Chapter 2

Computational Methodology

In the present thesis, we employ the density functional theory (DFT) \[122, 123\] and the time-dependent density functional theory (TDDFT) \[175\] based calculations to study the ground state and optical response properties of the nanostructures, respectively. In this chapter, we give a brief introduction to the basics of DFT and TDDFT based calculations.

It is well known that the physical and chemical properties of materials are determined by the behavior of electrons which glue the atoms together to form a variety of molecules and solids. These electrons interact among themselves and also with the nuclei of the constituent atoms present in the system. The electronic structure calculations based on quantum mechanical theory play an important role in understanding many physical and chemical properties of materials. In quantum mechanics, the ground state properties of many-particle systems, like molecules and solids containing electrons and nuclei, are described by the time-independent Schrödinger Equation

\[
\mathcal{H} |\Psi\rangle = E |\Psi\rangle
\]  

with the Hamiltonian ($\hat{H}$)

\[
\mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I=1}^{N_I} \nabla_i^2 I + \frac{1}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{e^2}{|r_i - r_j|} + \frac{1}{4\pi\epsilon_0} \sum_{I<J}^{N_I} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \frac{1}{4\pi\epsilon_0} \sum_{i,I}^{N,N_I} \frac{Z_I e^2}{|r_i - R_I|}
\]  

where

\( \hbar \) & \( \epsilon_0 \) - Planck’s constant and permittivity of vacuum.

\( r_i \) & \( R_I \) - positions of electrons and nuclei.

\( m_e \) & \( M_I \) - masses of electrons and nuclei.
$e$ & $Z_I e$ - charges of electrons and nuclei.

$N$ & $N_I$ - numbers of electrons and nuclei in the system.

Now onwards, we use atomic units in which the following fundamental constants - $\hbar$, $e$, $m_e$, and $\frac{1}{4\pi\epsilon_0}$ are taken as unity. In the above equation, the first two terms represent the kinetic energy operators for electrons and nuclei. The next two terms correspond to the repulsive potentials due to electron-electron and nucleus-nucleus interactions. The attractive interaction between the electrons and nuclei is described by the last term. Solving the many-body Schrödinger equation (2.1) associated with the full Hamiltonian (2.2) for any realistic system is a formidable task. It requires dealing with $3(N+N_I)$ degrees of freedom to obtain a desired solution. The complexity arises due to the electrostatic interaction terms which couple the degrees of freedom of the particles among themselves and also with those of others. As a result, one needs to look for reasonable approximations to simplify the complex situation. Fortunately, in many physical problems, we can decouple the nuclear and electronic degrees of freedom with the Born-Oppenhemier approximation\cite{176} and solely focus attention on the Schrödinger equation for the electrons.

### 2.1 Born-Oppenhemier Approximation

According to this approximation\cite{176}, the electrons move much faster than the nuclei since the mass of an electron is much smaller than that of a nucleus. Thus the motion of electrons can be treated as instantaneous with respect to the motion of the nuclei. Moreover, it is assumed that the electrons remain always in the same adiabatic state during the motion of nuclei. Hence, the degrees of freedom of these two particles can be considered to be decoupled. By using this approximation, one can neglect the kinetic energy of nuclei from the Hamiltonian. Furthermore, the positions of the nuclei can be treated as parameters and thus the nucleus-nucleus interaction term becomes constant for a fixed set of nuclei. Then, the Hamiltonian which governs the electronic structure of the matter can be represented as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}^{N,N_I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

(2.3)
Even after invoking the Born-Oppenheimer approximation, finding the solution of many-electron Schrödinger equation with this Hamiltonian (2.3) is still a difficult task. Again, the reason for the difficulty is due to the second term which couples the coordinates of electrons. This term prevents the reduction of a many-electron problem to an effective single-electron problem.

2.2 Solving Many-Electron Problems

2.2.1 Wave Function Based Methods

In order to solve the Schrödinger equation for a many-electron system, an independent particle approach was introduced by D. R. Hartree\cite{Hartree177} (called Hartree method) and then it was modified by V. Fock (called Hartree-Fock (HF) method)\cite{Fock178}.

Within the Hartree method, the electrons are considered as independent and they interact with each other only via a mean-field Coulomb potential. Thus, the many-body wave function $\Psi(r_1, r_2, \ldots, r_N)$ can be written as a product of single-particle orbitals $\phi_i(r)$

$$\Psi(r_1, r_2, \ldots, r_N) = \phi_1(r_1)\phi_2(r_2)\cdots\phi_N(r_N)$$

(2.4)

Minimization of the energy expectation value

$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

(2.5)

with the wave function in Eq. (2.4) and subject to the orthonormalization condition

$$\int \phi_i^*(r)\phi_j(r)\,dr = \delta_{ij}$$

(2.6)

leads to a single-electron-like Schrödinger equation,

$$\left( -\frac{\nabla^2}{2} + V_{\text{mean}}(r) \right) \phi_i(r) = \epsilon_{ij}\phi_i(r)$$

(2.7)
By an unitary transformation \( \phi_i = \sum_j^N U_{ij} \phi_j' \) (\( U_{ij} \) is unitary matrix i.e. \( U^\dagger U = I \)), we get

\[
\left( -\frac{\nabla^2}{2} + V_{\text{mean}}(r) \right) \phi_i'(r) = \epsilon_i \phi_i'(r)
\]

(2.8)

where \( V_{\text{mean}}(r) \) is the mean field potential in which the electron moves. This potential includes the following two terms. (a) The external potential due to the electron-nuclear interaction and (b) the Hartree potential due to classical electrostatic repulsion between the electrons

\[
V_H(r) = \frac{1}{2} \int dr' \frac{n(r')}{|r - r'|}
\]

(2.9)

It is to be noted that this term includes the spurious effect due to the self-interaction.

The electron density of a system can be written as a sum of squares of the single-particle orbitals

\[
n(r) = \sum_i^N |\phi_i'(r)|^2
\]

(2.10)

To solve Eq.(2.8), one should know the \( V_{\text{mean}}(r) \) which depends on \( n(r) \). However, the calculation of density requires the knowledge of single-particle orbitals \( \phi_i(r) \) - which are the solutions of the equation we intend to solve. Hence, the equation is solved self-consistently.

The major problem with the Hartree method is that the Hartree wave function does not satisfy one of the fundamental properties of many-body wave function for the Fermions i.e the anti-symmetry property. In the HF method, the anti-symmetry property is incorporated by forming a Slater determinant\[179\] of the single-particle orbitals

\[
\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \ldots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \ldots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \ldots & \phi_N(x_N) \end{vmatrix}
\]

(2.11)

where \( x_i \equiv (r_i, \sigma_i) \) includes spatial and spin-coordinates (\( \sigma_i \)). The above wave function
is normalized. Similar to the previous case, the minimization of the energy expectation value with the above wave function leads to the single-particle HF equation

\[
\left(-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r})\right) \phi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}) - \sum_j \delta_{\sigma_i, \sigma_j} \int d\mathbf{r}' \frac{\phi^*_j(\mathbf{r}')\phi^*_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})
\] (2.12)

In the above equation, the first two terms correspond to the kinetic energy and the external potential respectively. The third term is the Hartree potential due to classical Coulomb electrostatic repulsion between the electrons. The last term on the left-hand side is called the exchange term which arises due to the inclusion of the Pauli’s exclusion principle through the anti-symmetric wave function. This term adds considerable complexity in the Hartree-Fock equation due to its non-local character. Physically, because of the exclusion principle the electrons with same spin avoid each other and thus, a depleted region of the charge density in the immediate vicinity of a given electron is created which is called the exchange hole. The exchange energy is considered due to the interaction between the exchange hole and the electrons. Within the HF method, a definite meaning can be assigned to the eigen values of single-particle orbitals with the help of Koopman’s theorem. The theorem states that each eigen value gives the energy required to remove an electron from the corresponding single-electron state.

There are two major improvements in the HF method as compared to the Hartree method. First, it includes the anti-symmetry property of the many-body wave function and thus exactly takes into account of the contribution due to the exchange effect. Secondly, there is no self-interaction in HF method since the self-interaction contribution present in the Hartree potential is exactly equal and opposite to that in the exchange potential and thus they cancel each other. However, it is important to note that the complex many-body wave function can never be a single Slater determinant of single-particle orbitals or a simple combination of few determinants. Thus, the energy obtained from the HF method is always higher than the true value. The error in the calculations of the HF energy with respect to the true one is called the correlation energy which arises due to the many-body correlation between the electrons[180]. Later on, several Post-
Hartree-Fock methods were developed to include the effect of correlations\textsuperscript{181}. Some of these methods are (i) Configuration interaction (CI), (ii) Coupled cluster (CC) and (iii) Møller-Plesset perturbation theory (MP2, MP3, MP4, etc.). The performance of these methods is impressive and they are able to produce accurate results. However, the practical applicability of these methods is strongly restricted to a system of few atoms or molecules since these methods are computationally expensive due to an unfavorable scaling with the size of the system\textsuperscript{182}. For example, the scaling of computational time in CI method goes as $M^6$ for single and double excitations, and as $M^8$ and $M^{10}$ for triply and quadruple excitations, respectively, where $M$ is the size of the basis set used in the calculations. Similarly, the computational time in $n^{th}$ order Møller-Plesset perturbation theory scales as $M^{n+3}$. Thus, in order to carry out the electronic structure calculations for a wider range of materials, one requires an alternative theory which can handle much larger systems containing many electrons more efficiently.

### 2.2.2 Density Based Method - Density Functional Theory

Density functional theory is an alternative way to study the electronic structure of matter in which the ground state electron density of a system is used as a basic variable instead of a many-body wave function. Conceptually, it is easy to work with density rather than a many-body wave function since the former is a function of three variables in contrast to the $3N$ variables of the latter. This theory has become a widely popular tool for the electronic structure calculations of condensed matter. DFT has also become popular in quantum chemistry due to recent developments in the modern approximate functionals\textsuperscript{125}. The calculations based on DFT with these approximate functionals provide an useful balance between accuracy and computational cost. Thus, it allows us to perform calculations on much larger systems, which are not possible with wave function based \textit{ab initio} methods, while retaining much of their accuracy.

For the first time, a theory based on the ground state electronic density $n(r)$ was proposed by Thomas\textsuperscript{183} and Fermi\textsuperscript{184, 185} in 1927. In this theory, the kinetic energy functional is derived from non-interacting electrons in homogenous electron gas. However, this theory does not include the quantum effects such as exchange and correlation. The
theory is unable to predict the stability of the molecular systems since the total energy of a molecule is higher than its constituent atoms. Over the years, several attempts have been made to improve the Thomas-Fermi like density based approach by including better kinetic energy functional as well as the effect of exchange and correlation\cite{186–188}. However, the theory lacks formal justifications for using the ground state electronic density $n(r)$ as a basic variable.

**Foundations of DFT**

The theoretical foundation for the density functional theory was laid by P. Hohenberg and W. Kohn in 1964\cite{122}. The theory is based upon the following two theorems.

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

Since the Hamiltonian is thus completely determined with a constant shift in the energy, it follows that the many-body wave functions for all the states of the system are determined. Hence, all the properties of the system are functionals of density and they can be completely determined if the ground state particle density $n(r)$ is known.

**Theorem 2:** (Variational Principle) There exists an universal functional $F[n]$ for any valid 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 the total energy functional $E[n]$, and the density $n(r)$ that minimizes the functional is the exact ground state density.

The proofs of these theorems for the non-degenerate ground state are very simple. Let us assume that there are two different external potentials $V_{ext}(r)$ and $V'_{ext}(r)$ which differ by more than an additive constant and both give the same ground state density $n(r)$. For the external potential $V_{ext}(r)$, the Hamiltonian $\hat{H}$ has the ground state energy $E_0$ and ground state wave function $\Psi$. Similarly, $E'_0$ and $\Psi'$ are the ground state energy and ground state wave function corresponding to $H'$ with the external potential $V'_{ext}(r)$. The Hamiltonians for the above mentioned two systems are given by

$$\hat{H} = \hat{T} + \hat{W} + V_{ext}(r) \quad ; \quad \hat{H}' = \hat{T} + \hat{W} + V'_{ext}(r) \quad (2.13)$$
where \( \hat{T} \) and \( \hat{W} \) represent the kinetic energy and the electron-electron repulsive potential respectively. Since \( \Psi' \) is not the ground state wave function of \( \hat{H} \), it follows that

\[
E_0 = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle \quad (2.14)
\]

The inequality in the above equation is strictly valid due to the assumption that the system has non-degenerate ground state. One can re-write the last term in above equation as

\[
\langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H'} | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H'} | \Psi' \rangle \quad (2.15)
\]

\[
= E'_0 + \int d^3r \left[ V_{\text{ext}}(r) - V'_{\text{ext}}(r) \right] n(r) \quad (2.16)
\]

Substituting Eq.(2.16) in Eq.(2.14), we get

\[
E_0 < E'_0 + \int d^3r \left[ V_{\text{ext}}(r) - V'_{\text{ext}}(r) \right] n(r) \quad (2.17)
\]

One can estimate the expectation value of \( \hat{H'} \) with the wave function \( \Psi \) and we arrive at a similar result as above

\[
E'_0 < E_0 + \int d^3r \left[ V'_{\text{ext}}(r) - V_{\text{ext}}(r) \right] n(r) \quad (2.18)
\]

Now, adding Eq.(2.17) and Eq.(2.18) we get the following contradictory inequality

\[
E_0 + E'_0 < E'_0 + E_0 \quad (2.19)
\]

This proves the fact that there cannot be two different external potentials, differing by more than an additive constant, which yield the same ground state density. Thus, there should be a one-to-one correspondence between the external potential and the ground state density.
Universal Functional

The total energy functional of the system can be written as

\[ E[n] = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle + \int d^3r V_{\text{ext}}(r)n(r) \]  

(2.20)

\[ = F[n] + \int d^3r V_{\text{ext}}(r)n(r) \]  

(2.21)

where \( T[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle \) and \( W[n] = \langle \Psi[n] | \hat{W} | \Psi[n] \rangle \) are the kinetic and electron-electron interaction energy functionals respectively. The functional \( F[n] = T[n] + W[n] \) is called universal functional since it is independent of the external potential and consequently of the system. The ground state energy of a system can be obtained by minimizing the above energy functional. The ground state density is the one which minimizes the \( E[n] \) and hence satisfy the Euler-Lagrange equation

\[ \frac{\delta F[n]}{\delta n(r)} + V_{\text{ext}}(r) = \mu \]  

(2.22)

where \( \mu \) is the Lagrange multiplier associated with the constraint

\[ \int n(r) dr = N \]  

(2.23)

If we know the exact form of \( F[n] \), Eq.(2.22) can be solved exactly to obtain the ground state density and thus, the ground state energy. Unfortunately, the exact form of the universal functional is not known.

2.2.3 The Kohn-Sham Approach

In 1965, soon after the discovery of the DFT, a practical approach of utilizing DFT for performing the electronic structure calculations was proposed by Kohn and Sham (KS)\[123\]. This approach has made DFT the most widely used tool in computational material science. In this approach, KS has ingeniously mapped the problem of a complicated interacting system onto a problem of much easier-to-solve non-interacting system. They have considered a fictitious auxiliary non-interacting system, with an effective po-
tential $V_{ks}$, having the same density $n(r)$ as that of the original interacting system. The main idea behind the KS approach is that the universal functional is written in terms of the kinetic energy $T_s[n]$ of the fictitious auxiliary non-interacting system.

\[
= T_s[n] + (T[n] - T_s[n]) + E_H[n] + (W[n] - E_H[n]) \\
= T_s[n] + E_H[n] + E_{xc}
\]  

(2.24)

where $E_{xc}$ is the exchange-correlation functional

\[
E_{xc}[n(r)] = T[n] - T_s[n] + W[n] - E_H[n]
\]  

(2.25)

and $E_H[n]$ represents the Hartree energy due to the classical Coulomb interaction between the electrons. Though $T_s[n]$ is not the true kinetic energy of the system, it can be exactly determined by

\[
T_s[n] = -\sum_i^N \int \phi_i^*(r) \left( \frac{\nabla^2}{2} \right) \phi_i(r) dr
\]  

(2.26)

Then, the small error or difference between the kinetic energies of the original interacting and fictitious auxiliary non-interacting systems is clubbed into the $E_{xc}[n]$. However, we do not know the form of this functional and thus one needs to use an approximation for it.

The single-electron eigen states $\phi_i(r)$ corresponding to the auxiliary non-interacting system are obtained by solving the Kohn-Sham equation

\[
\left( -\frac{\nabla^2}{2} + V_{ks}[n(r)] \right) \phi_i(r) = \epsilon_i \phi_i(r)
\]  

(2.27)

and then the density of the system (interacting and non-interacting) can be written as sum of squares of the occupied orbitals

\[
n(r) = \sum_i^N |\phi_i(r)|^2
\]  

(2.28)
By incorporating the first Hohenberg-Kohn theorem, the Kohn-Sham potential \( V_{ks} \) of the fictitious system can be related to the external potential \( V_{ext} \) of the real system in the following manner since both these two potentials correspond to the same density.

\[
V_{ks}[n(r)] = V_{ext}[n(r)] + V_H[n(r)] + V_{xc}[n(r)]
\]  
(2.29)

where \( V_H[n(r)] = \frac{1}{2} \int \frac{n(r')}{|r - r'|} dr' \) and \( V_{xc}[n(r)] = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \)  
(2.30)

are the Hartree and the exchange-correlation potentials respectively.

The total energy of the system can be obtained from the solutions of the KS equation and it is given by

\[
E[\phi_i(r)] = \sum_i \int \phi_i^*(r) \left[ -\frac{\nabla^2}{2} \right] \phi_i(r) dr + \int V_{ext}(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} dr dr' + E_{xc}[n(r)] + E_{NN}
\]

where \( E_{NN} \) is the energy due to the interaction between the nuclei.

2.2.4 Exchange-Correlation Functional

Within the Kohn-Sham scheme, all the quantum mechanical effects are included in the exchange-correlation functional. However, the exact form for \( E_{xc} \) as a functional of density is not known. Though the DFT is exact in principle, it is required to use an approximation to the unknown \( E_{xc} \) functional for the practical applications. Till date, several approximations to the exchange-correlation functional have been proposed in the literature[123, 189–196].

Local Density Approximation

A simplest approximation to the exchange-correlation functional is the local density approximation (LDA) which is suggested by KS in their seminal paper. Within the LDA,
the exchange-correlation functional is written as

\[ E_{xc}[n(r)] = \int n(r) \, \epsilon_{homo}^{xc}(n, r) \, dr \] (2.32)

where the exchange-correlation energy density \( \epsilon_{xc}[n(r)] \) of a system at each point is replaced by the exchange-correlation energy density \( \epsilon_{homo}^{xc}(n, r) \) of a homogeneous electron gas with density at that point. In this sense, the functional is purely local. Within the DFT formalism, the exchange-correlation density \( \epsilon_{xc} \) can be divided into two contributions namely the exchange \( \epsilon_x \) and the correlation \( \epsilon_c \). The exact form of the exchange part for homogeneous gas is given by Dirac and it is called the Dirac exchange\[186\]. In case of correlation, the analytical form is available only for low and high density limits. However, highly accurate numerical quantum Monte-Carlo simulations of the homogeneous electron gas are available from the work of Ceperly and Alder\[197\]. Based on the results of this work, the analytical expressions for the correlation energy density have been obtained by using sophisticated interpolation schemes. The most widely used representation is VWN, developed by Vosko, Wilk, and Nusair\[189\] while the recent one has been given by Perdew and Wang\[190\].

The LDA can be extended to the spin polarized case which is called as the local spin density approximation (LSDA) in which the up and down spins are treated separately.

\[ E_{xc}[n^\uparrow(r), n^\downarrow(r)] = \int n(r) \, \epsilon_{homo}^{xc}(n^\uparrow(r), n^\downarrow(r)) \, dr \] (2.33)

The performance of LDA/LSDA is quite satisfactory. It is expected that it would provide good results for the homogeneous system like nearly-free-electron metal. However, it is found to give reasonably good results for the inhomogeneous systems like atoms and molecules as well. One of the reasons for the success is that it obeys the sum rules for the exchange and correlation holes. It typically underestimates the contribution of exchange energy and overestimates the contribution of correlation energy which result in cancellation of errors. This leads to unexpectedly good results for the \( E_{xc} \) values. However, there are some failures of LDA, namely it tends to overestimate the binding energy but underestimate atomic ground-state energies, ionization energies and bang gaps.
Generalized Gradient Approximation

After the LDA, a further improvement to the approximation of exchange-correlation energy leads to the generalized gradient approximation (GGA) in which the exchange-correlation energy density depends not only on the density of the electrons, but also on the gradient of the density ($|\nabla n^\uparrow(r)|, |\nabla n^\downarrow(r)|$). Thus, the GGA is expected to give better results for the inhomogeneous systems.

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

$$= \int n(r) \epsilon_{xc}^{homo} F_{xc}(n^\uparrow(r), n^\downarrow(r), |\nabla n^\uparrow(r)|, |\nabla n^\downarrow(r)|) \, dr \quad (2.34)$$

where $F_{xc}$ is a dimensionless quantity and it satisfies the sum rules. Numerous forms of the $F_{xc}$ have been proposed in the literature\[191, 195\]. In many systems, the GGA gives improved results for the binding energies and the bond lengths as compared to the LDA. For most of our calculations for the ground state properties, we use one of the most popular GGA forms given by Perdew-Burke-Ernzerhof (PBE)\[195\].

### 2.2.5 Solving the Kohn-Sham Equation

In practice, the Kohn-Sham equation is solved numerically by an iterative procedure which is called as the self-consistent field (SCF) method. The steps involved in the SCF calculations are given below. The flow chart of these steps is also given in Figure 2.1.

1. Choose the approximate geometric structure of a system
2. Make an initial guess for the electron density $n(r)$
3. Construct the Kohn-Sham potential based on this density
4. Solve the Kohn-Sham equation to obtain the Kohn-Sham orbitals and energies
5. Construct a new density using these orbitals
6. Check the self-consistency. If the difference between the total energy of the system in two consecutive cycles is smaller than the threshold value, the self-consistency is achieved. Otherwise, go to step 7
7. Obtain new density by mixing the densities of the present and previous cycles. Then go back to step 3
Figure 2.1: The flow chart of the steps involved in DFT calculations including geometry optimization.

The procedure will be continued until self-consistency is reached. These calculations have been performed for the initial geometry (with a set of fixed nuclei) and it may not
correspond to the correct geometric structure of the system. In order to obtain the correct geometric structure, we calculate the Hellmann-Feynman force on each of the atoms at the end of the SCF cycle. If the forces are more than the threshold value, new geometric structure is created by appropriately moving the corresponding atoms. Now, the above mentioned steps in the SCF calculations are followed for the new geometric structure. The outer geometry loop is continued until we obtain the optimized geometric structure of the given system. At the end of these calculations, we can obtain all the ground state properties of the system from the KS orbitals and energies.

To solve the Kohn-Sham equation, we use a few numerical codes. Here, we summarize some of the salient features of these codes which we have used in our calculations. Though all the below mentioned codes solve same KS equation, the practical implementations are different. The main differences arise due to (a) the type of basis sets used to expand the KS orbitals (plane waves vs atom-centered basis functions ) and (b) the way in which the interaction between the nucleus and electrons is treated (full-potential vs pseudopotential/projector augmented wave). For most of our electronic structure calculations based on the DFT, we use the PBE[195] XC potential.

**WIEN2k**

We have used WIEN2k package[198] to perform the all-electron DFT based electronic structure calculations for the periodic solids. It employs the full-potential linearized augmented plane-wave (FP-LAPW) and local-orbitals as basis set to solve the Kohn-Sham equation. In this method, the unit cell is divided into two regions, namely (i) non-overlapping atomic spheres and (ii) an interstitial region. Atomic orbitals and plane waves are used as basis sets in the regions (i) and (ii) respectively. This method is considered to be one of the most accurate schemes for band structure calculations. We also include the relativistic effects in our calculations. The SCF calculations are performed with the convergence criterion for the total energy to be less than 0.1 mRy. The structures are optimized by minimizing the Hellmann-Feynmann forces till the forces on individual atoms are small (below 5 mRy/a.u).
Vienna Ab initio Simulation Package (VASP)

Using VASP[199], we have performed the electronic structure calculations for periodic solids within the framework of the projector augmented wave (PAW) method. PAW method considerably reduces the number of plane wave required for the calculations. In this code, the convergence criteria for energy in SCF cycles is chosen to be $10^{-6}$ eV. All the structures are optimized by minimizing the forces on individual atoms with the criterion that the total force on each atom is below $10^{-2}$ eV/ Å.

Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA)

We have also used SIESTA package[200–202] for performing a fully self-consistent DFT calculation by solving the standard Kohn-Sham equations. The KS orbitals are expanded using a linear combination of pseudoatomic orbitals proposed by Sankey and Niklewski[203]. All our calculations have been carried out by using triple-zeta basis set with polarization function. The standard norm conserving Troullier-Martins pseudopotentials[204] have been utilized.

Amsterdam Density Functional (ADF)

We use the ADF package[205] to perform the ground state and response properties calculations for the finite non-periodic systems, within the framework of DFT / TDDFT. For ground state properties, we use the triple-$\xi$ Slater-type orbital (STO) basis set with two added polarization functions (TZ2P basis set of ADF basis set library[205]). We use the Mayer formalism[206] as implemented in the ADF package[205] for the calculations of bond order. For these calculations, the convergence criteria for the norm of energy gradient and energy were fixed at $10^{-4}$ atomic units (a.u.) and $10^{-6}$ a.u., respectively.

Super-cell Approach

Many of the above mentioned codes use periodic boundary conditions to simulate three-dimensional periodicity of the bulk solids. But, the low dimensional nanostructures either lack or possess periodicity along only one or two directions. In order to simulate these low-dimensional nanostructures using the periodic code, we use super cell approach in which
Figure 2.2: Unit and super cells of low dimensional nanostructures: graphene (a, b) - two-dimensional system with vacuum in one direction, carbon nanotube (c, d) - one-dimensional system with vacuum in two directions, and fullerene (e, f) - zero-dimensional system with vacuum in all the three directions.

an artificial unit cell is constructed with a large vacuum along the non-periodic directions.

The vacuum is provided along the non-periodic directions to avoid the interaction between the nanostructures in the adjacent unit cells. In case of two-dimensional planar structures (along x- & y- axes), a vacuum space is given along the direction (z-axis) perpendicular to the plane. Similarly, for one (along x-axis) and zero-dimensional structures, the vacuum space is given in two (along y- and z-axes) and all the three (along x-, y- and z-axes) non-periodic directions respectively. In Figure 2.2, we give examples for unit cells (first
column) and super cells (second column) of low-dimensional systems such as graphene (a, b), carbon nanotube (c, d) and fullerene (e, f).

2.3 Time Dependent Density Functional Theory

In this section, we briefly describe the basics of the time-dependent density functional theory (TDDFT) which has been employed to calculate the frequency dependent polarizability.

Foundations

Formal foundation of TDDFT is based on the Runge-Gross (RG) theorem (1984)\(^{175}\) and it is the time-dependent analogue of the Hohenberg-Kohn (HK) theorem (1964)\(^{122}\). The RG theorem shows that, for a given initial wavefunction, there is an unique mapping between the time-dependent external potential of a system and its time-dependent density. This implies that one can work with time-dependent density (3 variables) instead of the many-body wavefunction (3N variables). Hence, all the properties of a system can be determined from the knowledge of the density alone. Unlike in DFT, there is no general minimization principle in the time-dependent case. Consequently, the proof of the RG theorem is more involved than that of the HK theorem. It has been shown by many people, namely Ghosh, Deb, Bartolotti, Runge, Gross, Kohn and others\(^{207-214}\) that several important concepts in the ground state DFT can be extended to time-dependent case in a rigorous manner. Thus, the TDDFT can be used to calculate the dynamic response properties such as polarizability, hyper-polarizability, excited state energies, optical absorption spectra and strength of the van der Waals interaction.

The evolution of many-body wavefunction with time is given by the time-dependent Schrödinger equation

\[
\hat{H}(t)|\Psi(t)\rangle = i \frac{\partial}{\partial t} |\Psi(t)\rangle, \quad \text{with} \ |\Psi(t = 0)\rangle = |\Psi(0)\rangle.
\] (2.35)
and the Hamiltonian $\hat{H}(t)$ of a system is given by

$$\hat{H}(t) = \hat{T} + \hat{W} + \hat{V}_{\text{ext}}(t),$$

(2.36)

where $\hat{T}$, $\hat{W}$ and $\hat{V}_{\text{ext}}(t)$ are the kinetic energy, the electron-electron repulsive and time-dependent external potentials respectively. The time-dependent density can be obtained from the many-body wave function as

$$n(r, t) = N \int dr_2 \ldots \int dr_N |\Psi(r, r_2, \ldots, r_N, t)|^2$$

(2.37)

and it has the interpretation that $n(r, t) dr$ is the probability of finding an electron in a region $dr$ around $r$ at a time $t$. Then, the density is normalized to the total number of electrons

$$\int n(r, t) dr = N$$

(2.38)

### 2.3.1 Runge-Gross Theorem

The RG theorem states that two densities $n(r, t)$ and $n'(r, t)$ evolving from a common initial state $|\Psi(0)\rangle$ under the influence of two Taylor expandable external potentials $V_{\text{ext}}(r, t)$ and $V'_{\text{ext}}(r, t)$, respectively, will be different if the potentials differ by more than a purely time-dependent ($r$-independent) function

$$V_{\text{ext}}(r, t) - V'_{\text{ext}}(r, t) \neq c(t) \Rightarrow n(r, t) \neq n'(r, t)$$

(2.39)

Now, in this situation, there is a one-to-one correspondence between the time-dependent density and potential. In order to prove this theorem, let us first show that current densities corresponding to these potentials must differ. The current density can be written as

$$j(r, t) = N \int dr_2 \ldots \int dr_N \Im \left( \Psi(r, r_2, \ldots, r_N, t) \nabla \Psi^\dagger(r, r_2, \ldots, r_N, t) \right)$$

(2.40)

where $\Im$ denotes the imaginary part and the corresponding continuity equation for the
current density is given by

\[ \frac{\partial}{\partial t} n(r, t) + \nabla \cdot j(r, t) = 0 \]  

(2.41)

Since the Hamiltonians of the two systems considered here differ only in their one-body external potentials, the equation of motion for the difference in their current densities can be written in the following manner

At \( t = 0 \)

\[ \frac{\partial}{\partial t} \{ j(r, t) - j'(r, t) \}_t=0 = -i \langle \Psi(0) | \left[ j(r, 0), \{ \hat{H}(0) - \hat{H}')(0) \} \right] | \Psi(0) \rangle \]

\[ = -i \langle \Psi(0) | \left[ j(r, 0), \{ V_{\text{ext}}(r, 0) - V'_{\text{ext}}(r, 0) \} \right] | \Psi(0) \rangle \]

\[ = -n(r, 0) \nabla \left\{ V_{\text{ext}}(r, 0) - V'_{\text{ext}}(r, 0) \right\} \]  

(2.42)

where \( n(r, 0) \) is the initial density. It is seen from the above equation that if the two potentials differ (by more than just a constant) at the initial time, then the first derivative of the currents must be different. Similarly, we can also show that the higher order derivative of current densities will differ by

\[ \frac{\partial^{k+1}}{\partial t^{k+1}} \{ j(r, t) - j'(r, t) \}_t=0 = -n(r, 0) \nabla \frac{\partial^k}{\partial t^k} \left\{ V_{\text{ext}}(r, t) - V'_{\text{ext}}(r, t) \right\}_t=0 \]  

(2.43)

If the equation (2.39) is satisfied and the two external potentials are Taylor expandable about \( t = 0 \), then there must be some finite \( k \) for which the right hand side (RHS) of equation (2.42) does not vanish, so that

\[ j(r, t) \neq j'(r, t) \]  

(2.44)

Thus, the two Taylor-expandable potentials, different by more than just a trivial constant, give two different current densities. In other words, there must be a one-to-one correspondence between the current densities and external potentials.

Substituting the equation of continuity in (2.43), we get

\[ \frac{\partial^{k+2}}{\partial t^{k+2}} \{ n(r, t) - n'(r, t) \}_t=0 = -\nabla \cdot \left\{ n(r, 0) \nabla \frac{\partial^k}{\partial t^k} \left\{ V_{\text{ext}}(r, t) - V'_{\text{ext}}(r, t) \right\}_t=0 \right\} \]  

(2.45)
If the RHS of the above equation is non-zero for some value of \( k \), then the two densities will be different. In order to show that the RHS is non-vanishing, let us assume that

\[
\nabla \cdot [n(r,0)\nabla f(r,t)] = 0 \quad (2.46)
\]

where the function \( f(r) \) is defined as

\[
f(r) = \frac{\partial^k}{\partial t^k} \{V_{ext}(r,t) - V'_{ext}(r,t)\}_{t=0} \quad (2.47)
\]

Now, consider the following integral

\[
\int f(r,t)\nabla \cdot \{n(r,0)\nabla f(r,t)\} dr = \int n(r,0)f(r)\nabla f(r,t) \cdot dS - \int n(r,0)[\nabla f(r,t)]^2 dr \quad (2.48)
\]

We use the Green’s theorem to obtain the RHS of the above equation. The left-hand side of the above equation should be zero due to our initial assumption in Eq.(2.46). The first term on RHS with surface integral vanishes since both the density and potential decay to zero as \( r \to \infty \). Equality in the above equation requires that the second term should also go to zero. But, the second term on RHS will vanish only when density or \( \nabla f \) is zero. The first choice is obviously ruled out. The second possibility contradicts our assumption that the two potentials differ by more than a time-dependent constant. Hence, there exists a one-to-one correspondence between the time-dependent density and the time-dependent potential. In other words, any two potentials which differ by more than a time-dependent constant will always give two different densities and vice versa. This completes the proof of the RG theorem.

### 2.3.2 Time Dependent Kohn-Sham Equation

Consider a fictitious non-interacting Kohn-Sham system with a potential \( V_{ks}(r,t) \) having a time-dependent density \( n(r,t) \). Then the time-dependent Kohn-Sham (TDKS) equation is given by

\[
i\frac{\partial}{\partial t} \phi(r,t) = \left[ -\frac{\nabla^2}{2} + V_{ks}[n](r,t) \right] \phi(r,t) \quad (2.49)
\]
where the time-dependent density is defined as

\[ n(r, t) = \sum_{i=1}^{N} |\phi_i(r, t)|^2 \]  \hspace{1cm} (2.50)

The \( V_{ks}(r, t) \) and the initial condition are chosen such that the time-dependent density of non-interacting system is equal to that of a real interacting system with a time-dependent potential \( V_{ext} \). Now, by virtue of the one-to-one correspondence proven in the previous subsection, the potential \( V_{ks}(r, t) \) can be written as

\[ V_{ks}(r, t) = V_{ext}(r, t) + V_H(r, t) + V_{xc}(r, t) \]  \hspace{1cm} (2.51)

where \( V_H \) and \( V_{xc}(r, t) \) are the time-dependent Hartree and exchange-correlation potentials respectively. To solve the above TDKS equation, one requires a knowledge of the \( V_{xc}(r, t) \). Unfortunately, the exact form of the function is not known and hence in practice we need to use an approximation for it.

### 2.3.3 Linear Response Theory and Adiabatic Local Density Approximation

When the strength of perturbing potential is weak, we can employ the linear response theory using perturbation theory to study the dynamic response properties of a system. We assume here that the initial state of the system is non-degenerate ground state and then we can expand the density \( n(r, t) \) close to the initial state as

\[ n(r, t) = n^{GS}(r, t) + \delta n(r, t) \]  \hspace{1cm} (2.52)

where \( \delta n(r, t) \) is the first order change in the ground state density due to a small change in the external potential,

\[ \delta n(r, t) = \int dt' \int dr' \chi[n^{GS}](r, r', t - t') \delta V_{ext}(r', t') \]  \hspace{1cm} (2.53)
In the above equation, the $\chi$ represents the susceptibility of the system which tells us how the density of the system changes at a point $\mathbf{r}$ and time $t$ due to the change in the external potential at an arbitrary point $\mathbf{r}'$ and at time $t'$. Here, $t > t'$. Similarly, the response of density due to a small change in the KS potential is determined by $\chi_{KS}$. It is to be noted that the susceptibility of a real interacting system $\chi$ is different from that of a fictitious non-interacting system. However, both these susceptibilities should yield same response to the density.

\[
\delta n(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi_{KS}[n^{GS}] (\mathbf{r}, \mathbf{r}', t - t') \delta V_{KS}(\mathbf{r}', t')
= \int dt' \int d\mathbf{r}' \chi_{KS}[n^{GS}] (\mathbf{r}, \mathbf{r}', t - t') \{ \delta V_{ext}(\mathbf{r}', t') + \delta V_{H}(\mathbf{r}', t') + \delta V_{xc}(\mathbf{r}', t') \}
\] (2.54)

Taking Fourier transform of Eq. (2.53) and (2.54), and then comparing these two equations, we get

\[
\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_{KS}(\mathbf{r}, \mathbf{r}_1, \omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right\} \chi(\mathbf{r}_2, \mathbf{r}', \omega)
\] (2.55)

where $f_{xc}$ is called the exchange-correlation kernel and it is given by

\[
f_{xc}[n](\mathbf{r}, \mathbf{r}', t - t') = \frac{\partial V_{xc}[n]}{\partial n(\mathbf{r}, t)}
\] (2.56)

The expression (2.55) is central equation in the linear response theory within the TDDFT. This is a Dyson-like equation. The $\chi(\mathbf{r}, \mathbf{r}', \omega)$ has poles at the excitation energies of the system and the strengths of the poles are related to the intensity of optical absorption.

The susceptibility of the KS system can be written in terms of the ground state KS eigen functions and eigen values

\[
\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) = 2 \lim_{\eta \to 0^+} \sum_i \sum_{\alpha} \left\{ \frac{\phi_i(\mathbf{r}, t)\phi_{\alpha}(\mathbf{r}, t)\phi^*_i(\mathbf{r}', t')\phi^*_\alpha(\mathbf{r}', t')}{\omega - \omega_{i\alpha} + i\eta} + \frac{\phi_i(\mathbf{r}, t)\phi_{\alpha}(\mathbf{r}, t)\phi^*_i(\mathbf{r}', t')\phi^*_\alpha(\mathbf{r}', t')}{\omega + \omega_{i\alpha} - i\eta} \right\}
\] (2.57)
where $\phi_i(r, t)$ and $\omega_i$ are the eigen functions and the corresponding eigen values of the KS states. The suffixes $i$ and $a$ represent the occupied and unoccupied KS states respectively.

It is clear from the equations (2.55) and (2.57) that the TDDFT based response property calculations require approximation for the XC functional at two levels. The first one is the static XC potential required to calculate the ground-state Kohn-Sham (KS) orbitals and orbital energies. The second approximation is needed to represent the XC kernel $f_{xc}(r, r', \omega)$.

The exact exchange-correlation potential depends on the entire history of the density, as well as the initial wave functions of both the interacting and the Kohn-Sham systems. However, the dependence of initial wave functions can be lifted if we start from a non-degenerate ground state (in both interacting and non-interacting systems) where the initial wave functions themselves are functionals of the initial density. Still, $V_{xc}(r, t)$ has a functional dependence not just on $n(r, t)$ but on $n(r', t')$ at an arbitrary point $r'$ in space and $t > 0$. Thus this potential is non-local in both space and time. In other words, this potential remembers all the densities in past, and hence it has memory. Therefore, the $V_{xc}$ in TDDFT is much more complex than that in DFT.

**Adiabatic Local Density Approximation**

A widely used approximation for the XC kernel $f_{xc}$ is the adiabatic local density approximation (ALDA). In this approximation, the functional derivative of the $V_{xc}$ is taken as static i.e XC kernel $f_{xc}$ is frequency independent. Thus, the adiabatic approximation ignores the dependence of density in the past and the $V_{xc}$ depends only on the instantaneous density.

$$ V_{xc}^{ALDA}[n](r, t) = V_{xc}[n(r)] $$ (2.58)

Thus, the above functional is local in time. For the exchange-correlation kernel, the $V_{xc}[n](r)$ of the homogeneous electron gas is used

$$ f_{xc}^{ALDA}(r, r', t) = \frac{\partial V_{xc}^{LDA}[n(r), r]}{\partial n(r')} \delta(t - t') $$ (2.59)
This approximation is expected to perform better for slowly changing potentials. Now, it is being regularly used to study several optical response properties of the finite systems and the results obtained from these calculations are quite satisfactory \cite{215, 216}.

### 2.3.4 Response Property Calculations

In this thesis, we study the optical response properties such as static electric dipole polarizability and strength (through $C_6$ coefficient) of the van der Waals interaction of nanostructures (non-periodic systems) by employing TDDFT based calculations. The average dipole polarizability ($\bar{\alpha}$) and its anisotropy ($\Delta \alpha$) can be expressed in terms of second-rank polarizability tensor ($\alpha$).

\[ \bar{\alpha}(\omega) = \frac{\alpha_{xx}(\omega) + \alpha_{yy}(\omega) + \alpha_{zz}(\omega)}{3} \]  
\[ |\Delta \alpha| = \left[ \frac{3 \text{ Tr} \alpha^2 - (\text{Tr} \alpha)^2}{2} \right]^{\frac{1}{2}} \]

The strength ($C_6$) of attractive van der Waals interaction between two neutral systems (A and B) is obtained via Casimir-Polder expression\cite{217} which relates $C_6$ with the dynamic polarizability of the interacting systems evaluated at imaginary frequency.

\[ C_6 = \frac{3}{\pi} \int_0^{\infty} \tilde{\alpha}^A(i\omega) \tilde{\alpha}^B(i\omega) \ d\omega \]

where $\tilde{\alpha}^A(\omega)$ and $\tilde{\alpha}^B(\omega)$ are the isotropic average dynamic polarizability of the systems A and B respectively. For the calculations of polarizability of nanostructures, we use the RESPONSE module\cite{218} available in the ADF package. This module employs the linear response theory of many-body systems and uses exact analytical expressions for polarizability in terms of the moment of the first-order induced density. For the calculations of the Kohn-Sham orbitals and energies, we use several approximate exchange-correlation functionals, ranging from simple local density approximation to asymptotically correct model potential - statistical average of orbital potential (SAOP)\cite{219, 220}. For the XC kernel $f_{xc}$, we use the above mentioned adiabatic local density approximation (ALDA).
For these response property calculations, we use one of the largest basis sets, namely, the all electron even tempered basis set ET-QZ3P-2DIFFUSE (ET) with two sets of diffuse functions as available in the ADF basis set library [205].

In this chapter, we have briefly discussed the basics of the DFT and TDDFT which we have employed in the electronic structure calculations to study several ground state and optical response properties of the nanostructures. The results of these investigations will be discussed in the following chapters. In Chapter 3, we start our discussion on the properties of two-dimensional graphene-like honeycomb structure made up of silicon atoms.