A MOLECULAR MODELING METHODS

A.1 Introduction

Modeling has gained significant importance in basic and applied sciences research. In the past, the term ‘model’ was thought as a prototype, made of different shapes of plastic/metal/wooden objects, of some complex molecule or of a structure. However, in today’s scientific research, it implies a set of mathematical equations that are capable of describing a phenomenon/system under investigation. Most of the models are so complex that an analytical solution is essentially impossible. Hence, numerical methods are used to obtain the solution and the iterative nature of these methods makes them convenient to be used on computers. A computational model can be of a small system like a molecule, a crystal lattice or a polymer chain, or can be of a macroscopic system like a liquid solution or a reactor and can be of any phenomenon, may it be a chemical reaction, a phase transition/separation, adsorption or a mechanical failure. In any computational modeling effort, a balance between simplicity and accuracy and that between the system size and the phenomenon under investigation need to be sought. For example, a model investigating the reaction pathway between two molecules may need to and can explicitly take into account the sub-atomic particles of the system, but a model investigating a hydrodynamic failure may not need to go to that a small length scale and can treat the system (made up of infinite number of small atoms and molecules) as one continuous medium. Multiscale computational modeling combines the modeling approaches at these different length scales in two different ways. (i) Material properties calculated using atomic level modeling are used as input parameters for
the higher length scales modeling. (ii) An area of interest in the system that needs more accurate treatment is modelled at an atomic level and the rest of the system is treated as one continuous medium. Figure A.1 shows the computational modeling approaches at different length scales. It has to be noted that with increasing precision and decreasing length scale, the time scale of the modeling methods also decreases.

**A.2 Molecular Modeling methods**

Matter is composed of molecules and molecules can be thought of as composed of individual atoms or of positively charged nuclei and negatively charged electrons. Different molecules contain different atoms (or same atoms in different spatial positions) or they contain different nuclei and different number of electrons (or same nuclei and same number of electrons in different spatial positions). These two different ways of looking at molecules give rise to the two most popular molecular modeling methods. The former is called as Force Field Method or Molecular Mechanics and the later is called as Electronic Structure Calculation or First–principles or *Ab initio* Method. In molecular mechanics, an individual atom is treated as the basic particle and the potential energy is calculated as a parametric function of the atomic coordinates. The dynamics of the atoms in molecular mechanics is modelled by classical Newton’s laws of motion.
However, in electronic structure calculation methods, the positively charged nuclei and the negatively charged electrons are the fundamental particles and the interaction between these charged particles give rise to the potential energy. The following subsections describe the technical details of molecular mechanics and electronic structure calculations.

**A.2.1 Molecular Mechanics**

Force field calculations are called as molecular mechanics since molecules in force fields calculations are described using a ‘ball and spring’ type of model where the atoms are the “balls” of different sizes and the bonds are the “springs” of different lengths and stiffness. The non-bonded interactions like the van der Waals interaction and the
electrostatic interaction are also taken into account in the force field calculations.

Figure A.2: An illustration of energy terms in molecular mechanics (Adapted from Frank Jensen 7).

The energy in force field calculations is given by a sum of different terms, where each term contributes for the specific type of deformation in the species, as given in the following equation.

\[
E_{MM} = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{torsion}} + E_{vdW} + E_{\text{electrostatic}} \tag{A.1}
\]

where \( E_{\text{stretch}} \) is the energy for stretching a bond between two atoms, \( E_{\text{bend}} \) is the energy for bending an angle formed by three bonded atoms, \( E_{\text{torsion}} \) is the energy for twisting around a bond and \( E_{vdW} \) and \( E_{\text{electrostatic}} \) are the energies accounting for van der Waals interaction and electrostatic interaction between two atoms. Figure A.2 shows a graphical illustration of the basic terms involved in calculating force field energy. Since the energy is a function of atomic coordinates, the minimum in the energy corresponding to the most stable configuration can be calculated by minimizing \( E_{MM} \) as a function of atomic coordinates.

The stretching energy between two bonded atoms 1 and 2, when written as a Taylor expansion at the equilibrium bond length, is given as 7
\[ E_{\text{stretch}}^{12} = E_0 + \frac{dE}{dl} \bigg|_{l_0^0} \left( l_{12}^2 - l_0^0 \right) + \frac{1}{2!} \frac{d^2E}{dl^2} \bigg|_{l_0^0} \left( l_{12}^2 - l_0^0 \right)^2 + \ldots \]  
\[ (A.2) \]

The first derivative at \( l_0^0 \) is zero and \( E_0 \) is usually set zero since it is a zero point in the energy scale. Hence, equation (A.2) can be written as

\[ E_{\text{stretch}}^{12} = \frac{1}{2!} \frac{d^2E}{dl^2} \bigg|_{l_0^0} \left( l_{12}^2 - l_0^0 \right)^2 = K_{\text{stretch}} \left( l_{12}^2 - l_0^0 \right)^2 \]  
\[ (A.3) \]

where \( K_{\text{stretch}} \) is the force constant. Equation (A.3) is in the form of a harmonic oscillator. A similar expression for an angle bending is given as

\[ E_{\text{bend}}^{123} = K_{\text{bend}} \left( \theta_{123}^0 - \theta_0^0 \right)^2 \]  
\[ (A.4) \]

The harmonic form for stretching and bending, though simple, may not always be sufficient. In such cases the functional form is extended to include higher order terms or instead of using a Taylor series expansion, a Morse potential type function is used which is given below.

\[ E_{\text{Morse}}^{12} = E_{\text{diss}} \left( 1 - e^{-\alpha \left| l_{12}^2 - l_0^0 \right|} \right) \]  
\[ (A.5) \]

where \( E_{\text{diss}} \) is the dissociation energy and \( \alpha \) is related to the force constant.

Torsion energy associated with the twisting around bond 2-3, in a four atom sequence 1-2-3-4 where 1-2, 2-3, and 3-4 are bonded atoms, is physically different from the bending and stretching energy because (i) the rotation along the bond can have contributions from bonded and non-bonded interactions and (ii) the torsion energy has to be periodic, since after rotating along the bond for 360°, the energy should return to the same value. To take into account the periodicity, the torsion energy is usually given as

\[ E_{\text{torsion}}^{1234} = K_{\text{torsion}} \left( 1 - \cos(n\omega) \right) \]  
\[ (A.6) \]

where \( K_{\text{torsion}} \) is the constant, \( \omega \) is angle of rotation and \( n \) determines the periodicity.
The van der Waals energy, due to the repulsion and attraction between the two non-bonded atoms, is usually given in the form of the popular Lennard-Jones potential as follows

\[ E_{vdW}^{12} = 4E_{min}^{L-J} \left( \left( \frac{R^0}{R^{12}} \right)^{12} - \left( \frac{R^0}{R^{12}} \right)^6 \right) \]  \hspace{1cm} (A.7)

where \( E_{min}^{L-J} \) is the depth of the minimum in the potential and \( R^0 \) is the distance at which the potential is zero. The electrostatic energy between two atoms is usually given by the Coulomb potential as

\[ E_{\text{electrostatic}}^{12} = \frac{Q_1 Q_2}{\varepsilon_{\text{dielec}} R^{12}} \]  \hspace{1cm} (A.8)

where \( Q_1 \) and \( Q_2 \) are the atomic charges and \( \varepsilon_{\text{dielec}} \) is the dielectric constant.

Assigning numerical values to different parameters in the above described functions is also equally important in force field calculations. Parameterization of the force field is usually done by reproducing the structure, relative energies, vibrational spectra obtained from the electronic structure calculation data and the experimental data. However, it is also required that the parameters which are fitted in any force field are transferable amongst different molecules and environments. A compromise between accuracy and generality needs to be sought. Different force fields have been developed over the years and some of the main differences in these force fields are the functional forms of the energy terms, the number of additional energy terms (other than the basic ones described above) and the information used to fit the parameters in the force field. Force fields containing simple functional forms, as described above, are often called as “Harmonic” or “Class I” type Force fields and those containing more complicated functional forms, additional terms and sometimes heavily parameterized using electronic structure
calculation methods are called as “Class II” type. Depending upon these factors, there are different force fields for different types of molecules and Table A.1 lists a few of them.

Table A.1: A list of few common force fields in molecular modeling.

<table>
<thead>
<tr>
<th>Force Field</th>
<th>Developers</th>
<th>Systems</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM2, MM3,</td>
<td>Prof. Norman</td>
<td>Organics/General Hydrocarbons</td>
<td>II</td>
</tr>
<tr>
<td>MM4</td>
<td>Allinger</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AMBER</td>
<td>Prof. Peter Kollman</td>
<td>General</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organics/Proteins</td>
<td></td>
</tr>
<tr>
<td>UFF</td>
<td>Prof. William Goddard</td>
<td>General</td>
<td>Between I and II</td>
</tr>
<tr>
<td>CHARMM</td>
<td>Prof. Martin Karplus</td>
<td>Proteins</td>
<td>I</td>
</tr>
<tr>
<td>GROMOS</td>
<td>University of Groningen and ETH Zurich</td>
<td>Proteins, Nucleic Acids and Carbohydrates</td>
<td>I</td>
</tr>
<tr>
<td>CFF, TRIPOS</td>
<td>Commercial</td>
<td>General</td>
<td>II</td>
</tr>
</tbody>
</table>

Force field methods are very widely used in computational modeling community and their ability to provide an understanding of atomic and molecular motions in different (and large) systems and phenomena, at a modest computational cost, has contributed greatly to the scientific research in last two decades. These methods are very popular in investigating systems containing small organic molecules, large biomolecules like proteins and DNA, polymers etc. They are also several orders of magnitude faster than the electronic structure calculation methods. However, there also certain limitations associated with the force field/molecular mechanics methods. They are as follows:
1) Out-of-ordinary/Unusual situation: Force field methods are based on various approximate functional forms and their parameters. Since the parameters are determined using experimental data, these methods are empirical. Force field methods perform extremely well when a lot of information about the system under investigation already exists in the force field. For molecules that are “exotic” or a little “unusual” and for which there is little information known, the force field methods may perform poorly. To summarize, the interpolative force field methods may lead to serious errors when used for extrapolation.

2) Diverse types of molecules: Parameterization of a force field needs a balance between generality and accuracy. The generality/transferability of a force field can be improved by including diverse types of molecules in the parameterization process but with a given functional form of the energy terms, including additional data may not help. On the other hand, changing the functional form or using additional terms, may remove the cancellation of the error effect in the simpler forms. Most of the force fields are restricted for specific types of molecules.

3) Chemical reactions: While performing force field calculations, the input consists of (i) types of atoms, (ii) interactions between those atoms (bonded or non-bonded) and (iii) the geometry. The first two factors are crucial in assigning an appropriate functional form to each interaction in the system. The force field calculations are appropriate when the type of every atom and its types of interactions do not change with changes in atomic coordinates. However, during the course of a chemical reaction, covalent bonds are formed and are broken. Hence, a chemical reaction leads to different energy functions in reactants and products for the same atom. The electronic structure of the system also changes significantly thereby changing the type of an atom (e.g. a carbon that was sp³ before the
reaction may become \(sp^2\) or \(sp\) after the reaction and vice-versa). These two factors in a chemical reaction change the fundamental information on which the force field energy was calculated and thus the energy will not remain smooth and continuous during the chemical reaction. Hence force field calculations fail to model a system in which chemical reactions occur. The harmonic description of the stretching energy would make it impossible to find parameter values describing the dissociation of a molecule.

4) Metal systems: Force field methods are believed to be difficult, if not impossible, to apply to metal compounds and complexes and especially to transition metal systems. The bonding in metals is much different than in organic systems. In the case of metal-ligand complexes, the metal forms a coordinate bond with the complex while in pure metallic systems, the bonding may vary with the size of the metal cluster. Since electronic effects can not be taken into account explicitly in force field calculations, they need to be taken into account implicitly. The key reasons for less successful implementation of force field methods to model metal (including transition metals) complexes and compounds are as follows:

- Varied coordination numbers and geometries: In metal-complexes, (organic or inorganic) coordination number of a metal is the number of atoms in the ligand to which the metal is bound and in case of metal clusters, it is defined as the number of nearest neighbour atoms. Transition metals may exhibit coordination numbers ranging from 1 to 12. There are also more than one ways to organize ligand atoms around the central metal species, giving rise to isomerism. In case of pure metal clusters, multiple structures, very close in energy, are present. The geometry may also differ significantly depending upon the physical state of the system (solid phase/solution/gas phase). Unlike organic compounds, metal
coordinated compounds possess a much wider structural flexibility and hence a variety of structural motifs are observed.\textsuperscript{22-24} This leads to difficulty in defining the energy functional forms to describe them. Force field methods are successfully applied to quite a few specific systems \textsuperscript{20,21,25-27} and a few generalized approaches\textsuperscript{28-30} have also been developed to tackle the problem.\textsuperscript{23,31} However, whenever force field methods need to be applied to a new system, very frequently a significant modification is required to be performed and the predictive power still remains questionable.\textsuperscript{9,14}

- Varied oxidation states and electronic structures: Another problem in using force field methods is that transition metals exhibit multiple oxidation numbers and electronic states (e.g. palladium has oxidation states of 0, 1, 2 and 4) and separate parameterization needs to be performed (similar to carbon with \textit{sp}, \textit{sp}\textsuperscript{2}, and \textit{sp}\textsuperscript{3} hybridization). The problem is further magnified due to multitude of transition metal complexes, thus making the parameterization even more difficult.\textsuperscript{9,19,32,33}

  Also in pure metallic systems, the nature of bonding and electronic structure change as the number of atoms in the metal cluster changes (e.g. \textit{Pd}_{2} has a spin multiplicity of 3, \textit{Pd}_{11} has a spin multiplicity of 7 and \textit{Pd}_{12} has a spin multiplicity of 5).\textsuperscript{34}

- The \textit{d}-shell electrons \textsuperscript{10,11}: In the case of transition metal systems, the effects due to \textit{d}-orbital electrons pose further problems in using force field methods. The structural, spectroscopic and magnetic properties of transition metal complexes are significantly affected by the \textit{d}-orbital electrons. Some significant issues are the Jahn-Teller distortion, \textit{s}-\textit{d} orbital mixing etc. Some efforts have been directed towards tackling these problems in force field methods and the POS (points on a sphere) model and the LFMM (ligand field augmented molecular mechanics) model have garnered relatively more attention.\textsuperscript{11} However, these modifications are
very specific and need significant code writing since they can not be implemented in standard force field method softwares and to make these approaches more diversified a lot of parameterization is needed. Another situation that may hamper the use of these methods is when the system under investigation contains both, the transition metal complexes and some routine organic molecules.

A.2.2 Electronic Structure Calculations

To model chemical reactions taking place in a system containing novel transition metal clusters and complexes and routine organic compounds, at an atomic level, there is no substitution to the electronic structure calculation methods. Since it explicitly takes into account the electronic structure, it also offers an additional advantage of probing and predicting the bonding and electronic structure changes in the system. The following sub-sections describe the necessary background material of electronic structure calculations and give a detailed description of the methods.

A.2.2.1 Electronic Structure of Atom and Wave-particle duality

An atom consists of electrons, protons and neutrons (Protons and neutrons are not the most fundamental particles of matter and they are made up of even smaller particles called quarks. However, these details are not required and are beyond the scope of this document). Electrically neutral neutrons and positively charged protons are bound together forming a positively charged nucleus and the negatively charged electrons arrange themselves around the nucleus. There exists electromagnetic interaction amongst these species. The wave-particle duality is known to exist for a long time to describe matter and energy in physics and chemistry and an appropriate mathematical form to describe an object depends upon its mass (and velocity when relativistic effects need to be
considered). Heavy objects can be treated as “particles only” and hence can be modelled using classical Newtonian mechanics. However, the borderline mass for Newtonian mechanics is the mass of a proton (and the velocity as a fraction of the velocity of light, to neglect relativistic effects). Electrons are a few orders of magnitude lighter than the neutrons and protons (and hence the nucleus) and hence they display both wave and particle like characteristics. The famous **double slit-experiment** was the first experimental proof of electrons behaving like a wave. Given the wave like behaviour of electrons, it is not possible to mathematically treat electrons using classical Newtonian mechanics and hence they need a special treatment, i.e. quantum mechanics.

### A.2.2.2 Postulates of Quantum Mechanics

Quantum mechanics is nothing but a set of underlying principles that can describe some of the most fundamental aspects of matter at a sub-atomic level. The postulates of quantum mechanics are as follows:  

1. Associated with any particle (like an electron) moving in a force field (like the electromagnetic forces exerted on an electron due to the presence of other electrons and nuclei) is a wave function \( \Psi \) which determines everything that can be known about the particle.

2. With every physical observable there is an associated operator, which when operating upon the wavefunction associated with a definite value of that observable will yield that value times the wavefunction \( (Q\Psi_n = q_n \Psi_n) \).

3. Any operator associated with a physically measurable property will be Hermitian \( (\int \Psi_a^* Q \Psi_b \, dr = \int (Q \Psi_a)^* \Psi_b \, dr) \).

4. The set of eigenfunctions of the operator will form a complete set of linearly independent functions \( (Q \Psi_j = q_j \Psi_j \text{ and } \Psi = \sum c_j \Psi_j) \).
5. For a system described by a given wavefunction, the expectation value of any property can be found by performing the expectation value integral with respect to that wavefunction \( \langle q \rangle = \int \Psi^* Q \Psi \, dr \).

### A.2.2.3 Schrödinger Equation

The Schrödinger equation,\(^{35}\) which is a second order partial differential equation, is the most important equation in quantum mechanics and can describe the spatial and temporal evolution of the wavefunction of a particle in a given potential. It is given as,

\[
H \Psi (r,t) = i \hbar \frac{\partial}{\partial t} \Psi (r,t) \tag{A.9}
\]

where \( \hbar \) is the reduced Planck’s constant, \( \Psi \) is the wavefunction and \( H \) is the Hamiltonian operator which is given as follows:

\[
H = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(r) \right) \tag{A.10}
\]

The first term in the Hamiltonian operator is the kinetic energy operator and the second term is the potential energy operator. Since equation (A.9) is a partial differential equation, if the separation of variables method is used, the wavefunction can be separated into spatial and temporal part as

\[
\Psi (r,t) = \Psi (r) f (t) \tag{A.11}
\]

Inserting equation (A.11) into equation (A.9) gives

\[
\frac{1}{\Psi (r)} H \Psi (r) = \frac{1}{f(t)} i \hbar \frac{d}{dt} f(t) \tag{A.12}
\]

The left hand side of equation (A.12) depends only on space while the right hand side depends only on time. Since these two are completely independent variables, equation (A.12) can only be true when both the sides of the equation are constant, i.e.

\[
\frac{1}{\Psi (r)} H \Psi (r) = E; \quad H \Psi (r) = E \Psi (r) \tag{A.13}
\]
\( E \) is a constant in equation (A.13). According to postulate number 2 of quantum mechanics, with every physical observable there is an associated operator. Since the Hamiltonian is an energy operator, it is intuitive that the constant \( E \) is nothing but the energy of the system. The solution of the time dependant right hand side part of equation (A.12) can be given as 
\[ f(t) = e^{-iEt/\hbar} \]
and inserting this solution in equation (A.11) gives,
\[ \Psi(r, t) = \Psi(r) e^{-iEt/\hbar} \tag{A.14} \]
Thus the wavefunction is written as a function with amplitude \( \Psi(r) \) and phase \( e^{-iEt/\hbar} \). Inserting equation (A.14) into equation (A.9) gives the time independent Schrödinger equation as
\[ H\Psi(r) = E\Psi(r) \tag{A.15} \]
and the time dependence can be written as a product of the time independent function and the phase factor. The phase factor is usually neglected for time-independent problems.

A nucleus is much heavier than electrons and this large mass difference also indicates that its velocity is much smaller than that of the electrons. Hence nuclei exhibit small quantum effects and can be treated classically. The electrons can adjust instantaneously to any change in the nuclear coordinates. If we write the time-independent Schrödinger equation for a system where \( n \) denotes nuclei and \( e \) denotes electrons and the nuclear coordinates are denoted as \( R_n \) and the electronic coordinates are denoted as \( r_e \) then,
\[ H_{\text{sys}} \Psi_{\text{sys}}(r_e, R_n) = E_{\text{sys}} \Psi_{\text{sys}}(r_e, R_n) \tag{A.16} \]
where
\[ H_{\text{sys}} = T_n + T_e + V_{ee}(r_e) + V_{en}(r_e, R_n) + V_{nn}(R_n) = T_n + H_e \tag{A.17} \]
\( T \) denotes the kinetic energy operator and \( V \) denotes the potential energy operator (coulombic interactions between electron-electron, electron-
nucleus and nucleus-nucleus). The total wavefunction of the system depends on the coordinates and velocities of the electrons and the nuclei. However, due to the separation of time scales between the electronic and nuclear motion (nuclei moving much slower than the electrons) it can be assumed that the nuclei are almost stationary with respect to the electrons. If the total wavefunction of the system is written as

$$\Psi_{sys} = \Psi_e (r_e, R_n) \Psi_n (R_n)$$ \hspace{1cm} (A.18)

then the Schrödinger equation in a static arrangement of nuclei can be written as

$$H_e \Psi_e (r_e, R_n) = E_e \Psi_e (r_e, R_n)$$ \hspace{1cm} (A.19)

Here the energy $E_e$ and the wavefunction $\Psi_e$ depend only on the nuclear coordinates and not on nuclear velocities. The total energy of the system then can be computed from the following equation.

$$(T_n + E_e) \Psi_n (R_n) = E_{sys} \Psi_n (R_n)$$ \hspace{1cm} (A.20)

The energy $E_e$ is often called the adiabatic contribution to the energy of the system and it is shown that the non-adiabatic contributions contribute very little to the energy. The error in hydrogen molecule is of the order of $10^{-4}$ a.u. and as the molecule gets bigger, the nuclei become heavier and thus the error decreases. Thus, with the separation of nuclear and electronic motion, we can compute the energy $E_e$ as a function of different nuclear coordinates. This way of computing the energy using $\Psi_e$ provides a potential energy surface on which the nuclei move. The separation of electronic and nuclear motion in a system, as described above, is called as the Born-Oppenheimer approximation. Most of the electronic structure calculations are performed using this approximation (i.e. using equation A.19 instead of equation A.16) and all the electronic structure calculation methods described henceforth in this will be using the Born-Oppenheimer approximation.
A.2.2.4 Solution for Hydrogen atom and Approximate Solution for Helium

The hydrogen atom is the simplest system on which electronic level calculations can be performed by solving the Schrödinger equation. For the hydrogen atom, with one electron and a nucleus of charge +1, the time independent Schrödinger equation can be written as,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right] \Psi(r) = E \Psi(r) \tag{A.21}$$

where $r$ is the distance of the electron from the nucleus and the potential energy operator takes into account the columbic interaction between the electron and the nucleus ($U(r) = -1/r$). The analytical solution for the wavefunction in spherical coordinates is given as,

$$\Psi_{nlm}(r, \theta, \phi) = \sqrt{\frac{2}{na_0}} \frac{(n-l-1)!}{2n(n+1)!} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_{l,m}(\theta, \phi) \tag{A.22}$$

where $n$, $l$ and $m$ are the principal, azimuthal and magnetic quantum numbers, $a_0$ is the Bohr radius, $\rho = 2r/na_0$, $L_{n-l-1}^{2l+1}(\rho)$ are Laguerre polynomials and $Y_{l,m}$ are spherical harmonics.

Once the wavefunction is determined, the square of the wavefunction at any point gives the probability of finding an electron at that point. Hence,

$$\int \Psi^* \Psi d\tau = 1 \tag{A.23}$$

The physical quantity that is associated with the Hamiltonian operator $H$ is the energy and is given as

$$E = \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau} = \int \Psi^* H \Psi d\tau = \langle \Psi | H | \Psi \rangle \tag{A.24}$$

It is a customary to write the integrals using a “Bra-ket” notation, as shown in equation (A.24).
The solution of Schrödinger equation for a system containing more than one electron is more complicated since no analytical solution exists. An approximate solution needs to be determined even for the helium atom which contains two electrons and a nucleus. The Schrödinger equation for this atom can be written as

\[
\left( -\frac{1}{2}\frac{\nabla^2_{\mathbf{r}_1}}{\hbar^2} - \frac{Z}{r_1} \right) + \left( -\frac{1}{2}\frac{\nabla^2_{\mathbf{r}_2}}{\hbar^2} - \frac{Z}{r_2} \right) + \frac{1}{r_{12}} \Psi (\mathbf{r}_1, \mathbf{r}_2)
\]

(A.25)

where \( Z \) denotes the charge on the nucleus, subscripts 1 and 2 represent electrons 1 and 2 and \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) represent their positions in space. If we assume that the two electrons in the atom interact with the nucleus but do not interact with each other, i.e. \( H = h_1 + h_2 \), then equation (A.25) becomes separable and an exact solution of the individual electron’s wavefunction can be obtained. The two separate equations are

\[
h_1 \phi_1 (\mathbf{r}_1) = E_1' \phi_1 (\mathbf{r}_1) \quad \text{and} \quad h_2 \phi_2 (\mathbf{r}_2) = E_2' \phi_2 (\mathbf{r}_2)
\]

(A.26)

and the total wavefunction then can be assumed as a product of individual wave functions \( \Psi (\mathbf{r}_1, \mathbf{r}_2) = \phi_1 (\mathbf{r}_1) \phi_2 (\mathbf{r}_2) \). The total energy of the helium atom with non-interacting electrons then can be given as \( E' = E_1' + E_2' \). To include the correction for repulsion between the two electrons in helium atom, an additional term can be defined as,

\[
U_{12}^{\text{eff}} = \int \phi_2 \frac{1}{r_{12}} \phi_2 d\tau \quad \text{and} \quad U_{21}^{\text{eff}} = \int \phi_1 \frac{1}{r_{12}} \phi_1 d\tau
\]

(A.27)

Since \( \phi_1 \) and \( \phi_2 \) are known from the non-interacting system, integrals in equation (A.27) can be evaluated. Using equation (A.27), the effective Hamiltonian that takes into account the electron-electron repulsion can be defined as
\[ H_1^{\text{eff}} = h_1 + U_1^{\text{eff}} \quad \text{and} \quad H_2^{\text{eff}} = h_2 + U_2^{\text{eff}} \]
\[ H_1^{\text{eff}} \varphi_1 = E_1 \varphi_1 \quad \text{and} \quad H_2^{\text{eff}} \varphi_2 = E_2 \varphi_2 \Rightarrow E_1, E_2, \varphi_1, \varphi_2 \]

Thus the total energy of the system with interacting electrons, \( E \), can be calculated as

\[
E_1 + E_2 = \langle \Psi | H_1^{\text{eff}} + H_2^{\text{eff}} | \Psi \rangle = \langle \Psi | h_1 + h_2 + \frac{2}{r_{12}} | \Psi \rangle \\
= \langle \Psi | H + \frac{1}{r_{12}} | \Psi \rangle = \langle \varphi_1 \varphi_2 | H + \frac{1}{r_{12}} | \varphi_1 \varphi_2 \rangle \\
= \langle \varphi_1 \varphi_2 | H | \varphi_1 \varphi_2 \rangle + \langle \varphi_1 \varphi_2 | \frac{1}{r_{12}} | \varphi_1 \varphi_2 \rangle \\
= E + \int \varphi_1 \varphi_2 \frac{1}{r_{12}} \varphi_1 \varphi_2 d\tau = E + J_{12} \\
\therefore E = E_1 + E_2 - J_{12}
\]

\( J_{12} \) is called as the Coulomb integral. It can be seen that the exact solution of hydrogen atom plays an important role in calculating an approximate solution for the helium atom.

Both the electrons in helium are in the 1s orbital and it means that they have the same principal, azimuthal and magnetic quantum numbers. However, they differ in the spin since one has a +1/2 spin and the other has −1/2 spin. In the above discussion, the total wavefunction of the helium atom is written as the product of individual electron wavefunctions as

\[
\Psi(r_1, r_2) = \varphi_1(r_1) \varphi_2(r_2) = 1s(1)\overline{1s}(2) \quad \text{(A.30)}
\]

where the wavefunctions/orbitals 1s and \( \overline{1s} \) differ in spin. Pauli’s exclusion principle states that, for two electrons, the total wavefunction is antisymmetric \( (\Psi(r_1, r_2) = -\Psi(r_2, r_1)) \). However, if \( \Psi \) is defined as in equation (A.30) and we exchange electrons 1 and 2, we get

\[
\Psi(r_1, r_2) = 1s(1)\overline{1s}(2) \text{ and } \Psi(r_2, r_1) = 1s(2)\overline{1s}(1) \\
\therefore \Psi(r_1, r_2) \neq -\Psi(r_2, r_1) \quad \text{(A.31)}
\]
Equation (A.31) does not obey Pauli’s exclusion principle. Hence the representation of the total wavefunction needs to be changed. A correct representation would be

\[
\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left[ 1s(1)1\bar{s}(2) - 1s(2)1\bar{s}(1) \right]
\]

The determinant in equation (A.32) is called as Slater determinant. If the correct representation of the total wavefunction is put in equation (A.29), we get

\[
E_1 + E_2 = \left\langle \Psi \left| H^\text{eff}_1 + H^\text{eff}_2 \right| \Psi \right\rangle = \left\langle \Psi \left| h_1 + h_2 + \frac{2}{r_{12}} \right| \Psi \right\rangle = \left\langle \Psi \left| H + \frac{1}{r_{12}} \right| \Psi \right\rangle
\]

\[
= \left\langle \Psi \left| H \right| \Psi \right\rangle + \frac{1}{2} \left\langle 1s(1)1\bar{s}(2) - 1s(2)1\bar{s}(1) \right\rangle \frac{1}{r_{12}} \left\langle 1s(1)1\bar{s}(2) - 1s(2)1\bar{s}(1) \right\rangle
\]

\[
= E + \frac{1}{2} \left\langle 1s(1)1\bar{s}(2) \right\rangle \frac{1}{r_{12}} \left\langle 1s(1)1\bar{s}(2) \right\rangle + \frac{1}{2} \left\langle 1s(2)1\bar{s}(1) \right\rangle \frac{1}{r_{12}} \left\langle 1s(2)1\bar{s}(1) \right\rangle
\]

\[
- \frac{1}{2} \left\langle 1s(1)1\bar{s}(2) \right\rangle \frac{1}{r_{12}} \left\langle 1s(2)1\bar{s}(1) \right\rangle - \frac{1}{2} \left\langle 1s(2)1\bar{s}(1) \right\rangle \frac{1}{r_{12}} \left\langle 1s(2)1\bar{s}(1) \right\rangle
\]

\[
= E + J_{12} - K_{12}
\]

\[
\therefore \quad E = E_1 + E_2 - J_{12} + K_{12}
\]

(A.33)

A.2.2.5 Linear Combination of Atomic Orbitals (LCAO)

The discussion in the above section is limited to Helium, containing only two electrons; however, any realistic system will be a polyelectronic system. Any system consists of molecules and when more than one atoms form a molecule (by forming electron sharing and non electron sharing bonds), their electronic structure gets modified. For example, when two H atoms form a covalent bond to make an H\(_2\) molecule, the electronic
structure is different than that of an individual hydrogen atom. According to the valence bond theory, the individual orbitals of two atoms overlap and the shared electrons are localized in the overlapped region (the bond) between the two atoms. However, in electronic structure computations, the molecular orbital theory is used. According to this theory, the electrons are not assigned to individual bonds and are considered to arrange themselves around the molecule, under the influence of the nuclei. Similar to orbitals in an atom, every molecule is considered to have a set of molecular orbitals and these molecular orbitals (wavefunction) are a mathematical construct of the individual atomic orbitals. Molecular orbitals are expressed as a linear combination of atomic orbitals (LCAO), as if each atom were on its own.

\[
\chi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \ldots + c_n\phi_n
\]  

(A.34)

where \( \chi \) is the molecular orbital, \( \phi_i \) is an atomic orbital and \( c_i \) is the coefficient associated with the atomic orbital \( \phi_i \). To make sure that the orbitals follow the antisymmetric constraint, they are expressed as Slater determinants (similar to equation A.32). If there are \( N \) electrons in the system with spin orbitals \( \chi_1, \chi_2, \ldots, \chi_N \), then the total wavefunction is given as,

\[
\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} 
\chi_1(1) & \chi_2(1) & \ldots & \chi_N(1) \\
\chi_1(2) & \chi_2(2) & \ldots & \chi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(N) & \chi_2(N) & \ldots & \chi_N(N) 
\end{vmatrix}
\]

(A.35)

Since in a polyelectronic system, it is not possible to obtain analytical solution, assuming non-interacting electrons (the way it is obtained in the case of Helium), the atomic orbitals are expressed in the form of basis functions. A basis function can be of any type; exponential, Gaussian,
polynomial, cube function, planewaves, to name a few. Though these basis functions need not be an analytical solution to an atomic Schrödinger equation, they should properly describe the physics of the problem and these functions go to zero when the distance between the nuclei and the electron becomes too large. The two types of basis functions commonly used to construct atomic orbitals are the Slater type orbital and the Gaussian type orbital. The functional form of the Slater type orbitals is as follows

$$\varphi_{z,n,l,m}(r,\theta,\phi) = NY_{i,m}(\theta,\phi)r^{n-1}e^{-\zeta r}$$

(A.36)

where $N$ is a normalization constant, $\zeta$ is a constant related to the effective charge of the nucleus and $Y_{i,m}$ are spherical harmonic functions. The Gaussian type orbitals are given as follows

$$\varphi_{z,n,l,m}(r,\theta,\phi) = NY_{i,m}(\theta,\phi)r^{2n-2-l}e^{-\zeta r^2}$$

(A.37)

The Slater type basis functions are superior to the Gaussian type basis function since less number of Slater orbitals are required to get a given accuracy and the physics of the system is better described using the Slater type orbitals. The minimum number of basis functions that are needed to describe any system is that which can just accommodate the number of electrons present in the system. For ex. two sets of $s$ functions ($1s$ and $2s$) and a set of $p$ functions ($2p_x$, $2p_y$ and $2p_z$) are required to describe the first row elements in the periodic table. Increased accuracy can be obtained using a larger number of basis functions. A detailed overview on different types of basis functions is beyond the scope of this document and hence not discussed here. The basis functions used in condensed phase and periodic systems are planewaves and the pertaining details will be discussed in section A.2.4.
A.2.2.6 Hartree-Fock Calculations

While performing electronic structure calculations in a polyelectronic system, we are aiming to calculate the molecular orbitals (and the energy). Once the type and numbers of basis function are decided, the molecular orbitals are formed as a linear combination of atomic orbitals, as in equation (A.34), and the wavefunction is expressed in the form of Slater determinant, as in equation (A.35). Since there is no “exact” wavefunction, we need to determine the coefficients of equation (A.34) which will give the best possible solution. The variational principle is used to calculate these coefficients and ultimately the wavefunction. It states that the energy calculated from an approximate wavefunction will always be bigger than the “true” energy of the system. This implies that the closer the approximate wavefunction to the actual solution, lower will be the energy of the system. Hence to obtain the best possible wavefunction, we need to determine the set of coefficients that will result in the minimum energy of the system i.e. the electronic energy of the system is minimized with respect to the coefficients. The numerical procedure is as follows.

If there is an \( N \) electron system for which the Hamiltonian is given as

\[
H = \sum_{i}^{N} \frac{-1}{2} \hat{\nabla}^2 - \sum_{i}^{N} \sum_{a}^{\alpha} \frac{Z_{a}}{r_{i} - r_{a}} + \sum_{i}^{N} \sum_{j}^{N} \frac{1}{\hat{h}_{ij}, g_{ij}}
\]  \tag{A.38}

and the wave function is expressed as a Slater determinant, as in equation (A.35), then the energy is given as,
\[ E = \left\langle \Psi \left| \sum_{i}^{N} h_{i} \right| \Psi \right\rangle + \left\langle \Psi \left| \sum_{i}^{N} \sum_{j} g_{ij} \right| \Psi \right\rangle \]

\[ = \sum_{i}^{N} \left\langle \chi_{i} (1) \chi_{j} (2) \ldots \chi_{N} (N) \right| h_{i} \left| \chi_{i} (1) \chi_{j} (2) \ldots \chi_{N} (N) \right\rangle + \sum_{i}^{N} \sum_{j}^{N} \left\langle \chi_{i} (1) \chi_{j} (2) \ldots \chi_{N} (N) \right| g_{ij} \left| \chi_{i} (1) \chi_{j} (2) \ldots \chi_{N} (N) \right\rangle \]

\[ = \sum_{i}^{N} \left\langle \chi_{i} \left| - \frac{\nabla_{i}^{2}}{2} \right| \chi_{i} \right\rangle + \sum_{i}^{N} \left\langle \chi_{i} \left| \frac{-Z_{a_{i}a_{j}}}{r_{a_{i}a_{j}}} \right| \chi_{i} \right\rangle + \sum_{i}^{N} \sum_{j}^{N} \left( J_{ij} - K_{ij} \right) \]

where

\[ J_{12} = \left\langle \chi_{1} (1) \chi_{j} (2) \left| \frac{1}{r_{12}} \right| \chi_{1} (1) \chi_{j} (2) \right\rangle \text{ and } K_{12} = \left\langle \chi_{1} (1) \chi_{j} (2) \left| \frac{1}{r_{12}} \right| \chi_{2} (1) \chi_{1} (2) \right\rangle \]

\[ (A.39) \]

If every orbital is doubly occupied then,

\[ \left\langle \Psi \left| H \right| \Psi \right\rangle = \sum_{i}^{n} 2h_{i} + \sum_{i,j}^{n} \left[ 2J_{ij} - K_{ij} \right] \]

\[ (A.40) \]

Varying the electronic energy as a function of orbitals and equating it to zero we get,

\[ \Im \left[ \xi \right] = \sum_{i}^{n} 2h_{i} + \sum_{i,j}^{n} \left[ 2J_{ij} - K_{ij} \right] + \sum_{i,j}^{n} 2\lambda_{ij} \left[ \left\langle \chi_{i} \left| \chi_{j} \right\rangle - \delta_{ij} \right\rangle \right] \]

\[ \frac{\partial \Im \xi}{\partial \chi_{i}} = 0 \Rightarrow \left[ h_{i} + \sum_{j}^{n} \left( 2J_{j} - K_{j} \right) \right] \chi_{i} = \sum_{j}^{n} \lambda_{ij} \chi_{j} \]

\[ (A.42) \]

where \( \lambda_{ij} \) are the Lagrange multipliers that are introduced because the minimization of the energy needs to be performed under the constraint that the molecular orbitals remain orthogonal and normalized.

Since the wavefunction is a determinant, the matrix \( \lambda_{ij} \) can be brought into diagonal form as \( \lambda_{ij} = 0 \) and \( \lambda_{ii} = \epsilon_{i} \),

\[ \left[ h_{i} + \sum_{j}^{n} \left( 2J_{j} - K_{j} \right) \right] \chi_{i} = \sum_{j}^{n} \lambda_{ij} \chi_{j} \]

\[ (A.43) \]

Expressing \( \chi_{i} = \sum_{\nu}^{M} c_{\nu} \varphi_{\nu} \) we get,
\[
F_i \sum_{\nu}^M {c}_{ij} \phi_{\nu} = \varepsilon_i \sum_{\nu}^M {c}_{ij} \phi_{\nu} \tag{A.44}
\]

where \(c_{ij}\) are the coefficients and \(M\) is the number of basis functions.

Multiplying equation (A.44) by a specific basis function and integrating gives the following equation

\[
F_\alpha = S_\alpha \varepsilon \]

\[
F_{\alpha \beta} = \left\langle \phi_\alpha | F | \phi_\beta \right\rangle \quad \text{and} \quad S_{\alpha \beta} = \left\langle \phi_\alpha | \phi_\beta \right\rangle \tag{A.45}
\]

where \(F\) is called as the Fock Matrix and \(S\) is called as the overlap matrix. Equation (A.45) is an eigenvalue problem and the Fock matrix needs to be diagonalized to get the coefficients of the molecular orbitals. But it has to be noted that the Fock matrix can only be calculated if the coefficients are known. Hence, the Hartree-Fock procedure to perform electronic level calculations starts with an initial guess for the coefficients, then calculating the Fock matrix and then recalculating the new set of coefficients by diagonalizing the Fock matrix. The procedure is repeated till the coefficients used to form the Fock matrix are the same to those emanating from the diagonalization of the Fock matrix. The convergence on the coefficients implies that the system is at the minimum energy.

A.2.2.7 Semi-empirical methods

The electronic structure calculation methods, like the Hartree-Fock method described above, are computationally very expensive and a significant amount of computational effort is needed to calculate and manipulate the integrals that are calculated in the process. Hence, to reduce the computational cost of electronic structure calculations, some approximations are made to these integrals, particularly to the two-electron, multicentre integrals. These integrals are either neglected or are parameterized using empirical data. Such methods are called as semi-
Some common semi-empirical methods are Zero-differential overlap (ZDO), Complete neglect of differential overlap (CNDO), Intermediate neglect of differential overlap (INDO), Neglect of diatomic differential overlap (NDDO), Modified neglect of diatomic overlap (MNDO), Austin model-1 (AM1), Parametric model-3 (PM3) etc. A detailed discussion of all these methods is not included here. However, these semi-empirical methods share a limitation of force field methods, i.e., their performance on unknown species. The extent of this limitation is not as severe as in the case of force field calculations though. Most of these methods also use the minimal basis function only.

A.2.2.8 Post Hartree-Fock

The electronic structure calculations are performed in the Hartree-Fock procedure by selecting the type and number of basis functions, forming a Slater determinant and then obtaining the coefficients in an iterative fashion, as explained in the previous section. The accuracy of these calculations can be improved (or the energy of the system can be further lowered) by increasing the number of basis functions used. The Hartree-Fock wavefunction can provide 99% accuracy in calculating the “true” energy of the system and hence suffices the purpose in a lot of cases. However, in certain situations, this 1% difference becomes very crucial to describe correctly the physics of the system. In order to further improve the accuracy of electronic structure calculation methods beyond the Hartree-Fock procedure, it is required to identify the root cause of this slight inaccuracy. Assuming that a sufficiently large basis set is used, the other possible source of error is due to electron-electron interaction treatment in the Hartree-Fock procedure. Though the electron-electron interaction is taken into account, as can be seen in equation (A.39), it has to be noted that each electron in the Hartree-Fock procedure sees an average
field of all other electrons and the motion of each and every electron is not correlated. In other words, an electron does not see each and every other electron as individual point charge so as to avoid it as much as possible. It also does not allow electrons to cross each other. Hence, any method that can improve the electron correlation this way will definitely lead to a lower energy of the system than that calculated using the Hartree Fock procedure. These methods are called as electron correlation methods and the electron correlation energy is the difference between the “true” energy of the system and the energy calculated using the Hartree Fock procedure.

One of the ways to further improve the electron correlation effects in electronic structure calculations is to include additional (Slater) determinants. Addition of determinants in the mathematical formulation can also be seen physically as addition of some unoccupied/virtual orbitals to the system, something very similar to addition of excited state orbitals to the ground state orbitals of the system.

\[
\Psi_{\text{correlation}} = \tilde{c}^0 \Psi^{\text{HF}} + \tilde{c}^1 \Psi^1 + \tilde{c}^2 \Psi^2 + \ldots 
\]  

(A.46)

where \(\Psi^{\text{HF}}\) is the single determinant wavefunction obtained using the Hartree-Fock procedure and \(\Psi^i\) are the additional determinants. There are 3 main methods that are used to take into account electron correlation effects, viz., Configuration Interaction (CI)\(^{37}\), Coupled Cluster (CC)\(^{38}\) and Møller-Plesset (MP)\(^{39}\) and they differ in ways to calculate the coefficients in equation (A.46). Further details of these methods are beyond the scope of this document and hence not provided here.

A.2.3 Density Functional Theory (DFT)

The previous section described the electronic structure calculation methods (Hartree-Fock, Semi-empirical and Post-Hartree-Fock) based on the multielectron wavefunction of the system. However, there exists one more theoretical approach to perform electronic structure calculations and
it is called as density functional theory. As the name suggests, the energy of the system containing \( N \) electrons that repel each other, get attracted to the nuclei by Columbic interaction and follow Pauli’s exclusion principle is calculated using the density of electrons instead of the wavefunction. The following sections describe the mathematical formulation of the density functional theory and the necessary details.

A.2.3.1 Origin and formulation of DFT

The Schrödinger wave equation for an \( N \) electron system is given as

\[
\left[ \sum_{i} \frac{1}{2} \nabla^2 - \sum_{i,j} \frac{1}{r_{ij}} + \sum_{i} \frac{Z}{r_{i}} \right] \Psi = E \Psi \tag{A.47}
\]

and, as mentioned before, the ground state electronic density of the system can be calculated as

\[
\rho(r_{i}) = N \int dx_{1} d_{2} \ldots d_{N} \psi^{*}(r_{i},x_{1},2,\ldots,N) \psi(r_{i},x_{1},2,\ldots,N) \tag{A.48}
\]

Equations (A.47) and (A.48) show that for a given potential \( \nu(\bar{r}) \), it is possible to compute the ground state density \( \rho(\bar{r}) \), via the electronic wavefunction \( \Psi \). However, Hohenberg and Kohn\(^{40}\) showed that there exists an inverse mapping with which it is possible to obtain an external potential, if the ground state density is provided. In their seminal paper,\(^{40}\) they also showed that this inverse mapping can be used to calculate the ground state energy of a multielectron system using the variational principle, without having to resort to calculate the wavefunction. If the wave function is expressed as

\[
\Psi = \Psi(\nu) \tag{A.49}
\]

then since \( \nu = \nu(\rho) \), the wavefunction can be written as
\[ \Psi = \Psi(\nu[\rho]) = \Psi(\rho) \tag{A.50} \]

Using the variational principle, the energy of the system can be calculated as,
\[
E = \min_{\rho} \langle \Psi[H|\Psi \rangle = \min_{\rho} \langle \Psi[\rho][H|\Psi[\rho] \rangle
= \min_{\rho} \langle \Psi[\rho][T + V + V_{ee}|\Psi[\rho] \rangle \tag{A.51}
\]
where \( T = \left( \frac{-\nabla^2}{2} \right), \nu = \left( \frac{-Z}{r} \right) \) and \( V_{ee} = \frac{1}{r_{ee}} \).

Equation (A.51) can be separated as,
\[
E = \min_{\rho} \left\{ \langle \Psi[\rho][\nu|\Psi[\rho]\rangle + \langle \Psi[\rho][T + V_{ee}|\Psi[\rho]\rangle \right\} \tag{A.52}
= \min_{\rho} \left\{ \int \Delta T \rho(r) \nu(r) + F[\rho] \right\}
\]
The energy is thus minimized over the density and not over the wavefunction. However, in equation (A.52), the functional form of \( F(\rho) \) is unknown.

The inverse mapping of density on potential is also valid for a system of non-interaction electrons and Thomas-Fermi,\textsuperscript{41, 42} even before the Hohenberg-Kohn theorem,\textsuperscript{40} provided a way to calculate the energy of such a non-interacting system by replacing the wavefunction with electron density as follows. For a non-interacting system,
\[
E = \sum_{i=1}^{N} \int d^3r \chi(i)^2 \left( \frac{-\nabla^2}{2} \right) \chi(i)^2 + \sum_{i=1}^{N} \int d^3r \chi(i) \chi(i)^2 \nu(r) \tag{A.53}
\]
As shown in equation (A.53), Thomas-Fermi just replaced the wavefunction with the electron density. They also showed that the kinetic energy part of a homogeneous electron gas is given as,
\[ T_s = \frac{3}{10} (3\pi^2)^{2/3} \int d^3 r \rho^{5/3} (\vec{r}) \] (A.54)

Hence according to Thomas-Fermi approach the energy of the non-interacting system can be given in terms of the electron density as,

\[ E(\rho) = \sum_{i=1}^{N} \frac{3}{10} (3\pi^2)^{2/3} \int d^3 r \rho^{5/3} (\vec{r}) + \int d^3 r \rho(\vec{r}) \psi(\vec{r}) \] (A.55)

This Thomas-Fermi approach of calculating the kinetic energy part of the non-interacting system of electrons is used to develop a scheme to evaluate the functional \( F(\rho) \) (for a system with interacting electrons) and the details are provided in the following section.

A.2.3.2 Kohn-Sham formulation

To calculate the unknown functional \( F(\rho) \) consisting of the electronic kinetic energy part and the electron-electron interaction part, Kohn and Sham\(^{43} \) came up with a scheme which calculates the total energy of the system using a combination of the density functional theory and orbital/wavefunction approach. A detailed description is as follows.

Kohn-Sham introduced a non-interacting system for which the Hamiltonian can be given as

\[ h_{ks} = -\frac{1}{2} \nabla^2 + v_{ks} (\vec{r}) \] (A.56)

If an orbital corresponding to the above Hamiltonian (usually referred as Kohn-Sham orbitals) is given in the form of a determinant as

\[ \chi_{ks} = |\chi_1(1) \chi_2(2) \chi_3(3)...\chi_N(N)| \] (A.57)

then the Schrödinger equation will be

\[ h_{ks} \chi_{ks} = E_{ks} \chi_{ks} \] (A.58)

In the Kohn-Sham formulation, the potential \( v_{ks} (\vec{r}) \) is defined in such a way that the electron density calculated using the Kohn-Sham orbitals \( \chi_{ks} \) is equivalent to the exact density of the electron-interacting system with
the actual potential \( \nu(\vec{r}) \). Using the Kohn-Sham orbitals, the kinetic energy of the non-interacting system can be given as

\[
T_s = \langle \chi_{KS} | T | \chi_{KS} \rangle \tag{A.59}
\]

From equations (A.56-A.59), with the actual wavefunction of the system as \( \Psi \), the ground state electronic energy of the system can be given as,

\[
E = \langle \Psi | T + \nu + V_{ee} | \Psi \rangle = \langle \Psi | T | \Psi \rangle + \int d^3r \rho(\vec{r}) \nu(\vec{r}) + \langle \Psi | V_{ee} | \Psi \rangle
\]

\[
= T_s + \int d^3r \rho(\vec{r}) \nu(\vec{r}) + \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} U[\rho]
\]

\[
+ T_k - T_s + \langle \Psi | V_{ee} | \Psi \rangle - U[\rho]
\]

\[
E_{xc}[\rho]
\]

where \( T_s \) is the kinetic energy which can be calculated using the Kohn-Sham orbitals. \( E_{xc}[\rho] \) is the only unknown function in the above equation that needs to be approximated. It accounts for less than 10% of the total energy.\(^8\)

It is possible to calculate the total ground state energy of the interacting system using the following steps:

(i) Define the Kohn-Sham non-interacting system

(ii) Calculate the density and kinetic energy of the system and

(iii) Calculate the ground state energy

However, it is only possible if the Kohn-Sham potential \( \nu_{KS}(\vec{r}) \) is known.

The methodology to determine the potential is as follows. From equations (A.56) and (A.58) we get

\[
E_{KS} = \min_{\rho} \left\{ T_s[\rho] + \int d^3r \rho(\vec{r}) \nu_{KS}(\vec{r}) \right\} \tag{A.61}
\]

where \( \frac{\delta E_{KS}}{\delta \rho} = 0 \Leftrightarrow \frac{\delta T_s}{\delta \rho} + \nu_{KS} = 0 \tag{A.62} \)
From equation (A.60), the actual ground state energy of the system is given as

\[
E = \min_{\rho} \left\{ T_s[\rho] + \int d^3 r \rho(\vec{r}) v(\vec{r}) + U[\rho] + E_{xc}[\rho] \right\} \tag{A.63}
\]

where

\[
\frac{\delta E}{\delta \rho} = 0 \Rightarrow \frac{\delta T_s}{\delta \rho} + v(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}}{\delta \rho} = 0 \tag{A.64}
\]

Combining equations (A.62) and (A.64), the Kohn-Sham potential can be obtained as

\[
v_{ks}(\vec{r}) = v(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}}{\delta \rho} \tag{A.65}
\]

If an approximate functional for \( E_{xc}[\rho] \) is known, the Kohn-Sham non-interacting system can be solved to obtain the Kohn-Sham orbitals \( \chi_{ks} \) and the density \( \rho \). Using this information the total energy of the system can be calculated using equation (A.63). However, since the Kohn-Sham potential depends on density \( \rho \) the above equations need to be solved iteratively.

To use the Kohn-Sham Density Functional theory, it is needed to have an appropriate functional form for \( E_{xc}[\rho] \) and the following section describes the approaches to obtain it.

A.2.3.3 Local density approximation and Generalized Gradient Approximation

From equation (A.60) it can be seen that the \( E_{xc}[\rho] \) term accounts for (i) the difference between the actual/exact electronic kinetic energy of the system and the Kohn-Sham non-interacting electronic kinetic energy \( (T_k - T_s) \) and (ii) the difference between the exact electron-electron interaction energy and \( U[\rho] \) (analogous to the Coulomb integral term \( J \) in the Hartree-Fock method, as shown in equation A.39). In other words, it accounts for the exchange-correlation energy \( (E_{xc} = E_x + E_c) \). The two
common approximations for the functional $E_{xc}[\rho]$ are the local density approximation (LDA) and the generalized gradient approximation (GGA).\textsuperscript{44}

As described in section A.2.3.1, the energy of non-interacting, homogeneous electron gas is given using equation (A.55) as

$$
\frac{3}{10}\left(3\pi^2\right)^{2/3}\int d^3r \rho^{4/3}(\bar{r}) + \int d^3r \rho(\bar{r})\nu(\bar{r}).\quad (\text{A.55})
$$

However, it only takes into account the kinetic energy part and the electron-nuclear interactions and neglects the electron-electron interaction energy. A next step in this procedure is to take into account the Coulomb interaction energy given by the term $U[\rho]$, thus extending the Thomas-Fermi energy to

$$
E_{TF} = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int d^3r \rho^{4/3}(\bar{r}) + \int d^3r \rho(\bar{r})\nu(\bar{r}) + \frac{1}{2}\int d^3r d^3r' \frac{\rho(\bar{r})\rho(\bar{r}')}{|\bar{r} - \bar{r}'|}.\quad (\text{A.66})
$$

Equation (A.66) is a step ahead from the completely non-interacting system but it still does not take into account the exchange and correlation energy. Dirac\textsuperscript{45} developed an exchange energy formula for the uniform electron gas as

$$
E_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\bar{r})d\bar{r}\quad (\text{A.67})
$$

Since,

$$
\frac{\delta E_x}{\delta \rho} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho(\bar{r})^{1/3}
$$

Ceperley and Alder\textsuperscript{46} determined the exact values of $\frac{\delta E_c}{\delta \rho}$ using numerical simulations and Vosko et al.\textsuperscript{47} interpolated those values to obtain an analytical function for the same. This analytical expression is given in the
spin-dependant form (if the electrons have spins \( \alpha \) and \( \beta \), then the total electron density is given as \( \rho = \rho_\alpha + \rho_\beta \) as

\[
\frac{\delta E_C}{\delta \rho}(r, \zeta) = \varepsilon_c(r, \zeta) \\
= \varepsilon_c(r, 0) + \varepsilon_s(r) \left[ \frac{f_2(\zeta)}{f_2(0)} (1 - \zeta^4) \right] + \left[ \varepsilon_c(r, 1) - \varepsilon_c(r, 0) \right] f_2(\zeta) \zeta^4
\]  

(A.69)

where

\[
f_2(\zeta) = \left\{ \frac{\frac{1}{2} \left[ (1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} \right] - 2}{(2^{4/3} - 1)} \right\}
\]

\[\varepsilon_{c/\alpha}(x) = A \left\{ \ln \frac{x^2}{x^2 + bx + c} + \frac{2b}{\sqrt{4c - b^2}} \tan^{-1} \left( \frac{\sqrt{4c - b^2}}{2x + b} \right) - \right\}
\]

\[\frac{bx_0}{x_0^2 + bx_0 + c} \ln \frac{(x - x_0)^2}{x^2 + bx + c} + \frac{2(b + 2x_0)}{\sqrt{4c - b^2}} \tan^{-1} \left( \frac{\sqrt{4c - b^2}}{2x + b} \right) \right\}
\]

\[x = \sqrt{r_s} \quad \text{and} \quad A, x_0, b, c \quad \text{are fitting constants.} \quad r_s \quad \text{is the effective volume containing an electron and the spin polarization} \quad \zeta \quad \text{is given as} \quad \left( \rho_\alpha - \rho_\beta \right)/\left( \rho_\alpha + \rho_\beta \right). \quad \text{Thus, for a uniform electron gas, the total energy of the system can be given as,}
\]

\[
E_{TF} = \frac{3}{10} \left( 3\pi^2 \right)^{2/3} \int d^3r p^{5/3}(\bar{r}) + \int d^3r \rho(\bar{r}) v(\bar{r})
\]

\[+ \frac{1}{2} \int d^3rd^3r' \frac{\rho(\bar{r}) \rho(\bar{r}')}{|\bar{r} - \bar{r}'|} + \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(\bar{r}) d^3r + \int \rho(\bar{r}) \left( \frac{\delta E_c}{\delta \rho} \right) d^3r
\]

(A.71)

In the Kohn-Sham density functional theory approach (as discussed in section A.2.3.2), when the exchange correlation term \( E_{xc}[\rho] \) in equation (A.60) is assumed to be equal to that of the uniform electron gas
\[ E_{xc}[\rho] = \frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int \rho^{\frac{1}{3}}(r) d^3r + \int \rho(r) \left(\frac{\partial E_c}{\partial \rho}\right) d^3r \] as shown in equation (A.69), it is referred to as Local Density Approximation or LDA.

The Generalized gradient approximation or GGA is an improvement over the LDA since it implements the gradient correction as
\[
E_{xc}^{GGA} = \int d^3r \ g(\rho, \nabla \rho) \quad (A.72)
\]
For the GGA to be practically useful, it is again important that it has an analytical form like LDA. Different popular formats of the GGA\(^{48-54}\) are used in the electronic structure calculations, but only the Perdew-Burke-Ernzerhof approximation\(^{52}\) will be discussed here.

Similar to the LDA, the \(E_{xc}[\rho]\) term is again separated into the exchange and correlation parts in GGA and in the Perdew-Burke-Ernzerhof approximation,\(^{52}\) the correlation term is given as
\[
E_c^{GGA} = \int \rho \left[ \epsilon_c(r, \xi) + H(r, \xi, t) \right] d^3r \quad (A.73)
\]
where \(t\) is the dimensionless density gradient given as \(t = |\nabla \rho|/(2 \phi k \rho)\), \(\phi\) is the scaling factor given as \(\phi(\xi) = \left[ (1 + \xi)^{\frac{1}{3}} + (1 - \xi)^{\frac{1}{3}} \right]/2\) and \(k = \sqrt{4(3\pi^2 \rho)^{\frac{1}{3}}/\pi \left(\hbar^2/me^2\right)}\). The functional form of \(H\) in equation (A.73) is given as
\[
H = \left( e^2/(\hbar^2/me^2) \right) 0.031091 \phi^3 \ln \left[ 1 + \frac{0.066725}{0.031091} \frac{t^2}{1 + \bar{A} t^2 + \bar{A}^2 t^4} \right] \quad (A.75)
\]
where \(\bar{A} = 0.066725 \exp \left[ -\epsilon_c/\left( 0.031091 \phi^3 \left( e^2/(\hbar^2/me^2) \right) \right) \right] - 1 \right]^{-1}\)

The exchange energy term for this GGA approximation is defined as
\[
E_x^{GGA} = \int \rho \epsilon_x(\rho) F_x(s) d^3r \quad (A.76)
\]
where \(s\) is another type of reduced density gradient given as \((r \ h^2 \me^2)^{0.5} \phi t / 1.2277\) and the functional form of \(F_x\) is as follows.
\[ F_x (s) = 1 + 0.804 - \frac{0.804}{1 + \frac{0.2195s^2}{0.804}} \] (A.77)

### A.2.4 Planewave-pseudopotential Methods

The above sections describe the multielectron system’s electronic structure calculations using the Kohn-Sham density functional theory within the framework of Born-Oppenheimer approximation. Even though the density functional theory takes into account the electron correlation at the computational cost of Hartree-Fock theory, it is computationally still a difficult task to apply this method to an extended system like crystals or bulk soft matter. The solution to this problem is to define a tractable size of system, which when repeated periodically in all spatial directions will represent the bulk i.e. to apply periodic boundary conditions to the cell containing a set of atoms/molecules. If the cell is defined by vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \), then its volume is given as \( \Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \). General lattice vectors are integer multiples of these vectors as
\[
\mathbf{L} = N_1 \mathbf{a}_1 + N_2 \mathbf{a}_2 + N_3 \mathbf{a}_3, \tag{A.78}
\]

A particular atomic arrangement which is repeated periodically, to mimic the actual system of interest, can reduce the computational cost of the calculations since the computations are restricted to the lattice. However, in such an arrangement the effective potential also has a periodicity as
\[
v_{eff} (\mathbf{r} + \mathbf{L}) = v_{eff} (\mathbf{r}) \tag{A.79}
\]
The resultant electron density will also be periodic. Given the periodic nature, the potential can be expanded as a Fourier series as \(^\text{55}\)
\[
v_{eff} (\mathbf{r}) = \sum_{\mathbf{G}} v_{eff} (\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \]  
where \( v_{eff} (\mathbf{G}) = \frac{1}{\Omega} \int v_{eff} (\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} \ d^3 \mathbf{r} \)  
(A.80)

where the vector \( \mathbf{G} \) forms the lattice in the reciprocal space which is generated by the primitive vectors \( \mathbf{b}_1, \mathbf{b}_2 \) and \( \mathbf{b}_3 \) in such a way that
\[ \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}, \]  
\[ \delta_{ij} \] being the Kronecker delta. Thus, the volume of the primitive cell in the reciprocal space is given as \[ \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = (2\pi)^3 / \Omega. \]  

Bloch’s theorem states that if \( \nu(\mathbf{r}) \) is a periodic potential \[ \{ \nu(\mathbf{r} + \mathbf{L}) = \nu(\mathbf{r}) \} \], then the wavefunction of a one electron Hamiltonian of the form \( \left( -\frac{1}{2} \nabla^2 + \nu(\mathbf{r}) \right) \) is given as planewave times a function with the same periodicity as the potential. Mathematically it can be written as
\[ \psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r}) \text{ where } u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{L}) \]  

(A.81)

Alternatively the Bloch’s theorem can be written as
\[ \psi_k(\mathbf{r} + \mathbf{L}) = e^{i\mathbf{k} \cdot \mathbf{L}} \psi_k(\mathbf{r}) \]  

(A.82)

It also has to be noted that planewaves are the exact orbitals for homogeneous electron gas. Since the function \( u_k(\mathbf{r}) \) is periodic, it can be expanded as a set of planewaves as
\[ u_k(\mathbf{r}) = \frac{1}{\Omega} \sum_G c_G^* e^{i\mathbf{G} \cdot \mathbf{r}} \]  

(A.83)

Combining equations (A.81) and (A.83) we get,
\[ \psi_k(\mathbf{r}) = \frac{1}{\Omega} \sum_G c_G^* e^{i\mathbf{G} \cdot \mathbf{r}} \]  

(A.84)

where \( c_G^k \) are complex numbers. While performing electronic structure calculations of a system with periodic boundary conditions (periodic potential) using the Kohn-Sham implementation of density functional theory and planewaves as basis functions, \( \psi_k(\mathbf{r}) \) can be seen as the Kohn-Sham orbitals. In that case the Kohn-Sham density functional theory equations can be rewritten as
\[ \left( -\frac{1}{2} \nabla^2 + \nu_{\text{eff}}(\mathbf{r}) \right) \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}) \]  

(A.85)
where \( \nu_{\text{eff}}(\vec{r}) \) accounts for nucleus-electron and electron-electron interactions and the electron density is given as

\[
\rho(\vec{r}) = 2 \frac{\Omega}{(2\pi)^3} \int \left| \psi_k(\vec{r}) \right|^2 \delta(E_F - \varepsilon_k) d^3k
\]  

(A.66)

Factor 2 in the above equation is to take into account both the electron spins and \( \delta \) is the step function which 1 for positive and 0 for negative function arguments. The integration in equation (A.66) is over the Brillouin zone (primitive cell in the reciprocal space).

As explained above, using the Bloch’s theorem, a problem of an extended system with an extended number of electrons is transformed into a problem within a small periodic cell. This improvement may not be very satisfactory if the integration in equation (A.66) needs to be performed at each and every point in the reciprocal space or the k-space since there are infinite numbers of k-points. However since the electronic wavefunction at k-points close to each other will be very similar, it is possible to replace the above integral as a discrete sum over limited number of k-points.

\[
\frac{\Omega}{(2\pi)^3} \int \left| \psi_k(\vec{r}) \right|^2 \delta(E_F - \varepsilon_k) d^3k \quad \rightarrow \quad \frac{1}{N_{k\text{-point}}} \sum f_k
\]  

(A.67)

The error due to this approximation can be minimized by using large number of k-points. Usually it is practised to converge the energy of the system with respect to the number of k-points in the calculation. However, as the size of the simulation cell in real space gets larger the size of the reciprocal space cell becomes smaller. This implies that as the simulation cell in real space becomes bigger, the k-space and hence the number of k-points becomes smaller. If the simulation cell is large enough then a single k-point (often referred as \( \Gamma \)-point) is also good enough for the calculation purpose.
A finite number of planewaves are required to perform the computations. Since the accuracy of the Kohn-Sham potential is dependant on the accuracy of basis set used for Kohn-Sham orbitals, it is apparent that a larger basis set would result in a more accurate Kohn-Sham potential. If plane waves are the basis set then the Kohn-Sham potential needs to be converged with respect to the number of planewaves. From equation (A.84), it can be seen that a higher modulus of $\vec{G}$ would result in higher number of planewaves. Hence, a limit is placed in the calculations where the $\vec{G}$ vectors with a kinetic energy lower than the specified cut-off are only considered for a calculation.

$$\frac{\hbar^2}{2m} |\vec{G}|^2 \leq E_{\text{cut}}$$  \hspace{1cm} (A.88)

The precision of the planewave implementation of Kohn-Sham density functional theory approach is thus dependant on the parameter $E_{\text{cut}}$, as per equation (A.88). Some of the advantages and disadvantages of using planewaves as basis functions are

- Planewaves are orthonormal and energy independent.
- Planewaves are not biased to any particular atom. Hence the entire space is treated on an equal footing and hence does not cause the basis set superposition error (due to overlap of individual atom’s basis set)
- The conversion between real and reciprocal space representations can be efficiently performed using Fast-Fourier transform algorithms and hence the computational cost can be decreased by performing the calculations in the reciprocal space.
- However, it can not take advantage of the vacuum space in the simulation cell by avoiding having a basis set in that region.
- Since the planewaves are independent of the positions of atoms, Hellman-Feynman theorem can be used to compute the forces\textsuperscript{15}, thereby reducing the computational cost. In other words, if a basis set
is dependant on the nuclear coordinates, then while calculating the forces the derivatives of the coefficients (with respect to nuclear coordinates) associated with the basis set also need to be computed. However if the basis set is independent, the variationally minimized coefficients can be used, as it they are, to compute the forces.

\[
\frac{\partial \langle E \rangle}{\partial R_n} = \frac{\partial}{\partial R_n} \left( \sum_i c_i^* \phi_i | H | \sum_j c_j \phi_j \right) \quad \Rightarrow \quad \sum_i \sum_j c_i^* c_j \left< \phi_i^* \frac{\partial H}{\partial R_n} \phi_j \right> \quad (A.89)
\]

- The valence wavefunctions are nodal in the core region of the atom (Pauli’s exclusion principle) and hence a large number of planewaves are needed to represent these large oscillations.

For a practical application of planewaves approach, a solution to the *nodal structure of valence wavefunctions* problem needs to be identified. The solution is to use the frozen core approximation i.e. to treat the core electrons and the nucleus as a *pseudocore*. The consequence is that the electron-nuclear potential will also have to replaced by a *pseudopotential*. Since this pseudopotential eradicates the core electrons from the system, it is very important that the pseudopotential takes into account the electron-nucleus interaction (as if shielded by the core electrons) and the electron-electron interaction (the classical Columbic and exchange-correlation interaction between the valence and core electrons). Hence the pseudopotential is angular momentum dependant as well. Due to this pseudopotential, the all electron wave function also gets replaced by the *pseudo-wavefunction*. Outside a certain cut-off radius the pseudopotential matches the true potential of the system and the pseudo-wavefunction matches the true wavefunction of the system (*cf*. Fig. A.3).

Additionally, it is worth noting that the contribution of core electrons to chemical bonding is negligible and only the valence electrons play a significant part in it. The core electrons play an important part in
the calculation of the total energy though and this implies that the removal of core electrons will also result in lower energy differences between different configurations, thereby reducing the efforts in achieving the required accuracy. As mentioned before, less number of planewaves is required than with the all-electron electron approach.

Figure A.3: The wavefunction of the system under the nuclear potential and under the pseudopotential \( \Psi_{AE}[Z/r] \) and \( \Psi_{pseudo}[\nu_{pseudo}] \).
Hamann, Schluter and Chiang\textsuperscript{58} laid down a set of conditions for a good pseudopotential. Those are

1. The all electron and pseudo valence eigenvalues agree for a particular atomic configuration.

2. The all electron and pseudo-wavefunction agree beyond a chosen core radius $r_{\text{cut}}$.

3. The logarithmic derivative of both the wavefunctions agree at $r_{\text{cut}}$, i.e.

$$
\left. \frac{d}{dr} \ln \Psi_{AE} \right|_{r_{\text{cut}}} = \left. \frac{d}{dr} \ln \Psi_{\text{pseudo}} \right|_{r_{\text{cut}}} \Rightarrow \left. \frac{\Psi'_{AE}}{\Psi_{AE}} \right|_{r_{\text{cut}}} = \left. \frac{\Psi'_{\text{pseudo}}}{\Psi_{\text{pseudo}}} \right|_{r_{\text{cut}}}.
$$

4. Though inside $r_{\text{cut}}$ the pseudo and all electron wavefunctions and the respective potentials differ, the integrated charge densities for both agree i.e.

$$
\int_{0}^{r_{\text{cut}}} |\Psi_{AE}|^2 \, d^3r = \int_{0}^{r_{\text{cut}}} |\Psi_{\text{pseudo}}|^2 \, d^3r.
$$

5. The first energy derivatives of the logarithmic derivatives of both the wavefunctions agree at $r_{\text{cut}}$.

All the pseudopotentials that satisfy condition 4 are called as norm-conserving pseudopotentials since the “norm” is conserved. When a pseudopotential is developed, above conditions (equivalency of energies and the first derivatives) are satisfied for the reference energy, however, with a change in the chemical environment of the atoms, the eigenstates will be at a different energy. Hence, for practical application of the pseudopotential, it has to have the capability of reproducing the above equalities with the all electron wavefunction in different chemical environments and in a wider range of energies. It was shown that the norm-conserving condition enhances this transferability\textsuperscript{58}. The two key aspects associated with any pseudopotential are “softness” and “transferability”. A soft pseudopotential means that fewer planewaves are needed, more electrons are frozen in the pseudocore and a large $r_{\text{cut}}$ is
employed. However, to make the pseudopotential more transferable, fewer electrons should be frozen in the *pseudocore* (more electrons treated explicitly), small $r_{\text{cut}}$ is employed and hence more planewaves are required. A balance need to be sought between softness and transferability, while developing the pseudopotential.

In addition to the conditions listed above, Hamann, Schluter and Chiang\textsuperscript{58} also provided with a methodology to generate the norm-conserving pseudopotentials. Generation of pseudopotential begins with the all electron calculations. The atomic potential is multiplied by a cut-off function so as to eliminate the strong attractive part. The parameters of the cut-off function are adjusted to give eigenvalues equal to the all electron calculations and the pseudowavefunctions which will agree with the all electronic wavefunction after the cut-off radius. The total potential is then calculated by inverting the Schrödinger equation. The total pseudopotential acting on the valence electrons is then screened by subtracting the classical Columbic potential and the exchange-correlation potential, to obtain the ionic pseudopotential. Kerker\textsuperscript{59} and Troullier-Martins\textsuperscript{60} simplified the above procedure of constructing the pseudopotential by modifying the valence wavefunction instead of modifying the potential, as suggested by Hamann-Schluter and Chiang.\textsuperscript{58}

The Troullier-Martins wavefunction is of the following form

$$\psi_l(r) = r^{l+1} \exp \left( c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12} \right)$$  \hfill (A.90)

where the coefficients are determined using the Hamann-Schluter-Chiang conditions.

Since the norm-conserving pseudopotential that can be developed using the above procedure, while satisfying the Hamann, Schluter and Chiang criteria, is angular momentum dependant (spherical symmetry
due to the potential of the nucleus and angular momentum dependency (due to the core electrons), it can be written in a generalized form as:

\[ v_{\text{pseudo}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} v^l (r) P^{lm} (\omega) \]  

(A.91)

where \( l \) is the azimuthal quantum number \( (s, p, d, f) \), \( m \) is the magnetic quantum number and \( P^{lm} (\omega) \) is a projector on angular momentum functions. An approximate way is to treat one specific angular momentum (typically the highest value of \( l \) for which the pseudopotential is generated) as the local part and the non-local part then consists of the difference between this local part and the actual angular momentum dependant pseudopotential. The pseudopotential is then written as

\[ v_{\text{pseudo}} = v_{\text{local}} (r) + \sum_{l,m} \Delta v^l (r) P^{lm} (\omega) \]

(A.92)

Thus, the local potential describes the interaction outside the pseudocore and the non-local part describes the interaction with core electrons. This type of pseudopotential is also called as semi-local pseudopotential since (i) the local part has one specific angular momentum and (ii) the projection operators act only on the angular variables of the position vector. The energy resulting from the local part of the pseudopotential can be calculated conveniently as \( \left( \int d^3 r \rho (r) v_{\text{local}} (r) \right) \), however, the non-local part is slightly more complicated due to the fact that the operator in the planewave basis set does not have a simple form in both, the real and the \( k \)-space. The two methods used to calculate the contribution of the non-local part of the pseudopotential to the energy are as follows:

1. Gauss-Hermite Integration:

The energy associated with the semi-local potential \( v_{\text{semilocal}} \) is given in the reciprocal space as
\[ E_{\text{semilocal}} = \sum_i \langle \varphi_i | V_{\text{semilocal}} | \varphi_i \rangle = \sum_i \sum_{G} \sum_{G'} \langle \varphi_i | \tilde{G} | \tilde{G'} \rangle \langle \tilde{G'} | V_{\text{semilocal}} | \varphi_i \rangle = \frac{1}{\Omega} \sum_i \sum_{G} \sum_{G'} c_i^* (\tilde{G}) c_i (\tilde{G'}) \hat{v}_{\text{semilocal}} (\tilde{G}, \tilde{G'}) \] (A.93)

If the angular momentum projector operator is given in the form of
\[ P_{lm} (\tilde{G}) = \langle Y_{lm} | \tilde{G} \rangle \], where \( Y_{lm} \) are spherical harmonics, and a spherical wave expansion for \( \tilde{G} \) is used then a simplified form (analogous to \( v_{\text{semilocal}} \) in equation A.92) for \( \hat{v}_{\text{semilocal}} \) is given as,
\[ \hat{v}_{\text{semilocal}} = \frac{16 \pi^2}{\Omega} \sum_{l,m} Y_{lm}^* (\tilde{G}) S^* (\tilde{G}) \sum_{l',m} Y_{lm} (\tilde{G'}^*) S (\tilde{G'}) \times \int r^2 dr \Delta v^I (r) J_l (Gr) J_l (G'r) \] (A.94)
where \( J_l \) is the Bessel function of the first kind with integer order \( l \). The first part of equation (A.94) can be calculated analytically, however, the second part is numerically integrated using the Gaussian quadrature formula such that \( \int r^2 f(r) dr \approx \sum_i w_i f (r_i) \).

2. Kleinman-Bylander method\textsuperscript{63}:

The scheme proposed by Kleinman and Bylander involves the following potential operator which substitutes the potential operator \( \hat{v}_{\text{semilocal}} \).
\[ V_{KB} = \frac{\langle \tilde{G} | \delta v^I \Psi_{l,m} \rangle \langle \delta v^I \Psi_{l,m} | \tilde{G'} \rangle}{\langle \Psi_{l,m} | \delta v^I | \Psi_{l,m} \rangle} \] (A.95)
where \( \Psi_{l,m} \) is the atomic pseudowavefunction and \( \delta v^I = v_{\text{pseudo}} - v_{\text{local}} \). The energy associated is then given as
\[ E_{KB} = \sum_i \langle \varphi_i | V_{KB} | \varphi_i \rangle \]
\[ = \sum_i \sum_{G} \sum_{G'} c_i^* (\tilde{G}) c_i (\tilde{G'}) \sum_{l,m} C_{l,m} \langle \tilde{G} | \delta v^I \Psi_{l,m} \rangle \langle \delta v^I \Psi_{l,m} | \tilde{G'} \rangle \] (A.96)
If a unit operator is inserted between the bra and ket of the element \( \langle \bar{G} | \delta v' \Psi_{l,m} \rangle \), the wavefunction \( \Psi_{l,m} \) is written in the form of radial wavefunction and spherical harmonics as \( |\Psi_{l,m}\rangle = |\chi_l\rangle |Y_{l,m}\rangle \) and a spherical wave expansion for \( \bar{G} \) is used then
\[
\langle \bar{G} | \delta v' \Psi_{l,m} \rangle = 4 \pi i \int \delta(\bar{G}) Y_{l,m} \left( \bar{G} \right) r^2 dr J_1(Gr) \delta v' \chi_l
\]
(A.97)
Substituting equation (A.97) into equation (A.96), we get the final expression for the energy as
\[
E_{KB} = \frac{16 \pi^2}{\Omega} \sum_i \sum_{G} \sum_{G'} \sum_{l,m} C_{i,m} c_i \left( \bar{G} \right) c_i' \left( \bar{G}' \right) S' \left( \bar{G} \right) S \left( \bar{G}' \right) \times
Y'_{l,m} \langle \bar{G} \rangle Y_{l,m} \left( \bar{G} \right)' \left( \int r^2 dr J_1(Gr) \delta v' \chi_l \right) \left( \int r'^2 dr' J_1(G'r') \delta v' \chi_l \right)
\]
(A.98)
It has to be noted that the Kleinman-Bylander scheme is computationally more efficient than the Gauss-Hermite numerical integration scheme to calculate the energy contribution of the semi-local part of the pseudopotential, however, constructing an accurate and transferable pseudopotential using the Kleinman-Bylander scheme can be challenging due to its complex form.64

It is also possible to generate the pseudopotential directly in an analytical form in such a way that it fulfils the Hamann-Schluter-Chiang conditions. The pseudopotential is separated in such a way that the local part is completely independent of the angular momentum and the non-local part accounts for the angular momentum. One of the most popular pseudopotential with this type of construction is the Goedecker pseudopotential65,66 where the local part is given as
\[
v_{\text{local}}(r) = \frac{-Z_{\text{ion}}}{r} \text{erf} \left( \frac{r}{r_{\text{local}} \sqrt{2}} \right) + \exp \left[ -\frac{1}{2} \left( \frac{r}{r_{\text{local}}} \right)^2 \right] \times
\left[ c_1 + c_2 \left( \frac{r}{r_{\text{local}}} \right)^2 + c_3 \left( \frac{r}{r_{\text{local}}} \right)^4 + c_4 \left( \frac{r}{r_{\text{local}}} \right)^6 \right]
\]
(A.99)
where $Z_{ion}$ is the charge on the pseudocore and $r_{local}$ is the range of the ionic charge distribution. The non-local part of the pseudopotential is given as

$$v_{non-local}(r, r') = \sum_{l,m, i,j=1}^{l+1} Y_{lm} \sqrt{2} \left\{ \frac{r^{l+2i-2} \exp\left(-\frac{1}{2} \left( \frac{r}{r_j} \right)^2 \right)}{r_j^{l+(4i-1)/2} \sqrt{\Gamma(l+(4i-1)/2)}} h_{ij}^l \right\} \left( \frac{r'^{l'+2j-2} \exp\left(-\frac{1}{2} \left( \frac{r'}{r_j'} \right)^2 \right)}{r_j'^{l'+(4j-1)/2} \sqrt{\Gamma(l'+(4j-1)/2)}} Y_{lm}' \right) \quad (A.100)$$

where $Y_{lm}(r)$ are spherical harmonics and $\Gamma$ is the gamma function. The benefit of the above pseudopotential is that it has an analytical expression in the Fourier space (or k-space) as well. The parameters of the above pseudopotential are computed by minimizing the objective function which could be a sum of differences of properties calculated using the pseudopotential and the all electron calculations.

### A.2.5 Optimization techniques

The electronic structure calculation methods described in sections A.2.2 – A.2.4 are used to calculate the ground state energy of the system at a particular nuclear (atomic) configuration. The energy calculated using the electronic structure calculation methods is a function of the nuclear configurations only. However, an arbitrarily chosen nuclear configuration/geometry may not be the most stable (lowest energy) one and hence it is needed to minimize the system energy with respect to the nuclear configuration. Finding the stationary point of the system where the first derivative of energy with respect to the nuclear configuration is
zero \( \nabla E(\vec{R}) = 0 \) is an important aspect of molecular modeling. Finding the nearest stationary point of the domain in which the system is lying can be done with some of the most common minimization/optimization methods like the Newton-Raphson, Steepest-Descent etc. For example, if a Newton-Raphson method is used then the steps involved in the optimization process will be as follows:

1. Calculate \( E(\vec{R}_{\text{initial}}) \)

2. Calculate numerically \( \nabla E(\vec{R})\big|_{\vec{R}_{\text{initial}}} \) and \( \nabla H(\vec{R})\big|_{\vec{R}_{\text{initial}}} \) where \( \nabla H \) is the Hessian matrix.

3. Continue the iteration scheme \( \vec{R}_i = \vec{R}_{\text{initial}} - \nabla^{-1}(\vec{R})\big|_{\vec{R}_{\text{initial}}} \nabla E(\vec{R})\big|_{\vec{R}_{\text{initial}}} \) till the convergence is reached \( \nabla E(\vec{R}) = 0 \).

This type of energy minimization leads to a local minimum and the minimized configuration may not be the “true” configuration which lies at the global minimum. Two of the most widely used methods in molecular simulations to find the global minimum more reliably are Molecular Dynamics and Monte-Carlo. Monte-Carlo method is based on making random changes to the system configuration. A specific criterion is defined to accept or reject these random changes, thus helping the system to move towards lower energy configuration states. Molecular dynamics on the other hand is a more physical method since every atom (nucleus) is assigned a finite velocity at the initial system configuration. Consecutive configurations are then generated by solving the Newton’s equations of motion for all the atoms. The velocity of the atoms is dependent on the kinetic energy of the system, which in turn governs the experimentally measurable quantity of the system, i.e. the temperature.
\( E_{\text{kinetic}} = \left( \frac{1}{2} m V^2 \right) = \frac{1}{2} k_B T \). Thus, molecular dynamics also accounts for the finite temperature effect on the system. In molecular dynamics, the system explores the potential energy surface part with the energies lower than the kinetic energy of the system. Molecular dynamics is also a better representation of the physical state of the system since most of the systems are at some finite temperature and the temperature dependant dynamics observed in this method are the real dynamics of the system. The forces acting on every atom of the system are calculated from the kinetic energy and the potential energy (the energy calculated using the electronic structure calculations or force field methods) of the system at each configuration during the molecular dynamics run. Details of the molecular dynamics method are described in the next section.

![Energy Trial Configuration](image.png)

**Figure A.4:** An illustration of a 1-dimensional potential energy surface of a system.
### A.2.5.1 Molecular Dynamics algorithm

As mentioned before, nuclei are orders of magnitude heavier than electrons and hence they can be treated using the classical Newtonian mechanics i.e. their motion can be calculated using Newton’s equations of motion. If the system contains $n$ atoms with coordinates $\vec{R}(R_1, R_2, \ldots, R_n)$ and the potential energy calculated from electronic structure calculations at a fixed configuration $\vec{R}$ is $E(\vec{R})$, then the Newton’s second law of motion $\text{Force} = \text{mass} \times \text{acceleration}$ can be written in the differential form as

$$- \frac{dE}{d\vec{R}} = m \frac{d^2 \vec{R}}{dt^2} \quad (A.101)$$

It can be shown that equation (A.101) conserves the total (kinetic+potential) energy of the system. If $T^R$ is the kinetic energy then,

$$\frac{d(E + T^R)}{dt} = \frac{dE}{dt} + \frac{dT^R}{dt} = \frac{dE}{d\vec{R}} \frac{d\vec{R}}{dt} + \frac{d}{dt} \left[ \frac{1}{2} m \left( \frac{d\vec{R}}{dt} \right)^2 \right]$$

$$\therefore \frac{dE}{d\vec{R}} = -m \frac{d^2 \vec{R}}{dt^2} \quad \text{from equation (2.101)} \quad (A.102)$$

$$\therefore \frac{d(E + T^R)}{dt} = -m \frac{d^2 \vec{R}}{dt^2} \frac{d\vec{R}}{dt} + m \frac{d\vec{R}}{dt} \frac{d^2 \vec{R}}{dt^2} = 0$$

To calculate the evolution of atomic positions with time, equation (A.101) needs to be solved. The procedure is described below and is shown in Fig. A.5. The advancement of nuclear coordinates in a small timestep $\Delta t$ can be given by the Taylor series expansion as,

$$\vec{R}_{i+1} = \vec{R}_i + \frac{d\vec{R}_i}{dt} \left( \Delta t \right) + \frac{1}{2} \frac{d^2 \vec{R}_i}{dt^2} \left( \Delta t \right)^2 + \frac{1}{3!} \frac{d^3 \vec{R}_i}{dt^3} \left( \Delta t \right)^3 + \ldots \quad (A.103)$$

If we go one timestep back, then a similar expression can be written as

$$\vec{R}_{i-1} = \vec{R}_i - \frac{d\vec{R}_i}{dt} \left( \Delta t \right) + \frac{1}{2} \frac{d^2 \vec{R}_i}{dt^2} \left( \Delta t \right)^2 - \frac{1}{3!} \frac{d^3 \vec{R}_i}{dt^3} \left( \Delta t \right)^3 + \ldots \quad (A.104)$$

Adding equations (A.103) and (A.104) gives,
\[ \ddot{\mathbf{R}}_{t+1} = \left( 2 \dot{\mathbf{R}}_t - \dot{\mathbf{R}}_{t-1} \right) + \frac{d^2 \ddot{\mathbf{R}}}{dt^2} \left( \Delta t \right)^2 + \ldots \]  

(A.105)

It can be seen that equation (A.105) calculates the configuration at a particular timestep using the configurations of two previous timesteps and the error is of the order \( (\Delta t)^4 \). To start the molecular dynamics calculations this way, the configuration at a timestep before the starting configuration has to be known and it can be approximated as \( \ddot{\mathbf{R}}_{t-1} = \ddot{\mathbf{R}}_0 - \left( \frac{d\ddot{\mathbf{R}}_0}{dt} \right) (\Delta t) \).

![Diagram of the Velocity Verlet Molecular dynamics algorithm](image)

**Figure A.5:** The Velocity Verlet Molecular dynamics algorithm.

The numerical method described above is also referred as Verlet algorithm. However, some of the disadvantages of this method are that it requires storage of two sets of positions and velocities do not appear explicitly (which is needed when a simulation needs to be run at a
constant temperature). It may also give rise to a numerical instabilities since a small number \((\Delta t)^2\) containing term is added to the difference between two large numbers \((2\vec{R}_i - \vec{R}_{i-1})\). Hence the Velocity Verlet algorithm,\(^{68}\) as described below, is a more popular scheme to solve molecular dynamics equations.

\[
\vec{R}_{i+1} = \vec{R}_i + \left( \frac{d\vec{R}}{dt} \right) (\Delta t) + \frac{1}{2!} \left( \frac{d^2\vec{R}}{dt^2} \right) (\Delta t)^2
\]

\[
\frac{d\vec{R}_{i+1}}{dt} = \left( \frac{d\vec{R}_i}{dt} \right) + \frac{1}{2} \left( \frac{d^2\vec{R}_i}{dt^2} + \frac{d^2\vec{R}_{i+1}}{dt^2} \right) (\Delta t)
\]

(A.106)

A more general formulation of the above described equations of motion can be done in the form of Lagrangian. Lagrangian, in classical mechanics, is defined as the difference between the kinetic energy and the potential energy of the system. The benefit of using Lagrangian formulation is that it is not restricted to a particular type of coordinate system. If \(q\) are the coordinates and \(\dot{q}\) are their time derivatives then the Lagrangian can be written as\(^7\)

\[
\mathcal{L}(q, \dot{q}) = T^g(q) - E(q)
\]

(A.107)

The equations of motion in the Lagrangian formulation can be obtained from the following Euler-Lagrange equation.

\[
\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{q}} \right) - \frac{\partial \mathcal{L}}{\partial q} = 0
\]

(A.108)

where \(\dot{q}\) is treated as a variable. In Cartesian coordinates \(q = \vec{R}\) and \(\dot{q} = d\vec{R}/dt\) and in that case equation (A.108) reduces to the Newton’s equation (A.101) as follows.
\[
\frac{d}{dt} \left( \frac{\partial \mathbf{L}}{\partial \dot{\mathbf{q}}} \right) - \frac{\partial \mathbf{L}}{\partial \mathbf{q}} = 0 \quad \Rightarrow \quad \frac{d}{dt} \left( \frac{\partial \mathbf{L}}{\partial \dot{\mathbf{q}}} \right) = \frac{\partial \mathbf{L}}{\partial \dot{\mathbf{q}}} 
\]

\[
\Rightarrow \quad \frac{d}{dt} \left( \frac{dR}{dt} \right) = -\frac{\partial \mathbf{L}}{\partial \dot{\mathbf{q}}} = -\frac{dE}{d\mathbf{R}} 
\]

A.2.5.2  **Nose-Hoover thermostat**

As shown above, the molecular dynamics algorithm described in the previous section conserves the total energy. Hence the system falls naturally under the microcanonical ensemble where the total number of atoms, the system’s volume and its total energy are conserved. Since the kinetic energy is the difference between the total energy (constant) and the potential energy (changing with atomic positions) of the system, it may vary significantly during the course of a molecular dynamics run, thereby causing temperature variations. When the objective of any simulation study is to support/validate/predict the experimental data, it is more appropriate to be able to perform the simulations at constant temperature condition. One of the most popular ways to perform molecular dynamics simulations at constant temperature is to integrate the system with a heat bath. Heat transfer occurs between the system and the heat bath so as to keep the system at a constant temperature. The mathematical formulation for such a heat bath was provided by Nose and Hoover\(^{69, 70}\) and hence is commonly referred as Nose-Hoover thermostat. In this formulation, to the physical system of \(n\) particles with coordinates \(\mathbf{R}\), potential energy \(E\)
and velocities \( \frac{d\vec{R}}{dt} = \dot{\vec{R}} \), an artificial dynamical variable \( \dot{s} \) representing the heat bath is added. This additional variable has mass \( M \) (actual unit of \( M \) is \( \text{energy} \times \text{time}^2 \)) and velocity \( \dot{s} \). The interaction between the actual system and the heat bath is obtained through this parameter \( \dot{s} \). It acts as a time scaling parameter as \( \Delta t = \dot{s}^{-1} \Delta \tilde{t} \) where \( \Delta t \) is the time interval in the real system and \( \Delta \tilde{t} \) is the time interval of the extended system containing the real system and the heat bath. As a consequence, the atomic coordinates remain similar in both the cases but the velocities are modified as

\[
\vec{\tilde{R}} = \vec{R} \quad \text{and} \quad s = \sqrt{s}
\]

(A.110)

The definition of parameter \( \dot{s} \) and its interaction with the real system as a heat bath is more intuitive in equation (A.110) where it can be seen as a velocity scaling parameter \( [\text{Temperature} \propto (\text{velocity})^2] \). With such an integrated heat bath, the extended Lagrangian of the system, analogous to equation (A.107), becomes

\[
\mathcal{L}(\vec{R}, \dot{\vec{R}}, \dot{s}, \ddot{s}) = \frac{1}{2} \sum_{i=1}^{n} m \dot{s}^2 \dot{R}_i^2 - E(\vec{R}) + \frac{1}{2} M \dot{s}^2 - \phi k_b T \ln \dot{s}
\]

(A.111)

where \( \phi \) is equal to the degrees of freedom \( (\phi = \text{DOF}_{\text{real}} \quad \text{or} \quad \phi = \text{DOF}_{\text{real}} + 1) \), the first two terms are the kinetic and potential energies of the real system and the last two terms are the kinetic and potential energies of the heat bath. It was shown that this form of the potential energy of the heat bath results in canonical ensemble of the real system.\(^70\) It has to be noted that the sign of \( \dot{s} \) determines the direction of heat flow. If \( \dot{s} < 0 \) then heat flows into the real system and if \( \dot{s} > 0 \) then heat flows out of the real system. The equations of motion derived from the Lagrangian of equation (A.111) are
\[
\ddot{R}_i = m_i^{-1} s^{-2} \left( -\frac{\partial E}{\partial R_i} - 2s^{-1} \dot{s} \dot{R}_i \right) 
\]

\[
\ddot{s} = M^{-1} \dot{s}^{-1} \left[ \sum_{i=1}^{n} m_i \dot{s}^2 \dot{R}_i^2 - \varphi k_u T \right] 
\]

where the first term represents the equation of motion of the real variables and the second term represents the equation of the \( \dot{s} \) variable. Equation (A.112), representing the extended system, can be numerically integrated based on the timestep \( \Delta \tau \). However, the atomic coordinates and velocities of the real system will evolve at a timestep of \( \Delta t = s^{-1} \Delta \tau \). This implies that, if the molecular dynamics algorithm is implemented using the thermostat of equation (A.112), then the real system will evolve at uneven time intervals. Hence the equations were reformulated\(^6\) from extended system to real system as follows. Since \( \Delta t = \dot{s}^{-1} \Delta \tau \), \( \frac{d}{dt} = \dot{s} \left( \frac{d}{d\tau} \right) \).

\[
s = \tilde{s}, \quad \dot{s} = \tilde{s} \dot{\tilde{s}}, \quad \ddot{s} = \tilde{s}^2 \ddot{\tilde{s}} + \tilde{s} \dot{\tilde{s}}^2, \quad \tilde{R} = \dot{\tilde{R}} \\
\dot{\tilde{R}} = \dot{s} \tilde{R}, \quad \ddot{\tilde{R}} = \dot{s}^2 \ddot{\tilde{R}} + \dot{s} \dot{\tilde{s}}^2 \tilde{R} \quad \text{and} \quad \frac{dE}{dR} = \frac{dE}{d\tilde{R}} 
\]

The Lagrangian equations of motion (A.112) according to above transformation then become

\[
\ddot{R}_i = m_i^{-1} \left( -\frac{\partial E}{\partial R_i} \right) - \xi \dot{R}_i 
\]

\[
\ddot{s} = -M^{-1} \left[ \sum_{i=1}^{n} m_i \dot{R}_i^2 \right] \left[ k_u \Theta \frac{T}{\sum_{i=1}^{n} m_i \dot{R}_i^2} - 1 \right] 
\]

where \( \xi = s^{-1} \dot{s} \). It can be seen that the magnitude of parameter \( M \) determines the coupling between the heat bath and the real system. A very large value of \( M \) will result in poor temperature control (or a microcanonical or \( \text{NVE} \) ensemble) whereas a very small value of \( M \) will result in high frequency oscillations.
The Nose-Hoover thermostat, as described above, is one of the most widely used thermostat method in molecular dynamics simulations. However, it has been reported that this type of thermostat suffers from the problem of non-ergodicity\(^{72,73}\) for systems with certain types of Hamiltonians. A very similar thermostat method, called as Nose-Hoover chain thermostat\(^{72}\) cures this problem. In this method, the thermostat applied to the real system is thermostatted by another similar thermostat and so on. The mathematical formulation for the Nose-Hoover chain thermostat is given as follows.

\[
\dot{R}_i = m_i^{-1}\left(-\frac{\partial E}{\partial R_i} - \xi_i \dot{R}_i\right)
\]

\[
\dot{\xi}_1 = -M_1^{-1}\left(\sum_{i=1}^{n} m_i \dot{R}_i^2\right) \left(k_B T \sum_{i=1}^{n} m_i R_i^2 - 1\right) - \xi_1 \xi_2
\]

\[
\dot{\xi}_2 = M_2^{-1}\left[M_1 \xi_1^2 - k_B T\right] - \xi_2 \xi_3
\]

(A.115)

\[\text{A.2.6 Car-Parrinello Molecular Dynamics}\]

Molecular dynamics in atomic level modeling can be classified into following two main categories:

1. Classical molecular dynamics using force field: The potential energy \(E(\vec{R})\) and forces \(dE/d\vec{R}\) are calculated using force-field methods or molecular mechanics, as described in section A.2.1 and the equations of motion are solved as described in section A.2.5.

2. Ab Initio molecular dynamics: The potential energy and forces are calculated using electronic structure calculations described in sections A.2.2 – A.2.4 and the equations of motion are solved as described in section A.2.5.
Classical molecular dynamics is computationally much less expensive than \textit{ab initio} molecular dynamics since ab-initio molecular dynamics require electronic structure calculations. This also means that the time and length scales that can be accessed by classical molecular dynamics are much larger than those by \textit{ab initio} molecular dynamics. However, as mentioned before, classical molecular dynamics is inadequate to model chemically complex systems (where electronic structure and bonding patterns change due to reactions, system contains transition metal compounds and simulations give rise to many novel molecular species) and hence \textit{ab initio} molecular dynamics remains the only option. In \textit{ab initio} molecular dynamics, when the electronic structure calculations (optimizing the wavefunction for a fixed nuclear configuration) are performed after every molecular dynamics time step, it is called as Born-Oppenheimer molecular dynamics and the Lagrangian associated with the Born-Oppenheimer molecular dynamics (without the thermostat) is

$$
\mathcal{L}_{\text{BO}} = \frac{1}{2} \sum_i m_i \dot{R}_i^2 - \langle \Psi | H | \Psi \rangle
$$

(A.116)

The above Lagrangian is appended to include the thermostat when \textit{ab initio} molecular dynamics is performed in a canonical ensemble. The electronic structure calculations in the Born-Oppenheimer molecular dynamics can be performed using Hartree-Fock, semi-empirical or Kohn-Sham DFT methods and can be performed explicitly for all the electrons or using the planewave-pseudopotential approach. Born-Oppenheimer molecular dynamics has the capability to significantly leverage the field of molecular dynamics by extending it to incorporate complex, diverse and less known systems in material science and chemistry. However, due to the associated computational expense, it did not gain the popularity that would justify its usefulness. A breakthrough in the field of \textit{ab initio} molecular dynamics was brought by Car-Parrinello\textsuperscript{74} with the
introduction of a modified method that would reduce the computational cost of \textit{ab initio} molecular dynamics. Unlike Born-Oppenheimer molecular dynamics, the Car-Parrinello scheme does not require the optimization of the wavefunction (or density) to be performed after every molecular dynamics timestep and it ensures that the electronic wavefunction stays close to the optimized value throughout the course of the molecular dynamics simulation. The details of Car-Parrinello method are given in the following section.

A.2.6.1 \textit{Car-Parrinello Scheme}

Born-Oppenheimer molecular dynamics is a combined modeling approach where the electronic motion is treated purely quantum mechanically and the nuclear motion is treated classically and hence electronic structure calculations (or wavefunction optimization) are required after every molecular dynamics step. If this quantum-classical two component system is mapped on to a completely classical formulation such that the \textit{movement} of the electronic structure (optimized before the molecular dynamics) also can be followed \textit{classically}, then it might be possible to avoid the electronic structure calculation after every time step and is needed only once. In other words, instead of optimizing the wavefunction for the modified Hamiltonian $H$ of the system after every molecular dynamics step, the wavefunction is directly propagated using a classical formalism. This is the fundamental idea behind the Car-Parrinello scheme.\textsuperscript{74}

The (potential) energy of the system, calculated using electronic structure calculations, is a function of nuclear coordinates but it can also be considered as a functional of the wavefunction which in turn consists of individual atom wavefunctions (as a Slater determinant). As discussed before, the forces on the nuclei are calculated by differentiating the
Lagrangian with respect to nuclear coordinates. Similarly, if a Lagrangian is defined such that it encompasses the motion of nuclei and the propagation of the electronic structure, then the forces on the wavefunction (so as to propagate it along time) can be calculated by taking a functional derivative of the Lagrangian with respect to the wavefunction. In this way the quantum mechanically calculated electronic wavefunction can be propagated classically. Car and Parrinello formulated this Lagrangian as

\[ \mathcal{L}_{cp} = \sum_i m_i \dot{R}_i^2 + \sum_j \frac{1}{2} \mu_j \langle \dot{\chi}_j | \dot{\chi}_j \rangle - \langle \Psi | H | \Psi \rangle + \text{constraints} \quad (A.117) \]

where \( \chi_j \) is the orbital/wavefunction of the \( j^{th} \) electron in the system, \( \mu \) (unit of \( \mu \) is \( \text{energy} \times \text{time}^2 \)) is the fictitious mass associated with the wavefunction and the constraints in equation (A.117) can be some external constraints on the system or internal constraints like orthonormality. It has to be noted that the kinetic energy term \( \sum_j \frac{1}{2} \mu_j \langle \dot{\chi}_j | \dot{\chi}_j \rangle \) has no relation with the physical quantum kinetic energy and is completely fictitious. The Euler-Lagrange equations will then be

\[ \frac{d}{dt} \frac{\partial \mathcal{L}_{cp}}{\partial R_i} = \frac{\partial \mathcal{L}_{cp}}{\partial \dot{R}_i} \quad \text{and} \quad \frac{d}{dt} \frac{\partial \mathcal{L}_{cp}}{\partial \dot{\chi}^*_i} = \frac{\partial \mathcal{L}_{cp}}{\partial \dot{\chi}^*_i} \quad (A.118) \]

From equation (A.118), the equations of motion become

\[ m_i \ddot{R}_i = -\frac{\partial}{\partial R_i} \langle \Psi | H | \Psi \rangle + \frac{\partial}{\partial R_i} \text{(constraints)} \]

\[ \mu \ddot{\chi}_i = -\frac{\partial}{\partial \dot{\chi}^*_i} \langle \Psi | H | \Psi \rangle + \frac{\partial}{\partial \dot{\chi}^*_i} \text{(constraints)} \quad (A.119) \]

Equation (A.119), in conjunction with the Nose-Hoover thermostat as described in section A.2.5.2, can then be numerically solved using the velocity verlet algorithm, as described in section A.2.5.1. The kinetic energy of the nuclei (and the system) is \( \sum_i m_i \dot{R}_i^2 \) and thus the temperature
of the system $T \propto \sum_{i} m_{i} \dot{R}_{i}^{2}$. Similarly the fictitious temperature associated with the wavefunction is $\propto \sum_{j} \frac{1}{2} \mu_{i} \langle \dot{\chi}_{i} | \dot{\chi}_{i} \rangle$. A very small value of $\mu$ is chosen so as to keep the fictitious temperature of the wavefunction very low. The reason for this choice will become clear later. The main concerns about the Car-Parrinello scheme would be as follows: (i) If the electronic wavefunction follows the Born-Oppenheimer surface throughout the molecular dynamics simulation, (ii) How the forces calculated using Car-Parrinello Lagrangian are equal to Born-Oppenheimer molecular dynamics forces and (iii) How the total energy of the system is conserved (microcanonical ensemble).\textsuperscript{15,75}

At the beginning of the Car-Parrinello molecular dynamics scheme, the electronic wavefunction is optimized for the initial nuclear configuration. When the nuclei start moving, their motion changes the electronic structure of the system thereby changing the wavefunction representing the minimum in the energy at an instantaneous nuclear configuration. According to the Car-Parrinello Lagrangian, the wavefunction is also propagated classically according to equation (A.119). As mentioned before, the Car-Parrinello molecular dynamics will follow the Born-Oppenheimer molecular dynamics when the wavefunction propagated using the Car-Parrinello scheme will result in the same electronic energy as that from the wavefunction which is optimized for the modified Hamiltonian. This is only possible when no additional energy from an external system (i.e. from the classical nuclear system) is transferred to the classically propagated quantum electronic system; because if the energy transfer occurs then the quantum system which is propagated classically need to be treated quantum mechanically so as to bring the electronic system to its minimum energy level. Also the “extra” energy transferred to the wavefunction will result in larger forces on the
wavefunction (in addition to \( \frac{\delta}{\delta \chi^*_i} \langle \Psi | H | \Psi \rangle \)), thereby deviating from the Born-Oppenheimer surface. In other words, if the energy from the nuclei is not transferred to the electronic system, the Car-Parrinello scheme should follow the Born-Oppenheimer molecular dynamics. This adiabaticity is achieved due to the virtue of the timescale difference between the very fast electronic motion and the slow nuclear motion. It is shown that when a small perturbation in the minimum energy state of a system results in some force on the wavefunction, then the minimum frequency related to the dynamics of the orbital is

\[
\omega_{\text{min}} \propto \left( \frac{E_{\text{gap}}}{\mu} \right)^{\frac{1}{2}}
\]

(A.120)

where \( E_{\text{gap}} \) is the energy difference between the highest occupied and the lowest unoccupied orbital. The parameter \( E_{\text{gap}} \) in equation (A.120) is determined by the physics of the system, however, the parameter \( \mu \) is completely fictitious and hence can be fixed to an arbitrary value. The frequency range of the orbital dynamics thus can be switched towards the higher side by choosing a very small value of \( \mu \). If a sufficiently small value is chosen then the power spectra emerging from the wavefunction dynamics (fast motion, high frequency) can be completely separated from that emerging from the nuclear dynamics (slow motion, low frequency). If these two power spectra do not have any overlap in the frequency domain then there will not be any energy transfer from the nuclei to the wavefunction. Thus the fictitious kinetic energy of the wavefunction

\[
\sum_j \frac{1}{2} \mu_j \langle \dot{x}_j | \dot{x}_j \rangle
\]

will remain constant. This fictitious kinetic energy is also a measure of the correctness of the Car-Parrinello implementation. In this way if the wavefunction or electronic structure during the Car-Parrinello
molecular dynamics follows the Born-Oppenheimer surface then the forces acting on the nuclei \( \frac{\partial}{\partial R_i} \langle \Psi | H | \Psi \rangle \) will be the same as Born-Oppenheimer molecular dynamics. The physical energy of the system is \( \sum_i m_i \dot{R}_i^2 + \langle \Psi | H | \Psi \rangle \), whereas the Car-Parrinello energy is \( \sum_i m_i \dot{R}_i^2 + \langle \Psi | H | \Psi \rangle + \sum_j \frac{1}{2} \mu_j \langle \dot{\chi}_j | \dot{\chi}_j \rangle \). Since

\[
\left\{ \sum_j \frac{1}{2} \mu_j \langle \dot{\chi}_j | \dot{\chi}_j \rangle \right\} - \left\{ \sum_i m_i \dot{R}_i^2 + \langle \Psi | H | \Psi \rangle \right\} = 0 \tag{A.121}
\]

and the fictitious kinetic energy remains constant, from statistical mechanical point of view, it can be said that the system is under microcanonical ensemble where the total energy of the system is conserved. Figure A.6 shows various energies of a model system of bulk crystalline silicon during the car-Parrinello run.

![Figure A.6: Variation of different energies during the Car-Parrinello molecular dynamics run of bulk silicon. Adapted from Pastore and Smargiass]({})

A minute inspection of Fig. A.6 shows that the oscillations in the fictitious kinetic energy are a mirror image of the oscillations in the
potential energy of the system (a few order of magnitude difference though). These can be attributed to the pull applied by the classically moving nuclei on the classically propagating wavefunction.

### A.2.7 Metadynamics

The Car-Parrinello molecular dynamics scheme, even though significantly reduces the computational cost of ab initio molecular dynamics, can not access the time scales more than a few picoseconds when hundreds of atoms are present in the simulation system (even with the state of the art computational servers). With the technological evolution in computer hardware and reduction in costs, researchers are hoping to increase the accessible length and timescales of ab-initio molecular dynamics simulations. However, to run a simulation equivalent to hundreds of nanoseconds (which is possible using classical force field molecular dynamics) and to be able to simulate realistic phenomena which take place at much larger timescales than that can be accessed by ab initio molecular dynamics, in addition to the development of computational hardware, it also becomes necessary to implement methods that can accelerate the events somehow to make them happen earlier. Ab-initio molecular dynamics is usually employed when chemical reactions are taking place in the system and if the reaction of interest is associated with a large energy barrier then the timescale for the reaction is large and thus becomes difficult to be accessed using ab initio molecular dynamics. Hence, a system may be stuck in a local minimum in the energy surface and may take too long computational time to cross the energy barrier to reach the global minimum (cf. Figure A.6).

The molecular dynamics simulation can be run at a higher temperature so as to accelerate the event which is expected to take place at a longer timescale in real system, however, this may cause some
undesirable and unrealistic events to happen in the system. There are several methods that have been implemented in the literature in the past to overcome this difficulty including umbrella sampling, nudged elastic band, finite temperature string method, transition path sampling, milestone, multiple timescale accelerated molecular dynamics, to name a few. The most recent of all these methods is called metadynamics and it has the following advantages:

1. It encompasses several benefits of all the above mentioned methods
2. It can accelerate the rare events so as to be able to see them in a realistic computational simulation time.
3. It can also be used to reconstruct the energy surface so as to get quantitative information about the energy landscapes and barriers.
4. It is coupled with the Car-Parrinello molecular dynamics by Iannuzzi et al. very recently.

The following two sub-sections describe the concept and mathematics behind the metadynamics technique.
A.2.7.1 Concept

The metadynamics technique, as described by Laio and Gervasio,\textsuperscript{82} is based on the principle of filling up the energy surface with potentials. As shown in Figure A.8, if the energy surface is plotted as a one dimensional function of a particular reaction coordinate and the system is residing in the potential well ‘A’ from which it is taking too long to escape due to the energy barriers then (cf. Figure A.7),

1. The potential well ‘A’ is filled up with small potentials so that system slowly comes to a higher energy position.
2. As soon as the middle potential well is filled up, the system escapes to the potential well ‘B’ on the left through the saddle point $S_1$.
3. The potential well ‘B’ is then gradually filled till the saddle point $S_2$ is reached then the system escapes to the potential well ‘C’.
4. Gradually, well ‘C’ is filled.
5. The system is forced to cross the energy barriers to reach the global energy minimum by filling up the potentials and if the potentials and the positions of their deposition are tracked, then the energy well can be reconstructed.\textsuperscript{84, 85}

![Energy landscape diagram](image)

**Figure A.8:** The system initially placed in well A goes to the global minimum in well C after filling up the energy surface. Adapted from Laio and Gervasio\textsuperscript{82}

\textbf{A.2.7.2 Extended Car-Parrinello Lagrangian for metadynamics}

As described above, the metadynamics technique is based on filling up the energy surface by dropping potentials at small time intervals in the coordinate space of interest. Though this method can be implemented in any type of molecular dynamics techniques (classical and \textit{ab initio}), the mathematics relevant to the implementation of this method in the Car-Parrinello scheme is described here, as originally given by Ianuzzi et al.\textsuperscript{83}
and further extended by Laio et al.\textsuperscript{82, 86-88} If \( \mathbf{\xi} \) is a vector of the collective variables (coordinates of interest) that form the energy well to be filled or that form the energy surface of interest (for ex. it can be the bond distance between two hydrogen atoms if the dynamics and energy surface of hydrogen dissociation is studied or it can be some coordination number if a more complex phenomenon like protein conformation is studied), the metadynamics approach treat them as additional variables in the system and the car-Parrinello Lagrangian is then extended as\textsuperscript{83}

\[
\mathcal{L}_{MTD} = \mathcal{L}_{CP} + \sum_{cv} m_{cv} \dot{\mathbf{\xi}}_{cv} - \frac{1}{2} \sum_{cv} k_{cv} \left[ \mathbf{S}_{cv} \left( \mathbf{\bar{R}}_{cv} \right) - \mathbf{S}_{cv} \right]^2 + v_{cv}(t, \mathbf{\xi}) \tag{A.122}
\]

where \( \mathcal{L}_{CP} \) is the Lagrangian defined in equation A.117, the first term indicates the kinetic energy of the collective variables, the second term is the harmonic restraining potential and the last term is the potential that is dropped to fill the energy well in the collective variable \( \mathbf{\xi} \) space at different time intervals. Defining the kinetic and potential energy of the additional collective variables allows controlling their dynamics in the canonical ensemble using a suitable thermostat. The dynamics of ionic and electronic (fictitious) motion are separated in the Car-Parrinello molecular dynamics by choosing an appropriate value for the mass associated with the fictitious kinetic energy of the wavefunction (as described in section A.2.6.1). Analogous to the original Car-Parrinello scheme, the dynamics of the collective variables are separated from the ionic and fictitious electronic motion by choosing an appropriate value for the fictitious mass \( m_{cv} \) of the collective variables. If the fictitious mass \( m_{cv} \) is large then the dynamics of the collective variables will be slow and thus can be separated from the ionic dynamics. The forces acting on the collective variables are due to the potential energy \( k_{cv} \left[ \mathbf{S}_{cv} \left( \mathbf{\bar{R}}_{cv} \right) - \mathbf{S}_{cv} \right] \), and due to the potential drops \( v_{cv}(t, \mathbf{\xi}) \). Hence the dynamics of the collective variables are
also dependant on $k_{cv}$. It has been shown that the extra term in metadynamics introduces an additional frequency for the motion of collective variables as $\sqrt{k_{cv}/m_{cv}}$\textsuperscript{86}. The force constant $k_{cv}$ is chosen such that the collective variables are close to the actual coordinates of the system. If a small $k_{cv}$ is used, it will result in a large variation in the collective coordinate even with a small potential drop. However, a very large value may result in very small timestep and excessive long computational time. Since $k_{cv}$ is selected by the above constraints, it sets limitation on the value of $m_{cv}$ so as to maintain the adiabaticity.

The potential used to fill the energy well at a time $t$ is given as \textsuperscript{82}

$$
v_{cv}(t,s) = \sum_{i,j} H_{MTD} \exp \left[ -\frac{(s - s_j)^2}{2(\Delta w_{ij})^2} \right] \exp \left[ -\frac{(s - s_j')(s_{j+1} - s_j')^2}{2(\Delta w_{j+1})^2} \right] \quad (A.123)
$$

where parameter $H_{MTD}$ is the height of the Gaussian. The first term in the above functional form of the potential is a typical Gaussian which is then multiplied with another Gaussian of width $\Delta w_{ij} = (s_{j+1} - s_j)$. This mathematical manipulation narrows the width of the potential in the direction of the trajectory, thus depositing the potentials close to each other in the direction of the trajectory. The values of the height and width of Gaussian depends upon the topology of the energy landscape of the system under investigation\textsuperscript{86}.

Metadynamics using an extended Car-Parrinello Lagrangian has recently been implemented to study glycine and pyrite surface interactions\textsuperscript{89}, isomerisation of alanine dipeptide\textsuperscript{90}, azulene to naphthalene rearrangement\textsuperscript{91}, proton diffusion in molecular crystals\textsuperscript{92}, to name a few.
A.3 References


9. Comba, P.; Kerscher, M., Computation of structures and properties of transition metal compounds. *Coordination Chemistry Reviews* 2009, 253, (5-6), 564-574.


17. All the papers in Coordination Chemistry Reviews, vol. 212, Issue 1 In pp 1-168.


61. Hutter, J. *Lecture Notes: Introduction to ab-initio molecular dynamics*; Zurich, 2002; pp 1-119.


64. Raugei, S. *Implementation of DFT based Car-Parrinello molecular dynamics*; Trieste, Italy, 2007; pp 1-23.


