CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

The density functional theory (DFT) is broadly using in computational materials science at the present time. In this thesis, all quantum mechanical calculations are studied by based on the DFT electronic structure simulation code Quantum Espresso [73]. Hence, we aimed to provide necessary description of DFT approaches. The first part describes the important concepts of DFT. The subsequent sections explain additional associated computational methods such as electron localization function, $p_z$ occupancy and nudge elastic bands method.

This work isn’t solely based on DFT and also on experimental studies. To obtain a partial understanding of the carbon based hybrid structures, an extensive range of various experimental techniques are employed. This includes a utilization of a series of materials characterization methods to gain information about structural properties, chemical conformations and sample morphologies. The main techniques employed through this work are exclusively presented below.

3.2 THEORETICAL BACKGROUND

3.2.1 Many Body Problem

Primarily, the theoretical condensed matter physics could determine the physical properties of system which consist of M nuclei and N electrons by solving the many-body time independent Schrodinger equation

$$H\psi_i(r_1, r_2, ..., r_N, R_1, R_2, ..., R_M) = E_i\psi_i(r_1, r_2, ..., r_N, R_1, R_2, ..., R_M)$$

3.1

here, $H$ defines Hamiltonian operator and $\psi$ denotes the wavefunction of both electron and nuclear coordinates.

The Hamiltonian of a system made up of interacting nuclei and electrons is defined as

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_{i,j} \frac{Z_i e^2}{|r_i - R_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_i \frac{Z_i Z_j e^2}{|R_i - R_j|}$$

3.2
where ħ, e, Z, r, R, M_e and M_I are represents reduced Planck’s constant, electron charge, nuclear charge, position of electron, position of nuclei, mass of electron and mass of nuclei respectively. In the above equation, the first two terms signify the kinetic energy operators for electrons and nuclei. The remaining terms are interpretation of the coulombic interactions for electron-nuclei, electron–electron and nuclei-nuclei respectively. Using the above equation, we can solve single electron problem (ex: hydrogen) analytically but most of the realistic problems involve systems with number of electrons. Meanwhile, electrons are moving faster than heavier nuclei and it can be consider that the nuclei are fixed instantaneously in the moving electrons. The e’s adiabatically don’t experience any transitions between stationary states. It is called as adiabatic approximation or Born-Oppenheimer approximation which de-couples the nuclear and electronic degrees of freedom.

3.2.2. Born-Oppenheimer Approximation

In this theory, the wave function of electrons and nuclei that has been considered separately. The mass of nuclei is very high when compared to that of an electron in a system which results in the insignificant velocity for nuclei. The frozen field of nuclear motion is considered from this assumption. The last term of equation of 3.2 becomes constant and it can be merged into the third term. This develops, a fixed potential external to electrons \(U(r_i, r_j)\). The total wave function can be written as

\[ \Psi(r, R) = \Psi_e(r, R)\Psi_N(R) \]

where, \(\Psi_e(r, R)\) and \(\Psi_N(R)\) are electronic and nuclei wave function respectively. The electronic Hamiltonian is given by

\[
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i}^{N} U(r_i, r_j) \right] \Psi = E\Psi
\]

Here, the first step in this approximation is to fix the position of atomic nuclei and the wave function of electronic coordinate is operated by the Hamiltonian. However, this approximation could not overcome the dimensional curse.

To reduce the number of degrees of freedom of the many body H problem, we approach approximation called Hartree-Fock (HF) approximation which is based on the assumption of uncorrelated electrons system and antisymmetric feature of wavefunction upon the interchange of the coordinates of the two electrons. This approach gives the solution
to solve the problem by the self-consistent field scheme. The HF theory is one e− based subject to the average potential created by the nucleus and other e−s. However, it neglects inherent e− correlation and experiences difficulties in computing the exchange term due to the slow decay with respect to distance. Eventually, DFT incorporates the exchange and correlation effects of the electrons in the system which is described in detail in the following section.

3.2.3. Density Functional Theory

The DFT is progressed on the foundation of the unique idea introduced by Thomas and Fermi in 1927. The electron density is considered as the simple variable to define the many-body solid system in the ground state, whereas in the HF theory based on the wavefunction. The DFT depends on the Hohenberg and Khon (HK) theorem which is proposed in 1964.

3.2.4 Hohenberg –Kohn theorems

Hohenberg and Kohn introduced DFT by two theorems. Kohn and Sham extended this theory by some assumptions.

**Theorem 1**

The first theorem explains that ground state energy of the system directly depends on the electron density for the interacting electrons. And, there is a strong correlation between the potential and electron density of interacting electrons. If the number of electrons and the potential is available, then defining the electronic Hamiltonian is possible. Moreover, ρ(r) defines the number of electrons in the system, it also determines the wavefunction and total energy of the system E(ρ(r)). Hence, the energy can be written as a basic variable such as electron density,

\[ E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho] \]

Where, T[ρ], V_{ee}[ρ] and V_{ne}[ρ] are kinetic energy of electron, electron-electron interaction energy and electron-nuclei interaction energy respectively. The Hohenberg-Kohn functional is projected as

\[ F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] \]
If $F_{HK}[\rho]$ is recognized, then the solution for the Schrödinger equation can be obtained. The term $E_{ee}[\rho]$ consist of classical part of coulomb repulsion between electrons and self-interaction correction term.

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_2 - r_1} d r_1 d r_2$$ \hspace{1cm} 3.7

In Thomas Fermi model, the $J[\rho]$ is replaced for $E_{ee}[\rho]$ and $T[\rho]$ and is solved from non-interacting uniform electron gas model. This approach simplifies that if the electron density is known then the total energy can be obtained directly.

**Theorem 2**

This second theorem guides towards shortening the way of searching the ground state energy by using variational principle method. Here, the electron density is used as a single variable to search for the ground state energy. The minimum energy is essentially the global minimum of the electron density

$$E_0 = E[\rho_0(r)] \leq E[\rho(r)]$$ \hspace{1cm} 3.8

Moreover, these two theorems do not afford to give the exact form of energy functional and the way to estimate the form of this functional. Kohn and Sham suggested that the introduction of orbitals into this problem can correctly approximate the energy functional and still the development of approximation is progressed by many researchers.

### 3.2.5. Kohn-Sham Equation

To find the exact ground state density, the functional $F_{HK}[\rho]$ need to be solved. In 1965 the Kohn and Sham developed the differential equations for solving many body Schrödinger equation. The replacement of interacting particles by non-interacting particles with the same ground state density is the main idea proposed by Kohn and Sham. The kinetic energy term is first split into interacting ($E_{\text{kin}}^{\text{int}}$) and non-interacting ($E_{\text{kin}}^{\text{non}}$) term and it is written by

$$E_{\text{kin}} = E_{\text{kin}}^{\text{non}} + E_{\text{kin}}^{\text{int}}$$ \hspace{1cm} 3.9

And the kinetic energy of non-interacting electrons mainly depends on Kohn-Sham (K-S) orbital (single electron wavefunction) and is defined by

$$E_{\text{kin}}^{\text{non}} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle$$ \hspace{1cm} 3.10
Where $\phi_i$ are K-S orbitals. Regrouping the interacting terms together as single entity is called by exchange correlation energy, $E_{xc}$

$$E_{xc} = E_x + E_c^{int} + E_{kin}^{int} = E_x + E_c$$ \hspace{1cm} 3.11

In comparison with the Hatree-Fock method, the new terminology called correlation term ($E_c^{int}$) is included in the K-S approach,

$$E_H + E_x \rightarrow E_H + E_x + E_c^{int}$$ \hspace{1cm} 3.12

The final energy expression is written as

$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$ \hspace{1cm} 3.13

Or the energy with respect to density is explored by

$$E[\rho] = T_s[\rho] + \int \rho(r)V_{ext}(r)dr + J[\rho] + E_{xc}[\rho]$$ \hspace{1cm} 3.14

In summary, the first three terms are comparatively easy than the exchange correlation term and the appropriate assumption is needed to quantify the exact result. The final expression can be solved by a set of one-particle equation

$$\frac{1}{2}\sum_{i=1}^{N} \nabla^2 - V_{eff}(\mathbf{r})] \phi_i = \epsilon_i \phi_i$$ \hspace{1cm} 3.15

Here, the electronic density is directly related with K-S one electron orbitals. The self-consistent procedure for K-S approach is projected in Figure. 3.1.
3.2.6 Exchange-Correlation Functional

So far, it is practically possible to perform the self-consistent calculations using the K-S equation to determine the converged density which predicts the physical properties of the system. However, the exchange-correlation energy ($E_{XC}$) is the main problematic function which is actually unknown. We need a suitable approximation for certain systems that yields the actual solutions. There are many ways to define a function such as local density approximation (LDA), generalized gradient approximation (GGA), hybrid functional and GW approximation. Here, we are going to discuss in the following sections about LDA and GGA functional only which are employed in this thesis.

3.2.7 Local Density Approximation

Here, it approximates a system based on the simple idea of homogenous distribution of electrons where a density of e’s are same everywhere in the system. This good accuracy of $E_{XC}$ functional can be written as

$$E^{LDA}_{XC}[n(r)] = \int n(r)E_{XC}[n(r)]d^3r$$  \hspace{1cm} 3.16
Where $E_{XC}[n(r)]$ defines the exchange correlation energy as the functional of electron density. This exchange correlation functional works well for homogenous electron gas and it works well for system which has slowly varying potential. Similarly the exchange correlation potential can be defined as

$$V_{XC}(r) = \frac{\delta E_{XC}[n(r)]}{\delta n(r)} = \epsilon_{XC}[n(r)] + n(r) \frac{\delta \epsilon_{XC}[n(r)]}{\delta n(r)}$$

We could expect, LDA suits for the pretty uniform density of systems such as nearly free-electron metal. It provides accuracy account for some less homogeneous systems such as molecules, ionic crystals and semiconductors. This is because of LDA that achieves the correct sum rules for the $E_{XC}$ hole. However, it underestimates the equilibrium volume of crystal lattices by limited percent owing to their over binding glitches.

### 3.2.8 Generalized Gradient Approximation

The $E_{XC}$ energy depends on both electron densities and its gradients of density is called as the generalized gradient approximations (GGAs). Perdew, Burke and Ernzerhof (PBE) offered GGA-functional in 1996 which is widely used functional [74]. The conditions like charge density of a system changes rapidly and it can be solved by this generalized gradient approximation.

$$E_{XC}^{PBE}[n(r)] = \int d^3 r \epsilon^{hom}_{XC}[n(r), \nabla n(\tilde{r}, \zeta, s)] n(r)$$

where $\epsilon^{hom}_{XC}$ is the exchange energy term of uniform density of system, $\nabla n$ is the gradient of density of the system depends on the local Seitz radius $\tilde{r}$, relative spin polarization $\zeta$ that is approximated to be independent of $r$ and density gradient $s$ (dimensionless). This GGA functional conserves the exact features of LDA and includes the inhomogeneous contributions at the same time. Hence, the account of electron correlation in molecules or surfaces are improved by the GGA-PBE functional. In this thesis, we mainly engaged with GGA-PBE functional owing to its better description than LDA.

### 3.2.9 Van der Waals forces in DFT

A common disadvantage of GGA as well as hybrids functionals is substituting the portion of the local by nonlocal HF exchange which they can’t define long-range e’ correlations and it is reasonable account for van der Waals interactions. This section concentrates on specific approach, van der Waals (vdW) interactions within the framework of DFT. The vdW includes the following forces between molecules: (i) two permanent
dipoles (Keesom force), (ii) a permanent dipole and a corresponding induced dipole (Debye force), and (iii) two instantly induced dipoles (London dispersion force). So far, there are three main types of approaches have also been proposed for studies on vdW systems as following (i) explicit density functionals, (ii) DFT extended with atom-pair potentials, and (iii) perturbation theory, typically in the random-phase approximation.

In this thesis we focused on explicit density functionals with an the well-known Grimme’s DFT-D method [75]. The strong covalent bonds are well described by traditional approximations, like the GGAs and a pairwise atomistic correction that can be used to account for the vdW forces. In this method, there are two kinds of parameters that must be specified. The first kind are dispersion coefficients $C_6$, which characterize the asymptote, and the second kind are cutoff radii $r_{cut}$, which characterize the damping functions.

A semi-empirical dispersion potential is adding to the conventional K-S DFT energy and total energy equation becomes,

$$ E_{DFT-D} = E_{KS-DFT} + E_{Disp} $$

where $E_{KS-DFT}$ is the self-consistent K–S energy and $E_{Disp}$ is an empirical dispersion correction is given by

$$ E_{Disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{c_{ij}^6}{R_{ij}^6} \int dmp(R_{ij}) $$

Here, $N$ is the number of atoms in the system, $c_{ij}^6$ denotes the dispersion coefficient for atom pair i,j, $s_6$ is a global scaling factor that only depends on the density functional used and $R_{ij}^6$ is an interatomic distance.

The fixing $C_6$ values is very major limitations of the DFT-D approach when the electronic character of an atom in a molecule is very different from that of the free atom in its ground state.

### 3.3 Pseudopotentials

In general, most of the physical and chemical properties of the system are determined by the valence electrons than the core electrons which are tightly bound with nucleus. The idea of a pseudopotential is associated with substituting the effects of the core e’s with an effective potential. Using the K-S approach, we generated pseudopotential by starting with
the solution of the atomic problem. After obtaining K-S orbitals, we made an arbitrary dissimilarity between valence and core \( e^- \) states. The changes in the environment due to the presence of core \( e^- \) states are assumed to be very little. Hence, their effect were replaced by a transferable and model potential. The valence \( e^- \) states appear rapid oscillate close to the core states. Hence, the valence states become smoother by introducing the new potential. Hereafter, the computational cost is totally reduced by considering core electrons as treated as smoothened pseudo-core region up to a certain radial cutoff. The computational effort is improvised by using plane waves, which can smooth out this region. Moreover, the valence electrons experience smoother potential due to the effect of nuclear coulomb potential on valence electrons which brings that pseudopotential approximation is entirely for valence electrons (see Figure 3.2). The ultrasoft pseudopotential are widely used method and described in detail of the following section.

3.3.1 Ultra-Soft Pseudopotentials

The systems in the first-row and transition-metal elements of periodic table are found difficulties in the inadequacy of norm conserving pseudopotentials to represent the highly localized p and d orbitals. In 1990, Vanderbilt projected the ultra-soft pseudopotential which has the form of an addition of a few separable terms that becomes local and vanishes out. The transferability can be enhanced analytically by increasing the number of energies spanning the range of occupied state energies. The pseudopotential follows charge-state dependent and includes in the self-consistent screening process. These features permit the cut-off radius to be better by considering transferability for p and d orbitals.
3.4 TECHNIQUES USED TO ANALYSE THE LI STORAGE

3.4.1 Open Circuit Voltage, Volume Expansion and Formation Energy

The average voltage (or open circuit voltage (OCV)) for various Li content can be expressed as

$$\text{OCV}(x) = \frac{-\Delta G}{zF},$$

where $\Delta G$ is the Gibbs free energy of the system, $F$ is the Faraday constant and $z=1$ which is the electronic charge. The entropic contributions to the $\Delta G$ are small at low temperatures \[76\]. The Gibbs free energy can be approximated by the internal energy ($\Delta E$), $\Delta G \approx \Delta E$. The anodic cell reaction during Li intercalation can be written as,

$$\text{Li}_{x_1}C_6 + \text{Li} \rightarrow \text{Li}_{x_2}C_6$$

with $x_2 > x_1$,

The open circuit voltage (OCV) is expressed by

$$\text{OCV}(x_1, x_2) = \frac{[E(\text{Li}_{x_2}C_6) - E(\text{Li}_{x_1}C_6) - (x_2 - x_1)E(\text{Li})]}{(x_2 - x_1)} F,$$
where \( E(Li_{x_2}C_6) \) and \( E(Li_{x_1}C_6) \) are the total energies of the host materials (graphite) with the Li concentrations of \( x_2 \) and \( x_1 \) and can be obtained from first principles. The average lithium insertion voltage at \( x = ((x_1+x_2)/2) \) is calculated considering the Li concentration of \( x_1 \) and \( x_2 \). In all calculations, \( x_2 \) and \( x_1 \) are considered as lithiated and delithiated of single Li ions.

The volume expansion as a function of intercalated Li concentrations in host material is also computed by the calculated equilibrium volumes of the lithiated structures and it can be derived by,

\[
\Delta V = \frac{[V(G + nLi) - V(G)]}{V(G)},
\]

where \( V(G + nLi) \) and \( V(G) \) are the volume of the Li intercalated host material and pristine material. Here, \( n \) is the Li intercalated concentration in the host material.

In order to determine the stability, we calculate the formation energy (\( \Delta E_f \)) by

\[
\Delta E_f = \frac{6[E(G + nLi) - E(G) - nE(Li)]}{n_c},
\]

where \( E(G + nLi) \) and \( E(G) \) are the total energy of \( n \) Li atom/s intercalated in host material and pristine material respectively. Here, \( n_c \) is the number of carbon atoms in host material.

### 3.4.2 Theoretical Specific Capacity Calculations

The theoretical specific capacity (Sp .cap) can be calculated by using the following formula:

Specific theoretical capacity (mAh/g) = \( [(F \times n_{Li})/(M \times 3600)] \times 1000 \)

Where,

- \( F = \) Faraday’s constant (96,500 coulombs per gm equivalent).
- \( n_{Li} = \) Number of Li per formula \( (Li_xC_6) \) unit of the electrode material.
- \( n_{Li} = x = 6 \times (n/n_c) \)
- \( n \) = number of lithium atom adsorbed in the anode material.
- \( n_c \) = number of carbon atom in the anode material.
- \( M \) = Molecular mass of the electrode material.

Other way,

Specific Theoretical capacity (mAh/g) = \( (n_{Li} \times 26.801 \times 1000)/M \).
26.801 = Faradays constant / (Charging battery /1 hour)
= 96,500 / (3600).
If this has to be expressed in terms of current, divide that by 3600
F = 26.801 Ah/Mole
M = molecular weight
For mA, we multiply with 1000.

For example,

1. Graphite anode material for LiC₆:
   \[ n_{Li} = x = 6 \left( \frac{n}{n_a} \right) \]
   \[ = 6 \left( \frac{4}{24} \right) \]
   \[ = 1 \]
   Sp. cap = \( (1 \times 26.801 \times 1000) / (6 \times 12.011) = 372 \text{ mAh/g.} \)
   Six C atoms molecular weight = 6 \times 12.011.

2. SWCNT anode material for LiC₂:
   Sp. cap = \( (1 \times 26.801 \times 1000) / (2 \times 12.011) = 1116 \text{ mAh/g.} \)

3. Si doped T6 anode material can have conformation of Li_{1.7}SiC₅:
   Sp. cap = \( (1.7 \times 26.801 \times 1000) / (6 \times 12.011) = 632 \text{ mAh/g.} \)

3.4.3 Electron Localization Function (ELF)

Becke and Edgecombe constructed an ELF concept. It is a measure of a probability to find an e⁻ in the neighbourhood of another e⁻ with like-spin that provided a quantifiable description of the Pauli Exclusion Principle.

\[ ELF = \frac{1}{1 + (D/D_h)^2} \] 3.26

Where, D(r) and D_h(r) represent the excess local kinetic energy and Thomas fermi kinetic energy density and this can be defined as

\[ D(r) = \frac{1}{2} \sum_i |\nabla \Psi_i(r)|^2 - \frac{|\nabla n(r)|^2}{8n(r)}, \] 3.27

\[ D_h(r) = \frac{3}{10} (3\pi^2)^{2/3} n(r)^{5/3} \] 3.28

D can be sometimes termed as Pauli kinetic energy density and it becomes 0 when e⁻s are localized.
It proceeds value from 0 to 1, when ELF is 1 resembles to the perfect localization and \( \frac{1}{2} \) is for the uniform \( e^- \) gas. The functional required in different regions to identify values of ELF. A general observations are following:

(i) High ELF regions need a functional that can explain localized \( e^- \)s.

(ii) Intermediary ELF regions are precisely described by functional based on the uniform \( e^- \) gas.

(iii) Stumpy ELF regions require a functional which could treat pure quantum effects existing in the classically forbidden region (outer electronic surfaces)

**3.4.4 Nudged Elastic Band Method**

The minimum energy pathway for two local minima (initial and final structure) is calculated by Nudged Elastic band method. For the two local minima in the potential energy surface, chain of images is constructed by elastic band method. The NEB method is very much useful for estimating the transition state and reaction path in any chemical reaction. In elastic band method, the set of images \((r^0, r^1, ..., r^M)\) for the objective function can be expressed mathematically by

\[
S[r^{(0)}, r^{(1)}, ..., r^{(M)}] = \sum_{i=0}^{M} V[r^{(i)}] + \frac{k}{2} \sum_{i=1}^{M} [r^{(i)} - r^{(i-1)}]^2
\]

Where, \( k \) and \( V[r^{(i)}] \) defines the spring constant (stiffness of the harmonic spring) and total energy of the \( i^{th} \) image respectively. To minimize the object function, the endpoint images should be stationary and the force acting on the endpoint images should be zero, and for all the other images the force is nonzero which makes the lowest amount of energy to define the minimum energy path between two known minima. The usage of harmonic spring \( (k) \) is to fix the distance evenly between each image in the straight line. Moreover, the converged elastic band will cross the potential energy barrier if it is close to transition state and will easily follow the lowest energy path by choosing the correct value of spring constant. There are two main problems which deny its success: the first one is estimating the exact stiffness for the spring constant. This will cause the images in the straight line (chain) to slide downhill which results to cross the transition state and can produce the bad choice of minimum energy path near to the TS region (see Figure 3.3). The second problem is known as corner cutting which tends to drag the path away from the minimum energy direction which leads to overestimate the barrier energy for any process.
The above said two problems happens due to the high and low value of spring constant and it is very hard to estimate the optimal value for spring constant to scale down the two problems. By using nudged elastic band (NEB) method, the above said problem can be prevented by applying parallel and perpendicular force in the path of the images. The total force acting on the image is written by,

\[ f_{\text{NEB}}[r(i)] = f^V_{\parallel}[r(i)] + f^S_{\parallel}[r(i)] \]  

Then the normal physical force and parallel spring force is written as

\[ f^V_{\parallel}[r(i)] = -\nabla^{(i)}V[r^{(i)}] + (\nabla^{(i)}V[r^{(i)}], \hat{t})\hat{t} \]  
\[ f^S_{\parallel}[r^{(i)}] = k [(r^{(i+1)} - 2r^{(i)} + r^{(i+1)}), \hat{t}] \hat{t} \]

Where, the gradient mainly acts for image i only and tangent vector pointing along the line between two adjacent images [89]. From Figure 3.4, the spring force acting along the unit vector direction and the perpendicular force acts normal to the unit vector which result in the NEB force to drag the image i towards the minimum energy path. The climbing nudged elastic band method (C_NEB) is used to find the exact saddle points along the minimum energy path which is sometime hard to search by NEB method. In this C_NEB method, the highest energy image is lifted towards the saddle point [77]. Along the band direction, climbing image increases its energy and the energy is minimized in all the other directions. For the converged NEB calculation, all the images are in the MEP and have zero force in every image.
3.5 EXPERIMENTAL TECHNIQUES OF CHARACTERIZATION

3.5.1 X-ray Diffraction (XRD)

X-ray technique is used to analyse the crystalline/amorphous nature of nanomaterials. A XRD spectra aid to figure out the crystalline size of different phases occurs in nanomaterials. Solid materials can define as amorphous and crystalline. In amorphous, atoms arrange randomly as same as the disorder found in liquids. In crystalline, atoms arrange in an even pattern and repeats in three dimensions called as the crystal. The lowest volume part is called a unit cell and its dimensions are a, b, c of three axes and angles between them are termed as alpha, beta, and gamma. When an X-ray knocks out an atom in the material, the e’s start to fluctuate with the same frequency as the inward ray.

Hence, a diffracted ray can be described as a large number of scattered beam. X-ray reflections create from sequence of parallel planes in the crystal. Miller indices such as three integers h, k and l are used to define the orientation and inter-planar spacing’s of planes. For a cubic crystal structure, inter-planar spacing \( d_{hkl} \) can be described by,

\[
d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}
\]  

3.33
where \( a \) represents is the any one value of lattice parameter. The interatomic spacing \((d)\), incident wavelength \((\lambda)\) and angle of the diffracted ray \((\Theta)\) are connected with Braggs law can be expressed by,

\[
n\lambda = 2d \sin \Theta \tag{3.34}
\]

where \( n \) is integer. The positions and intensities of the peaks are considered to identify the fundamental structure of the material. For example, the diffraction lines of graphene differ from CNT, though both structures made of carbon atoms. This phase identify is significant since the material properties are extremely reliant on structure.

![Figure 3.5 a schematic diagram of X-ray diffraction (adopted from ref: [99])](image)

### 3.5.2 Transmission Electron Microscopy (TEM)

TEM is a technique to analyses the morphology of nanomaterials. A related method, scanning electron microscopy (SEM) has been extensively studied in the characterization of nanomaterials. Generally, TEM experimentations conduct in vacuum. In this technique, transmitted and diffracted e−s are used to analyses a surface of nanomaterials. A primary high energy beam of e−s (-100 to 300 KeV) pass through a condenser to yield parallel beam which impact on the sample materials. The incident e−s ionize atoms on the surface of samples by removing one of the strongly bound core-shell e−s from the nucleus that causes a production of secondary signals (see Figure 3.6). The e−s transfer through the samples are giving more information. The order of magnification size in TEM is \( \sim 10^5 \sim 10^6 \) and diameter of incident e− beam is approximately 1 to 10 nm. The contrast in transmission mode is triggered by attenuation of e−s and also owing to density and thickness differences of samples.
3.5.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS technique is based on the Photo-electric effect. When a sample irradiate with X-rays, photo-electrons are consequently eject from atoms in the nearby surface (see Figure 3.7). The kinetic-energy (K.E) of an irradiated photo-electron is equivalent to the difference between energy of photon and binding energy of the $e^{-}$. From the obtained XPS spectra, we analyse the elemental composition at the parts per thousand range and oxidation state of the exist elements that inside the compound. At present, an ambient-pressure XPS is available that analyse materials at pressures of a limited tens of millibar.

The average depth of investigation for an XPS is ~ 5 nanometre. It can be investigated up to a few microns by linking the method with ion milling. It offers information about surface layers which is significant for industry and research applications such as photovoltaics, catalysis and energy storage materials.
Figure 3.7 Working Principles of the XPS technique (adopted from: [101])

For, Gas \[ KE = h\nu - IP \]
Solid \[ KE = h\nu - BE - \Phi \]