First-principles study on electronic, magnetic and optical properties of terbium phosphide

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Abstract

In this work, the first-principles calulations have been performed to predict the structural, electronic, magnetic and optical properties of terbium phosphide (TbP) by using PBE-GGA approaches based on density functional theory (DFT) as implemented in WIEN2k package. The spin-polarization calculation shows that TbP is stabilized in zinc blende structure with magnetic moment of 6 μB. The band structure of TbP shows half-metallic behaviour. The optical properties likes dielectric function, reflectivity, optical conductivity, refractive index and absorption coefficient were also calculated for TbP in the zinc blende structure.

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Chapter 1

Introduction

Semiconductors are fundamental elements of contemporary electronics, revolutionizing and advancing life on earth since they are a crucial component of devices. A wide range of intriguing uses in electronics, device fabrication, and thin-film solar cells [1] can be found for the well-known group II-VI and group III-V compounds as semiconductors. Semiconductor components are used in photonic, electronic and optoelectronic devices. They have electronic and optical properties. In addition to their distinctive electronic characteristics, semiconductors with exceptional optical properties are viewed as novel prospects for a variety of optoelectronic devices, including light-emitting and laser diodes [2], IC's, electro-optic waveguide modulators [3], high-electron-mobility-transistor (HEMT), metal-oxide-semiconductor capacitor (MOSCAP) [4] and heterostructure lasers [2]. Nowadays, material having the properties for development of multifunctional device. The material which have spintronic behaviour that are considered to be half metals using spin of electrons rather than focusing on their conventional charge property. The individual aspect of half-metal have two spin bands with different electronic structure. The majority spin band behaves like metals and the minority spin band behaves semiconducting trait along with a gap in the fermi level [5]. Researchers investigated zinc blende (ZB) and rock salt (RS) type structures for half-metallic ferromagnetic compounds because group III and V are stable in zinc blende or rock salt type structure as the conventional binary semiconductors [6].

Since their early research helped close the gap between magnetism and quantum mechanics [7], rare-earth elements have played a significant role in the periodic table and more recently, their potential for enhanced energy storage has been explored. By using the full potential linearized augmented plane wave (FP-LAPW) method, the structural, electronic and optical properties of TbP have been studied based on density functional theory (DFT) [8]. At first, we have studied the TbP structure and stated the theoritical procedure for obtaining the structural properties and total energies where we have used total energy minimization. In the present paper the electronic band structure, the density of states and the optical properties have been studied.

Chapter 2

Theoretical background

2.1 Schrödinger's equation

Schrödinger wave equation is one of the most fundamental equations of quantum physics. The equation also called the Schrödinger equation is basically a differential equation and widely used to solve problems based on the atomic structure of matter. The Schrödinger wave equation describes the behaviour of a particle in field of force or the change of a physical quantity over time. Erwin schrödinger who developed the equation in 1926. Now, the time-depedent schrödinger equation [9] is represented as

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t) \tag{2.1}$$

The Hamiltonian for a single particle

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t) \tag{2.2}$$

leads to the time-dependent single-particle Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = [-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t)]\Psi(\vec{r},t) \tag{2.3}$$

For N particles in three dimensions, the Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{p_i^2}}{2m_i} + V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i} + V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) \tag{2.4}$$

The corresponding Schrödinger equation reads

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = [-\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i}\vec{\nabla}_i^2 + V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t)]\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) \tag{2.5}$$

The solutions of the time-independent Schrödinger equation are special cases, where the Hamiltonian itself has no time-dependency (which implies a time-independent potential $V(\vec{r}_1, \vec{r}_2, ...\vec{r}_N)$, and the solutions therefore describe standing waves which are called stationary states or orbitals).

The time-independent equation is obtained by the approach of separation of variables, i.e. the spatial part of the wave function is separated from the temporal part [10]

$$\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)\tau(t) = \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)e^{-i\omega t} \tag{2.6}$$

Furtheremore, the left hand side of the equation reduces to the energy eigenvalue of the Hamiltonian multiplied by the wave function, leading to the general eigenvalue equation

$$E\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \hat{H}\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.7}$$

Again, using the many-body Hamiltonian, the Schrödinger equation becomes

$$E\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = [-\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i}\vec{\nabla}_i^2 + V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)]\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.8}$$

2.2 The wave function

The state of a particle is completed described by (time-dependent) wave function, i.e. the wave function contains all information about the particle's state. The Born probability interpretation of the wave function, which is a major principle of the

Copenhagen interpretation of quantum mechanics, provides a physical interpretation for the square of the wave function as a probability density [11]

$$|\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 ... d\vec{r}_N \tag{2.9}$$

Equation (2.9) describes the probability that particles $1, 2, ..., N$ are located simultaneously in the corresponding volume element $d\vec{r}_1 d\vec{r}_2 ... d\vec{r}_N$ [12]. If the positions of two particles are exchanged, the overall probability density can not depend on such an exchange, i.e.

$$|\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_i, \vec{r}_j, ..., \vec{r}_N)|^2 = |\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_i, \vec{r}_j, ..., \vec{r}_N)|^2 \tag{2.10}$$

There are only two possibilities for the behavior of the wave function during a particle exchange. The first one is symmetrical wave function, which does not change due to such an exchange. This corresponds to bosons (particles with integer or zero spin). The other possibility is an anti-symmetrical wave function, where an exchange of two particles causes a sign change, which corresponds to fermions (particles which half-integer spin). [13]

The anti-symmetric fermion wave function leads to the Pauli principle, which states that no two electrons can occupy the same state, whereas state means the orbital and spin parts of the wave function. [14] Another consequence of the probability interpretation is the normalization of the wave function. If equation (2.9) describes the probability of finding a particle in a probability of one, i.e. all particles must be found somewhere in space. This corresponds to the normalization condition for the wave function.

$$\int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N |\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)|^2 = 1 \tag{2.11}$$

Equation (2.11) also gives insight on the requirements a wave function must fulfill in order to be physical acceptable. Wave functions must be continuous over the full spatial range and square-integratable. [15]

Another very important property of the wave function is that calculating expectation value of the corresponding observable for that wave function. For an observable

$O(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$, this can generally be written as

$$O = \langle O \rangle = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{O} \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.12}$$

2.3 Many-body system and Born-Oppenheimer (BO) approximation

The Hamiltonian of a many-body system consisting of nuclei and electrons can be written as [16]

$$H_{tot} = -\sum_I \frac{\hbar^2}{2M_I} \vec{\nabla}^2_{\boldsymbol{R}_I} - \sum_i \frac{\hbar^2}{2M_e} \vec{\nabla}^2_{\boldsymbol{r}_i} + \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\boldsymbol{R}_I - \boldsymbol{r}_i|} \tag{2.13}$$

where the indexes I, J run on electrons, $\boldsymbol{R}_I$ and M_I are positions and masses of the nuclei, $\boldsymbol{r}_i$ and M_e of the electrons, Z_I the atomic number of number of nucleus I. The first term is the kinetic energy of the nuclei, the second term is the kinetic energy of the electron, the third term is the potential energy of nucleus-nucleus Coulomb interaction, the fourth term is the potential energy of electron-electron Coulomb interaction and the last term is the potential energy of nucleus-electron Coulomb interaction. [17] The time-independent Schrödinger equation for the system:

$$H_{tot} \Psi(\{\boldsymbol{R}_I\}, \{\boldsymbol{r}_i\}) = E \psi(\{\boldsymbol{R}_I\}, \{\boldsymbol{r}_i\}) \tag{2.14}$$

where $\psi(\{\boldsymbol{R}_I\}, \{\boldsymbol{r}_i\})$ is the total wavefunction of the system. Everything about the system is known if one can solve the above Schrödinger equation. However, it is impossible to solve it in practice. A so-called Born-Oppenheimer (BO) approximation was made by Born and Oppenheimer [18] in 1927. Since the nuclei are much heavier than electrons, the nuclei move much slower than the electrons. Therefore we can separate the movement of nuclei and electrons. When we consider the movement of electrons, it is responsible to consider the positions of nuclei are fixed, thus the total wavefunction can be written as:

$$\psi(\{\boldsymbol{R}_I\},\{\boldsymbol{r}_i\}) = \Theta(\{\boldsymbol{R}_I\})\phi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_I\}) \tag{2.15}$$

where $\Theta(\{\boldsymbol{R}_I\})$ describes the nuclei and $\phi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_I\})$ the electrons. With the BO approximation, Eq. (2.15) can be divided into two separate Schrödinger equations:

$$H_e\phi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_I\}) = V(\{\boldsymbol{R}_I\})\phi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_I\}) \tag{2.16}$$

where

$$H_e = -\sum_i \frac{\hbar^2}{2M_e}\vec{\nabla}^2_{\boldsymbol{r}_i} + \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{I,i}\frac{Z_I e^2}{|\boldsymbol{R}_I - \boldsymbol{r}_i|} \tag{2.17}$$

and

$$[-\sum_I \frac{\hbar^2}{2M_I}\vec{\nabla}^2_{\boldsymbol{R}_I} + V(\{\boldsymbol{R}_I\})]\Theta(\{\boldsymbol{R}_I\}) = E'\Theta(\{\boldsymbol{R}_i\}) \tag{2.18}$$

Eq.(2.16) is the equation for the electronic problem with the nuclei positions fixed. The eigenvalue of the energy $V(\{\boldsymbol{R}_I\})$ depends on the positions of the nuclei. After solving Eq. (2.22), $V(\{\boldsymbol{R}_I\})$ is known and by applying it to Eq. (2.18), which has no electronic degrees of freedom, the motion of the nuclei is to obtained.

The significance of the BO approximation is to separate the movement of electrons and nuclei. The electrons are moving in a static external potential $V_{ext}(\boldsymbol{r})$ formed by the nuclei, which is the starting point of DFT. The BO approximation was extended by Bohn and Huang known as Born-Huang (BH) approximation [19] to take into account more nonadiabatic effect in the electronic Hamiltonian than in the BO approximation.

2.4 The Hartree-Fock approach

Observables in quantum mechanics are calculated as the expectation values of operators. [11] The energy as observable corresponds to the Hamiltonian operator, therefore the energy corresponding to a general Hamiltonian can be calculated as

$$E = \langle \hat{H} \rangle = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.19}$$

The central idea of the Hartree-Fock approach is that the energy obtained by any (normalized) trial wave function, different from the actual ground state wave function, is always an upper bound, i.e. higher than the actual ground state energy. If the trial function happens to be the desired ground state wave function, the energy are equal

$$E_{trial} \geq E_0 \tag{2.20}$$

with

$$E_{trial} = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*_{trial}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi_{trial}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.21}$$

and

$$E_0 = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*_0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi_0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.22}$$

The expressions above are usually inconvenient to handle. For the sake of a compact notation, the following the bra-ket notation of Dirac is introduced. [20]

In that notation, equation (2.20) to (2.22) are expressed as

$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = E_{trial} \geq E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \tag{2.23}$$

Proof: The eigenfunctions ψ_i of the Hamiltonian $\hat{H}$ (each corresponding to an energy eigenvalue E_i) form a complete basis set, therefore any normalized trial wave function ψ_{trial} can be linear combination of those eigenfunctions.

$$\psi_{trial} = \sum_i \lambda_i \psi_i \tag{2.24}$$

The assumption is made that the eigenfunctions are orthogonal and normalized.

Hence it is requested that the trial wave function is normalized, it follows that

$$\langle\psi_{trial}|\hat{H}|\psi_{trial}\rangle = 1 = \langle\sum_i \lambda_i\psi_i|\sum_j \lambda_j\psi_j\rangle = \sum_i\sum_j \lambda_i^*\lambda_j\langle\psi_i|\psi_j\rangle = \sum_j |\lambda_j|^2 \quad (2.25)$$

On the other hand, following (2.23) and (2.25)

$$E_{trial} = \langle\psi_{trial}|\hat{H}|\psi_{trial}\rangle = \langle\sum_i \lambda_i\psi_i|\hat{H}|\sum_j \lambda_j\psi_j\rangle = \sum_j E_j|\lambda_j|^2 \quad (2.26)$$

Together with the fact that the ground state energy E_0 is per definition the lowest possible energy, and therefore has the smallest eigenvalue ($E_0 \leq E_i$), it is found that

$$E_{trial} = \sum_j E_j|\lambda_j|^2 \geq E_0\sum_j |\lambda_j|^2 \quad (2.27)$$

what resembles equation (2.23).

Equations (2.19) to (2.27) also include that a search for the minimal energy value while applied on all allowed N-electron wave-functions will always provide the ground-state wave function (or wave functions, in case of a degenerate ground state where more than one wave function provides the minimum energy). Expressed in terms of functional calculus, where $\psi \longrightarrow N$ addresses all allowed N-electron wave functions, this means [21]

$$E_0 = \min_{\psi\rightarrow N} E[\psi] = \min_{\psi\rightarrow N}\langle\psi|\hat{H}|\psi\rangle = \min_{\psi\rightarrow N}\langle\psi|\hat{T}+\hat{V}+\hat{U}|\psi\rangle. \quad (2.28)$$

For N-electron systems this search is, due to the large number of possible wave functions on the one hand and limitations in computational power and time, practically impossible. What is possible is the restriction of the search to a smaller subset of possible wave function, as it is done in the Hartree-Fock approximation.

In the Hartree-Fock approach, the search is restricted to approximations of the N-electron wave function by an antisymmetric product of N (normalized) one-electron wave-functions, the so called spin-orbitals $\chi_i(\vec{x}_i)$. A wave function of this type is called Slater-determinant, and reads

$$\psi_0 \approx \phi_{SD} = (N!)^{-\frac{1}{2}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \tag{2.29}$$

It is important to notice that the spin-orbitals $\chi_i(\vec{x}_i)$ are not only depending on spatial coordinates but also on a spin coordinate which is introduced by a spin function, $\vec{x}_i = \vec{r}_i, s$

The ground state energy approximated by a single slater determinan becomes

$$E_0 = \min_{\phi_{SD}\to N} E[\phi_{SD}] = \min_{\phi_{SD}\to N} \langle\phi_{SD}|\hat{T} + \hat{V} + \hat{U}|\phi_{SD}\rangle \tag{2.30}$$

A general expression for the Hartree-Fock energy is obtained by usage of the Slater determinant as a trial function

$$E_{HF} = \langle\phi_{SD}|\hat{H}|\phi_{SD}\rangle = \langle\phi_{SD}|\hat{T} + \hat{V} + \hat{U}|\phi_{SD}\rangle \tag{2.31}$$

The final expression for the Hartree-Fock energy contains three major parts

$$E_{SD} = \langle\phi_{SD}|\hat{H}|\phi_{SD}\rangle = \sum_i^N (i|\hat{h}|i) + \frac{1}{2}\sum_i^N\sum_j^N [(ii|jj) - (ij|ji)] \tag{2.32}$$

with

$$(i|\hat{h}|i) = \int \chi_i^*(\vec{x}_i)[-\frac{1}{2}\vec{\nabla}_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}}]\chi_i(\vec{x}_i)d\vec{x}_i, \tag{2.33}$$

$$(ii|jj) = \int\int |\chi_i(\vec{x}_i)|^2 \frac{1}{r_{ij}} |\chi_j(\vec{x}_j)|^2 d\vec{x}_i d\vec{x}_j, \tag{2.34}$$

$$(ii|jj) = \int\int \chi_i(\vec{x}_i)\chi_j^*(\vec{x}_j)\frac{1}{r_{ij}}\chi_j(\vec{x}_j)\chi^*(\vec{x}_i)d\vec{x}_i d\vec{x}_j, \tag{2.35}$$

Finally, one arrives at

$$\hat{f}\chi_i = \lambda_i\chi_i, i = 1, 2, ..., N \tag{2.36}$$

with

$$\hat{f}_i = -\frac{1}{2}\vec{\nabla}_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + \sum_{i}^{N}[\hat{J}_j(\vec{x}_i) - \hat{K}_j(\vec{x}_i)] = \hat{h}_i + \hat{V}^{HF}(i) \tag{2.37}$$

the Fock operator for the i-th electron. In similarity to (2.32) to (2.35), the first two terms represent the kinetic and potential energy due to nucleus-electron interaction, collected in the core Hamiltonian h_i, whereas the latter terms are sums over the Coulomb operators $\hat{J}_j$ and the exchange operators $\hat{K}_j$ with the other j electrons, which form the Hartree-Fock potential $\hat{V}^{HF}$.

The two electron repulsion operator from the original Hamiltonian is exchanged by a one-electron operator $\hat{V}^{HF}$ which describes the repulsion in average. [21]

2.4.1 Limitation and failings of the Hartree-Fock approach

Atoms as well as molecules can have an even or odd number of electrons. If the number of electrons is even and all of them are located in double occupied spatial orbitals ϕ_i the Compound is in a single state. Such systems are called closed-shell systems. Compounds with an odd number of electrons as well as compounds with single occupied orbitals, i.e. species with triplet or higher ground state, are called open-shell system respectively. These two types of systems correspond to two different approaches of the Hartree-Fock method. In the restricted HF-method (RHF), all electrons are considered to be paired in orbitals whereas in the unrestricted HF (UHF)- method this limitation is lifted totally. It is also possible to describe open-shell systems with a RHF approach where only the single occupied orbitals are excluded which is then called a restricted open-shell HF (ROHF) which is an approach closer to reality but also more complex and therefore less popular than UHF. [21]

The size of the investigated system can also be a limiting factor for calculations. Kohn states a number of $M = p^5$ with $3p10$ parameters for a result with sufficient accuracy in the investigation of the H_2 system. [22] For a system with $N = 100$ (active) electrons the number of parameters rises to

$$M = p^{3N} = 3^{300} to 10^{300} \approx 10^{150} to 10^{300} \tag{2.38}$$

Since a many electron wave function cannot be described entirely by a single Slater determinant, the energy obtained by HF calculations is always larger than the exact ground state energy. The most accurate energy obtainable by HF-methods is called the Hartree-Fock-limit. The difference between E_{HF} and E_{exact} is called correlation energy and can be denoted as [23]

$$E_{corr}^{HF} = E_{min} - E_{HF} \tag{2.39}$$

Despite the fact that E_{corr} is usually small against E_{min}, as in the example of a N_2 molecule where

$$E_{corr}^{HF} = 14.9eV < 0.001.E_{min}, \tag{2.40}$$

it can have a huge influence. [24]

For instance, the experimental dissociation energy of the N_2 molecule is

$$E_{diss} = 9.9eV < E_{corr} \tag{2.41}$$

which corresponds to a large contribution of the correlation energy to relative energies such as reaction energies which are of particular interest in quantum chemistry. [24] The main contribution to the correlation energy arises from the mean field approximation used in the HF-method. That means one electron moves in the average field of the other ones, an approach which completely neglects the intrinsic correlation of the electron movements. To get a better understanding what that means, one may picture the repulsion of electrons at small distances which clearly cannot be covered by a mean-field approach like the Hartree-Fock-method. [21]

2.5 The electron density

The electron density (for N electrons) as the basic variable of density functional theory is defined as [25]

$$n(\vec{r}) = N \sum_{s_1} \int d\vec{x}_2 ... \int d\vec{x}_N \psi^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)\psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) \tag{2.42}$$

If additionally the spin coordinates are neglected, the electron density can even be expressed as measurable observable only dependent on spatial coordinates [26]

$$n(\vec{r}) = N \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.43}$$

which can e.g. be measured by X-ray diffraction. [21]

Before presenting an approach using the electron density as variable, it has to be ensured that it truly contains all necessary informations about the system. In detail that means it has to contain information about the electron number N as well as the external potential characterized by $\hat{V}$. The total number of electrons can be obtained by integration the electron density over the spatial variables

$$N = \int d\vec{r} n(\vec{r}) \tag{2.44}$$

2.6 Thomas-Fermi-Dirac approximation

In 1927, the predecessor to DFT was the Thomas-Fermi (TF) model proposed by Thomas [27] and Fermi [28]. They used the electron density $n(\boldsymbol{r})$ as the basic variable instead of the wavefunction. The total energy of a system in an external potential $V_{ext}(\boldsymbol{r})$ is written as a functional of the electron density $V_{ext}(\boldsymbol{r})$ as:

$$E_{TF}[n(\boldsymbol{r})] = A_1 \int n(\boldsymbol{r})^{\frac{5}{3}} d\boldsymbol{r} + \int n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) d\boldsymbol{r} + \frac{1}{2} \int \int \frac{n(\boldsymbol{r}) n(\boldsymbol{r})'}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' \tag{2.45}$$

where the first term is the kinetic energy of the non-interacting electrons in a homogeneous electron gas (HEG) with $A_1 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$ in atomic units. The kinetic energy density of a HEG is obtained by adding up all of the free electron energy state $\epsilon_k = \frac{k^2}{2}$ up to the Fermi wavevector $k_F = [3\pi^2 n(\boldsymbol{r})]^{\frac{1}{3}}$ as:

$$\begin{aligned} t_0[n(\boldsymbol{r})] &= \frac{2}{(2\pi)^3} \int_0^{k_F} \frac{k^2}{2} 4\pi k^2 dk \\ &= A_1 n(\boldsymbol{r})^{\frac{5}{3}} \end{aligned}$$

The second term is the classical electrostatic energy of the nucleus-electron Coulomb interaction. The third term is the classical electrostatic Hartree energy approximated by the classical Coulomb repulsion between electrons. In the original TF method, the exchange and correlation among electron was neglected. In 1930, Dirac [29] extended the Thomas-Fermi method by adding a local exchange term $A_2 \int n(\boldsymbol{r})^{\frac{4}{3}} d\boldsymbol{r}$ to eq.(2.45) with $A_2 = -\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}$, which leads eq. (3.4) to

$$E_{TFD}[n(\boldsymbol{r})] = A_1 \int n(\boldsymbol{r})^{\frac{5}{3}} d\boldsymbol{r} + \int n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) d\boldsymbol{r} + \frac{1}{2} \int\int \frac{n(\boldsymbol{r}) n(\boldsymbol{r})^{'}}{|\boldsymbol{r} - \boldsymbol{r}^{'}|} d\boldsymbol{r} d\boldsymbol{r}^{'} + A_2 \int n(\boldsymbol{r})^{\frac{4}{3}} d\boldsymbol{r} \tag{2.46}$$

The ground state density and energy can be obtained by minimizing the Thomas-Fermi-Dirac equation (2.46) subject to conservation of the total number (N) of electrons. By using the technique of Lagrange multipliers, the solution can be found in the stationary condition:

$$\delta\{E_{TFD}[n(\boldsymbol{r})] - \mu(\int n(\boldsymbol{r}) d\boldsymbol{r} - N)\} = 0 \tag{2.47}$$

where μ is a constant known as a Lagrange multipliers, whose physical meaning is the chemical potential (or Fermi energy at T = 0 K). Eq. (2.47) leads to the Thomas-Fermi-Dirac equation,

$$\frac{5}{4} A_1 n(\boldsymbol{r})^{\frac{2}{3}} + V_{ext}(r) + \int \frac{n(\boldsymbol{r}^{'})}{|\boldsymbol{r} - \boldsymbol{r}^{'}|} d\boldsymbol{r}^{'} + \frac{4}{3} A_2 n(\boldsymbol{r})^{\frac{1}{3}} - \mu = 0 \tag{2.48}$$

which can be solved directly to obtain the ground state density.

2.7 Hohenberg-Khon (HK) theorems

In 1964, DFT was proven to be an exact theory of many-body systems by Hohenberg and Khon [30]. It applies to condensed-matter systems of electrons with fixed nuclei, and also to any system of interacting particles in an external potential $V_{ext}(\vec{r})$. The theory is based upon two theorems.

2.7.1 The HK theorem I

The ground state particle density $n(\vec{r})$ of a system of interacting particle in an external potential $V_{ext}(\vec{r})$ uniquely determines the external potential $V_{ext}(\vec{r})$, except for a constant. Thus the ground state particle density determines the full hamiltonian, except for a constant shift of the energy. In principle, all the states including ground and excited states of many-body wavefunctions can be calculated. This means that the ground state particle density uniquely determines all properties of the system completely.

Proof of the HK theorem I

For simplicity, consider the case that the ground state of the system is nondegenerate. It can be proven that the theorem is valid for systems with degenerate ground states. [31] The proof is based on minimum energy principle. Suppose there are two different external potentials $V_{ext}(\vec{r})$ and $V'_{ext}(\vec{r})$ which differ by more than a constant and lead to the same ground state density $n_0(\vec{r})$. The two external potentials would give two different Hamiltonians, $\hat{H}$ and $\hat{H}'$, which have the same ground state density $n_0(\vec{r})$ but would have different ground state wavefunctions, Ψ and Ψ', with $\hat{H}\psi = E_0\psi$ and $\hat{H}'\psi' = E'_0\psi'$. Since ψ' is not the ground state of $\hat{H}$, it follows that

$$\begin{aligned} E_0 &< \langle\Psi'|\hat{H}|\Psi'\rangle \\ &< \langle\Psi'|\hat{H}'|\Psi'\rangle + \langle\Psi'|\hat{H} - \hat{H}'|\Psi'\rangle \\ &< E'_0 + \int n_0(\boldsymbol{r})[V_{ext}(\boldsymbol{r}) - V'_{ext}(\boldsymbol{r})]d\boldsymbol{r} \end{aligned} \tag{2.49}$$

Similarly

$$\begin{aligned} E'_0 &< \langle\Psi|\hat{H}|\Psi\rangle \\ &< \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}' - \hat{H}|\Psi\rangle \end{aligned} \tag{2.50}$$

$$< E_0 + \int n_0(\boldsymbol{r})[V'_{ext}(\boldsymbol{r}) - V_{ext}(\boldsymbol{r})]d\boldsymbol{r}$$

Adding eq. (2.49) and (2.50) lead to the contradiction

$$E_0 + E'_0 < E_0 + E'_0 \tag{2.51}$$

Hence, the ground state density determines the external potential $V_{ext}(\vec{r})$, except for a constant. There is one-to-one mapping between the ground state density $n_0(\vec{r})$ and the external potential $V_{ext}(\vec{r})$, although the exact formula is unknown.

2.7.2 The HK theorem II

There exists a universal functional $F[n(\boldsymbol{r})]$ of the density, independent of the external potential $V_{ext}(\vec{r})$, such that the global minimum value of the energy functional $E[\Psi'] \equiv \int n(\boldsymbol{r})V_{ext}(\boldsymbol{r})d\boldsymbol{r} + F[n(\boldsymbol{r})]$ is the exact ground state energy of the system and the exact ground state density $n_0(\boldsymbol{r})$ minimizes this functional. Thus the exact ground state energy and density are fully determined by the functional $E[\Psi']$.

Proof of the HK theorem II

The universal functional $F[n(\boldsymbol{r})]$ can be written as

$$F[n(\boldsymbol{r})] \equiv T[n(\boldsymbol{r})] + E_{int}[n(\boldsymbol{r})] \tag{2.52}$$

where $T[n(\boldsymbol{r})]$ is the kinetic energy and $E_{int}[n(\boldsymbol{r})]$ is the interaction energy of the particles. According to variational principle, for any wavefunction Ψ', the energy functional $E[\Psi']$:

$$E[\Psi'] \equiv \langle\Psi'|\hat{T} + \hat{V}_{int} + \hat{V}_{ext}|\Psi' \tag{2.53}$$

has its global minimum value only when Ψ' is the ground state wavefunction ψ_0 with the constraint that the total number of the particle is conserved. According to HK theorem I, Ψ' must correspond to a ground state with particle density $n'(\boldsymbol{r})$ and external potential $V'_{ext}(\boldsymbol{r})$, then $E[\Psi']$ is a functional of $n'(\boldsymbol{r})$. According to variational principle:

$$
\begin{aligned}
E[\Psi'] &\equiv \langle\Psi'|\hat{T}+\hat{V}_{int}+\hat{V}_{ext}|\Psi' \\
&= E[n'(\boldsymbol{r})] \\
&= \int n'(\boldsymbol{r})V'_{ext}(\boldsymbol{r})d\boldsymbol{r} + F[n'(\boldsymbol{r})] \qquad (2.54) \\
&> E[\Psi_0] \\
&= \int n_0(\boldsymbol{r})V_{ext}(\boldsymbol{r})d\boldsymbol{r} + F[n_0(\boldsymbol{r})] \\
&= E[n_0(\boldsymbol{r})]
\end{aligned}
$$

Thus the energy functional $E[\Psi'] \equiv \int n(\boldsymbol{r})V_{ext}(\boldsymbol{r})d\boldsymbol{r} + F[n(\boldsymbol{r})]$ evaluated for the correct ground state density $n_0(\boldsymbol{r})$ is indeed lower than the value of this functional for any other density $n(\boldsymbol{r})$. Therefore by minimizing the total energy functional of the system with respect to variations in the density $n(\boldsymbol{r})$, one would find the exact ground state density and energy. [32]

2.8 The Kohn-Sham equations

The framework by Hohenberg and Kohn is exact, yet not very useful in actual calculations. The only possibility would be the direct use of the second Hohenberg-Kohn theorem for energy minimization, a way that is possible in general but has proven itself to be impractical. [16]

The Hartree-equations are clearly wave-function based and not directly related to the work of Hohnberg and Kohn, yet they have been proven very useful. Hartree's approximation assumes that every electron moves in an effective single-particle potential of the form

$$v_H(\vec{r}) = -\frac{Z}{|\vec{r}|} + \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} \tag{2.55}$$

The first term is an attractive Coulomb potential of a nucleus with atomic number Z, whereas the integral term corresponds to the potential caused by the mean electron density distribution $n(\vec{r})$.

The mean density can be denoted in terms of the single particle wave functions

$$n(\vec{r}) = \sum_{j=1}^{M} |\phi_j(\vec{r})|^2 \tag{2.56}$$

Since the electron-electron interactions are taken into account in the potential term, the N-electron and therefore (neglecting the spin coordinates) 3N-dimensional Schrdinger equation can be approximately replaced by N 3-dimensional single particle equations for electrons moving in an effective potential defined in (2.55):

$$[-\frac{1}{2}\vec{\nabla}^2 + v_H(\vec{r})]\phi_j(\vec{r}) = \epsilon_j \phi_j(\vec{r}) \tag{2.57}$$

Therefore, Kohn and Sham investigated the density functional theory applied to a system of N non-interacting electrons in an external potential, similar to Hartree's approach. The expression for the energy of such a system is of the form

$$E_{v(\vec{r})}[n'(\vec{r})] \equiv \int v(\vec{r}) n'(\vec{r}) d\vec{r} + d\vec{r} + T_S[n'(\vec{r})] \geq E \tag{2.58}$$

where $n'(\vec{r})$ is a v-representable density for non-interacting electrons and $T_S[n'(\vec{r})]$ the kinetic energy of the ground state of those non-interacting electrons. [26]

Setup of the Euler-Lagrange equation [33] for the non-interacting case (2.58) with the density defined in (2.56) as argument provides [26]

$$\delta E_v[n'(\vec{r})] \equiv \int \delta n'(\vec{r})[v(\vec{r}) + \frac{\delta}{\delta n'(\vec{r})} T_S[n'(\vec{r})]|_{n'(\vec{r})=n(\vec{r})} - \epsilon] d\vec{r} = 0 \tag{2.59}$$

For a system of non-interacting electrons, the total ground state energy and particle density can therefore simply be denoted as the sums

$$E = \sum_{j=1}^{N} \epsilon_j \tag{2.60}$$

and

$$n(\vec{r}) = \sum_{j=1}^{N} |\phi_j(\vec{r})|^2 \tag{2.61}$$

In addition, Kohn and Sham used the universal functional as an alternative formulation, [8]

$$F[n^{'}(\vec{r})] \equiv T_S[n^{'}(\vec{r})] + \frac{1}{2} \int \frac{[n^{'}(\vec{r})][n^{'}(\vec{r}^{'})]}{|\vec{r} - \vec{r}^{'}|} d\vec{r} d\vec{r}^{'} + E_{xc}[n^{'}(\vec{r})]. \tag{2.62}$$

In (2.62) T_S $[n^{'}(\vec{r})]$ is the kinetic energy functional of non-interacting electrons (which is not even for the same density $n(\vec{r})$ the true kinetic energy of the interacting system) and the second term is the so-called Hartree term which describes the electrostatic self-repulsion of the electron density. [34] The last term is called exchange-correlation term. It is implicitly defined by (2.62) and can in practice only be approximated. The quality of the approximation for $E_{xc}[n^{'}(\vec{r})]$ is therefore one of the key issues in DFT. [26]

Construction of the Euler-Lagrange equations for the interacting case in equation (2.62) provides

$$\delta E_v[n^{'}(\vec{r})] \equiv \int \delta n^{'}(\vec{r})[v_{eff}(\vec{r}) + \frac{\delta}{\delta n^{'}(\vec{r})} T_S[n^{'}(\vec{r})]|_{n^{'}(\vec{r})=n(\vec{r})} - \epsilon] d\vec{r} = 0 \tag{2.63}$$

with

$$v_{eff}(\vec{r}) \equiv v(\vec{r}) + \int \frac{[n(\vec{r})]}{|\vec{r} - \vec{r}^{'}|} d\vec{r} + v_{xc}(\vec{r}) \tag{2.64}$$

and the functional derivative

$$v_{xc}(\vec{r}) \equiv \frac{\delta}{\delta n^{'}(\vec{r})} E_{xc}[n^{'}(\vec{r})]|_{n^{'}(\vec{r})=n(\vec{r})} \tag{2.65}$$

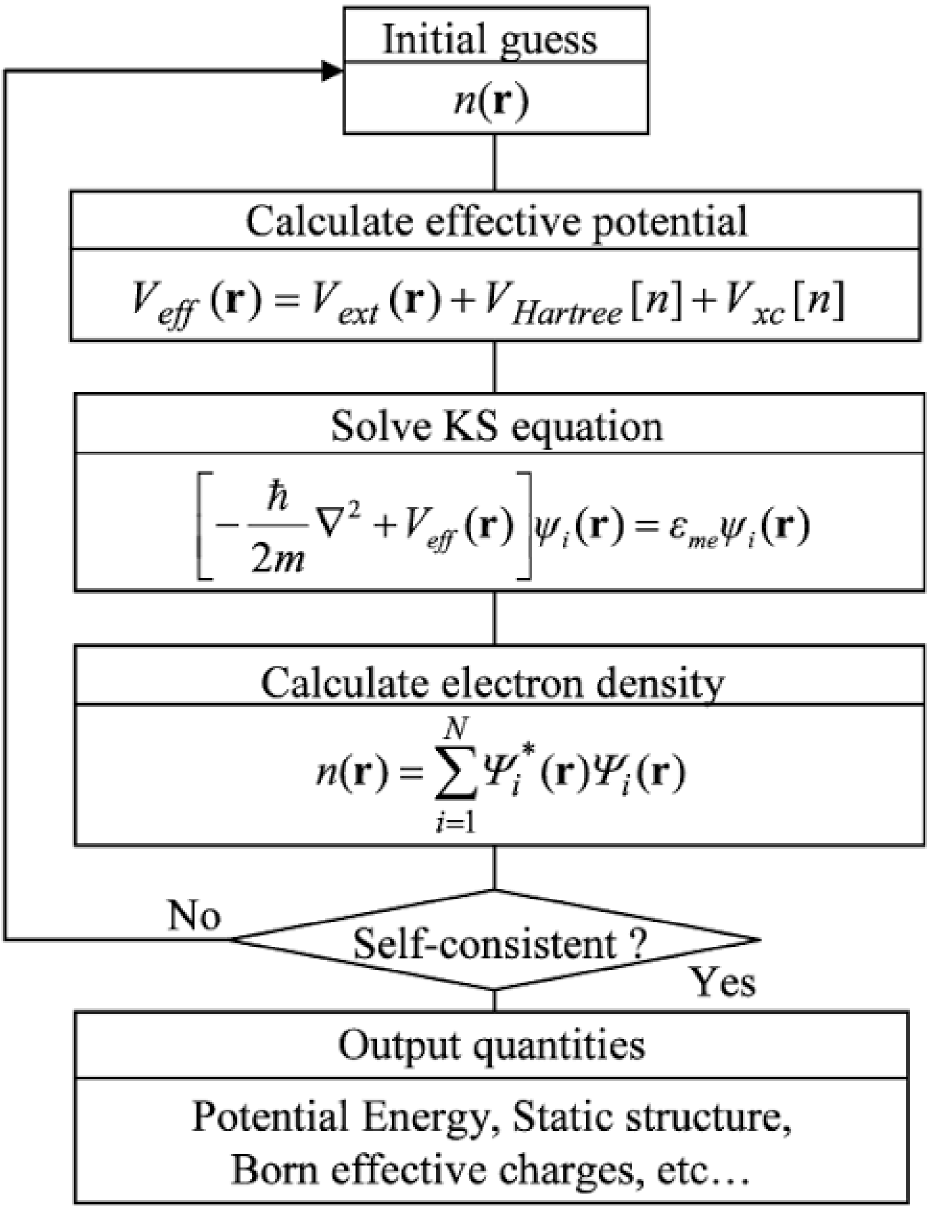

Figure 2.1: Flowchart of self-consistency loop for solving KS equations

whereas the Euler-Lagrange equation resembles (2.59) up to the potential term.

Because of that, the minimizing density can be calculated in a way similar to the Hartree- approach described in equations (2.55) to (2.57). The corresponding equations are the single-particle Schrödinger equations

$$[-\frac{1}{2}\vec{\nabla}^2 + v_{eff}(\vec{r})]\phi_j(\vec{r}) = \epsilon_j\phi_j(\vec{r})j = 1, ..., N \tag{2.66}$$

as well as the defining equation for the particle density

$$n(\vec{r}) = \sum_{j=1}^{M} |\phi_j(\vec{r})|^2, \tag{2.67}$$

which form together with the effective potential $v_{eff}(\vec{r})$ in (2.64) the self-consistent Kohn-Sham equations. [8]

The accurate ground state energy, as one of the most important quantities, can be expressed as [26]

$$E = \sum_j \epsilon_j + E_{xc}[n(\vec{r})] - \int v_{xc}(\vec{r}) n(\vec{r}) dv - \frac{1}{2} \int \frac{[n^{'}(\vec{r})][n^{'}(\vec{r}^{'})]}{|\vec{r} - \vec{r}^{'}|} d\vec{r} d\vec{r}^{'}. \tag{2.68}$$

Equation (2.68) can be seen as an generalization of the energy expression obtained with the Hartree-approach (note that the neglect of $E_{xc}[n(\vec{r})]$ and $v_{xc}(\vec{r})[n(\vec{r})]$ leads back to equation (2.60)). [26]

2.9 Exchange-correlation functional

The major problem in solving the Khon-Sham equations is that the true form of the exchange-correlation functional is not known. Two main approximation methods have been implemented to approximate the exchange-correlation functional. The local density approximation (LDA) is first approach to approximate the exchange-correlation functional in DFT calculations. The second well known class of approximations to the Khon-Sham exchange-correlation functional is the generalized gradient approximation (GGA). In the GGA approximation the exchange and correlations energies include the local electron density and the local gradient in the electron density. [35]

Chapter 3

The electronic, magnetic and optical properties of TbP

3.1 Method of calculations

Under the framework of density of density functional theory, the structural, electronic, optical properties of the TbP are investigated using full potential linearized augmented plane (FP-LAPW) method, approach implemented in the WIEN2k package. The generalized gradient approximation (GGA) for determining the exchange and correlation potential energy in Khon-Sham equation that gives the final result. The generalized gradient approximation is used to optimize the parameters (RK_{max}, K-point, and lattice constant). For Tb and P, the RMT values are taken 2.3 and 2.1 respectively. We set R$K_{max} = 8.5$ after optimization of energy where, R is the smallest radius of muffin-tin sphere and K_{max} is the largest reciprocal lattice vector that used in the expansion of flat wave-function. Moreover, the number of K-point is selected to 1000 in Brillouin zone. When the total energy of the system is stable within the energy of 10^{-4} Ry then self-consistent equations is converged.

3.2 Geometric structure and volume optimization

The rare earth TbP has two types of structures. Rock salt (RS) type structure with the space group (225, $Fm\bar{3}m$) with Tb atoms located at $(0, 0, 0)$ and P atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and in zinc blende type structure belonging to cubic crystal system with the space group (216, $F4\bar{3}m$), though the Tb atoms occupies the same $(0, 0, 0)$ position, P atoms occupies $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position. Figure 3.1(a, b) shows the representation of the structure of the TbP. The Murnaghan equation of state is used to compute energy as a function of latice constant in order to determine the stability of the compound in the structure under investigation before moving on to any electronic or magnetic properties. The volume optimization is provided with WIEN2k package that determines the minimum energy possessed by a system by plotting volume vs energy graph. It is clear that every system tries to in its minimum energy level, and so we plotted total energy vs volume plots from non-magnetic (NM), and ferromagnetic (FM) calculation are shown in Figure 3.2(a-d) for TbP. From energy vs volume plot we obtain lattice constant. Table 3.1 represents the calculated total energy and lattice constant.

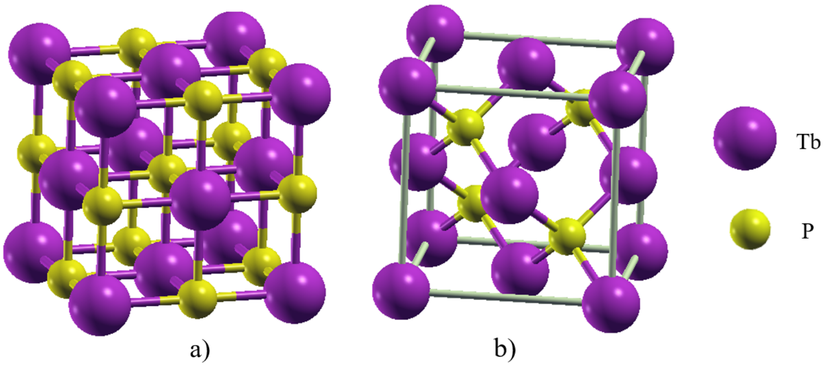

Figure 3.1: Crystal structure of TbP a) rock salt and b) zinc blende type structure

Compound	Structure type	Phase	Total energy (Ry)	Lattice constant (Å)
TbP	RS	NM	-24122.229336	5.673
		FM	-24122.660121	5.696
	ZB	NM	-24122.138711	6.313
		FM	-24122.561569	6.305

Table 3.1: Calculated total energy and lattice constant of TbP

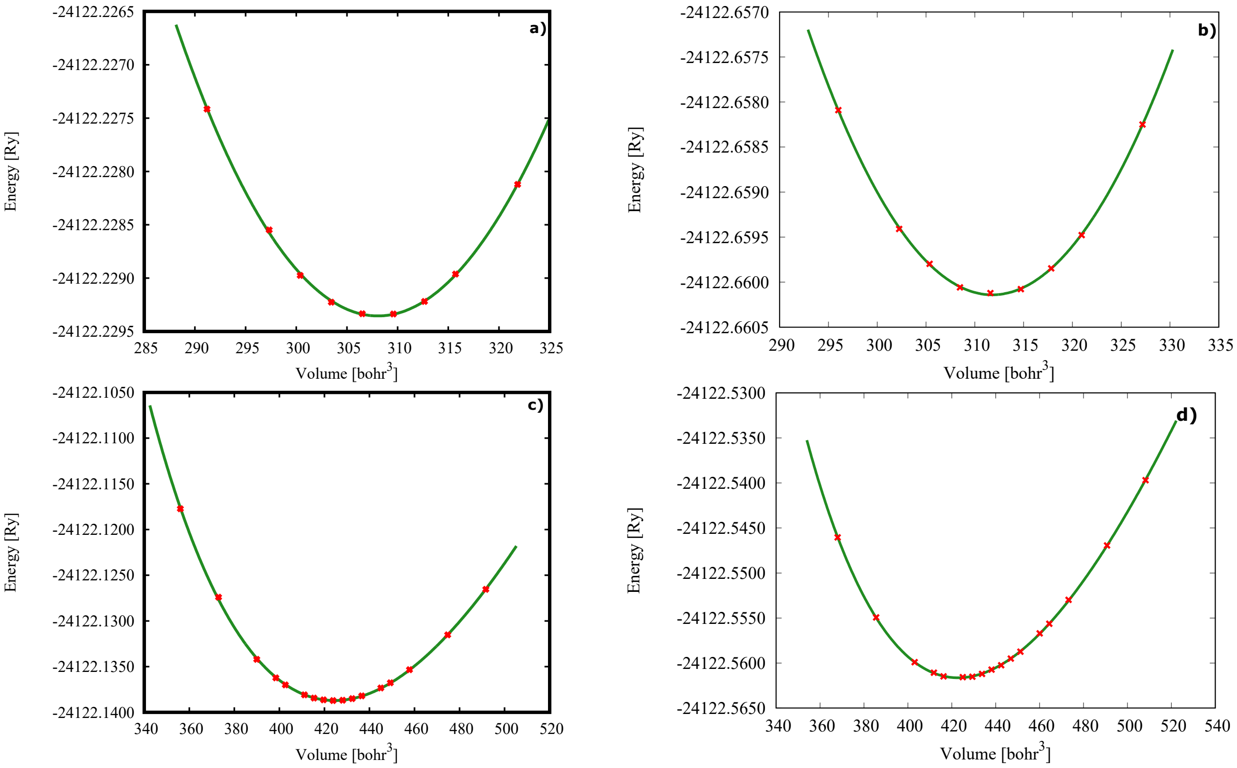

Figure 3.2: Volume optimization of TbP a) non-magnetic and b) magnetic phases for RS type structure, c) non-magnetic and b) magnetic phases for ZB type structure

3.3 Electronic properties

We must use generalized gradient approximation GGA, which is available as Perdew-Burke-Ernzerhof (PBE) functional, to calculate the spin polarization band structure and total density of state (TDOS) in order to understand the electrical properties of TbP.

3.3.1 Band structures

Understanding the physical characteristics of crystalline solids, which nearly entirely define optical as well as transport aspects, requires research of the electronic band structures. The spin polarization band structure of TbP for both the spin-up and down channels at equilibrium state along high symmetry direction in the first Brillouin zone are represented in Figure 3.3. Zero is chosen as fermi level. For rock salt type structure, spin polarization calculation shows that the valency bands overlap with conduction band in both sipn-up and spin-down band structures and the fermi level passing through the overlapping region shown in Figure 3.3(a, b). For this

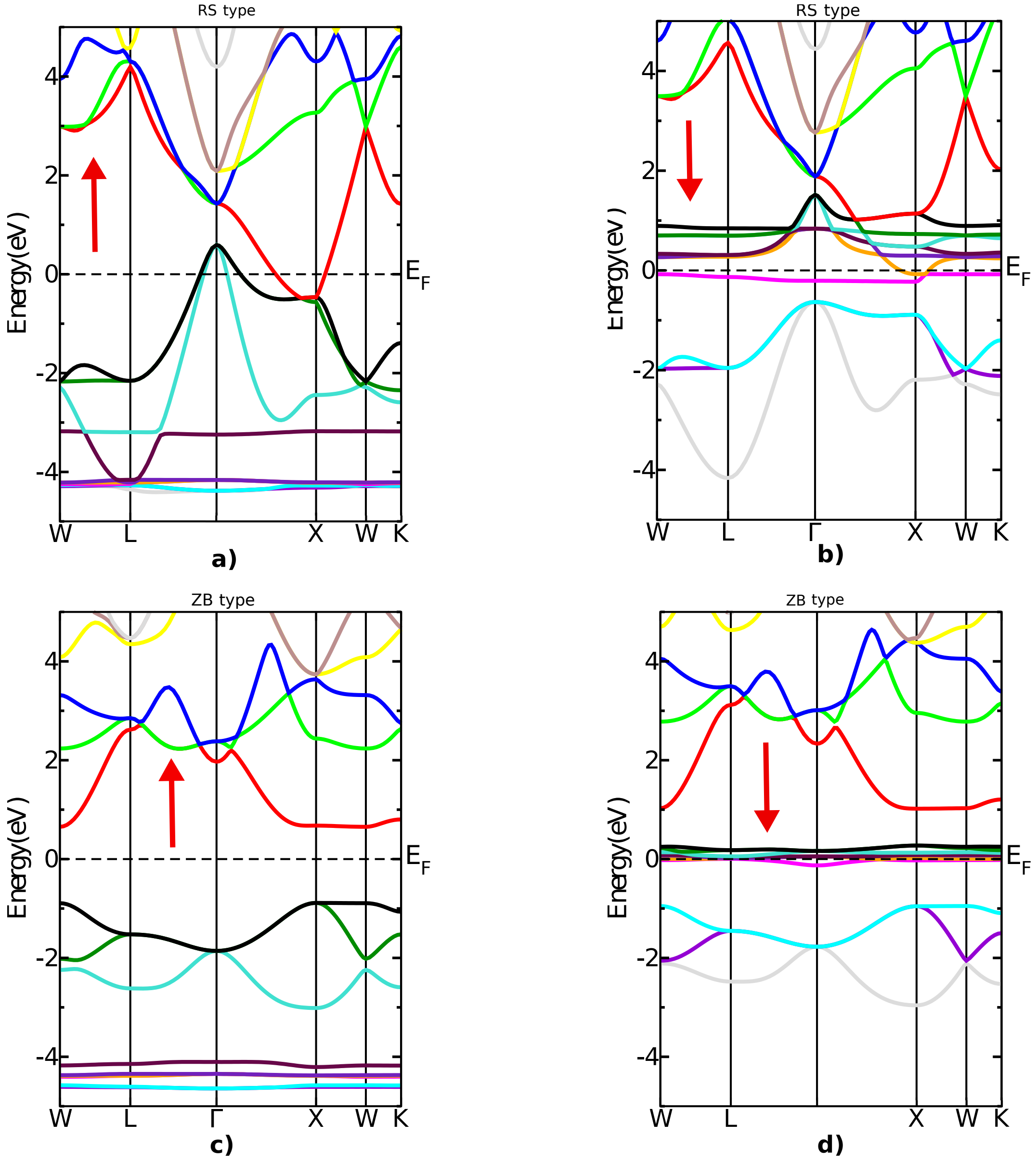

Figure 3.3: Calculated band structures of TbP a) spin-up and b) spin-down for RS type structure, c) spin-up and d) spin-down for ZB type structure

reason, there is no band gap. For zinc blende type structure, in Figure 3.3(c) spin polarization calculation shows that there is a band gap between valence band and the conduction band in spin-up band structures but spin-down band structures shows no bandgap shown in Figure 3.3(d) which indicates these compound is half-metallic.

3.3.2 Density of states

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy.

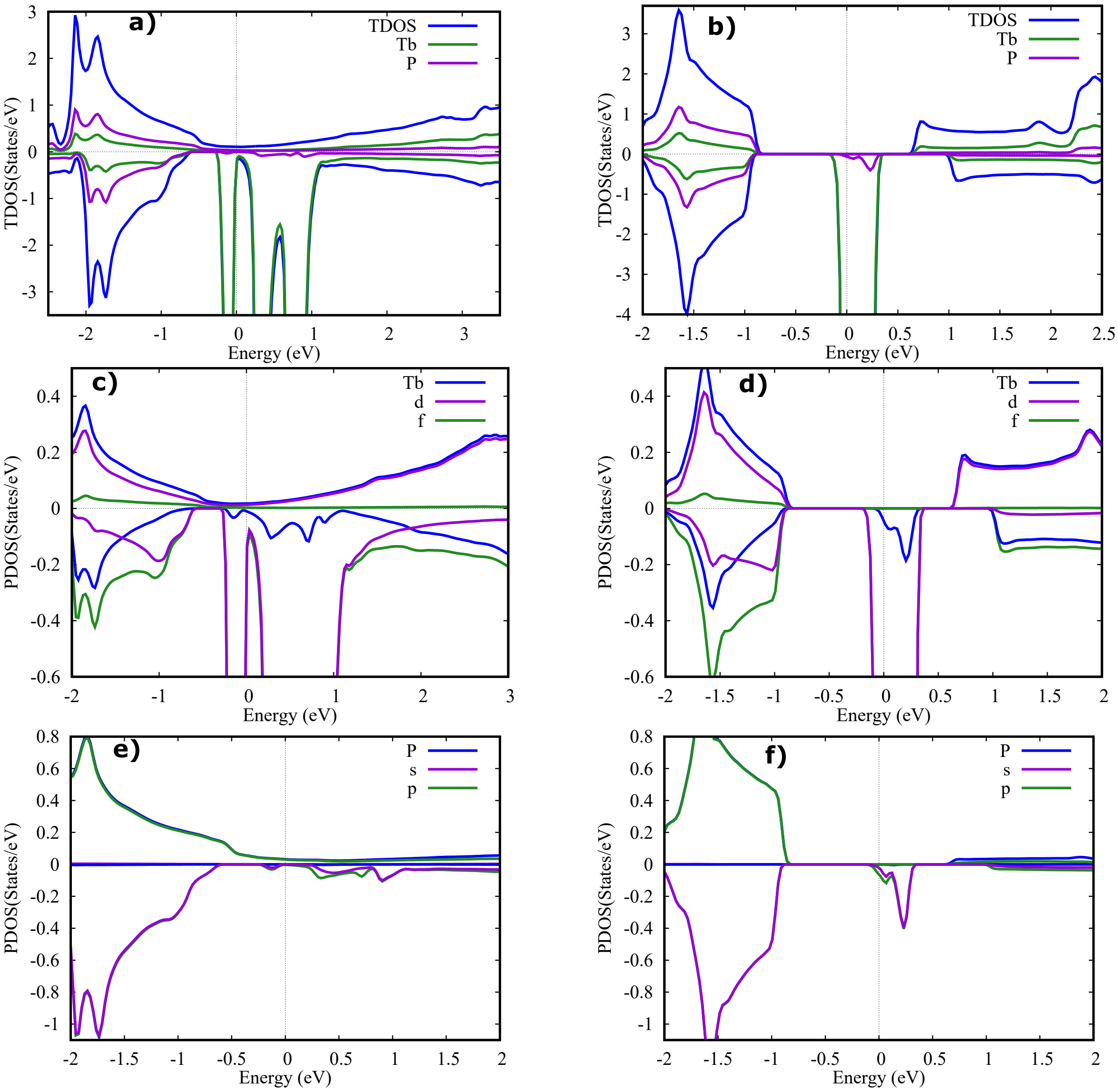

Figure 3.4: (a, b) Total density of states (DOS) of TbP for RS and ZB type structure, and (c, d) partial density of states of Tb atoms and (e, f) partial density of states of P atoms for RS and ZB type structures

Calculating the total density of states and partial density of state with GGA is required for the study of materials' electronic characteristics. Figure 3.4(a-f), shows the corresponding total density of states and partial density of states. The PDOS of Tb contains orbital d, f electrons for spin-up and spin-down for TbP is plotted in Figure 3.4(c) and Figure 3.4(d). Similarly the PDOS of P is also plotted in Figure 3.4(e) and Figure 3.4(f). The lower portion indicates the minority spin density while the upper portion indicates the majority spin density. For rock salt type of structure

Compound	Individual magnetic moments(μB)	
TbP	Site	GGA
	Intersititial	0.11863
	Tb	5.87454
	P	0.00847
	Total	6.00164

Table 3.2: Total spin magnetic moment of TbP in GGA approach

of TbP, in Figure 3.4(a) depicts the conduction band and valence band overlaps at fermi level. This indicates that the system is matelic. Figure 3.4(b) shows shows the system is half metallic.

3.4 Magnetic properties

The ferromagnetic ordering in the TbP is indicated by the spin-polarized calculations. The ferromagnetic TbP cell produced a magnetic moment of 6μB. The electronic configuration of Tb is $[X_e]3s^2 3p^3 6s^2$ where as for P the electronic configuration is $[N_e]3s^2 3p^3$. The valence electron of Tb plays an important role in increase in the magnetic moment in TbP. The total spin magnetic moment was found out to be 6.00163 μB in GGA approach. Using PBE potential, the magnetic moment of Tb atom is 5.87454 μB which is positive and 0.00847 μB is the magnetic moment of P atom that express the ferromagnetic ordering of the magnetic state. The total spin magnetic moment from spin polarization calculation of zinc blende type structure is shown in Table 3.2.

3.5 Optical properties

The optical properties of a material defines how it interacts with light. We have studied the dielectric function, reflectivity, optical conductivity, refractive index, absorption coefficient, and electron energy loss for understanding the optical properties of TbP by means of the FP-LAPW method and generalized gradient approximation (GGA).

3.5.1 Dielectric function

The correlation between energy band structure and optical transition is expressed by the complex dielectric function of a material.The complex dielectric function of the semiconductor material is

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \tag{3.1}$$

The complex dielectric function,real dielectric function and imaginary dielectric function are denoted by $\epsilon(\omega)$, $\epsilon_1(\omega)$ and $i\epsilon_2(\omega)$ respectively. Based on the band-structure results, the dielectric function can be calculated. The imaginary part of the dielectric function is obtained from the electronic structure. The real part of the dielectric function is calculated by the Kramers-Kronig relation. The imaginary part of the dielectric function depends on the joint density of state and the momentum matrix elements, while the real part is obtained from the Kramers-Kronig relation. It indicates the changing inter-band transitions in the semiconductor. The real part and imaginary parts between 0 and 12 eV are shown in Figure 3.5(a, b) where energy is plotted in the X-direction, real and imaginary dielectric function is plotted in Y-direction.

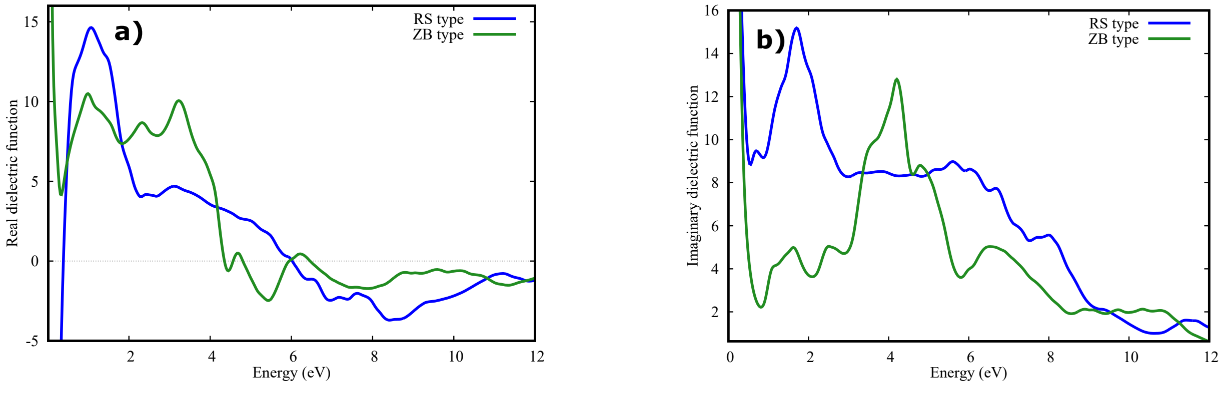

Figure 3.5: Dielectric function of TbP a) real b) imaginary

The real dielectric function represents the degree of polarization and energy dissipation amplitude is represented by imaginary dielectric function. The positive part of the real dielectric function indicates that TbP conducts at low energy levels, where the negative part of the real dielectric function indicates that it is insulating at high energy levels. Real dielectric function is maximum in infra-red region for rock salt and zinc blende type structure shown in Figure 3.5(a) where the propagation of electromagnetic wave is maximum at 1.5 eV. Figure 3.5(b) shows the imaginary dielectric function is maximum in infra-red region at 2 eV for RS type structure whereas ZB type structure shows maximum values in ultra-violet region at 4.1 eV. The maximum value represents charge carriers shifting from filled to empty bands.

3.5.2 Reflectivity and optical conductivity

Optical reflectivity helps to measure that a substance can be used for shielding purposes as an anti-reflecting coating. The optical reflectivity versus photon energy is shown in Figure 3.6(a) by using PBE functional. The reflectivity is being minimum in infra-red and visible region for both type of structure. For zinc blende type structure, the reflection occurs minimum at 0.5 eV. Whereas for rock salt type structure, the minimum reflection occurs at 11 eV. At higher energy region the reflectivity is maximum that means the system reflects more light. The maximum reflectivity occurs in UV region at 10 eV for rock salt type structure and at 12 eV for zinc blende type structure. High optical reflectivity represents strong metallic properties of the compound TbP.

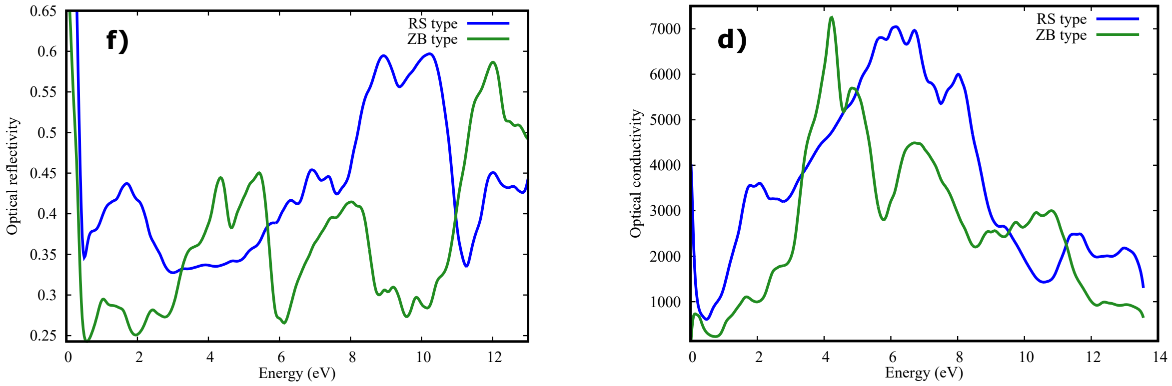

Figure 3.6: Calculated c) optical reflectivity and d) optical conductivity of TbP

The ability of a medium to initiate a phenomenon of conduction as the electromagnetic radiation try to propagate through it determines by optical conductivity. The dielectric function leads to the conclusion that the optical conductivity. It is given by,

$$\sigma(\omega) = -(i\omega/4\pi)\varepsilon(\omega) \tag{3.2}$$

The curve of the optical conductivity vs energy calculated with PBE approximation are shown in Figure 3.6(b) for TbP. The optical conductivity spectra using the imaginary part of the dielectric function have been studied. A range of energies between 0 eV to 16 eV has been calculated. This figure also shows the conductivity increased as energy increases. The curve represent several peak because electron crossing from the valence to conduction band. For zinc blende type structure the maximum peak obtained in UV region at 4 eV. Optical conductivity begins to decrease and reaches zero for higher energy values. According to the optical conductivity curve, the absorbed light spent conductivity in the ultraviolet range.

3.5.3 Refractive index and absorption coefficient

The refractive index is the measure of bending of a light ray when passing from one medium to another medium. It describes the optical properties of any given material. The refractive index of the material, gives how much a path of light is bent when it enters that material. Figure 3.7(e) shows refractive index vs energy plot. The refractive index is inversely related to bandgap, if refractive index increases corresponding bandgap decreases. Refractive index is maximum in infra-red region for rock salt type structure at the energy range 1 eV compared with zinc blende type structure. It is clearly seen that the refractive index has high value in low energy limit.

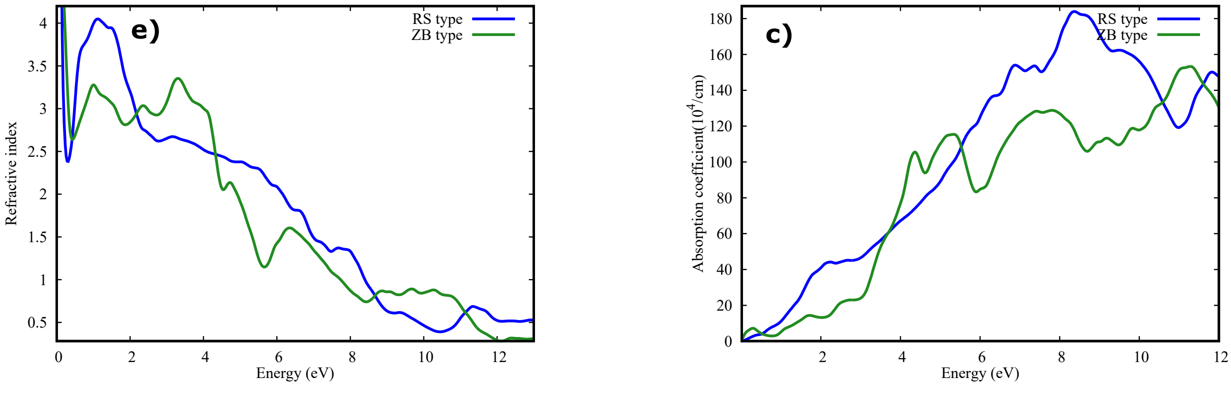

Figure 3.7: Calculated e) refractive index and f) absorption coefficient of TbP

When the photon energy ($h\nu$) of the incident beam is greater than the energy band gap (Eg), then absorption is produced. The form of the spectral components of the absorption coefficient by using PBE approch is plotted in Figure 3.7(b) in the energy range from 0 to 12 eV. From the characteristics of the curves, there is a considerable quantity of absorption occuring between 4 eV and 15 eV corresponding to the ultraviolet region. The zero absorption coefficient for the compound is remarked for photons possessing energies below the energy band gap in the infra-red region. The results of the absorption coefficient shows that this compound having the properties of good absorber.

Chapter 4

Conclusions

We studied the electronic, magnetic and optical properties of TbP by using density functional theory (DFT) and the PBE approximation approach. For ZB structure of TbP gives bandgap only for up spin that behaves as semiconductor while in down-spin channel there is no bandgap and behaves as metal. As a result, the TbP system behaves as half metal. The magnetic moment of TbP for spin polarization calculation is very high nearly 6 μB for (ZB ferromagnetic structure type) compared to RS type structure. The real and imaginary dielectric functions, optical absorptivity, conductivity, reflectivity, refractive index are also calculated for the system.

List of Abbreviations

BH : Born-Huang
BO : Born-Oppenheimer
BZ : Brillouin Zone
DFT : Density Functional Theory
DOS : Density of States
FP-LAPW : Full Potential Linearized Augmented Plane
GGA : Generalized Gradient Approximation
HEMT : High-Electron-Mobility-Transistor
HF : Hartree-Fock
HK : Hohenberg-Kohn
KS : Kohn-Sham
LDA : Local Density Approximation
MOSCAP : Metal-Oxide-Semiconductor Capacitor
PDOS : Partial Density of States
RHF : Restricted Hartree-Fock
RS : Rock Salt
TF : Thomas-Fermi
UHF : Unrestricted Hartree-Fock
XC : Exchange Correlation
ZB : Zinc Blende

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