Investigation of Structural, Electronic and Optical Properties of Silicon(Si) using DFT and TDDFT

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(**Condensed matter**)

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June 2022

DECLARATION

I, the undersigned declare that, this research paper entitled "**Investigation of Structural, Electronic and Optical Properties of Silicon(Si) using DFT and TDDFT** " is my own original work and it has not been submitted for the award of any academic degree or the like in any other institution or university, and that all the sources I have used or quoted have been indicated and acknowledged.

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ABSTRACT

Silicon is an indirect band gap semiconductor belonging to group III-V. It is commonly used in light emitting diodes (LED) and many optoelectronic devices fabrications. In this thesis, the structural, electronic and optical properties of silicon are investigated using DFT and TDDFT with the help of Quantum ESPRESSO. A number of convergence test were performed to establish the optimal value of various parameters in the numerical calculations. Firstly, the total minimum energy of Silicon per atom was calculated as a function of cutoff energy and k-points sampling. The results of calculations show that the total minimum energy of Silicon per atom is monotonically decreasing with increasing cutoff energy due to variational principle.However, this trend can not be predicted from increasing the k-point sampling.Secondly, the optimal lattice constants of bulk silicon was calculated using the results obtained from energy convergence test (i.e 50 Ry and 6 x 6 x 6 k-points).The equilibrium lattice constant was 5.43 Angestrom. The obtained result was overestimated as compared to the experimental result. Moreover the band structure and density of states of Silicon have been calculated based on the frame work of density functional theory.The calculated band gap Energy of Silicon is 0.83 eV, which is closer to the experimental value (1.12 eV). Finally the real, and imaginary parts of the dielectric function and the electron energy loss function(EELS) were calculated using TDDFT .

Keywords: Silicon, density functional theory, pseudopotentials, plane wave self-consistent field, Quantum Espresso Package,time dependent density functional theory(TDDFT)and, turboEELS.

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Introduction

1.1 General back ground of the study

Silicon is an important electronic material. It plays a crucial role in solar cell indus-
try, and has been widely applied as a photovoltaic material in solar cell devices be-
cause of its high abundance and stability. Looking for direct band gap silicon is still
a very active field in material science. As the third generation of solar cells, quan-
tum dot solar cells have great potential in improving the efficiency of photoelectric
conversion[1]. The need to produce more cost efficient electronic devices with sim-
ple processing techniques has fostered the development of new materials to become
an attractive and useful alternative to inorganic semiconductors, organic materials, in-
cluding conjugated polymers, organic small molecules (SMs) and self-assembling or-
ganic semiconductors, have intrigued an increasing attention because of their poten-
tial to enable the fabrication of flexible, light weight, semi transparency and large-area
devices[2].These advantages prove attractive for organic and printable electronics in-
dustries which have been on an exponential growth curve for many years and vari-
ety of applications has expanded such as organic photovoltaic cells (OPVs), organic
light-emitting diodes (OLEDs), flexible displays, integrated Smart systems and various
sensors. Particularly,OPVs composed of organic materials have recently brought con-
siderable attention to their potential to become an economically viable source of af-
fordable, clean, and renewable energies. Quantum chemical modelling by DFT and
time-dependant DFT (TDDFT) has become a powerful tool to allow qualitative and
quantitative studies of materials at the molecular level[2]. DFT has been employed suc-
cessfully to explain and predict detailed morphological information for known conju-

gated organic molecules, such as molecular geometries, electronic structure, frontier molecular orbital (FMO) energy levels, absorption spectra, and intramolecular charge transfer (ICT)[2]. The examination of geometric structures, electronic, optical and vibrational properties of Silicon can be carried out by DFT and TDDFT calculations promoting a reasonable interpretation of the experimental results and subsequently better understanding of the relationship between the structure and resulting properties. Moreover, the absorption spectra, lowest excitation energy gaps and oscillator strength have been studied on the excited states via TDDFT method[3]. Time-dependent density functional theory (TDDFT) can be used to obtain the optical spectra from relaxed geometries. TDDFT is an exact reformulation of time-dependent quantum mechanics, in which the fundamental variable is no longer the many-body wave function but the time-dependent density. TDDFT is an extension of DFT with the time-dependent domain to describe what happens when a time-dependent perturbation is applied. For the sake of completeness, the essentials of this method can be summarized explicitly. In TDDFT, the basic variable is the one electron density $n(r,t) = \Sigma_{i=1}^{N} |\psi(r,t)|^2$, which is obtained with the help of a fictitious system of non interacting electrons, the Kohn-Sham system[5].

1.2 Statement of the problem

This study focusses on the structural, electronic and optical properties of silicon(Si); which belongs to **many body problem**. **Many body problems** are complicated and challenging to solve. Because of this the state of motion cannot be solved analytically for systems in which three or more masses are interacting. To solve this many body problems, the density functional theory is preferred as an accurate and reliable tool. The basic purpose of DFT is that any property of the interacting systems can be viewed as a functional of the ground state density n_o(r). The semiconductor material, silicon (Si) plays significant role in the production of organic photovoltaic cells (OPVs), organic light-emitting diodes (OLEDs), flexible displays, integrated Smart systems and various sensors. However studying the structural, electronic and optical properties of Si is very crucial to widen its application in future technologies. So it is aimed to investigate the

structural, electronic and optical properties of silicon (Si) using DFT and the time dependent DFT with the help of Quantum ESPRESSO package

1.3 Basic research questions

- What is the computed value of the total minimum energy of silicon(Si) per atom with respect to cutoff energy?

- What is computed value the total minimum energy of silicon(Si) per atom with respect to K-points sampling?

- Obtain the lattice constant of Silicon(Si) per atom?

- What is band structure of Silicon(Si) per atom?

- what is density of state of Silicon(Si) per atom?

- What is the real and imaginary part of the dielectric function and EELS of silicon?

1.4 Objectives of the study

1.4.1 General objective

The general objective of this study is to investigate the structural,electronic,and optical properties of silicon(Si) using density functional theory (DFT) and time dependent-density functional theory.

1.4.2 Specific objective

- Determinig the total minimum energy of Silicon(Si) per atom with respect to cutoff energy

- Determining the total minimum energy of Silicon(Si) per atom with respect to K-points

- To calculate the lattice constant of Silicon(Si) per atom

- To calculate band structure of Silicon(Si) per atom

- To calculate the density of state of Silicon(Si) per atom

- To determine the real and imaginary part and the electron energy loss of the dielectric function of silicon.

1.5 Significance of the study

Understanding the structural, electronic and optical properties of many electron system(silicon) helps to know about the system in detail. Moreover it helps to develope computational skills for solving many body problems.

1.6 Scope of the study

This study concerned the structural,electronic and optical properties of silicon per atom using Density functional theory DFT and the time dependent density functional theory TDDFT. Each and every computations are guided by quantum espresso package.Mainly the band structure of silicon, density of state of Silicon(DOS) and absorption spectrum are illustrated theoretical as welell as practically as visible output.

2

Review of related literature

2.1 Introduction

This chapter focuses on the basic Quantum mechanical description of many-body system up to the theoretical background of the structural, electronic and optical calculation methodologies. For approximately solving many electron problems, the Hartree-Fock, Hohenberg kohn, Thomas-Fermi, the Kohn-Sham, the modern DFT and some other theories are discussed in some detail.Finally to perform calculations of a system, a plane wave basis set and pseudo-potential can be reviewed

2.2 General properties of silicon(Si)

Silicon is a crystalline semi-metal or metalloid. One of its forms is shiny, grey and very brittle (it will shatter when struck with a hammer). It is a group 14 element in the same periodic group as carbon, but chemically behaves distinctly from all of its group counterparts. Silicon shares the bonding versatility of carbon, with its four valence electrons, but is otherwise a relatively inert element. Silicon exhibits metalloid properties, is able to expand its valence shell, and is able to be transformed into a semiconductor; distinguishing it from its periodic group members. As mentioned above, Silicon(Si) is an attractive material, which is now in a fast developing stage. In this work, general properties of Silicon (Si) is stated as basic concepts, including chemical, mechanical, thermal, optical, electrical and structural properties[4].

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Chemical property of silicon(Si)

Silicon is much more reactive than carbon. At high temperatures, Si combines with $O_2, F_2, Cl_2, Br_2, I_2, S_8, N_2, P_4$, C and B to give binary compounds. Silicon liberates H_2 from aqueous alkali, but is insoluble in acids other than a mixture of concentrated HNO$_3$ and HF[7].

$$Si + 4\left[OH\right]^- \longrightarrow \left[SiO\right]^{4-} + 2H_2$$
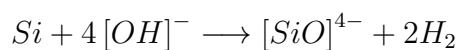
The table below gives the general properties of silicon(Si)

TableGeneral properties of silicon

Table 2.1: properties of silicon

Property	Value
Group	14 (Carbon Family)
Electron Configuration	$[Ne]3s^2 3p^2$
Atomic Density	$5x10^{22}cm^{-3}$
Atomic Weight	28.09
Density (ρ)	$2.328gcm^{-3}$
Energy Bandgap E_G	1.1242 eV
Lattice constant	0.543095nm
Melting point	1415^oC

2.2.1 Crystal structure of silicon(Si)

Because of the importance of semiconductors in our everyday lives, it is important to draw attention to the structural similarities that exist within group 14 materials.The silicon element exhibit diamond structure type. In this prototype structures, atoms are in tetrahedral environments. Diamond-type structures are adopted by Si and Ge, and the addition of dopants[7].

2.2.2 Application of silicon(Si)

- Silicon is a vital component of modern day industry. Its abundance makes it all the more useful. Silicon can be found in products ranging from concrete to computer chips.

- In modern day technologies,pure silicon discretely control the number and charges of current that passes through it. This makes silicon important in devices such as transistors ,solar cells,integrated circuits, microprocessors, and semiconductor devices for proper performance

- silicon is used in manufacture of glass

- ultra-high purity glass is ultra pure silica, and is used to make fiber optic cables

- Silicon plays an integral role in the construction industry. Silicon, specifically silica, is a primary ingredient in building components such as bricks, cement, ceramics, and tiles.

- Silicone polymers are generally characterized by their flexibility, resistance to chemical attack, impermeability to water, and their ability to retain their properties at both high and low temperatures Silicone polymers are used in insulation, cookware, high temperature lubricants, medical equipment, sealants, adhesives, and even as an alternative to plastic in toys.[6]

2.3 Density Functional Theory (DFT)

Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators[8,9]. The great advantage of DFT is that it can be applied to a wide variety of systems, ranging from transition metal complexes to solids, surfaces and metallo-proteins. In DFT,Computational methods are now used extensively by experi-mental chemists. The computation time is not excessive, and the results are generally reliable. (DFT) focuses on the electron density distribution in a system rather than on many-electron wavefunctions. Information that can be calculated includes the equilibrium geometry of a molecule, transition state geo-metries, heats of formation, composition of molecular orbitals, vibrational frequencies, electronic spectra, reaction mechanisms and (from molecular mechanics calculations) strain energies[8]. All properties of the many-body system are determined by the ground state density $\rho_0(r)$. Each property is a functional of the ground state density $\rho_0(r)$[8,9,10]. DFT follows different approaches to attain its central target. Some of theories or approaches were encountered with some drawbacks. One of these is the Thomas-Fermi theory, which is the poor approximation of kinetic energy functional.DFT in principle, is an ab-initio method that it does not use any experimental results on chemical bonding. It works with the electron density only. There are significant advantages to a computational theory based on electron densities.The first is in relation to efficiency; the

electron density depends on the three spatial variables in contrast to the 4N variables that wave functions depends on (three spa-tial and one spin per electron).Therefore large system can be theoretically modeled .In addition, electron correlation is conceptually easier to include in DFT. It has achieved a certain status as a standard first method. The first principle calculations have gained great success in studying the equilibrium properties of matter, though there are still many challenges to DFT[10,11,12,13]

2.4 Many electron system

The ultimate goal of most approaches in solid state physics, quantum chemistry and in this electronic structural calculation of silicon(si) is the solution of the time independent, non relativistic Schrödinger equation [13,14,15]. The electronic Schrödinger equation of a system of N electrons reads,

$$H\psi\left(r_1, r_2, ...r_N\right) = E\psi\left(r_1, r_2, ...r_N\right) \tag{2.1}$$

Where H is Hamiltonian of the system, E is energy, r_N is coordinate of the electron with index N and $\psi\left(r_1, r_2, ...r_N\right)$ is the many particles wave function.

$$\widehat{H} = \widehat{T}_e + \widehat{V}_{ne} + \widehat{V}_{ee} + \widehat{T}_n + \widehat{V}_{nn} \tag{2.2}$$

where,

$\widehat{T}_e = -\Sigma^{iN}\frac{1}{2}\nabla^2$,

$\widehat{V}_{ne} = \Sigma_a^{iN_{nuc}}\Sigma_i^{N_e}\frac{ZA}{[Ra-r_i]}$,

$\widehat{V}_{ee} = \Sigma_i^{N_e}\Sigma_{j>i}^{N_e}\frac{e}{|r_i-r_j|}$,

$\widehat{T}_n = \Sigma_a^{N_{nu}} - \frac{1}{2}\nabla_i^2$ and

$\widehat{V}_{nn} = \Sigma_a^{iN_{nuc}}\Sigma_{b>a}^{N_{elec}}\frac{Z_AZ_B}{|R_a-R_b|}$ in atomic unit.

2.5 The Thomas Fermi theory

The Thomas Fermi theory is the simple example of a DFT. It emerges when we ignore the exchange energy and make the simplest possible approximation for the kinetic energy [16]. For a solely varying density function the kinetic energy density will only depend on the number of density at the same position. Taking the specific function from

the Fermi gas, we arrive at the kinetic energy functional[16].

$$T\left[n\left(r\right)\right]=\int\frac{3}{10}\frac{\left(3\pi^2\right)^{\frac{2}{3}}}{m}n\left(r\right)^{\frac{5}{3}}d^3 \tag{2.3}$$

And the sum of the KE and potential energy terms will give us the total energy within the Thomas Fermi approximations

$$E\left[n\left(r\right)\right]=\int\frac{3}{10}\frac{\left(3\pi^2\right)^{\frac{2}{3}}}{m}n\left(r\right)^{\frac{5}{3}}d^3+\frac{e^2}{2}\int\frac{n\left(\overrightarrow{r}\right)n\left(\overrightarrow{r}\prime\right)}{|\overrightarrow{r}-\overrightarrow{r}\prime|}d^3\overrightarrow{r}\prime d^3\widehat{r}+\int n\left(r\right)V_N\left(r\right)d^3r \tag{2.4}$$

Where the first term is kinetic energy of the electrons, the second term is the potential energy of the electrons due to their mutual electric repulsion and the third term is the potential energy of an atom's electrons, due to the electric attraction of positively charged nucleus. Note that the expression only depends on density n(r). Unfortunately, this theory has limited validity due to its poor approximation of kinetic energy functional [10]

2.6 Hartree - Fock theory

. HF theory is the Variational theory obtained by the expectation value of the Hamiltonian,allowing all wave functions that can be represented as Slater determinants. This theory was developed by two individuals, Hartree and Fock. Fock applied the slater determinant to the Hartee method and proposed the Hartree- Fock method and involves antisymmetric natures of waves, spin orbital (slater determinant), orthogonality and angular momentum [17].One of the strategies of HF is, the self-consistent solutions are obtained by employing variational principle, which is given by;

$$\delta\left\langle\psi^N|H|\psi^N\right\rangle=0 \tag{2.5}$$

2.7 The Hohenberg-Kohn theorem

The foundation of the DFT method is the Hohenberg-kohn theorem, which states that for each given electronic density $\rho(r)$, there is one and only one corresponding potential. All properties of the many body system are determined by ground state density. The H-K theorem implies that the ground- state for any system can be determined by varying the charge density until the global minimum in the energy functional is found.

2.7.1 First theorem of Hohenberg-Kohn

The ground state energy of many body system is a unique functional of the particle density. In principle all properties of the ground state can be expressed as functional of the ground state spin density matrix ρ_o . Therefore, the ground state wave function ψ (which can be determined by the density function theory) minimizing the energy functional [19].

$$E\left[\psi\right] = \left\langle \psi | \widehat{H} | \psi \right\rangle \tag{2.6}$$

Using$\psi_o \rho_o$ one can determine all properties by calculating;

$$\left\langle \widehat{o} \right\rangle \left[\rho_o\right] = \left\langle \psi_o \left[\rho_o\right] | \widehat{o} | \psi_o \left[\rho_o\right] \right\rangle \tag{2.7}$$

Where $\widehat{o}$ is an arbitrary operator.

2.7.2 Second theorem of Hohenberg- kohn

A universal functional for the energy $E[n]$ interms of the density n(r) can be defined, valid for any external potential $V_{ext}(r)$. For any particular $V_{ext}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density that minimize the functional is the exact ground state density n_o (r) [19]. The total energy can be written as,

$$E\left[n\right] = T\left[n\right] + V_{ne}\left[n\right] + V_{ee}\left[n\right] = F_{HK}\left[n\right] + V_{N_e}\left[n\right] \tag{2.8}$$

Where ;$F_{HK}\left[n\right] = T\left[n\right] + V_{ee}\left[n\right]$ which is universal functional

2.8 The kohn-sham approach/ theory

Kohn and Sham (KS) proposed to put wave mechanics in to the kinetic energy functional, but retain the density variable n(r) elsewhere. Their theory was tightly linked to HF slater approximation of many body fermions theory [19,20]. The weakest part of the Thomas Fermi theory was the treatment of the kinetic energy functional in this theory. Kohn-sham considered the exchange and correlation energies and supposed to calculate the exact kinetic energy of a non interacting reference system with the same density as the real interacting system.

$$E_{KS}\left[\phi_1, \phi_2...\phi_N\right] = \Sigma_a^N \frac{\hbar^2}{2m} \int d^3 r \nabla \phi_a^*$$

$$.\nabla\Phi_a + \frac{1}{2}\int d^3 r \frac{e^2}{|r-r\prime|} n\left(r\right) n\left(t\prime\right) + E_{xc}\left[n\right] + \Sigma_a \int d^3 r v_{ext}\left(r\right)|\phi_a|^2 \qquad (2.9)$$

Which is used together with the definition $n\left(r\right)\Sigma_a^N|\phi_a\left(r\right)|^2$ Accurate values of the exchange and correlation energies obtained for chemically interacting.systems are essential for analysis of the effect of electron correlation with in Kohn-sham (KS) theory. Two of the earliest density functional are the local density approximation (LDA) andgeneralized gradient approximation (GGA).

2.9   The exchange- correlation energy

The exchange-correlation energy E_{xc} of a many- electron system is the quantity of DFT. In context of Kohn-Sham theory, E_{xc} is defined as a functional of the electron density ρ. In K-S expression the total electronic energy $E\left[\rho\right]$ is;

$$E\left[\rho\right] = T_s\left[\rho\right] + V\left[\rho\right] + W\left[\rho\right] + E_{xc} \qquad (2.10)$$

Where; T_s - is the kinetic energy of a non-interacting particle system with density ρ, V is the energy of electron-nuclear attraction, W H is the coulomb or Hartree energy and E_{xc} is the exchange-correlation energy. An accurate values of the exchange and correlation energies obtained for chemically interacting systems are essential for analysis of the effect of electron correlation with the Kohn-sham theory and in order to test and calibrate various DFT approximation (Local Density Approximation and Generalized Gradient Approximation)(LDA) and Generalized Gradient Approximation(GGA)).

2.10   The Local Density Approximation (LDA)

The first family of exchange correlation functional is the LDA functional [35]. The idea of this functional is the first look at the case of a homogenous electron gas. In such a system, one considers the electron moving in uniform external potential. In DFT, the electron density rather than the wave function is the basic variable.

$$E_{xc}^{LDA}\left[n\right] = \int n\left(r\right) E_{xc}\left[n\left(r\right) d\widehat{r}\right] \qquad (2.11)$$

In LDA, there is no known formula to calculate the total energy of many electrons moving in an external potential using the density. Hohnberg and Kohn proved that there

exist a universal functional of the density called,$G[\rho]$ such that:

$$E[\rho_r] = \int v(r)\rho d^3r + \frac{1}{2}\int \frac{\rho r \rho r\prime}{|r - r\prime|}d^3r d^3r\prime + G[\rho] \tag{2.12}$$

Where the first term on the right hand side is the energy due to external potential while the second term is the classical coulomb energy of the electron system. The main deficiency of the LDA was the strong over binding with bond energies in error by about 1ev. On the one hand this renders LDA useless for most applications in condensed matter physics. On other hand, the problem was hardly visible in solid state physics where bonds are rarely broken, rearranged so that the errors canceled.

2.11   The generalized gradient approximation (GGA)

This functional (GGA) depends on the local electron density as the spatial variation of the electron density that is represented by density gradient. The idea behind this functional was to improve the approximation of LDA by considering not only the electron density, but also the local gradient of that density [21,22]. The GGA functional can be written as;

$$E_{xc}^{GGA}[n] = \int n(r)E_{xc}[n(r)\nabla_n]d\overrightarrow{r} \tag{2.13}$$

The $E_{xc}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas. The GGA gives better total energies. When a bond between two atoms is broken, the surface is increased. In GGA, this bond-breaking process is more favorable than in LDA and hence bond is weakened. Thus the GGA cures the over binding error of the LDA. These gradient corrections greatly improved the bond energies and made density functional theory useful also for chemists. The most widely distributed GGA functional is the Perdew Burke-Ernzerhof (PBE) functional [21,22,24].

2.12   Plane wave basis sets and Pseudo potentials

2.12.1   Plane wave basis set

In calculations of solid states or condensed matter, the DFT will be applied with plane wave basis sets [33]. When dealing with a crystal which has atoms periodically arranged, the electrons are in a periodic potential U(r), where $U(r + R) = U(r)$ and R is

the Bravais lattice. As the Bloch theorem states below that, a discrete plane- wave basis sets are used to expand the electronic wave function at each K-points. In principle, an infinite plane wave basis sets is required to expand the electronic wave function. However, the coefficients $C_i, K + G$ for the plane waves with small kinetic energy, $\frac{\hbar}{2m}|K + G|^2$ are typically more important than those with large kinetic energy. Thus, plane-wave basis sets can be truncated to include only plane wave that have kinetic energy less than some particular cut-off energy.

2.12.2 The pseudo-potential

Pseudo potentials have been introduced to avoid describing the core elements explicitly and to avoid the rapid oscillation of the wave function near the nucleus, which normally require either complicated or large base sets. Due to this, the fundamental idea of pseudo potential is the replacement of one problem with another. Its primary application in electronic structure is to replace the strong coulomb potential of the nucleus and the effects of tightly bound core electrons by an effective ionic potential acting on the valence electron [24,25,26]. The pseudo potential approximation is motivated by the fact that the behavior of valence electrons in the bonding region primarily determines the electronic structure and the structural properties of many materials. In a pseudo-potential formulation, the effect of the core electrons and that of nuclear potential are combined to form an effective ionic pseudo-potential. The pseudo potentials are commonly constructed, so that outside of a core region the valence pseudo wave functions match the corresponding states derived from all electron calculation, inside the region they are smooth functional. This formulation makes pseudo-potential calculations quite efficient, since the core orbital do not need to be recomputed. The relaxation correction takes in to account the relaxation of the electron system up on the excitation of an electron. The orthogonalized plane waves $(OPW)_{\phi_n}$ is defined by $e^{ik.\overrightarrow{r}} + \Sigma_c b_c \psi_k^c (\overrightarrow{r})$ where $\psi_k(r)$ is the core wave function the sum is over all core levels with Bloch wave vector k, and we require that ϕ_k are orthogonal to every core level.

$$d(\overrightarrow{r}) \psi_k^{\phi c^*} (\overrightarrow{r}) \phi_k (\overrightarrow{r}) = 0 \qquad (2.14)$$

The starting point for pseudo potential calculations and analysis is the application of nearly free electron (NFE) theory to find the valence levels (ϕ_k^v). The pseudo potential is the sum of the actual periodic potential and V^R Where; $v^R = \Sigma_c \left(E_k^v - E_c\right) \left(\int dr \psi_K^{c*} \phi\right) \psi_k^c$

$$H + V^R = -\frac{\hbar^2}{2m} + U + V^R \tag{2.15}$$

Where; $U + V^R = V spendo$, U- is negative near ion cores while V^R is always positive. Moreover pseudo potentials have been introduced to avoid the rapid oscillations of the wave function near the nucleus, which normally require either complicated or large basis sets and to avoid describing the core electrons explicitly.Hamann, Schluter and Chiang showed in 1979 how pseudo potentials can be constructed in such a way that their scattering properties are identical to that of an atom to first order in energy. These first principles pseudo potentials relieved the calculation from the restrictions of empirical parameters. Highly accurate calculations have become possible especially for semiconductors and simple metals. An approach by Zunger and Cohen towards first principles pseudo potentials precedes other approaches[26].

2.13 Periodic super cells

We would define the shape of the cell that is repeated periodically in space, the super cell,by lattice vector $\vec{a_1}, \vec{a_2} and \vec{a_3}$. If we solve the Schro?dinger equation for this periodic system, the solution must satisfy a fundamental property known as Bloch's theorem.

2.14 Bloch theorem

A Bloch function is the generalization of a plane wave for an electron in periodic potential. Bloch- theorem states that in a periodic solid each electronic wave function can be written as the product of cell periodic and wave like part.

$$\psi_k \left(r\right) = e^{iG.\vec{r}} U_k \left(r\right) \tag{2.16}$$

Where $U_k \left(\hat{r}\right)$ is the periodic potential in space with the same periodicity as the supper cell. That is;

$$U_k \left(\hat{r}\right) = U_k \left(\vec{r} + n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3}\right) \tag{2.17}$$

, where for any integer $\overrightarrow{a_1}, \overrightarrow{a_2} and \overrightarrow{a_3}$

2.15 Energy cutoffs and K- Points

Energy cut-offs limit the number of plane wave components. The minimum length scale depends on the elements in the system. Our discussion of k-space would begin with Bloch's theorem,which tells us the solutions of the Schorödinger equations for a super cell that have the form $\psi_k(r) = e^{iG.\overrightarrow{r}}U_k(r)$ where $U_k(r)$ is periodic in space with the same periodicity as the supper cell. It is now time to look at this part of the problem more carefully. The periodicity of $U_k(r)$ means that it can [i(K + G).r] be expanded in terms of a special set of plane waves.$U_k(r) = \Sigma C_{i'G}e^{i(K+G).r}$ Where the summation is over all vectors defined by; $\overrightarrow{G} = n_1b\overrightarrow{b} + n_2\overrightarrow{b} + n_3\overrightarrow{b}$ With integer values n_i... The set of vectors defined by $\overrightarrow{G}$ in reciprocal space are defined. So that for any real space lattice vector, combining the two equations above giveWith integer values n_i. The set of vectors defined by G in reciprocal space are defined. So that for any real space lattice vector, combining the two equations above give

$$\overline{\Psi}_k(r) = \Sigma_G C^{ik+Ge}\left(\left(i\overrightarrow{K} + \overrightarrow{G}\right)\overrightarrow{r}\right) \tag{2.18}$$

According to this expression, evaluating the solution at even a single point in k-space involves a summation over an infinite number of possible values of G. This does not use for practical calculations. here are solutions with kinetic energy.

$$E = \frac{(\hbar)^2}{2m}|\overrightarrow{K} + \overrightarrow{G}|^2 \tag{2.19}$$

It is reasonable to expect that the solutions with lower energies are more physically important than solutions with very high energies. As a result, it is usual the infinite sum above to include only solutions with kinetic energies less than some value; The infinite sum then reduces to

$$\psi_k(r) = \Sigma_{|G+K|<G}CG + Ke^{[i(\overrightarrow{K}+\overrightarrow{G})r]} \tag{2.20}$$

This expression includes slightly different numbers of terms for different values of k the discussion above has introduced one more printer that must be defined whenever a DFT calculation is performed the cutoff energy (E_{cu}). The solution that is used most

widely was developed by monk-horst pack in 1976. The symmetry of the cell may be used to reduce the number of k-points which are needed. Using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulators or semiconductor by calculating the electronic states at a very small number of k-points. The electronic potential and total energy are more difficult to calculate if the system is metallic because a dense set of k-points is required to define the Fermi surface precisely. The magnitude of any error in the total energy due to inadequacy of the k-points sampling can always be reduced by using a denser set of k-points. The computational cost of performing a very dense sampling of k-points can be significantly reduced by using the k-point total energy method [25, 26].

2.16 The time dependent density functional theory(TDDFT)

Time-dependent density functional theory (TDDFT) can be viewed as an exact reformulation of time-dependent quantum mechanics, where the fundamental variable is no longer the many-body wave-function but the density.This time-dependent density is determined by solving an auxiliary set of non-interacting Schrödinger equations, the Kohn-Sham equations.The non-trivial part of the many body interaction is contained in the so called exchange correlation potential, for which reasonably good approximations exist. Within TDDFT two regimes can be distinguished: i) If the external time-dependent potential is "small "the complete numerical solution of the time-dependent Kohn-Sham equations can be avoided by the use of linear response theory. This is the case, e.g., for the calculation of photo-absorption spectra. ii) For a "strong "external potential, a full solution of the time dependent Kohn-Sham equations is in order. This situation is encountered, for instance, when matter interacts with intense laser fields. It was in 1964 that Hohenberg and Kohn discovered that to fully describe a stationary electronic system it is sufficient to know its ground-state density. Another breakthrough occurred when Kohn and Sham proposed the use of an auxiliary non-interacting system, the Kohn-Sham system, to evaluate the density of the interacting system. Within the Kohn-Sham system, the electrons obey a simple,one-particle,Schrödinger equation with an effective external potential, v_{KS} . As v_{KS} is a functional of the electronic den-

sity, the solution of this equation has to be performed self-consistently. The effective potential, v_{KS}, is usually decomposed in the form

$$v_{KS} = v_{ext}(r) + v_{Hartree}(r) + v_{xc}(r) \tag{2.21}$$

The non-relativistic many-body Schrödinger equation is

$$i\frac{\partial}{\partial t}\Psi(\{r\}, t) = \widehat{H}(\{r\}, t)\Psi(\{r\}, t) \tag{2.22}$$

where $\widehat{H}$ is the Hamilton operator of the system and $\{r\} = \{r_1, ..., r_N\}$ are the spatial coordinates of the N electrons. The Hamiltonian is naturally decomposed into three parts, $\widehat{H}(\{r\}) = \widehat{T}(\{r\}) + \widehat{W}(\{r\}) + \widehat{V}(\{r\}) + \widehat{V}_{ext}(\{r\}, t)$ The first two are the kinetic energy and the electron-electron interaction,

$\widehat{T}(\{r\}) = -\frac{1}{2}\Sigma_{i=1}^{N}\nabla_1^2, \widehat{W}(\{r\}) = \frac{1}{2}\Sigma_{i,j=1 i,j\neq o}^{N}\frac{1}{|r_i - r_j|}$

The third term can be written as a sum of one-body potentials, $\widehat{V}_{ext}(\{r\}, t) = \Sigma_{i=1}^{N}v_{ext}(r, t)$ and can be used, for example, to describe the Coulomb interaction of the electrons with a set of nuclei,

$v_{ext}(r, t) = -\Sigma_{v=1}^{N_n}\frac{z_v}{|r - R_v(t)|}$

where z_v and R_v denote the charge and position of the nucleus v, and N_n stands for the total number of nuclei in the system.

3

Research Methodology

3.1 Computational Methodology

To study the system we used the QUANTUM ESPRESSO package as our first principal code. Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations based on density functional theory, plane waves basis sets and pseudopotentials to represent electron ion interactions,. It is free, open-source software distributed under the terms of the GNU General Public License (GPL)[33]. All the ground state relaxed structures were obtained after performing geometry optimization to get an ideal relaxation structure[34-37], all in Cartesian coordinates. This optimized structure is then used to calculate the electronic and optical properties, in particular the energy gap and absorption spectrum linear response..All the computational approaches were successfully done in real space[39]. The core electrons with strong coulombic effect were treated using the Troullier and Martins pseudo potentials [39]. For the ground state calculation, the computational parameters were used exactly [40] to solve for the Kohn-Sham eigenvalues. Then the time-dependent calculations of the perturbed system are conducted. Subsequently, the time reversal symmetry propagator in the algorithms was used to approximate the evolution operator. The wave functions representation in real space was mapped onto a uniform grid with a spacing of 0.175 Å and spheres of radius 4 Å around every atom. The system was perturbed by short electrical pulses 0.01 $\mathring{A}^{-1}$. A time step of 0.0017 femtoseconds ensured the stability of the time propagation, and a total propagation time of 10 femtoseconds allowed a resolution of about 0.01 eV in the resulting energy spectrum with almost 6000 steps.Next up,by the use of optimized turboEELS code which supports two levels of parallelization: i) a

plane-wave parallelization, which is implemented by distributing real- and reciprocal-space grids across the processors, and ii) a k points parallelization, which is implemented by dividing all processors into pools, each taking care of one or more k points as a components of the Quantum ESPRESSO package,the ground-state calculations are performed then the Lanczos recursion calculations,then the post-processing spectrum calculation are performed for the optical property calculation. The computation takes place in such a way that input file is given for the soft-ware (quantum ESPRESSO Package). The input file is composed of three name lists; **control, system, and electrons** followed by three cards ATOMIC SPECIES, ATOMIC POSITIONS, K-POINTS. During computation the system follows Algorithm of Self-Consistent Iteration. Self-consistent iterations to solve this problem consist of starting with an initial guess of the charge density n(r), then obtaining a guess for V_{ext} and solving Kohn-Sham equation for wave function ψ_i(r) to update charge density and external potential. Then, Kohn-Sham equation is solved again for the new wave function and the process is carried on until the difference between two consecutive external potential is below a certain tolerance (equivalently, the wave functions are close to stationary)[42]. The SCF method is an iterative procedure which yields a self-consistent set of wave functions and orbital energies. Flow chart scheme of SCF to iterate Kohn-Sham equations for a set of fixed nuclear (ionic) positions is shown in the figure below.
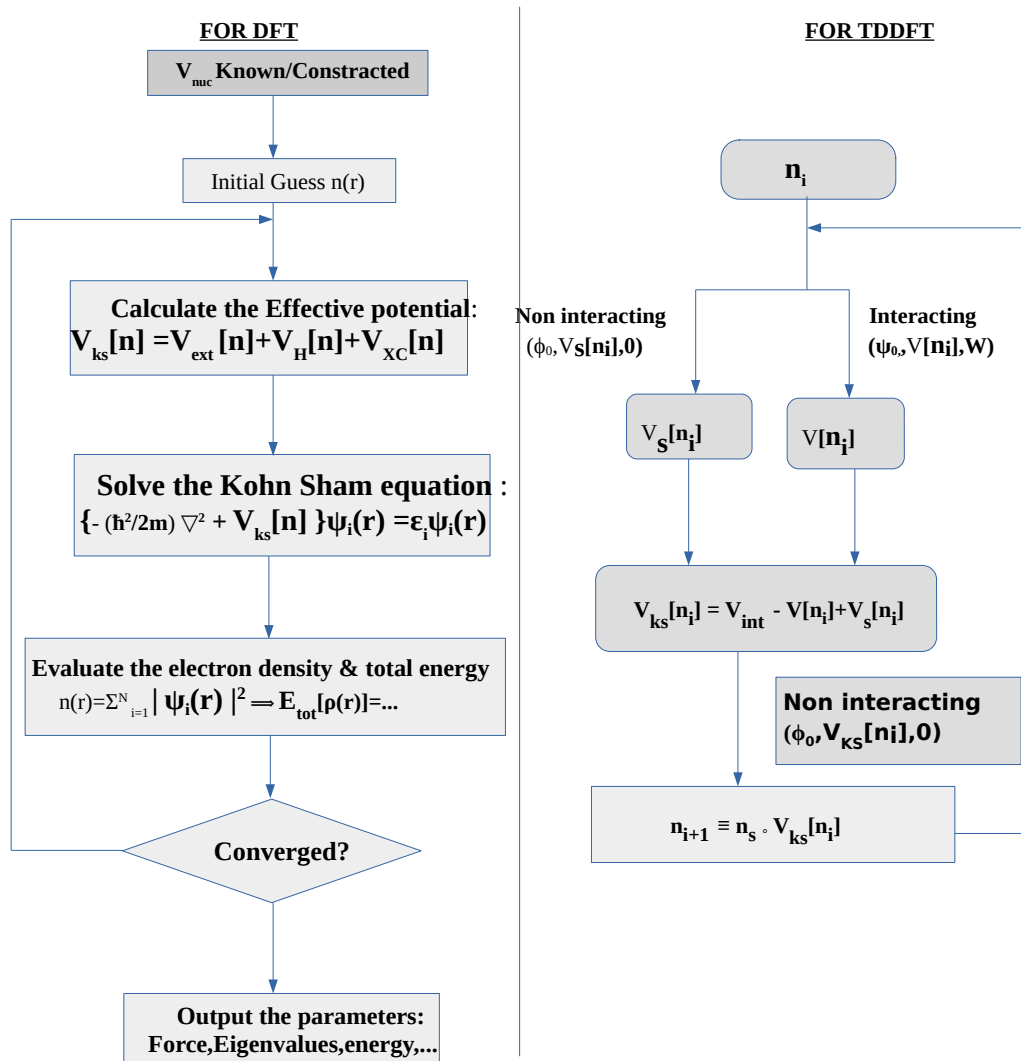
Contents

Figure 3.1: Flow chart scheme of SCF to iterate Kohn-Sham equations for a set of fixed nuclear (ionic) positions

4

Results and Discussions

4.1 Introduction

In this thesis DFT and TDDFT are applied for the investigation of the electronic, structural and optical properties of Silicon(Si) using Quantum espresso package. The plane wave self-consistent field (PWscf) code was implemented as our first principle energy code which uses ultra-soft pseudopotentials (US-PP) within density functional theory and the norm conserving pseudopotentials with in TDDFT. The main features of pseudising process is to eliminate the effects of rapid oscillations of the core electrons near the nuclei or to replace the strong coulomb potential with the weaker one. Thus the ultra-soft pseudopotentials with Perdew-Burke- Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange correlation functional were employed to calculate the electronic, structural and optical properties of silicon(Si). The convergence issue was checked in two ways. Firstly by varying cutoff energy from 20 Ry to 100 Ry for fixed Monk-Pack mesh grid (K-points) and lattice constants. Secondly, by varying K-point samplings (2 to 12) keeping cutoff energy and lattice parameters constant. The equilibrium lattice constant was calculated by fixing cutoff energy at 50 Ry and K-point at 6 x 6 x 6. Finally the band structure and density of states of silicon have been investigated based on DFT and the optical property is then investigated using the TDDFT.

4.1.1   Total minimum energy of Silicon per atom with respect to energy cutoff

The total minimum energy of Silicon per atom with respect to cutoff energy was calculated for fixed values of K-Points and lattice constant. The calculation was done using different energy cutoff values from 20 Ry to 100 Ry.

Table 4.1: The computed results of total minimum energy with respect to energy cutoff

Energy cutoffs(Ry)	Total energy(Ry)
20 Ry	-15.74127690 Ry
30 Ry	-15.74183109 Ry
40 Ry	-15.74189663 Ry
50 Ry	-15.74190667 Ry
60 Ry	-15.74191231 Ry
70 Ry	-15.74191618 Ry
80 Ry	-15.74191874 Ry
90 Ry	-15.74192006 Ry
100 Ry	-15.74192104 Ry

Convergence test of total minimum energy of Silicon per atom with respect to cutoff energy

The convergence test of the total minimum energy of Silicon with respect to the plane wave cutoff energy was investigated. An increment of energy cutoff for wave function is made until the convergence is achieved. The total minimum energy converged at 50 Ry plane wave cutoff energy and the total ground state energy had its minimum at -15.74190667 Ry. The calculated results show that the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function as shown in Fig.4.1. The accuracy of the ground state energy depends on the number of basis functions. We can realize that when the number of basis functions approaches infinity, energy is close to the ground state energy
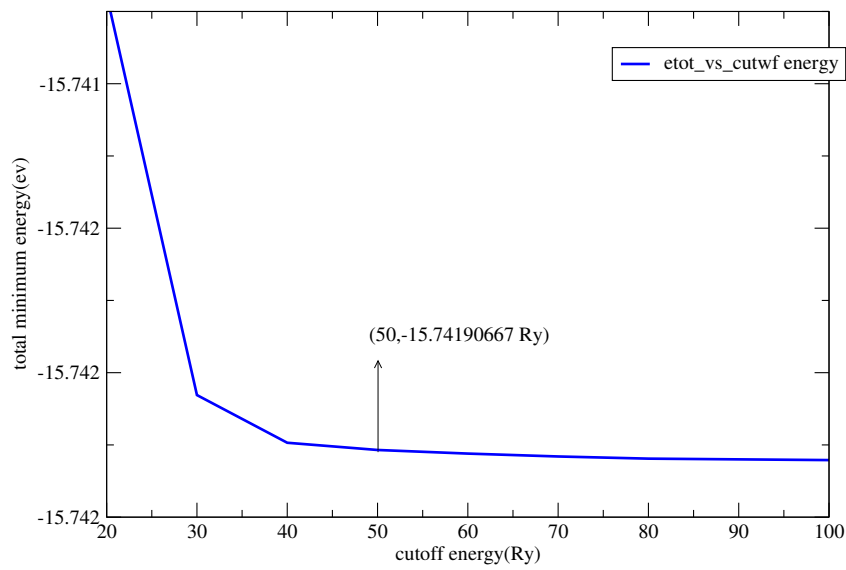
Figure 4.1: Total minimum energy of Silicon per atom with respect to energy cutoff

4.1.2 Total minimum energy of Silicon per atom with respect to K-point grids

In this case, the calculation was done using different k- point grids from 2 x 2 x 2 to 12 x 12 x 12 mesh grids. Here the other variables such as lattice constant and energy cutoff were kept fixed. The result is described in Table 4.2.

Table 4.2: The computed results of total minimum energy with respect to k-points sampling

K-points grid	Total energy(Ry)
2 x 2 x 2	-15.73041441 Ry
3 x 3 x 3	-15.74064271 Ry
4 x 4 x 4	-15.74172587 Ry
5 x 5 x 5	-15.74188015 Ry
6 x 6 x 6	-15.74190657 Ry
7 x 7 x 7	-15.74191153 Ry
8 x 8 x 8	-15.74191259 Ry
9 x 9 x 9	-15.74191282 Ry
10 x 10 x 10	-15.74191287 Ry
11 x 11 x 11	-15.74191287 Ry
12 x 12 x 12	-15.74191288 Ry

Convergence test of total minimum energy of Siliocon per atom with respect to K-points sampling

A convergence test of total energy for k-point sampling was performed on Silicon. The total energy of Silicon atom was calculated using various sets of k-points ranging from 2 x 2 x 2 to 12 x 12 x 12. In each of these cases the plane wave kinetic energy cutoff of 50 Ry was used. The total minimum energy of Silicon is calculated as a function of k-points grid size using PWscf code. For this calculations, the other variables (lattice constant,energy cutoff) are kept constant. Convergence of the total energy with respect to the discrete Brillouin zone sampling was achieved for 6 x 6 x 6 Monkhorst-Pack mesh grid. The total ground state energy has its minimum at -15.74190657 Ry as given in Fig.4.2

4.1.3 The equilibrium lattice constant of Silicon atom

In order to determine the optimal lattice constant (parameters) in thetrahedral crystal structure of Silicon, the total energy was optimized in function of the volume of the unit
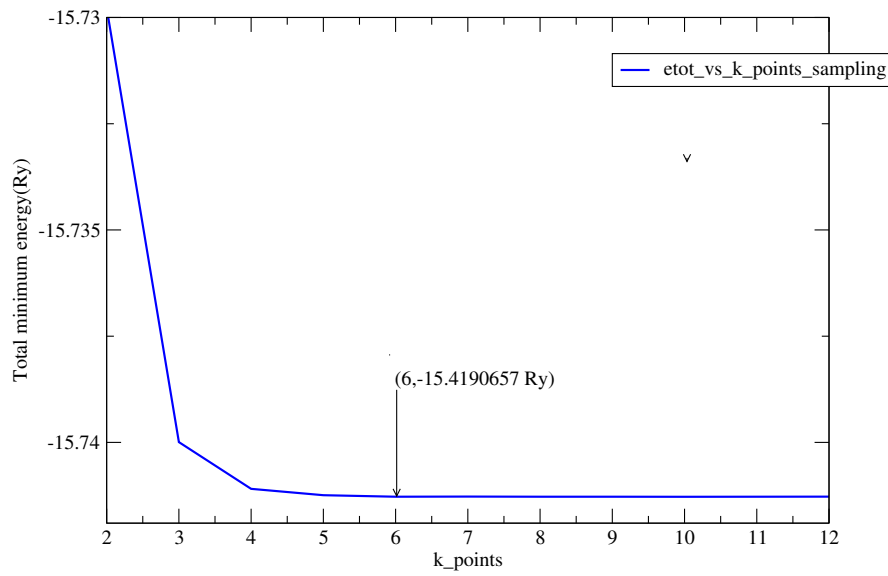
Figure 4.2: Total minimum energy of Silicon per atom with respect to k-point sampling

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cell. The calculation was performed for a series parameters. To carry out the calculation, a plane wave kinetic energy cutoff of 50 Ry and a Monkhorst-Pack grid of 6 x 6 x 6 were fixed and used.
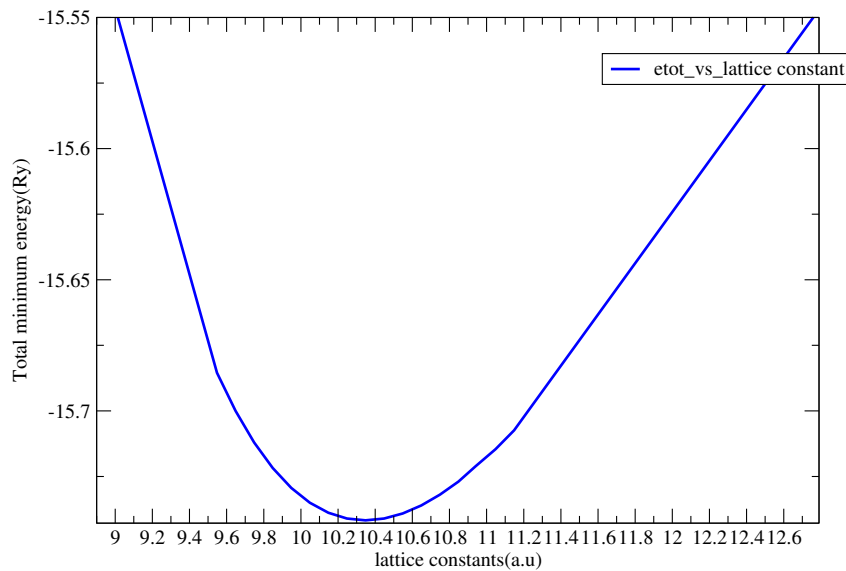
Figure 4.3: plot of total minimum energy of Silicon with respect to lattice constant

4.2   Band structure of Silicon

To find the band structure the k-points are generated along high symmetry points us-
ing k-point path with the help of xcrysden software. The energy band structure of bulk
Silicon is presented in figure 4.4. Energy gap between occupied and unoccupied energy
levels is among the ways that we can determine the difference between electrical prop-
erties of metals, semiconductors and insulators. The band gap has been calculated as
the difference between the energies for the minimum of the conduction band and the
maximum of the valence band. From the band structure of three dimensional Silicon,
we calculated the band gap energy which is 0.83 ev. The calculated result is closer to the
experimental value (1.12 eV). As the result of calculation shows that Silicon has an indi-
rect band gap which makes it an interesting material for application in optoelectronics.
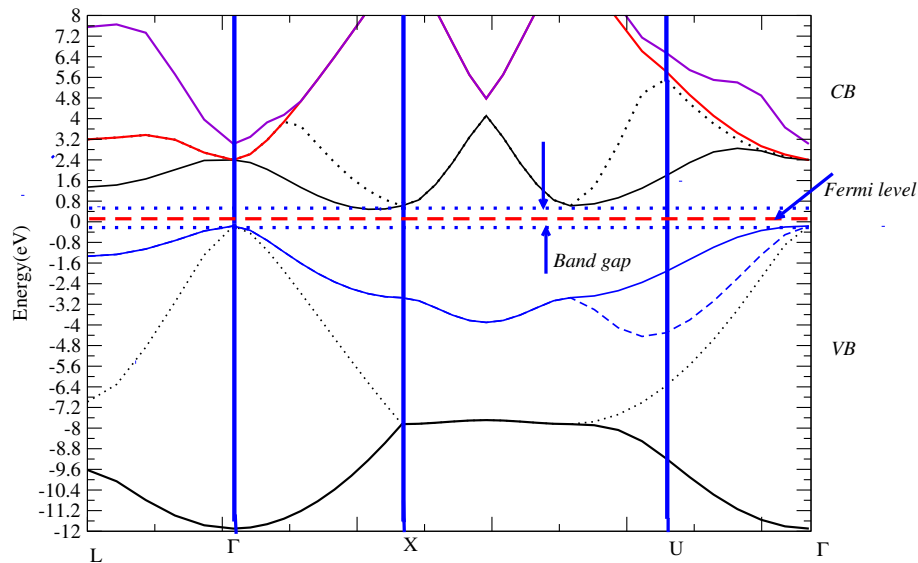
Figure 4.4: The band structure of silicon

4.3 Density of states of Silicon

As to our computation we see that the density of states of Silicon(DOS) is the investigation of its electronic transport properties. In figure 4.5, we see that before the Fermi level enters the conduction band, there is an insulating region. The Fermi level (E_f) was referenced at 0 eV. Determining the density of state of material is useful to classify materials as metal, semiconductor and insulator. If the density of states is continuous(different from zero) near the Fermi level(from conduction band to valence band) the material is metal. If there is discontinuity near the Fermi level either it is either a semi conductor or an insulator based on the band gap value. Here our calculation shows that silicon is an indirect band gap semi conductor.
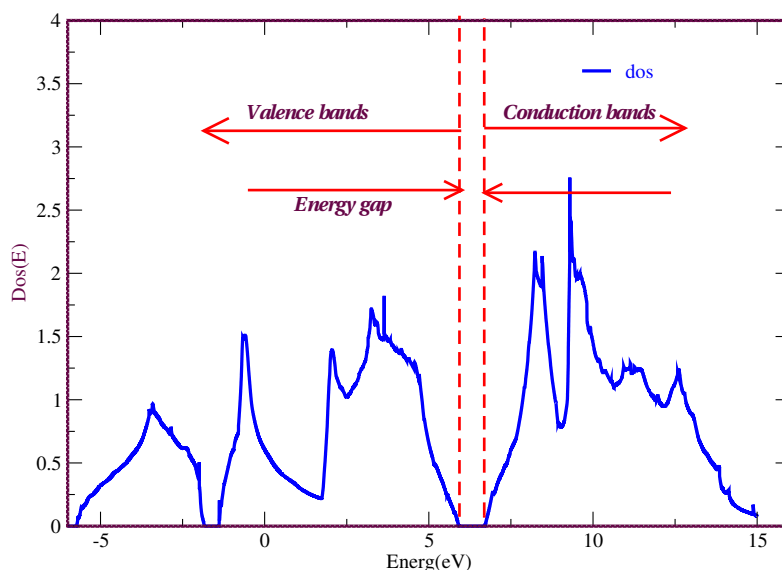
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Figure 4.5: The density of state of silicon

Table 4.3: Comparison of calculated properties of Silicon in this study to others

project	Reference	calculated value	Error in percent
Crystal constant (Fcc)	5.431Å [5]	5.475 Å or 10.263Bohr	4.4
Density gcm^{-3}	2.329 [5]	2.272	5
Band gap(eV)	1.12eV [5]	0.83	29

4.4 The real and imaginary parts of the dielectric function and the EELS of silicon

To find the real and imaginary part of the dielectric function of silicon, we have used the optimized turboEELS code which supports two levels of parallelization: i) a plane-wave parallelization, which is implemented by distributing real- and reciprocal-space grids across the processors, and ii) a k points parallelization, which is implemented by dividing all processors into pools, each taking care of one or more k points as a components of the Quantum ESPRESSO package. The real part of the dielectric function is related to the transimitance and the imaginary part of the dielectric function corresponds to the absorption. The absorption is related to the transition of neutral electron from valence

band to the conduction band according to the Fermi golden rule. However the electron energy loss function corresponds to the inelastic scattering of electrons. It is related to the plasmon excitation as illustrated in figure 4.6. Next,discussing the optical response of Silicon crystal structure; the imaginary and real parts of the dielectric function are illustrated in Figure 4.6 shown by legends Re(eps) and Im(eps). Our results show that the Im(eps) is the sum of all transitions from the valence bands (VBs) to the conduction bands (CBs).The maximum of Im(eps) for this structure is located at the energy 5.51eV, which is in the visible range of light for silicon.The absorption edge of this structure occurs at an energy of 1.01 eV that is related to the optical transition from the VB to the CB . In the Drude model,the plasma frequencies are defined by the roots of Re(eps) with the x = 0 line and for this system it is calculated to be 10.4 eV. Another root of Re(eps) with the x = 0 line for this system occurs at an energy of 15.59 eV which is related to the main plasma frequencies for the plasmon energy. It is clear that at these energies, the Re(eps) goes through zero. The electron energy loss spectroscopy EELS technique is useful in revealing plasma resonance phenomena as distinct from normal interband transitions. It is known that the sharp peaks in the energy-loss function are associated with plasma oscillations and consistent with the roots of Re(eps) with the x =0 line. It is obvious that the Silicon bulk system has one main peak in the EELS spectra which is associated with the plasma oscillations.
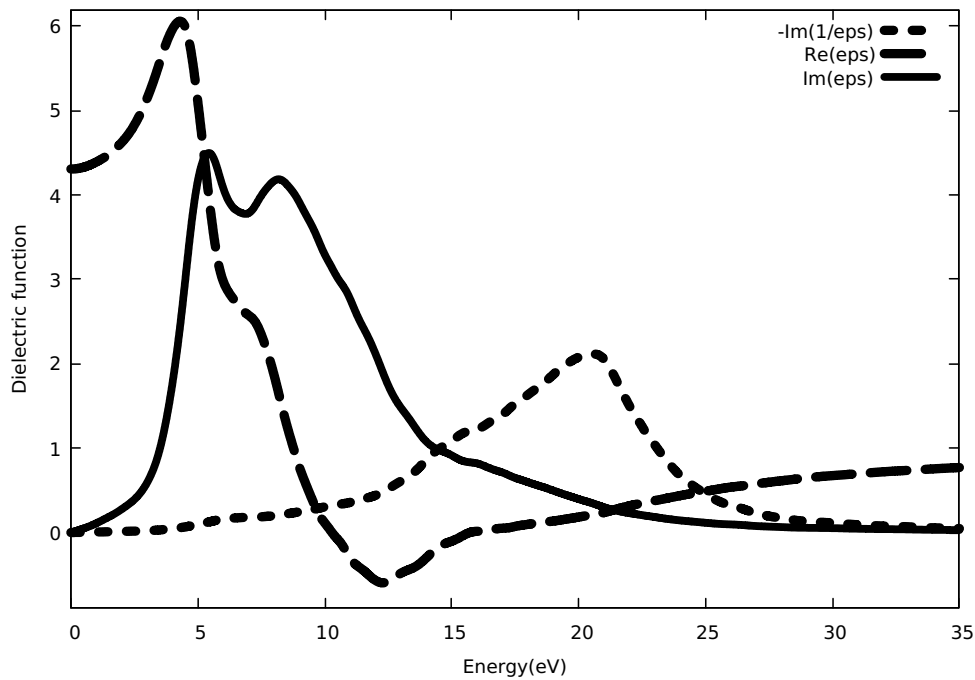
Figure 4.6: The real and imaginary parts of the dielectric function and The EELS

The electron energy loss function EELS for Silicon atom along the polarization is also plotted in Figure 4.6 which is indicated by -Im(1/eps). It is evident that this material possesses a strong absorption in the visible region of light.The main peak of the absorption spectrum along all directions occurs around 5.84 eV, which exhibits significant UV absorption for this atom and in the EELS spectra it is associated with the plasma oscillation for the plasmon energy.

5

conclusion

The density functional theory(DFT) and the time dependent density functional theory(TDDFT) were used to investigate the electronic, structural and optical properties of Silicon. The plane wave self-consistent field (PWSCF) and ultra-soft pseudopotentials with generalized gradient approximation (GGA) were implemented in Quantum Espresso package. All calculations have been carried out using Quantum Espresso package. The total minimum energy calculation was performed as a function of cutoff energy and k-point samplings. The total energy convergence test was achieved at the energy cutoff 50 Ry and at 6 x 6 x 6 k-point grid size. The total minimum energy of Silicon per atom is -15.74190667 Ry with respect to energy cutoff and -15.74190657 Ry with respect to k-point grid size. The computational results show that the total minimum energy per atom is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-point sampling.The optimal lattice constant of silicon was calculated using the above total energy convergence test by varying lattice parameter.From the result the equilibrium lattice constant is 5.475 Å. The obtained result is overestimated as compared to the experimental result 5.431 Å due to the approximate nature of the applied DFT. The band structure was determined by generating k-points along high symmetry points using K-point path with the help of xcrysden software. The computed values of band gap of Silicon is 0.83 eV. It shows the calculated result is in good agreement with experimental value(1.12 eV). The calculated band structure shows Silicon is an indirect band gap material. That is the valance band maximum and the conduction band minimum occurs at different position. The discontinuity of density of states from valance

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band maximum to the conduction band minimum near the Fermi level shows Silicon is semi conductor.Our results show that this material possesses strong absorption in the visible region of light, suggesting its potential for applications in optoelectronics, photovoltaics, and nano electronics.

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If failed, give reasons and indicate plans for re-examination.

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