

T.R.
BOLU ABANT İZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
Department of Physics



**AB INITIO CALCULATIONS ON LATTICE DYNAMICAL
PROPERTIES OF LANTHANIDES**

DOCTOR OF PHILOSOPHY

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ABSTRACT

**AB INITIO CALCULATIONS ON LATTICE DYNAMICAL PROPERTIES
OF LANTANIDES
PHD THESIS
SERPİL ERYİĞİT**

**BOLU ABANT İZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF PHYSICS
(SUPERVISOR: PROF.DR. CİHAN PARLAK)**

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In this thesis, we report the results of several in-depth studies on the quantum mechanical properties of rare-earth metals. Studies are carried out in the frameworks of density functional theory (DFT), DFT plus static Coulomb correlation as formulated by a Hubbard model, and dynamical mean-field theory. The aim of the study was to assess the possibility of using a pseudopotential formulation of the DFT with mean-field-level corrections for the strong electronic correlations to account for the structural, electronic, magnetic, and elastic properties of rare-earth metals. The results presented in the thesis indicate that projected augmented waves produced by a multi-objective evolutionary optimization algorithm provide a satisfactory electron-nuclei interaction potential to describe the aforementioned properties of cerium in addition to the widely discussed $\alpha - \gamma$ isostructural phase transition.

KEYWORDS: DFT+U, Lanthanides, Cerium, Phase Transitions

ÖZET

**LANTANİTLERİN ÖRGÜ DİNAMİĞİ ÖZELLİKLERİ ÜZERİNE AB
INITO HESAPLAMALAR
DOKTORA TEZİ
SERPİL ERYİĞİT
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LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ
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(TEZ DANIŞMANI: PROF. DR. CİHAN PARLAK)**

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Bu tezde, nadir toprak metallerinin kuantum mekanik özellikleri üzerine birkaç derinlemesine çalışma yapılmıştır. Çalışmalar, yoğunluk fonksiyonel teorisi (DFT), DFT artı bir Hubbard modeli tarafından formüle edilen static Coulomb korelasyonu ve dinamik ortalama alan teorisi, çerçevesinde yürütülmüştür. Çalışmanın amacı, nadir toprak metallerinin yapısal, elektronik, manyetik ve elastik özelliklerini hesaba katmak için güçlü elektronik korelasyonlar için ortalama alan düzeyinde düzeltmelerle DFT'nin sözde potansiyel formülasyonunu kullanma olasılığını değerlendirilmiştir. Tezde sunulan sonuçlar, çok amaçlı bir evrimsel optimizasyon algoritması tarafından üretilen yansıtılmış artırılmış dalgaların, yaygın olarak tartışılan α - γ izoyapısal faz geçişine ek olarak seryumun yukarıda belirtilen özelliklerini açıklamak için yeterli bir elektron çekirdeği etkileşim potansiyeli sağladığını göstermektedir.

.

ANAHTAR KELİMELEER: DFT+U, Nadir-toprak elementler, Seryum, Faz Geçişleri

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LIST OF ABBREVIATIONS AND SYMBOLS

BAIBU	: Bolu Abant Izzet Baysal University
cDFT	: Constrained Density Functional Theory
cRPA	: Constrained Random Phase Approximation
DFT	: Density Functional Theory
DFT+U	: Density Functional Theory plus Hubbard U
DMFT	: Dynamical Mean Field Theory
EOS	: Equation of States
LDA	: Local Density Approximation
GGA	: Generalized Gradient Approximation
PAW	: The Projector Augmented Wave

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1. INTRODUCTION

15 of the elements of the periodic table starting with lanthanum (atomic number 57) and ending with lutetium (atomic number 71) are named rareearth or the lanthanides. Lanthanides and their compounds have interesting electronic and magnetic properties [1] that are utilized in developing various advanced devices. Most of the electronic and magnetic properties of this group are determined by the interesting physics of 4f electrons. While La has no 4f electrons, starting with Ce (one 4f electron) the 4f shell is completely filled in Lu. Aim of the research in the present thesis is to study various properties of these elements by using the state of the art electronic structure methods.

The most widely used method for theoretical investigation of properties of materials has been the density functional theory (DFT) developed in early 1960s. DFT is a single-particle theory and proven to be very successful in predicting structural, electronic and magnetic properties of the most of the materials. But, materials, such as transition metals, lanthanides and actinides which have localized d and f electrons show strong correlations between those electrons and need many-body techniques to be described adequately. Density Functional Theory plus Hubbard U (DFT+U) and Density Functional Theory plus Dynamical Mean Field Theory (DFT+DMFT) are two relatively new approaches developed to amend the shortcomings of the DFT in treating strongly correlated electron systems.

Aim of the present thesis research is to investigate three interrelated properties of lanthanide series of elements in DFT+U and DFT+DMFT frameworks to delineate the role of strong correlations in electronic and magnetic properties for the 4f electron systems. Below, a brief summary of each problem, its importance and study plan is given.

First Principles Calculation of Hubbard Interaction Parameter U and Optimization of Occupation Matrices for the 4f Orbital of Rare-Earth Elements

The simplest way to treat the localization effect is to assume a static Hubbard interaction (U) for the localized orbitals.

The net effect of such an interaction is to open a gap between the occupied and the unoccupied manifolds of the bands originating from the aforementioned orbitals. There are various approaches to determining U for a given element: The simplest approach is to consider U as an adjustable parameter and compute whatever physical property one is interested for a series of U values and choose the value of U as the one that makes the calculated property agree with the experiment the best. This particular approach breaks the 'first principles' character of the computations and has no predictive power. Two methods, namely constrained density functional theory (cDFT) [2,3] and constrained random phase approximation (cRPA) [4, 5], have been develop to calculate ab-initio values of U . Both methods have been used to calculate U values for some elements [6–10] of the lanthanide series, but the reported results depend on the technical details of the computational set up used in the study.

Our aim in this part of the study is to obtain a set of consistent Hubbard U parameters for the whole lanthanide series. Towards that end, we will utilize both cDFT and cRPA methods to calculate the Hubbard interaction. In the cDFT approach, U is the energy difference between the electron removal and addition to the correlated shell:

$$U = E(f^{n+1}) + E(f^{n-1}) - 2E(f^n) \quad (1.1)$$

where $E(f^n)$ is the total energy of the system when f shell is occupied with n electrons. The difference can be formulated as the second derivative of the total energy with respect to the electron number n [3].

The cRPA approach depends on the calculation of the screened Coulomb interaction between the correlated electrons with certain constraints. This technique constrains the polarization effects in the calculation of screened interactions to transitions involving the non-local states and uses random phase approximation to compute the polarization of the electronic system.

Computations for the Hubbard U parameter will be carried out in density functional framework within the projected augmented waves approach for the description of the electron-nuclei interactions. One of the difficulties of such

calculations for the strongly correlated f electron systems has been the difficulty of reaching a unique global minimum state in selfconsistency cycles of the computations. Starting the cycle from a known symmetry ground state for the correlated orbitals is the most widely used method to guide the electronic system to a global minimum. We will use a genetical algorithm to optimize initial occupation matrix of f orbitals. Preliminary calculations indicate that such optimization would produce better initial states compared to random starting density.

As output of the first problem, we aim to find:

- A set of optimum initial occupation matrices
- cRPA and cDFT Hubbard U and Hund J parameters

for the f orbitals of lanthanide series elements. These quantities would be useful both for understanding of the physics of strongly correlated electronic systems and guide the investigation of further properties of rare-earths.

Effect of Strong Correlations on the Structural and the Electronic Properties of Lanthanides

The most obvious deficiency of DFT and such single-particle approaches in describing the strongly correlated electronic systems is their failure to explain the photoemission spectra of such systems. In the second problem, we will use the results of the first problem to investigate the electronic spectral function of lanthanides in DFT+DMFT framework. In this framework, DFT is used to compute the parameters of tight-binding like many-body Hamiltonian for the correlated orbitals of the system under consideration. This manybody system will be solved by using a Quantum Monte Carlo method to obtain the many-body spectral function which will be compared with the DFT electronic density of states to delineate the effects of manybody interactions in the electronic structure. Also, frequency dependent screened interactions and equilibrium volume and bulk modulus will be calculated by using DFT+DMFT energies to assess whether many-body effects have any roles in the structural details of the lanthanides.

Effect of Strong Correlations on the Elastic Properties of the Lanthanides

Elastic properties of materials describe the stress response of the solid to applied strain and important in various applications. In the third problem, we plan to investigate the possible effects of the strong electronic correlations on the strain response of the lanthanides.

There are three main approaches to elastic tensors calculation of the solids: Linear response approach developed by Hamann has been implemented in DFT framework with norm-conserving pseudopotentials and in PAW formalism only for if exchange-correlation function is taken in local density approximation. The second and the third approaches both use finite strains and fit the calculated total energy or the stress to the applied strain to find the elements of the elastic tensor. The formulation of stress in DMFT framework is complicated and its implementation in electronic structure codes is not common. So, we will use DFT+DMFT finite strain approach to investigate the role of strong correlations in the elastic behaviour of lanthanides.

2. THEORETICAL FRAMEWORK

2.1 Density Functional Theory

Density Functional Theory (DFT) is a computational quantum mechanical modeling method used in physics, chemistry, and materials science to investigate the electronic structure (or behavior) of many-body systems. It is based on the idea that the behavior of a many-electron system can be accurately described by using a density function, rather than the wave function of each individual electron. DFT has become a popular method in condensed matter physics and computational chemistry, as it is less computationally demanding than other methods and can still provide accurate results for many systems. DFT is a powerful tool for studying the electronic structure of materials, molecules and other systems. It allows researchers to calculate the ground state properties of a system, such as its total energy, charge density and chemical bonding, as well as its excited state properties, such as its optical spectra and electronic transitions. DFT can also be used to investigate the properties of systems under extreme conditions, such as high pressures and temperatures.

DFT is a widely used method in many areas of physics and chemistry and has contributed to many important advances in our understanding of the electronic structure of matter.

Density Functional Theory (DFT) was developed in the early 1960s by the physicists Kohn and Sham [11], and Kohn was awarded the Nobel Prize in Chemistry in 1998 for this work. The basic idea behind DFT is that the behavior of a many-electron system can be accurately described by using a density function rather than the wave function of each individual electron. This density function can be calculated using a set of mathematical equations known as the Kohn-Sham equations.

Kohn-Sham equation used in density functional theory to describe the behavior of electrons in a general external potential. It is given by the following equation:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r) \quad (2.1)$$

Here, $\hbar$ is the reduced Planck constant, m is the mass of an electron, ∇^2 is the Laplacian operator, $v_{\text{eff}}(r)$ is the total potential energy experienced by the electrons, $\phi_i(r)$ are the wave functions of the electrons, and ϵ_i are the energies of the electrons. The development of DFT is a breakthrough in computational quantum mechanics, as it allows researchers to study the electronic structure of complex many-electron systems more efficiently and accurately than possible. Before the development of DFT, researchers had to use computationally demanding methods, such as the Hartree-Fock method, to study the electronic structure of such systems. DFT is less computationally demanding than these methods and can still provide accurate results for many systems.

The Hartree-Fock method is used to approximate the ground state wave function and energy of a many-body quantum system. This method is based on the Hartree approximation, which assumes that the wave function of a many-body

system can be written as a product of single-particle wave functions. The Hartree-Fock method is based on the following equations:

$$\hat{H}\Psi = \left(\sum_{i=1}^N \hat{h}(i) + \sum_{i<j}^N V_{\text{int}}(i,j) \right) \Psi = E\Psi \quad (2.2)$$

The single-particle Schrödinger equation:

$$\hat{h}_i \phi_i = \epsilon_i \phi_i \quad (2.3)$$

Here, $\hat{H}$ is the total Hamiltonian operator for the many-body system, Ψ is the wave function for the many-body system, $\hat{h}_i$ is the single-particle Hamiltonian operator for the i th particle, ϕ_i is the single-particle wave function for the i th particle, $V_{\text{int}}(i,j)$ is the interaction operator between particles i and j , and E is the total energy of the system. The Hartree-Fock method involves solving the single-particle Schrödinger equation for each particle in the system and then using these solutions to construct the wave function for the many-body system. Using the Hartree-Fock equation, this wave function is then used to calculate the system's total energy. This process is repeated iteratively until the wave function and energy converge to a stable solution.

Applications of Density Functional Theory

Many different DFT methods have been developed, each with its strengths and weaknesses. Some popular methods include local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals. These methods differ in how they treat exchange and correlation effects, which are important for describing the behaviour of the electron density in a manybody system. DFT methods are widely used in chemistry, physics, and materials science to study the electronic structure of atoms, molecules, and solids.

Since its development, DFT has been refined and extended in many ways. For example, researchers have developed more accurate versions of the Kohn-Sham equations and methods for incorporating relativistic and quantum electrodynamic effects into DFT calculations. In addition, many efficient algorithms and computational tools have been developed to make it easier to perform DFT calculations on large and complex systems.

The development of DFT has significantly impacted many areas of physics and chemistry and continues to be an important tool for studying the electronic structure of matter.

One important application of DFT in chemistry is studying chemical reactions. DFT can be used to calculate the potential energy surfaces of chemical reactions, which can help chemists understand the mechanisms and rates of chemical reactions. DFT can also be used to predict the structures and properties of stable and unstable molecules and to study the properties of complex systems such as enzymes and catalysts.

In addition, DFT can be used to study the electronic structure of materials, such as metals, semiconductors, and insulators. This can help chemists to understand the properties of these materials, such as their electrical conductivity, optical properties and reactivity. DFT can also be used to study the electronic structure of large biomolecules, such as proteins and nucleic acids, which are important for understanding many biological processes.

In materials science, DFT is a powerful tool for predicting and understanding the properties of materials, including their structures, energies, and electronic structures. DFT can study various materials, including metals, semiconductors, insulators, and even complex, disordered materials. Some of the specific applications of DFT in materials science include: Investigating material's structural and energetic properties, such as crystal structure, lattice parameters, and cohesive energies. Predicting the electronic structure and properties of materials, including the band gap, electronic density of states, and electrical conductivity. Modelling the response of materials to external stimuli, such as strain, temperature, and electric and magnetic fields.

Another application of DFT in quantum mechanics is predicting atoms, molecules, and solids ground state and excited state energies. Investigating the electronic structure and properties of atoms, molecules, and solids, including their bonding patterns and electron density distributions. Modeling the response of quantum systems to external stimuli, such as electric and magnetic fields,

temperature, and pressure. Investigating the behavior of defects and impurities in quantum systems and their impact on the systems properties.

2.2 Projector Augmented Wave (PAW) Approach

The PAW approach is an attempt to write the 'valence' electron wave functions of an atom in terms of wave functions and auxiliary functions in the region close to the nucleus, where they vary rapidly in terms of smoother but identical chemical and physical properties. Below is a summary of this approach.

Let $\hat{H}$ be the electronic Hamiltonian. From the solution of the eigenvalue problem $\hat{H}|\Psi_n\rangle = \epsilon_n|\Psi_n\rangle$ electronic energy levels ϵ_n and all-electron wave functions $|\Psi_n\rangle$ can be obtained. Suppose that $\hat{T}$ transformation operator transforms a smooth wave function $|\widetilde{\Psi}_n\rangle$ into a fast-changing $|\Psi_n\rangle$ all electron wave function:

$$|\Psi_n\rangle = \hat{T}|\widetilde{\Psi}_n\rangle \quad (2.1)$$

here we use the index n instead of the orbital or band number, wave vector k , and spin index, as appropriate. $\hat{T}$ conversion under Kohn-Sham equations can be written as,

$$\hat{T}^\dagger \hat{H} \hat{T} |\widetilde{\Psi}_n\rangle = \epsilon_n \hat{T}^\dagger \hat{T} |\widetilde{\Psi}_n\rangle \quad (2.2)$$

In order for the $|\widetilde{\Psi}_n\rangle$ functions, which are the solution of this equation, to be the desired smoothness, what should be the properties of the $\hat{T}$ transformation?

First, since all-electron wavefunctions change slowly outside the core region, $\hat{T}$ should only be active in regions close to the nucleus. We can define the region where the $\hat{T}$ transformation will take effect as a sphere of diameter r_c with the core being the center. Let's call this sphere augmentation sphere. In this case, the $\hat{T}$ transformation in a system consist of different atoms can be written as

$$\hat{T} = 1 + \sum_a \hat{T}^a \quad (2.3)$$

where a is over the types of atoms in the system. Here $\hat{T}^a$ is the transformation specific to the a atom, operating only within the augmentation sphere of radius r_c^a .

Suppose the electronic wave function of the atom a includes partial wave functions ϕ_i^a (we use the index i in place of the fundamental quantum numbers n_i, l_i , etc.). The smooth functions corresponding to these partial all-electron wave functions are also generated via $\hat{T}$

$$|\phi_i^a\rangle = (1 + \hat{T}^a)|\tilde{\phi}_i^a\rangle \quad (2.4)$$

it can be written as. From this equation, the $\hat{T}$ operator can be written as

$$\hat{T}^a|\tilde{\phi}_i^a\rangle = |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \quad (2.5)$$

that is, if $|\phi_i^a\rangle$ and $|\tilde{\phi}_i^a\rangle$ are known, the operator $\hat{T}$ can be calculated.

If the set of smooth partial waves has closure within the augmentation sphere, then the smooth total electronic wave vector in terms of the elements of this set, with the expansion coefficients P_{ni}^a lets define as

$$|\tilde{\Psi}_n\rangle = \sum_i P_{ni}^a |\tilde{\phi}_i^a\rangle \quad (2.6)$$

If we apply the $\hat{T}$ transformation to this expansion,

$$\hat{T}|\tilde{\Psi}_n\rangle = |\Psi_n\rangle = \sum_i P_{ni}^a \hat{T}|\tilde{\phi}_i^a\rangle = \sum_i P_{ni}^a |\phi_i^a\rangle \quad (2.7)$$

becomes. That is, the expansion coefficients of the all-electron wave function in terms of all-electron partial wave functions and the expansion coefficients of the smooth wave function in terms of smooth partial waves are the same. To get the coefficients P_{ni}^a

$$P_{ni}^a = \langle p_i^a | \tilde{\Psi}_n \rangle = \int dr p_i^a(r) \tilde{\Psi}_n(r) \quad (2.8)$$

Here, the projector function corresponding to the partial state i of atom a with $p_i^a(r)$ is defined. In light of this information, we can define the smooth electronic wave function in terms of partial waves and projectors can be defined as

$$|\Psi_n\rangle = \sum_i |\tilde{\phi}_i^a\rangle \langle p_i^a | \tilde{\Psi}_n \rangle \quad (2.9)$$

This expression means that is $\sum_i |\tilde{\phi}_i^a\rangle \langle p_i^a | = \hat{I}$ and $\langle p_i^a | \tilde{\phi}_j^a \rangle = \delta_{ij}$. In other words, projectors and pseudo part wave functions form a complete set within the augmentation sphere, and these functions are perpendicular to each other.

Projectors can be considered zero-valued as they do not operate outside of this sphere. Using this information, the system transformation operator $\hat{T}$ is defined a

$$\hat{T} = 1 + \sum_{i,a} (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle p_i^a| \quad (2.10)$$

For a DFT calculation using PAW datasets, the necessary all-electron partial wave $|\phi_i^a\rangle$, smooth pseudo partial wave $|\tilde{\phi}_i^a\rangle$ and projector $|\phi_i^a\rangle$ functions should be given for each atom in the system to generate this $\hat{T}$ operator. The data set consisting of this information and the correction factors to be explained below regarding the potential is called the PAW dataset. Now let's look at the answer to the question of how to find the elements of this data set for a particular atom in practice. PAW dataset generation starts with finding the wave function and state energies of all electrons in the atom. These quantities are given by solving an equation like the Schrödinger equation in the context of DFT; Where relativistic effects may be significant, a scalar-relativistic or relativistic formulation can also be used. Equations to be solved is

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r) \right) |\phi_i\rangle = \epsilon_i |\phi_i\rangle \quad (2.11)$$

where

$$v_{\text{eff}}(r) = -\frac{Ze^2}{r} + e^2 \int dr' \frac{n_c(r') + n(r)}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}(n_c(r) + n(r)) \quad (2.12)$$

While writing these equations, we divided the electrons into two groups as core and valence electrons and showed the density of core electrons as $n_c(r)$ and the density of valence electrons as $n(r)$. μ_{xc} is the exchange-correlation energy. PAW datasets will be generated for the $|\phi_i\rangle$ states selected as the valence electron in the 2.11 equation.

2.3 Pseudopotential

To generate smooth partial wave and projector functions from partial all electron functions, it is necessary to define a pseudopotential first. There are three prominent methods in the literature for how $V^{\text{PS}}(r)$ can be calculated. The first of these is the norm-conserved pseudopotential approach developed by Troullier and

Martins. In this approach, first of all, it is determined which reference energy E_{loc} and angular momentum channel (l_{loc}) will be used to construct the pseudopotential, and it is determined within the augmentation sphere of the pseudopotential assumed to be in the form

$$\phi_{PS}(r) = r^{l_{loc}+1} \exp(p(r)) \quad (2.13)$$

$p(r) = \sum_{i=1}^6 C_i r^{2i}$ is a 12th order even polynomial. The coefficients of C_i are found by pairing the whole electron partial wave $\phi_{AE}(r)$ with $\phi_{PS}(r)$ and its derivatives on the augmentation sphere surface ($r = r_c$). As a result, the pseudopotential $V^{PS}(r)$ can be found by reversing the Schrödinger equation as

$$V^{PS}(r) = E_{loc} + \frac{\hbar^2}{2m} \left(\frac{d^2 p}{dr^2} + \left(\frac{dp}{dr} \right)^2 + \frac{2(l_{loc}+1)}{r} \frac{dp}{dr} \right) \quad (2.14)$$

at the values of $l = l_{loc}$ and $E = E_{loc}$. Another common method for calculating $V^{PS}(r)$, is similar to Vanderbilt's ultrasoft pseudopotential approximation, the pseudo partial wavefunction is defined as

$$\phi_{PS}(r) = r^{l_{loc}+1} \sum_{i=0}^3 C_i r^{2i} \quad (2.15)$$

in the $r < r_c$ region and $V^{PS}(r)$ is obtained similarly to the Troullier-Martins method.

Another common pseudopotential generation method is to derive $V^{PS}(r)$ directly in terms of the whole electron potential $V^{AE}(r)$. In this approach, $V^{PS}(r)$ is defined

$$V^{PS}(r) = \alpha \frac{\sin qr}{r} \quad (2.16)$$

as a zero-order Bessel function. In the pseudopotential generation stage of PAW dataset generation, there are two parameters (E_{loc} and l_{loc}) and the freedom to choose one of three different methods.

2.4 Pseudo Partial Wave and Projectors

In the production of PAW datasets, there are two methods, called Vanderbilt and Blöchl approaches, which are also commonly used to generate pseudo partial wave $\tilde{\phi}_{n_i l_i}(r)$ and the corresponding projector $p_i r$. In these approaches, either the

projectors are assumed to be perpendicular to the pseudo wave (Vanderbilt) or the partial wave is found by assuming the projector's shape (Blöchl).

2.5 Vanderbilt Approach

In the Vanderbilt approach, first of all, a partial wave function $\tilde{\phi}_{n_i l_i}(r)$ is created for each partial wave at the chosen matching point $r_{n_i l_i}$ which itself and its derivatives will be equal to the whole electron partial wavefunction $\phi_{n_i l_i}(r)$. There are three commonly used approaches to the form of $\tilde{\phi}_{n_i l_i}(r)$. The first method is the polynomial form

$$\tilde{\phi}_{n_i l_i}(r) = r^{l_i+1} \sum_{m=0}^6 C_m r^{2m} \quad (2.17)$$

used in the reference pseudopotential generation above. As the second form, similar to the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) approach [12], $\tilde{\phi}_{n_i l_i}(r)$ can be written as the sum of Bessel functions

$$\tilde{\phi}_{n_i l_i}(r) = \sum_{m=0}^p r \alpha_m j_{l_i}(q_m r) \quad (2.18)$$

Finding projectors that will satisfy the steepness and completeness condition from pseudo partial waves obtained by any of the above three methods in the Vanderbilt approach is as follows: For each $\tilde{\phi}_{n_i l_i}(r)$ found, the $\chi_{n_i l_i}$ auxiliary function

$$|\chi_{n_i l_i}\rangle = (\epsilon_{n_i l_i} - \hat{T} - V^{\text{PS}}) |\tilde{\phi}_{n_i l_i}\rangle \quad (2.19)$$

to be used to find the corresponding projector, this quantity is non-zero only in the $r < r_{n_i l_i}$ region. i, j element with the help of $\tilde{\phi}_{n_i l_i}(r)$ pseudo partial wave and $\chi_{n_j l_j}(r)$ auxiliary functions Let's define the matrix B , which is

$$B_{i,j} = \langle \tilde{\phi}_{n_i l_i} | \chi_{n_j l_j} \rangle \quad (2.20)$$

In this case, it has been shown by Vanderbilt that the projector defined as

$$p_{n_j l_j}(r) = \sum_i \chi_{n_i l_i} (B^{-1})_{i,j} \quad (2.21)$$

automatically satisfies the $\langle \tilde{\phi}_{n_i l_i} | p_{n_j l_j} \rangle = \delta_{ij}$ steepness condition.

2.6 Blöchl Approach

The Blöchl approach assumes the shape of the projector functions and has pseudo partial waves perpendicular to them. $k(r)$ function to be zero outside the Augmentation zone Pseudo partial wave $\tilde{\phi}_{n_i l_i}(r)$ with the help of

$$k(r) = \left(\frac{\sin\left(\frac{\pi r}{r_c}\right)}{\frac{\pi r}{r_c}} \right)^2 \quad (2.22)$$

$k(r)$ is similar to the Schrödinger equation. It can be found by solving equation

$$(\hat{T} + V^{\text{PS}} - \epsilon_{n_i l_i}) |\tilde{\phi}_{n_i l_i}\rangle = C_{n_i l_i} k(r) |\tilde{\phi}_{n_i l_i}\rangle \quad (2.23)$$

$C_{n_i l_i}$ constants are chosen to make the logarithmic derivatives of the respective partial all-electron and pseudo wave functions equal on the augmentation sphere. If we define the projector

$$p_{n_i l_i}(r) = \frac{k(r) \tilde{\phi}_{n_i l_i}(r)}{\langle \tilde{\phi}_{n_i l_i} | p_{n_j l_j} \rangle} \quad (2.24)$$

corresponding to $\tilde{\phi}_{n_i l_i}(r)$, the $\langle \tilde{\phi}_{n_i l_i} | p_{n_i l_i} \rangle = 1$ condition is automatically satisfied. The projector and partial waves obtained from the steepness condition can be achieved using Gram-Schmidt or a similar steepening method.

2.7 Core Density and Unscreened Potential

The required quantities in the PAW atomic data set are all-electron and pseudo-core electron density and n_c , $\tilde{n}_c$ ve $v_H[\tilde{n}_{Zc}]$ quantities, which are the core Hartree potential. n_c can be obtained directly from the whole electron wave function from the atomic solution of the Schrödinger equation, $\tilde{n}_c$ can be obtained

from the polynomial pseudoization. There are two approaches to obtaining $v_H[\tilde{n}_{Zc}]$. According to the Blöchl method, it is defined as

$$v_H[\tilde{n}_{Zc}] = V^{\text{PS}} - v_H[\tilde{n} + \tilde{n}_c + \hat{n}_B] - v_{\text{xc}}[\tilde{n} + \tilde{n}_c] \quad (2.24)$$

H in subscripts indicates Hartree and xc indicates exchange-correlation potential. One of the important parameters of this equation is the compensation charge density $\hat{n}_B$ added to the pseudo core density so that it has the same multipole values as the all-electron core density. $\hat{n}_B$ in the form of

$$\hat{n}_B(r) = g_0(r) \int_0^{r_c} (n(r) - \tilde{n}(r) + n_c(r) - \tilde{n}_c(r) + n_Z(r)) dr \quad (2.25)$$

we can define. Where n_Z is the core charge density and $g_0(r)$ is the compensation load shape function. There are three different forms in common use for this function: 1. sinc

$$g(r) = \left(\frac{\sin(\pi r/r_c)}{\pi r/r_c} \right)^2 \quad (2.26)$$

$g(r)$ in Gaussian, with d scale constant,

$$g(r) = \exp(-(r/d)^2) \quad (2.27)$$

and in Bessel functions it can be defined as

$$g(r) = \sum_{i=1}^2 \alpha_i j_0(q_i r) \quad (2.28)$$

Another definition of the $v_H[\tilde{n}_{Zc}]$ unscreened potential was defined by Kresse-Joubert as

$$v_H[\tilde{n}_{Zc}] = V^{\text{PS}} - v_H[\tilde{n} + \hat{n}_K] - v_{\text{xc}}[\tilde{n} + \hat{n}_K + \tilde{n}_c] \quad (2.29)$$

Here, the compensation load density is defined as

$$\hat{n}_K(r) = g(r) \int_0^{r_c} (n(r) - \tilde{n}(r)) dr \quad (2.30)$$

An important criterion for compatibility between the ability of pseudopartial waves and all electron partial waves to describe the same physical properties is that

their logarithmic derivatives are compatible with as wide an energy range as possible.

2.8 Optimization Process

To summarize each step of the PAW dataset production process described above in terms of number of parameters and type of method:

1. In the local pseudopotential selection stage, three parameters as r_c , E_{loc} and l_{loc} and three different pseudopotential types as Troulliers-Martins, ultrasoft and Bessel
2. For each angular momentum channel during the generation of partial pseudo-wave and projectors, the cut-off radius r_{ni} , l_i and reference energy E_{ni} , l_i . In practice two pseudo partial waves and projector functions are defined per angular momentum channel For GW type calculations, it is recommended that this number be three at the most. Since one of these channels is taken as a bound state per each angular momentum number, the reference energy of these states is certain. However, other states are defined for non-connected states and reference energies need to be optimized. In the partial pseudo wave generation process, there are two types as Vanderbilt and Blöchl approaches, and in the Vanderbilt process there are also two types in the subheadings of polynomial and Bessel.
3. The shape function of the compensation charge density can be selected among three different types as sinc, Gaussian or Bessel.

If we look at the characteristic dimensions of the relevant parameters in order to understand the dimensions of the parameter space to be examined in the optimization process; The number of angular momentum channels is four in the systems envisaged to be examined. r_c and r_{ni} , l_i parameters are expected to be between [2,3] Bohr, and E_{loc} and E_{ni} , l_i parameters are expected to be between 0.1 Rydberg. Assuming a resolution of 0.05 Bohr for position parameters and 0.1 Rydberg for energy parameters, an optimization using 2 projectors per angular momentum channel would require a minimum in a very high dimensional space

such as F. Considering the number of methods that can be chosen as combinations, it is clear that it is not possible to find a minimum based on brute force in such a large space. Approximate methods, which are generally referred to under the title of evolutionary algorithms and which are used to find the parameters that will optimize a given objective function by methods inspired by biological evolution, are not differentiable in this type and serve to find the best approximate functions defined in multidimensional spaces [24].

Optimizing PAW datasets with genetic algorithm algorithmically:

1. Randomly selected from the above-given limits of E_{loc} , E_{ni} , l_i , r_c and r_{ni} , l_i parameters PAW dataset generated at values (let's call each of them an individual, and this set of N individuals, let's call it the initial generation).
2. As the fitness of each member of the generation, the fit of the logarithmic derivatives of the all-electron and pseudo wave functions, the lattice parameters calculated using that data set, the fit of the bulk modulus and magnetic moment with the FP-LAPW calculation, and the convergence cut-off energy required for the DFT calculation It will be calculated according to a function created from the values. These values will be a measure of how "fit" each individual is.
3. Repeat the following operations until sufficient fitness is reached:
 - (a) Select individuals with the best fit-values to be parents of the next generation.
 - (b) Bring these individuals by crossover or mutation to create a new generation.
 - (c) Determine the eligibility of new individuals according to the criteria mentioned above.
 - (d) Replace the old generation with the worst fit-values with the new generation.

3. PAW FOR LANTHANIDES

3.1 Electronic Structure of Cerium

The ground state of the cerium atom is $[\text{Ce}] = [\text{Xe}]4f^4 5d^1 6s^2$. Since $4f$ shell contains only a single electron with $L = 3$ and $S = 1/2$, if one does not consider the spin-orbital momentum interaction, there would be two degenerate energy levels with S parallel and anti-parallel to the orbital momentum. Because of the spin-orbit interaction, the good quantum number to describe the state of $4f$ electron is the total angular momentum J . Since the $4f$ shell is filled less than half, according to Hund's rule, it would split into $J = L - S = 5/2$ ($^2F_{5/2}$, S anti-parallel to L) and $J = L + S = 7/2$ ($^2F_{7/2}$, S parallel to L) states. $^2F_{5/2}$ has 300 meV lower energy compared to the $^2F_{7/2}$ state.

When the atom is in a crystal environment, the average electric field from the surrounding ions and electrons can be modeled as a crystal field which would lift the $2j + 1$ degeneracy of those levels.

When spin-orbit interaction is neglected, there are seven $4f$ orbitals that correspond to m_l values of $0, \pm 1, \pm 2, \pm 3$. A simple linear combination of the nonzero m_l values along with $m_l = 0$ form the general set of $4f$ orbitals. The cubic set of $4f$ orbitals are chosen as xyz (A_{2u}), x^3, y^3, z^3 (T_{2u}) and $z(x^2 - y^2), x(z^2 - y^2), y(z^2 - x^2)$ (T_{1u}).

When a cerium atom is placed at the center of the cube, as shown in Fig. 3.1a, the t_{1u} would have lobes pointing directly to the legends at the faces of the cube which would make those the highest energy states. Similarly, the eight lobes of the a_{2u} orbital point directly to the corners of the cube, so

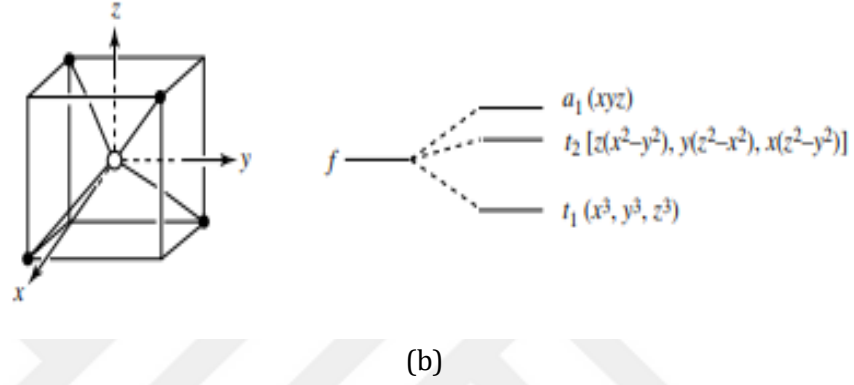
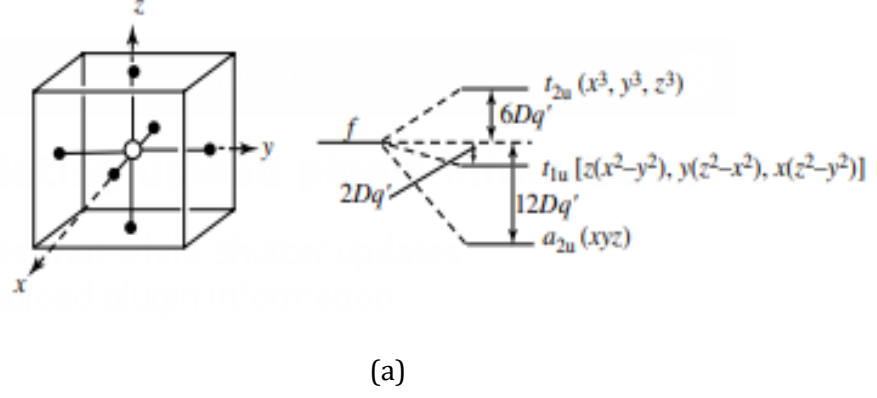


Figure 3.1: Splitting of 4f levels in given crystal field.

these states are expected to be the lowest energy state while t_{2u} states are the intermediate between a_{2u} and t_{2u} . The situation in tetrahedral symmetry can be analyzed similarly, as can be seen from Fig. 3.1b, the lowest energy state is t_{1u} while the highest one is a_{2u} .

Spin-dependent GGA+U calculations have difficulty converging to a global minimum due to the complicated energy landscape. Constraining the occupation matrix of the correlated manifold to a particular form for a number of initial self-consistency iterations has been used as a way to nudge the system towards the desired ground state. From the local symmetry properties of the Ce atom in the fcc structure, we have tried following initial f-occupations:

1. $|\psi_1\rangle = -\frac{1}{4} (\sqrt{6}|-1\rangle + \sqrt{10}|-3\rangle)$
2. $|\psi_2\rangle = \frac{1}{4} (\sqrt{10}|-1\rangle - \sqrt{6}|-3\rangle)$
3. $|\psi_3\rangle = \frac{1}{4} (\sqrt{10}|1\rangle + \sqrt{6}|3\rangle)$
4. $|\psi_4\rangle = -\frac{1}{4} (\sqrt{6}|1\rangle - \sqrt{10}|3\rangle)$
5. $|\psi_5\rangle = |-2\rangle$
6. $|\psi_6\rangle = |2\rangle$
7. $|\psi_7\rangle = |0\rangle$

The set $(|\psi_1\rangle, |\psi_4\rangle, |\psi_7\rangle)$ forms the t_2 group of cubic $4f$, while the set $(|\psi_2\rangle, |\psi_3\rangle, |\psi_6\rangle)$ has t_1 symmetry and $|\psi_5\rangle$ is a_{2u} .

Occupation matrices for $|\psi_i\rangle$ are:

1. $\rho_{\psi_1}(1,1) = 0.6, \rho_{\psi_1}(3,3) = 0.4, \rho_{\psi_1}(1,3) = \rho_{\psi_1}(3,1) = 0.45$
2. $\rho_{\psi_2}(1,1) = 0.4, \rho_{\psi_2}(3,3) = 0.6, \rho_{\psi_2}(1,3) = \rho_{\psi_2}(3,1) = -0.45$
3. $\rho_{\psi_3}(5,5) = 0.6, \rho_{\psi_3}(7,7) = 0.4, \rho_{\psi_3}(5,7) = \rho_{\psi_3}(7,5) = 0.45$
4. $\rho_{\psi_4}(5,5) = 0.4, \rho_{\psi_4}(7,7) = 0.6, \rho_{\psi_4}(5,7) = \rho_{\psi_4}(7,5) = -0.45$
5. $\rho_{\psi_5}(2,2) = 1$
6. $\rho_{\psi_6}(6,6) = 1$
7. $\rho_{\psi_7}(4,4) = 1$

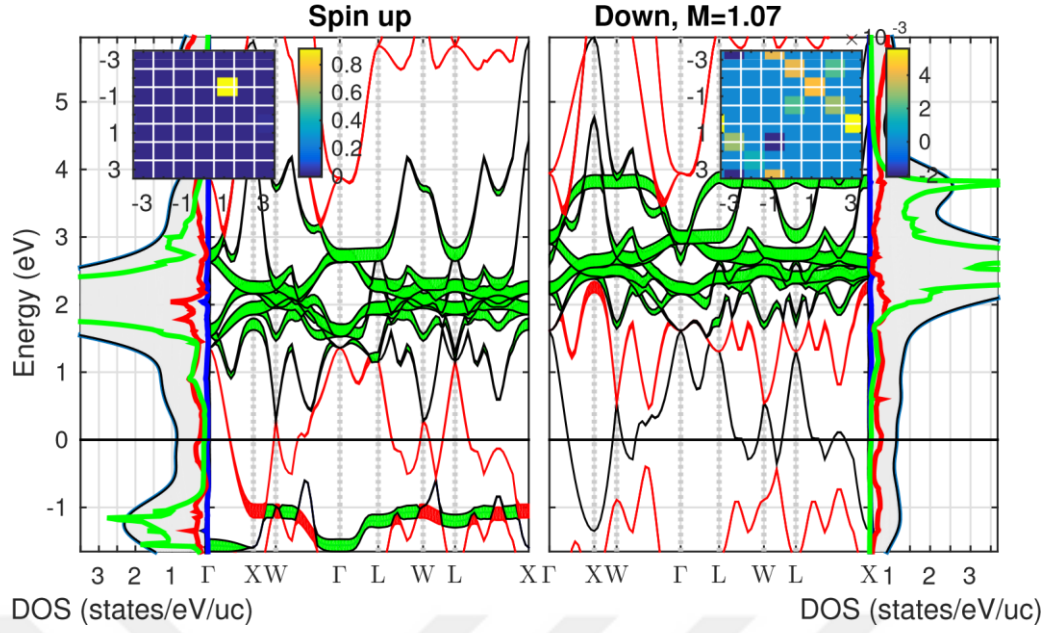


Figure 3.2: DOS and fat bands of Ce in sGGA+U approximation ($U=4$, $J=0.65$ eV). The width of the green and the red strips represents the 4f and 5d weights of the bands, respectively. Only bands 6-15 contain appreciable 4f contribution. So, the Wannier functions will be constructed out of those bands. The matrices in the insets are the 4f occupation matrices of the up and down spin channels.

3.2 Calculation of Hubbard U and Hund J for Cerium

Calculation of Hubbard U for α and γ cerium. The magnitude of Hubbard U is very important for DFT + U calculations on the properties of the cerium metal. From our previous computations, it is found that at low values of U the system has zero net magnetic moment and the DFT equation of state calculations converge to the volume of α cerium, while for $U > 3.25$ eV, the same methodology approaches to the volume of the γ phase with a net magnetic moment of 1 Bohr magneton. We have used the constrained random phase approximation (cRPA) to determine the Hubbard U and exchange J of Ce from the first principles. cRPA aims to determine U and J by calculating the screening of the Coulomb interaction by constraining the electronic transitions to those that do not involve the correlated 4f orbitals. The difficulty of isolating 4f states which are hybridized with 5d and 6s states makes the

calculations somewhat difficult. Using two different approximations to disentangle the 4f orbitals, we have obtained $J = 0.7$ eV and $U = 2.1$ and 4.5 eV. Here, we provide a short review of the calculation of the Hubbard U and Hund exchange J parameters for Ce. Calculation of U and J parameters starts with a well converged LDA or GGPWA calculation with high number of bands included in the model. The details of such calculations are presented in Ref. [13]. The relevant Abinit parameters of the calculations will be presented below for ease of reproduction of the results.

3.3 Dataset 1: Well Converged LDA Calculation

```
#####General parameters #####
nband      54
nline      5#well converged wfks
nnscllo    5#well converged wfks
#####LDA+U parameters #####
pawoptosc  1#Shishkin-Kresse oscillator mat
ucrpa      1#screening(Wannier)
symchi     0
upawu      0.0 eV
usepawu    1#LDA+U(for prt usefull quants)
##### k-grid parameters #####
ngkpt      3*8
```

The first dataset is a simple calculation of the density using GGA with 54 bands. We do not use symmetry in this calculation, so $nsym=1$. If symmetry is used ($nsym=0$), then the calculation of U and J will be valid, but the full interaction matrix described later will not be correct.

3.4 Dataset 2: Definition of Wannier functions

Two important physical parameters relevant to this dataset: Diagonalization of the Kohn-Sham Hamiltonian and definition of Wannier functions.

```
##### Wannier calculation #####
dmftbandi2      6 #Wannier func. (start)
dmftbandf2      20#Wannier func. (end)
getden2         -1
iscf2           -2
kssform         3
nbandkss2       -1#No of bands in KSS file
nbdbuf2         4
tolwfr2         1.0d-15#conv. criteria
usedmft2        1#to compute Wannier funcs.
```

To obtain well-converged eigenstates of the Kohn-Sham Hamiltonian, we use relatively high criteria of tolwfr2 1.0d-15. At this point one needs to determine which bands to be included in the construction of the Wannier functions. One needs to investigate the orbital character of the bands to decide which bands could form the correlated orbitals. The fat bands displayed in Fig. 3.2 can be used as guide for the choice. The width of the stripes in the figure indicate the magnitude of 5d (red) and 4f (green) character of the band. Although not discernable from the graph, only the bands from 6th to the 20th contain any 4f character and they are used to construct Wannier functions.

3.5 Dataset 3: Screening Calculation

Computation of the constrained polarizability and the dielectric function.

```
##### Screening calculation #####
ecuteps3        11.0# cut for dielectric mat.
freqremax3      10 eV
freqremin3      0 eV
getwfk3         -1
gwcaltyp3       2
gwpara3         1
nfreqim3        0
nfreqre3        1
optdriver3      3#Screening calculation
```

ucrpa_bands 3 6 20

Convergence of polarizability: nband and ecutepts are the two main variables that should be converged. Note that one must study the role of these variables directly on the effective interaction parameters to determine their relevant values. ucrpabands defines the bands for which the transitions are neglected.

3.6 Dataset 4: Effective Interaction

```
#####Effective interaction calculation #####
ecutsigx4      40.0#cut-off for Sigma_x
freqspmax4     10 eV
freqspmin4     0 eV
getscr4        3#SCR file(pre ds)
getwfk4        2#WFK file(ds2)
gwcaltyp4      2# activate HF or ucrpa
gwpara4        2
mqgrid4        300# Reduced
mqgriddg4      300# Reduced
nfreqsp4       1
nkptgw4        0#the GW correction: all BZ
optdriver4     4#Self-Energy calculation
```

ecutsigx is thus the main convergence parameter for this dataset. Note that as discussed in Appendix A of [13], high values of ecutsigx can be necessary because oscillator matrix elements in PAW contains the Fourier transform of (a product of) atomic orbitals.

To present an example of range of physical quantities calculated in such computations, below we present some of the outputs for the most relevant quantities:

3.7 Results

For an atomic wfn truncated at rmax =	100.0000
The norm of the wfn is =	1.0000
The bare interaction (no renormalization) =	23.1478 eV
The bare interaction (for a renorm. wfn) =	23.1478 eV
For an atomic wfn truncated at rmax =	2.5585
The norm of the wfn is =	0.9663
The bare interaction (no renormalization) =	22.7827 eV
The bare interaction (for a renorm. wfn) =	24.3990 eV

Here, the bare interaction is found to be 23.15 eV (which will be compared to the one calculated from the Wannier functions below.

$U^*=U(m_1, m_2, m_1, m_2)$ for the bare interaction

	1	2	3	4	5	6	7
1	24.640	23.112	22.483	22.167	22.492	23.152	24.296
2	23.112	23.802	23.116	22.860	23.123	23.269	23.124
3	22.483	23.116	24.419	23.481	22.909	23.153	22.496
4	22.167	22.860	23.481	23.951	23.487	22.898	22.178
5	22.492	23.123	22.909	23.487	24.436	23.161	22.502
6	23.152	23.269	23.153	22.898	23.161	23.884	23.164
7	24.296	23.124	22.496	22.178	22.502	23.164	24.665

Hubbard bare interaction $U=1/(2l+1) \sum U(m_1, m_2, m_1, m_2) = 23.1641$
0.0000

(Hubbard bare interaction $U=1/(2l+1) \sum U(m_1, m_1, m_1, m_1) =$
24.25680.0000)

Diagonal bare interactions are similar to the bare interaction on atomic orbitals (23.15 eV, as discussed above). It shows that the Wannier functions (obtained within bands 6-20) are localized similar to the atomic orbitals.

Hund coupling $J=U(m_1, m_1, m_2, m_2)$ for the bare interaction

-	12	3	4	5	6	7
---	----	---	---	---	---	---

```

1  24.640 0.734 0.521 0.355 0.524 0.741 0.172
2  0.734 23.802 0.551 1.013 0.591 0.278 0.735
3  0.521 0.551 24.419 0.300 0.738 0.557 0.524
4  0.355 1.013 0.300 23.951 0.300 1.010 0.356
5  0.524 0.591 0.738 0.300 24.436 0.555 0.522
6  0.741 0.278 0.557 1.010 0.555 23.884 0.742
7  0.172 0.735 0.524 0.356 0.522 0.742 24.665
(bare int) J= U-1/((2l+1)(2l)) sum_m1,m2 (U(m1,m2,m1,m2)
-U(m1,m2,m2,m1)) = 0.7449

```

Similarly, for the cRPA interaction, we obtain:

```

U'=U(m1,m2,m1,m2) for the cRPA interaction
-      1 2      3      4      5      6      7
1  5.084 3.817 3.349 3.192 3.356 3.816 4.732
2  3.817 4.512 3.868 3.734 3.873 3.949 3.820
3  3.349 3.868 5.004 4.262 3.714 3.864 3.353
4  3.192 3.734 4.262 4.804 4.267 3.729 3.195
5  3.356 3.873 3.714 4.267 5.017 3.869 3.356
6  3.816 3.949 3.864 3.729 3.869 4.510 3.818
7  4.732 3.820 3.353 3.195 3.356 3.818 5.092
Hubbard cRPA interaction for w=1, U=1/(2l+1) **2 sum
U (m1, m2, m1, m2) = 3.9161    0.0000

```

```

(Hubbard cRPA interaction for w=1, U=1/(2l+1)
sum U (m1, m1, m1, m1) = 4.8604 -0.0000)

```

```

Hund coupling J = U (m1, m1, m2, m2) for the cRPA interaction
-      1      2      3      4      5      6      7
1  5.084 0.625 0.470 0.344 0.474 0.634 0.172
2  0.625 4.512 0.483 0.844 0.521 0.272 0.629
3  0.470 0.483 5.004 0.280 0.632 0.491 0.474
4  0.344 0.844 0.280 4.804 0.280 0.837 0.345

```

```

5  0.474 0.521 0.632 0.280 5.017 0.487 0.471
6  0.634 0.272 0.491 0.837 0.487 4.510 0.632
7  0.172 0.629 0.474 0.345 0.471 0.632 5.092

```

```

cRPA int. J=U-1/((2l+1) (2l)) sum_m1, m2(U (m1, m2, m1, m2)
-    U (m1, m2, m2, m1)) = 0.6524    -0.0000

```

Average U and J as a function of frequency

omega	U(omega)	J(omega)
0.000	3.9161	0.0000

Table 3.1: Convergence of U and J with respect to E_c , number of bands $nband$, and reciprocal grid size $ngkpt$.

E_c	nband	ngkpt	U	J	E_c^e	E_c^Σ
20	54	3*8	3.92	0.65	10.8	39.9
30	54	3*8	3.91	0.65	21.6	39.9
30	54	3*16	3.76	0.65	21.6	39.9
30	74	3*8	3.86	0.65		
30	54	3*8	3.91	0.66	10.8	39.9

4. PAW OPTIMIZATION

The optimization process of an element's PAW datasets starts with the solution of the Schrödinger or scalar Dirac equations to determine the wave function and energy levels of the electrons in that element atom. In this study, atomic structures were investigated by solving the scalar Dirac equation, with the expectation that the high atomic numbers of the examined elements could show the effect of relativity, and for this purpose the atompaw program was used. Pseudopotential, electronic wave function and projection functions were also calculated with the same program. For this reason, it would be appropriate to describe the optimization process of PAW datasets through the elements of the input set of this program. As an example, the input file of the program atompaw for the Pr element is shown below.

```

Pr 59
LDA-PW scalarrelativistic loggridv4 1201 logderivrange -5 5 1000

```

6 5 4 4 0 0	!n for last occupied s,p,d,f,g,h orbitals
4 3 3	!3 electron in 4f
0 0 0	!end of partial occupations.
c	!core 1s
c	!core 2s
c	!core 3s
c	!core 4s
v	!valence 5s
v	!valence 6s
c	!core 2p
c	!core 3p
c	!core 4p
v	!valence 5p
c	!core 3d
c	!core 4d
v	!valence 4f
3	!basis contains s, p, d, f partial waves
2.4592 2.0264 2.429 2.0112	!rpaw, rshape, rvloc, rcore
n	
y	
0.3580	!p projector energy
n	
y	
0.7778	!d projector energy
y	
1.5948	!d projector energy
n y	
1.2513	!f projector energy
n custom polynom 2 5 15 vanderbiltortho sinc	
4 -1.1528 ultrasoft	
2.2137	!s1 match radius
2.0504	!s2 match radius
2.1795	!p1 match radius
2.0967	!p2 match radius
2.1801	!d1 match radius
2.1439	!d2 match radius
2.2077	!f1 match radius

2.3567

!f2 match radius

XMLOUT

DEFAULT

END

The purpose of the optimization process is to obtain a total of 21 parameters, shown in red in the given example, in such a way as to minimize the error of the PAW dataset to be obtained. First of all, let's open a little bit about what these 21 parameters are. The line defined as **2.4592 2.0264 2.429 2.0112** *!rpaw, rshape, rvloc, rcore* shows various distance values where all-electron and pseudo waves are selected identically. *rpaw* is the radius of the augmentation sphere, *rshape* is the cutoff point of the shape function to compensate for the charge density, *rvloc* is the mapping point of the local potential to the all electron potential, and *rcore* is the pseudo charge of the all-electron charge density. Describes the point at which it will be selected equal to its density. These four parameters play an important role in the suitability of the PAW dataset to describe the properties of the relevant element.

The next 3 or 4 parameters of the input are related to the definition of orbital projector functions. In the current study on the lanthanide series, we took $6s5s5p5d^n4f^m$ as the valence electron configuration. As shown in the table above, $n = 0$ for most of the elements. In this study, it was generally considered appropriate to produce two projectors per valence orbital. Therefore, 2 (5s and 6s) +1 (5p) +1 (4f)=4 or 5 (d orbitals) of the projector functions are for bound states and the energies of these projectors are bound to state energies. The remaining 3 or 4 projector energy are among the parameters that can be changed in the input set. Since there are no bonded d orbitals in the above example, the 4 unbound projector functions are described at positive energy.

The **custom polynom 2 5 15 vanderbiltortho sinc** line contains the technical details for generating projector functions. Here **polynom 2 5 15** describes how to generate pseudo partial waves and can be one of three different values **polynom, polynom2, rrkj**. **vanderbiltortho** describes the details of creating and erecting projectors and can be one of the **vanderbiltortho, svdortho, gramsschmidtortho**

options. The sinc part is the shape function and can be selected as sinc, gaussian, besel.

The line `-1.1528 ultrasoft` determines the type of local energy and pseudopotential. The ultrasoft part can be selected as ultrasoft or trouilliersmartin. In all calculations, the radius values are between [2.0,2.6] Au, the unbound projector energy values are between [0,10] Ha, and the local energy values are between [-2,10] Ha.

However, the 'error of a given PAW dataset' is not a well-defined quantity. Within the scope of the project in this study, various definitions of 'error' were studied and their effects on the equilibrium volume, bulk modulus, electronic structure and lattice vibration frequencies of the resulting PAW datasets were tried to be clarified. To better explain these 'error' definitions, it is necessary to describe the elements of the PAW dataset. Programs that calculate the properties of solidstate systems with quantum mechanical principles and mostly within the scope of density functional theory, various approximations are used to describe the electrons of the system and their interaction with the nucleus. In the PAW approach, which is one of them, the pseudo-wave and projector functions for all electrons selected as valence electrons for each atom type forming the system and the description of the pseudopotential of the atom form the elements of the PAW data set. The important difference between pure pseudopotential approximations and PAW sets is that different angular momentum dependent wave and projector functions are used in PAW set, whereas norm-protected pseudopotential approximations use only angular momentum dependent potentials. The primary selection criterion of the pseudo wave and projector functions that make up the PAW dataset is that the atomic properties calculated with these approximations and the all electron properties calculated without approximation are as close to each other as possible. This proximity is usually checked using two quantities. The most important of these quantities is the logarithmic derivative of all-electron and pseudo wave functions with respect to energy. The fact that these derivatives are identical over as wide an energy range as possible means that the electron binding and scattering properties of the atom can be made by the pseudo-wave description. Again, the small

difference between the all-electron and pseudocalculated energy levels indicates that the pseudo-description is sufficient to describe the structure of the atom.

Figure 4.1 shows the logarithmic derivatives of all-electron and pseudo wave functions calculated with random input parameters of the Ce element. In this example, it is seen that while there is agreement between the two derivatives

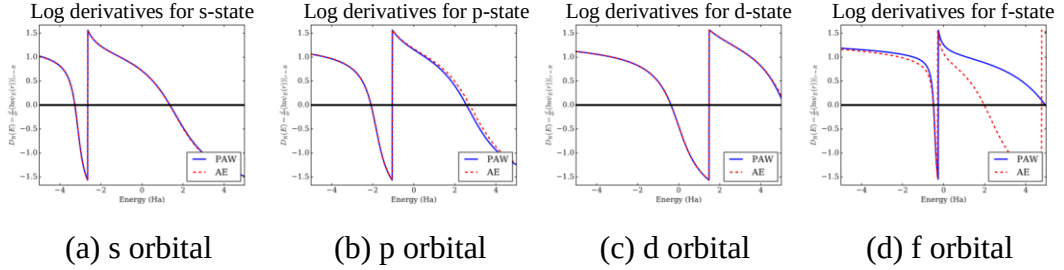


Figure 4.1: The inverse tangent of the logarithmic derivative of the all-electron and pseudo wave functions for the element Cerium.

for the s and d orbitals, the derivatives of the p and f orbitals are different. One of the important minimization quantities of the optimization process is the sum of the differences between these derivatives. Logarithmic derivatives are calculated at 1000 points in the $[-5.5]$ Hartree energy range to find this sum. At each point, the difference of the inverse tangent of all-electron and pseudo wave derivatives PAW was taken and the error was determined as the sum of these differences. The sum of these errors over four orbitals is defined as the total logarithmic error for the given input set.

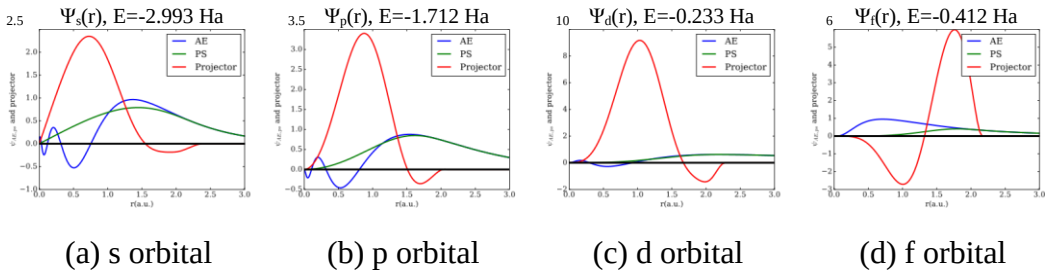


Figure 4.2: Projector functions with all-electron and pseudo wave functions for the element Cerium.

Another feature of good PAW dataset is that the ratio between the maximum value of the projection functions and the maximum amplitude of the all-electron and pseudo wavefunctions does not differ by more than one, that is, the projection function and wavefunctions are of comparable size. In Figure 4.2, some of the

projection functions with all-electron and pseudo waves of the Cerium atom PAW series whose logarithmic derivatives are given above are shown. In figure 4.2, all-electron, pseudo-wave and projector function sizes are comparable for the s orbital, It is seen that the maximum value of the projector function is very high, especially for the d and f orbitals. In the optimization process, the ratio of the maximum value of each projector function to the maximum of that orbital's all-electron and/or pseudo partial wave is also taken as one of the optimization variables. Let's call this value r_i . We have taken the value to be minimized as $P_i (1 - r_i)^2$ since it would be meaningless if the projector was too low.

We can define a general optimization problem as finding the values of x that will minimize the value of the function $f(x)$ attached to a vector x with n elements. Here $f(x)$ is called the objective function. In the problem we are examining, the elements of the vector x are 21 different parameters given in the example input above. However, it is not very clear what to choose as $f(x)$, and as an optimization problem, the most challenging part of the PAW dataset problem is to predetermine the quantity or quantities to be minimized, namely the objective function, as described above. In this direction, we have created various objective functions by considering properties such as logarithmic derivatives, amplitude ratios, all-electron and partial wave energy differences, equilibrium volume and bulk modulus. These objective functions were constructed from different combinations of logarithmic derivative differences (4), amplitude ratios (8), energy difference (1), unit cell volume (1) and bulk modulus (1) error variables. Of these combinations, we reviewed the most as

1. $f_1 : R^{21} \rightarrow R^{15}$
2. $f_2 : R^{21} \rightarrow R^2$
3. $f_3 : R^{21} \rightarrow R^1$

Here, the objective function R^{21} has 21 real number inputs, and R^{15} is logarithmic derivative differences (4), amplitude ratios (8), energy difference (1), unit cell volume (1) and bulk modulus means that it has 15 outputs with (1) error. In the definition of the objective function R^2 , the two output elements are chosen either as

the sum of the logarithmic derivative differences over the orbitals and the sum of the amplitude ratios over the 8 projectors, or as the relative error of the calculated equilibrium volume and bulk modulus relative to the experimental data. The objective function R^1 was evaluated as the sum of the logarithmic derivative differences (4), amplitude ratios (8), energy difference (1) variables. It should be noted here that the objective function f_1 and f_2 is multi-purpose, while the f_3 function is single-purpose. Single and multi-objective optimization algorithms are quite different. Optimizing multiple purposes at the same time is difficult; It is common for one goal to improve while the other worsens. We used genetic algorithms for both single- and multi-objective improvements. The main study subject of genetic algorithms is populations created from problem inputs. The algorithm tries to create new generations by mating fit individuals, considering the degree of fitness of individuals in the population and mutations, and to ensure that the individuals in the population are the best in terms of purpose as the number of generations increases. The optimization workflow, in general terms defined as:

1. Establishment of the initial population. Each individual of this population represents a PAW dataset and is represented by the 21 parameters in the example input given above. To have sufficient genetic diversity in the initial population, the parameter values of the individuals should be determined randomly within the limits given above for the relevant parameter. For genetic algorithms to sample an appropriately wide parameter space, the population number must be more than a certain multiple of the number of parameters that define each individual. In this study, we examined populations of 40, 120, and 300 individuals. Again, the initial individual fitness for purpose values needs to be calculated with the chosen objective function $f_i(x)$.
2. Creating a new generation population by mating some of the best ones determined from the current population, preserving some of them with random mutations and calculating the fitness for purpose values of individuals in the new population. There are different approaches in the

literature regarding technical details such as ranking of individuals in terms of fitness for purpose and mutation rate.

3. Repetition of process 2 according to predetermined criteria. This criterion can be the total number of generations, or it can be chosen as the difference between the generations in the objective function value below a certain threshold, that is, the new generations do not produce more fit individuals.

In this way, logarithmic derivatives, energy-volume curves and Bulk modulus values obtained from PAW data sets obtained as a result of the optimization process, all electron, pseudo wave functions and graphs of reflectors, electronic state densities for up and down spin states, electronic band structures, as well as a graphical representation of the matrix, which is an indicator of the placement of electrons in the f-state, and the values of some other parameters used in the production of PAW data sets are given below, respectively, for the elements mainly analysed in this study as examples.

4.1 Elastic Constants of Lanthanides

In this section, we present the results of elastic constant calculations for all the lanthanides, except lanthanum, which does not have any 4f electrons. All the calculations reported in this section were obtained by using PAWs as obtained from the optimization procedure outlined in the previous subsection.

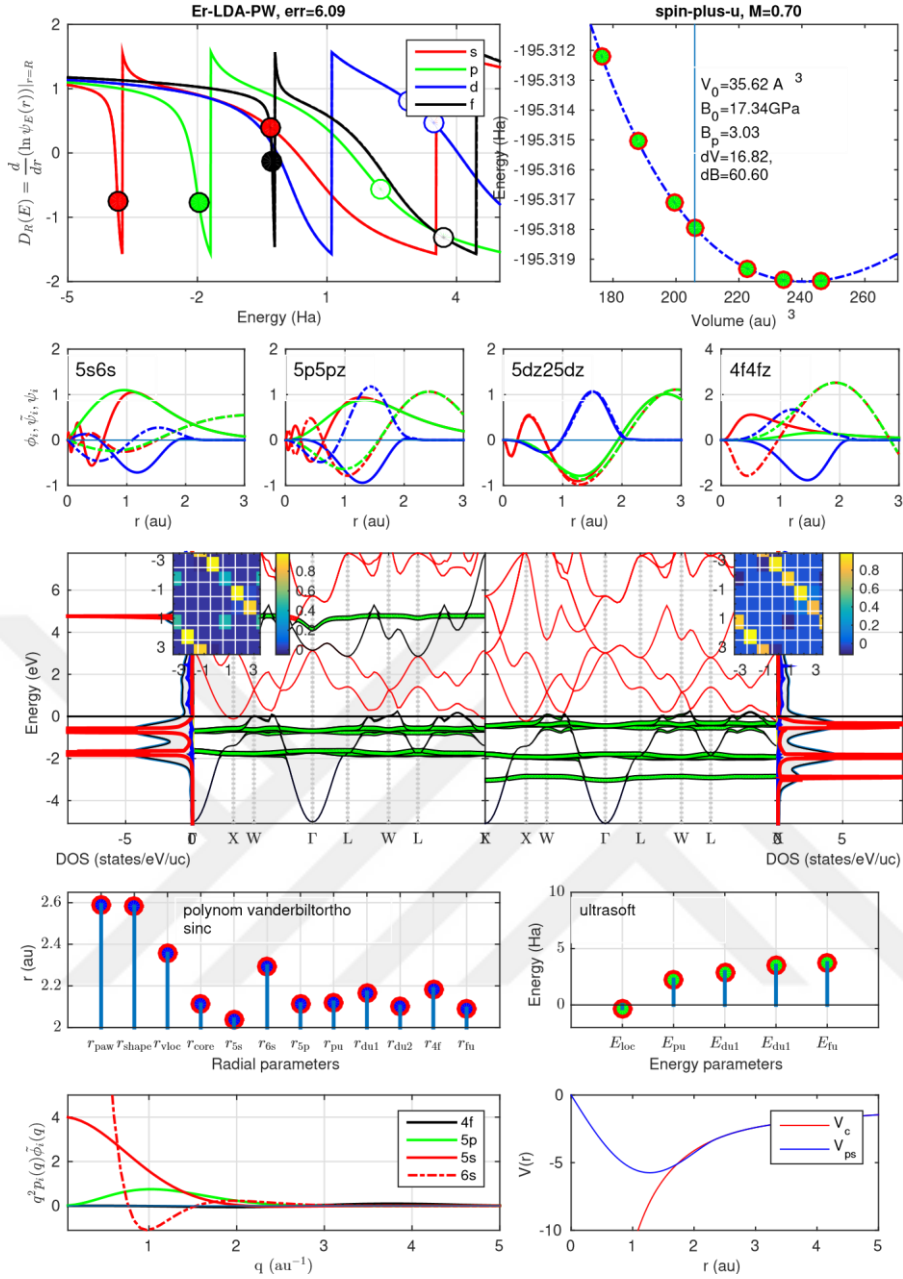


Figure 4.3: All the atomic and solid-state related quantities considered in the optimization of the PAW set for the element Er. From the top, the tangent of the logarithmic derivatives and EOS fit (first row), all electron and pseudo waves (second row), fat band structure, electronic density of states, and 4f occupation matrices (third row), optimized parameters for Vanderbilt and ultrasoft pseudo schemes (fourth row), Fourier transform of the smooth wavefunctions and pseudopotential (the last row).

Table 4.1: Lattice constants (a and c in $^{\circ}\text{\AA}$), elastic tensor components (C_{ij} in GPa), bulk modulus (B in GPa), and root mean square error of theoretical calculations for lanthanides Ce to Nd. The rows labeled Calc. are those calculated in this thesis.

Ce	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	r_{RMS}	a	c	B	Ref.
Calc.	21	17			18					18.33	
Exp.								5.16			[14]
	24.1	10.2			19.4			5.16		14.83	[15]
	26.01	14.26			17.30					18.18	[16]
Theo.	23.8	10.4			15.2					14.8	[17]
	32.5	17.2			14.3			5.29		22.3	[18]DFT
	37.9	26.4			20.9					30.2	[19]DFT
	24.15	15.33			18.19			5.16		18.27	[20]
	43.46	23.59			21.71			5.29		30.2	[21]DFT
	24.4	5.5			18.3					14.8	[22]
Pr											
Calc.	51.2	18.0	13.8	52.6	12.3	18.4	19	3.73	11.99	26.2	
Exp.								3.67	11.83		[14]
	49.35	22.95	14.3	57.40	13.60	13.20				28.8	[23]
Theo.	60.77	25.36	17.88	67.34	17.4		22			34.57	[21]
Nd											
Calc.	61.08	19.69	16.88	66.36	17.14	21.52	10 21	3.65	11.75	32.12	
Exp.								3.65	11.79		[14]
	58.78	24.58	16.20	65.13	16.20					30.66	[24]
	54.82	24.62	16.60	60.86	15.03	15.10				31.8	[24]
Theo.	59.9	29.8	16.5	72.2	18.8		13 17	3.69	11.87	31.63	[25]DFT
	55.2	27.9	14.2	65.1	18.5		9 10	3.67	11.80	28.32	[25]DFT
	65.24	25.88	17.77	71.77	19.11		12 17			36.12	[21]DFT

First, we present the results for the first three elements of the series, namely Ce, Pr, and Nd, in Table 4.1. While Ce crystallizes in the face-centered cubic structure under ambient conditions, Pr and Nd have a double hexagonal closed-packed structure as the ground state. The crystal symmetry determines the number of nonzero elements of the elastic constant tensor. There are three independent nonzero C components for cubic structures (C_{11} , C_{12} , and C_{44}). For the hexagonal lattice, in addition to those elements C_{13} , C_{33} , and C_{66} are also expected to be nonzero. The column of root mean square error r_{RMS} in the table is a measure of the error in the calculations with respect to the reported experimental data and is the square root of the sum of the squares of the differences between the experimental and theoretical data. From Table 4.1, it can be seen that for cerium, the reported elastic constants calculated with the DFT show a wide range of values, especially for C_{11} and C_{12} . Also, the experimentally reported values for C_{12} differ by more than 40 %. These experimental disagreements for the elastic constants are found in most of the lanthanides data, which makes a sound comparison of the two difficult. For Pr and Nd, our results for the lattice parameters a and c are found to be in excellent agreement with the values in the literature, while the average error in reproducing the elastic tensor components is satisfactory.

As the second group of results, we present the results of the set of calculations for the rest of lanthanides series of elements from Pm to Lu in Table 4.2. Most of the elements in this series also have a simple hexagonal or double hexagonal close-packed structure and have six independent elastic tensor components. Eu and Yb are the exceptions to this rule, while Eu crystallize in body-centered cubic structure, Yb has the fcc structure and both have only three independent and nonzero elastic constants. As can be seen in the table, elements in the hexagonal class have C_{11} and C_{33} around 60-80 GPa and off-diagonal responses around 20 GPa. The elastic constants of the cubic structure are found to be around 20 GPa. The difference in elastic constants is also seen in the bulk modulus data, which is expected because both quantities are measures of the structure's response to external mechanical disturbances, albeit different in character. The results reported in Table 4.2 show that our optimized PAW sets are able to reproduce the structural as well as elastic properties of the lanthanide series of 4f elements extremely well in a systematic

way. The agreements between our calculated lattice parameters and the experimental measurements are especially good. One should note that the experimental data on the lattice parameters have much less error compared to those on the elastic data due to the methods used to obtain them and the number of studies reported.

Table 4.2: Lattice constants (a and c in Å), elastic tensor components (C_{ij} in GPa), bulk modulus (B in GPa), and root mean square error of theoretical calculations for lanthanides Pm to Lu. The rows labeled Calc. are those calculated in this thesis.

Pm	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	r_{RMS}	a	c	B	Ref.
Calc.	52.91	15.93	19.64	63.76	17.01	18.33		3.62	11.66	32.03	
Exp.								3.65	11.65		[14]
Theo.	70.36	24.63	18.62	77.17	21.00		23			37.96	[21]DFT
Sm											
Calc.	68.77	24.92	31.35	93.77	19.74	20.54		3.68	5.85	46.79	
Exp.								3.61	11.66		[14]
Theo.	61.81	21.27	24.56	68.58	18.64		23			36.91	[21]
Eu											
Calc.	16	12			15			4.56			
	18	13			15			4.56		14.7	
Exp.								4.58			[14]
Theo.	16.46	10.55			16.34					12.52	[21]
	17.79	14.67			6.37					15.71	[26]
Gd											
Calc.	64.53	21.49	21.89	71.97	17.88	21.94	21	3.62	5.78	36.92	
Exp.								3.63	5.78		[14]
	78.80	31.45	19.10	78.99	23.78					38.43	[27]
Theo.	68.26	21.00	30.04	80.3	21.01		31			41.73	[21]
Tb											
Calc.	69.48	16.85	21.5	78.7	26.17	24.54	19 17	3.62	5.63	38.48	
Exp.								3.61	5.70		[14]
	78.36	27.77	20.05	82.43	25.18					37.93	[27]
	67.88	24.32	22.99	72.25	21.40	21.78				38.8	[28]
Theo.	67.88	24.32	22.99	72.25	21.4		14 0	3.59	5.69	38.29	[29]
	73.8			80	23.1	20.4					[30]
	78.8	23.3	22.8	94.8	19.9		15 16			43.22	[31]
	68.43	20.07	28.59	79.25	21.85		24 14			40.87	[21]
Dy											
Calc.	72.52	35.05	31.06	96.77	24.86	27.68	31 31 28	3.59	5.55	46.71	
Exp.								3.59	5.65		[14]
	80.1	36.7	18.6	85.1	26.8					38.88	[32]
	81.04	37.40	18.75	85.06	26.77					39.09	[33]
	70.7	25.4	20.8	78.9	24.7	24.6				38.11	[34]
Theo.	74.7	26.2	22.3	78.7	23.1	24.3	17 18 5			39.96	[35]
	74.7	26.2	22.3	78.7	24.3	24.3	17 17 4			39.95	[36]
	74.4	19.0	23.4	91.7	17.4		29 30 20			41.06	[31]
	70.93	20.53	28.75	84.67	23.97		32 32 19			42.14	[21]
	70.7	21.93	17.6	70.5	21.27	28.88	22 23 13			35.24	[37]

Ho														
Calc. Exp.	88.90	31.39	29.97	83.37	25.55	30.28	30	23	25	30	3.57	5.52	48.76	
	76.12	26	20.72	80.15	25.92	25.06					3.57	5.62	40.8	[14]
Theo.	76.1	24.8	20.6	77.6	25.7								39.10	[38]
	79.90	26.60	18.45	82.23	28.47								39.12	[32]
	77.2			84.4	27.5	26.2		5	7	3				[33]
	75.3	19.6	24.3	93.8 ³⁵	17.7			21	21	26			41.98	[39]
	75.40	22.30	29.63	85.06	26.74			20	21	28			44.12	[31]
														[21]
Er														
Calc. Exp.	75.2	12.4	12.8	80.4	28.5	28.5	31	33	33				34.12	
	86.3	30.5	22.7	85.5	28.1	27.9					3.56	5.69	43.40	[14]
Theo.	87.00	29.00	23.12	81.20	27.60								43.35	[40]
	83.88	29.26	24.21	84.32	26.45								43.53	[27]
	77.8	20.2	25.8	97.3	19.7								43.69	[41]
	81.54	24.27	28.34	88.05	28.85			22	22	20			45.82	[31]
								15	14	12				[21]
Tm														
Calc. Exp.	88.68	49.06	18.27	88.49	24.45	25.14		29			3.75	5.79	39.54	
	86.3	31.0	24.5	84.0	27.7						3.53	5.55	44.32	[14]
Theo.	77.3	19.7	16.9	96.0	25.6			23					39.63	[42]
	88.44	25.58	28.04	94.21	30.28			11					48.23	[31]
														[21]
Yb														
Calc. Exp.	19.0	8.29			15.61			14			5.16		11.86	
	18.62	10.36			17.72						5.48			[14]
Theo.	11.62	6.47			11.06			38			5.45		13.11	[43]
	18.7	10.6			18.8			4					8.3	[44]
	18.1	10.6			18.5			3					13.3	[17]
	18.6	10.4			17.7			0					13.1	[45]
	23.21	12.91			17.44			20					13.13	[22]
													16.34	[21]
Lu														
Calc. Exp.	84.46	31.53	12.85	86.67	26.16	29.63		24			3.49	5.42	37.51	
	86.23	32.03	28.0	80.86	26.79	27.10					3.51	5.54	47.6	[14]
Theo.	82.2	20.2	25.5	99.49	16.8			26					44.86	[46]
	95.84	31.38	28.73	98.11	32.69			15					51.94	[31]
														[21]

Table 4.3: Calculated bulk (B) and shear (G) moduli, Young moduli (E), in GPa, compressibility (β , in 1/GPa), the Pugh's indexes (G/B), Poisson's ratio (ν), and Zener anisotropy factor (A),

Pro.	Pr	Nd	Pm	Sm	Gd	Tb	Dy	Ho	Er	Tm	Lu
B_V	27.3	32.8	31.1	45.2	36.8	37.5	48.5	49.3	34.09	48.6	41.1
G_V	16.3	20.33	18.06	21.31	20.67	25.57	26.91	27.90	29.37	27.88	30.250
B_R	25.1	31.40	32.95	48.41	36.99	39.47	44.96	48.20	34.15	30.52	33.90
G_R	15.5	19.94	17.97	20.97	20.37	25.48	26.74	27.74	29.27	26.77	29.53
B_{av}	26.2	32.12	32.03	46.79	36.92	38.48	46.71	48.76	34.12	39.54	37.51
G_{av}	15.9	20.14	18.02	21.14	20.53	25.51	26.83	27.82	29.32	27.32	29.89
E	39.7	49.96	45.51	55.12	51.96	62.68	67.55	70.12	68.38	66.62	70.85
ν	0.25	0.24	0.26	0.30	0.27	0.23	0.26	0.26	0.16	0.21	0.19
β	0.039	0.031	0.031	0.020	0.027	0.03	0.021	0.021	0.03	0.025	0.027
G/B	0.61	0.63	0.56	0.45	0.56	0.66	0.57	0.57	0.86	0.69	0.80
mach:	2.13	1.87	1.88	2.37	2.06	1.47	1.88	1.91	1.20	1.62	1.43
A	0.65	0.73	0.88	0.79	0.77	1.00	0.93	0.91	0.88	0.70	0.72
f:	1.07	0.95	0.67	0.50	0.84	0.76	0.69	1.13	0.92	1.44	1.22
Au:	0.32	0.14	-0.03	0.01	0.07	-0.04	0.11	0.05	0.02	0.80	0.34

Finally, we report the derived elastic properties which are obtained from the calculated values in Tables 4.2 and 4.1 in Table 4.3 from Pr to Lu in the series. Data for Ce and Eu are missing from the table.

5. PROPERTIES OF CERIUM METAL

Cerium metal undergoes an interesting fcc to fcc (γ to α) phase transition with approximately 18% volume collapse under 0.8 GPa pressure at room temperature or when the temperature is lowered below 100 K under ambient pressure conditions. The mechanism for the transition has been the subject of many experimental and theoretical investigations over the years. The equation of state (EOS) and the pressure dependent elastic properties of elemental cerium have been studied by many groups over the last five decades by using various experimental techniques [15,16,47–60] to understand this peculiar phase transition, and the isostructural phase transition of Ce has also been investigated by measurements of the elastic constants as function of pressure. While the reported equilibrium volumes for the α - and γ -phases agree with each other in these studies, the bulk modulus there are significant differences among the reported bulk modulus values, which might be due to the insufficiency of the EOS model used to fit the data. Jeong *et. al.* [55] claimed that $C^* = (C_{11} - C_{12})/2$ the shear modulus is insensitive to pressure around the phase transition point, while Lipp *et. al.* [60] have studied the pressure dependent elastic properties of Ce at high temperatures. Contrary to Jeong *et. al.* [55], claim that C_{11} does not decrease under pressure, so a change in C_{12} must be the source of pressure dependence of the bulk modulus.

Almost all electronic structure method has been used to study the energetics and the change in spectral properties of Ce around the $\gamma - \alpha$ transition [49,61–84]. The approach in these studies range from the most basic density functional theory (DFT) with local density approximated exchange correlation functional to the DFT + dynamical mean field (DMFT) level which has been developed to account for the strongly-correlated electrons. Among the many early electronic structure studies, [61] and [49] are the first two reports of the self-consistent electronic structure of Ce. Glotzel [49] have used the linear muffin-tin orbital method (LMTO) and the local spin density approximation for the exchange-correlation to investigate the structural and magnetic properties of Ce. They have observed, similar to what we found, that at the γ -volume, $4f$ band spin polarises with an approximately 1 Bohr magneton per atom. (Similar results were reported by Refs. [62–64]). Tian *et. al.*

[74] have used the LDA + Gutzwiller method, which accounts for the strong correlation effects in the $4f$ shell, to study the zero temperature phase diagram of Ce and reported values V (28.49) and B (27.6) values in good agreement with the experimental data for the phase α . Various DFT+ U and DFT+DMFT studies report lattice constants that are close to the α - or the γ -volume, but the bulk modulus contains generally high errors [72,76,78,80,81].

The elastic constants of α - and γ -phases of Ce have also been investigated by a number of groups [17–22,85,86] theoretically. Ref. [18] uses the linear response in the density functional perturbation theory framework to deduce the elastic constants. Baria *et. al.* [17] have used a phenomenological pseudopotential method to calculate phonon dispersions and deduce elastic properties. Dupont *et. al.* [20] have used molecular dynamics with embedded atom model potential parameters to calculate the elastic properties of Ce. Ouyang *et. al.* [21] presented the elastic constants of γ -Ce along with those of other lanthanides. Similar to the disagreements for the bulk modulus, there exist large discrepancies between the reported theoretical and experimental elastic constants for the metallic Ce.

There have been a number of controversial issues concerning the theoretical studies on Ce: The ground state at zero temperature and ambient pressure is the α -phase, which does not have a net magnetic moment. At room temperature and ambient pressure, Ce exists in the γ phase with net magnetic moment. At both LDA and GGA levels of DFT, most of the studies find the α -phase as the lowest energy state. Since the very early SLDA calculations, it has been found that DFT results indicate the emergence of a net magnetic moment for unit cell volumes around V_γ . Some studies indicate a double-well structure in the EOS (centered around V_α and V_γ). Amending LDA and GGA with Hubbard and Hund corrections (+ U method) was found to solve some of the problems, such as the location of Hubbard satellites in the electronic structure around the Fermi surface for sufficiently large U values, but leads to the ground state being γ -phase of zero temperature, contrary to the experimental findings. Although several first-principles methods have been developed to determine the value of U , it has been difficult to compute a unique value of U that can be used to solve the problem of ground state and spectra problem simultaneously. Another contentious issue in theoretical studies on Ce was the

importance of spin-orbit interaction; while some studies found that its inclusion was crucial [76,78], others claimed its role is minimal in obtaining agreement with the experimental results [87]. It has long been understood that DFT has deficiencies in describing the physics of strongly correlated systems, and many-body techniques are needed to properly describe the peculiarities of such systems. LDA+ U , LDA+DMFT, and LDA+G as well as LDA+GWA methods.

Our aim in the present study is to investigate the volume-dependent elastic properties of metallic cerium with different approximations, such as GGA, sGGA, GGA+ U , sGGA+ U and sGGA+ U +SO, to assess the suitability of those approximations in describing the energy of a model strongly-correlated electron system. The elastic constants and EOS of a solid are determined by the strain derivatives of the total energy.

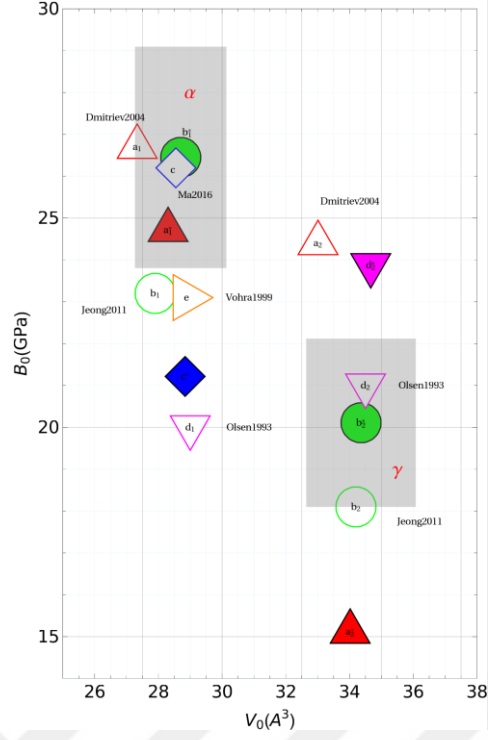
5.1 Review of the Literature

In this subsection, we provide a brief overview of the experimental and theoretical literature on the ground-state structure of the α - and γ -phases of the elemental cerium metal. Since various values for the equilibrium volume and bulk modulus for both phases are quoted in the literature, our aim here is to make a critical assessment of those reported experimental results by using several equation-of-state formulations. Furthermore, we analyze the findings of a wide spectrum of theoretical studies to investigate the possible sources of the failure of density functional methods to reproduce the experimentally observed structural properties of cerium in a consistent manner.

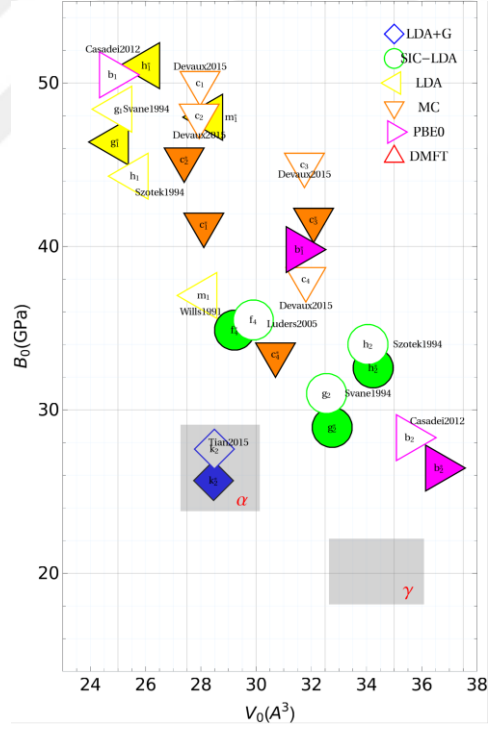
5.2 Structural Properties

We have considered a number of equations of state formulations that are widely used in describing the energy-volume or pressure-volume relation for solids. The list of models is given in Table 5.1. Figure 5.1a) presents the bulk modulus and equilibrium volume values obtained by fitting the experimental pressure dependent volume data of Refs. [53–56,59]. The empty and shaded plot markers in the figure indicate the B and V values quoted in the relevant reference and the result of our re-fit procedure, respectively, while the gray rectangles illustrate the region with $\pm 5\%$ volume $\pm 10\%$ bulk modulus error for the α - and γ -phases. Figure 5.1a) indicates

that although both our fits and the original fits produce very similar equilibrium volumes for both phases, there are appreciable differences for the bulk modulus (up to 15% for γ - and 30 % for α -phase) among the original data sets. It is interesting to note that none of the bulk modulus data that we obtain, except for the α Ce data of Dmitriev *et.al.* [56], agrees well with the results reported in the literature. Furthermore, none of the EOS considered in the present study fits the data of Ref. [53,54] reasonably well. We have checked that the norms of the fit residuals are smaller for the parameters we obtained compared to those reported. After a careful examination of all the available data, we claim that the best reference equilibrium volume and bulk modulus data for both phases of cerium are the results of our best fit to the data of Ref. [55] to $B_0=26.5$ GPa, $V_0=28.70 \text{ }^\circ\text{A}^3$ for the α - and $B_0=20.1$ GPa, $V_0=34.02 \text{ }^\circ\text{A}^3$ for the γ -phase. It is generally accepted that the bulk moduli measured at room temperature and the one calculated in the DFT framework (which is essentially a zero temperature calculation) would differ due to zero-point vibrations and thermal effects, which can be deduced by using phenomenological formulas [89]. The combination of these effects is found to be 1.1 and 0.8 GPa for the α - and γ -phases, respectively. Therefore, one would expect the zero temperature bulk moduli of α - and γ -Ce to be 25.5 and 19.3 GPa, respectively.



(a) Experimental



(b) Theory

Figure 5.1: Equilibrium volume and the zero pressure bulk modulus of cerium from various experimental (a1,a2: [56], b1,b2: [55], c: [59], d1,d2: [61], e: [54]) and theoretical data (b1,b2: [87], c1,c2,c3,c4: [84], h1,h2: [67], f1,f2: [71], g1,g2: [66], k2: [81], m1: [88]). Solid plot marks indicate our re-fitted V_0 and B_0 values while the empty marks show the original values reported in the relevant study.

Table 5.1: Equations of States (EOS) used in this study ($x = (V/V_0)^{1/3}$).

Equation	$E(V)$
Birch-Euler [93]	$E_0 - \frac{9B_0V_0}{16x^6} (x^2 - 1)^2 [(B'_0 - 6)x^2 - B'_0 + 4]$
Birch-Lagrange [93]	$E_0 - \frac{9}{16}B_0V_0 (x^2 - 1)^2 (B'_0 (x^2 - 1) - 2)$
Mie-Gruneisen [94]	$E_0 - \frac{9B_0V_0}{3B'_0-8} \left(\frac{1}{x} - \frac{x^{7-3B'_0}}{3B'_0-7} - 1 \right)$
Pack-Evans-James [95]	$E_0 + \frac{B_0V_0}{(B'_0-1)^2} [e^{-3(B'_0-1)(x-1)} + 3(B'_0-1)x - 3B'_0 + 2]$
Poirier-Tarantola [96]	$E_0 - \frac{9}{2}B_0V_0 \ln(x)^2 [(B'_0 - 2) \ln(x) - 1]$
Tait [97]	$E_0 + \frac{B_0V_0}{(B'_0+1)^2} \left[(B'_0 + 1)x^3 + e^{-(B'_0+1)(x^3-1)} - B'_0 - 2 \right]$
Vinet [98]	$E_0 + \frac{2B_0V_0}{(B'_0-1)^2} \left[2 + e^{-\frac{3}{2}(B'_0-1)(x-1)} (-3B'_0(x-1) + 3x - 5) \right]$

Almost all ab initio electronic structure calculation methods that employ density functional theory and its extensions have been used to study the peculiar structure of cerium in the last 40 years [48]. We have chosen a small subset of those computations for further analysis and present the reported equilibrium volume and the bulk modulus values along with the results of our re-fits to the reported total energy versus volume data in figure 5.1b. Note that the $E - V$ data we use in the fits are picked digitally from the published curves, which introduce some errors. The considered set of methods include the bare bone density functional methods such as LDA [66, 67, 88], as well as various computational techniques developed for the calculation of the energy of strongly correlated electronic systems, such as self-interaction corrected LDA [66, 67, 71], Hubbard corrected DFT (LDA+ U) [71] or dynamical mean-field theory (LDA+DMFT) [77], LDA+Gutzwiller approach (LDA+GA) [74, 79, 81], Monte Carlo [84] methods and DFT with hybrid functionals or exact exchange formulation (EX+cRPA@PBE0) [87]. Our fits agree reasonably well with the most of the reported results; only for the EX+cRPA@PBE0 results of Casadei *et.al.* [87], we find a large difference in both the volume and the bulk modulus. With the exception of Ref. [81], none of the considered methods were found to reproduce the experimental V_0 and B_0 values simultaneously as can be seen from Figure 5.1b). However, data can be group into

two different sets according to the agreement for the volume; one set of calculations predicts the volume of the α -phase well (LDA [86], MC [86], SIC-LDA [71], LDA+G [81]) while another set describes the volume of the γ -phase (SIC-LDA [66,67] and EX+cRPA@PBE0 [87]) in good agreement with the experiments. The bulk modulus is found to be overestimated by almost all the methods, with the exception of the LDA + GA calculations of Ref. [81]. Although B_0 values reported by Refs. [87] and [66] are close to the $\pm 10\%$ limits of the α Ce bulk modulus, the corresponding volumes for those calculations are close to that of the γ -phase. A surprising finding from Fig. 5.1 is that the SIC-LDA which is one of the oldest methods in the considered set is also the one of the best performing in terms of predicting the experimental B_0 and V_0 values of Ce.

5.3 Pressure Dependence of Bulk Modulus

As an elastic property of the material, the bulk modulus B can be defined as the second volume derivative of the total energy $B = V d^2E/dV^2$. Under (over)-estimation of B calculated at a given level of theory indicates under(over)-binding for the interactions considered at that level of the theory. As the interesting physics of $\gamma - \alpha$ iso-structural phase transition in Ce is related with the change in the binding properties of the single $4f$ electron, all theoretical methods considered can be analyzed in terms of their performance to produce the relation between the pressure and the bulk modulus. From the set of theoretical calculations investigated in the present study, it is found that the equilibrium volume bulk modulus for the γ -phase is lower than that for the α -phase, which might support the claim that the $4f$ electron participates in bonding for the α phase while it is inert in the γ phase.

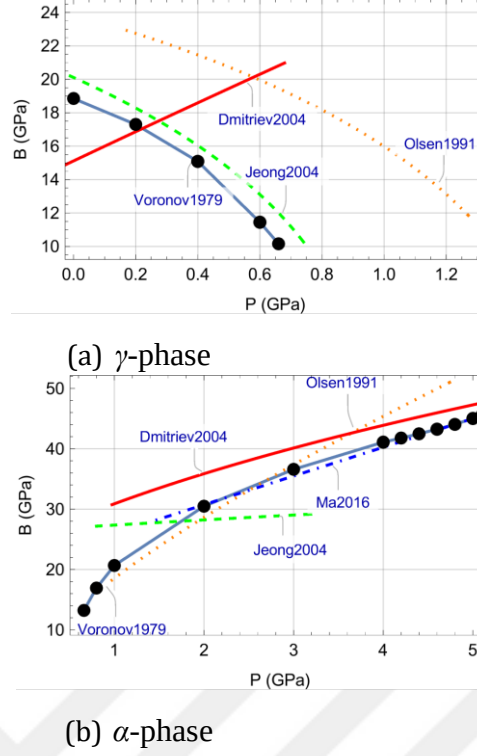


Figure 5.2: Bulk modulus as function of the pressure calculated from the equation of state formula.

We have used the best-fit EOS functions to calculate the volume-dependent bulk modulus of the α - and γ -phases of the Ce metal from the definition $B = V d^2E/dV^2$ and display the results in Fig. 5.2a) and b), respectively. We should note that a similar study was carried out by Jeong *et.al.* [55] by fitting to a third-order polynomial, but we have found that such fits would produce unreasonable results for the other data sets considered in the present study. One would expect the bulk modulus to decrease (increase) with increasing volume for the α (γ)-phase, which seems to be the case for all experimental data sets except for the γ -phase data of Dmitriev *et.al.* [56]. Ma *et.al.* [59] and Dmitriev *et.al.* [56] data suggest similar slopes for the volume-bulk modulus relationship, while the data reported in Ref. [55] (Ref. [53]) indicate a very weak (strong) volume dependence for the bulk modulus of α -Ce. One can observe from Fig. 5.2b that three of these sets (Refs. [53,56,59]) that almost meet at the same point (≈ 26.5 GPa) around the equilibrium volume 190 (a.u.³). It is well known that the γ phase undergoes an isostructural

phase change with increasing pressure, which is accompanied with a decrease in bulk modulus.

Fig. 5.2 b indicates that only the data of Refs. [53] and [55] obey the expected B - V relation, while the Ref. [56] behaves exactly oppositely, which could be due to the limited number of data points in that set. Furthermore, one can see the more reliable bulk modulus value of γ -phase is 20.1 GPa in figure.

We have used the best-fitting EOS functions to calculate the volumedependent bulk modulus of the α - and γ -phases of the Ce metal from the definition $B = -V \frac{dP}{dV}$, one expects B to decrease with increasing pressure until $P_c \approx 0.75$ GPa for the γ -phase and to increase with increasing pressure after the transition to α -phase. But none of the considered equations of states is formulated for the structures undergoing phase transitions. To investigate whether one could deduce any phase transition related structures from the bulk modulus versus pressure data, we fit the energy-volume data to the 4th, 5th, and 6th order polynomials and calculate the pressure ($-dE/dV$) and bulk modulus ($V d^2E/dV^2$). Additionally, the $B_{P=0}$ values obtained from the fourth-order fits for most of the sets are similar to those obtained from the standard EOS fits but show significant differences for some of the data sets [81,87]. We should note that the fits become noisy and quite oscillatory gradually as the order of the polynomial increases beyond 5. The findings of this section suggest that it might be problematic to calculate the equation of state by using the standard formulation when there exists a phase transition within the considered pressure range.

5.4 Method

The results reported in this section were obtained in the DFT framework using the ABINIT suite of programs. The projector augmented wave (PAW) data set for cerium in the $[\text{Xe}] 5s^3 5p^6 4f^1 5d^1 6s^2$ valence configuration has been generated using the Atompaw program and multiobjective evolution algorithms of Matlab. The generalized gradient approximation of Perdew-Burke-Ernzerhof with exchange modifications is used as the exchange-correlation function. We have used a relatively high energy cutoff of 30 Hartree for the plane wave expansion and a

fine $16 \times 16 \times 16$ Γ centered Monkhorst-Pack mesh for the integration over the first Brillouine zone, which ensures that the calculated volume and elastic property values are converged to 1% of their reported values. The implementation of the LDA+ U method in ABINIT is described in.

5.4.1 Elastic Properties

Elastic constants are tensorial properties of the material that describe its response to finite strains. Under strain η the lattice vectors of the unit cell transforms to

$$r' = r \cdot \eta \quad (5.1)$$

where r is the matrix whose columns are the lattice vectors of the unit cell.

There are various ways to calculate the elastic properties of crystals. One method is strain-stress method that is used in this study based on fitting the strain-stress relation of deformed crystals ($\sigma_i = c_{ij}\epsilon_i$ where σ_i , ϵ_i and c_{ij} are strain, stress and single-crystal elastic constants, respectively, and $i, j = 1, 2 \dots 6$). Here, the six strain components ϵ_i span a 6-dimensional strain space, with the strain tensors as vectors in the space. Similarly, the calculated stress tensors represent vectors in a 6-dimensional stress space. The elastic constants matrix (c_{ij}) is a mapping between the two spaces. The stress tensor can be obtained from either first-principles or empirical potential methods. Once the stress is calculated for each strain, the single-crystal elastic constants are retrieved by linear least-squares fitting using singular value decomposition.

The strain energy method [101] for crystals of a face-centered cubic structure, there are only three independent components of the elasticity tensor; namely C_{11} , C_{12} , and C_{44} in Voigh notation. These components can be deduced from a set of 3 different strains: C_{44} and $C_{11}-C_{12}$ can be calculated from the volume conserving strains, while $(C_{11} + 2C_{12}) = 3B_0$, where B_0 is the bulk modulus can be obtained from hydrostatic pressure calculations. For the $C_{11}-C_{12}$ quantity, we use the strains that conserve volume in the following form:

$$\eta = \begin{pmatrix} 1+x & 0 & 0 \\ 0 & 1-x & 0 \\ 0 & 0 & 1+\frac{x^2}{1-x^2} \end{pmatrix} \quad (5.2)$$

to the unit cell, where x ranges from -0.025 to 0.025 in 8 steps, the resulting (x, E_k) data are fitted to a quadratic polynomial of the form:

$$E(x) = a_0 + a_1x + a_2x^2 \quad (5.3)$$

where $C_{11}-C_{12} = \frac{a_2}{V_k}$.

In detail, the bulk modulus B_k at volume V_k is calculated from its definition $B_k = V_k(d^2E/dV_k^2)$ by the finite difference formula:

$$B_k = \frac{V_k}{12\Delta V}(-E_{k-2} + 16E_{k-1} - 30E_k + 16E_{k+1} - E_{k+2}) \quad (5.4)$$

E_k is the total energy of the unit cell of volume V_k .

Similarly, to compute C_{44} , we use the orthorhombic volume-conserving strain of the form:

$$\eta = \begin{pmatrix} 1 & \frac{x}{2} & 0 \\ -\frac{x}{2} & 1 & 0 \\ 0 & 0 & 1+\frac{x^2}{4-x^2} \end{pmatrix} \quad (5.5)$$

again, x changes from -0.025 to 0.025 in 8 steps. And the resulting (x, E_k) data is fitted to the quadratic polynomial given Eq.5.3 and C_{44} obtained as $\frac{2a_2}{V_k}$.

5.4.2 Structural Properties

First, we study the Hubbard U dependence of equilibrium volume and the related bulk modulus of Ce at spin GGA+ U level and present the graphs of V_0 and B_0 as functions of U in Fig. 5.3a-b. It is interesting to note that the U dependence of the equilibrium volume (Fig. 5.3b) looks qualitatively similar to the α - γ phase transition of Ce. It is well known that the spin-polarized DFT calculations for cerium indicate the emergence of magnetic order for lattice constants above 5.1 Å [65]. On the other hand spin polarization, here, develops at all considered unit cell

volumes for U larger than a critical value U_c that is found to be around 3.25 eV in the present work which is similar to the U_c reported in Ref. [102]. U -dependence of both V_0 and B_0 show a discontinuity around U_c , as can be seen from the figure. Below U_c , V_0 is close to the volume of the α -Ce while above it is close that of the γ -Ce. The bulk modulus is found to increase with increasing U until U_c and suddenly decreases to a value smaller than the $U = 0$ case at U_c and gradually increases to saturation with increasing U above U_c . The behavior of B_0 for $U < U_c$ is especially interesting because as U increases, B_0 increases, but V_0 remains almost constant, which is related to the change in density of $4f$ states around the Fermi level. Chen [103] carried out a similar study for the fcc phase of Pu. Interestingly, they have found very similar U dependence for the equilibrium volume and the bulk modulus. Even the critical values of U for Ce and Pu are approximately equal. Its highly probable that the phenomenon is related to the f electrons, but considering the fact that Ce has a single $4f$ electron while Pu has six $5f$ electrons, the similarity in U_c should be considered as fortuitous.

Below the critical value U_c , after detailed test calculations with different U parameters, we found that an interesting effect of U on the bulk modulus and volume of the unit cell. In Figure 5.3, we display the U -dependence of V_0 and B_0 . When $U < 3.25$ eV, the volume of the unit cell does not show any changes with the U parameter, and we can say that in this area the volume is not related to U and it shows the expected value of α -phase volume but after that values the system jumps at γ -phase volume and getting sensitive with U parameter. Conjugate with this behavior of volume as a function of the U parameter, the bulk modulus values of the system show linear increase until $U = 3.25$ eV and one can say that these values of the bulk modulus, around expected values of the α - phase bulk modulus, and dramatically fall the expected γ -phase bulk modulus values (20.1 GPa). Overall, with this observation we can say that magnitude of U determines the definition of the phase of Ce, when $U < 3.25$ eV system define the α -phase and greater values of U produces the γ -phase.

We have done energy versus volume calculations for basic GGA, GGA with spin-orbit interaction (GGA+SO), GGA+ U and spin GGA+ U with different U values in the range [0,6] eV and spin-orbit calculations to determine the basic structural parameters, such as equilibrium volume V_0 , zero-pressure bulk modulus (B_0) and its pressure derivative for Ce. In Figure 5.4, we plot the $E - V$ curves for those calculations (only the $U = 4$ eV and $J = 0.65$ curves of the calculations + U are shown). The nonlinear least squares fit to the EOS in Table 5.1 for the GGA, GGA+ U , spin+ U with $U < 3.25$ eV computations converge to similar equilibrium volumes of $V_0 = 27.2 \text{ \AA}^3$ which is close to the unit cell volume of α -Ce (28.30) [88] and is in good agreement with the results of various calculation at the similar level of theory [49,65,86,104]. The bulk modulus and its pressure derivative for these three sets of calculations are found to be somewhat different; $B_0 = 25.16, 25.25$ and 35.02 GPa, for GGA,

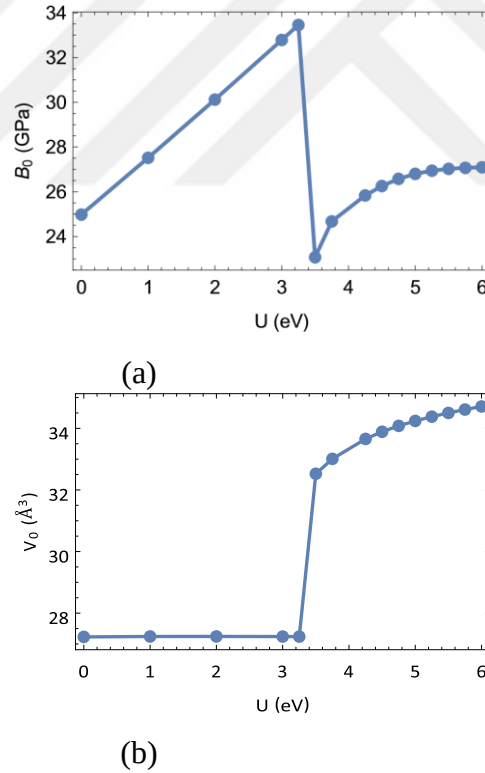


Figure 5.3: Bulk Modulus and equilibrium volume versus U

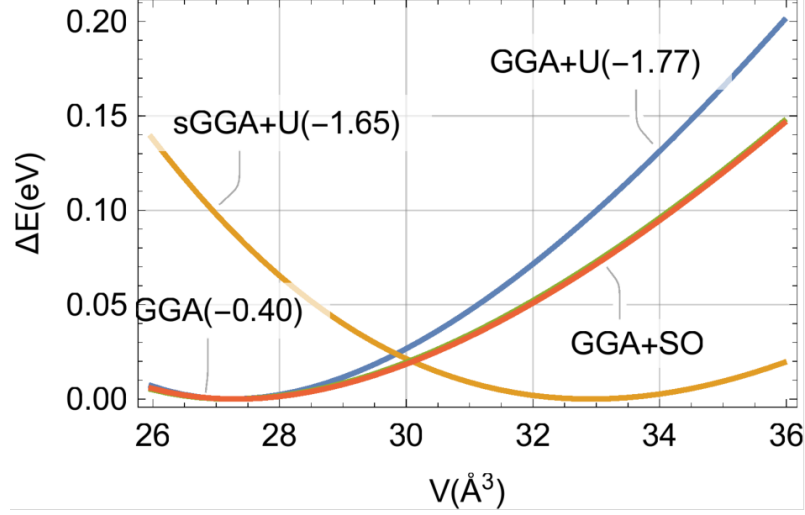


Figure 5.4: Energy versus volume for GGA, GGA+ U , sGGA+ U and GGA+SO calculations. $U = 4$, $J = 0.65$ eV in all + U computations. The curves are shifted vertically by the numbers in parenthesis which indicate the difference from the minimum of the GGA+SO calculation.

GGA + SO and GGA + U , respectively. Additionally, pressure derivatives of B_0 are found to be $B'_0 = 3.31, 3.26, 3.54$. It is interesting to compare V_0 and B_0 calculated here with the ones in the literature which were calculated in the same theoretical framework. Full-potential linear muffin-tin orbital technique (FP-LMTO) (37.0 GPa, 28.1 Å^3) [86], GGA+ U method with PAW (40.98 GPa, 27.09 Å^3) [42] and LDA+ U study with PAW (41.72 GPa, 27.07 Å^3) [86]. From these analyses, generally all calculated volume data agree well with each other and our calculations, but the bulk modulus values are higher than the expected value for the α -phase. As the compared computations use similar techniques with differences in details, such as computational parameters, it is not easy to disentangle the reasons for such large discrepancies. There have been reports on the effect of spin-orbit interaction on the properties of Ce, which claimed that it was essential to include it for a satisfactory description of its ground state in the DFT framework [65]. Here, it is found that including the spin-orbit interaction in GGA has very little effect on the equilibrium structural properties. As can be seen from Fig. 5.4, sGGA+ U calculations indicate an equilibrium volume 32.91 Å^3 which is close to the V_0 of γ Ce (34.48 Å^3) [52]. The sGGA+ U results for B_0 and B'_0 are calculated as 24.34 GPa and 2.19, respectively. We should note that the total energy curves in Fig. 5.4 indicate that the lowest energy state at the GGA+ U level has the volume of the γ phase, which is in contradiction with the experimental findings (at zero temperature

Ce is found to be in α phase). This shortcoming of the GGA+ U approximation is well known and dealt with [73] by reducing U , which creates inconsistencies in spectral calculations.

We calculate the elastic constants of both α - and γ -phase Ce from the basic GGA, GGA+ U and spin-polarized GGA+ U calculations, and the elastic constants information studied in the present work is provided in Table 5.2 and compared to the available experimental and other theoretical values. To the best of our knowledge, there is no published experimental report on the elastic properties of the Ce phase α -. As a comparison between calculations and two experimental data sets (γ -phase) we give the r_{RMS} deviations in mentioned table, from this values one can say that our GGA+ U calculations agree with the experimental data especially for Ref. [13] ($r_{RMS}=1.58$) and the better results for DFT based calculations. In the table r_{RMS} value of Ref. [17,20] looks well for a experimental data set but we should say that they used phenomenological models and they have fitted their parameters with the experimental data.

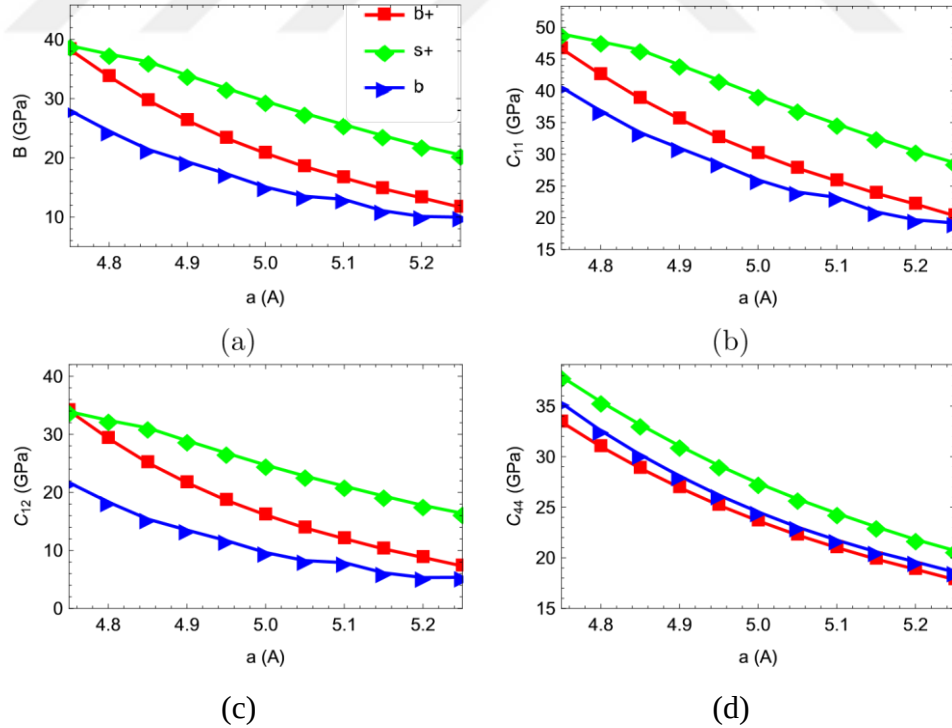


Figure 5.5: Bulk modulus and elastic constants as function of the lattice constant calculated at the GGA (b), GGA+ U (b+) and spin-polarized GGA+ U (s+) levels. $U = 4$ eV, $J = 0.65$ eV

The lattice constant-dependent bulk modulus and the elastic constants of Ce are displayed in Fig.5.5 for GGA, GGA+ U and spin-polarized GGA+ U calculations. All three sets of calculations show similar volume dependence on the considered elastic properties; they decrease with increasing lattice constant which is expected. The pure GGA calculation without U -correction or spin effects produces the lowest values while spin GGA+ U for all four quantities (B_0 , C_{11} , C_{12} , and C_{44}) results in the highest values. We should note that the results presented in Fig. 5.5 are obtained for a single value of U and do not show any sign of discontinuity around the lattice constant of γ -Ce.

6. PHASE TRANSITION

The isostructural (fcc) $\gamma \rightarrow \alpha$ phase transition in cerium exhibits an approximately 17% volume collapse, a transformation from a ferromagnetic to paramagnetic state, and an abrupt decrease of elastic constants. It is universally accepted that this peculiar transition is due to the existence of a single $4f$ electron in the electronic configuration of Ce. Although many experimental [103–106] and theoretical [13, 19, 21, 22, 25, 49, 64, 66–69, 71, 73, 74, 76–80, 84–86, 88, 94, 102, 104, 106, 109–122] techniques have been used to understand how f electrons affect the transition over the last century, there still are controversies about the exact contribution of various physical processes and the role of f electrons in those processes in the phase transition [123]. The Mott transition (MT) and the Kondo volume collapse (KVC) models, are the leading candidates that claim to explain the transition [123–125]. In the Mott scenario, the mechanism of the transition is the competition between the intersite hybridization and the on-site Coulomb interaction of f electrons, while in the Kondo volume collapse (KVC) model, the variation of the hybridization between the conduction electrons and the $4f$ electron with volume is claimed to be the driver of the transition. Recent studies, based on the similarities observed in spectral functions and magnetic moments in Hubbard model (MT) and Anderson impurity model (KVC) calculations, indicate that these two models might capture complementary features of the transition [115].

The first principles calculations based on density functional theory (DFT) alone [88] and with various improvements of it, such as DFT+self-interaction correction (SIC) [66,67,71], DFT+U [72,73,114], DFT+dynamical mean field theory (DMFT) [13,77,82,84,106,115–117,126–128], hybrid functionals [87] and DFT+Gutzwiller (G) [79,81], have been used since mid-seventies to better understand these two phases and the transition between them. Although early DFT calculations in the local and generalized gradient approximations (LDA and GGA) were able to reproduce the experimental magnetic structure at V_α and V_γ , only a single minimum near V_α was found in the equation of state (EOS) that was attributed to the self-interaction problem of DFT which tends to delocalize electrons. Various groups [66,67,71] have found that self-interaction corrections would stabilize the γ phase and combining LSD and SIC-LSD results could account for the EOS of both phases. Taking into account of the strongly correlated nature of $4f$ electron of Ce, Hubbard U corrections were shown, similar to SIC-LSD, to reproduce the properties of the γ phase reasonably well [72,73,114] and the results of LDA and LDA+U calculations were associated with the α and γ phases, respectively, and were used to study phase diagram of cerium [73]. Further improvements in theory of strongly correlated systems with advances in dynamical mean field theory [13,77,82,106,115–117,126–128] and techniques such as Gutzwiller variational method [76,78,81] and Jastrow wave functions [84] were able to account for the spectral features and EOS parameters of α and γ phases. Also, hybrid functionals and exact exchange plus correlations in the random phase approximation were found to reproduce the EOS of Ce within a single theory [87,121]. Despite ever increasingly sophisticated methods have been used to characterize the properties of α and γ phases, it has been difficult to find a driver of the transition [121].

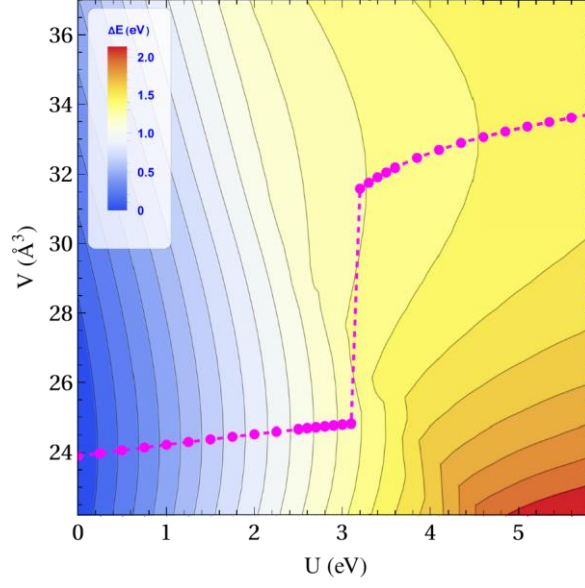
One of the essential ingredients of first principles calculations that reproduce some of the properties of α - and γ - Ce is the inclusion of orbital polarization effects [87] in the form of a definite $4f$ occupation symmetry or large electronic smearing factor. For instance, using QMC with Jastrow wave function, Deveraux *et al.* [84] have shown that the symmetry of f electron occupation is an essential indicator in the phase transition mechanism. They found that in the γ -phase, f electron resides in t_{1u} orbital which has a larger spread compared to the one

in α phase. Furthermore, Luders *et al.* [71] have calculated the EOS of Ce by using LDA and SIC-LDA methods by restricting the symmetry of $4f$ occupation to A_{2u} , T_{1u} and T_{2u} for SIC-LDA calculations and found that A_{2u} occupation would reproduce the γ -phase while the LDA equilibrium volume was close to that of the α -phase. Aim of the present study is to investigate whether DFT+U level theory coupled with the control of f electron occupation symmetry might be used to explain the change in the properties, such as volume, magnetic moment, electronic spectral features and elastic properties of cerium, for the $\gamma - \alpha$ phase transition. The results reported below indicate that a small change in U around a U_c leads to large changes in the equilibrium volume, magnetic moment, f -electron occupation, local f entanglement entropy, and elastic constants similar to those observed in $\gamma - \alpha$ transition.

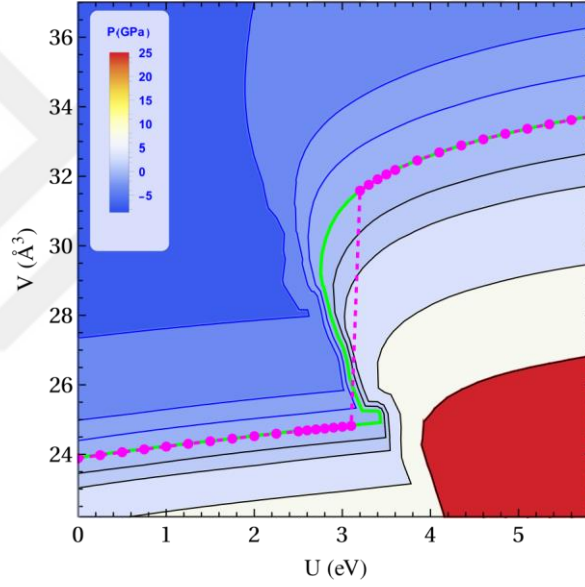
Results reported in this study were obtained in the DFT framework by using ABINIT [129] suite of programs. The projector augmented wave (PAW) data set for cerium in $[Xe]5s^35p^64f^15d^16s^2$ valance configuration has been generated by using the Atompaw [81] program and multiobjective evolution algorithms. Generalized gradient approximation of Perdew-Burke-Ernzerhof with exchange modifications [93] is used as the exchange-correlation functional. We have used a relatively high energy cut-off of 30 Hartree for the plane-wave expansion and a fine $16 \times 16 \times 16$ Γ -centered Monkhorst-Pack mesh for the integration over the first Brillouine zone which ensures that the calculated volume and elastic property values are converged to 1% of their reported values. The implementation of DFT+U method in ABINIT is described in Ref. [94]. For the calculation of the elastic constants, we adopt the method developed by Sin'ko [130].

First, we present the unit cell volume and Hubbard U -dependence of the total energy and pressure in Fig. 6.1a) and Fig. 6.1b), respectively. The displayed data are obtained by calculating the total energy of the unit cell over the $21 a_0$ (4.46 to 5.29 $^\circ A$) by $24 U$ (0 to 6 eV) grid for three different initial $4f$ occupation configurations (A_{2u} , T_{1u} , and T_{2u}). All three initial occupation symmetries were found to produce the same $E - V$ curves for $U < 3$ eV while A_{2u} configuration was found to be at lower energy for $U > 3.25$ eV. Overlaid dotted lines with the filled circles

in both figures show the equilibrium volume V_0 obtained from the nonlinear fit of the volume-energy data at a given U to the Vinet equation of state [100]. One of the peculiar properties of cerium metal that was tried to be shown by using first principles methods is the double-minimum in the volume-energy relation. Existence of broken orbital symmetry in the initialization of the system seems to be one of the common aspects of calculations, such as Hartree-Fock, DFT+U [114], SIC-LSD [64,65], LDA+GA [79,81] and hybrid functional calculations [121] that produce EOS with double minima. As can be seen from Fig. 6.1a) and b), in our calculations, the double well structure appears around $U_c = 3.25$ eV for only the A_{2u} initial $4f$ configuration. The global minimum in $E - V$ curve is found to be at lower volume for $U < U_c$ and at higher volume for $U > U_c$ eV. The change in V_0 around U_c is reminiscent of the γ - α phase transition which is accompanied by volume collapse. The change in volume is larger than the experimental value, because the lower volume is underestimated in the present study. Including the spin-orbit interaction did not change the results appreciably except for U_c and the symmetry of the $4f$ occupation which were found to be 2.75 eV and A_{2u} below and T_{2u} above $U = 3.5$ eV, respectively. Thus, contrary to the findings in Refs. [76,77,79,81] the inclusion of spin-orbit interaction does not seem to be essential in reproducing the structural properties of cerium in the DFT+U framework.



(a) Total energy



(b) Pressure

Figure 6.1: U and volume dependence of the total energy (a) and the pressure (b) for cerium. Contour lines in (a) start from zero on the left bottom corner and are separated by 100 meV. Tick green line in (b) denotes $P = 0$. Blue and black contour lines denote $(-1, -2, -5 \text{ and } -10)$ and $(1, 2, 5, 10)$ GPa, respectively.

Magnetization is another property that shows a sudden change in $\gamma - \alpha$ transition; α -phase is paramagnetic while the higher volume γ -phase exhibits a net magnetic moment. In figure 6.2a), we display the U and V -dependence of magnetization M . It is well established that the DFT calculations predict a magnetic unit cell with a large enough lattice constant even in the absence of Hubbard

corrections [49]. The dotted contours in figure 6.2a) indicate that M increases from 0.05 to $1.1\mu_B$ as U is increased beyond U_c .

The entanglement entropy of the $4f$ electron is defined as $S = -k_B \sum_i \lambda_i \ln \lambda_i$ where λ_i are the eigenvalues of the $4f$ occupation matrix. S is displayed in Fig. 6.2b) as function of U and V . Entropy change is one of the most studied aspects of the γ - α transition [55,57,58,72,77,131,132]. Electronic, lattice, disorder and magnetic entropy of both phases were calculated or measured with widely differing values. The Clausius–Clapeyron relation would give the total entropy change as $dP/dT = \Delta S^{\gamma-\alpha}/\Delta V^{\gamma-\alpha} = 1.5k_B$. In our calculations, the phase transition is found to be accompanied with an entropy reduction from 2.20 to 0.6 (6.2b)), which is inline with the emergence of magnetic order.

Since the magnetization in cerium is mainly due to f electrons, co-existence of magnetic moment and the low occupation entropy can be understood as an approach to integer occupation.

The number of f electrons n_f as function of U and V is displayed in Fig. 6.2c) which shows that the change in n_f is relatively small across the critical line. $U - V$ dependence of n_f is different compared to those of P , M and S . At low volumes, as U is increased from zero to U_c , n_f decreases from

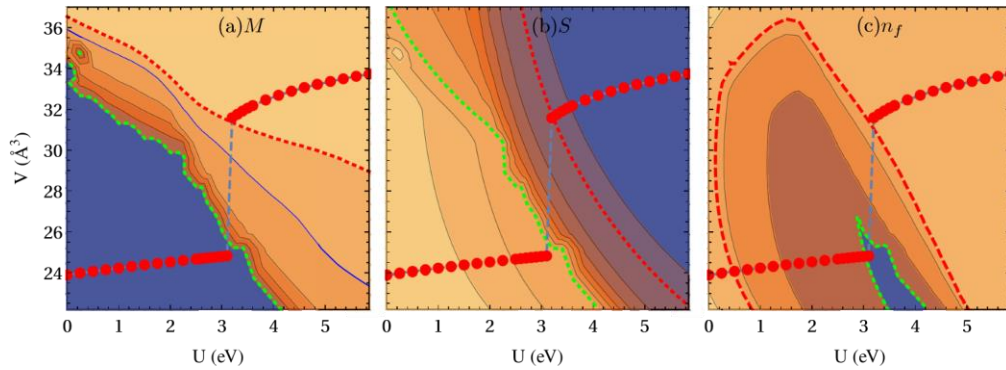
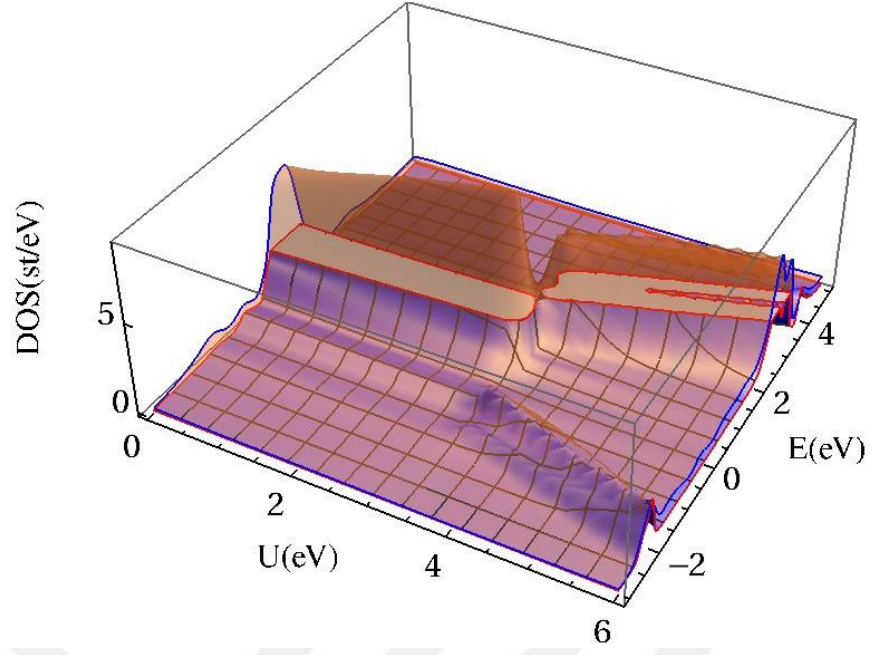


Figure 6.2: U and volume dependence of the unit cell magnetization (a), entanglement entropy of $4f$ electrons (b) and the number of $4f$ electrons (c) for cerium.

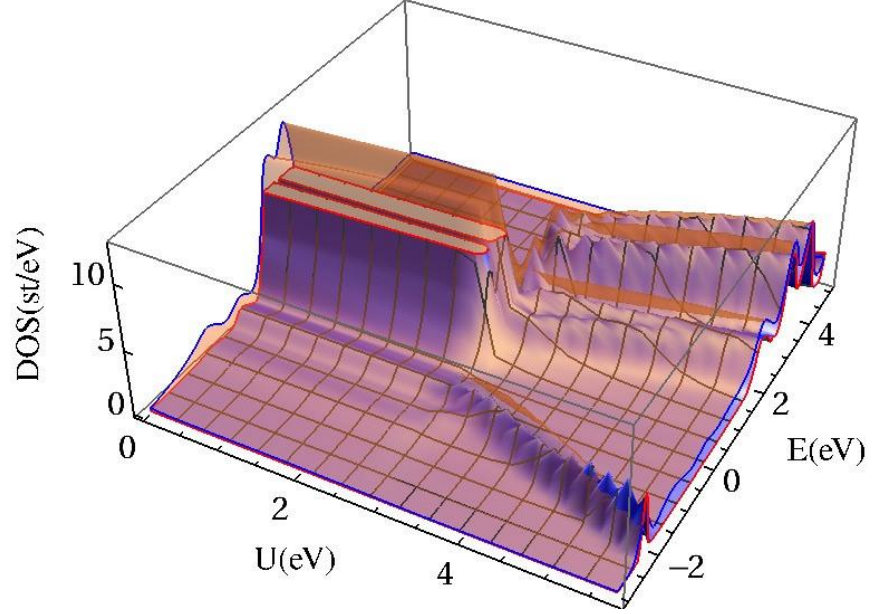
0.96 to 0.84 and jumps from 0.84 to 0.96 at the critical U . These values are interestingly very similar to the Compton and neutron scattering results $n_f^\alpha = 0.8$ and $n_f^\gamma = 1$ of Ref. [133].

To further elucidate the behaviour of the $4f$ electron in the transition, we display the total and the $4f$ partial density of states (PDOS) for the ferromagnetic and spin-orbit coupling calculations as function of U in Fig. 6.3. Based on photoemission and inverse photoemission measurements, Ce exhibits three prominent peaks around Fermi level: a lower Hubbard band around -2 eV, a higher Hubbard band at 2-4 eV, and a Kondo resonance and its spin-orbit split replica at 0.25 eV below Fermi level [106,122,134,135]. The peak around Fermi level is considered to be due to $f - c$ hybridization and its strength is an indication of the degree of the hybridization which is stronger in α -phase. Figures 6.3a) and b) show that the $4f$ PDOS has a small value around 0.4 eV below Fermi level and a large component centered around 2 eV above Fermi level for $U < U_c$ and those values are not very sensitive to the magnitude of U . Above U_c , PDOS splits in to four parts and the energy of the center of nonzero PDOS increase (decrease) linearly with U above (below) Fermi level. The lower Hubbard band at -2 eV attributed to f state in both α and γ -phases is found to be mostly due to $5d$ electrons for $U < U_c$ in contradiction to the widely accepted inference from PES and IPES spectra.

We present the U -dependence of elastic constants C_{11} , C_{12} and C_{44} along with the bulk modulus $B_0 = (C_{11} + 2C_{12})/3$ in Fig. 6.4. As with all quantities reported so far, the elastic constants also experience a discontinuous drop with



(a) Spin up



(b) Spin-orbit

Figure 6.3: Total (transparent and outlined in blue) and the 4f partial (outlined in red) density of states as function of U for the majority spin component (a) and calculated with spin-orbit coupling (b). $E = 0$ is the Fermi level.

U increasing beyond U_c . Elastic anisotropy $A = 2C_{44}/(C_{11} - C_{12})$ for cerium is reported by Greiner *et al.* as 2.94 [16]. From Fig. 6.4, the elastic anisotropies are found to be 2.8 and 2.5 for α and γ -phases, respectively. Another interesting change in the elastic constants is seen in the Cauchy pressure which is defined through the Cauchy relation $C_{44} - C_{12} = 2P$ where P is the Cauchy pressure. We have found that α -Ce (γ -) has negative (positive) Cauchy pressure.

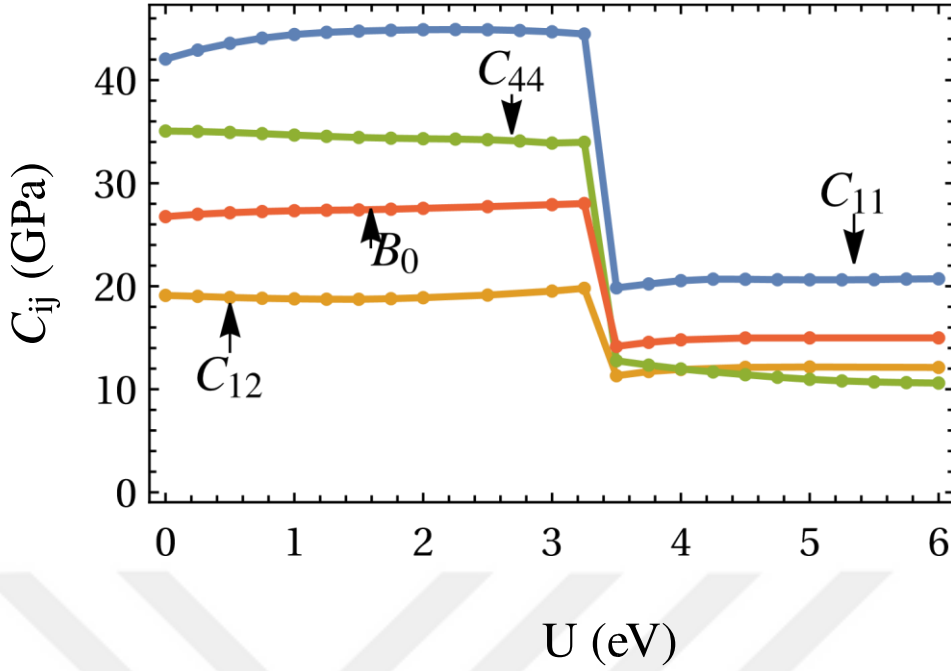


Figure 6.4: U -dependence of equilibrium elastic constants.

It is also interesting to note that the bulk modulus calculated from the elastic constants for the low and high volumes are very close to B_0 of α and γ phases of cerium.

We have investigated the structural, magnetic, and electronic properties of cerium in DFT+ U framework to understand the isostructural $\gamma - \alpha$ phase transition. It is found that many aspects of the changes in those properties at the transition could be reproduced with a small change in Hubbard U around 3.25 eV which suggests that U correction plays the role of external perturbations such as pressure and temperature for this particular transition. While the structural and magnetic properties across the transition are well reproduced, the increase in the $4f$ partial density of states at lower Hubbard band at -2 eV is achieved only at higher U values. U_c found here is low compared to the one used commonly (6 eV) to account for the results of photoemission studies [104].

7. CONCLUSIONS

From the first-principles calculations with the projector augmented wave (PAW) formalism, we tried to analyze the structural and elastic properties of α - and γ -phases of elementary cerium which is an exotic material due to the existence of a single $4f$ electron. We have used a number of well-known equations of state formulas to fit the available experimental and theoretical data $P - V$ and $E - V$ and tried to obtain valid reference values for the equilibrium volume, bulk modulus, and the pressure derivative of the bulk modulus for both phases of cerium. The results of the fits indicate that the most consistent experimental data is the one reported in Ref. which can be fitted with $V_0=28.70 \text{ \AA}^3$, $B_0=25.5 \text{ GPa}$, and $V_0=34.02 \text{ \AA}^3$, $B_0=19.3 \text{ GPa}$ for α - and γ -phases for the equilibrium volume and bulk modulus when the zero-point vibrations and the thermal corrections are considered. We have also analyzed the EOSs calculated by using various ab initio schemes and found that although the early DFT and recent LDA+GA calculations are better in describing EOS of Ce, most of those calculations over-estimate the bulk modulus. We have carried out similar EOS calculations at the levels of GGA, spin GGA, GGA+ U , spin GGA+ U and spin GGA with spin-orbit coupling plus U to investigate the source of errors in the failure to account for the bulk modulus of cerium by DFT and its variants. The calculated EOSs for the spin-polarized GGA+ U approach was found to display interesting behaviour as function of the Hubbard U . Perhaps the most important finding of this study is the interesting Hubbard U dependence of the equilibrium volume and the related bulk modulus of Ce. We found that U -dependence of both V_0 and B_0 show a discontinuity around $U_c=3.25 \text{ eV}$. Below U_c , V_0 is close to the volume of the α -Ce while above it is close to that of the γ -Ce. The behavior of B_0 for $U < U_c$ is especially interesting, because as U increases, B_0 increases but V_0 remains almost constant, which is related to the change in density of $4f$ states around the Fermi level. The most important such behavior is the two-well structure found in the volume dependence of the total energy for $U < 3.5 \text{ eV}$. Interestingly, the local minima of the well are located close to the experimental volumes of the α and γ phases. U -dependence of the total energy is found to display a phase-transition like structure; as U is increased from 0 to $U_c = 3.35 \text{ eV}$, the two-well structure develops with minima located near V_α . Further increasing U shifts the minima to near V_γ .

We have also calculated the elastic constants of both α - and γ -phase Ce in the basic GGA, GGA+ U and spin-polarized GGA+ U frameworks. The results of the GGA+ U calculations are found to be in good agreement with the available experimental data. In addition, we have done GGA, GGA+ U and spin-polarized GGA+ U calculations, the lattice constant-dependent bulk modulus, and the elastic constants of Ce. We found the basic GGA calculations for B_0 , C_{11} , C_{12} and C_{44} give the lowest values, while the GGA+ U calculations give the highest values. We have also investigated the pressure dependence of elastic constants and found that the equation of state formulations around phase transition pressures are not able to describe the phase transition effects. The Vancouver citation system was used in this thesis.

8. REFERENCES

The Vancouver citation system was used in this thesis.

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