

Chapter 2

Theoretical Methods and Methodology

2.1 Density functional theory methods

DFT is a fundamental premise including the motion and pair correlation to achieve electronic ground state, which primarily utters in terms of total electron density [1, 2]. Since the beginning, DFT gained enormous attention in realizing ground state electronic density, energy of any system such as clusters, solids, atoms and molecules in presence or absence of external perturbations [2]. The basis of DFT is based on Hohenberg-Kohn (HK) theorem [3], Kohn-Sham (KS) principle [4], local density approximation (LDA) and PAW method [5], generalized gradient approximation (GGA) [6] and pseudopotential (PP) method, which are discussed in the present chapter for in-depth understanding of this *ab initio*-based simulation. These particulars required to contrive the basis sets in DFT simulation utilizing Quantum ESPRESSO (QE) package [7]. DFT is a complementary approach to the traditional methods, which disentangle the complexities of many-body problem in quantum systems.

In this regard, using the contemporary computational codes it becomes challenging task to achieve the electronic properties of a system considering a many-body problem. A complete quantum-mechanical approach of a system is required considering nuclei and electronic wavefunctions; however, the mass of an atomic nucleus is much higher than that of mass of electron. Therefore, to reduce vast majority of simulation and obtain high accuracy, Born-Oppenheimer approximation (BOA) [8] is included and their properties are decoupled from the valence electrons and ions (discarding the core electrons and nuclei). In this case, solving the many-body problem still remains

challenging and unclear because it separates electronic and ionic degree of freedom and considers low mass electron instead ions for complex quantum systems. We consider BO approximation in entire *ab initio* based DFT simulations that has been implemented to achieve the objective of present thesis work.

Initially, the strongly correlated electron system was explained by Thomas-Fermi (TF) model [9, 10] and Hartree-Fock-Slater [11] method, which are considered to be the ancestor of latest DFT method. As per the TF model, the class of system containing interacting electrons without relativistic effect in Schrödinger equation can be written as,

$$H \equiv \hat{T} + \hat{U}_{en} + \hat{U}_{ee} \quad (2.1)$$

$$H = -\frac{1}{2}\sum_j \nabla_j^2 + \sum_j u_{ext}(\mathbf{r}_j) + \frac{1}{2}\sum_{j \neq k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \quad (2.2)$$

Here, $\hat{T} = -\frac{1}{2}\sum_j \nabla_j^2$ denotes the kinetic energy operator, $\hat{U}_{en} = \sum_j u_{ext}(\mathbf{r}_j)$ is potential energy due to electron-nuclei interaction and $\hat{U}_{ee} = \frac{1}{2}\sum_{j \neq k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}$ is potential energy due to electron-electron interaction. With the help of TF approximation, the kinetic energy $T[n(r)]$ is approximated for a non-interaction system with electron density $n(r)$. In TF model, the exchange-correlation energy term is ignored and the Hartree approximation remains identical to TF model. In this regard, this technique fails to realize the shell model and stabilization of molecules.

The aforementioned shortcomings can be overcome by generalizing the TF model implementing in modern DFT approach. The modern DFT approach is found to be an exact approach for solving many-electron problem. This approach solves the set of equations via iterative scheme, which is based preferably on KS scheme. The precursor to modern DFT approach is associated with the previous work of Thomas [10], Fermi [9], Dirac [12], von Weizsacker [13] and Slater [14]. The beginning of DFT approach was evolved from the

ground-breaking research of Hohenberg and Kohn in the year 1964 [3] and Kohn and Sham in 1965 [4]. The HK theorem published in 1964 describes that the energy ground state is a functional of electron density, where combination of energy and electron density can be acquired by minimizing the energy as a function of the density at fixed functional. The paper published in 1965 set a stage to form the electronic ground state density by considering non-interacting orbitals, basically the KS wave functions. The preliminary understanding of the HK theorem and KS scheme constructs the ideal system for non-interacting Fermions having density $n(r)$ equivalent to interacting Fermions. Taking into account the superiority of both the works, the respective theorems are explained below for detail understanding.

2.1.1 Hohenberg-Kohn Theorems

The first theorem states as:

Theorem 2.1.1: *The ground state energy E_0 is the unique functional of the ground state electron density $E_0 = \langle \Psi_0[n_0] | H | \Psi_0[n_0] \rangle = E_0[n]$.*

The Coulombic potential present between electrons for determining the electronic nature of solids, basically depends on HK functional. Moreover, the interacting nucleus, molecules, crystals depend on the effective potential operator. Therefore, the HK functional is named as unique functional, because it attains constant value for all systems. The non-degenerate ground state electron density can be constructed from the Hamiltonian operator, which determines the information of expectation values for all states of the system.

The second theorem states as:

Theorem 2.1.2: *The ground state energy E_0 can be proved via Variational principle: the electron density $n(r)$, that minimizes the total energy, is the true ground state energy $E_0[n_0] \leq E[n]$.*

The external potential universally constructs the ground state wavefunctions, which establishes all observables of the system such as kinetic energy. Moreover, the HK theorems are expanded to more crystal systems and dimensions from bulk to low-dimensions, which incorporates various parameters such as SOC, spin-polarization etc. Moreover, HK theorems are extremely robust, but practically they do not have any provision to compute the ground state electron density. In this regard, Kohn and Sham provides a simple iterative method scheme for performing *ab initio* DFT calculations.

2.1.2 Kohn-Sham approach

Kohn and Sham advocate the following scheme:

Theorem 2.1.3: *The theorem formulates that for each interacting system S with distinct functional, there exist non-interacting system R , described by Hamiltonian $\widehat{H}_S = \widehat{T} + \widehat{V}_S$, where \widehat{V}_S yields the same true ground state electron density $n_S(r)=n_R(r)$.*

The HK theorem determines uniquely the ground state electron density of the system. It is important to obtain suitable potential energy to describe the electron density $n_R(r)$. The additional system exhibits noninteracting kinetic energy functional, the density of that energy functional collects from single-particle equation to obtain KS orbitals. The single-particle equation relies on the electron density $n(r)$, also depends solely on KS orbitals. In this regard, it is important that the single-particle equation must be solved self-consistently by means of iterative scheme. The ground state energy and electron density can be obtained exactly, if the exchange-correlation (X_C) term is exactly recognized. It is necessary to know the exact value of X_C term, because it has all the quantum mechanical origin for various fictitious non-interacting and interacting systems. Therefore, it has an utmost need to find an appropriate and descent approximation to determine the X_C term. The simple and mostly employed approximation are mentioned in the next subtopics of this chapter.

2.1.3 Exchange-Correlation term

The KS-DFT approach is mainly to solve many-electron Schrödinger equation by separating out the discrete single-particle kinetic energy term and Hartree term from the interacting X_C functional. However, an appropriate discussion on X_C functional can be understood by quantum mechanical adiabatic process. The Hamiltonian for electron density varies adiabatically to reach the ground state more rapidly than the motion of nucleus. The X_C term accounts for remaining interacting and non-interacting kinetic and electrostatic terms, which creates a bridge by determining the scaling factor (ξ) to obtain the electron-electron coupling term. The interacting and non-interacting terms are transformed between 0 and 1, where density is constant under adiabatic process. This inference suggests the equation for exchange-correlation energy term,

$$E_{XC}[n(r)] = \frac{1}{2} \int n(r) dr \int \frac{n_{XC}(r,r')}{r-r'} dr' \quad (2.3)$$

Here, $n_{XC}(r, r')$ corresponds to the average X_C interaction factor. Thus, we can determine the exchange-correlation density as,

$$\epsilon_{XC} [n(r)] = \frac{1}{2} \int \frac{n_{XC}(r,r')}{|r-r'|} dr' \quad (2.4)$$

The n_{XC} term can be decomposed into two disparate parts expressed as $n_{XC}(r, r') = n_X(r, r') + n_C(r, r')$, where $n_X(r, r')$ is the exchange term and $n_C(r, r')$ is correlation term obtained linearly. The exchange term (n_X) can be characterized by considering the Hartree-Fock (HF) energy term as,

$$E_{XC}[n(r)] = \frac{1}{2} \int n(r) dr \int \frac{n_X(r,r')}{r-r'} dr' \quad (2.5)$$

The exchange-correlation term X_C can be described as $E_{XC} = \int n(r) \epsilon_{XC} [n(r)] dr$. The true ground state can be obtained by employing the approximations to know the exact X_C functional. It is important to realize exchange-correlation density for each electron to construct appropriate approximations to realize the

quantum mechanical origin. The various approximations are discussed in the next section of this chapter.

2.1.4 Local density approximation (LDA)

In KS-DFT, the ground state energy and electron density are determined for many-body system, the exchange-correlation energy functional is required to approximate for practical implications. LDA is the simplest approximation to scrutinize the unknown value of χ_C energy density by considering KS orbitals. In this regard, the exchange-correlation energy is determined by approximating locally the summation of electron density for exchange as well as correlation energy of homogeneous electron gas (HEG) model. It is known that HEG can be formulated by considering N interacting electrons in a volume V to maintain the system neutrality in presence of homogeneously positive charge background. To approximate the exchange-energy term in the system, the exchange term can be written as,

$$E_X^{LDA}[n] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(r)^{4/3} dr \quad (2.6)$$

The correlation energy is expressed analytically in the limits of high and low density corresponds to weak and strong correlation. The modest χ_C functional can be described as,

$$E_{XC}^{LDA}[n(r)] = \int n(r) \epsilon_{XC}[n(r)] dr \quad (2.7)$$

The high-density limit for correlation energy density is written as,

$$\epsilon_C = A \ln(r_s) + B + r_s(C \ln(r_s) + D) \quad (2.8)$$

The low limit density,

$$\epsilon_C = \frac{1}{2} \left(\frac{d_0}{r_s} + \frac{d_1}{r_s^2} + \dots \right) \quad (2.9)$$

Here, $[n(r)]$ is the electron density; ϵ_{XC} is the exchange-correlation energy term for density $n(r)$, r_s is the dimensionless quantity named as Wigner-Seitz

parameter. However, QMC is parameterized over electron density $n(r)$ for obtaining accurate results.

The LDA potential decays slowly in a Coulombic manner with different electron density. However, LDA is an effective method for obtaining accurate results for inhomogeneous systems. In LDA calculations, the density is assumed to remain same throughout, which indicates that the exchange energy is considered to be undervaluing. Meanwhile correlation energy is overvalued, they tend to cancel each other [15]. Though LDA can describe many physical quantities, but it does not support Rydberg series underestimating the band gaps and lattice constants. Therefore, LDA provides less description for electron-rich species described from band gaps and interplanar distances between the atoms and layers stated in this thesis work. In this regard, more generalized approximation (discussed in the next section) is required for defining exchange-correlation functional in complex systems.

2.1.5 Generalized gradient approximation (GGA)

LDA has limitations in its accuracy for determining most of the physical quantities which needs considerable precision. To overcome the limitations of LDA, a modification in the approximation was implemented by Hohenberg and Kohn [3] by expanding the higher order terms via Fourier series in order to obtain the gradient of electron density known as gradient expansion approximation (GEA). The GEA method fails to give the accuracy because integration of exchange term leads to -1, which contravenes the sum rule. Even if the GEA method disobeys the sum rule, it somehow opens an opportunity to manifest generalized gradient approximation (GGA) exchange-correlation term by determining cut-off parameter of GEA exchange term. The GGA is commonly explained in terms of gradient of electron density to obtain true electron density in inhomogeneous system. This expansion leads to GGA and can be written as,

$$E_{XC}^{GGA}[n(r)] = \int F_{XC}(n(r), \nabla n(r)) n(r) \epsilon_{XC} [n(r)] d^3r \quad (3.0)$$

Here, $F_{XC}(n(r), \nabla n(r))$ is the exchange enhancement factor proposed by Perdew and Wang [16], later it was revised to much modest form known as PBE suggested by Perdew, Burke and Ernzerhof for solving the equation. The GGA term is composed by parameterizing correlation energy and gradient electron density for HEG [6]. The shortcomings of LDA are modified by implementing GGA for understanding various physical quantities such as surface energies, phase stability, magnetic and electronic properties etc. Moreover, GGA and LDA schemes are the simplest approximations till date but these are scanty to determine the insulator band gap modelled specifically for rare-earth compounds. To overcome such drawbacks, hybrid functional must be implemented along with augmented recursion method.

2.1.6 The Plane-wave Pseudopotential approach

To introduce DFT practically on real systems, it is essential to solve KS equations in a computationally efficient way *via* iterative scheme with highest accuracy in the results. The calculation carried out in all the chapters of this thesis considers the plane wave pseudopotential method to solve the KS equations. This method involves plane wave basis set to characterize the atomic orbitals and pseudopotential designate the nucleus and core electrons. Alternative methods to describe plane wave pseudopotential does exist in simulations include localized basis function for sole atomic orbitals [17]. Although the alternate methods are computationally favourable, but these methods suffer due to incomplete basis set creating hindrance in obtaining truly converged ground state energy as a function of basis set. In this regard, plane wave pseudopotential approach is highly considerable over the alternate basis sets. Combination of plane waves with pseudopotential can extensively modify the exactness of DFT calculation.

Currently pseudopotential, also known as effective potential, constructed from first-principles calculations by solving KS equation and simplifies the information regarding complex systems. The manifestation of pseudopotential gives an effort to modify the complication of the motion of core electrons and nucleus creating an effective potential term, which modifies the Schrödinger equation instead of Coulomb potential term. The atomic orbitals exhibiting spherical symmetry conduct the task and express its wavefunction as the product of radial and spherical function. The Schrödinger equation can be solved by reducing to one-electron particle considering radial function by integrating numerically. A schematic illustration of corresponding many-electron wavefunction expressed with respect to Coulomb potential shown in Figure 2.1. The prime motive is to reduce many-electron problem within a sphere of effective potential having core electrons with radius $r_{cut-off}$ by a debilitated potential having same ground state wave function for similar energy eigen value as the initial many-electron wave function outward $r_{cut-off}$ (shown in Figure 2.1 with dotted line). Pseudopotentials with higher electron core cut-off radius is softer, which converges more promptly. Due to its rapidness, the accuracy is compromised to produce realistic characteristics

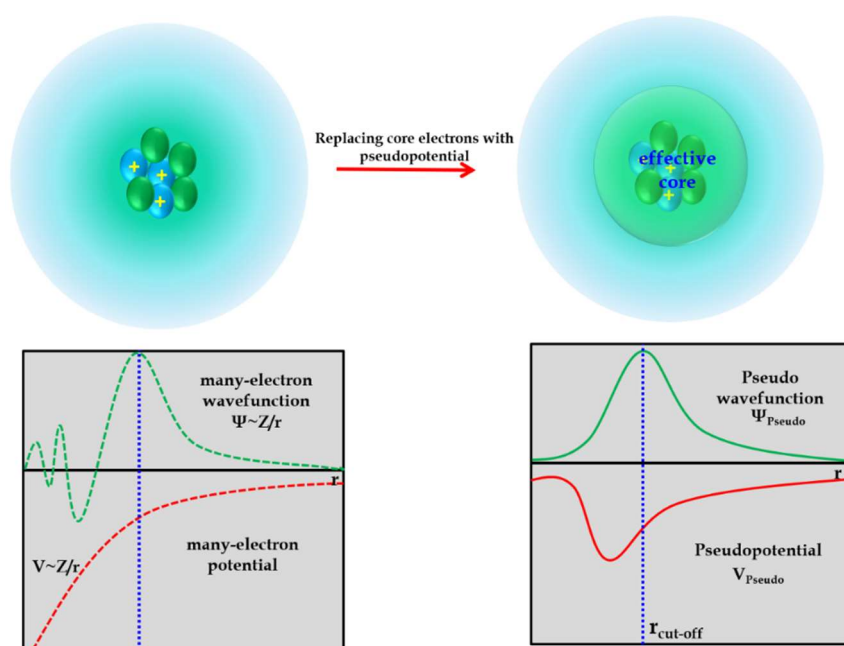


Figure 2.1: Displaying the schematic representation of many-electron wave function shown in green dashed line and corresponding pseudo wave function, Ψ_{Pseudo} (green solid line) combining with Coulomb potential shown in red dashed line and pseudopotential (red solid line).

The concept of pseudopotential approximation was first introduced in 1934 by Hans Hellmann. The commonly used pseudopotential in modern DFT is norm conserving pseudopotentials (NCP) and ultrasoft pseudopotential (USPP). The former pseudopotential basically includes the creation of nodeless pseudo wave function Ψ_{Pseudo} by conserving the norms of many-electron wave functions. These pseudopotentials commonly allow basis-set by considering lower cut-off energy for describing the electronic wave functions with proper convergence with reasonable computing resources. However, NCP was first introduced in 1979 by Hamann, Schlüter and Chiang (HSC) [18]. The norm conserving pseudopotential generates by inverting the Schrödinger equation at many-electron Eigen values, given as

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_l(r) - \epsilon \sim \frac{Z}{r} \right] \Psi \sim \frac{Z}{r}(r) = 0 \quad (3.1)$$

$$\hat{V}_l(r) = \sum_m \sum_n |Y_{mn} \rangle V_{mn}(r) \langle Y_{mn}| \quad (3.2)$$

The norm-conserving pseudopotential acquired here is semi-local with high degree of tunability, which performs utilizing single-electron wave functions in the similar manner. However, to minimize computational cost Kleinman and Bylander [19] reframed the equations independently in non-local form.

The challenge remains when all elements are treated with nodeless valence electrons within pseudopotential framework. In this case, the wavefunctions of pseudopotential and many-electron must be commensurate. The electrons in valence state are predominantly localized in ionic core making it computationally expensive for carrying out the calculations. To overcome the limitation of NCP, Vanderbilt developed an advanced pseudopotential named Vanderbilt ultrasoft pseudopotential (USPP), where the need of including ionic

cores has been relaxed [20, 21]. In this case, USPP considers small portion of wave function, which is simulated instead of illustrating the full potential wave function using plane waves. This helps in reducing the cut-off energy of plane wave in the simulations. The compensation in plane wave cut-off energy lowers the cost of computation in many other computational efforts needed for improvement.

2.1.7 The projector augmented wave (PAW) method

The PAW method is a technique, which manoeuvre by reducing the linear augmented plane wave method (LAPW) and pseudopotential method allows for *ab initio* DFT calculations with higher computational efficacy. The PAW approach was first proposed by P. E. Blöchl in the year 1994 [5]. The linear methods basically allot full-wave potential functions, while pseudopotential method combined with plane wave basis set simplifies the computational effort of many-electron system. The amalgamation of both the aforementioned method avoids use of wave functions in vicinity to ion cores and oscillates rapidly due to the orthogonality required to express electron wavefunctions. In this context, while simulating the electron wavefunction it requires higher computational expense to describe the valence electron states involving plane wave basis sets. The PAW method overcome the aforementioned issue by reconstructing faster oscillating wavefunctions into tranquil wavefunction, which is evidently convenient for high-end computation and promotes many-body wavefunction from these tranquil wavefunctions. Moreover, the PAW method sheds apotheosis in step-by-step manner for clarity in understanding [22].

The formalism of PAW method is considered by mapping Hilbert space (HS) exhibiting robust oscillatory behaviour for many-electron wavefunctions, which reduces the wavefunction for orthogonal core electrons named as pseudo (ps) HS. The valence state wavefunction is transformed linearly to PS wavefunctions making it computationally efficient than many-electron wavefunction. The

linear transformation alter ps wave function to many-electron wavefunction can be written as,

$$|\Psi\rangle = T|\widetilde{\Psi}\rangle \quad (3.3)$$

Here, $T = 1 + \sum_R \hat{T}_R$ and R is the atomic position, \hat{T}_R is non-zero value within augmented region Ω_R . This signifies that the $|\Psi\rangle$ and $|\widetilde{\Psi}\rangle$ coalesce outside the augmented sphere. The full set of ps wavefunction can be considered inside $|\widetilde{\Psi}\rangle$, which maintains the orthogonality with core electrons. Near the edge of each atom, ps wavefunction is mapped into ps partial waves given as, $|\Psi\rangle = [1 + \hat{T}_R]|\widetilde{\Psi}_c\rangle$, c represents the small explication of atomic position R. The linear transformation can be identified and transform radial Schrödinger equation $|\Phi_i\rangle$. The linear operator can be termed as,

$$T = 1 + \sum_i (|\Phi_c\rangle - |\widetilde{\Phi}_c\rangle)\langle p'_c| \quad (3.4)$$

Here, $\langle p'_c|$ is the projector operator and can be expressed as $\langle p'_c| = \sum_d (\langle f_k|\widetilde{\Phi}_l\rangle_{cd})^{-1}\langle f_d|$ with the condition $\langle p'_c| = \delta_{cd}$.

Here, $\langle f_d|$ is an arbitrary and linear arrangement of equations.

2.1.8 van der Waals interaction in DFT

The exchange-correlation formalism discussed in section 2.1.3 fails to analyze vdW interaction in strongly correlated system, which is predominantly an important phenomenon to understand. To agree upon such systems, random phase approximation (RPA) is utilized to realize the correlation energy of strongly correlated system [23] and solves the many-body perturbation theory through density functional perturbation theory (DFPT). Till date, various methods have been characterized to treat vdW corrections with DFT. This particularly varies from meticulous dispersion functionals extract from *ab initio* DFT calculations to parameterizing fully empirical corrections. Most efficient description of dispersion correction is explained explicitly by non-local correlation functional. The adiabatic connection-fluctuation dissipation theorem

(ACFDT) mostly elevated due to its determination of the correlation energy term extending a computationally effective approach describing various structural information of crystals, lattice constants and atomic energies [24]. In this regard, it is likely to mention that ACFDT-RPA approach balances well with ionic, metallic, vdWs interacted systems and gives an effective information of weak binding energy on metallic surfaces [25], binding energies in layered Fermi systems such as graphene [26] and ferromagnetic systems like CrBr₃ [27].

The vdWs density functional theory method (vdW-DFT) [28] provides a conclusive non-local interaction straightly into the X_C functional, contrary to ACFDT-RPA approach. The vdW-DFT can be expressed in terms of exchange, correlation and non-local term in X_C energy [29],

$$E_{XC} = E_X^{GGA/Ex} + E_C^{LDA/GGA} + E_C^{nl} \quad (3.5)$$

Here, the first term described as exchange contribution from GGA or in true form, the second term is the correlation contribution characterized locally within LDA or GGA and the third term is the non-local term to be approximated [30]. Moreover, vdW-DFT has various applications and can solve many-body problem by modifying LDA or GGA along-side dispersion correction required to analyse variety of physical properties of solids [31] with efficient computational expense. The modified dispersion correction with empirical parameters is used promptly named as DFT-D method [32]. Grimme proposed an alternate empirical method named DFT-D2 for illustrating the binding energies extracted from experiments [51]. The inclusion of vdW correction solely depend to the total energy of solid having strong interatomic interaction with high accuracy, simple and post-processing data.

2.1.9 Coulomb interaction in DFT

Beyond HF, the electron-electron coupling in strongly correlated systems, such as lanthanides and actinides, transition metals, organometallic, can be constructed from *ab initio* DFT simulations, but fails to achieve the correlation

effect in such systems. The electrons act anonymously in such strongly correlated systems. In strongly correlated systems, the condition of particular electron relies robustly on the condition of neighbouring electrons of the system, which interacts or correlates with each other *via* Coulomb interaction. The orbitals such as s and p consisting of electrons behave like a wave and can be conveyed to a single-particle picture. In this regard, the weakly correlated systems are dissipated over the entire solid and reasonably explained within DFT framework. On the other hand, the f and d orbitals accumulate in the edge of atoms and are strongly correlated to each other. In this regard, LDA fails to depict strong correlation between excited and ground state energy properties, because the electrons act as wave like nature.

In general, strongly correlated systems can be understood from electronic band structure containing electronic states with attenuated bands. These attenuated bands exist near the Fermi level for such strongly coupled Coulomb materials. In this case, it is not feasible to disregard the correlation effect for understanding various physical phenomenon like electronic, magnetic, topological and transport properties. The limitations of DFT with strongly correlated systems are repercussions of scanty exchange-correlation energy approximations, irrespective of LDA or GGA formalism. In this regard, it is important to add a correction term to reduce computational expenses suggested by DFT+U approach [33, 34]. This correction term includes the total energy subtended from KS orbitals, which identifies electron-electron interaction term in a constant field and double counting term. Apart from DFT+U, it has another approximate method named GW approximation [35] similar to RPA method [36]. The DFT+U method is the buoyant method for utilizing high-end computational simulation efficiently for replicating electronic and structural properties of correlated systems. However, its calculation restricts itself when the calculation is performed beyond static mean-field theory [37]. In this regard, Hubbard model and DFT++ provides an interface to model Hamiltonians to handle computational efficacy and solve the dynamical mean field theory

(DMFT) maintaining the periodicity in bulk to low-dimensions [38]. The magnetic behaviour in monolayer limit coupled with metallic material can be understood by Anderson impurity model (AIM) as a prototypic model for electronically localized states.

2.2 Wannier tight binding Hamiltonian method (WTBH)

The tight-binding method (TB) is a semi-empirical technique to investigate electronic states by expressing Hamiltonian onto localized atomic orbitals. There are various conventions to establish TB models such as Slater-Koster approach [39], discrete $k.p$ model [40] and maximally localized Wannier functions (MLWF) [41] onto a crystal lattice. In this regard, we consider MLWF method alongside *ab initio* DFT calculation mentioned in the subsequent chapter of current thesis work. The introduction of Wannier functions (WF) [42] were propelled in the year 1937 and manifested to be one of the potent methods to study various phenomenon in condensed matter physics such as topological phases, magnetization, polarizability [41]. The WFs consider fully orthonormalized basis set that behaves as a connection between delocalized plane wave illustration from First-principles DFT simulation, basically used to determine various physical properties and a localized atomic orbital more likely to describe the forces and bonds associated with it. The Wannier tight binding Hamiltonian (WTBH) can be initiated using Wannier90 package [43] to construct MLWF, established on *ab initio* DFT calculations. Moreover, to obtain MLWF it needs various options to automate wannierization of energy bands in a particular energy range by disentangling the bands to investigate various physical properties such as topology, magnetic properties etc.

Computationally, Wannier function bears several advantages because of maximally localized atomic orbitals. This allows WTBH to regulate comparatively coarse real-space grid by performing Fourier transform of the Hamiltonian and derive over first Brillouin zone at high-symmetry points [44]. In this regard, this method is computationally very much efficient to carry out

simulations of higher computational cost, such as determining Chern number, Z_2 invariant, Berry phase, spin-texture, chirality, Landau level etc. Such interesting physical quantities can be achieved based on localized phenomenon [45] like defects [46], excitons [47], electron-electron interaction [48], electron-phonon coupling [49] and proximity effect [50], which can be easily modelled in Wannier basis sets.

2.2.1 Modelling of Wannier tight binding Hamiltonian method (WTBH)

The preliminary formalism of wannierization of band is well validated. A set of Bloch eigenvectors $|\psi_{n,k}\rangle$ pronounces the single-particle state for periodic crystal system exhibiting translational symmetry with band index n and crystal momenta k . The behaviour of jumping of electrons from one orbital state to another can be parameterized by considering localized atomic orbitals instead of Bloch electrons because the hindmost is delocalized. WFs are one of the most essential tools to choose localized orbitals with high accuracy and can be modelled by inverse Fourier transform of a Bloch electron state. In this regard, the real-space Wannier TB Hamiltonian can be constructed by discretizing the electron state via Fourier transform [41],

$$|\mathbf{R}_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} |\psi_{n,k}\rangle \exp(-i\mathbf{k} \cdot \mathbf{R}) d\mathbf{k} \quad (3.6)$$

Here, \mathbf{R} is the unit cell constructed from WFs, V depicts volume of the unit cell. The unitary matrix considers the Bloch states in momentum space to a transformed Bloch state $|\psi_{n,k}\rangle$ depending on the gauge transformation of WFs [41],

$$|\psi_{n,k}\rangle = \sum_m U_{mn}^{(k)} |\psi_{m,k}\rangle \quad (3.7)$$

Here, n and m are band indices. It is important to construct MLWFs, $U_{mn}^{(k)}$ is taken into consideration to minimize the Wannier spread functional. The TB

Hamiltonian $H_{ab}(\mathbf{k})$ for reciprocal space can be obtained by Fourier transforming the real-space Hamiltonian $H_{ab}(\mathbf{R})$ to momentum space,

$$H_{ab}(\mathbf{k}) = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot (\mathbf{R} + T_b - T_a)) H_{ab}(\mathbf{R}) \quad (3.8)$$

Here, the parenthesis ab denotes hopping of electron from orbital a of variational cell and b in unit cell of Wannier TB Hamiltonian.

$$\Omega = \sum_n [\langle r^2 \rangle_n - \bar{r}_n^2] \quad (3.9)$$

Here, $\bar{r}_n = \langle 0n | \mathbf{r} | 0n \rangle$ and $\langle r^2 \rangle_n = \langle 0n | r^2 | 0n \rangle$. The minimum energy is obtained iteratively, constructed on primary guess of localized orbitals.

Wannier tight binding Hamiltonian method promotes the energy bands and eigenvectors very much accurately. This method has many advantages over simpler TB method without erroneously, but Wannier functions creates bridge between localized orbital and *ab initio* technique making complicated calculations much easier and computationally efficient.

2.3 Concluding Remarks

In conclusions, advances in scaling quantum materials by solving quantum mechanical equations as a function of size restricts their novel aspects in understanding coupled systems like 2D vdW heterostructures. In this regard, solving many-body problem quantum mechanically from DFT and WTBH approach, are one of the substantial tools to investigate electronic, topological and magnetic properties of vdW quantum systems. For solving HK and KS theorems, DFT is legitimately precise technique for calculation of electronic properties using pseudopotential plane wave basis sets. While WTBH method rely on localized Wannier basis sets with coarse real-space grid using full potential basis sets. Thus, integration of DFT and WTBH provides an exact accuracy and reducible simulation to achieve various properties of complicated vdW quantum systems, where the computational cost becomes less expensive. This creates a bridge between First-principles simulations and WTBH for

determining various properties (topological, magnetic, electronic and transport) of strongly correlated systems.

References

- [1] Becke, A. D. Perspective: Fifty years of density-functional theory in chemical physics. *Journal of Chemical Physics*, 140:18A301, 2014.
- [2] Kohn, W., Becke, A. D., Parr, R. G. Density Functional Theory of Electronic Structure. *Journal of Physical Chemistry*, 100 (31):12974, 1996.
- [3] Hohenberg, P. and Kohn, W. Inhomogeneous electron gas. *Physical Review*, 136: B864-B871, 1964.
- [4] Kohn, W. and Sham, L. J. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140: A1133-A1138, 1965.
- [5] Blöchl, P. E. Projector augmented-wave method. *Physical Review B*, 50: 17953, 1994.
- [6] Perdew, J. P., Burke, K. and Ernzerhof, M. Generalized Gradient Approximation made simple. *Physical Review Letter*, 77:3865, 1996.
- [7] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G. L., Cococcioni, M., Dabo, I., Corso, A. D., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A. P., Smogunov, A., Umari, P., and Wentzcovitch, R. M. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502, 2009.
- [8] Born, M. and Oppenheimer, R. Quantum theory of molecules. *Annales de Physique-Berlin*, 84:04570484, 1927.

-
- [9] Fermi, E. Un metodo statistico per la determinazione di alcune propriet dell' atomo. *Rend. Accad. Naz. Lincei*, 6:602-607, 1927.
- [10] Thomas, L. H. The calculation of atomic fields. *Mathematical Proceedings of the Cambridge Philosophical Society*, 23(5):542-548, 1927.
- [11] Kaplan, T. A. and Kleiner, W. H. Hartree-Fock Theory: Slater determinants of Minimum energy. *Physical Review*, 156:1, 1967.
- [12] Rehn, D. A., Wills, J. M., Battelle, T. E. and Mattsson, A. E. Dirac's equation and its implications for density functional theory-based calculations of materials containing heavy elements. *Physical Review B*, 101:085114, 2020.
- [13] Jones, W. and Young, W. H. Density functional theory and the von Weizsacker method. *Journal of Physics C: Solid State Physics*, 4:1322, 1971.
- [14] Slater, J. The theory of complex spectra. *Physical Review*, 34 (2): 1293, 1929.
- [15] Hood, R. Q., Chou, M. Y., Williamson, A. J., Rajagopal, G., Needs, R. J., and Foulkes, W. M. C. Quantum monte Carlo investigation of exchange and correlation in silicon. *Physical Review Letter*, 78:3350-3353, 1997.
- [16] Perdew, J. P., Chevary, J. A., Vosko, S. H., Jackson, K. A., Pederson, M. R., Singh, D. J., and Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Physical Review B*, 46:6671-6687, 1992.
- [17] Soler, J. M., Artacho, E., Gale, J. D., Garcia, A., Junquera, J., Ordejon, P., and Sanchez-Portal, D. The SIESTA method for ab initio order-materials simulation. *Journal of Physics: Condensed Matter*, 14(11):2745-2779, 2002.
- [18] Hamann, D. R., Schluter, M., and Chiang, C. Norm-conserving pseudopotentials. *Physical Review Letter*, 43:1494-1497, 1979.
- [19] Kleinman, L. and Bylander, D. M. Efficacious form for model pseudopotentials. *Physical Review Letter*, 48:1425-1428, 1982.

-
- [20] Laasonen, K., Pasquarello, A., Car, R., Lee, C., and Vanderbilt, D. Carparinello molecular dynamics with vanderbilt ultrasoft pseudopotentials. *Physical Review B*, 47:10142-10153, 1993.
- [21] Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41:7892-7895, 1990.
- [22] Kresse, G. and Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*, 59:1758-1775, 1999.
- [23] Harl, J. and Kresse, G. Accurate bulk properties from approximate many-body techniques. *Physical Review Letter*, 103:056401, 2009.
- [24] Callen, H. B. and Welton, T. A. Irreversibility and generalized noise. *Physical Review*, 83:34-40, 1951.
- [25] Kresse, G. et al. Accurate surface and adsorption energies from many-body perturbation theory. *Nature Materials*, 9:741-744, 2010.
- [26] Polini, M., Tomadin, A., Asgari, R. and Macdonald, A. H. Density-Functional theory of Graphene sheets. *Physical Review B*, 78:115426, 2008.
- [27] Ghazaryan, D., Greenaway, M. T., Wang, Z., Guarochico-Moreira, V. H., Vera-Marun, I. J., Yin, J., Liao, Y., Morozov, S. V., Kristanovski, O., Lichtenstein, A. I., Katsnelson, M. I., Withers, F., Mishchenko, A., Eaves, L., Geim, A. K., Novoselov, K. S. and Misra, A. Magnon-assisted tunnelling in van der Waals heterostructure based on CrBr₃. *Nature Electronics*, 1:344, 2018.
- [28] Dion, M., Rydberg, H., Schroder, E., Langreth, D. C., and Lundqvist, B. I. Van der waals density functional for general geometries. *Physics Review Letter*, 92:246401, 2004.
- [29] Klimes, J. c. v., Bowler, D. R., and Michaelides, A. van der Waals density functionals applied to solids. *Physical Review B*, 83:195131, 2011.

-
- [30] Lee, K., Murray, E. D., Kong, L., Lundqvist, B. I., and Langreth, D. C. Higher-accuracy van der Waals density functional. *Physical Review B*, 82:081101, 2010.
- [31] Langreth, D. C., Lundqvist, B. I., Chakarova-Kck, S. D., Cooper, V. R., Dion, M., Hyldgaard, P., Kelkkanen, A., Kleis, J., Kong, L., Li, S., Moses, P. G., Murray, E., Puzder, A., Rydberg, H., Schrder, E., and Thonhauser, T. A density functional for sparse matter. *Journal of Physics: Condensed Matter*, 21(8):084203, 2009.
- [32] Douketis, C., Scoles, G., Marchetti, S., Zen, M., and Thakkar, A. J. Intermolecular forces via hybrid hartreefock scf plus damped dispersion (hfd) energy calculations. an improved spherical model. *The Journal of Chemical Physics*, 76(6):3057-3063, 1982.
- [33] Anisimov, V. I., Aryasetiawan, F., and Lichtenstein, A. I. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the $d+d+u$ method. *Journal of Physics: Condensed Matter*, 9(4):767-808, 1997
- [34] Anisimov, V. I., Zaanen, J., and Andersen, O. K. Band theory and mott insulators: Hubbard u instead of stoner i . *Physical Review B*, 44:943-954, 1991.
- [35] Hedin, L. New method for calculating the one-particle green's function with application to the electron-gas problem. *Physical Review*, 139: A796-A823, 1965.
- [36] Caruso, F., Rohr, D. R., Hellgren, M., Ren, X., Rinke, P., Rubio, A., and Scheffler, M. Bond breaking and bond formation: How electron correlation is captured in many-body perturbation theory and density-functional theory. *Physical Review Letter*, 110:146403, 2013.
- [37] Hewson, A. C. The kondo problem to heavy fermions. 1993.
-

-
- [38] Georges, A., Kotliar, G., Krauth, W., and Rozenberg, M. J. Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions. *Review Modern Physics*, 68:13-125, 1996.
- [39] Slater, J. C. and Koster, G. F. Simplified LCAO method for the Periodic potential problem. *Physical Review*, 94:1498, 1954.
- [40] Willatzen, M. and Lew Yan Voon, L.C. The k.p Method-Electronic Properties of Semiconductors, Vol. 53, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009, pp. 1689-1699.
- [41] Marzari, N., Mostofi, A.A., Yates, J.R., Souza, I. and Vanderbilt D. Maximally localized Wannier functions: Theory and applications. *Review Modern Physics*, 84:1419-1475, 2012.
- [42] Wannier, G. H. The structure of electronic excitation level in insulating crystals. *Physical Review*, 52:191, 1937.
- [43] Mostofi, A. A., Yates, J. R., Lee, Y-S., Souza, I., Vanderbilt, D. and Marzari, N. Wannier90: A tool for obtaining maximally-localized Wannier functions. *Computer Physics Communications*, 178:685, 2008.
- [44] Yates, J. R., Wang, X., Vanderbilt, D. and Souza, I. Spectral and Fermi surface properties from Wannier interpolation. *Physical Review B*, 75:195121, 2007.
- [45] Pacchioni, G. J. T. Modeling doped and defective oxides in catalysis with density functional theory methods: Room for improvements. *Journal of Chemical Physics*, 128:182505, 2008.
- [46] Gay, J. and Smith, J. Generalized-Wannier-function solutions to model surface potentials. *Physical Review B*, 11:4906, 1975.
- [47] Dvorak, M., Wei, S.-H. and Wu, Z. Origin of the variation of exciton binding energy in semiconductors. *Physical Review Letter*, 110:016402, 2013.

- [48] Şaşıoğlu, E., Schindlmayr, A., Friedrich, C., Freimuth, F. & Blügel, S. Wannier-function approach to spin excitations in solids. *Physical Review B*, 81:054434, 2010.
- [49] Agapito, L. A. and Bernardi, M. *ab initio* electron-phonon interactions using atomic orbital wave functions. *Physical Review B*, 97:235146, 2018.
- [50] Zutic, I., Matos-Abiague, A., Scharf, B., Dery, H. and Belaschenko, K. Proximitized materials. *Materials Today*, 22:85, 2019.
- [51] Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry*, 27(15):1787–1799, 2006.