<td>2.0</td>
<td>−12.60</td>
<td>−10.30</td>
<td>−11.62</td>
<td>−8.93</td>
</tr>
</tbody>
</table>

H. Phonon studies of PaO and PaO$_2$

The phonon dispersion for Pa, PaO and PaO$_2$ is calculated within the GGA (PBE) scheme. The lattice dynamics studies is not carried out for both the LDA and DFT + $U$ scheme. This is because, the inclusion of $U$ parameter does not lead to significant changes in the phonon frequency of these systems. The phonon dispersion calculated exploits the linearity relationship between the induced forces on the atoms in the crystal and the displacement of the atoms from their equilibrium position, which holds within the harmonic regime.

In Fig. 11a, no negative phonon modes for Pa are observed in the phonon dispersion plot, hence this structure is dynamically stable. The maximum frequency for the acoustic modes is about 4.5 THz due to the large mass of Pa atom which does not undergo significant perturbation.

In Fig. 11b, no negative phonon modes for PaO are observed in the phonon dispersion plot, hence this structure is dynamically stable. The low lying frequency modes are governed by the dynamics of heavy Pa atoms. The higher frequencies, on the other hand, are governed by the dynamics of the oxygen atoms which are much lighter compared to Pa atoms. The difference
in the frequency of oxygen atoms compared to the Pa atoms is rather large. This suggests that instability in the system can arise from a small perturbation of the crystal structure.

In Fig. 11c, no negative phonon modes for PaO$_2$ are observed in the phonon dispersion plot, hence this structure is dynamically stable. The low lying frequency modes are governed by the dynamics of heavy Pa atoms, whereas the higher frequencies are governed by the dynamics of lighter oxygen atoms. The difference in the frequency of oxygen atoms compared to the Pa atoms is lower compared with PaO. This implies that the extra oxygen atom has led to the stabilization of the structure.

IV. CONCLUSIONS

The structural, mechanical and electronic properties of Pa have been studied within the DFT method. Inclusion of SP and SOC give an adequate description of this system. As far as the structural properties are concerned, the inclusion of the Hubbard $U$ parameter is not relevant here. We determined that Pa is elastically and dynamically stable.

The structural, mechanical and electronic properties of PaO have been studied within the DFT + $U$ approximation. The inclusion of SP and SOC gives an adequate description of this system. Our calculations show that the properties of this system can be described accurately with an effective $U$ parameter of 2.5 eV within the GGA + $U$. The results using LDA + $U$ were unsatisfactory. PaO is dynamically stable as shown by the phonon dispersion data. PaO is also stable to isotropic stress because of its positive bulk modulus. However, PaO has a low shear modulus. The charge density plot shows the presence of strong ionic bonding in this system. We conclude that PaO structure will readily oxidize to PaO$_2$ structure, which is the more stable form. This is in line with observed experimental results.

The SOC inclusion together with the Hubbard $U$ parameter is essential for the accurate determination of the total energy, electronic and magnetic properties of PaO$_2$. Within the LDA + $U$ (SOC scheme) at $U = 4.0$ eV, the lattice parameter is 5.501 Å, which is approximately equal to the experimental result. However, the results for the band gap and the energy of formation are found to be unsatisfactory within this scheme. On the other hand, within the GGA + $U$ (SOC scheme) at $U = 2.0$ eV, the lattice parameter is 5.553 eV, which is approximately 0.78 % above the experimental value. Within this scheme we derive accurate results for the electronic, elastic and mechanical properties of the system. This method predicts PaO$_2$ as an insulator with a band gap
of 3.48 eV.

Hence, to obtain an accurate description of the PaO and PaO$_2$, we have shown that the inclusion of the Hubbard $U$ parameter is paramount. In general, the GGA is better suited for the incorporation of the Hubbard $U$ parameter for these systems.

ACKNOWLEDGMENTS

This work is supported by the University of Pretoria. We gratefully acknowledge Material Design Inc. support in particular Rene Windiks, Walter Wolf, Paul Saxe and the members of the Computational and Theoretical Physics group at the University of Pretoria. Also, we are thankful to Dr. Jannie Pretorius for help with the use of the computational resources. NC is grateful to the National Institute for Theoretical Physics for support.

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7 Per Söderlind, G. Kotliar, K. Haule, P. M. Oppeneer, and D. Guillaumont. Computational modeling of


35 Denis Gryaznov, Eugene Heifets, and David Sedmidubsky. Density functional theory calculations


FIG. 10: (Color online) The total and projected densities of states (DOS) for the SP and SP + SOC of PaO$_2$ in the AFM ordered phase within the descriptions of GGA and GGA + $U$ approximations at an energy cutoff of 400 eV. All the DOS are calculated at the optimized geometry for the given density functional and magnetic ordering. The Fermi energy level is set at zero and is represented by the dashed line. It contains two unique Pa atoms (label $Pa_1$ and $Pa_2$) due to the spin configuration and the O atoms are same.
FIG. 11: (Color online) The phonon dispersion plot of PaO and PaO₂, showing the lattice dynamics of Pa and O atoms.
This concludes the studies on Pa and its oxides. The next chapter presents a comparative study of various actinide mononitride and dinitride compounds. It shows the significance of the Hubbard $U$ parameter in the proper description of these actinide systems with $5f$ electrons. These material have important technological application in nuclear energy generation (considered as possible nuclear fuel material).
Chapter 6

GGA + U studies of the early actinide mononitrides and dinitrides

This section was published as\textsuperscript{[10]} “Obodo, K. O. and Chetty, N. (2013). GGA + U studies of the early actinide mononitrides and dinitrides. Journal of Nuclear Materials, 442(1-3), 235244.”
GGA + $U$ studies of the early actinide mononitrides and dinitrides

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Abstract. We present a detailed comparative study of the electronic and mechanical properties of the early actinide mononitrides and dinitrides within the framework of the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA [PBE]) and GGA + $U$ implementations of density functional theory with the inclusion of spin-orbit coupling. The dependence of selected observables of these materials on the effective $U$-parameter is investigated in detail. The properties include the lattice constant, bulk modulus, charge density distribution, hybridization of the atomic orbitals, energy of formation and the lattice dynamics. The inclusion of the Hubbard $U$ parameter results in a proper description of the 5f electrons, and is subsequently used in the determination of the structural and electronic properties of these compounds. The mononitrides and dinitrides of the early actinides are metallic except for UN$_2$, which is a semiconductor. These actinide nitrides are non-magnetic with the exception of UN, NpN, PuN, NpN$_2$ and PuN$_2$ that are magnetic systems with orbital-dependent magnetic moments oriented in the z-axis. We observed that ThN$_2$ is elastically unstable to isotropic pressure. We discovered that UN$_2$ is thermodynamically unstable, but may be stabilized by N vacancy formation.

Submitted to: J. Phys.: Condens. Matter

PACS numbers: 62.20.D-, 63.20.D-, 71.15.Mb, 71.20.-b, 71.27.+a
1. Introduction

The investigation of actinide-based materials is an area of active research. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] The effects of 5f-electrons in the actinide nitrides are of significant interest to both theorists and experimentalists, [12, 13, 14] because exotic properties often arise from the strong electron-electron interactions paving the way for interesting physics and novel applications. The actinide metals exhibit increased 5f electronic localization with increasing atomic number which has a direct bearing on the orbital overlap and electronic band structure of these systems.

Actinide nitrides are set to become a major component in large-scale energy generation devices in nuclear power stations as an alternative to the current fuel sources that are being used. [15, 16] The Generation-IV nuclear reactors (fast neutron fission reactors) are developed to use the actinide nitrides as the primary fuel source. [17] Actinide nitrides release a larger amount of fissile products (neutrons) compared to its consumption, and the long-lived fission products have a higher probability to transmute leading to higher usable energy densities.

Based on the importance of the actinide nitrides from both a scientific and technological point of view, the understanding of the electronic and structural properties is important to harness, control, and effectively use these materials. The presence of 5f electrons poses a considerable challenge in the theoretical description of the actinide compounds. This is mainly due to the improper account of the electron-electron interactions by the local spin density approximation (LSDA) and the generalized gradient approximation (GGA) approaches implemented in density functional theory (DFT). The DFT $+$ $U$ [18, 19, 20] (LDA $+$ $U$ and GGA $+$ $U$) approach has been shown to overcome some of the shortcomings and shows a lot of promise in the studies of the 5f electron systems.

In this work, the actinide nitrides of interest are the early actinide mononitrides (AcN) and dinitrides (AcN$_2$) where (Ac = Th, Pa, Np, U and Pu). At low temperatures, the AcN crystallizes in the NaCl crystal structure, while the AcN$_2$ mainly exists in the fluorite structure. There also exist other actinide compounds that crystallize in the NaCl crystal structure such as the mono-carbides, mono-pnictides, mono-chalcogenides, etc.

To the best of our knowledge, a detailed analysis of these systems within the DFT $+$ $U$ approach is lacking. [21, 22, 9, 23] Petit et al. [9] investigated some actinide mono-carbides and mononitrides using the self-interaction corrected (SIC) local spin-density approximation. These authors observed ionic character in the mononitrides, increased localization in PuN, and an itinerant picture for UN. Silva et al., [4] recently synthesized NpN and confirmed the existence of other phases of neptunium nitrides using both experimental and computational techniques. These authors showed the importance of the Hubbard $U$-parameter (accounting for onsite interactions) along with relativistic effects to accurately describe these compounds.

Atta-Fynn et al. [21] treated all the nitrides on equal footing at different magnetic configurations with and without spin orbit coupling (SOC). They showed that the type-I antiferromagnetic (AFM) configuration gives similar results to the type-II AFM configuration and results in a more energetically favorable configuration with the inclusion of SOC.

In our work, we have therefore considered the type-I AFM structure within the projector augmented wave (PAW) method to analyze the mononitride systems. We compare our results with available experimental data as well as with other theoretical results. All calculations are based on density functional theory with and without the inclusion of the Hubbard $U$-parameter (DFT $+$ $U$). We evaluate the heat of formation, the structural, electronic, elastic, and mechanical properties of the various actinide nitrides. Of interest is how well our zero temperature DFT $+$ $U$ computations predict these properties. Previous studies proposed that PaN has a more covalent character compared to UN, NpN, PuN that are predominantly ionic.
Therefore, by scrutinizing the valence charge density distributions, we examine the AcN and AcN₂ compounds to give an account of the bonding character of these systems. The Hubbard U-parameter is shown to be important in the prediction of the structural properties of the actinide nitrides. The lattice dynamics of these systems gives an indication of the mechanical stability.

The rest of this paper is organized as follows: in Section 2, we present a description of the computational methodology. The calculated ground state properties of AcN and AcN₂ compounds, and the effect of the Hubbard U-parameter are given in Section 3 and 4 respectively. Finally, we make our concluding remarks in Section 5.

2. Computational Details

The calculations are performed using density functional theory [24] as implemented in the VASP code [25]. The PAW approach of Blöchl in the implementation of Kresse and Joubert is used to describe the electron wave functions. [26] The semi-core electrons and the valence electrons of the actinides are represented by plane waves. The PBE [27] form for the GGA and the GGA + U is used in the description of the exchange-correlation potential.

The unit cell parameters and atomic positions are optimized with an energy tolerance of $10^{-7}$ eV. The calculations are performed with an energy cut-off of 500 eV and 550 eV for AcN and AcN₂ respectively. The Brillouin zone (BZ) integrations are performed using a spacing of 0.2 Å⁻¹ for the Monkhorst-Pack [28] grid. Fractional electron occupancies and integration of the bands at the Fermi level are determined using the Methfessel-Paxton smearing method with a smearing parameter of 0.2 eV. The AcN and AcN₂ with SOC (spin-orbit coupling) calculations are performed within the constraints of symmetry. The lifting of the symmetry constraints lead to no significant change in the total energy and electronic properties, with an exception of PuN and UN₂ were the calculation is performed with the symmetry constraints lifted [3]. The total energy, electronic band structure and density of states (DOS) were calculated using the tetrahedron integration method with Blöchl corrections.

We use the Dudarev et al. [29] simplified rotationally-invariant form for the Hubbard correction to account for the on-site Coulomb interactions. This approach combines the Hubbard U and Hund’s J to give the $U_{\text{eff}} = U - J$. The rotational invariance is preserved within this formalism because the $U$ parameter depends on the trace of the occupation matrixes and their products. The generic expression for the energy functional in the DFT + U formalism is represented by

$$E_{\text{DFT} + U} = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}},$$

where $E_{\text{DFT}}$ is the DFT (LDA or GGA) contribution to the total energy and $E_{\text{Hub}}$ is the electron-electron interaction from the Hubbard term. $E_{\text{dc}}$ is a double counting term, introduced because part of the electron-electron interaction is taken into account in $E_{\text{DFT}}$. The last two terms depend on the occupation matrix of the correlated orbitals of the system under consideration. In this study, the calculated Hubbard $U_{\text{eff}}$ parameter (henceforth referred to as the Hubbard $U$) is optimized with respect to the experimentally determined lattice constant for each of the actinide nitrides that we considered. The optimized $U$ parameter is used to determine the structural, electronic, elastic and mechanical properties of the compounds. This results in a better qualitative and quantitative description of the various properties.

Relativistic effects are important for the actinides. This leads to lower calculated ground state total energies compared to non-relativistic calculations. In this study, we present results using the GGA and the GGA + U forms for the exchange correlation potential together with spin-polarization (SP) and spin orbit coupling (SOC).
A method using the least squares fit, [30] as implemented in the MedeA-MT module, was used to obtain the elastic constants. The elastic properties are calculated from the Hill values, which are a geometric mean of the Voigt and Reuss values. The eigenvalues of the stiffness matrix give an indication of the mechanical stability of the systems under consideration. The Hill values [31] were used in the estimation of longitudinal, shear and mean sound velocities and the Debye temperatures. [32]

The energy of formation for each structure was calculated by taking the difference between the total energy of the actinide compound and the energies of its constituents in their corresponding bulk elemental forms:

$$\Delta E_f = E_{\text{tot}}(\text{AcN}_n) - N_{\text{Ac}} E_{\text{bulk}}^{\text{(Ac)}} - N_{\text{N}} E_{\text{bulk}}^{\text{(N)}},$$

where $n$ is either 1 or 2 for the mononitride and dinitride, respectively, and $N_{\text{Ac}}$ and $N_{\text{N}}$ are the number of Ac atoms and N atoms in the calculational unit cell of the compound, respectively. $E_{\text{bulk}}^{\text{(Ac)}}$ is the energy per Ac atom in its ground state structure, and $E_{\text{bulk}}^{\text{(N)}}$ is the energy per N atom in the nitrogen molecule.

The phonon frequencies are calculated using the direct approach of lattice dynamics based on linear response theory, as implemented in the MedeA-PHONON package. [33] This exploits the fact that within the harmonic regime, there is a linear relationship between the induced forces on the atoms and the displacement of the atoms from their equilibrium positions. We discovered that using GGA $+ U$ only has a marginal effect on the quantitative description of the phonon frequencies. Therefore, we have only presented results for the phonon frequencies within the GGA approximation.

We applied our methods to the study of the ferromagnetic (FM) and the antiferromagnetic (AFM) configurations for the actinide mononitrides and dinitrides. The non-magnetic (NM) systems consistently resulted in higher energies of formation for all the structures considered. Therefore NM results are not presented in this study.

### 3. AcN

The AcN crystal structures are presented in Fig. 1. The ferromagnetic phase is the cubic NaCl structure with the $Fm-3m$ space group, and the antiferromagnetic phase is cubic NaCl with the $Pm3m$ space group.

#### 3.1. Energy of Formation

In Table 1, the calculated equilibrium lattice constant, energy of formation, magnetic moment, bulk and shear moduli, and Debye temperature are presented. The energy of formation for all the AcN investigated, calculated using equation 2, is negative. This implies that the formation of these structures is energetically favorable.

Also, in Table 1 we observe that ThN and PaN evolve to their non-magnetic ground states with the AFM structure being slightly more energetically favorable than the FM structure. UN to PuN give various degrees of magnetization due to the 5f orbitals, with the magnetic orientation along the z-axis in both the AFM and FM ordering. This is attributed to strong electron-electron correlations of the 5f electrons at each atomic site resulting in net local magnetic moments. We observe that the degree of magnetization is over-estimated using the PAW (GGA $+ U$) approach compared to all-electron (AE) calculations and experimental data. For the UN to PuN compounds, the total energy with PAW (with and without the Hubbard $U$) results in the FM structure having the lowest energy of formation.
Table 1: The Hubbard $U$ (eV), optimize lattice parameters $a$ (in Å), calculated energy of formation $\Delta E_f$ (eV), total magnetic moment $\mu_B$ (Bohr magnetons), bulk and shear moduli (GPa), and the Debye temperature $\theta_D$ (K) using GGA + $U$ within the SOC scheme. Where AE results is from Ref [21] and the PAW results is our data.

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<th>Compound</th>
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<th>$U$</th>
<th>$a_0$</th>
<th>$\Delta E_f$</th>
<th>$\mu_B$</th>
<th>bulk</th>
<th>shear</th>
<th>$\theta_D$</th>
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<tr>
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<td>4.26</td>
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3.2. Structural Properties

We present the lattice constants calculated using the PAW method (GGA with and without the inclusion of Hubbard $U$-parameter) in Table 1. We find a favorable comparison with the AE [21] results for the various AcN compounds considered. For ThN, we obtain reasonable results without the inclusion of the Hubbard $U$ parameter. This is understandable since Th lacks $5f$ electrons. Also for PuN, the lattice constant is not affected much by the inclusion of the $U$. This is understood in terms of its relative position in the actinide series.

The inclusion of the Hubbard $U$ parameter of 1 eV in UN and NpN results in lattice constants that compare very well with experiment. The experimentally determined lattice constant [34, 35] and the calculated result of our lowest energy structure in parenthesis for ThN, UN, NpN and PuN are 5.154 Å (5.172 Å), 4.889 Å (4.889 Å), 4.894 Å (4.909 Å) and 4.905 Å (4.907 Å) respectively.

3.3. Elastic Properties

The calculated bulk modulus, shear modulus and Debye temperature for the AcN compounds are presented in Table 1. They are all positive, which indicates that the compounds are all elastically stable. The inclusion of the $U$ parameter leads to an overall better agreement of the calculated elastic properties with other available theoretical and experimental data [35, 36, 21, 7]. For instance, the experimentally determined bulk modulus and the calculated result of our lowest energy structure in parenthesis for ThN and UN are 175 GPa [37] (178 GPa) and 193 GPa [35] (198 GPa) respectively.

PaN has the highest Debye temperature $\theta_D$ of 358 K of the systems that we considered. This is associated with complex covalent bonding behavior in this system that will be further explored in our discussion on the valence charge density. PaN, followed by UN, have the highest calculated bulk modulus that also points to the inherent covalent bonding in these systems.
3.4. Density of States

The partial density of states (PDOS) for the $5f$ and $6d$ states for the actinides and the $2p$ states of the nitrogen are presented for the ground state AcN compounds. All the compounds studied within GGA and GGA + $U$ are found to be metallic. There is a systematic increase in the $5f$ electron density of states at the Fermi level with increasing atomic number, and there is a contribution from the N $2p$ states below the Fermi level.

As shown in Fig. 2 for the AFM structure of ThN, the metallicity of ThN is determined mainly by the hybridization of the $5f$ and $6d$ states from the actinide with a very minute contribution from $2p$ states of the nitrogen at the Fermi level.

![Figure 2: (Color online) Partial density of states for ThN in the AFM structure. The Fermi level is the vertical line through $E = 0$](image)

From PaN to PuN, we have a higher $5f$ electron contribution at the Fermi level compared to the other orbitals in both the GGA and GGA + $U$ descriptions shown in figures 3. This is attributed to increased localization of the $5f$ electrons in the actinides. However, other experimental and theoretical studies [13, 14, 6] of UN have confirmed that the U $5f$ states have some itinerant character that is attributed to the presence of U $5f$ states at the Fermi-level therefore preserving some band character. [14]

In Fig 4, we present the partial DOS for PuN in the AFM structure. There is a significant difference in the peaks of the two actinide atoms of the $5f$ states (minority and majority spin) compared to the AFM PDOS of ThN that has no difference in the peaks. This is an indication of AF magnetic ordering in this system. Similar features are observed in the AFM structure of UN to PuN.
Figure 3: (Color online) Partial density of states for PaN, UN and NpN in the FM structure. The Fermi level is the vertical line through $E = 0$

3.5. Valence charge densities

In Fig. 5, we show the valence charge density plots for the compounds that we investigated. This gives us an indication of the character of the bonding. The charge density distribution is computed in the (001) plane for the AFM configuration. The scale in Fig. 5f is such that blue is devoid of electrons and red indicates a high concentration of electrons. The charge densities plotted are for the valence states summed over both spin orientations.

In general, we observe near-spherical charge density distributions around the actinide and nitrogen atoms with significant charge depletion between the atoms, which is characteristic of the rock-salt structure with predominant ionic bonding. Between the actinide and nitrogen...
atoms there is a subtle charge density bridge, attributed to the slight covalent character in the actinide nitrides. There is charge transfer from the actinide metals to the non-metallic nitrogen atoms. As the atomic number increases (Th to Pu) resulting in higher valence localized $5f$ electrons, there is a noticeable increase in the charge accumulation at the actinide site.

3.6. Phonon Studies

In Fig. 6, no negative phonon modes for the various $\text{AcN}$ structures are observed in the phonon dispersion plot. Therefore, these compounds are dynamically stable. The low-lying frequency modes are governed by the dynamics of the heavy $\text{Ac}$ atoms, and the higher frequencies by the lighter N atoms. There is a significant difference in the frequency of N atoms compared to the Ac atoms due to the large mass differences. This suggests that instability in the system can arise from a small perturbation of the crystal structure.

$\text{PuN}$ has the lowest acoustic velocity corresponding to the lowest bulk modulus and overall strength of all the $\text{AcN}$ systems that we studied. There are "flatish" sections of the optical branches in all systems that suggest low group velocities for these modes involving N.

4. $\text{AcN}_2$

In Fig. 7, we present the $\text{AcN}_2$ crystal structures. The ferromagnetic (FM) phase is the cubic fluorite structure with space group $Fm-3m$, while the antiferromagnetic phase (AFM) is a double tetragonal unit cell with space group $P4/mnm$, and the magnetic ordering is in the $z$-axis.
4.1. Energy of Formation

In Table 2, the calculated equilibrium lattice constant, energy of formation, magnetic moment, bulk and shear moduli, and Debye temperature are presented. The calculated energy of formation for the AcN$_2$, using equation 2, is negative, which implies that the structures are energetically favorable. The difference in the energy of formation of the AcN$_2$ within the GGA approach using the AFM and FM structures is about one-hundredth of an eV. The introduction of the Hubbard U parameter results in a difference of about one-tenth of an eV in the energy of formation between the AFM and the FM structures. We conclude that the AFM structures are slightly more energetically favorable with the exception of ThN$_2$ for which the FM is more energetically favorable.

ThN$_2$ to UN$_2$ compounds evolve to the non-magnetic ground state irrespective of the starting magnetic configuration. We observe that the magnetic orientation has little effect on the structural, elastic and mechanical properties. For NpN$_2$ and PuN$_2$, the AFM structure results in zero net magnetization. But, the FM structure for NpN$_2$ gives a net magnetic
moment of 0.19 \( \mu_B \) and 0.95 \( \mu_B \) for GGA and GGA + \( U \) respectively. The FM structure for PuN\(_2\) gives a net magnetic moment of 1.74 \( \mu_B \) for GGA and 2.04 \( \mu_B \) for GGA + \( U \). The magnetic orientation in these compounds is along the \( z \)-axis.

Comparing the energy of formation for the actinide mononitrides and dinitrides, we observe that the dinitrides are more energetically stable with the exception of ThN\(_2\) that is later shown to be elastically unstable. PuN\(_2\) has a slightly lower energy of formation than
4.2. Structural Properties

In Table 2, we present the calculated equilibrium lattice constant, magnetic moment, bulk and shear moduli and Debye temperature. The lattice constant using the PAW approach obtained for the various AcN$_2$ compounds considered is calculated using GGA and GGA + U. The experimentally determined lattice constant and the calculated result with the Hubbard $U$ parameter of our lowest energy structure in parenthesis for UN$_2$ [34, 38] and NpN$_2$ [4] are 5.308 Å (5.302 Å) and 5.3236 Å (5.32 Å) respectively. To the best of our knowledge, no experimental data on the lattice parameters of ThN$_2$, PaN$_2$ and PuN$_2$ is available.

4.3. Elastic properties

The AcN$_2$ considered are all elastically stable except for ThN$_2$, which is elastically unstable to shear stress due to the negative shear modulus. The Debye temperature therefore cannot be calculated for this system. This is consistent with experimental findings that suggest the existence of two stable alloys of thorium and nitrogen, namely ThN and Th$_3$N$_4$, [39]

The bulk and shear moduli increases from ThN$_2$ to UN$_2$, then subsequently decreases to PuN$_2$. The calculated bulk modulus, shear modulus and Debye temperature with and without the $U$ parameter for PaN$_2$ and UN$_2$ are consistent for the AFM and the FM phases as shown in Table 2. Also, for NpN$_2$ without the $U$ parameter, the elastic properties are consistent for the AFM and FM phase. However, we discovered that the FM phase for both NpN$_2$ and PuN$_2$ are highly sensitive to structural optimization, which leads to significant structural distortion.

4.4. Density of States

The partial density of states (PDOS) for the 5$f$ and 6$d$ states for the actinide atom and the 2$p$ states of the nitrogen atom is presented for AcN$_2$ in the ground state structures. We observe
GGA + U studies of the early actinide mononitrides and dinitrides

Table 2: The Hubbard $U$ (eV), optimize lattice parameters $a$ (in Å), calculated energy of formation $\Delta E_f$ (eV), total magnetic moment (scalar norm) $\mu_B$ (Bohr magnetons), bulk and shear moduli (GPa), and the Debye temperature $\theta_D$ (K) using GGA + $U$ within the SOC scheme.

<table>
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<th>Compound</th>
<th>Theory</th>
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<th>$a_0$</th>
<th>$\Delta E_f$</th>
<th>$\mu_B$</th>
<th>bulk</th>
<th>shear</th>
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that AcN$_2$ within the GGA and GGA + $U$ are metallic with the exception of UN$_2$ which has a band gap.

In Fig. 10, an insulating character is observed for UN$_2$ with a GGA band gap of 0.56 eV and an increase in the band gap to 0.64 eV on the inclusion of the Hubbard $U$ of 2 eV. This is comparable to the band gap obtained by Weck et al. [22] of 0.94 eV using the AE approach and by Lu et al. [7] of 0.75 eV using a Hubbard $U$ of 4 eV. If we consider the FM structure, which is less energetically favorable, a GGA band gap of 0.73 eV and a band gap of 0.83 eV on inclusion of the Hubbard $U$ of 2 eV (figure not presented) is obtained. The top of the valence band is determined mainly by the hybridization of the U 5f and N 2p states, while the electronic properties of UN$_2$ is governed mainly by the 5f states because they dominate the conduction band minimum and valence band maximum.

The metallicity of ThN$_2$ is determined mainly by the 2p states as shown in Fig. 8. There is significant hybridization of the 5f and 6d states for the thorium atom and the 2p states of the nitrogen atom at the Fermi level.

While in PaN$_2$ as shown in Fig. 9, there is approximately equal participation of the 5f and 6d states around the Fermi level compared to the other orbitals in both the GGA and GGA + $U$. The inclusion of the Hubbard $U$ of 2 eV leads to an increase in the 5f states in the conduction band but no noticeable change at the Fermi level.
GGA + U studies of the early actinide mononitrides and dinitrides

Figure 8: (Color online) Partial density of states for Th\(\text{N}_2\). The Fermi level is the vertical line through \(E = 0\)

The Np\(\text{N}_2\) and Pu\(\text{N}_2\) compounds results in metallic behavior as presented in Fig. 11 and 12 with the Fermi level dominated by the 5f states. There is weak hybridization of the actinide 5f and 6d states at the Fermi-level in Np\(\text{N}_2\) and a significant hybridization of the actinide 5f and 6d states with the nitrogen 2p state in Pu\(\text{N}_2\) compound.

4.5. Valence charge densities

In Fig. 13, we show the valence charge density plots for all the compounds considered to investigate the bonding character. The density distribution is computed in the (100) plane for the AFM configuration. We observe that the bonding character is not dependent on the magnetic configuration of the systems that we investigated. The scale in Fig. 13f is such that blue is devoid of electrons and red indicates a high concentration of electrons. The charge densities plotted are for the valence states summed over both spin orientations.

We observe significant distortion in the spherical charge distribution around the actinide compared to the nitrogen atoms. Between the actinide and nitrogen atom there is a subtle charge density bridge, attributed to the slight covalent character in the actinide nitrides. This charge density bridge along with the actinide charge density increases with increase in the atomic number of the actinide metal (Th to Pu) compared to the rest of the interstitial region. This results in increased covalent bonding character of the actinide nitride with increase in the atomic number. However, the Ac\(\text{N}_2\) studied are all predominantly ionic compounds.

4.6. Phonon Studies

The calculated phonon dispersion curves along the W-L-\(\Gamma\)-X-W-K directions for Ac\(\text{N}_2\) are presented in Fig. 14 within the GGA approach. Generally, the phonon frequencies for all the compounds considered are split roughly into two halves, where the lower frequencies are governed by the dynamics of the heavy Ac atoms and the higher frequencies by the dynamics of the N atoms.

The Ac\(\text{N}_2\) are dynamically stable with no negative phonon modes in the dispersion plot with the important exception for UN\(\text{N}_2\), which has a small fraction of imaginary phonon frequencies. This is due to the transverse modes of the nitrogen atoms.
GGA + U studies of the early actinide mononitrides and dinitrides

Figure 9: (Color online) Partial density of states for PaN$_2$. The Fermi level is the vertical line through $E = 0$

Figure 10: (Color online) Partial density of states for UN$_2$. The Fermi level is the vertical line through $E = 0$
GGA + U studies of the early actinide mononitrides and dinitrides

Figure 11: (Color online) Partial density of states for NpN\textsubscript{2}. The Fermi level is the vertical line through $E = 0$

Figure 12: (Color online) Partial density of states for PuN\textsubscript{2}. The Fermi level is the vertical line through $E = 0$
This result contradicts the theoretical observation by Lu et al.[40] that predicts a thermodynamically stable structure for UN$_2$. Our result corroborates experimental evidence by Rundle et al. [34], Tagawa et al. [15, 16] and more recent studies [41, 42] that suggests UN$_2$ has never been prepared as a stoichiometric compound. Experimentally, it has been concluded that the correct stoichiometry may be UN$_{1.75}$. UN$_2$ is nonstoichiometric and was assigned a hypothetical CaF structure on the basis of the experimental data for the actinide dinitrides with N/U = 1.75 – 1.78 with the understanding that the non-stoichiometry arises from the presence of nitrogen vacancies in UN$_2$. This is consistent with our theoretical observation that the nitrogen atom is the source of the instability.

A trend of reduced gap in the phonon frequency between the modes of the heavy actinide
metal and the light nitrogen atom is observed with increasing atomic number. Also, the difference in the frequency of nitrogen atoms compared to the actinide atoms is low compared to their AcN analogue. This implies that the addition of the extra nitrogen atom to the structure has led to the further stabilization of the structure.

5. Concluding remarks

We studied the ground state electronic, structural and mechanical properties of the AcN and AcN$_2$ early actinide nitrides. The calculated lattice parameters with the inclusion of the Hubbard $U$ parameter agree well with available experimental data where that data exists. There is the exception of ThN, PuN and ThN$_2$ compounds where GGA gives agreeable results for the actinide mononitrides and dinitrides. In general, all the actinide nitrides studied are energetically favorable, and are elastically and mechanically stable with the exception of ThN$_2$. 

Figure 14: Phonon dispersion for AcN$_2$ crystalline structures
that is unstable to isotropic pressure. Notably UN$_2$ is thermodynamically unstable and has been speculated to stabilize under N-vacancy formation. This will be investigated in a future study.

Comparison of the calculated and experimental magnetic properties of these systems shows that the GGA + $U$ with and without SOC gives a good qualitative account of the properties compared with experiment, but not an accurate quantitative account. Therefore, going beyond DFT + $U$ is important to quantitatively determine the magnetic moments.

An analysis of the valence charge density distribution of the actinide nitrides shows the presence of ionic bonding predominantly, with the dinitrides having higher covalent character compared to the mononitrides. Also, we observe a consistent increase in the charge density distribution at the actinide sites for the actinide mononitrides and dinitrides with increasing atomic number.

All the actinide nitrides considered are metallic in nature with the exception of UN$_2$.

Acknowledgments

We thank the University of Pretoria for financial support. KO gratefully acknowledges the support of Obodo T. Joshua and the members of the Computational and Theoretical Physics group at the University of Pretoria for useful discussions. Also, we thank Dr Jannie Pretorius and Prof. Walter Meyer for assistance with the computational hardware and software resources. Finally, NC is grateful to the National Institute for Theoretical Physics for support.

References


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Based on the discussion from the last four chapters, the general conclusions are drawn about the various actinide systems investigated. These are given in the next chapter.
Chapter 7

General conclusions

In this study, we use first principle pseudopotential-based approach within the DFT and DFT+U based approaches to determine the total energy for various actinide systems. The fully converged total energy with respect to the kinetic energy cutoff and k-points sampling is used to determine the structural, mechanical, elastic and electronic properties. The following motivated the study: (i) the search for ordered alloys of Th-Ti systems, (ii) the understanding of Th-N based compounds and (iii) the effect of 5f electrons on the actinide systems.

Conclusions drawn from these studies are given at the end of each chapter focused on the results and discussion. This chapter presents the highlights of the study, which are divided are into two broad headings: (i) Thorium and its alloys, (ii) Other actinide compounds.

7.1 Thorium and its alloys

In this section the inclusion of the effective Hubbard $U$ parameter for the accurate determination of the systems under investigation was found to be insignificant. This is due to the absence of an 5f electron in the thorium system.

This work is motivated by the usefulness of various compounds of Th and N in the generation of energy. Also, it validates the $ab initio$ technique used in the study. Th$_3$N$_4$, Th$_2$N$_3$ and Th$_2$N$_2$NH systems were investigated to determine the structural, elastic, and electronic properties and the formation energy of these Th-N based compounds. The inclusion of SP and SOC results in no significant change in the calculated properties of these compounds. Therefore, the non-magnetic case was used in this investigation. We determined that Th-N based compounds are elastically stable, with a negative heat of formation. Th$_3$N$_4$ has the lowest
value of $a_0$, followed by $\text{Th}_2\text{N}_3$, then $\text{Th}_2\text{N}_2\text{NH}$. $\text{Th}_3\text{N}_4$ is the most energetically stable nitride of thorium considered. Using the valence charge density distribution, the bonding properties were accurately determined, which shows the presence of a predominantly ionic bonding character. $\text{Th}_3\text{N}_4$ and $\text{Th}_2\text{N}_2\text{NH}$ are insulating, while $\text{Th}_2\text{N}_3$ is metallic. The insulating character of $\text{Th}_2\text{N}_2\text{NH}$, which is crystallographically similar to the metallic sesquinitride is attributed to the effect of the -(NH) group on the electronic structure. There is significant hybridization of the thorium 6$d$ and 5$f$ states with the nitrogen 2$p$ in the Th-N based compounds.

Next, the elemental, 50:50 and off 50:50 Th-Ti systems were investigated in order to determine the possibility of formation of an ordered alloy involving a ThTi system. This work is motivated by the usefulness of various alloys of Th and Ti. The structural stability was established using arguments based on elastic constants, phonon frequencies, electron localization function, valence charge density, band structure, density of states and heat of formation. Using the valence charge density and electron localization function plots, the bonding properties were accurately determined. The bonding character is described further from the electronic properties. From the MT-module, the elastic properties were determined. The calculation of elastic properties and phonon dispersions correctly determined the elastic stability and dynamic stability for ThTi$_3$ (in the Cr$_3$Si structure). ThTi$_3$ (in the Cr$_3$Si structure) was found to be metallic. Using arguments based on the calculated heat of formation, the investigated structure is predicted to be meta-stable.

### 7.2 Other actinide compounds

In this section the inclusion of the effective Hubbard $U$ parameter for the accurate determination of the systems under investigation was found to be essential. This is due to the presence of a partially filled 5$f$ orbital in the early actinide system.

The structural, mechanical and electronic properties of Pa, PaO and PaO$_2$ have been studied within the DFT and DFT+$U$ approach. As far as the structural properties for Pa are concerned, the inclusion of the Hubbard $U$ parameter is not relevant here, but has been found relevant to describe PaO and PaO$_2$ accurately. Pa, PaO and PaO$_2$ are elastically and dynamically stable. They are all metallic within the DFT approach. The inclusion of the effective Hubbard $U$ parameter results in a band gap of 3.48 eV for the PaO$_2$ system using PBE (GGA). To accurately describe PaO and PaO$_2$, the inclusion of the effective Hubbard $U$ parameter is essential.
Next, the ground state electronic, structural and mechanical properties of the early actinide mononitrides and dinitrides were studied using DFT+U. The calculated lattice parameters with the inclusion of the Hubbard $U$ parameter agree well with available experimental data where that data exists. There is the exception of ThN, PuN and ThN$_2$ compounds where GGA gives acceptable results for the actinide mononitrides and dinitrides. In general, all the actinide nitrides studied are energetically favorable, and are elastically and mechanically stable, with the exception of ThN$_2$ that is unstable to isotropic pressure. Notably, UN$_2$ is thermodynamically unstable and has been speculated to stabilize under N-vacancy formation. This will be investigated in a future study. Comparison of the calculated and experimental magnetic properties of the actinide nitrides indicates that the GGA + $U$ with and without SOC gives a good qualitative account of the properties compared with experiment, but not an accurate quantitative account. Looking at the valence charge density distribution of the actinide nitrides, the presence of ionic bonding is predominant with the dinitrides having higher covalent character compared to the mononitrides. Also, there is a consistent increase in the charge density distribution at the actinide sites for the actinide mononitrides and dinitrides with increasing atomic number. All the actinide nitrides considered are metallic in nature, with the exception of UN$_2$.

### 7.3 Conclusions

Firstly, the electronic and elastic properties of Th-N based alloys have been studied in detail. We established that Th$_2$N$_2$(NH) is insulating, unlike the crystallographically equivalent Th$_2$N$_3$, which is metallic. Next, we have demonstrated that the formation of an ordered alloy of a Th-Ti based compound is plausible. This provided information on the electronic, elastic and mechanical properties of this ordered alloy. This has furnished more information on the bulk systems of these compounds.

Thereafter, we investigated the effect of the Hubbard $U$ parameter on the Protactinium and its oxides, and various actinide nitrides. We find that to accurately describe these systems the inclusion of the $U$ parameter is essential. Finally, a comparative study was presented on the early actinide mononitrides and dinitrides.
7.4 Future investigations

The various studies undertaken open up an avenue for further investigations. Future work involves searching for other candidate stoichiometry structure of various actinide elements and other alloying elements. The stability of the ordered alloys would be investigated using the method presented in chapter 4.

The investigation of various actinide systems will be carried out. This will involve studying how the Hubbard $U$ parameter describes the various actinide carbides. An in-depth analysis of UN$_2$, looking at the effect of pressure, temperature on the stabilization of the UN$_2$ structure will be undertaken. Use of other available techniques such as dynamic mean field theory, GW approach, etc. to investigate the electronic and magnetic properties of actinide compounds that fails using the DFT+$U$ approach will be considered.
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