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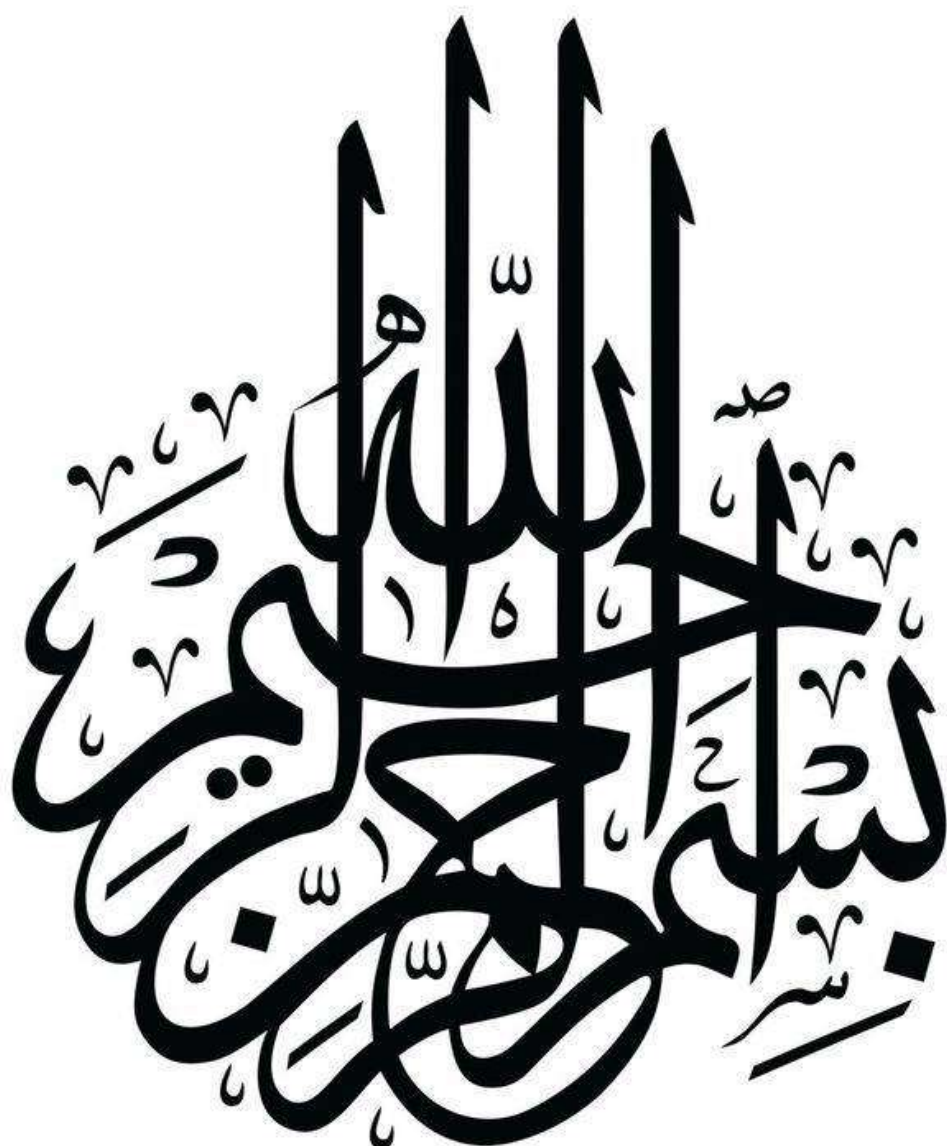
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○ **Dedication :**

I dedicate this modest work to the dearest people in my life,

*To my beloved father **Bachir**, who has always been my source of strength and support,
and to my dear mother **Khadra**, whose prayers and kindness have illuminated my
path.*

*To my dear brothers: **Walid, Khaled, Areslan, Reyadh, Kamel, Samir**,
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*To all those who have contributed, directly or indirectly, to the accomplishment of this
work,*

I dedicate the fruit of my efforts, hoping it meets your expectations.



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○ **List of Symbols**

- **H** : Hamiltonian of the system
- **ϕ** : Wave function of the system
- **E** : Total energy of the system
- **$\hbar$** : Planck constant (reduced Planck constant)
- **$\mathbf{r}_i$** : Position vector of electrons
- **m_e** : Electron mass
- **M_a** : Nuclear mass
- **$\mathbf{R}_a$** : Position vector of nuclei
- **Ω_i** : Potential energy of an electron (i) under the influence of the field
- **ψ_e** : Electronic wave function
- **V_{ext}** : External potential
- **H_i** : Hamiltonian of each electron
- **E_i** : Energy of each electron
- **$\rho(\mathbf{r})$** : Electron density
- **V_{ext}** : Unique external potential
- **$F[\rho]$** : Universal functional of Hohenberg and Kohn
- **E_{KH}** : Kohn–Sham energy
- **V_H** : Hartree potential
- **E_{XC}** : Exchange–correlation energy
- **E_{XC}^{LDA}** : Exchange–correlation energy in LDA
- **E_{XC}^{GGA}** : Exchange–correlation energy in GGA
- **ε_{XC}** : Exchange–correlation energy density
- **Ω** : Volume of the unit cell
- **$V(\mathbf{r})$** : Muffin-Tin (MT) potential
- **∇^2** : Laplacian
- **$V_{ext}(\mathbf{r})$** : External potential
- **$\rho_0(\mathbf{r})$** : Electron density of the ground state
- **E_0** : Ground-state energy
- **$T[\rho]$** : Kinetic energy of the system
- **DFT**: Density Functional Theory
- **LDA**: Local Density Approximation
- **GGA**: Generalized Gradient Approximation
- **V_{eff}** : The effective potential
- **Ω** : The cell volume
- **$Y_{l,m}$** : The spherical harmonics
- **$R_{n,l}$** : The radial part

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• Abstract

During this study, the structural and thermodynamic properties of **BaTiO₃** were investigated using the pseudopotential method within the framework of **(DFT)**, employing the Generalized Gradient Approximation **(GGA-PBE)** for the description of **exchange-correlation energy**.

The structural calculations revealed that the lattice parameter reached **a=4.0391Å**, while the bulk modulus was estimated to be **B=160.087GPa**. These results showed good agreement with previously published theoretical and experimental values, confirming the accuracy of the adopted computational methodology.

Furthermore, the thermodynamic properties of the compound were studied, including the heat capacity at constant volume, entropy, internal energy, free energy, and thermal expansion coefficient as a function of temperature. The obtained results indicated that the heat capacity, entropy, and thermal expansion coefficient increase progressively with increasing temperature due to the activation of lattice vibrations within the crystal structure. In contrast, the free energy decreases with increasing temperature, whereas the internal energy continuously increases as a consequence of the rise in vibrational energy of the atoms.

The obtained results confirm the effectiveness of Density Functional Theory and the pseudopotential method in describing the structural and thermodynamic properties of perovskite materials. The good agreement achieved with previously reported theoretical and experimental results demonstrates the reliability and accuracy of the computational approach adopted in the study of this type of material.

• Résumé

Au cours de cette étude, les propriétés structurales et thermodynamiques du composé BaTiO₃ ont été étudiées en utilisant la méthode du pseudopotentiel dans le cadre de Théorie de la fonctionnelle de la densité (DFT), avec l'approximation du gradient généralisé (GGA-PBE) pour la description de l'énergie d'échange-corrélation.

Les résultats des calculs structuraux ont montré que la constante de réseau est égale à ($a = 4.0391 \text{ \AA}$), tandis que le module de compressibilité a été estimé à ($B = 160.087 \text{ GPA}$) Ces résultats présentent un bon accord avec les valeurs théoriques et expérimentales publiées dans les références scientifiques, ce qui confirme la précision de la méthodologie de calcul adoptée.

Par ailleurs, les propriétés thermodynamiques du composé ont été étudiées, notamment la capacité calorifique à volume constant, l'entropie, l'énergie interne, l'énergie libre et le coefficient de dilatation thermique en fonction de la température. Les résultats obtenus montrent que la capacité calorifique, l'entropie et le coefficient de dilatation thermique augmentent progressivement avec l'élévation de la température en raison de l'activation des vibrations du réseau cristallin. En revanche, l'énergie libre diminue lorsque la température augmente, tandis que l'énergie interne augmente continuellement sous l'effet de l'accroissement de l'énergie vibrationnelle des atomes.

Les résultats obtenus confirment l'efficacité de la théorie de la fonctionnelle de la densité et de la méthode du pseudopotentiel dans la description des propriétés structurales et thermodynamiques des matériaux pérovskites. Le bon accord avec les résultats théoriques et expérimentaux publiés démontre la fiabilité et la précision de l'approche de calcul adoptée pour l'étude de ce type de matériaux.

• ملخص

خلال هذه الدراسة تم حساب الخصائص البنيوية والترموديناميكية للمركب BaTiO_3 باستعمال طريقة الجهد الكاذب (Pseudopotential) في إطار DFT ، مع اعتماد تقريب التدرج المعمم (GGA-PBE) لوصف طاقة التبادل والارتباط.

أظهرت نتائج الحسابات البنيوية أن قيمة ثابت الشبكة بلغت $a=4.0391 \text{ \AA}$ في حين قُدرت قيمة معامل الانضغاط بـ $B=160.087 \text{ GPa}$ ، وقد سجلت هذه النتائج توافقاً جيداً مع القيم النظرية والتجريبية المنشورة في المراجع العلمية، مما يؤكد دقة المنهجية الحسابية المعتمدة.

كما تم التطرق إلى دراسة الخصائص الترموديناميكية للمركب، والمتمثلة في السعة الحرارية عند حجم ثابت، الإنتروبيا، الطاقة الداخلية، الطاقة الحرة ومعامل التمدد الحراري بدلالة درجة الحرارة. وقد بينت النتائج أن السعة الحرارية والإنتروبيا ومعامل التمدد الحراري تزداد تدريجياً مع ارتفاع درجة الحرارة نتيجة تنشيط الاهتزازات الشبكية داخل البنية البلورية، بينما تنخفض الطاقة الحرة مع زيادة درجة الحرارة، في حين تزداد الطاقة الداخلية بشكل مستمر بفعل تزايد الطاقة الاهتزازية للذرات.

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General introduction

General Introduction

Physics is regarded as one of the fundamental sciences dedicated to explaining natural phenomena and understanding the laws that govern the behavior of matter and energy across different scales, ranging from the atomic level to macroscopic systems. With the rapid advancement of **quantum mechanics** and **solid-state physics**, **materials physics** has emerged as a major branch of modern applied physics, focusing on the relationship between the microscopic structure of materials and their **physical** and **chemical properties** [1].

Materials physics plays a pivotal role in both scientific research and technological innovation, as it provides a deep understanding of how atomic and electronic configurations influence macroscopic properties. These include **structural**, **electronic**, **thermal**, and **mechanical characteristics**. Establishing this link between **microscopic** and **macroscopic scales** is essential for the design and optimization of advanced materials used in applications such as microelectronics, energy storage systems, solar cells, and smart sensing devices [2].

The investigation of material properties relies on three complementary approaches. The first involves **experimental methods**, which are based on laboratory techniques such as **X-ray diffraction (XRD)**, scanning electron microscopy (**SEM**), transmission electron microscopy (**TEM**), as well as spectroscopic and thermal analyses. While these methods provide accurate and reliable data on **structure** and **properties**, they are often costly, require sophisticated instrumentation, and may not be easily applicable under extreme conditions.

The **second approach** is based on **theoretical methods**, which rely on the fundamental principles of quantum mechanics, particularly the **Schrödinger equation**. Although this framework offers a rigorous description of the electronic behavior in materials, solving the equation exactly for many-electron systems remains computationally challenging, thereby limiting its direct applicability [3].

To address **these challenges**, **computational methods** have become indispensable in modern materials science. These approaches are based on **numerical simulations** that model physical systems using theoretical foundations. Among them, **ab initio methods** are particularly significant, as they do not depend on empirical parameters but are derived directly from first principles.

Within this framework, Density Functional Theory (**DFT**) represents one of the most successful and widely employed approaches in **materials physics**. Developed by **Kohn and**

Sham, this theory introduced a major simplification by replacing the complex many-electron wave function with the electron density as the central variable of the system [4].

DFT is founded on two fundamental theorems: the first establishes that **the ground-state energy** is a unique functional of the electron density, while the second demonstrates that this density can be obtained from an equivalent non-interacting system. In practical implementations, **exchange–correlation** effects are approximated using functionals such as the Local Density Approximation (**LDA**) and the Generalized Gradient Approximation (**GGA**), which offer a reasonable compromise between computational efficiency and accuracy [5].

In this context, **perovskite materials** have attracted considerable interest due to their rich and diverse physical properties. Among them, Barium Titanate (**BaTiO₃**) is one of the most extensively studied **ferroelectric** compounds.

BaTiO₃ crystallizes in the **perovskite structure** and exhibits pronounced **ferroelectric** behavior, which originates from the displacement of **ions** within the unit cell, leading to the formation of a permanent electric dipole moment. Furthermore, it undergoes structural phase transitions as a function of temperature, such as the transition from the cubic to the tetragonal phase, which significantly affects its **structural** and **thermal properties** [6].

These features make **BaTiO₃** an ideal model system for investigating the interplay between **crystal structure** and **physical properties**, particularly **thermal** and **structural** behavior. It is widely utilized in various technological applications, including multilayer ceramic capacitors, pressure and temperature sensors, piezoelectric devices, advanced electronic components, and non-volatile memory technologies.

Numerous theoretical and **experimental studies** have demonstrated that Density Functional Theory provides an accurate description of the properties of **BaTiO₃**, with results that show good agreement with experimental observations, especially in terms of **structural stability**, phase transitions, and thermal behavior. This highlights the reliability of **DFT**-based methods in the study of **ferroelectric materials** [7].

In the present work, the **structural** and **thermal properties** of **BaTiO₃** are investigated using Density Functional Theory within the pseudopotential formalism. The calculations are carried out using the **ABINIT code**, which is widely employed for **electronic structure** calculations in materials science [5].

In addition, **the GIBBS program** is utilized to evaluate the thermal properties of the material based on energy–volume data obtained from **DFT** calculations, within **the quasi-harmonic approximation**. This approach enables the determination of key **thermodynamic quantities** such as **heat capacity**, **thermal expansion coefficient**, and **Debye temperature**, which characterize the thermal response of the material as a function of temperature [8].

The primary objective of this study is to explore the relationship between the **crystal structure** and the **thermal properties** of **BaTiO₃**, to understand how **structural variations** influence its **thermal stability**, and to compare the obtained results with those reported in the literature in order to assess the validity and reliability of the adopted methodology.

This manuscript is organized into **three main chapters**, in addition to a general **introduction** and a **conclusion**. The **first chapter** presents the theoretical background of the ab initio approach, particularly Density Functional Theory (**DFT**) [9], along with the principal approximations used to describe exchange–correlation effects, namely **LDA** and **GGA**. The **second chapter** is devoted to the computational methodology, focusing on the pseudopotential approach implemented within **the ABINIT code**, with a brief overview of different types reported in the literature. **The final chapter** presents the results obtained for the **BaTiO₃** compound, along with their analysis and comparison with previously published data.

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Chapter I :

*Theoretical concepts in Density
Functional Theory (DFT)*

The description of the dynamical behavior of electrons and atomic nuclei within matter is essential for understanding the microscopic properties that govern physical systems. In this context, **Erwin Schrödinger**[1] established the mathematical foundation of quantum mechanics through his well-known equation, which remains a cornerstone in the study of quantum systems. However, exact analytical solutions of this equation are limited to very simple systems, particularly those containing a single electron, which restricts its direct application to more complex systems.

When dealing with solid materials composed of a large number of atoms and interacting electrons, the problem becomes a highly complex many-body quantum system. A direct solution of the Schrödinger equation in such cases is practically unfeasible due to its enormous mathematical and computational complexity. This challenge necessitates the use of well-established approximation methods that allow for an accurate yet computationally manageable description of the physical properties of materials.

This chapter provides a systematic presentation of the main theoretical and computational approaches used to investigate material properties from first principles within the framework of quantum mechanics. We begin by discussing the limitations of methods based on the many-body wave function, whose complexity increases dramatically with the number of particles in the system.

Subsequently, we introduce **Density Functional Theory (DFT)**, founded on the theorems formulated by **Pierre Hohenberg** and **Walter Kohn**, which demonstrate that the ground-state electron density is, in principle, sufficient to determine all properties of a quantum system. This shift from the many-body wave function to the electron density represents a profound conceptual advancement in the understanding of interacting systems.

Finally, we detail the mathematical formalism of this theory and derive the **Kohn–Sham equations**, which reformulate the interacting-electron problem into an equivalent system of non-interacting electrons moving within an effective potential. This approach achieves a careful balance between theoretical rigor and computational efficiency, making it a fundamental tool for studying the structural, electronic, and energetic properties of solid materials.

I.1 Schrödinger Equation:

Solids are composed of an arrangement of fundamental particles, namely ions (atomic nuclei) with positive charge and much lighter electrons with negative charge. The

main challenge lies in determining the properties of this complex system (ions + electrons) based on the principles of quantum mechanics. This theoretical description relies on **the Schrödinger equation**, which relates the system's Hamiltonian to its wave function ψ and the corresponding energy E

$$H\psi = E\psi \quad (\text{I.1})$$

E represents the ground-state energy of the particles described by the wave function ψ

H denotes the exact Hamiltonian of the system, which accounts for all electrostatic interactions between the particles, whether attractive or repulsive, depending on the charges of the ions and electrons.

$$H = T_N + T_e + V_{N-N} + V_{N-e} + V_{e-e} \quad (\text{I.2})$$

The terms T_N , T_e , V_{N-N} , V_{N-e} and V_{e-e} describe the different contributions to the total energy of the system: the kinetic energies of the nuclei and electrons, the repulsive energy between nuclei, the attractive energy between electrons and nuclei, and the repulsive energy between electrons, respectively.

$$\bullet \quad T_e = \frac{-\hbar^2}{2m} \sum_i^N \Delta_i \quad (\text{I.3})$$

$$\bullet \quad T_N = -\frac{\hbar^2}{2M} \sum_K^M \Delta_K \quad (\text{I.4})$$

$$\bullet \quad V_{N-N} = \frac{1}{2} \sum_k^M \sum_{l=k}^M \frac{e^2 Z_k Z_l}{4\pi\epsilon_0 |\vec{R}_k - \vec{R}_l|} \quad (\text{I.5})$$

$$\bullet \quad V_{e-e} = \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (\text{I.6})$$

$$\bullet \quad V_{e-N} = -\sum_k^M \sum_{i \neq k}^N \frac{Z_k e^2}{4\pi\epsilon_0 |\vec{R}_k - \vec{r}_i|} \quad (\text{I.7})$$

The symbols e , m , and M represent the electron's charge, the electron's mass, and the nucleus's mass, respectively.

These symbols are also used to specify the positions of the electrons (i) and (j) and the nuclei (k) and (l), while the atomic numbers indicate the identity of each nucleus (k) and (l).

An exact solution of **the Schrödinger equation(I.1)** is possible only for single-electron systems, such as hydrogen-like atoms. For multi-electron systems, the **Born–Oppenheimer** approximation is commonly employed, which assumes that the nuclei move much more slowly than the electrons. This allows the electronic motion to be treated independently from the nuclear motion, simplifying the analysis of the system's quantum properties[1].

$$H = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{r_{Ai}} + \sum_{i,j \neq i} \frac{e^2}{r_{ij}} + \sum_{A,B \neq A} \frac{Z_A Z_B e^2}{R_{A,B}} \quad (\text{I.8})$$

The general form of the Schrödinger equation (I,1) is extremely difficult to solve directly, mainly due to the strong interactions between electrons and nuclei within a material. To simplify the treatment of the system's Hamiltonian, **Max Born and Robert Oppenheimer** proposed an approximation method, known as the Born-Oppenheimer approximation (or adiabatic), which allows the separation of the motion of electrons from that of nuclei, thus greatly facilitating the solution of the equation [1,2].

I.1.1 Born–Oppenheimer Approximation

The Born–Oppenheimer approximation is based on the large difference between the mass of the nucleus and that of the electron, where the nuclear mass M exceeds the electron mass m by several orders of magnitude (approximately 10^3 to 10^4 times greater), their dynamical behaviors occur on significantly different time scales. Electrons, owing to their much smaller mass, respond far more rapidly to external forces, whereas the much heavier nuclei move comparatively slowly.

Based on this fundamental distinction, it is reasonable, as a first approximation, to consider the nuclei as fixed while analyzing electronic motion. This assumption provides a physically justified simplification, allowing the separation of electronic and nuclear motions and thereby facilitating the solution of the Schrödinger equation for a many-particle system[4].

Under this approximation, the nuclear kinetic energy term T_N is neglected, and the nucleus–nucleus interaction term V_{N-N} is treated as a constant. Consequently, the total Hamiltonian of the system can be written as:

$$H_{tot} = H_e + V_{N-N} \quad (I.9)$$

where the electronic Hamiltonian is given by:

$$H_e = T_e + V_{N-e} + V_{e-e} \quad (I.10)$$

In this formulation, the analysis focuses exclusively on the motion of electrons in the Coulomb field generated by fixed nuclei, providing a simplified yet physically accurate framework for describing the electronic structure of atomic and molecular systems.

The operator H_e represents the electronic Hamiltonian of the system, and the main task is therefore to determine the electronic eigenvalues and eigenfunctions, i.e., to solve the equation:

$$H_e \psi = E_e \psi \quad (I.11)$$

By employing the **Born–Oppenheimer approximation**, the system can be simplified from $(Z+1)N$ particles to a system of ZN electrons with fixed nuclei. Nevertheless, solving this equation remains highly challenging, as an exact analytical solution is not feasible, and direct numerical solutions are extremely difficult due to the complexity of electron–electron interactions.

To overcome these difficulties, several approximate methods have been developed, most notably **the Hartree method**, which represents the total wavefunction as a product of single-electron wavefunctions while respecting **the Pauli** exclusion principle. This approach provides a practical and efficient framework for studying electronic interactions with reasonable accuracy and computational feasibility.

I.1.2 Hartree Approximation

We are dealing with a many-electron system, for which solving the exact Schrödinger equation is extremely difficult because of electron–electron interactions. To simplify the problem, Hartree proposed an approximation in which each electron moves independently in an average potential created by the nuclei and all other electrons.

Within this approximation, the total electronic wavefunction is expressed as the product of single-electron wavefunctions:

$$\psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots \dots \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2) \dots \dots \dots \psi_N(\mathbf{r}_N) \quad (\text{I.12})$$

Consequently, the many-body Schrödinger equation is transformed into a set of independent one-electron equations:

$$H_i \psi_i = E_i \psi_i \quad (\text{I.13})$$

Or equivalently

$$\left[-\frac{\hbar^2}{2m} \Delta_i + U_i(\mathbf{r}_i) + V_i(\mathbf{r}_i) \right] \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i) \quad (\text{I.14})$$

Here:

- $U_i(\mathbf{r}_i)$: represents the Hartree field created by other electrons in the system.
- $V_i(\mathbf{r}_i)$: is the potential energy of electron i due to fixed nuclei at positions R .

Although the Hartree approximation significantly simplifies the problem, it neglects the antisymmetric nature of the electronic wavefunction and does not explicitly account for exchange effects. Therefore, two important aspects must be considered [5]:

Coulomb repulsion between electrons:

Each electron experiences electrostatic repulsion from all other electrons. A more accurate treatment of this interaction improves the description of the electronic structure.

Pauli exclusion principle:

According to this principle, no two electrons can occupy the same quantum state simultaneously. Therefore, the total electronic wavefunction must be antisymmetric with respect to the exchange of any two electrons.

I.1.3 Hartree–Fock Approximation:

To overcome the limitations of the Hartree approximation, Fock [6] introduced an improved method that incorporates the Pauli exclusion principle through the use of a Slater determinant. The electronic wavefunction is written as [7]:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \dots & \Psi_N(1) \\ \Psi_1(2) & \Psi_2(2) & \dots & \Psi_N(2) \\ \dots & \dots & \dots & \dots \\ \Psi_1(i) & \Psi_2(i) & \dots & \Psi_N(i) \\ \dots & \dots & \dots & \dots \\ \Psi_1(N) & \Psi_2(N) & \dots & \Psi_N(N) \end{vmatrix} \quad (\text{I.15})$$

Here, the factor $\frac{1}{\sqrt{N!}}$ is a normalization constant. The determinant automatically guarantees the antisymmetry of the wavefunction under the exchange of any two electrons and therefore satisfies the Pauli exclusion principle.

Compared with the Hartree approximation, the Hartree–Fock method provides a more realistic description of electronic systems by incorporating exchange effects while remaining computationally tractable.

I.1.4 Hohenberg and Kohn Approximation :

The total energy of a system in its ground state is a unique universal functional that depends solely on the electronic density, and can therefore be written as:

$$E_0 = E \left[\rho(\vec{r}) \right] \quad (\text{I.17})$$

For a fixed external potential V_{ext} and a given number of electrons N , the total energy of the system reaches its minimum value when the density

$\rho(\mathbf{r})$ corresponds to the exact ground-state density. Thus,

$$E_0 \left(\rho(\vec{r}) \right) = \min E \left(\rho(\vec{r}) \right) \quad (\text{I.18})$$

The energy functional can also be expressed in terms of the many-body wavefunction ψ and the Hamiltonian operator as:

$$E[\rho(\mathbf{r})] = \langle \psi | H | \psi \rangle = \langle \psi | T_e + V_{e-e} + V_{ext} | \psi \rangle \quad (\text{I.19})$$

Here, the external potential V_{ext} includes the Coulomb interaction between electrons and nuclei, as well as the interactions among the nuclei themselves. Accordingly, the energy functional may be decomposed as:

$$E[\rho(\mathbf{r})] = \langle \psi | T_e + V_{e-e} | \psi \rangle + \langle \psi | V_{ext} | \psi \rangle \quad (\text{I.20})$$

The total energy can also be written in terms of a universal density functional as:

$$E = \left[\rho(\vec{r}) \right] = F \left[\rho(\vec{r}) \right] + \int \rho(\vec{r}) V_{ext} d(\vec{r}) \quad (\text{I.21})$$

where the universal functional $F[\rho]$ is given by:

$$F[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[\rho] \quad (\text{I.22})$$

Due to the repulsive electron–electron interaction, $F[\rho]$ represents the universal functional introduced by **Pierre Hohenberg** and Walter Kohn [8], which contains contributions from both kinetic and potential energies.

The functional $G[\rho]$ accounts for the kinetic energy together with the difference between the true electron–electron interaction energy and that obtained within the Hartree approximation. Importantly, the functionals $F[\rho]$ and $G[\rho]$ remain valid regardless of the form of the external potential or the number of electrons in the system.

However, the two **Hohenberg–Kohn** theorems do not provide an explicit analytical expression for the energy functional $E(\rho(\mathbf{r}))$ [9]. Consequently, a practical treatment requires the use of an approximate scheme. For this purpose, one proceeds to the Kohn–Sham approximation.

I.1.5 Kohn–Sham Approximation:

In 1965, **Walter Kohn** and **Lu Jeu Sham**[10] introduced a simplified formalism for calculating electron density.

Although the **Hohenberg–Kohn** theorem provides a fundamental foundation, it does not offer a practical and explicit procedure for constructing the mapping from the electron density

$\rho(\mathbf{r})$ to the many-body wave function $\psi(\rho)$. To overcome this conceptual limitation, **Kohn** and **Sham** proposed in 1965 an alternative formulation based on replacing the real interacting electronic system with an auxiliary fictitious non-interacting system, provided that both systems share the same ground-state electron density. This theoretical construction preserves both the ground-state energy and the electron density of the real system, while significantly simplifying the treatment of complex electron–electron interactions through the introduction of an effective potential.

Within this framework, the energy functional of the interacting system can be expressed as follows [11]:

$$F[\rho(r)] = T_s [\rho(r)] + E_H[\rho(r)] + E_{xc}[\rho(r)] + V_{ext}[\rho(r)] \quad (I.23)$$

where:

- $T_s [\rho(r)]$: represents the kinetic energy of a non-interacting electron system having the same density.
- $E_H[\rho(r)]$: denotes the classical electrostatic (**Hartree**) energy.
- $E_{xc} [\rho(r)]$: is the exchange–correlation energy, which incorporates all remaining **quantum** mechanical effects not included in the non-interacting kinetic energy **and Hartree** terms.
- $V_{ext}[\rho(r)]$: corresponds to the energy arising from the external potential acting on the system.

The importance of **equation (I.23)** lies in the fact that, through the variational principle of energy minimization, it leads to the **Kohn–Sham** equations, which are solved self-consistently. These equations take a form analogous to the single-particle Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r) \right] \psi_i = \varepsilon_i \psi_i(r) \quad (I.24)$$

Here,

ψ_i are the **Kohn–Sham** orbitals, and ε_i are their corresponding eigenvalues, representing single-particle energy levels within the non-interacting reference system.

The **Hartree** potential, which describes the average electrostatic interaction arising from the electron density distribution, is given by:

$$V_H(r) = \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d\mathbf{r}d\mathbf{r}' \quad (I.25)$$

The exchange–correlation potential is obtained as the functional derivative of the exchange–correlation energy with respect to the electron density:

$$V_{xc}[\rho(r)] = \left[\frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \right] \quad (I.26)$$

These relations emphasize a central idea: each electron moves under the influence of an effective potential that accounts for the collective effect of all other electrons. **Accordingly**, the **Kohn–Sham** equation can be written in compact form as:

$$\hat{H} \psi_i = \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \psi_i = \varepsilon_i \psi_i \quad (I.27)$$

where the effective potential is defined as:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (\text{I.28})$$

Thus, the Kohn–Sham formulation provides a coherent and practical theoretical framework for investigating many-electron systems, reducing the complexity of electron–electron interactions to an effective potential while preserving the essential physical characteristics of the real system.

I.1.6 Local Density Approximation (LDA):

Within the framework of Density Functional Theory (DFT), **Kohn** and **Sham** proposed in 1965 the Local Density Approximation (LDA) as a practical formulation for representing the exchange–correlation energy functional $E_{xc}[\rho(\mathbf{r})]$ [12]. This approximation is based on the assumption that the electronic density $\rho(\mathbf{r})$ varies slowly on a microscopic scale, allowing each point in the system to be treated locally as a homogeneous electron gas with the same density.

Under this assumption, the exchange–correlation energy is expressed as

$$E_{xc} = \int \rho(\mathbf{r}) E_{xc}[\rho(\mathbf{r})] d\mathbf{r} = \int \rho(\mathbf{r}) \{E_x[\rho(\mathbf{r})] + E_c[\rho(\mathbf{r})]\} d\mathbf{r} \quad (\text{I.29})$$

where $E_{xc}[\rho(\mathbf{r})]$ denotes the exchange–correlation energy per electron of a homogeneous electron gas with density ρ . This quantity is decomposed into two contributions: the exchange term $E_x[\rho(\mathbf{r})]$ which can be derived analytically from the homogeneous electron gas model, and the correlation term $E_c[\rho(\mathbf{r})]$, which was determined with high numerical accuracy using Quantum Monte Carlo techniques in the work of Ceperley and Alder, and subsequently parameterized in forms suitable for practical calculations [13].

The **LDA** is particularly appropriate when density gradients are small, since the local electronic properties are then expected to resemble those of the reference homogeneous electron gas. Although this approximation neglects explicit dependence on spatial derivatives of the density, it has demonstrated remarkable effectiveness in describing inhomogeneous systems, especially in solid-state physics. Its practical success has established it as one of the foundational approximations in DFT and has motivated the development of more advanced approaches that incorporate gradient corrections explicitly [14].

I.1.7 Generalized Gradient Approximation (GGA):

Although the Local Density Approximation (**LDA**) has provided satisfactory results in a wide range of applications, its limitations become evident in systems where the electronic density exhibits significant spatial variations. This is primarily because **LDA** depends exclusively on the local value of the electron density $\rho(\mathbf{r})$, neglecting the influence of its spatial gradient, which may lead to noticeable deviations from experimental data in certain cases. To address this shortcoming, the Generalized Gradient Approximation (**GGA**) was developed with the aim of improving the description of the exchange–correlation energy by incorporating the effects of density inhomogeneity.

Within the **GGA** framework, the exchange–correlation energy functional depends not only on the electron density but also on its spatial gradient. It is expressed as:

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) E_{xc}^{hom}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r}^3 \quad (\text{I.30})$$

where

E_{xc}^{hom} represents the local **exchange–correlation** energy density including gradient effects. The inclusion of density derivatives enables a more accurate description of inhomogeneous systems compared to **LDA**. In particular, it improves the prediction of structural and energetic properties, especially in materials characterized by directional chemical bonding or pronounced variations in electron distribution.

Several functional forms have been proposed within the **GGA family**. Among them are **Becke's B88 functional** [15], the **Perdew–Wang formulation** known as **GGA-PW** or **GGA91** [16], and the widely used **Perdew–Burke–Ernzerhof (PBE) functional**, commonly referred to as **GGA-PBE** or **GGA96** [17]. Additional variants include the **RPBE functional** developed by Hammer and co-workers [18], the **GGA-WC** or **GGA06 functional** proposed by Wu and Cohen [19], and the revised **PBEsol** or **GGA08 functional** introduced by Perdew et al. for improved solid-state calculations [20].

In general, **GGA** provides a noticeable improvement over **LDA** in the calculation of total energies, binding energies, and lattice **parameters**. In the present work, the **GGA-PBE functional** [17] was adopted due to its balanced compromise between computational efficiency and accuracy, as well as its ability to yield results in close agreement with experimental observations.

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CHAPTER II:

Plane Wave and Pseudopotential Methods

II.1. Plane Wave Method (PW) :

Following the theoretical developments within the framework of Density Functional Theory (DFT), the Kohn–Sham equations were established. These equations have a form similar to the Schrödinger equation for a single particle. They are solved using a self-consistent procedure, starting from a practical description of the physical system composed of nuclei and electrons. The equations are written as follows :

$$H_{eff} Q_i \left(\vec{r} \right) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff} \left(\vec{r} \right) \right] Q_i \left(\vec{r} \right) = \varepsilon_i \left(\vec{r} \right) \varphi_i \left(\vec{r} \right) \quad (II.1)$$

Where

- V_{eff} represents the effective potential acting on the electrons. This potential is composed of several contributions and can be expressed as:

$$V_{eff} \left(\vec{r} \right) = V_{pseudo} \left(\rho \left(\vec{r} \right) \right) + V_H(\rho(\vec{r})) + V_{xc}(\rho(\vec{r})) \quad (II.2)$$

In the case of a perfect crystal, the Kohn–Sham equations describe the behavior of valence electrons moving in a periodic potential generated by the periodic arrangement of nuclei, which are often represented using pseudopotentials, in addition to the contribution of the other electrons in the system. However, describing a crystalline system that contains an infinite number of electrons moving in a field generated by an infinite number of nuclei remains a significant challenge. In principle, this would require determining a wave function for each electron, which makes a direct solution of the problem impractical.

To overcome this difficulty, the periodic nature of crystalline systems is exploited. This property makes it possible to simplify the theoretical treatment of the problem. By taking advantage of the crystal symmetry, the computational complexity of the system can be significantly reduced, which facilitates the study of the electronic properties of crystalline materials [1,2].

II.2. Introduction of Pseudopotential Method :

The pseudopotential theory, initially developed by Enrico Fermi in the study of atomic energy levels, represents an effective approach for analyzing and understanding the electronic properties of solids. The physical properties of crystalline materials are predominantly determined by valence electrons, while core electrons, being strongly bound, contribute minimally to chemical bonding [3-6].

In this framework, core electrons are grouped together with the nucleus to form rigid ions, according to the so-called frozen-core approximation [3]. This approximation accounts

for the interactions between the nucleus and the core electrons, the Hartree potential arising from these electrons, as well as a partial exchange-correlation contribution reflecting the interactions between core and valence electrons, particularly to include certain relativistic effects.

This simplification allows for an efficient treatment of the core electrons problem, enabling the study to focus on the behavior of valence electrons within a potential partially screened by the inner electrons. Therefore, the pseudopotential method relies on the approximation that replaces the Coulomb potential of the nucleus and the effects of the strongly bound core electrons with an effective potential that interacts solely with the valence electrons [7].

II. 3. Cut-off Energy

The accurate representation of the electronic wavefunction necessitates the deployment of an extensive plane-wave basis set. From a physical standpoint, the expansion coefficients $C_{\vec{k}+\vec{G}}$

for plane waves with low kinetic energy are inversely proportional to their kinetic energy

$\frac{\hbar^2}{2m} \left| \vec{k} + \vec{G} \right|^2$ [8]. Consequently, for computational feasibility, the basis set is truncated to include only those plane waves whose kinetic energy remains below a predefined threshold, known as the cut-off energy, according to the following criteria:

$$\frac{\hbar^2}{2m} \left| \vec{k} + \vec{G} \right|^2 \leq E_{cut-off} \quad (\text{II.3})$$

$$E_{cut-off} = \frac{\hbar^2}{2m} \left| \vec{k} + \vec{G} \right|^2 \quad (\text{II.4})$$

The selection process of these plane waves involves defining a sphere in reciprocal space with a radius of $|G_{max}|$ centered at the origin, such that all vectors within this sphere satisfy the condition $|k + G| \leq G_{max}$. The total number of plane waves N_{pw} contained within this boundary is given by the following expression:

$$N_{pw} \approx N_K \times \frac{1}{2\pi^2} \Omega E_{cut-off}^{\frac{3}{2}} \quad (\text{II.5})$$

Where N_K and Ω represent the number of sampled $\vec{k}$ within the first Brillouin zone and the volume of the simulation cell, respectively. A rigorous selection of the cut-off energy is fundamental, as it ensures the convergence of the total energy and directly dictates the degree of numerical precision in the calculations.

II-4. The Pseudopotential Method

Building upon the fundamental concepts established in the first chapter, a principal framework can be defined to determine the electronic ground state of an arbitrary system within the Kohn-Sham formulation. A primary challenge arises as calculations become increasingly computationally expensive with larger atomic sizes. This escalation is attributed, on one hand, to the increased number of electrons, and on the other, to the highly localized nature of certain orbitals, such as the d-orbitals. Consequently, while some periodic table elements can be modeled with high efficiency, heavy elements and transition metals necessitate significantly more powerful computational resources. This section provides an overview of the pseudopotential approximation, which is predicated on the physical principle that a material's properties are primarily determined by its valence electrons. When investigating a system composed of **{nucleus + electrons}**, the external energy is calculated as follows:

$$E_{ext} [\rho(r)] = \frac{1}{\Omega} \int V_{ext}(r) \rho(r) dr \quad (\text{II.6})$$

Where:

- V_{ext} : The Coulomb potential generated by the bare nuclei.
- Ω : The volume of the simulation cell.

Methodologically, a distinction is made between two types of electrons: core electrons and valence electrons. Core orbitals are characterized by lower energy levels and are strictly localized near the nucleus; they exhibit minimal sensitivity to the chemical environment and do not participate in chemical bonding. Furthermore, they are difficult to represent using a plane-wave basis set due to their rapid oscillations near the atomic nuclei. Conversely, valence orbitals are less localized, extending far from the nucleus, and are the primary determinants of the system's physicochemical properties.

The concept proposed by Fermi involves simplifying electronic structure calculations by eliminating core states, thereby reducing computation time—a method known as the "frozen core approximation." Within this framework, the effect of core electrons is replaced by an effective pseudopotential. The system under consideration is no longer a {bare nucleus

+ all electrons} system, but rather **{ions (nucleus + core electrons) + valence electrons}**. We seek to replace the strong electron-nucleus potential with a "weaker" potential that accounts for the screening of the nucleus by the core electrons.

In modeling the external potential $V_{ext}(r)$, several models have been established. In pseudopotential-based methods, one begins with the atomic states of an isolated atom, defining a cutoff radius r_c to distinguish between the core and valence regions. Subsequently, by expanding wavefunctions on a plane-wave basis and imposing the Orthogonalized Plane Wave (OPW) condition, the pseudopotential is constructed [9,10,11].

These eigenfunctions, termed pseudowavefunctions, possess the same scattering properties as the real (all-electron) wavefunctions outside the core region. The transferability of a pseudopotential refers to its capacity to accurately predict or reproduce a wide range of properties across diverse chemical environments.

Figure (II.1) illustrates the profile of a pseudowavefunction in comparison to the exact wavefunction and the corresponding potentials [8].

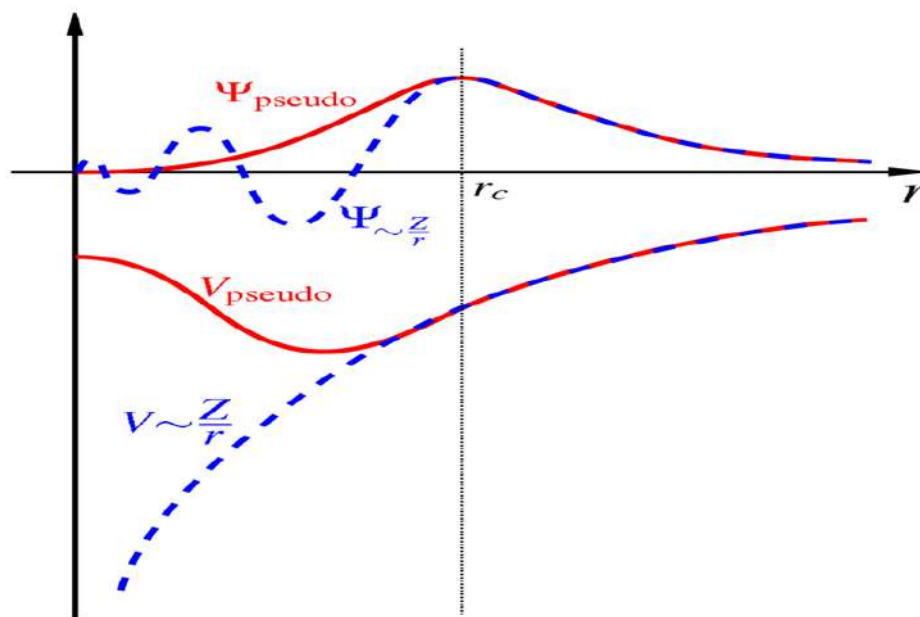


Figure (II.1): Pseudization of valence electron wavefunctions and the corresponding potential.

Four major families of pseudopotentials have been developed:

- Norm-conserving pseudopotentials, introduced by Hamann et al. [12].

- Vanderbilt ultra-soft (US) pseudopotentials [13].
- Projector Augmented Wave (PAW) methods, which do not strictly conserve the norm [14].
- Dual-space Gaussian pseudopotentials, introduced by Goedecker et al. [15,16].

In this work, norm-conserving pseudopotentials were preferred due to their conceptual clarity and straightforward numerical implementation.

II-5. Norm-Conserving Pseudopotentials

We proceed within a spinless formalism, where each eigenstate of the atomic Schrödinger equation is characterized by three quantum numbers (n, l, m). The total wavefunction is expressed as:

$$\phi_{nlm}(r, \theta, \varphi) = R_{n,l}(r)Y_{l,m}(\theta, \varphi) \quad (\text{II.7})$$

Where

$R_{n,l}$ represents the radial part and $Y_{l,m}$ denotes the spherical harmonics, defined by:

$$Y_{l,m}(\theta, \varphi) = g(\theta)e^{im\varphi} \quad (\text{II.8})$$

To ensure that the $Y_{l,m}$ functions are well-defined, m must be an integer ($m \in \{Z\}$). Furthermore, since m and l are known to be either both integers or both half-integers, it follows that l must also be an integer.

In this framework, we utilize a radial Schrödinger-type equation involving only the radial component $R_{n,l}$. The family of norm-conserving pseudopotentials must satisfy the following fundamental conditions:

1- Equality of Eigenvalues: The pseudo-eigenvalues (PS: pseudopotential) and the real eigenvalues (AE: All-Electron) must be identical for a given electronic configuration:

$$\epsilon_{n,l}^{AE} = \epsilon_{n,l}^{PS} \quad (\text{II.9})$$

2- Convergence of Wavefunctions: The real and pseudo-wavefunctions must be identical beyond a chosen cutoff radius r_c . That is, for $r > r_c$

$$R_{n,l}^{AE}(r) = R_{n,l}^{PS}(r) \quad (\text{II.10})$$

2- Norm Conservation: The integrals of the real and pseudo-charge densities must agree within the cutoff radius for each valence state[8]:

$$\int_0^{r_c} |R_{n,l}^{AE}(r)|^2 r^2 dr = \int_0^{r_c} |R_{n,l}^{PS}(r)|^2 r^2 dr \quad (\text{II.11})$$

A direct consequence of this condition is that the logarithmic derivatives of the real and pseudo-wavefunctions, as well as their first derivatives with respect to energy, must agree for $r > r_c$.

Once the pseudo-wavefunction is obtained, the screened pseudopotential $V_{scr,l}^{PS}$, as seen by the valence electrons, is determined by inverting the radial Schrödinger equation:

$$V_{scr,l}^{PS} = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_l^{PS}(r)} \frac{d}{dr} [r R_l^{PS}(r)] \quad (\text{II.12})$$

The resulting pseudopotential is non-singular except at the origin, allowing for the inversion of the equation. The ionic pseudopotential is then derived by removing the screening effect of the valence electrons from the screened pseudopotential. This is achieved by subtracting the Hartree potential $V_H^{PS}(r)$ and the exchange – correlation potential $V_{xc}^{PS}(r)$, both calculated from the pseudo-wavefunctions:

$$V_{ion,l}^{PS}(r) = V_{scr,l}^{PS}(r) - V_H^{PS}(r) - V_{xc}^{PS}(r) \quad (\text{II.13})$$

For each angular momentum component, the wavefunction experiences a distinct potential within the core region. Consequently, the ionic pseudopotential is generally expressed as a combination of a local part (dependent only on r) and a non-local part (accounting for the l -dependence). The semi-local form of the pseudopotential is written as:

$$V_{ion,l}^{PS}(r) = V_{ion,local}^{PS}(r) + \sum_l V_{nonlocal,l}^{PS}(r) \hat{P}_l \quad (\text{II.14})$$

Where:

- $V_{ion,local}^{PS}(r)$: denotes the local pseudopotential.
- $V_{nonlocal,l}^{PS}(r) = V_{ion,l}^{PS}(r) - V_{ion,local}^{PS}(r)$: represents the non-local potential for the l -th angular momentum component.
- $\hat{P}_l$: is the projection operator onto the l -th angular momentum component.

Various parameterized forms of norm-conserving pseudopotentials exist. In this work, we have utilized the Troullier-Martins pseudopotentials.

II.6. Troullier-Martins Pseudopotential

The pseudo-wavefunctions, for each orbital angular momentum l , take the following form within the core region ($r \leq r_c$) [17]:

$$R_l^{PS}(r) = r^{l+1} e^{p(r)} / r \leq r_c \quad (\text{II.15})$$

Where $p(r)$ is defined as a twelfth-order polynomial, consisting only of even powers to ensure proper physical behavior and symmetry at the origin:

$$P(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12} \quad (\text{II.16})$$

The coefficients c_n of the polynomial $p(r)$ are determined by satisfying the following physical and mathematical constraints:

1. Norm-Conservation Condition

The integrated probability density of the pseudo-wavefunction within the core region must match that of the all-electron (true) wavefunction :

$$\int (R_l^{PS}(r))^2 dr = \int (R_l(r))^2 dr \quad (\text{II.17})$$

2. Continuity of the pseudo-wavefunction and its first four derivatives at r_c : To ensure maximum smoothness of the potential, continuity conditions are imposed at the cut-off as radius (r_c) follows :

$$\frac{d^n R_l^{PS}(r_c)}{dr^n} = \frac{d^n R_l(r_c)}{dr^n} \quad n = 0, \dots, 4 \quad (\text{II.18})$$

Wavefunction Continuity:

$$R_l^{PS}(r_c) = r_c^{l+1} e^{p(r_c)} = R_l(r_c) \quad (\text{II.19})$$

Which allows for the determination of the polynomial value at the boundary:

$$P(r_c) = \ln \left[\frac{R_l(r_c)}{R_c^{l+1}} \right] \quad (\text{II.20})$$

Continuity of the First Derivative:

By differentiating equation (II.15), the first derivative of $p(r)$ at r_c is determined according to the relationship:

$$\begin{aligned} \frac{dR_l^{PS}}{dr} &= (l+1)r^l e^{p(r)} + r^{l+1} e^{p(r)} p'(r) = \frac{l+1}{r} R_l^{PS}(r) + p'(r) R_l^{PS}(r) \\ \Rightarrow p'(r_c) &= \frac{1}{R_l^{PS}(r_c)} \frac{dR_l}{dr} - \frac{l+1}{r_c} \end{aligned} \quad (\text{II.21})$$

Continuity of the Second Derivative:

Expanding the differentiation and relating it to the Schrödinger equation (where $V(r)$ is the potential and ε is the energy eigenvalue), we obtain:

$$\frac{d^2 R_l^{PS}(r)}{dr^2} = l(l+1)r^{l-1} e^{p(r)} + 2(l+1)r^l e^{p(r)} p'(r) + r^{l+1} e^{p(r)} [p'(r)]^2 + r^{l+1} e^{p(r)} p''(r)$$

$$\Rightarrow p''(r) = 2 \left(\frac{1}{2r^{l+1} e^{p(r)}} \frac{d^2 R_l^{PS}(r)}{dr^2} - \frac{l(l+1)}{2r^2} \right) - \frac{2(l+1)}{r} p'(r) - [p'(r)]^2 \quad (\text{II.22})$$

$$\Rightarrow p''(r) = 2(V(r) - \varepsilon) - \frac{2(l+1)}{r} p'(r) - [p'(r)]^2 \quad (\text{II.23})$$

Higher-Order Derivatives:

The mathematical expression for the third derivative $p'''(r)$ is derived to ensure the required smoothness:

$$p''(r) = 2V'(r) + 2\frac{(l+1)}{r^2} p'(r) + \frac{2l^2+l+1}{r^3} 2p'(r)p''(r) - 2\frac{(l+1)}{r} p'''(r) \quad (\text{II.24})$$

3. Final Screened and Unscreened Pseudopotential

The derivation concludes with the determination of the fourth derivative of $p(r)$ according to the following expression:

$$p''''(r) = 2V''(r) - 4\frac{l+1}{r^3} p'(r) 2\frac{l+1}{r^2} p''(r) - 2\frac{l+1}{r} p'''(r) - 2[p''(r)]^2 2p'(r)p''(r) \quad (\text{II.25})$$

In the final stage, the ionic pseudopotential corresponding to the angular momentum l is obtained by subtracting the valence electron contributions from the screened potential:

$$V_l^{PS}(r) = V_{SC/L}^{PS}(r) - V_H[n^{PS}(r)] - V_{XC}[n^{PS}(r)] \quad (\text{II.26})$$

Where $n(r)$ denotes the electronic pseudo-density constructed from the generated pseudo-wavefunctions.

II-7. Hartwigsen-Goedecker-Hutter (HGH) Pseudopotential

Hartwigsen, Goedecker, and Hutter introduced minor modifications to the analytical form of the Bachelet-Hamann-Schlüter pseudopotential. Their construction [18] also incorporates the norm-conservation property originally proposed by Bachelet and Schlüter [17].

The local component of the pseudopotential is defined by the following expression:

$$V_{loc}(r) = \frac{-Z_{ion}}{r} \text{erf}\left(\frac{r}{\sqrt{2}r_{loc}}\right) + \exp\left[-\frac{1}{2}\left(\frac{r}{r_{loc}}\right)^2\right] \times [c_1 + c_2\left(\frac{r}{r_{loc}}\right)^2 + c_3\left(\frac{r}{r_{loc}}\right)^4 + c_4\left(\frac{r}{r_{loc}}\right)^4] \quad (\text{II.27})$$

- **Variables definition:**

- erf : The error function
- Z_{ion} : The ionic charge of the atomic core (representing the total charge minus the valence charge).

- **The non-local contribution** to the pseudopotential is given by:

$$V_l(r, r') = \sum_{i=1}^{i=3} \sum_{j=1}^{j=3} \sum_{m=-1}^{m=+1} Y_{l,m}(r) P_l^i(r) h_{l,j}^l P_j^l(r') Y_{l,m}^*(r') \quad (\text{II.28})$$

Where:

- $Y_{l,m}$: The spherical harmonics.
- $\mathbf{l}$: The angular momentum.

The projectors $P_i^l(\mathbf{r})$ are defined in the Gaussian form as follows:

$$P_i^l(r) = \frac{\sqrt{2} r^{l+(i-1)} \exp\left(-\frac{r^2}{2r_l^2}\right)}{r_l^{1+(4i-1)/2} \sqrt{\Gamma\left(1+\frac{4i-1}{2}\right)}} \quad (\text{II.29})$$

Where Γ denotes the gamma function. In this construction, the parameters are determined by minimizing the discrepancy between the eigenvalues and the charges within the core region for both the atom and the pseudoatom. A distinctive feature of this pseudopotential is that the parameters are "fitted" directly from the eigenvalues and charges calculated by accounting for all electrons. This approach is used instead of performing an analytical or numerical fit to reproduce the pseudofunctions, which are themselves constructed from these calculations.

II. 8. Advantages of the Pseudopotential Approach

The implementation of the pseudopotential method in electronic structure calculations offers several computational and physical advantages over all-electron methods, namely:

Efficiency of Plane-Wave Basis Sets: By smoothing the potential within the core region, the rapid oscillations of the wavefunctions are eliminated. This allows for the effective use of plane-wave basis sets, significantly reducing the computational requirements (the energy cutoff) needed for convergence.

Simplified Implementation of Forces and Stress: The use of plane waves within this framework facilitates the direct formulation and calculation of Hellmann-Feynman forces and virial pressures, owing to the mathematical simplicity of the plane-wave representation.

Enhanced Relative Precision of Total Energy: Since the massive, constant energy contributions from the core electrons are excluded, the calculation focuses solely on the valence electrons. This enables achieving the necessary physical precision in total energy per atom with only five significant figures, a degree of accuracy that would require far higher precision in all-electron approaches.

Spectral Integrity: The pseudopotential concept ensures the stability of the energy spectrum by preventing the emergence of ghost bands during electronic structure calculations [22].

II.9. Definition and Objective of the GIBBS Program

The equation of state (EOS) and chemical potential are essential thermodynamic properties that describe the behavior of solids under pressure (p) and temperature (T).

The EOS defines the response of crystalline phases to variations in these macroscopic parameters, while the chemical potential μ , equivalent to the molar Gibbs free energy G_m , determines phase stability and transformations.

From a theoretical viewpoint, evaluating the EOS and chemical potential from first principles is fundamental in crystal physics. Under fixed temperature and hydrostatic pressure, thermodynamic equilibrium is obtained by minimizing the Gibbs free energy [23]

$$G^*(\mathbf{X}; p; T) = E(\mathbf{X}) + P\mathbf{v}(\mathbf{X}) + A_{vib}(\mathbf{X}; T)$$

where

$\mathbf{x}$ represents the internal structural parameters of the crystal. In this expression,

$E(\mathbf{x})$ is the total energy, $pV(\mathbf{x})$ denotes the pressure contribution, and A_{vib}

is the vibrational Helmholtz free energy, given in the quasi-harmonic approximation by [23]

$$A_{vib}(\mathbf{x}; T) = \int_0^\infty \left[\frac{1}{2} \hbar \omega + KT \ln(1 + e^{-\hbar \omega / KT}) \right] g(\mathbf{x}; \omega) d\omega \quad (\text{II.30})$$

with

$g(\mathbf{x}; \omega)$ being the phonon density of states.

In practical calculations, vibrational effects are often neglected in a first approximation, reducing the Gibbs free energy to

$$G_{static}^*(\mathbf{x}; p) = E(\mathbf{x}) + pV(\mathbf{x})$$

which is minimized with respect to $\mathbf{x}$. Although this static model provides useful predictions, it does not fully reproduce experimental results because thermal contributions remain significant even at low temperatures.

To overcome this limitation, several quasi-harmonic methods have been proposed [24], yet their application in first-principles calculations remains computationally expensive. Therefore, alternative simplified models were introduced to include thermal effects using calculated energy–volume data [25,26,27,,20,28].

II.10. The Quasi-Harmonic Debye Model

II.10.1. Basic input of the model: static optimisations

The implementation of the quasi-harmonic Debye model assumes the availability of an appropriate approximate algorithm (e.g., ab initio methods [19,29,30,31,21]) to compute the

total energy $E(x)$. Before the model can be applied, this multivariable energy surface must be transformed into a strain-energy or energy-volume $E(V)$ curve. This transformation can be achieved through two equivalent computational pathways:

- **Fixed-volume optimisations:** This involves minimizing $E(x)$ for a set of discrete, fixed volumes by optimizing internal coordinates, angles, and cell length ratios (e.g., c/a and b/a). This procedure yields an $E(V) = E(x_{pot}(V))$ curve, representing the minimum energy points across different constant V hyperplanes.

- **Constant-pressure optimisations:** Static optimisations are performed at various constant pressures using the non-equilibrium Gibbs function (equivalent to the static enthalpy H_{static}^*):

$$G_{static}^*(x; p) = G_{static}^*(x; p) = E(x) + pV(x) \quad (\text{II.31})$$

This leads to the static equation of state (EOS) $V(p)$, from which the corresponding (E, V) pairs are derived.

Both procedures are physically equivalent since G_{static}^* acts as the Lagrange function for minimizing E under the constraint of constant V , where pressure p serves as the Lagrange multiplier. For numerical stability in subsequent minimization procedures, a homogeneous distribution of V points spanning values above and below the static zero-pressure equilibrium volume V_0 is preferred. Fixed-volume optimisations are generally recommended to avoid the inclusion of unphysical negative pressures required to sample points above V_0 .

II.10.2. Thermal effects: quasi-harmonic Debye model

Following the static calculations, the non-equilibrium Gibbs function G^* is expressed as a function of $(V; p, T)$:

$$G^* = (x_{opt}(V); p, T) = E(x_{opt}(V)) + pV + pV + A_{vib}(x_{opt}(V); T)$$

The vibrational contribution A_{vib} is formulated using the Debye model of the phonon density of states [25,26,27,20,28]:

$$A_{vib}(\theta; T) = nKT \left[\frac{9}{8} \frac{\theta}{T} + 3 \ln(1 - e^{-\theta/T}) - D(\theta/T) \right]$$

Where the Debye integral $D(y)$ is defined as:

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$$

The Debye characteristic temperature Θ is related to the average sound velocity and can be computed for an isotropic solid, assuming a constant Poisson ratio σ [32], as follows [25]:

$$\Theta = \frac{\hbar}{k} \left[6\pi^2 V^{\frac{1}{3}} n \right]^{\frac{1}{3}} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (\text{II.32})$$

Where M is the molecular mass per formula unit, B_s is the adiabatic bulk modulus, and $f(\sigma)$ is given by [27,28]:

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2}{3} \frac{1+\sigma}{1-2\sigma} \right)^{\frac{3}{2}} + \left(\frac{1}{3} \frac{1+\sigma}{1-2\sigma} \right)^{\frac{3}{2}} \right]^{-1} \right\}^{\frac{1}{3}}$$

The adiabatic bulk modulus B_s is often approximated by the static compressibility derived from the $E(V)$ curve:

$$B_s \simeq B_{static}(X) \simeq B_{static}(X_{opt}(V)) = \left(\frac{d^2 E(X_{opt}(V))}{dV^2} \right) = V \left(\frac{d^2 E(V)}{dV^2} \right) \quad (\text{II.33})$$

$$B_T(p, T) = V_{opt} \left(\frac{\partial^2 G^*(V; p, T)}{\partial V^2} \right)_{p, T} (V_{opt}) \quad (\text{II.34})$$

II.10.3 .Computational Scheme

To simplify the minimization and derivation involved in **Eqs. (II.33)–(II.34)**, analytical functions of V are fitted to the numerical data of $G^*(V; T, p)$ and $E(V)$. To reduce fitting errors, particularly at large volumes, the reduced parameter

$$X = (V/V_{erf})^{1/3}$$

is adopted, where V_{erf} is the equilibrium volume corresponding to the minimum energy in the (E, V) dataset.

To improve accuracy, polynomial fittings of different orders are performed and averaged using weighted factors given by

$$p_i = e^{-\omega_i^2} / \sum_i e^{-\omega_i^2} \quad (\text{II.35})$$

With

$$\omega_i = \left[\frac{(n_i+1)}{N_i} \right] \left[\frac{\sigma_i}{\sigma_{min}} \right]$$

And

$$\sigma_{min} = \min\{\sigma_i\}$$

This method ensures stable numerical results for the function minimum and its derivatives.

The same fitting procedure is applied to static and thermal data, where

$$A^*(V; T) = E(V) + A_{vib}(\Theta(V); T)$$

If

$$f(x) = \sum_i a_i x^i$$

fits the (E, x) data, then for $(E+pV, x)$ at $p \neq 0$, the third-order coefficient becomes

$$a'_3 = a_3 + pV_{ref}$$

Since

$$Pv = px^3 V_{ref}$$

After obtaining $E(x)$, the function $\Theta(x)$ is derived analytically, allowing construction of $(A^*(x; T), x)$ and determination of $G^*(x; p, T)$. Finally, the equation is solved using the bisection and Newton–Raphson methods, while $\ln\Theta$ versus $\ln V$ fitting is used to estimate the Grüneisen parameter (see below).

II.10 .4. Empirical Analytical Equations of State (EOS)

The gibbs program relies on fitting analytical expressions to the $p(V)$ data obtained. These models are based on the zero-pressure bulk modulus B_0 and its pressure derivatives $(B'_0, B''_0, \dots)$ as fitting parameters, allowing an alternative description of compressibility compared to that given in **Eq. (II.34)**.

These analytical relations can be used to determine various thermodynamic properties at any temperature T and pressure p . They can also be employed to calculate $\Theta(V)$ from **Eq. (II.32)** after performing an appropriate fit to the static data.

To assess the accuracy of the fitting, the $p(V)$ relationship can be analytically integrated to obtain the corresponding energy, namely the internal energy E in static calculations or the Helmholtz energy A^* in thermal calculations. The results are then compared with the original energy–volume data.

The gibbs program incorporates three main equations of state: the Vinet model [33], the Birch–Murnaghan model [32], and the spinodal model [34].

II.10.4.1. The Vinet Equation of State

The Vinet equation describes the relationship between pressure and volume as follows

$$\text{Ln} \left[\frac{px^2}{3(1-x)} \right] = \ln B_0 + \alpha(1-x) \quad x = \left(\frac{V}{V_0} \right)^{1/3} \quad (\text{II.36})$$

where

V_0 represents the zero-pressure equilibrium volume, while the fitting parameter is given by:

$$a = \frac{3(B'_0 - 1)}{2}$$

The isothermal bulk modulus and its pressure derivatives are defined as:

$$B_T = -x^{-2} B_0 e^{(1-x)} f(x) \quad (\text{II.37})$$

$$B'_T = \frac{1}{3} [(ax + 2) - x \frac{f'(x)}{f(x)}] \quad (\text{II.38})$$

$$B''_T = \frac{x}{9B_T} \left\{ x \frac{f''(x)}{f(x)} - a + \frac{f'(x)}{f(x)} [1 - x \frac{f'(x)}{f(x)}] \right\} \quad (\text{II.39})$$

where the function is defined as:

$$f(x) = x - 2 - ax(1-x)$$

II.10.4.2 . Birch–Murnaghan Equation of State

The second-order Birch–Murnaghan equation of state is employed to describe the pressure–volume relationship through a reduced function defined as:

$$F(f) = \frac{p}{3f(1+2f)^{5/2}} = \sum_{i=0}^2 a_i f^i$$

where

f represents the finite strain, and a_i are fitting parameters. These coefficients enable the determination of the zero-pressure bulk modulus and its pressure derivatives:

$$B_0 = a_0$$

$$B'_0 = 4 + \frac{2a_1}{3B_0}$$

$$B''_0 = \left[\frac{2}{3} \frac{a_2}{B_0} B'_0(B'_0 - 7) - \frac{143}{9} \right] / B_0 \quad (\text{II.40})$$

These relations highlight the fundamental role of the fitting parameters in characterizing the elastic properties of materials.

II.10.4.3. Spinodal Equation of State

The spinodal equation of state provides a description of material behavior near the mechanical stability limit, relating pressure and volume as follows:

$$V = V_{sp} \exp\left\{-\left[\frac{K^*}{1-\beta}\right](p - p_{sp})^{1-\beta}\right\}$$

The spinodal volume is given by:

$$V_{sp} = V_0 \exp\left\{\frac{\beta}{(1-\beta)}(p - p_s)^{1-\beta}\right\}$$

The spinodal volume is given by:

$$V_{sp} = V_0 \exp\left\{\frac{\beta}{(1-\beta)\beta'_0}\right\} \quad (\text{II.41})$$

where

p_{sp} , K^* , and β are fitting parameters. The bulk modulus and its derivatives are expressed as:

$$B_T = [K^*]^{-1}(p - p_{sp})^\beta$$

$$B'_T = \beta[K^*]^{-1}(p - p_{sp})^{\beta-1}$$

$$B''_T = \beta(\beta - 1)[K^*]^{-1}(p - p_{sp})^{\beta-2}$$

For numerical fitting, the logarithmic linear form is used:

$$\ln B_T = \beta \ln(p - p_{sp}) - \ln K^*$$

This formulation allows the determination of fitting parameters using linear least-squares methods.

II.10.5. Thermodynamic Properties (Quasi-Harmonic Debye Model)

Once the equilibrium state is determined, thermodynamic properties can be evaluated using the quasi-harmonic Debye model. The vibrational internal energy, heat capacity, and entropy are given by:

$$\bullet \quad U_{vib} = nkT \left[\frac{9}{8} \frac{\theta}{T} + 3D(\theta/T) \right] \quad (\text{II.42})$$

$$\bullet \quad C_{v,vib} = 3nk \left[4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (\text{II.43})$$

$$\bullet \quad S_{vib} = nk[4D(\theta/T) - 3 \ln(1 - e^{-\theta/T})] \quad (\text{II.44})$$

In conclusion, the **GIBBS program** represents a robust and efficient computational tool for predicting the thermodynamic behavior of solid-state materials. By integrating the quasi-harmonic Debye model with static energy-volume data, the program

successfully as the thermal expansion coefficient, heat capacities, and the Equation of State **(EOS)** without the prohibitive computational cost of explicit phonon calculations or molecular dynamics. Its flexibility in handling various analytical Equations of State, such as Vinet and Birch-Murnaghan, makes it an indispensable asset for studying materials under extreme conditions of pressure and temperature **[20,21]**. Ultimately, the use of this program enhances our understanding of phase stability and lattice dynamics, providing a reliable theoretical framework that complements experimental high-pressure research.

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Chapter III :
Results and Discussions

III.1. Crystal Description

In the preceding sections, a model describing the system composed of nuclei and electrons has been established. This approach leads to the Kohn–Sham equations, which are analogous to the single-particle Schrödinger equation and are solved self-consistently:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (\text{III.1})$$

where the effective potential is expressed as:

$$V_{eff}\left(\vec{r}\right) = V_{pseudo}\left(\rho\left(\vec{r}\right)\right) + V_H(\rho(\vec{r})) + V_{xc}(\rho(\vec{r}))$$

In an ideal crystal, the Kohn–Sham equations describe the valence electrons moving in a potential generated by the periodic lattice of pseudo-nuclei as well as by the other electrons. However, this formulation inherently involves an infinite number of electrons evolving in the field of an infinite number of nuclei, making a direct solution impractical.

To overcome this difficulty, it is essential to take advantage of the crystal's periodic nature. This is achieved by exploiting the symmetry properties of the crystalline lattice. A crystal is characterized by a basis (motif) and three primitive vectors $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$, which define the associated Bravais lattice.

Accordingly, the system can be reduced to a unit cell of parallelepiped shape containing ions and electrons, whose edges are defined by the vectors $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$

The potential then exhibits translational symmetry with respect to the lattice vectors

$$V(\vec{r}) = V(\vec{r} + \vec{R}) \quad (\text{III.2})$$

where

- $\mathbf{R}$ is a Bravais lattice vector given by

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

- with (n_1, n_2, n_3) being integers.

As a consequence, both the electronic density and the Kohn–Sham effective potential inherit this periodicity:

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{R}) \quad (\text{III.4})$$

$$V_{eff}(\vec{r}) = V_{eff}(\vec{r} + \vec{R}) \quad (\text{III.5})$$

This translational invariance of the effective potential constitutes the fundamental basis for the application of Bloch's theorem, which greatly simplifies the study of electronic properties in crystalline solids[1].

III.2. Bloch's Theorem

Bloch's theorem [2] is based on the periodic nature of the potential in a crystalline lattice, which makes it possible to reduce the mathematical description of electronic wave functions from an infinite set to a finite number equal to the number of electrons within the unit cell. According to this theorem, the electronic wave function can be expressed as the product of a plane wave and a periodic function having the same periodicity as the crystal lattice, as follows:

$$\varphi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) f_i(\vec{r}) \quad (\text{III.6})$$

where

$f_i(\vec{r})$ is a periodic function that satisfies the symmetry of the lattice. This function can be expanded as a discrete sum of plane waves whose wave vectors belong to the reciprocal lattice:

$$\varphi_i(\vec{r}, \vec{r}) = \sum_{\vec{G}} C_{i, \vec{k} + \vec{G}} \exp[i(\vec{k} + \vec{G}) \cdot \vec{r}] \quad (\text{III.7})$$

where

- $\vec{G}$ denotes the reciprocal lattice vectors, defined such that their components are integer multiples (with m being an integer). The vector $\vec{k}$ is referred to as the Bloch vector and characterizes the electronic state within the crystal.

III. 3. Sampling of the Brillouin Zone

Equation

$$H_{eff} Q_i(\vec{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff}(\vec{r}) \right] Q_i(\vec{r}) = \varepsilon_i(\vec{r}) \varphi_i(\vec{r}) \quad (\text{III.8})$$

is solved for each wave vector $\vec{k}$ within the Brillouin zone, and the corresponding eigenvalues are indexed by i . The system is thus described in terms of energy bands, where each atomic state gives rise to an energy band defined by .

From a numerical standpoint, it is not feasible to handle a continuous and infinite set of $\vec{k}$ -points. Therefore, the integrations are performed using a finite set of $\vec{k}$ -points distributed within the Brillouin zone, which constitutes a commonly adopted approximation.

The accuracy of the results obtained through a self-consistent approach strongly depends on the density of the k-point mesh used to solve Equation (III.8). In the case of semiconductors, a relatively small number of k-points is sufficient to obtain a reliable estimate of the total energy. In contrast, for metals, a finer sampling is required in order to properly describe the Fermi surface.

Thus, a balance must be achieved between computational cost and the number of k-points ensuring satisfactory convergence of the total energy. Several k-point sampling schemes have been proposed in the literature, including those of Chadi and Cohen [3], Joannopoulos and Cohen [4], Evarestov and Smirnov [5], and Monkhorst and Pack [6].

III.4. Crystal structure of Perovskite BaTiO₃ (Cubic)

In 1839, Gustav Rose discovered the mineral “perovskite” during his studies in the Ural Mountains. The mineral was named in honor of the Russian mineralogist Count Lev Aleksevich von Perovski [7]. Calcium titanate (CaTiO₃) is considered the first representative compound exhibiting this crystal structure [8].

Subsequently, the general formula ABO₃ was adopted to describe a broad class of oxides sharing the same crystal structure, in which the A and B cations occupy specific lattice sites within a three-dimensional oxygen framework. This classification was later extended to include non-oxide compounds that possess an analogous structural arrangement, which are also categorized as perovskites.

Perovskite compounds have attracted significant scientific interest due to their wide range of technological applications, particularly in electronics, refractories, and ceramics. This interest is largely attributed to the diversity of their physical properties, including superconductivity [9], catalytic and magnetic properties [10,11], ionic conductivity [12], as well as notable optical properties [13–15].

Perovskites are recognized as a fundamentally important class of ferroelectric materials [10]. These compounds are commonly represented by the general formula ABO₃, where the A-site is typically occupied by a mono- or divalent cation, while the B-site is occupied by a transition metal cation of higher valence, commonly tetravalent or pentavalent. The ideal perovskite structure adopts a cubic symmetry and is characterized by a relatively simple yet highly ordered arrangement.

Structurally, the perovskite lattice can be described as a three-dimensional network of corner-sharing BO₆ oxygen octahedra, forming a continuous framework. Within this framework, the B-site cations are located at the centers of the octahedra, whereas the A-site cations occupy larger interstitial sites with twelvefold coordination, situated between the

octahedral units. This arrangement gives rise to interpenetrating sublattices associated with the A and B cations.

One of the most notable features of perovskite materials is their exceptional structural adaptability, which enables them to undergo a variety of structural phase transitions. Experimental studies have demonstrated that perovskites can exhibit multiple phases, including ferroelectric and antiferroelectric states, as well as structural distortions related to the tilting of the oxygen octahedra, contributing to their rich and diverse physical behavior.

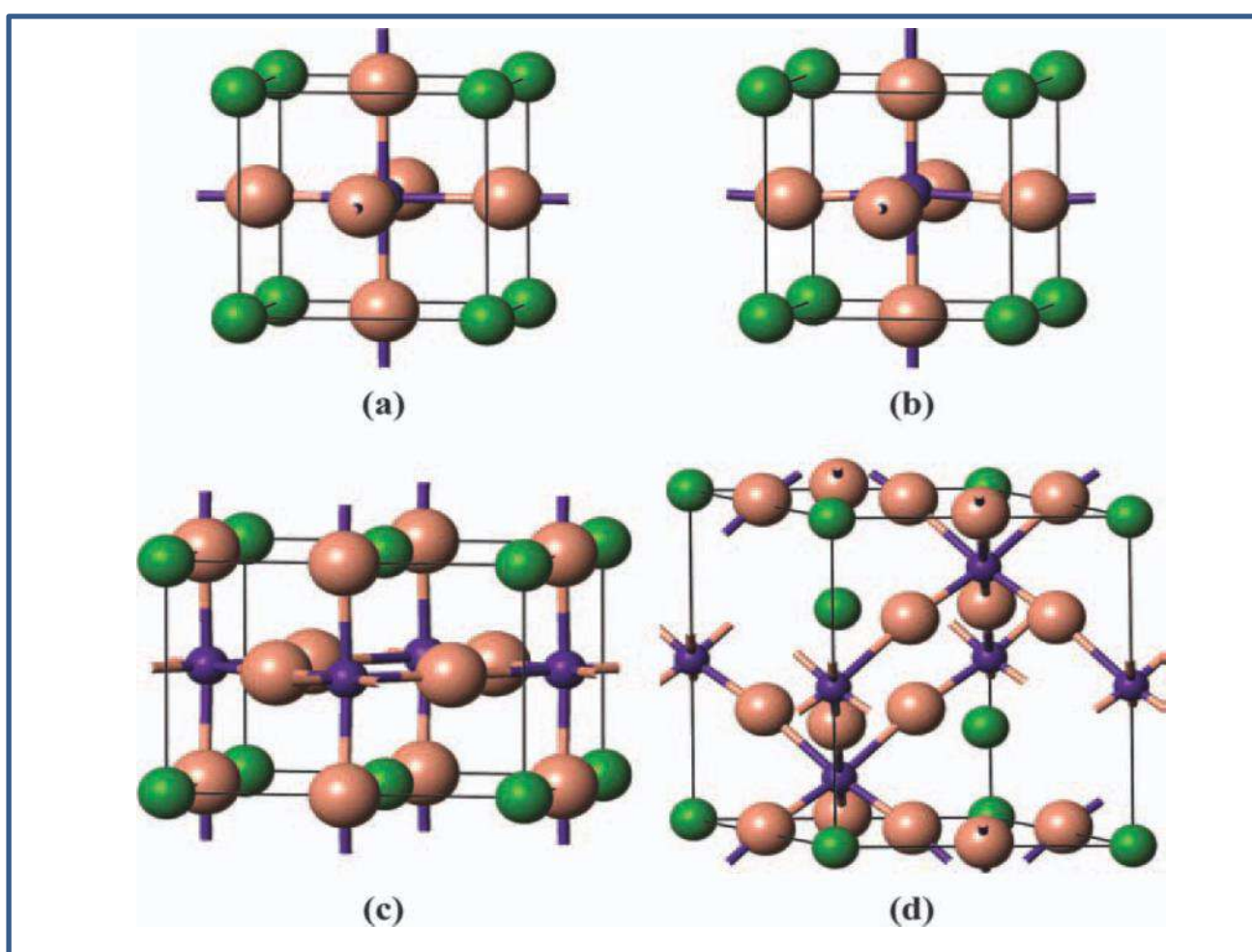
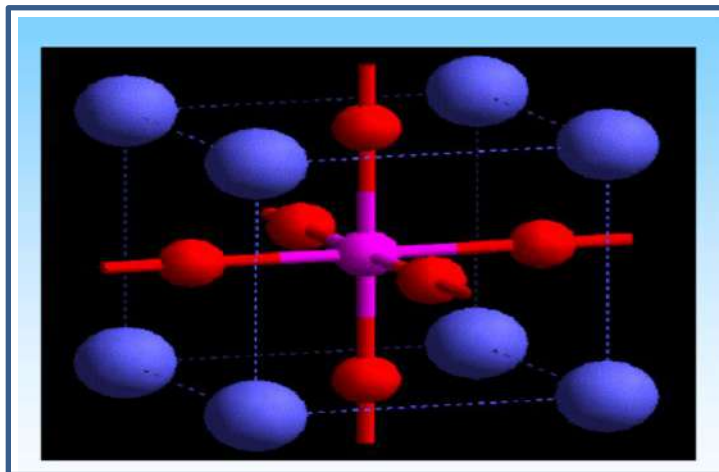
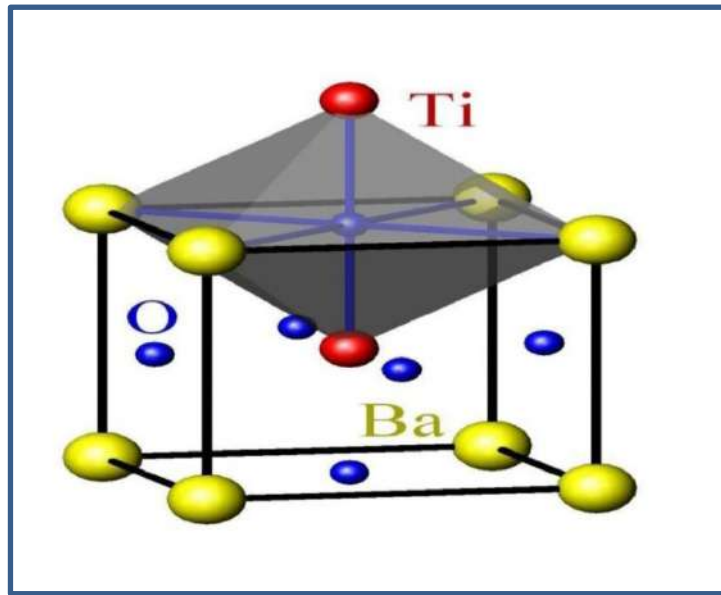


Figure (III.1) Structure of conventional unit cells for **a)** cubic, **b)** tetragonal, **c)** orthorhombic, and **d)** rhombohedral BaTiO_3 . Legend: Ti—small violet balls, Ba—middle green balls, O—large light-pink balls.



Figure(III.2): Structure cristalline de BaTiO3

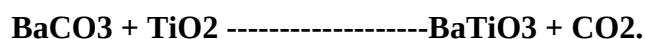
III.4.1. Unit cells BaTiO3 in cubic

- [Ba] : [Xe]6 s^2
- [Ti] : [Ar]3 d^2 4 s^2
- [O] :1 s^2 2 s^2 2 p^4

Table (III.1): Information about the perovskite material BaTiO₃

Density (g/cm³)	6,02
Melting temperature (0C)	1650
Molar mass (g/mole)	233,24
Young's modulus (Gpa)	67
Hardness (Molis)	5
Piezoelectric strain constant (pC/N)	78

❖ **Chemical interactions of the BaTiO₃ compound**



❖ **Goldschmidt tolerance factor**

$$\begin{cases} RA + RO = a \frac{\sqrt{2}}{2} \\ \quad \quad \quad et \\ RB + RO = a/2. \end{cases}$$

Donc : $\frac{RA+RB}{\sqrt{2}(RB+RO)} = 1$

$$\frac{(RA+RO)}{\sqrt{2}(RB+RO)} = t$$

Where

RA ;RB and RO are the ionic radii of the A-site cation, B-site cation, and oxygen anion, respectively

For BaTiO₃ :

- $O = O^{-2}, B=Ti^{4+}, A = Ba^{2+}$

The ionic radii used are :

- $R_{Ba^{2+}} = 1.61 \text{ \AA} (C_N = 12)$
- $R_{Ti^{4+}} = 0.605 \text{ \AA} (C_N = 6)$
- $R_{O^{2-}} = 1.40 \text{ \AA} (C_N=6)$

$$t \approx 1$$

The obtained value $t \approx 1.06$ indicates that the structure is close to the ideal cubic perovskite, with a slight deviation from perfect symmetry. This **deviation** is attributed to the off-centering of the **Ti⁴⁺ ion** within the **TiO₆** octahedron, which is responsible for the ferroelectric behavior of **BaTiO₃**[16].

III.5.Calculation details

To carry out this work, we employed the **ABINIT** package [17–19], which is based on Density Functional Theory (**DFT**). The Generalized Gradient Approximation (**GGA**) was used to describe the **exchange–correlation interactions**. The interaction between core and valence electrons, as well as the electron–nucleus interaction, was treated using the pseudopotential approach, in which the strong ionic potential is replaced by a weaker effective potential.

The investigation of the structural and electronic properties of **BaTiO₃**, which crystallizes in a **cubic perovskite structure**, within the pseudopotential framework requires the definition of appropriate input parameters. In the present study, **norm-conserving pseudopotentials** [19] were employed.

To ensure the convergence of the total energy E_T and related parameters, a series of tests

with respect to the plane-wave cutoff energy (**E_{cut}**) was performed until satisfactory convergence was achieved. **The Monkhorst–Pack scheme** [20] was used to sample the Brillouin zone, employing a **4×4×4 k-point grid**, and 40 Hartree for the number of E_{cut} which ensures good accuracy of the calculated results

III.5.1. Structural proprieties

The model cubic is the crystal lattice of perovskite compound BaTiO₃ (#221), The atom Ba is located in the position Ba 1a (0, 0, 0), Ti 1b ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and O 3c ($\frac{1}{2}$, $\frac{1}{2}$, 0).

The optimization of structural parameters is carried out by calculating the variation of energy as a function of the volume **V** and minimizing this energy to determine the set of optimal parameters. The energy values as a function of volume are fitted using the Murnaghan equation of state [21], which is given by:

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (\text{III.9})$$

Where B_0 represent the bulk modulus at equilibrium with respect to pressure, and V_0 is the equilibrium volume of the unit cell. **Figure (III.3)** shows the variation of the total energy as a function of volume for the BaTiO₃ compound.

The results obtained using the pseudopotential method for **BaTiO₃**, along with other calculations from various theoretical and experimental works, are summarized in **Table (III.2)**. It can be observed that the results obtained by this method are in good agreement with those available in the literature.

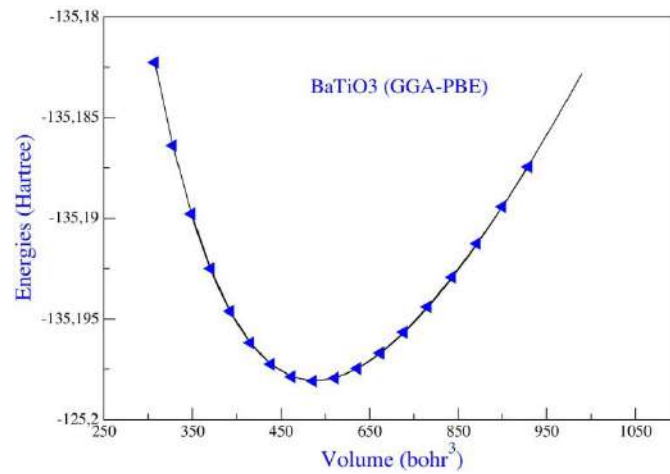


Figure (III.3) The variation of the total energy as a function of the unit cell volume.

Table (III.2): Structural parameters at equilibrium: lattice parameter a and bulk modulus B_0 for the compound BaTiO₃.

<i>BaTiO₃</i>	<i>This work</i>	<i>Other theoretical</i>	<i>Experiment</i>
<i>a ($\text{\AA}$)</i>	4.0391	3,95206 (LDA) [22] 4,03462 (SCAN) [22] 4,03661 (PBE) [22] 3,922 (LDA) [23] 4,008 (PBE) [23] 7,45 (FLAPW) [24] 7,456 [24]	4,03558 [25]
<i>B (GPas)</i>	160.087	200 [26]	162 [27]

III.6. Thermodynamic Properties

Thermodynamic properties provide an essential theoretical framework for understanding the behavior of materials across different physical states, enabling the characterization of equilibrium states and the analysis of changes induced by thermal or mechanical interactions.

In materials physics, these properties are extensively applied in the study of phase transformations and the determination of stability conditions. While state functions such as internal energy, entropy, and enthalpy serve as key analytical tools, the Gibbs free energy remains the most widely used function for predicting spontaneous transformations.

Thermal properties refer to the physical parameters that describe how a material responds to thermal effects. These include the ability to conduct heat, the capacity to store energy in the form of heat, and dimensional changes resulting from temperature variations. In materials science, thermal conductivity is a key indicator of heat transfer efficiency through a material. Specific heat capacity quantifies the energy required to alter a material's temperature, while thermal expansion explains how materials expand or contract upon temperature changes, which can significantly affect their mechanical performance [28].

III.7. Heat Specific with Constant Volume

Heat refers to a mechanism of energy transfer that takes place between a system and its surrounding environment solely as a consequence of a difference in temperature. In contrast to state functions, heat does not constitute an intrinsic attribute of the system; instead, it represents a path-dependent quantity that manifests exclusively during the process of energy exchange. This transfer occurs naturally from higher-temperature zones to lower-temperature zones, persisting until thermodynamic equilibrium is reached.

Within the framework of thermodynamics, heat plays a central role in characterizing energy interactions across physical systems, given that it is directly correlated with changes in internal energy and with the production of mechanical work [29].

According to the first law of thermodynamics:

$$\delta Q = dU + \delta W$$

For a system where only boundary work is considered:

$$\delta Q = dU + P dV$$

Where:

- **Q** : heat transfer (J)
- **U** : internal energy
- **W** : work
- **P** : pressure
- **V** : volume

Specific heat capacity is defined as the amount of thermal energy needed to raise the temperature of one unit mass of a material by one degree. It constitutes an intrinsic thermophysical characteristic that reflects a material's capacity to store heat.

Materials possessing a high specific heat capacity are capable of absorbing considerable quantities of heat while undergoing only minor temperature fluctuations. In contrast, those with a low specific heat capacity exhibit more substantial temperature variations when subjected to the same amount of thermal energy input. This property holds significant importance in thermal analysis and serves as a critical parameter for selecting and designing materials across a wide range of engineering applications.

The specific heat capacity is expressed as follows: [28]:

$$C = \frac{Q}{m \Delta T} \tag{III.10}$$

A constant-volume process refers to a thermodynamic transformation wherein the system's volume remains invariant throughout. Under such conditions, neither expansion nor compression takes place; as a result, the system does not perform any mechanical work.

In this type of process, the entirety of the heat supplied to the system is converted into a change in its internal energy. The heat capacity measured at constant volume describes the relationship between internal energy and temperature, and it represents a fundamental quantity in thermodynamic analysis [30].

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad (\text{III.11})$$

and for a small temperature change:

$$dU = C_v \, Dt \quad (\text{III.12})$$

Also, for a constant volume process:

$$Q = \Delta U \quad (\text{III.13})$$

Where:

- C_v = heat capacity at constant volume ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)
- U = internal energy
- T = temperature
- Q = heat added to the system

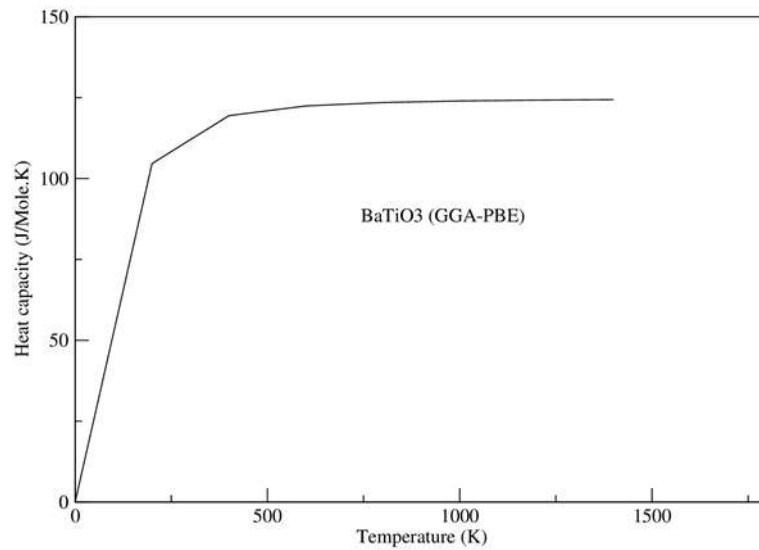


Figure (III.4) : Variation of the Heat Capacity as a Function of Temperature for BaTiO3 Calculated Using the GGA-PBE Approximation

This curve represents the variation of the constant-volume heat capacity C_v as a function of temperature for Perovskite compound BaTiO₃, calculated within the GGA-PBE approximation. The behavior reflects typical thermodynamic characteristics consistent with solid-state physics[31].

Regarding the contribution of lattice vibrations to the total heat capacity in perovskite compounds such as BaTiO₃, the behavior of the heat capacity at constant volume (C_v) can be divided into three main regions:

At low temperatures (below 250 K), C_v increases rapidly with temperature as the relation $C_v \propto T^3$ due to the progressive activation of lattice vibrational modes.

In the intermediate temperature range (above 250 K), C_v continues to increase more gradually as most vibrational modes become fully excited.

At high temperatures, C_v gradually approaches a constant value known as the Dulong–Petit limit[32], **the value of C_v at high temperature is around 124 J/mole.K**, which represents the expected behavior of crystalline solids at elevated temperatures.

III.8. Entropy

Entropy is a fundamental thermodynamic quantity that characterizes the degree of disorder within a system, as well as the fraction of energy that is unavailable for conversion into useful work. It plays a central role in determining the spontaneity and direction of thermodynamic processes.

According to the second law of thermodynamics, entropy increases in irreversible processes and remains constant in reversible transformations. This principle reflects the natural tendency of physical systems to evolve toward states of thermodynamic equilibrium and maximum disorder [30].

For a reversible process, entropy change is defined as

$$ds = \frac{\delta Q_{rev}}{T} \quad (III.14)$$

And for a finite change

$$\Delta S = \int \frac{\delta Q_{rev}}{T} \quad (III.15)$$

For an isolated system:

$$\Delta S \geq 0$$

Where:

- S : entropy
- Q_{rev} : reversible heat transfer
- T : absolute temperature

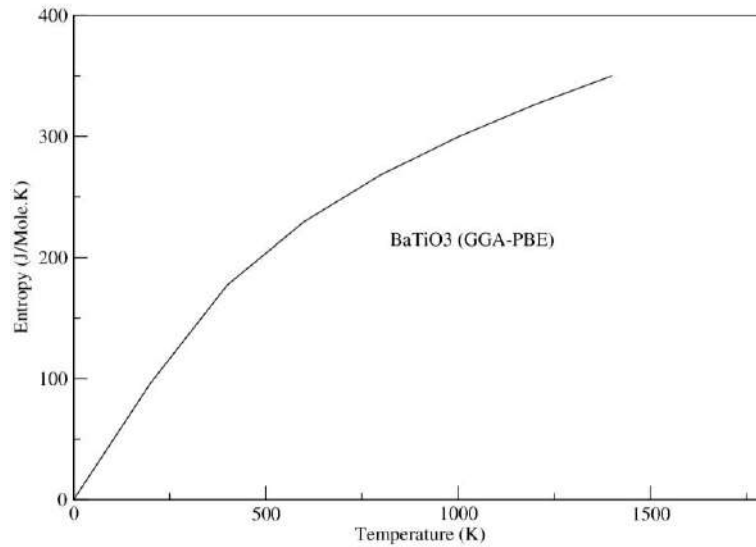


Figure (III.5): Variation of Entropy with Temperature in Barium Titanate (BaTiO_3) within the GGA-PBE Approximation

The calculated results show that the entropy values of Perovskite Compound (GGA-PBE) BaTiO_3 increase steadily with rising temperature as shown in figure (III.5), reflecting an increase in the degree of disorder in the system as thermal energy increases. The thermodynamic properties were evaluated over a temperature range from 0 to 1400 K.

III.9. Free Energy and Energy

Free energy is a thermodynamic potential that quantifies the portion of energy available within a system to perform useful work under conditions of constant temperature and pressure. It is a fundamental criterion for assessing the spontaneity of physical and chemical processes.

In particular, Gibbs free energy plays a central role in materials physics, as it enables the prediction of phase stability and phase transformation behavior. A decrease in Gibbs free energy signifies a spontaneous process, whereas thermodynamic equilibrium is attained when this potential reaches its minimum value.

The Gibbs free energy is defined as[33]:

$$G=H-TS$$

(III.16)

- **G:** Gibbs free energy
- **H :**enthalpy
- **T :** absolute temperature
- **S :** entropy

The condition for spontaneity is:

- $\Delta G < 0$

At equilibrium:

- $\Delta G = 0$

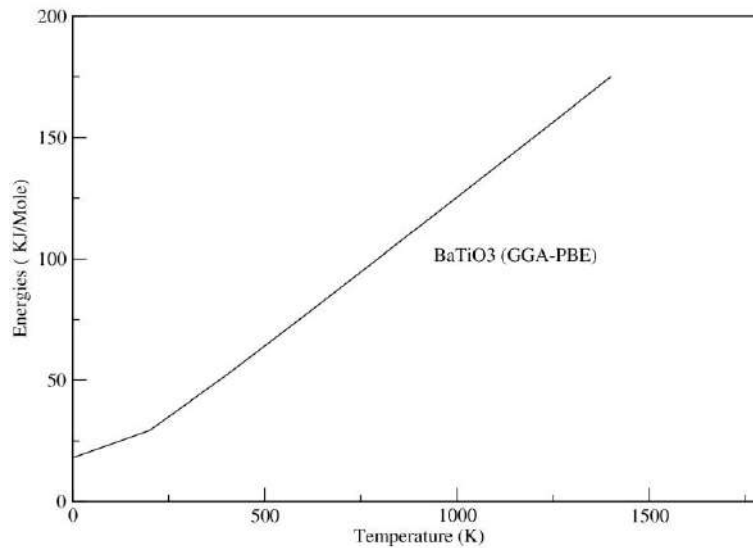


Figure (III.6) : Variation of Total Energy with Temperature in BaTiO3 (GGA-PBE)

The figure (III.6) represents the variation of vibrational energy with temperature for the perovskite compound BaTiO3 calculated using the GGA-PBE approximation. It is observed that the vibrational energy remains almost constant at temperatures below 100 K, which reflects the weak thermal excitation and the limited atomic motion in this low-energy regime[34]. In this region, the atoms are mainly confined to small oscillations around their equilibrium positions, and only low-frequency phonon modes are significantly active[34,35].

However, once this thermal threshold is exceeded, the vibrational energy starts to increase more noticeably with temperature, showing an approximately linear dependence.

This behavior is attributed to the progressive activation of additional vibrational modes within the crystal lattice as thermal energy increases. At higher temperatures, more phonon states become populated, leading to stronger lattice vibrations and a continuous increase in vibrational energy[34,36].

Overall, this trend highlights the important role of lattice dynamics in determining the thermal properties of BaTiO₃[37,34,35] . The observed behavior is consistent with the expected thermodynamic response of crystalline solids, where thermal energy is gradually converted into vibrational motion as temperature rises.

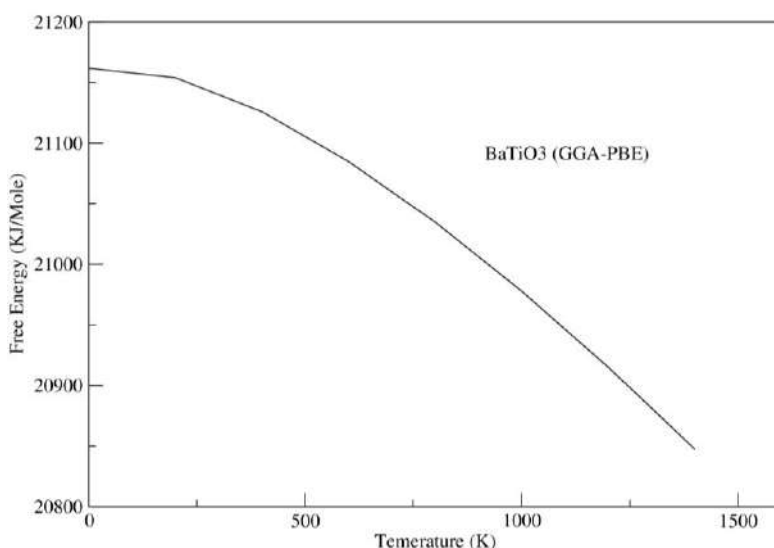


Figure (III.7) Free Energy Variation with Temperature for BaTiO₃ (GGA-PBE)

The variation of free energy with temperature for the perovskite compound BaTiO₃, as shown in Figure (III.7) and calculated using the GGA-PBE method, reveals a clear decreasing trend as temperature increases. This behavior is consistent with the theoretical expression of the Helmholtz free energy [38]: ($F = U - TS$), where the contribution of the entropy term (TS) becomes more significant at higher temperatures, leading to a reduction in the total free energy. The nearly linear decrease observed in the curve reflects the increasing influence of thermal (lattice) vibrations, which enhance the entropy of the system and consequently lower its free energy. This progressive decline indicates that the material attains greater thermodynamic stability at elevated temperatures, in agreement with the expected thermal response of crystalline solids.

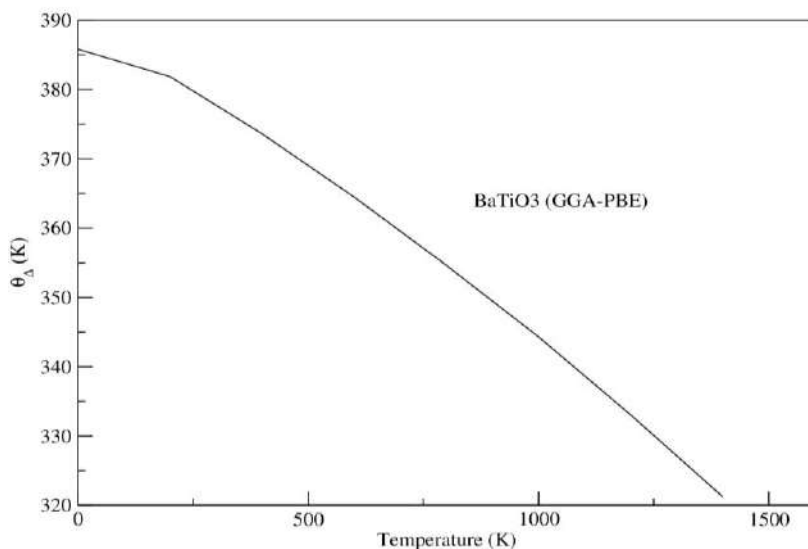


Figure (III.8_) Variation of the Debye Temperature (Θ_D) as a Function of Temperature for BaTiO3 (GGA-PBE)

for the perovskite compound BaTiO₃, calculated using the GGA-PBE approximation. The Debye temperature is an essential parameter in the quasi-harmonic Debye model, as it provides important insight into the vibrational characteristics of the crystal lattice and is closely related to the stiffness of the material and the average phonon frequency.

It can be observed that Θ_D decreases with increasing temperature, which is mainly attributed to the softening of lattice vibrations caused by thermal expansion and anharmonic effects at elevated temperatures. As temperature rises, the atomic bonds become less rigid, leading to a reduction in the average vibrational frequencies of the lattice and, consequently, a decrease in the Debye temperature. This behavior reflects the progressive weakening of interatomic forces under thermal excitation.

Figure (III.8_) represents the variation of the Debye temperature (Θ_D) as a function of temperature; the figure shows the decreasing trend, which indicates that the vibrational spectrum of BaTiO₃ becomes increasingly populated with low-energy phonon modes as temperature increases. The reduction in Θ_D also suggests enhanced phonon-phonon interactions and stronger anharmonicity in the crystal lattice, which play a significant role in determining the thermal properties of the material [39].

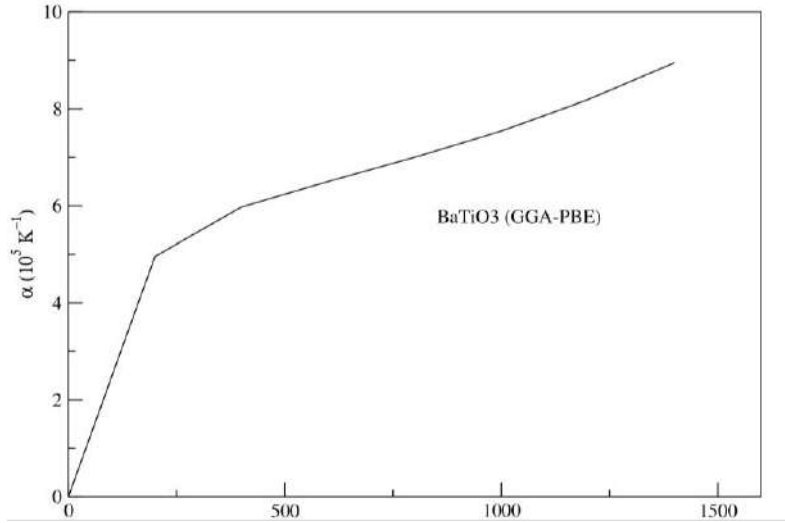


Figure (III.9): Variation of Thermal Expansion coefficient with Temperature for BaTiO₃

The figure(III.9) illustrates the variation of the thermal expansion coefficient (α) as a function of temperature for the perovskite compound BaTiO₃, calculated using the GGA-PBE approximation. It is observed that the thermal expansion coefficient increases progressively with increasing temperature, exhibiting low values in the low-temperature region, followed by a nonlinear increase at the initial stage, and then tending toward quasi-linear behavior at higher temperatures.

This behavior can be explained based on the fundamental physics of thermal expansion. As temperature increases, the amplitudes of atomic vibrations within the crystal lattice also increase, leading to an expansion of the interatomic distances. This phenomenon is primarily associated with anharmonic effects in the potential energy, which become more significant at elevated temperatures, thereby explaining the continuous increase in the thermal expansion coefficient.

Furthermore, the nonlinear behavior observed in the low-temperature region reflects the sensitivity of the crystal structure to thermal variations in this range. In contrast, the tendency toward quasi-linearity at higher temperatures indicates that the relationship between strain and temperature variation approaches the linear relationship expressed by the following equation:

$$\varepsilon_{ij} = \alpha_{ij} \Delta T$$

where the strain becomes approximately proportional to the temperature change within the studied temperature range. Moreover, this behavior may also be associated with possible structural changes or phase transitions known in this type of material.

Therefore, these results are consistent with the general theoretical framework of thermal expansion and confirm the validity of the adopted computational model, while preserving the reference **[40]**.

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General Conclusion

In this study, a comprehensive theoretical investigation of the structural and thermodynamic properties of the cubic perovskite compound BaTiO_3 was carried out using Density Functional Theory (DFT) as implemented in the ABINIT code, based on the pseudopotential and plane-wave approach. The main objective was to understand the stability and thermal behavior of this material through first-principles calculations within both ground-state and finite-temperature frameworks.

Firstly, the structural parameters, including the lattice constant and bulk modulus, were determined through total energy minimization and the Murnaghan equation of state. The obtained results show good agreement with available theoretical and experimental data reported in the literature, with small deviations that remain within acceptable error margins, confirming the reliability of the computational approach employed.

From the thermodynamic perspective, the quasi-harmonic Debye model was used to study the temperature dependence of the thermal properties. The results indicate that the internal energy increases with temperature, while the free energy decreases due to the increasing contribution of entropy. In addition, the entropy increases progressively with temperature, reflecting enhanced lattice vibrations and a higher degree of disorder within the crystal structure.

The heat capacity at constant volume exhibits a characteristic three-stage behavior: a rapid increase at low temperatures, a slower variation at intermediate temperatures, and finally an approach to the Dulong–Petit limit at high temperatures, indicating the full excitation of phonon modes in the crystal lattice.

Moreover, the Debye temperature decreases with increasing temperature, which is attributed to anharmonic lattice effects and phonon softening. The thermal expansion coefficient also increases gradually with temperature due to the progressive enlargement of interatomic distances induced by thermal vibrations.

Overall, the obtained results confirm the structural stability of BaTiO_3 and highlight its expected thermodynamic behavior under temperature variations. This study demonstrates the effectiveness of first-principles calculations combined with the quasi-harmonic Debye model in accurately describing the physical properties of perovskite materials and provides a deeper understanding of their behavior under different thermal conditions.