I don’t demand that a theory correspond to reality because I don’t know what it is. Reality is not a quality you can test with litmus paper. All I’m concerned with is that the theory should predict the results of experiment.

-Stephen Hawking

Recent developments in quantum mechanics have shown that many phenomenon in nature can be understood by knowing how electrons respond to the environment of surrounding electrons, ions, electromagnetic fields and forces. The behavior of electrons under any of above environment establish the physical properties of solids. It becomes very important to develop a valid quantum-mechanical description of these systems. This chapter describes the basic theoretical framework used. The chapter is organized as follows. In the beginning, the general concept of electronic structure calculations is introduced. This is discussed within the frameworks of density functional theory (Sec. 2.3) with the approximations used like exchange-correlation approximation, pseudopotential approximation, supercell approximation and the convergence with k-points. The section is followed by the techniques used to minimize the total energy of the macroscopic system (Sec. 2.6). The FLAPW method and magnetic interactions are discussed in Sec. 2.7 and Sec. 2.8, respectively. Section 2.9 describes the conductance calculations using Landauer-Büttiker formalism.

2.1 TOTAL ENERGY CALCULATIONS

At the atomic scale, the physical properties of matter can be determined by Schrödinger equation, \( \hat{H}\Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N) \) (in the non-relativistic form), with \( \Psi \) being \( N \) particle wave function (excluding its spin coordinate). The explicit form of the differential operator \( \hat{H} \), the many body Hamiltonian is well known, it is linear and second order. It takes the form as given below:

\[
\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i,l} \frac{Z_l}{|r_i - R_l|} + \frac{1}{2} \sum_{i\neq j} \frac{1}{|r_i - r_j|} - \sum_{i} \frac{1}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j} \frac{Z_iZ_j}{|R_i - R_j|} \tag{2.1}
\]

where the summation indices \( i \) and \( j \) correspond to the electrons, whereas \( I \) and \( J \) correspond to nuclei. The spatial differential operator \( \nabla \) represents the kinetic energy.
operator. The spatial vector positions of the \(i^{th}\) electron and \(I^{th}\) nuclei are denoted as \(r_i\) and \(R_I\), respectively. The terms can be identified in order as, the kinetic energy for electrons, the attractive electron-nuclei interaction, the electron-electron repulsive interaction, the kinetic energy of nuclei and the nuclei-nuclei repulsion. In compact form, the Eq. (2.1) can be written as,

\[
\hat{H} = \hat{T}_e(r) + \hat{V}_{\text{elN}}(r; R) + \hat{V}_{\text{ex}}(r) + \hat{T}_N(R) + \hat{V}_{\text{NN}}(R)
\]  

(2.2)

Where, operators \(\hat{T}\) and \(\hat{V}\) are kinetic and potential operators and depend on the positions of the electrons \((e)\) and nuclei \((N)\) at \(r\) and \(R\), respectively. The solution of the differential equation \((\hat{H}\Psi(r_1, r_2, .., r_N) = E\Psi(r_1, r_2, .., r_N))\) is a many body wave function \(\Psi\), which depends on the space and time variable for each nucleus as well as space and spin variable for each electron. The position of each electron (and nuclei) is a probability distribution which can be determined from the squared modulus of the wave function \(|\psi_i(r)|^2\). The expectation value of any physical observable can be determined directly in terms of this quantum state,[209] i.e., for the position \(r\), the expectation value is, \(\langle r \rangle = \int_{-\infty}^{+\infty} r |\Psi(r)|^2 dr\). However, the problem is that, the complexity of the equation does not allow to solve it exactly in practice, for realistic situation. In order to solve these equations, we require a set of approximations. The important approximations are discussed briefly in the thesis.

- **Born-Oppenheimer Approximation**: The Eq. (2.1), would be easy to solve if it were *separable*, but the electron-nuclei interaction term depends explicitly on the position of electron \((e)\) as well as the position of the nuclei \((N)\). In addition, the mass of the nucleus \((M_I)\) is so large \((10^3 - 10^5\) times) than the mass of the electron \((m_e)\), that the mass of the electron can be neglected. Thus, the nuclei, being orders of the magnitude heavier than the electrons can be assumed to be stationary from the point of view of electrons. As the nuclei changes its configuration spatially, we assume that the electrons will instantaneously find new spatial configuration adjusted to the respective nuclei. Thus in Born-Oppenheimer approximation,[210] the problem is reduced to, solving the Schrödinger equation for \(N_e\) electrons in a static potential. By fixing the nuclei, the interaction energy between nuclei \((E_{NN})\) becomes constant. The kinetic energy of nuclei can also be omitted from new parametrized Hamiltonian as

\[
\hat{H} = \hat{T}_e(r) + \hat{V}_{\text{elN}}(r; R_0) + \hat{V}_{\text{ex}}(r) + V_{\text{NN}} = \hat{H}_e + V_{NN}
\]

(2.3)

The new term, electronic Hamiltonian is denoted as \(\hat{H}_e\), and it contains the information of motion of electrons in a fixed external potential due to nuclei. The Hamiltonian can be written as,

\[
\hat{H}_e = \hat{T}_e(r) + \hat{V}_{\text{ext}}(r; R_0) + \hat{V}_{\text{int}}(r)
\]

(2.4)

where, \(\hat{V}_{\text{int}}\) is the internal potential.

- **Time Dependence**: In general, the ground states of systems are investigated independent of time. For time dependent applications such as, the non equilibrium electron transport calculations, the stationary state ground state act as the initial reference. The time dependent part is introduced in the product solution \(\Psi(t) = e^{-i\varepsilon t}\Psi\). Here, \(\varepsilon_i\) are the solutions of the time independent Schrödinger’s equation \(\hat{H}\Psi_i = \varepsilon_i \Psi_i\) corresponding to the \(i^{th}\) stationary state of the total energy \(\varepsilon_i\).
2.2 Hartree-Fock Approximation

- **Relativistic effects and core electrons:** Relativistic effects for atoms with atomic number less than about 25 (for Manganese) can be neglected, since the relativistic effects are important for the core electrons of nuclei of heavy elements.[211] These electrons are also chemically inert and are treated in frozen core approximation. The scalar relativistic description of the isolated atoms are used to obtain the reference orbitals of core electrons.

With reference to the Eq. (2.4), the potential term $V_{\text{int}}(r)$ can be re-written, if we assume the valence electron as a continuous distribution of electron charge with the density,

$$V_{\text{int}}(r) = -\int dr\ n(r') \frac{1}{|r-r'|} \quad (2.5)$$

Within the independent electron approximation, the contribution of the electron in the state $\Psi_i$ to the electron density would be,

$$n_i(r) = -|\psi_i(r)|^2 \quad (2.6)$$

with the total electron density to be $n(r) = -e \sum_i |\Psi_i(r)|^2$

The single particle Schrödinger equation is then written as,

$$\frac{1}{2} \nabla_i^2 \Psi_i(r) + \hat{V}_{\text{ext}}(r) \Psi_i(r) + \left[ \sum_j \int dr' \ |\Psi_j(r')|^2 \frac{1}{|r-r'|} \right] \Psi_i(r) = E_i \Psi_i(r) \quad (2.7)$$

These equations are called as Hartree equations for every occupied electron state. The Hartree equations need to be solved self consistently. However, these Hartree equations can not explain the screening phenomenon, which is due to configuration of $(N-1)$ electrons surrounding a particular electron. Besides this drawback, the exchange interaction between the electrons due to Pauli’s exclusion principle is also not included in the Eq. (2.7).

### 2.2 Hartree-Fock Approximation

For $N$ electrons, the average total energy for a state can be evaluated for a particular $\Psi$, as

$$E[\Psi] = \int \Psi^* \hat{H} \Psi \ dr \equiv \langle \Psi | \hat{H} | \Psi \rangle \langle \Psi | \Psi \rangle \quad (2.8)$$

The equation is valid provided the wave functions are normalized. The energy of any state is higher than that of the ground state, unless $\Psi$ is the ground state, according to the variational theorem, i.e., $E[\Psi] \geq E_0$. The energy $E[\Psi]$ is a functional of the wave function and the product of the wave function in Eq. (2.8) (omitting the spin dependence) is defined as,

$$\langle \Psi | \Phi \rangle = \int dr_1...dr_N \ \Psi^*(r_1,...,r_N) \Phi(r_1,...,r_N) \quad (2.9)$$

The Hartree equations (Eq. 2.7) follow from minimizing Eq. (2.8) over all $\Psi$, which has the form,

$$\Psi(r_1,...,r_N) = \psi_1(r_1)\psi_2(r_2)\psi_N(r_N) \quad (2.10)$$

where, $\psi_i$ represents the orthonormal single particle wave function. However this is incompatible with the Pauli’s exclusion principle which requires change in the sign upon change in any two coordinates.
2.3 Density Functional Theory

\[ \Psi(r_1, \ldots, r_i, \ldots, r_j, \ldots, r_N) = -\Psi(r_1, \ldots, r_j, \ldots, r_i, \ldots, r_N) \]  

(2.11)

Hartree-Fock theory considers the structure of \( \Psi \) to be an antisymmetric product of the functions \( \psi_i \), each of which depends on the coordinate of single particle.

\[ \Psi(r_1, \ldots, r_N) = \begin{pmatrix} \psi_1(r_1) & \psi_1(r_2) & \ldots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \ldots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \ldots & \psi_N(r_N) \end{pmatrix} \]  

(2.12)

With the orthonormal single electron wave functions as stated in Eq. (2.12), the expression for Hartree-Fock energy can be written as,

\[ E_{HF} = \sum_i \int d\mathbf{r} \, \psi_i^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 + \tilde{V}_{ext}(\mathbf{r}) \right) \psi_i(\mathbf{r}) \]

\[ + \frac{1}{2} \sum_{i,j} \int d\mathbf{r} \, d\mathbf{r}' \, \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2 \]

\[ - \frac{1}{2} \sum_{i,j} \int d\mathbf{r} \, d\mathbf{r}' \, \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i(\mathbf{r}) \]  

(2.13)

The second term in Eq. (2.13) is the classical Coulombic interaction energy in terms of orbitals and the last term represents the exchange energy. By applying the variation theorem to this energy gives the ground state orbitals when they are orthonormal. This leads to Hartree-Fock equations:

\[ \left[ \frac{1}{2} \nabla^2 + \tilde{V}_{ext}(\mathbf{r}) + \sum_{i,j} \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_j|} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}) \]

\[ = \sum_j \int d\mathbf{r}' \, \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) = E_i \psi_i(\mathbf{r}) \]  

(2.14)

where the additional term represents the exchange term. Thus, the Hartree-Fock equations describe the non-interacting electrons under mean field potential which contains classical Coulomb potential and non-local exchange-potential.

However, solving the problem of \( N \) electrons is not an easy task, because the numbers of degrees of freedom is still very large. In addition, the Schrödinger’s equation cannot be solved exactly because of non-local nature of electron-electron interaction (\( \tilde{V}_{ee} \)). This has been achieved with the development of density functional theory developed by Hohenberg and Kohn\[212\] and Kohn and Sham.[213]

2.3 DENSITY FUNCTIONAL THEORY

The density functional theory (DFT) presents a powerful method to determine the ground state of the system based on total energy calculations and other physical observable of many electron system. The many body problem (Eq. 2.1) is extremely complex for computation even for the system containing few atoms. The DFT makes the problem simple, since the basic quantity is not the the \( N \)-particle wave function \( \Psi(r_1, r_2, \ldots, r_N) \), but the corresponding electron charge density \( n(\mathbf{r}) \) such that,
Density Functional Theory

\[ n(r) = N \int \cdots \int d{r}_1 \, d{r}_2 \ldots d{r}_N \, \Psi({r}_1, {r}_2, \ldots, {r}_N)^\dagger \sum_{i=1}^{N} \delta(r - r_i) \, \Psi({r}_1, {r}_2, \ldots, {r}_N) \]  \quad (2.15)

Here, \( n(r) \) is a non-negative function and integrates to the total number of electron \( N \).

\[ \int_V d^3r \, n(r) \equiv N \]  \quad (2.16)

In order to determine the ground state physical properties, the minimization of the energy functional \( E[\Psi] \) is essential. But for \( N \) particle system, the external potential \( \hat{V}_{\text{ext}}(r) \) fixes the Hamiltonian and hence \( N \) as well as, \( \hat{V}_{\text{ext}}(r) \) are responsible for the ground state properties. Instead of determining \( N \) and \( \hat{V}_{\text{ext}}(r) \), Hohenberg and Kohn theorem shows that the density \( n \) contains the same information as that of the wave function \( \Psi \), with the condition that \( \Psi \) is the ground state solution of the Schrödinger equation. Hence it becomes possible to calculate all ground state properties without knowing the explicit form of the wave function \( \Psi \).

2.3.1 Theorems of Hohenberg and Kohn

- For any system of \( N \) interacting particles, under the external potential \( \hat{V}_{\text{ext}}(r) \), the ground state wave function \( \Psi \) can be uniquely determined by the ground state electron density \( n(r) \).
  The expectation value of any operator \( \hat{O} \) is a unique functional \( \mathcal{O}[n(r)] \) of the ground state charge density.

\[ \mathcal{O}[n(r)] = \left\langle \Psi[n(r)] \right| \hat{O} \left| \Psi[n(r)] \right\rangle \]  \quad (2.17)

- There is only one external potential \( \hat{V}_{\text{ext}}(r) \) that gives the electron density in the ground state \( (n(r)) \). [i.e., for every external potential \( V_{\text{ext}} \), there is always a functional \( E_{\text{tot}}[\tilde{n}(r)] \) that is minimum and equals to the ground state energy \( E_0 \), provided that, the variational density \( \tilde{n}(r) \) coincides with the ground state density \( n(r) \)

\[ \tilde{n}(r) \in \mathcal{N} \implies E_{\text{tot}}[\tilde{n}(r)] \geq E_{\text{tot}}[n(r)] = E_0 \]  \quad (2.18)

where \( \mathcal{N} \) denotes the space of \( N \)-representable densities, obtained from any antisymmetric \( N \)-body wavefunction.

The total energy can be written with separate term for potential energy as,

\[ E_{\text{tot}}[n(r)] = E_{\text{uni}}[n(r)] + \int d{r} \, V_{\text{ext}}(r) \, n(r) \]  \quad (2.19)

where, the universal functional \( E_{\text{uni}}[n(r)] \) depends on the electron density \( n(r) \) and not on the potential \( V_{\text{ext}}(r) \).

The theorems of Hohenberg and Kohn have some important implications.\,[2.14]

For the universal functional, \( E_{\text{uni}}[n(r)] \), a variational principle holds: the ground state charge density minimizes the ground state energy. Hence, the density functional theory reduces the \( N \)-body problem to the determination of 3-dimensional function \( n(r) \) that minimizes functional \( E[n(r)] \).
2.3.2 Kohn-Sham Equations

Kohn-Sham mapped the system of interacting electrons on to an auxiliary system of non-interacting electrons having the same electron density \( n(\mathbf{r}) \). The ground state electron density \( n(\mathbf{r}) \) is represented as a sum over single particle orbitals (KS orbitals) \( \Psi_i \), which obey orthonormality conditions,

\[
\Psi_i^*(\mathbf{r}) \Psi_j(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}
\]  \hspace{1cm} (2.20)

Kohn-Sham introduced the variational property of the energy \( E_{\text{tot}}[n(\mathbf{r})] \).[213] The energy functional can be written as,

\[
E_{\text{tot}}[n(\mathbf{r})] = T[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + E_{\text{ext}}[n(\mathbf{r})]
\]  \hspace{1cm} (2.21)

where,

\[
T[n(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^{N} \int \Psi_i^* \nabla^2 \Psi_i \, d\mathbf{r}
\]  \hspace{1cm} (2.22)

\[
E_H[n](\mathbf{r}) = \int d\mathbf{r} \, d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]  \hspace{1cm} (2.23)

\[
E_{\text{ext}}[n(\mathbf{r})] = \int d\mathbf{r} \, V_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r})
\]  \hspace{1cm} (2.24)

The electron-electron interaction consists of

\[
E_{\text{ee}}[n(\mathbf{r})] = E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]
\]  \hspace{1cm} (2.25)

The \( E_{\text{ee}} \) denotes the electron-electron interaction due to exchange and correlation, which is not included in the Hartree term \( E_H \). The explicit form of \( T[n(\mathbf{r})] \) and \( E_{\text{ee}}[n(\mathbf{r})] \) is not known. Kohn-Sham made some approximations by treating the complex many particle problem as a problem of non-interacting electrons that leads to the same electron density. The main advantage of this picture is that one can work with the single-particle wave functions \( \psi_i(\mathbf{r}) \). The auxiliary function \( \Psi_{KS} \) has the form of \( N \) particle wavefunction of non-interacting electrons:

\[
\Psi_{KS}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det(\psi_i(\mathbf{r}_i))_{i,i'} \quad \text{with} \quad \int d\mathbf{r} \, \psi_i(\mathbf{r})^\dagger \psi_i(\mathbf{r}) = \delta_{i,i'}
\]  \hspace{1cm} (2.26)

With the definitions of \( n(\mathbf{r}) \) as explained in Eq. (2.15), \( \Psi_{KS} \) leads to the densities

\[
n(\mathbf{r}) = \sum_{i=1}^{N} \psi_i(\mathbf{r})^\dagger \psi_i(\mathbf{r}),
\]  \hspace{1cm} (2.27)

The Kohn-Sham formalism is based on,

- The variation of \( E_{\text{tot}} \) is done with the set of trial densities as shown in Eq. (2.27)

- the kinetic energy of the \( \Psi_{KS} \) is used to approximate the major part of the kinetic energy:

\[
T[n(\mathbf{r})] = \sum_{i=1}^{N} \left( \Psi_{KS} \left[-\frac{1}{2} \nabla^2 \right] \Psi_{KS} \right) + T^{(1)}[n(\mathbf{r})] = \sum_{i=1}^{N} d\mathbf{r} \, \psi_i(\mathbf{r})^\dagger \left( -\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) + T^{(1)}[n(\mathbf{r})]
\]  \hspace{1cm} (2.28)
The correction term $T^{(1)}$ is approximated by a simple expression for local electron density. The Hartree potential is calculated as,

$$V_{H}(r) = 2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.29)$$

The exchange-correlation energy is calculated as

$$E_{xc}[n(\mathbf{r})] = E_{xc}[n(\mathbf{r})] + T^{(1)}[n(\mathbf{r})] = E_{xc}[n(\mathbf{r})] + \left( T[n(\mathbf{r})] - \sum_{i=1}^{N} \langle \Psi_{KS} | \nabla^{2} | \Psi_{KS} \rangle \right)$$

The ground state energy functional (Eq. 2.19) can be rewritten as

$$E_{tot}[\{ \psi_i \}] = \int d\mathbf{r} \left( \sum_{i=1}^{N} \psi_i(\mathbf{r})^\dagger \left( -\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) + \left( \frac{1}{2} V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) \right) n(\mathbf{r}) \right) + E_{xc}[n(\mathbf{r})] \quad (2.31)$$

The equation (2.31) is based on the approximation that the space $\mathcal{N}$ of $\mathcal{N}$-representable trial densities is restricted to the densities that are represented by $N$ non interacting electrons (Eq. 2.27). The main advantage of the functional form of $E_{tot}$ in Eq. (2.31) is that the major part of the kinetic energy is expressed explicitly, hence reducing the error due to an approximation to $E_{xc}$. The exchange-correlation energy $E_{xc}$ can be approximated further viz., local density approximation (LDA)\cite{213} and generalized gradient approximation (GGA)\cite{215} and is discussed in the next subsection.

In order to get variational properties of the energy, we find the set of orthonormal wave-functions $\{ \psi_i(\mathbf{r}) \}_{i \in [1,N]}$ that minimize the $E_{xc}$ as described in Eq. (2.30). For an arbitrary variation of $\psi_i(\mathbf{r})$ under the orthonormality constraints, (Eq. 2.26), the variation of $E_{tot}$ must vanish. This leads to the condition that, the functional derivative with respect to $\psi_i$ of constrained functional,

$$E' = E_{tot} - \sum_{ij} \lambda_{ij} \left( \int d\mathbf{r} \psi_i^{*}(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right) \quad (2.32)$$

where, $\lambda_{ij}$ are Lagrange multipliers and it will vanish with

$$\frac{\delta E'}{\delta \psi_i(\mathbf{r})} = \frac{\delta E'}{\delta \psi_i(\mathbf{r})} = 0 \quad (2.33)$$

Also, we use,

$$\frac{\delta n(\mathbf{r})}{\delta \psi_i^{*}(\mathbf{r}')} = \psi_i(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \quad (2.34)$$

The variation then comes out using the functional derivative (Appendix-A),

$$\frac{\delta T}{\delta \psi_i(\mathbf{r})} = -\frac{1}{2} \sum \nabla^2 \psi_i(\mathbf{r}) \quad (2.35)$$

$$\frac{\delta E_{H}}{\delta \psi_i(\mathbf{r})} = \int d\mathbf{r'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) \quad (2.36)$$

and we get Euler-Lagrange equation as,

$$\left( -\frac{1}{2} \nabla^2 + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})] + V_{ext}[n(\mathbf{r})] \right) \psi_i(\mathbf{r}) = \sum_{j} \lambda_{ij} \psi_j(\mathbf{r}) \quad (2.37)$$
and an exchange-correlation potential as

\[ V_{xc}[n(r)] = \frac{\delta E_{xc}}{\delta n(r)} \]  \tag{2.38}

The Lagrange multiplier \( \lambda_{ij} \) can be obtained by multiplying both sides of Eq. (2.37) by \( \psi_i^*(r) \) and integrating,

\[ \lambda_{ik} = \int dr \; \psi_i^*(r) \left( -\frac{1}{2} \nabla^2 + V_H[n(r)] + V_{xc}[n(r)] + V_{ext}[n(r)] \right) \psi_i(r) \]  \tag{2.39}

This gives the Kohn-Sham equations,

\[ \left( \hat{H}_{KS} - \epsilon_i \right) \psi_i(r) = 0 \]  \tag{2.40}

where, \( \lambda_{ij} = \delta_{ij} \epsilon_j \) and the operator \( \hat{H}_{KS} \) is called as Kohn-Sham Hamiltonian, and is defined as,

\[ \hat{H}_{KS} = -\frac{1}{2} \nabla^2 + V_H[n(r)] + V_{xc}[n(r)] + V_{ext}[n(r)] \equiv -\frac{1}{2} \nabla^2 + V_{KS}(r) \]  \tag{2.41}

and this is related to the functional derivative of the energy as,

\[ \frac{\delta E_{tot}}{\delta \psi_i^*(r)} = \hat{H}_{KS} \psi_i(r) \]  \tag{2.42}

### 2.3.3 Local Density Approximation

The exact form of the exchange-correlation energy functional \( E_{xc} \) is not known. A simple and powerful approximation is the local density approximation (LDA),\[213\] where the density is treated locally as an uniform electron gas and the \( E_{xc} \) at every point in the system is same as that of the uniform gas having the same electron charge density.

\[ E_{xc}[n(r)] \approx \int dr \; \epsilon_{xc}[n(r)] \; n(r) \]  \tag{2.43}

The function \( \epsilon_{xc} \) is exchange-correlation energy per particle and is purely local. The \( \epsilon_{xc} \) depends purely on electron density. Therefore, the exchange correlation potential becomes

\[ V^{LDA}_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} = \frac{n(r) \frac{\partial \epsilon_{xc}[n(r)]}{\partial n(r)}}{n(r)} \]  \tag{2.44}

and the Kohn-Sham orbital equation then becomes,

\[ \left[ -\frac{1}{2} \nabla^2 + V_H[n(r)] + V^{LDA}_{xc}[n(r)] + V_{ext}[n(r)] \right] \psi_i(r) = \epsilon_i \psi_i(r) \]  \tag{2.45}

The self consistent solution of Eq. (2.45) is called as Kohn-Sham local density approximation (KS-LDA),\[214\]

For the case of rapidly varying densities, the approximation (Eq. 2.43) needs to be improved. A generalization to a functional that depends also on gradients, Generalized Gradient Approximation (GGA),\[215\] has been made to give an improved description of systems when electron density is varying very rapidly. In this correction, the exchange-correlation functional is written as a function of the local density and of the local gradient of the density, which is an additional factor that multiplies the homogeneous electron densities:

\[ E_{xc}[n(r)] \approx \int dr \; \epsilon_{xc}[n(r), |\nabla n(r)|] \]  \tag{2.46}
The GGA functionals are simple extension of LDA to inhomogeneous electron densities. These functionals are not constructed to describe non-collinear magnetic densities unlike LDA functionals. Previous studies show that, GGA leads to less precise results in comparison with the LDA in the case of transition metals and magnetic materials.\[216\]

### 2.3.4 The Total Energy

The electronic energy $E_{\text{tot}}$ is given by functional (2.31). The Eq. (2.31) can be solved self consistently by converging the electron charge density $n$. Let's denote $n^{(\text{in})}$ being the charge density that is used to construct the effective potential ($V_{\text{eff}}$ shown in the following equation). It may differ from the density $n^{(\text{out})}$ that is constructed from the solutions of the $\{\psi_i\}$

\[
\left( -\frac{1}{2} \nabla^2 + V_H[n^{(\text{in})}] + V_{\text{ext}} + V_{xc}[n^{(\text{in})}] \right) \psi_i = \epsilon_i \psi_i \quad , \quad n^{(\text{in})} \neq n^{(\text{out})} = \sum_i \psi_i^\dagger \psi_i \quad (2.47)
\]

The difference between $n^{(\text{in})}$ and $n^{(\text{out})}$ can be minimized by inserting only one density in the Eq. (2.31). This will give $n^{(\text{out})}$. For the evaluation of $\sum_i \psi_i^\dagger \left( -\frac{1}{2} \nabla^2 \right) \psi_i$, the information about the wave function is required, which is not known for the $n^{(\text{in})}$. The density mixing process can be used to get the information about the wave function. Therefore the total electronic energy can be written as,

\[
E_{\text{tot}}[n^{(\text{out})}] = \int d\mathbf{r} \left( \sum_i \psi_i^\dagger \left( -\frac{1}{2} \nabla^2 \right) \psi_i + n^{(\text{out})} V_{\text{ext}} \right) + E_H[n^{(\text{out})}] + E_{xc}[n^{(\text{out})}] \quad (2.48)
\]

The kinetic energy term can be evaluated directly. The derivatives can be avoided because $\{\psi_i\}$ are solutions of Kohn-Sham equations:

\[
\left( -\frac{1}{2} \nabla^2 + V_{\text{eff}}[n^{(\text{in})}] \right) \psi_i = \epsilon_i \psi_i = \sum_i \psi_i^\dagger \left( -\frac{1}{2} \nabla^2 \right) \psi_i = \sum_i \psi_i^\dagger (\epsilon_i - V_{\text{eff}}[n^{(\text{in})}]) \psi_i \quad (2.49)
\]

The expression for $E_{\text{tot}}[n^{(\text{out})}]$ can be simplified as:

\[
E_{\text{tot}}[n^{(\text{out})}] = \sum_i \epsilon_i + \int d\mathbf{r} n^{(\text{out})} \left( -V_H[n^{(\text{in})}] - V_{xc}[n^{(\text{in})}] \right) + E_H[n^{(\text{out})}] + E_{xc}[n^{(\text{out})}] \quad (2.50)
\]

The right hand of the above equation can be interpreted as, a functional $\tilde{E}$ that depends on $n^{(\text{out})}, n^{(\text{in})}, \{\psi_i\}$

\[
\tilde{E}[n_1, n_2, \{\psi_i\}] = E_{\text{tot}}[n_1] \bigg|_{n^{(\text{in})}=n_2} \quad (2.51)
\]

The charge density is said to be converged well if,

\[
n^{(\text{out})} = n^{(\text{in})} + \delta n \quad \text{with} \quad \|\delta n\| \ll \|n^{(\text{in})}\| \quad (2.52)
\]

The equation for $E_{\text{tot}}[n^{(\text{out})}]$ can be approximated by,

\[\text{In Eq. (2.51), the entity } n_1 \text{ is the input density for the first self consistent cycle, whose output density is } n_2. \text{ In the next self-consistent cycle, } n_2 \text{ is taken as input density } n^{(\text{in})}_i, \text{ if the convergence is not achieved.}\]
\[ E_{\text{tot}}[\hat{n}^{\text{(out)}}, \hat{n}^{\text{(in)}}, \{\epsilon_i\}] \approx \tilde{E}[\hat{n}^{\text{(in)}}, \hat{n}^{\text{(in)}}, \{\epsilon_i\}] + \int d\mathbf{r}(\delta n) \frac{\delta \tilde{E}[\tilde{n}, \hat{n}^{\text{(in)}}, \{\epsilon_i\}]}{\delta \tilde{n}} \bigg|_{\tilde{n} = \hat{n}^{\text{(in)}}} + O((\delta n)^2) \quad (2.53) \]

The second term in above equation equals zero as:

\[ \frac{\delta \tilde{E}[\tilde{n}, \hat{n}^{\text{(in)}}, \{\epsilon_i\}]}{\delta \tilde{n}} \bigg|_{\tilde{n} = \hat{n}^{\text{(in)}}} = -V_H[\hat{n}^{\text{(in)}}] - V_{\text{xc}}[\hat{n}^{\text{(in)}}] + \left( \frac{\delta E_H[\tilde{n}]}{\delta \tilde{n}} + \frac{\delta E_{\text{xc}}[\tilde{n}]}{\delta \tilde{n}} \right) \bigg|_{\tilde{n} = \hat{n}^{\text{(in)}}} = 0 \quad (2.54) \]

Hence the expression

\[ E_{\text{tot}}[\hat{n}^{\text{(out)}}, \hat{n}^{\text{(in)}}, \{\epsilon_i\}] = \sum_i \epsilon_i - \int d\mathbf{r} \hat{n}^{\text{(in)}} \left( \frac{1}{2} V_H + V_{\text{xc}} \right) + E_{\text{xc}}[\hat{n}^{\text{(in)}}] \quad (2.55) \]

can be a good approximation in the case of well converged electron density. \[217\]

\( E_{\text{dc}} \) is a double-counting term, same as \( \int d^3 \mathbf{r} \frac{1}{2} v_H n \) in the Hartree method. The energy \( E \), that is relevant for the analysis of complete chemical, structural and magnetic configuration is the sum of electronic energy \( E_{\text{tot}} \) and the energy due to Coulombic interaction between the atomic nuclei \( E_{ii} \)

\[ E = E_{\text{tot}} + E_{ii} \quad (2.56) \]

With \( E_{ii} \) given as

\[ E_{ii} = \sum_{\mu, \mu' \in \{1,M\}, \mu \neq \mu'} \frac{Z(\mu)Z(\mu')}{|\mathbf{R}(\mu) - \mathbf{R}(\mu')|} \quad (2.57) \]

\[ \text{2.4 SPIN IN DENSITY FUNCTIONAL THEORY} \]

Open shell structures tend to show measurable magnetic moment which originates from their electronic structure. The electronic spin is responsible for the nonzero magnetic moment in the system, which as collective phenomenon makes the structure magnetic. Hence a development of DFT that includes the spin phenomenon was essential to investigate the magnetic properties in the system. In this section, we briefly highlight the spin structure in DFT beginning with the one electron wave function.

In non-relativistic framework, the spin is introduced in two component spinor wave function as,

\[ \psi(\mathbf{r}) = \begin{pmatrix} \psi_\alpha(\mathbf{r}) \\ \psi_\beta(\mathbf{r}) \end{pmatrix} \quad (2.58) \]

Where the component in above equation can be expressed as, \( \psi_\alpha(\mathbf{r}) = \psi_{\alpha+\frac{1}{2}} \), and \( \psi_\beta(\mathbf{r}) = \psi_{\alpha-\frac{1}{2}} \). Two spin functions can be defined with spin variable of \( \frac{1}{2} \) and \(-\frac{1}{2} \) such that,

\[ \alpha(\frac{1}{2}) = 1 \quad \text{and} \quad \alpha(-\frac{1}{2}) = 0 \quad (2.59) \]
\[ \beta(\pm \frac{1}{2}) = 0 \quad \text{and} \quad \beta(-\frac{1}{2}) = 1 \]  

(2.60)

\[ \psi(r,s) = \psi_\alpha(r)\alpha(s) + \psi_\beta(r)\beta(s) \]  

(2.61)

The non-relativistic one-electron Hamiltonian \( \hat{H} \) is spin independent and hence commutes with the spin operators, in particular \([\hat{H}, \hat{s}_z] = [\hat{H}, \hat{s}_2] = 0\) where, the operator \( \hat{s} \) is defined as,

\[ \hat{s} = -i \hbar \sigma = \frac{\hbar}{2} \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix} \]  

(2.62)

\( \sigma \)'s are Pauli’s matrices and expressed as,

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]  

(2.63)

### 2.4.1 Spin structure for many electron system

It is convenient to introduce the spin coordinates \( s_i \) that can be used to distinguish from spatial coordinates. The \( N \) electron wave function then depends on \( N \) spin coordinates along with \( N \) spatial coordinates as:

\[ \Psi = \Psi(r_1s_1, r_2s_2, ..., r_Ns_N) \]  

(2.64)

where \( r_is_i \) denotes the combination of space and spin coordinates, with each spin coordinate assuming the values of \(-1/2\) and \(+1/2\). In total, \( 2^N \) different combinations of the values are possible leading to \( 2^N \) components of the wave function.

### 2.4.2 Electron spin density

The total electron density as defined in Eq. (2.15) indicates the probability of finding any electron of a many electron system at certain position \( r \). The spin coordinate can be incorporated by treating the wave function as a two component spinor. The magnetization density is then three component and can be written as,

\[ m(r) = \int \int ... d\mathbf{r}_1 \ d\mathbf{r}_2 ... d\mathbf{r}_N \ \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)^\dagger \sigma \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \]  

(2.65)

Where, \( \sigma = (\sigma_x, \sigma_y, \sigma_z)^t \) denotes the Pauli matrices as discussed in above section.

Let us consider the magnetic field that acts on the spin of the electrons. The Hamiltonian of the system can be written as,

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\text{ext}}(\mathbf{r}_i) + 2\beta_e \sum_i \mathbf{B}(\mathbf{r}) \cdot \mathbf{s}_i \]  

(2.66)

where, \( \beta_e = \frac{e\hbar}{2mc} \) is the Bohr magnetron and \( s_i \) is the spin angular momentum.
The potential energy operator can be written as,

\[ \hat{\mathcal{V}} = \sum_i V_{\text{ext}}(\mathbf{r}_i) + 2\beta_e \sum_i \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i \]
\[ = \int d\mathbf{r} \ V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) - \int d\mathbf{r} \ \mathbf{B}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r}) \]  
(2.67)

For \( n(\mathbf{r}) \) and \( \mathbf{m}(\mathbf{r}) \) being the total electron density and the magnetization density, respectively, let's denote \( n^\alpha(\mathbf{r}) \) and \( n^\beta(\mathbf{r}) \) as the spin up and spin down electron densities respectively corresponding to the diagonal elements of \( \gamma_i \) in the spin space\(^2\). It can be said that, \( n^\alpha(\mathbf{r}) \) and \( n^\beta(\mathbf{r}) \) are the basic variables.[214]

In the context of the definitions of \( n^\alpha(\mathbf{r}) \) and \( n^\beta(\mathbf{r}) \), it can be proved that,[214]

\[ m(\mathbf{r}) = \beta_e [n^\beta(\mathbf{r}) - n^\alpha(\mathbf{r})] \]  
(2.68)

In spin density functional theory, the search for minimum of the energy is an extension of the non-spin case as:

\[ E_{\text{tot}} = \min_{n^\alpha, n^\beta} \left\{ \left| \mathbf{\Psi} - \frac{1}{2} \nabla_i \mathbf{\Psi} + \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \mathbf{\Psi} \right| - \int d\mathbf{r} \left( V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) - b(\mathbf{r}) m(\mathbf{r}) \right) \right\} \]

\[ = \min_{n^\alpha, n^\beta} \left\{ \min_{\mathbf{\Psi} \rightarrow n^\alpha, n^\beta} \left( \mathbf{\Psi} - \frac{1}{2} \nabla_i \mathbf{\Psi} + \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \mathbf{\Psi} \right) + \int d\mathbf{r} \left( V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) - b(\mathbf{r}) m(\mathbf{r}) \right) \right\} \]

\[ = \min_{n^\alpha, n^\beta} \left\{ F[n^\alpha, n^\beta] + \int d\mathbf{r} \left( V_{\text{ext}}(\mathbf{r}) + \beta_e b(\mathbf{r}) \right) n^\alpha(\mathbf{r}) + \left( V_{\text{ext}}(\mathbf{r}) - \beta_e b(\mathbf{r}) \right) n^\beta(\mathbf{r}) \right\} \]

(2.69)

where,

\[ F[n^\alpha, n^\beta] = \min_{n^\alpha, n^\beta} \left( \mathbf{\Psi} - \frac{1}{2} \nabla_i \mathbf{\Psi} + \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \mathbf{\Psi} \right) \]

In above equation, the \( n^\alpha, n^\beta \) helps to describe the ground state of the system. However, the form of \( F[n^\alpha, n^\beta] \) is unknown and approximations are necessary in order to evaluate it.

2.4.3 Kohn-Sham Method

The Kohn-Sham method can be used to handle the kinetic energy contribution in the energy functional \( F[n^\alpha, n^\beta] \). Hence, \( F[n^\alpha, n^\beta] \) can be written as,

\[ F[n^\alpha, n^\beta] = T_s[n^\alpha, n^\beta] + V_H[n^\alpha + n^\beta] + E_{xc}[n^\alpha, n^\beta] \]  
(2.70)

where, \( T_s[n^\alpha, n^\beta] \) is the kinetic energy functional, for densities \( n^\alpha, n^\beta \). The term \( V_H \) and \( E_{xc} \) represents the Hartree and exchange correction energy functional. The set \( \phi_{ia} \) and \( n_{ia} \) is defined such that,

\[ \sum_i n_{ia} |\phi_{ia}(\mathbf{r})|^2 = n^\alpha(\mathbf{r}), \quad \sum_i n_{ib} |\phi_{ib}(\mathbf{r})|^2 = n^\beta(\mathbf{r}) \]  
(2.71)

\(^2\gamma_i (\mathbf{r}_i, \mathbf{r}_1) = \sum_I \psi_i(\mathbf{r}_i) \psi_I^*(\mathbf{r}_1) \Rightarrow \) the first order reduced density matrix of Fock-Dirac density matrix
The total energy functional then becomes,

\[
E_{\text{tot}}[n^\alpha,n^\beta] = \sum_{i\alpha} n_{i\alpha} \int d\mathbf{r} \phi_{i\alpha}(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \phi_{i\alpha}(\mathbf{r}) + V_H[n^\alpha,n^\beta] + E_{xc}[n^\alpha,n^\beta] + \int d\mathbf{r} \left( V_{\text{ext}}(\mathbf{r}) + \beta_e b(\mathbf{r}) n^\alpha(\mathbf{r}) + (V_{\text{ext}}(\mathbf{r}) - \beta_e b(\mathbf{r})) n^\beta(\mathbf{r}) \right)
\]

The minimum of \( E_{\text{tot}}[n^\alpha,n^\beta] \) can be evaluated by variational theorem within the space of orbitals \( \phi_{i\alpha} \) provided that the normalization,

\[
\int d\mathbf{r} \phi_{i\alpha}(\mathbf{r}) \phi_{i\alpha}(\mathbf{r}) = 1
\]

The Kohn-Sham equations then become,[214]

\[
\hat{h}_{\text{eff}}^\alpha \phi_{i\alpha}(\mathbf{r}) = \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}^\alpha(\mathbf{r}) \right] \phi_{i\alpha}(\mathbf{r}) = \epsilon_{i\alpha}^\alpha \phi_{i\alpha}(\mathbf{r}), \quad i = 1,2,\ldots, N^\alpha
\]

Similarly,

\[
\hat{h}_{\text{eff}}^\beta \phi_{j\beta}(\mathbf{r}) = \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}^\beta(\mathbf{r}) \right] \phi_{j\beta}(\mathbf{r}) = \epsilon_{j\beta}^\beta \phi_{j\beta}(\mathbf{r}), \quad i = 1,2,\ldots, N^\beta
\]

The spin dependent effective potentials can be written as,

\[
\begin{align*}
V_{\text{eff}}^\alpha &= V_{\text{ext}}(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta E_{xc}[n^\alpha,n^\beta]}{\delta n^\alpha(\mathbf{r})} \\
V_{\text{eff}}^\beta &= V_{\text{ext}}(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta E_{xc}[n^\alpha,n^\beta]}{\delta n^\beta(\mathbf{r})}
\end{align*}
\]

\( \epsilon_{i\alpha}^\alpha \) are the Lagrange multiplier for the constraint, \( \int d\mathbf{r} \phi_{i\alpha}(\mathbf{r}) \phi_{i\alpha}(\mathbf{r}) = 1 \) and

\[
N^\alpha = \int d\mathbf{r} n^\alpha(\mathbf{r}), \quad N^\beta = \int d\mathbf{r} n^\beta(\mathbf{r})
\]

The variation of the total energy can be obtained only when

\[
N = N^\alpha + N^\beta
\]

In above treatment, the kinetic energy term \( T_0[n^\alpha,n^\beta] \) is treated exactly through the spin Kohn-Sham equations Eq. (2.75) and (2.76). We note that the \( E_{xc}[n^\alpha,n^\beta] \) exists, though yet unknown.

This method has certain advantages. First, the method can describe the many particle system under the presence of external magnetic field. The theory can incorporate the spin orbit effects and other relativistic effects. The expressions can be extended to obtain the effects even in the absence of the magnetic field. Hence the results should be identical for DFT and spin polarized DFT, when \( b = 0 \), provided the exact form of \( E_{xc}[n^\alpha(\mathbf{r}),n^\beta(\mathbf{r})] \) and \( n(\mathbf{r}) \) is used.
2.4.4 Relativistic Corrections to Kohn-Sham Equations

While dealing with the systems with heavy nuclei, relativistic effects become more important due to high kinetic energy of the electrons in the vicinity of the nucleus. Dirac-equation is used to derive the relativistic density functional theory.[218] Similar to the non-relativistic case, we can decompose the total energy term as a summation of single particle energies, the Hartree term and the exchange-correlation term. The Dirac equation is used to calculate the kinetic energy in the relativistic theory. Denoting $\sigma$ as a vector of Pauli spin-matrices, the wave function can be separated into 4-components with two spatial components and two spin components ($\psi_{i,\alpha}$ and $\psi_{i,\beta}$). A relativistic DFT[218] can be derived from Dirac equation,

$$\{c\alpha \cdot \hat{p} + \frac{1}{2} \beta c^2 + V_{\text{eff}}(\mathbf{r}) + B_{xc} \cdot \sigma\} \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r})$$

(2.79)

where, $c$ denotes the velocity of light, $\hat{p}$ denotes the momentum operator $(-\frac{1}{2} \nabla)$, $B_{xc} = \frac{\delta E_{xc}[n, n]}{\delta n(\mathbf{r})}$, and $E_i = \epsilon_i + \frac{1}{2} c^2$ is the eigen energy with an additional contribution from the rest mass. The spinor wavefunction $\psi(\mathbf{r})$ has 4 components and we define,

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(2.80)

Where $\sigma$ denotes the Pauli matrices as expressed in Eq. (2.63) and $\beta$ is the $(2 \times 2)$ identity matrix. The 4 component spinor wavefunction $\psi_i$ consists of two parts ($\psi_\alpha(\mathbf{r})$ and $\psi_\beta(\mathbf{r})$):

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_\alpha(\mathbf{r}) \\ \psi_\beta(\mathbf{r}) \end{pmatrix}, \quad \psi_\alpha(\mathbf{r}) = \begin{pmatrix} \psi_\alpha^\dagger \\ \psi_\alpha^\dagger \end{pmatrix}, \quad \psi_\beta(\mathbf{r}) = \begin{pmatrix} \psi_\beta^\dagger \\ \psi_\beta^\dagger \end{pmatrix}$$

(2.81)

The Kohn-Sham equation can be written as,

$$\mathcal{H}_{rel} \phi_i = \epsilon_i \phi_i$$

(2.82)

The spinor part of the wave function is expressed in terms of $\phi_i$'s as:

$$\psi_{i\alpha} = \left(1 - \frac{1}{2 c^2} \hat{p}^2\right) \phi_i + \mathcal{O}(c^{-4})$$

(2.83)

$$\psi_{i\beta} = \left(\frac{1}{c} (\sigma \cdot \hat{p}) + \frac{1}{c^2} \left(-\frac{1}{2} \hat{p}^2 + V - \epsilon_i\right)(\sigma \cdot \hat{p})\right) \phi_i + \mathcal{O}(c^{-5})$$

(2.84)

The Hamiltonian then becomes,

$$\mathcal{H}_{rel} = \mathcal{H}_{KS} + \frac{1}{c^2} \left(-\hat{p}^4 + \frac{1}{2} \nabla^2 (V_{\text{eff}} + \sigma \cdot B_{xc})\right) + \frac{1}{c^2} \sigma \cdot ((\nabla V_{\text{eff}}) \times \hat{p}) + \frac{1}{c^2} \mathbf{B}$$

(2.85)

In the above equation, $\mathcal{H}_{KS}$ represents the non-relativistic Kohn-Sham equation and $\mathbf{B}$ is the $(2 \times 2)$ matrix, whose elements are usually small compared to other corrections in the Hamiltonian and can safely be neglected. The second term in Eq. (2.85) is invariant under rotation in the spin space and this contribution is called as scalar-relativistic ($\mathcal{H}_{SR}$) approximation.[219] The invariance of $\mathcal{H}_{SR}$ under a rotation in spin space follow:
\[ U^{\dagger}\mathcal{H}_{SR}U = \mathcal{H}_{SR} \]  \hfill (2.86)

where, \( U \) is \((2 \times 2)\) matrix for spin rotation. The term \( \sigma \cdot \mathbf{B} \) commutes with \( U \), when we say that,

\[ \mathbf{B}_{xc} \parallel \mathbf{m} \quad \text{with} \quad \mathbf{m} = \sum_{i} \Psi_{i}^{\dagger} \sigma \Psi_{i} \]  \hfill (2.87)

The wave functions are rotated upon application of a rotation to a system, i.e., \( \Psi_{i} \rightarrow U \Psi_{i} \) and hence \( \mathbf{B}_{xc} \propto \sum_{i} \Psi_{i}^{\dagger} U^{\dagger} \sigma U \Psi_{i} \) is also rotated. Therefore, the term \( \sigma \cdot \mathbf{B}_{xc} \) is a scalar product and follows spin rotation invariance.

The spin orbit coupling operator can be written as

\[ \mathcal{H}_{so} = \frac{1}{c^2} \sigma \cdot ( (\nabla V_{\text{eff}}) \times \hat{\mathbf{p}} ) \]  \hfill (2.88)

In Eq. (2.88), the term for potential gradient \((\nabla V)\) is large for the region close to the core region of the atoms, the potential term can be approximated by its spherically symmetric average \((V_{\text{eff}}(r) \approx \tilde{V}_{\text{eff}}(r))\), where \( r = |\mathbf{r} - \mathbf{R}| \) With this, Eq. (2.88) can be simplified by using\(^3\)

\[ (\nabla V_{\text{eff}}) \times \hat{\mathbf{p}} \approx \left( \frac{d}{dr} \tilde{V}_{\text{eff}} \right) \mathbf{r} \times \hat{\mathbf{p}} = \left( \frac{d}{dr} \tilde{V}_{\text{eff}} \right) \hat{\mathbf{L}} \]  \hfill (2.89)

The spin orbit coupling operator takes the form,

\[ \mathcal{H}_{so} = v(r) \sigma \cdot \hat{\mathbf{L}} \]  \hfill (2.90)

where the spherically symmetric function is denoted by \( v(r) \) which decays fast for increasing distance \( r \) from the nucleus.

### 2.5 SuperCell and Pseudopotential Approximations

#### 2.5.1 Supercell Approximation

With the approximations discussed in above subsections, the problem still remains to solve the Kohn-Sham equations for infinite number of electrons if the system under investigation is bulk. In order to make the problem simpler, we assume that our system of interest can be represented by a box of atoms which can be repeated periodically in all Cartesian directions. For isolated systems like finite size systems or clusters, the domain in which the Kohn-Sham equations should be solved can be restricted to the region where the effective potential decays and vanishes at the boundary of the cell. For bulk systems, the infinite number of electrons move in a static potential of infinite number of nuclei. This problem can be solved by performing calculations on periodic systems and by applying Bloch’s theorem to the electronic wave function.

The box can be represented by three primitive vectors viz., \( \mathbf{a}_{1} \), \( \mathbf{a}_{2} \) and \( \mathbf{a}_{3} \). The volume of the box can be written as,

\[ \Omega = \mathbf{a}_{1} \cdot (\mathbf{a}_{2} \times \mathbf{a}_{3}) \]  \hfill (2.91)

\[ \nabla V_{\text{eff}}(r) \approx \sum_{\mu} \frac{\partial \tilde{V}_{\text{eff}}(r\mu)}{\partial r_{\mu}} \frac{\mathbf{r}^{\mu}}{r^{\mu}} \]
\[ T = N_1 \mathbf{a}_1 + N_2 \mathbf{a}_2 + N_3 \mathbf{a}_3, \quad N_i \equiv \text{Integers} \quad (2.92) \]

For finite systems, it is important to have enough vacuum in the supercells to prevent the structures in neighboring cells from interacting with each other.

### 2.5.2 Fourier representation

The computational cost of the Kohn-Sham equations can be reduced by using the translational symmetry of the atomic structures. The effective potential is a periodic function with the lattice, i.e.,

\[ V_{\text{eff}}(\mathbf{r} + \mathbf{T}) = V_{\text{eff}}(\mathbf{r}) \quad (2.93) \]

The effective potential \( V_{\text{eff}} \) can be expanded into Fourier series as, \[ V_{\text{eff}}(\mathbf{r}) = \sum_G V_{\text{eff}}(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}} \quad V_{\text{eff}}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \, V_{\text{eff}}(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} \quad (2.94) \]

The above equation fulfills the conditions \( \mathbf{G} \cdot \mathbf{T} = 2\pi M \) for all lattice vectors, where \( M \) is an integer. The vectors \( \mathbf{G} \) constitute the lattice also called as reciprocal lattice, using \( \mathbf{b}_1, \mathbf{b}_2 \) and \( \mathbf{b}_3 \) such that,

\[ \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}, \quad i, j = 1, 2, 3 \quad (2.95) \]

The volume of the reciprocal lattice is,

\[ \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\Omega} \quad (2.96) \]

### 2.5.3 Bloch’s theorem

Bloch’s theorem states that, in a periodic potential, an electron wave function can be written as the product of the cell-periodic part \( u_{k,j}(\mathbf{r}) \) and a wavelike part with wave vector \( \mathbf{k} \),\[ \psi_{k,j}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} u_{k,j}(\mathbf{r}) \quad (2.97) \]
The Bloch’s theorem restricts the calculations of the eigenfunctions within one unit cell. Using the translational vector $T$ defined in Eq. (2.92) the form of eigenfunctions in all other unit cells can be determined, with respect to single unit cell, [220]

$$\int_\Omega d\mathbf{r} |\psi_{k,j}(\mathbf{r})|^2 = 1$$  \hspace{1cm} (2.98)

The functions $u_{k,j}$ can be expanded in terms of plane waves as they are periodic in lattice. It can be written as,

$$\psi_{k,j} = \sum_G C_G^{k,j} e^{i(k+G)\cdot \mathbf{r}}$$ \hspace{1cm} (2.99)

The coefficients $C_G, C_{G+k}, C_{G+k'}, ..$ are the coefficients whose wave vector differ by $k$ and it couples to the reciprocal lattice vectors $G$ in the first Brillouin zone, for any fixed wavevector $k$.

The Kohn-Sham equations of the density functional theory can be written in terms of Bloch states:[220]

$$\left( -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_{k,j}(\mathbf{r}) = \epsilon_{k,j} \psi_{k,j}(\mathbf{r})$$ \hspace{1cm} (2.100)

with

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]$$

and

$$n(\mathbf{r}) = \frac{2}{(2\pi)^3} \int_{BZ} d\mathbf{k} |\psi_{k,j}(\mathbf{r})|^2 \Theta(E_f - \epsilon_{k,j})$$ \hspace{1cm} (2.101)

In above equation, $\Theta$ is a step function and its value is 1 for positive argument whereas, 0 for negative. $E_f$ is the Fermi energy up to which single particle energy states are occupied.

2.5.4 k-point sampling

Our problem of calculating eigenstates is not simple as there are an infinite number of $k$-points in the single unit cell. However, we use the information that, the electron wave function is very much similar for the $k$-points which are very close together.[222] Therefore, we can represent the wavefunction of certain region of $k$-space by the wave function at a single $k$-point belonging to that $k$-space. The mesh of $k$-points is thus defined at $N_{\text{kpt}}$ positions and summed over the Brillouin zone, replacing the integral by discrete sum in Eq. (2.101):[220]

$$\frac{\Omega}{(2\pi)^3} \int_{BZ} \ldots \Theta(E_f - \epsilon_{k,j}) \ d\mathbf{k} \quad \rightarrow \quad \frac{1}{N_{\text{kpt}}} \sum_k f_{k,j} \ldots$$ \hspace{1cm} (2.102)

where, $f_{k,j}$ are occupation numbers which can be either one or zero. Using this, the electronic states are calculated at only finite number of $k$-points. The error in the energy can be reduced by increasing the density of $k$-points mesh. Usually, it is a good idea to converge the mesh of $k$-point for a particular system and particular size of Brillouin zone. Increasing the supercell, decreases the size of the Brillouin zone and hence small number of $k$-points are needed.
2.5.5 *Representation of Kohn-Sham Equations in plane waves*

With the plane waves as a basis set, the Kohn-Sham equations (Eq. 2.40) take much simpler form. Using the form of the wavefunction as expressed in Eq. (2.99), into Eq. (2.101), and multiply from left with $\exp(-i(k+G') \cdot r)$. With the integration over $r$, we get matrix eigenvalue equation, \[ \sum_G \left( \frac{\hbar^2}{2m} ||k+G||^2 \delta_{G'G} + V_{\text{ext}}(G' - G) + V_H(G' - G) + V_{\text{xc}}(G' - G) \right) c_{G'}^{kj} = \epsilon_k^{ij} c_k^i \] (2.103)

In the above equation, the kinetic energy is nonzero only for diagonal elements and the potential energy terms are expressed in the form of Fourier transforms. The solution of Eq. (2.103) is obtained by diagonalizing the Hamiltonian matrix with the elements $H_{G'G}$. In practice, the Fourier expansion of the wavefunctions can be truncated by keeping only those plane wave vectors $(k+G)$ with a kinetic energy less than the cutoff $E_{\text{cutoff}}$:

\[ \frac{\hbar^2}{2m} ||k+G||^2 \leq E_{\text{cutoff}} \] (2.104)

2.5.6 *Pseudopotential Approximations*

It is well known that, the important physical properties are determined by the valence electrons rather than the core electrons. Therefore the cost of electronic structure calculations can be reduced significantly, if the core electrons are treated as frozen, and only valence electrons are treated explicitly. The pseudopotential approximation replaces the core electrons and the strong ionic potential by a much weaker pseudopotential which acts on a set of pseudo wave functions. The general idea is shown in Fig. 2.2. The valence wave function ($\Psi$ in Fig. 2.2) oscillates rapidly inside the core region due to strong ionic potential, in order to maintain the orthogonality between the core electron wave function and the valence wave function.

The idea of the pseudopotential method originated with the orthogonalized plane wave method, in which the valence wave function is expanded in the plane wave basis set, which are orthogonalized to the lowest core states.[223]

The Schrödinger equation for self consistent potential ($V_{\text{ext}}(r)$) can be written as,

\[ \hat{H}\psi_i = \left( -\frac{1}{2} \nabla^2 + V_{\text{ext}}(r) \right) \psi_i = \epsilon_i \psi_i(r) \] (2.105)

The core and conduction band states are distinguished by $\alpha$ and $k$ respectively[224]

\[ -\frac{1}{2} \nabla^2 \psi_\alpha(r) + V_{\text{ext}}(r) \psi_\alpha(r) = \epsilon_\alpha \psi_\alpha(r) \] (2.106)

The conduction band wave function can be expanded in terms of orthogonalized plane waves (OPWs). An OPW of wavenumber $k$ is defined as,

\[ \text{OPW}_k = |k\rangle - \sum_\alpha |\alpha\rangle \langle \alpha|k\rangle \] (2.107)

In the above equation,

\[ \langle \alpha|k\rangle = \frac{1}{\Omega} \int d\mathbf{r}' \psi_\alpha^*(\mathbf{r}') e^{i\mathbf{k} \cdot \mathbf{r}'} \] (2.108)
Using the above product, Eq. (2.107) can be written as,

$$\text{OPW}_k = e^{ikr} - \sum_a \psi_a(r) \int dr' \psi_a^*(r') e^{ikr'}$$  \hspace{1cm} (2.109)

This state is orthogonal to any state and can be verified,[224]

$$\int d\mathbf{r} \psi_\beta^*(\mathbf{r}) \text{OPW}_k = \int d\mathbf{r} \psi_\beta^*(\mathbf{r}) e^{ikr} - \sum_a \psi_\alpha^*(\mathbf{r}) \psi_\alpha^*(\mathbf{r}) \int d\mathbf{r}' \psi_\alpha^*(\mathbf{r}') e^{ikr'}$$

$$= \int d\mathbf{r} \psi_\beta^*(\mathbf{r}) e^{ikr} - \sum_a \psi_\alpha^*(\mathbf{r}) \psi_\alpha^*(\mathbf{r}) \int d\mathbf{r}' \psi_\alpha^*(\mathbf{r}') e^{ikr'}$$

$$= 0$$  \hspace{1cm} (2.110)

The normalized plane waves and core functions are:

$$|k\rangle = \frac{1}{\Omega} e^{ikr}$$

$$|\alpha\rangle = \psi_\alpha(r)$$  \hspace{1cm} (2.111)

Hence the OPWs using above notation becomes,

$$\text{OPW}_k = |k\rangle - \sum_a |\alpha\rangle \langle \alpha|k\rangle$$  \hspace{1cm} (2.112)

The OPW is written in terms of projection operator $\hat{P}$, that projects any function into core energy states.

$$\hat{P} = \sum_a |\alpha\rangle \langle \alpha|$$  \hspace{1cm} (2.113)

Therefore,

$$\text{OPW}_k = (1 - \hat{P})|\alpha\rangle$$  \hspace{1cm} (2.114)

The expansion of the wavefunction in sets of OPWs can be written as,

$$\psi_k = (1 - \hat{P}) \sum_k a_k |k\rangle$$  \hspace{1cm} (2.115)

This method converges fast i.e., $\sum_k$ have important contributions for small values of $k$ and any function $\phi_k = \sum_k a_k |k\rangle$ will be a smooth function. Here, we call $\phi_k$ as a pseudo wave function.

2.5.6.1 Pseudopotential Formulation

$$\psi_k = (1 - \hat{P})\phi_k$$  \hspace{1cm} (2.116)

Using this form in the Schrödinger’s equation,

$$-\frac{1}{2} \nabla^2 \phi_k + V_{\text{ext}}(\mathbf{r})\phi_k - \left( -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) \right) \hat{P}\phi_k = \epsilon \hat{P}\phi_k + \epsilon \phi_k$$  \hspace{1cm} (2.117)

In simplified form, it can be written as,

$$-\frac{1}{2} \nabla^2 \phi_k + W\phi_k = \epsilon \phi_k$$  \hspace{1cm} (2.118)
The Eq. (2.118) is called as Pseudopotential equation. The form of the pseudopotential is given as,

$$W = V_{ext}(\mathbf{r}) - \left( -\frac{1}{2} \mathbf{r}^2 + V_{ext}(\mathbf{r}) \right) \hat{P} + \epsilon \hat{P}$$ \hspace{1cm} (2.119)$$

Using the identity Eq. (2.113), the above equation for pseudopotential can be written as,

$$W = V_{ext}(\mathbf{r}) + \sum_a (\epsilon - \epsilon_a) |a\rangle \langle a|$$ \hspace{1cm} (2.120)$$

In the above equation (Eq. 2.120), the projection operator in the equations makes the potential very different than in the ordinary case.[224] The pseudopotential $W$ is nonlocal unlike the potential $V_{ext}(\mathbf{r})$. Also, $W$ is very small in comparison to $V_{ext}(\mathbf{r})$ (Eq. 2.119). The $V_{ext}(\mathbf{r})$ being the attractive potential, second term contains the difference $(\epsilon - \epsilon_a > 0, \hat{P} > 0)$, that will dominate the negative terms of the attractive potential $V_{ext}(\mathbf{r})$ (Fig. 2.2) This is the Kleinmann-Bylander form of pseudopotential whose generalization is known as ultrasoft pseudopotential.

2.5.7 Norm-conserving Pseudopotentials

Using the norm-conservation, the basic advantage is that, the usual normalized functions are defined so that they have correct amount of electron charge inside the core region. This helps in giving correct scattering properties using pseudopotentials over large range of energies. The norm conserving potential is $l$-dependent and is given as,[224]

$$V(\mathbf{r}, \mathbf{r'}) = \sum_{l,m} V_l(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r'}) Y_l^m(\theta, \phi) Y_l^{m*}(\theta', \phi')$$ \hspace{1cm} (2.121)$$

or in simplified form,

$$V_{NL} = \sum_{lm} |l, m\rangle V_l(\mathbf{r})$$ \hspace{1cm} (2.122)$$

2.5.8 Projector Augmented Wave (PAW) method

The formalism of ultrasoft pseuopotential is very complex. A more transparent approach is called as Projector Augmented Wave (PAW) method, which includes number
of methods to provide a simple and consistent way of reconstruction of all electron wave function from pseudo wave function. The PAW method unites the description of augmented wave methods as well as ultra-soft pseudopotentials. PAW works with smooth pseudo wave functions that can be expanded in few plane waves. The interesting property of the PAW method is that the full all-electron wave function is preserved within the core region. There is no need to deal with the inert core electrons. The valence pseudo wave functions are smooth and without nodes inside the augmented spheres. It gives access to full all electron wave function and density. In order to reduce the computational cost due to the all-electron wave function, Blöchl pointed out that, the true wave function, $\Psi$ and the pseudo wave function, $\tilde{\Psi}$ can be linked by a linear transformation. In PAW method, we map the complete wavefunction and a pseudo-wave function by a linear transformation. The pseudo wave function is smooth enough so that it can be expanded in the sets of fewer plane waves.

The root of the PAW method lies in the transformation ($T$), that maps the true wavefunction (along with the complete nodal structure) onto an auxiliary wave functions, which are convenient numerically. The aim is to get smooth auxiliary wave function that has rapid convergence with the plane wave expansion. Such transformation can be used to expand the auxiliary wave function into a convenient basis set, and then evaluate all physical properties after reconstruction of true wave function. At beginning, consider a single atom in the system. Lets call $R$ as the region centered around the atom. Then the mapping is defined as,

$$|\tilde{\phi}_l\rangle = (1 + T)|\phi_l\rangle \tag{2.123}$$

The functions $\tilde{\phi}_l$ are solutions of all electron atomic KS equation which are continuous at the origin, $\phi_l$ corresponds to the pseudo-functions which are smoother in the region $R$. By setting, $T = 0$ outside the $R$.

Within the region of $R$, the pseudo-wavefunction $\psi$ for system over the atomic pseudo-waves $\phi_l$ can be written as,

$$|\psi\rangle = \sum_l c_l|\phi_l\rangle \tag{2.124}$$

By applying the operator $(1 + T)$ to both the sides of above equation,

$$|\tilde{\psi}\rangle = \sum_l c_l|\tilde{\phi}_l\rangle \tag{2.125}$$

where, $\tilde{\psi}$ denotes the all electron wave function. Rearranging Eq. (2.125)

$$|\tilde{\psi}\rangle = |\psi\rangle + \sum_l c_l(|\tilde{\phi}_l\rangle - |\phi_l\rangle) \tag{2.126}$$

In order to define the coefficients $c_l$, the projectors $\beta_l$ are introduced such that,

$$\langle \beta_l | \phi_m \rangle = \delta_{lm}, \quad \sum_l |\phi_l\rangle \beta_l \langle \phi_l | = I \tag{2.127}$$

It can be verified that, $c_l = \langle \beta_l | \psi \rangle$, and we write,

$$|\tilde{\psi}\rangle = |\psi\rangle + \sum_l \langle \beta_l | \psi \rangle(|\tilde{\phi}_l\rangle - |\phi_l\rangle)$$

$$\begin{align*}
|\tilde{\psi}\rangle &= [I + \sum_l (|\tilde{\phi}_l\rangle - |\phi_l\rangle) \langle \beta_l |] |\psi\rangle 
\end{align*} \tag{2.128}$$
The term in the square bracket shows \((1 + T)\) operator, which replaces the pseudo states \(\phi\) from the pseudowavefunctions around the atoms by all electron states \(\phi\). The operator is purely local (atomic) and is obtained from \(\psi_i\) all electron states, respective pseudo states \(\phi_i\) and the projections \(\beta_i\).

Using the from of \(\psi\) in the Kohn-Sham energy functional and finding its energy minimum with respect to the variation of the smooth part of \(\psi\), the solution is obtained. In this case, the electron density is no more simple square of the orbitals but contains additional augmentation part,

\[
n(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{lm} \langle \psi_i | \beta_l \rangle q_{lm}(r) \langle \beta_m | \psi_i \rangle
\]

In the above equation, \(q_{lm}(r)\) is defined as,

\[
q_{lm}(r) = \tilde{\phi}_l(r) \tilde{\phi}_m(r) - \phi_l(r) \phi_m(r)
\]

2.6 Numerical Determination of the Kohn-Sham Ground state

2.6.1 Self Consistency loop and iterative methods

The calculation of Kohn-Sham ground state is split into two different problems: first is to determine the eigenfunctions and eigenvalues by minimizing the energy of the bands for a particular electron density, and the other is the calculation of self consistent electron density. At the beginning, a set of trial wave functions \(\{\psi_i | i = 1, ..., N_{\text{bands}}\}\) is chosen along with a initial guess of electron density \(n^{\text{in}}\). From the input electron density the local potential \(V_{\text{loc}}\) is evaluated

\[
V_{\text{loc}} = V_{\text{ion}}^{\text{loc}} + V^H[n^{\text{in}}] + V^{xc}[n^{\text{in}}]
\]

and also the the corresponding double counting corrections can be written as

\[
E_{\text{d.c.}}[n^{\text{in}}] = -E^H[n^{\text{in}}] + E^{xc}[n^{\text{in}}] - \int dr V^{xc}(r)n^{\text{in}}(r)
\]

In the next step, the trial wave functions are improved iteratively and new eigenenergies are used to calculate a new Fermi energy and new partial occupancies. The total free energy is calculated as the sum of band energies along with the entropy and double counting corrections,

\[
F = \sum_i f_i \epsilon_i^{\text{app}} - \sum_i \sigma S \left( \frac{\epsilon_i - H}{\sigma} \right) + E_{\text{d.c.}}[n^{\text{in}}] + \gamma_{\text{Ewald}}
\]

The HF functional (defined in Eq. 2.133) is non-self consistent and it requires the calculations of band energy for a fixed electron density \(n^{\text{in}}\). To get the exact Kohn-Sham ground state energy, the self consistency with respect to the input electron density needs the charge density residual vector \(R[n^{\text{in}}] \equiv n^{\text{in}} - n^{\text{out}}\) be zero. In principle, it is necessary to calculate the eigenfunctions \(\psi_i\) exactly for each new input electron density, making \(n^{\text{out}}\) and residual vector \(R\) functionals of the initial electron density \(n^{\text{in}}\) only. This is repeated iteratively until the residual vector \(R\) vanishes. The iterative methods for the diagonalization of the Kohn-Sham Hamiltonian is discussed in Appendix-B and Appendix-C.
2.7 Solving the Kohn-Sham equations using the FLAPW method

We will discuss another efficient method to solve the Kohn-Sham equations which uses a non-plane wave basis set, called as full-potential linearized augmented plane wave (FLAPW) method, which has certain advantages as follows: [152, 230–232] Plane waves are convenient to use as a basis set, because they are orthogonal and are eigenfunctions of the Laplace operator, which is contained in the Hamiltonian. However plane waves are eigenfunctions of the Schrödinger equation for a constant potential, but in many cases the potential is not constant and it diverges at the nuclei and it rapidly oscillates in these regions, which requires large number of basis functions for expansion. The APW-method and its improvement called as FLAPW method, deals with this deficiency of the plane waves. For simplicity, we initially discuss the methods for spinless Kohn-Sham equations:

$$\left( -\frac{1}{2}\nabla^2 + V_H[n] + V_{\text{ext}}[n] + V_{\text{xc}}[n] \right) \psi_i = \epsilon_i \psi_i$$  \hspace{1cm} (2.134)

Figure 2.3 – Flow-chart for calculating Kohn-Sham ground state.
2.7 Solving the Kohn-Sham equations using the FLAPW method

2.7.1 Solving the secular equation

Equation (2.134) is solved self consistently by starting with the initial electron density \( n^{(\text{in})} \) and by evaluating the density dependent potential \( (V_{\text{eff}}[n]) \). The eigenstates of Kohn-Sham equation (Eq. 2.134) are determined. For each wave vector \( \{k\} \), the secular equation is solved in the subspace that restricts \( \{\psi_{k,i}\} \) to the lattice periodic functions. After calculating the Fermi energy and the occupation number \( \omega_{k,i} \) of the \( i^{th} \) state, output density is determined by summing over all occupied states of all \( k \)-points

\[
n^{(\text{out})} = \sum_{k,i} n_{k,i} \psi_{k,i}^\dagger \psi_{k,i} \tag{2.135}
\]

A new input electron density is obtained by mixing the \( n^{(\text{in})} \) and \( n^{(\text{out})} \) and the self consistency performed until the electron density is converged.

In each loop of the self consistency cycle, the secular problem of Kohn-Sham Hamiltonian is solved. The treatment is done separately for core and valence states as described in the following subsections.

2.7.1.1 Core States

The relativistic effects are dominant in the core states. Therefore the Dirac equation (Eq. 2.82) is used and states are represented by spinors. The atoms can be treated as isolated atoms while solving the core states as these states are localized near the nucleus. Within certain distance (muffin-tin radius, \( R_{MT} \)), the spherical form of the potential is considered, and it is neglected beyond this distance.

2.7.1.2 Valence States

The valence states expanded in LAPW functions (as discussed in Sec. 2.7.2). These basis functions are finite, linearly independent however not orthogonal. The set of the basis functions depends on the Bloch vector \( k \). The \( j^{th} \) eigenstate of \( \mathcal{H} \) has the form \( |\psi_j\rangle = \sum_G C_{G,j} |G\rangle \) and the eigenvalue equation has the form,

\[
\mathcal{H} \sum_G C_{G,j} = \epsilon_j \sum_G C_{G,j} \langle G | \mathcal{H} | G \rangle \quad \implies \quad \sum_G \langle G | \mathcal{H} | G \rangle C_{G,j} = \epsilon_j \sum_G \langle G | G \rangle C_{G,j} \tag{2.136}
\]

In practice, the basis set used is finite, hence the exact eigenvalue equation is approximated by

\[
(H - \epsilon_j S) C_j = 0 \quad \text{where} \quad H_{G,G'} = \langle G' | \mathcal{H} | G \rangle, \quad S_{G,G'} = \langle G' | G \rangle \tag{2.137}
\]

The Hermitian matrices \( H \) and \( S \) are the Hamiltonian matrix and the overlap matrix, respectively. The \( S_{G,G'} \) is positive definite (since, \( S = T^\dagger T \), where \( T \) is transformation matrix from linearly independent LAPWs to an orthogonal basis set). The Eq. (2.137) is called generalized eigenvalue problem, and overlap matrix is an unit matrix in the standard secular equation. The diagonalization of the Hamiltonian is the most time consuming part of the calculations, which scales as the third power to the number of basis functions \( |G\rangle \).

2.7.2 LAPW basis functions

LAPW basis set gives better description of the wave functions near the nucleus. The interesting magnetic properties are due to spin orbit interaction and it originates from the region close to the nucleus where the potential gradient is very high. In

\[\text{November 2013}\]
Solving the Kohn-Sham equations using the FLAPW method

Figure 2.4 – Division of space in non-overlapping spheres and interstitial region. The muffin-tin sphere \( \mu \) is centered in \( \mathbf{R}^\mu \) at the nucleus of atom \( \mu \) and has the muffin-tin radius \( R^\mu_{MT} \). (Ref.: Marcus Heide, PhD thesis, 2006)[217].

The noncollinear magnetic calculations presented in this thesis, the wavefunctions are expanded using the LAPW basis set. In this formalism, the real space is divided into two major regions: In the transition region between atoms (the interstitial region), the basis functions are just the plane waves, (the solution of the Schrödinger equation with constant potential), whereas, in the spheres, the basis functions are constructed from the Schrödinger equation with spherical potential. This region is called as muffin-tin spheres.

The center of the \( \mu \)th sphere is denoted by \( \mathbf{R}^{(\mu)} \), the vector \( \mathbf{r} \) can be expressed in polar coordinates with notation \( \mathbf{r} = \mathbf{r}^{(\mu)} \left( \sin \delta^{(\mu)} \cos \phi^{(\mu)} \mathbf{e}_x + \sin \delta^{(\mu)} \sin \phi^{(\mu)} \mathbf{e}_y + \cos \delta^{(\mu)} \mathbf{e}_z \right) \).

With this, the LAPW basis set that corresponds to the wave vector \( \mathbf{k} \) in the interstitial region can be written as,

\[
\phi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} 
    e^{(i\mathbf{k} \cdot \mathbf{r})} & \mathbf{r} \in \text{interstitial region}, \\
    \sum_{l,m} \left( A_{k,l,m}^{(\mu)} u_l^{(\mu)}(r^{(\mu)}) + B_{k,l,m}^{(\mu)} \dot{u}_l^{(\mu)}(r^{(\mu)}) \right) Y_{l,m}(\delta^{(\mu)},\phi^{(\mu)}) & \mathbf{r} \in \text{muffin-tin sphere } \mu
\end{cases}
\] (2.138)

\( Y_{l,m} \) denote angular momentum dependent spherical harmonics and \( u_l^{(\mu)}, \dot{u}_l^{(\mu)} \) denote the radial dependent functions. The coefficients \( A_{k,l,m}^{(\mu)}, B_{k,l,m}^{(\mu)} \) are determined by matching the wavefunctions (\( \phi_{\mathbf{k}}(\mathbf{r}) \)) and its gradient (\( \nabla_\mathbf{r} \phi_{\mathbf{k}}(\mathbf{r}) \)) at the muffin-tin sphere boundary so that they are continuous. The solution of the Schrödinger equation with a radially symmetric potential \( V(r) \) is of the form,

\[
\left\{ -\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right\} r u_l(r) = 0 \] (2.139)

For each \( E_l \), the above equation has one solution \( u_l(r) \), which is regular at \( r = 0 \) for the reasonable potential. In practice of APW method, the regular solutions \( u_l \) are used as radial functions \( u \) in equation (2.138), whereas \( B_{k,l,m}^{(\mu)} \) is kept zero.[234] \( E_l \) is set to the band energy, so that same energy eigenstate can be represented in all regions in space. This forces to determine the band energies self consistently as they are different for different eigenstates.

2.7.3 LAPW basis for film geometries

In order to do ab initio calculations for low dimensional systems such as films and surfaces instead of bulk systems, one has to use supercell with enough vacuum, so
Figure 2.5 – Division of space in the film calculations. In the \(xy\)-plane, the crystal has the translational symmetry, the \(z\)-direction is infinitely extended. In this figure, \(y\) direction is perpendicular to the plane. The plane wave that describe the wavefunctions in the interstitial region have the periodicity \(\tilde{D}\) in \(z\)-direction but for \(r_z > \frac{1}{2}D\), the basis consists of the vacuum functions that decays as \(z\) approaches to infinity. The basis functions in the muffin tin are same as that for bulk case. \(\text{(Ref.}: \text{S. Blügel and G. Bihlmayer, Computational Nanoscience: NIC Series, 31, 85-129, (2006)).}\)

as to avoid the interaction between the repeated systems. This requires a very large basis set. In order to reduce the computational cost of such systems, LAPW basis set is introduced.\[157\] It permits to calculate a film/surface without the use of supercell in all the directions. The systems are finite in the third dimension. In the muffin-tin and interstitial region, two more regions (vacuum regions) are introduced in comparison with the APW method. They begin from both the sides of film and extend infinitely in the film. In these regions, the basis functions are constructed from the solutions of a Schrödinger equation with asymptotic decaying potential.

In this case, the Bloch theorem is applied in two dimension with translational symmetry. \(X\) and \(X_\parallel\) represents the component normal to the film and the 2-dimensional in-plane vector respectively. The wave functions according to two dimensional Bloch theorem can written as,

\[
\psi_{k,||}(r) = e^{i(k,||.r)} \sum_{G,||} c_{k,||,G,||}(r_z) e^{i(G,||.r_z)}
\]

(2.140)

In Eq. (2.140), the summation runs over all \(G,||\) vectors of the two dimensional unit cell. The functions \(c_{k,||,G,||}(r_z)\) are non-periodic in \(z\), however in the interstitial region (\(|z| < D/2\), they are expanded using the plane waves.

In the film geometry, the basis functions can be labeled by the plane wave vectors \(k\) like the bulk geometry. But now, \(k = k,|| + G,|| + G_z e_z = (k_x + G_x)e_x + (k_y + G_y)e_y + G_z e_z\).
\[ \phi_k(r) = \begin{cases} \epsilon^{(k \cdot r)} & r \in \text{interstitial region}, \\ \Sigma_{l,m} \left( A^{(\mu)}_{k,l,m} u^{(\mu)}_l(r^\mu) + B^{(\mu)}_{k,l,m} \hat{u}^{(\mu)}_l(r^\mu) \right) Y_{l,m}(\theta, \phi) & r \in \text{muffin-tin sphere } \mu \\ \epsilon^{(k \cdot r)} \left( A^{(\eta)}_{\text{vac}, \text{K}_1} u^{(\eta)}_{\text{vac}, \text{K}_1}(r_2) + B^{(\eta)}_{\text{vac}, \text{K}_2} u^{(\eta)}_{\text{vac}, \text{K}_2}(r_2) \right) & r \in \text{vacuum } \eta \end{cases} \] (2.1.41)

The vacuum coefficients \( A \) and \( B \) as well as the functions \( u_{\text{vac}} \) and \( \hat{u}_{\text{vac}} \) are constructed similar to the corresponding coefficients and functions in the muffin-tin spheres. The \( u_{\text{vac}} \) and \( \hat{u}_{\text{vac}} \) are determined by the one dimensional Schrödinger equation,

\[ \begin{cases} k^2 - \frac{\partial^2}{\partial r^2} + V_{\text{vac}}(r_z) - E_{\text{vac}} \end{cases} u_{\text{vac}}(r_z) = 0 \] (2.1.42)

and its energy derivative is

\[ \begin{cases} k^2 - \frac{\partial^2}{\partial r^2} + V_{\text{vac}}(r_z) - E_{\text{vac}} \end{cases} \hat{u}_{\text{vac}}(r_z) - u_{\text{vac}}(r_z) = 0 \] (2.1.43)

It is sufficient to describe all valence electrons with \( E^{(\eta)}_{\text{vac}} \) for every vacuum region.

### 2.7.4 Magnetic Calculations

If we neglect the external magnetic field, the Kohn-sham equation can be written as,

\[ \mathcal{H}_1 = -\frac{1}{2} \nabla^2 + V_H + V_{\text{ext}} + V_{\text{xc}}, \quad B_{\text{xc}} = |B_{\text{xc}}| \] (2.1.44)

The form of \( B_{\text{xc}} \) can be understood from Eq. (2.79). For non-magnetic case, \( B_{\text{ext}} = 0 \). The Kohn-Sham equation (Eq. 2.40) can be written as,

\[ \begin{pmatrix} \mathcal{H}_1 + B_{\text{xc}} \frac{m_x}{|m|} & B_{\text{xc}} \frac{m_x - im_y}{|m|} \\ B_{\text{xc}} \frac{m_x + im_y}{|m|} & \mathcal{H}_1 - B_{\text{xc}} \frac{m_x}{|m|} \end{pmatrix} \begin{pmatrix} \psi_i^\top \\ \psi_i^\top \end{pmatrix} = \epsilon_i \begin{pmatrix} \psi_i^\top \\ \psi_i^\top \end{pmatrix} \] (2.1.45)

In the non-magnetic cases, \( m = B_{\text{xc}} = 0 \), then Eq. (2.1.45) reduces to two equivalent equations of the form,

\[ \mathcal{H}_i \psi_i = \epsilon_i \psi_i \] (2.1.46)

The solutions of the above equation can be obtained as described in subsection (Sec. 2.7.1). These method can also be used for magnetic equation (2.1.45), where, for each \( \mathbf{k} \) vector two basis functions need to be constructed, each is zero in one component of the spinor. For collinear magnetic configurations, the magnetization \( \mathbf{m} \) can be written as,

\[ \mathbf{m}(r) = m(r) \mathbf{e}_m \quad \text{with} \quad \mathbf{e}_m = \text{constant} \] (2.1.47)

The restriction to collinear configurations reduces the computational cost to a great extent. As long as we neglect the spin orbit interaction, the orientation of the spin coordinate system (describing the vector \( \mathbf{m} \)) does not depend on the orientation. Hence we can choose, \( \mathbf{m}(r) = m(r) \hat{e}_z \). With this choice, the exchange correlation potential is diagonal in spin space and Eqn. (2.1.45) takes the form,

\[ \begin{pmatrix} \mathcal{H}_1 + B_{\text{xc}} & 0 \\ 0 & \mathcal{H}_1 - B_{\text{xc}} \end{pmatrix} \begin{pmatrix} \psi_i^\top \\ \psi_i^\top \end{pmatrix} = \epsilon_i \begin{pmatrix} \psi_i^\top \\ \psi_i^\top \end{pmatrix} \] (2.1.48)

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Here the Hamiltonian as well as the overlap matrix are block-diagonal. This reduces the diagonalization of the magnetic matrix to two matrices having half the size, which can written in form of the equations,

\[
(\mathcal{H}_1 + B_{xc}) \psi_i^\uparrow = \epsilon_i^\uparrow, \quad (\mathcal{H}_1 - B_{xc}) \psi_i^\downarrow = \epsilon_i^\downarrow.
\]  

(2.149)

In the case of non-collinear spin systems, the magnetization can not take a global axis and needs to be represented by a three dimensional vector \( \mathbf{m}(\mathbf{r}) \). The code used (FLEUR) for the calculations in this thesis restricts direction of the magnetization within the muffin-tin only.[235] The code used (FLEUR) for the calculations in this thesis restricts direction of the magnetization within the muffin-tin only.[236]

\[
\mathbf{m}(\mathbf{r}) = \begin{cases} 
\mathbf{m}(\mathbf{r}) & \text{interstitial and vacuum region,} \\
 m^{(\mu)}(\mathbf{r}) \hat{e}^{(\mu)} & \text{in muffin-tin sphere } \mu 
\end{cases}
\]  

(2.150)

The local coordinate system for every muffin-tin is introduced such that, the local \( \hat{z} \) axis points parallel to \( \hat{e}^{(\mu)} \). If the quantities in local coordinate frames are denoted by \( (\tilde{} \cdot) \), then a spin rotation matrix \( U_{MT\mu} \) binds the local spin to the global magnetic moment. The potential then can be written as

\[
\tilde{V} = U_{MT\mu}^\dagger V U_{MT\mu} = (V_H + V_{\text{ext}}) \mathbb{1} + \begin{pmatrix} V_{xc}^{\uparrow\uparrow} & V_{xc}^{\uparrow\downarrow} \\
 V_{xc}^{\downarrow\uparrow} & V_{xc}^{\downarrow\downarrow} \end{pmatrix}
\]  

(2.151)

The \( V_{xc}(\mathbf{r}) \) is determined mainly by its diagonal elements \( V_{xc}^{(\uparrow,\uparrow)}(\mathbf{r}), V_{xc}^{(\downarrow,\downarrow)}(\mathbf{r}) \). The functions \( u, \tilde{u} \) are constructed from the diagonal elements of \( \tilde{V} \).

The basis set for non-collinear magnetization direction is modified. The radial functions \( u_l \) and \( \tilde{u}_l \) are constructed in the local coordinate system. In the interstitial region, the basis functions are constructed from the global frame of reference and take the form,

\[
\phi_{\mathbf{k}}^\uparrow(\mathbf{r}) = \begin{pmatrix} e^{i\mathbf{k} \cdot \mathbf{r}} \\
 0 \end{pmatrix} \quad \text{and} \quad \phi_{\mathbf{k}}^\downarrow(\mathbf{r}) = \begin{pmatrix} 0 \\
 e^{i\mathbf{k} \cdot \mathbf{r}} \end{pmatrix}
\]  

(2.152)

Both the local spin component of the basis functions need to be matched at the interface of muffin-tin and interstitial region. It is possible also to add constraints into average magnetization direction without violating the theorem of Hohenberg and Kohn[212, 213]

\[
\tilde{M} = \frac{\mathbf{M}}{|\mathbf{M}|} = \frac{\int_{MT} d\mathbf{r} \mathbf{m}(\mathbf{r})}{\int_{MT} d\mathbf{r} \mathbf{m}(\mathbf{r})}
\]  

(2.153)

of a particular muffin-tin sphere. This is equivalent with the local coordinate frame of the muffin-tin as,

\[
\int_{MT} d\mathbf{r} m_\xi(\mathbf{r}) = \int_{MT} d\mathbf{r} m_\eta(\mathbf{r}) = 0
\]  

(2.154)

The energy functional \( E_{\text{tot}}[n,\mathbf{m}] \) can be extended with these constraints by introducing the Lagrange multipliers \( B_{c,\xi}, B_{c,\eta} \) as

\[
F[n,\mathbf{m}] = E_{\text{tot}}[n,\mathbf{m}] - B_{c,\xi} \int_{MT} d\mathbf{r} \mathbf{m}_\xi(\mathbf{r}) - B_{c,\eta} \int_{MT} d\mathbf{r} \mathbf{m}_\eta(\mathbf{r})
\]  

(2.155)

The variation of above functional leads to the Kohn-Sham equation for magnetic calculations.
2.7 Solving the Kohn-Sham equations using the FLAPW method

Figure 2.6 – The size of the chemical unit cell shown by a solid line rectangle, if treating different magnetic calculations without generalized Bloch theorem. The last row shows the spin spiral calculations when generalized Bloch theorem is used.

2.7.5 Generalized Bloch theorem and Spin Spirals

There are few materials which do not show a ferromagnetic or an antiferromagnetic ground state but rather a spin spiral structure. A spin spiral is a structure in which the magnetic moment is rotated by a constant angle from one lattice point to the next one. In the absence of spin orbit coupling, the rotation axis can be defined as the global z axis without loss of generality. Spin spirals can be characterized by a spin spiral vector $\mathbf{q}$ that defines the real space direction along which the magnetic moment rotates with a period of $2\pi|\mathbf{q}|^{-1}$. The magnetization direction can be written as

$$m(r) = |m(r)| \left( \begin{array}{c} \sin \delta \cos \varphi \\ \sin \delta \sin \varphi \\ \cos \delta \end{array} \right) \Rightarrow m(r + R) = |m(r)| \left( \begin{array}{c} \sin \delta \cos(\varphi + \mathbf{q} \cdot \mathbf{R}) \\ \sin \delta \sin(\varphi + \mathbf{q} \cdot \mathbf{R}) \\ \cos \delta \end{array} \right)$$

Here, $\mathbf{R}$ is the lattice vector of the chemical lattice and $\delta$ is the cone angle. It describes the deviation of the magnetization with the rotation axis. In case of planar spiral rotation, the cone angle is zero.

With the help of the generalized Bloch theorem,[237–239] the spin spirals can be computed without the explicit use of supercell, as shown in Fig. 2.6. The generalized Bloch theorem allows calculations in a chemical unit cell and can be proved only if SOC is neglected. The procedure is given in brief as follows:

The field $B_{xc}$ is parallel to $\mathbf{m}$. The magnetization given in Eq. (2.156) indicates that, $B_{xc}$ and total potential $V$ have the same rotation in the spin-space. A generalized translation $T_R$, which combines a lattice translation with a rotation in spin space,
where \( \psi \) commutes with the Hamiltonian in a scalar relativistic approximation,

\[
T_R = U(q \cdot R) \psi(r - R), \quad [T_R, H] = 0
\]

where

\[
U = \begin{pmatrix}
\exp(-i \frac{1}{2} \varphi) & 0 \\
0 & \exp(+i \frac{1}{2} \varphi)
\end{pmatrix}
\]

and it represents the spin rotation matrix that rotates a spinor by an angle \( \varphi \) around the \( z \)-axis. The rotation of spin spirals is shown in the third panel from top of Fig. 2.6. \( R \) is a lattice vector of the chemical lattice.

2.7 Solving the Kohn-Sham equations using the FLAPW method

The same basis set around the \( n \)-tin boundaries are different for ordinary non-collinear calculations and spin spiral calculations. The electron density and density dependent potential \( V \) can be constructed as,

\[
\left[ n, \begin{pmatrix} m_1 \\ n_1 \end{pmatrix}, \begin{pmatrix} m_2 \\ n_2 \end{pmatrix} \right]
\]

2.7.6 Spin-orbit Coupling

Spin orbit coupling (SOC), is implemented in FLAPW method as described below. The SOC is considered within the muffin-tins only, as the SOC effect is significant in the atomic core region. The spin orbit coupling is neglected in the interstitial region. In short, the matching conditions at the muffin tin boundaries are different for ordinary non-collinear calculations and spin spiral calculations. The electron density and density dependent potential \( V \) can be constructed as,

\[
\left\{ \begin{array}{c}
p^t_{\mu}(r) \psi_{\mu,i} \\
U(q \cdot r) \psi_{\mu,i}
\end{array} \right\}
\]

The same basis set \( \{ \phi_{\mu}^{q}, e, G \} \) is used to expand the functions of the form \( U(q \cdot r) \psi_{\mu,i} \) as in the non-collinear case. However, in practice, it is good to construct the radial functions \( u \), and \( \hat{u} \) in the muffin tins from the diagonal elements of \( U^{t}_{\mu MT} V U_{\mu MT} \) since the magnetization usually is approximately collinear within muffin-tin spheres and rotates mainly in the interstitial region. In short, the matching conditions at the muffin tin boundaries are different for ordinary non-collinear calculations and spin spiral calculations. The electron density and density dependent potential \( V \) can be constructed as,

\[
\left\{ \begin{array}{c}
p_{\mu}(r) \psi_{\mu,i} \\
U(q \cdot r) \psi_{\mu,i}
\end{array} \right\}
\]

2.7.6 Spin-orbit Coupling

Spin orbit coupling (SOC), is implemented in FLAPW method as described below. The SOC is considered within the muffin-tins only, as the SOC effect is significant in the atomic core region. The spin orbit coupling is neglected in the interstitial as well as vacuum region. With this approximation, we have,[240]

\[
H_{so} = \sum_{\mu} \Theta^{\mu}(r^{\mu}) \xi^{\mu}(r^{\mu}) \sigma \cdot L^{\mu}, \quad \text{with} \quad \Theta^{\mu}(r^{\mu}) = \begin{cases} 1 & \text{if } |r^{\mu}| < R^{\mu}_{MT} \\
0 & \text{else} \end{cases}
\]

where, \( r^{\mu} = r - R^{\mu} \), and \( R^{\mu} \) as well as \( R^{\mu}_{MT} \) are the center and radius of the muffin-tin sphere \( \mu \). The spin orbit coupling operator in each muffin tin with atom index \( \mu \) can be written as,

\[
H_{so} = \xi(r) \left( \begin{array}{cc}
\hat{L}_z \\
\hat{L}_+ & -\hat{L}_-
\end{array} \right), \quad \hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y
\]
A rotation \( U_{rs} \) has to be performed to rotate the global spin coordinate frame with respect to the lattice if the spin quantization axis is not \( z \)-matrix. It can be performed by rotation of the SOC operator,

\[
U_{rs}^\dagger H_{so} U_{rs} = \xi(r) U_{rs}^\dagger (\sigma \cdot \hat{L}) U_{rs} = \xi(r) \begin{pmatrix}
\hat{L}_{\uparrow\uparrow} & \hat{L}_{\uparrow\downarrow} \\
\hat{L}_{\downarrow\uparrow} & \hat{L}_{\downarrow\downarrow}
\end{pmatrix}
\]

(2.163)

In practice, the SOC correction added to the scalar relativistic Hamiltonian depends on the kind of investigation, e.g., magnetocrystalline anisotropy (MCA) or Dzyaloshinskii-Moriya interaction (DMI). The incorporation of SOC can be achieved from self consistent calculations and by employing the force theorem.

- A second variation for self consistency in collinear structures
- Self consistent noncollinear structures
- Force theorem by diagonalizing exactly the \( H_{so} \)
- Using the force theorem and treating \( H_{so} \) within perturbation approach

2.7.7 Second Variation

If the unperturbed solution of the Hamiltonian (Eq. 2.41) is known, the number of basis functions can be reduced. This advantage is used in the second variation. In this scheme, we first do a collinear calculation neglecting the SOC and eigenfunctions \( \psi_{i\uparrow} \) and \( \psi_{i\downarrow} \) are evaluated. As a next step, these functions are used as a basis set to set up the full Hamiltonian (i.e., Hamiltonian containing \( H_{so} \), having the form as Eq. 2.162) and diagonalize it. The spin orbit coupling Hamiltonian \( \hat{H}_{so} \) mixes the up- and down-components of the unperturbed solution into the new wave functions via \( \hat{L}_{\sigma\sigma'} \) through its off-diagonal elements. However, the elements of \( H_{so} \) are small since \( H_{so} \) is a small perturbation in comparison with the scalar relativistic Hamiltonian. This scheme is useful if the ground state of system without SOC is approximately collinear.

2.7.8 First order perturbation theory

Due to the small contribution of the spin-orbit coupling, it is treated as a first order perturbation. The effects like Dzyaloshinskii-Moriya interaction (discussed in next section), can be approximated by the expectation values,

\[
\Delta E_{k,j} = \langle \psi_j | H_{so} | \psi_j \rangle = \begin{pmatrix}
\psi_{k,j}\uparrow \langle \psi_{k,j}\uparrow | & \psi_{k,j}\downarrow \langle \psi_{k,j}\downarrow |
\end{pmatrix}
\begin{pmatrix}
H_{so}^{\uparrow\uparrow} & H_{so}^{\uparrow\downarrow} \\
H_{so}^{\downarrow\uparrow} & H_{so}^{\downarrow\downarrow}
\end{pmatrix}
\begin{pmatrix}
\psi_{k,j}\uparrow \rangle \\
\psi_{k,j}\downarrow \rangle
\end{pmatrix}
\]

(2.164)

Here, the eigenstate of the perturbed system is represented by \( | \psi_j \rangle \). Within the first order perturbation theory, it is convenient to deal with the spin spiral calculations for small \( q \) vectors. [241] If SOC is taken into account, the atoms of a spin spiral are not equivalent under a generalized Bloch theorem, and they can be distinguished by their spin orbit contribution. It can be seen from following treatment, that the corrections due to SOC to all band energies are the same for all atoms, in the first order perturbation.

The spin orbit operator \( H_{so}^{\sigma\sigma'} \) is a lattice periodic for all its 4 components. Applying the lattice periodic operator to a Bloch wave gives the same Bloch vector and lattice periodic part (Bloch function) \( v(r) \)

\[
H_{so}^{\sigma\sigma'} e^{i(k\cdot\mathbf{q}/2)} u_j^{(\sigma')}(|r\rangle = e^{i(k\cdot\mathbf{q}/2)} v_j^{(\sigma')}
\]

(2.165)
where the \(-\) corresponds to \(\sigma' = \uparrow (\downarrow)\). The integrals over the off-diagonal elements of \(\mathcal{H}_{so}\), e.g., \(\langle \psi_j^{(\uparrow)} | \mathcal{H}_{so} | \psi_j^{(\downarrow)} \rangle\) vanish, when summed up over \(N\) chemical unit cells, so that the magnetization in the unit cell is commensurate.

\[
\sum_{n=1}^{N} e^{i\mathbf{q} \cdot \mathbf{r}} \int_{MT} d\mathbf{r} \, e^{i\mathbf{q} \cdot \mathbf{r}} u_j^{(\uparrow)}(\mathbf{r})^* v_j^{(\downarrow)}(\mathbf{r}) = 0, \quad \mathbf{q} \cdot \mathbf{R} = 2\pi/N \quad \text{and} \quad \mathbf{q} \parallel \mathbf{R}
\]  

(2.166)

Hence, we consider only the diagonal elements.

\[
\langle \psi_j | \mathcal{H}_{so} | \psi_j \rangle = N \left( \langle u_j^{(\uparrow)} | v_j^{(\uparrow)} \rangle + \langle u_j^{(\downarrow)} | v_j^{(\downarrow)} \rangle \right)
\]  

(2.167)

Here the Bloch factors cancel each other, leading to the same contribution for every atom in the magnetic supercell. The resultant expression, is a lattice periodic and thus considers only the chemical unit cell. The expectation values shown in Eq. (2.167) are calculated in following way. In the LAPW basis, the wavefunctions are expressed as,

\[
\psi_{K_j}(\mathbf{r}) = \sum_L \left( A_{L}^{K_j,l,m}_{\sigma,\sigma'}(r) + B_{L}^{K_j,l,m}_{\sigma,\sigma'}(r) \right) Y_l(\hat{\mathbf{r}})
\]  

(2.168)

The quantum numbers \(l\) and \(m\) are abbreviated as \(L\) and \(K_j = \mathbf{G} + \mathbf{k}_j\). They are constructed in the local coordinate frame (denoted by \(-\)) Expanding the wavefunctions in this basis,

\[
\psi_j(\mathbf{r}) = \sum_{L} \left( \sum_G c_{j,G}^{(\uparrow)} \psi_{K_j}^{(\uparrow)} \right), \quad j = (K_j, \nu_j)
\]

When the wavefunctions are rotated from local to the global frame of reference, the muffin-tin coefficients \(A\)- and \(B\)- are read as

\[
a_{j,l,m}^{(\alpha',\alpha)} = U_{MT}^{(\alpha',\alpha)} T_{l,m}^{(\alpha',\alpha)} A_{L}^{(\alpha)}
\]  

(2.170)

\[
b_{j,l,m}^{(\alpha',\alpha)} = U_{MT}^{(\alpha',\alpha)} T_{l,m}^{(\alpha',\alpha)} B_{L}^{(\alpha)}
\]  

(2.171)

The expectation values then reads as

\[
\langle \psi_{j} | \mathcal{H}_{so} | \psi_{j} \rangle = \int_{MT} d\mathbf{r} \psi_{j}^{\dagger}(\mathbf{r}) U_{rs}^{\dagger} \mathcal{H}_{so} U_{rs} \psi_{j}(\mathbf{r})
\]  

(2.172)

This can be evaluated using the following abbreviations

\[
A_{j,l,m}^{(\alpha',\alpha)} = \int_{0}^{2\pi} d\delta \int_{0}^{2\pi} d\varphi \, (-\sin \delta) \, Y_l(\delta,\varphi)^* L^{(\alpha',\alpha)}(\delta,\varphi) Y_l(\delta,\varphi),
\]

\[
R_{j,l,m}^{(\alpha',\alpha)} = \int_{0}^{R_{MT}} \int_{0}^{R_{MT}} d\mathbf{r} \, r^2 \xi(\mathbf{r}) u_{l}^{(\alpha',\alpha)}(\mathbf{r}) u_{l}^{(\alpha)}(\mathbf{r})
\]  

(2.173)
2.8 Magnetic Interactions

In this section, we consider the different types of magnetic interactions which can be important in allowing the magnetic moments in a system to communicate with each other and produce long range order. The magnetization direction of an atom can be described by a classical unit vector \( \mathbf{S}_j \) (with \( |\mathbf{S}_j| = 1 \)). The energy of the arrangement of several spins is determined by interaction between these spins. The physical origin lies in Coulombic interactions of electrons whose wave functions overlap with the electron wave functions from the neighboring atoms. A general bi-linear interaction between two spins can be written as,

\[
\mathbf{S}_i^T \mathbf{V}_{ij} \mathbf{S}_j \quad \text{with} \quad \mathbf{V}_{ij} = \begin{pmatrix}
V_{i1} & V_{i2} & V_{i3} \\
V_{i1} & V_{i2} & V_{i3} \\
V_{i1} & V_{i2} & V_{i3}
\end{pmatrix}
\]

(2.175)

where the element of \( V_{ij} \) depends on the site of the spins \( i \) and \( j \). The Hamiltonian that considers spin of all pair interactions can be written as

\[
H = \sum_{i,j} \mathbf{S}_i^T \mathbf{V}_{ij} \mathbf{S}_j
\]

(2.176)

Let us split the interaction into: an isotropic part, \( I_{ij} \), a symmetric traceless part \( \mathbf{V}_{ij}^+ \) and an anti-symmetric part \( \mathbf{V}_{ij}^- \):

\[
I_{ij} = \text{Tr}(\mathbf{V}_{ij})/3
\]

\[
V_{ij}^+ = (\mathbf{V}_{ij} + \mathbf{V}_{ij}^T)/2 - I_{ij}
\]

(2.177)

\[
V_{ij}^- = (\mathbf{V}_{ij} - \mathbf{V}_{ij}^T)/2.
\]

With the above formulations, the Hamiltonian (Eq. 2.176) can be written as

\[
H = \sum_{i,j} \left( I_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{S}_i^T \mathbf{V}_{ij}^+ \mathbf{S}_j + \mathbf{S}_i^T \mathbf{V}_{ij}^- \mathbf{S}_j \right)
\]

(2.178)

In the above equation, the first part is isotropic Heisenberg model. Any anti-symmetric matrix can be expressed by a vector

\[
\begin{pmatrix}
V_{ij}^-
\end{pmatrix}_{m,n} = \sum_{i=1}^{3} D_{ij} \epsilon_{imn}
\]

(2.179)
where $\varepsilon_{lmn}$ is the Levi-Civita symbol, and the antisymmetric part of the equation can be written as

$$S_i^T \mathbf{V}_{ij} \mathbf{S}_j = \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) \quad (2.180)$$

The above interaction is called as Dzyaloshinskii-Moriya interaction[197, 198] and is determined by Dzyaloshinskii-Moriya vector $\mathbf{D}_{ij}$, and will be discussed in further subsections. The third part is the symmetric traceless part $\mathbf{V}^{+}_{ij}$, called as Pseudo-dipolar interaction or anisotropic exchange.[242] However it is a relativistic two particle effect and its contribution to the energy is very small. In contrast to the above, the magnetocrystalline anisotropy energy (MCA), which is the on-site term of $\mathbf{V}^{+}_{ij} = \mathbf{V}^{+}_{ii}$

$$H_{ani} = \sum_i S_i^T \mathbf{K}_i \mathbf{S}_i$$

where, $\mathbf{K}$ is a lattice dependent anisotropy tensor.

The energy is then described by the equation.

$$H = \sum_{i<j} \left( J_{i-j} S_i \cdot S_j + \mathbf{D}_{i-j} (\mathbf{S}_i \times \mathbf{S}_j) + \sum_i S_i^T \mathbf{K} \mathbf{S}_i \right) \quad (2.182)$$

2.8.1 Heisenberg Model

This is the simplest model to describe the magnetic interactions and can be written as

$$H = \sum_{i,j} J_{ij} S_i \cdot S_j = \sum_{i,j} J_{ij} \cos(\varphi_{ij}) \quad (2.183)$$

The exchange integral $J_{ij}$ is mainly determined by the overlap of wave functions of atoms at site $i$ and $j$ and decreases rapidly with increasing distance $R_{ij}$ of the two atoms. In metals, the interaction is long ranged and shows oscillatory behavior. In spin spiral ground state, the interactions beyond the nearest neighbor are also significant, and the direction of the magnetization can be written as,

$$\mathbf{M}(\mathbf{R}_i) = M_0 \begin{pmatrix} \cos(\mathbf{q} \cdot \mathbf{R}) \sin(\theta) \\ \sin(\mathbf{q} \cdot \mathbf{R}) \sin(\theta) \\ \cos(\theta) \end{pmatrix} \quad (2.184)$$

where, $\mathbf{q}$ is the spin spiral vector and $\theta$ is the cone angle. The $z$ axis is chosen to be the axis of rotation. In collinear alignment, $J_1 < 0$ leads to ferromagnetic ordering ($\varphi = 0$). On a square lattice, $J_1 > 0$, the antiferromagnetic order has lower energy ($\varphi = \pi$).

2.8.2 Dzyaloshinskii-Moriya Interaction

If the spin orbit coupling is taken into account, an antisymmetric interaction may occur with an energy contribution of the form

$$E_{DM} = \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) = (\mathbf{D}_{ij} \cdot \hat{n}) \sin(\varphi_{ij}) \quad (2.185)$$

This interaction is called as Dzyaloshinskii-Moriya interaction.[197, 198] Since spin orbit coupling is essential for this interaction, non-relativistic Pauli equation can not be used to describe such interaction. Without SOC, the spin reflection shows degenerate energy, whereas, $E_{DM}$ is invariant under spin reflections, i.e., if $\mathbf{D} = e_z, \mathbf{S}_1 = e_x, \mathbf{S}_2 = e_y,$

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Figure 2.7 – Flat spin spirals shown rotating in different directions with the axis \( R \). The initial spin spiral (left side of each pair) is mirrored with an appropriate mirror plane, the resulting spiral is same with the initial one except with a change of sign of \( q \). (Ref.: B. Zimmermann, Diploma Thesis, (2010)).

Then a spin reflection on the \((y, z)\) plane changes a sign of \( E_{DM} \).

The crystal field breaks the chiral symmetry of the magnetic structure, when the SOC is taken into account. If the chiral symmetry of the structure is not broken, then SOC contributes only to the symmetric exchange integral \( J \) in the Eq. (2.183). However, in the case of broken symmetry, it contributes to the symmetric term of Eq. (2.183) and to the antisymmetric term (Eq. 2.185).

The DMI vector vanishes if the chemical lattice is invariant under real space inversion. This can be seen from Fig. 2.7. In the first figure, the right- and left- handed spirals are mirror images to each other. If we take spin-orbit coupling into account, we need to consider the system consisting of a spiral and a substrate. For the first and middle panel of Fig. 2.8, the surface does not break the mirror symmetry, hence the spin spiral energy is still degenerate and corresponding components of DM-vector vanish. For the last panel, the surface breaks the mirror symmetry and hence the component of DM-vector survives and it is along the rotation axis of the spiral vectors. In addition, if the system would have inversion symmetry, this mirror plane would have been preserved, that would lead all components of DM-vector to vanish.

The directions of the DM-vector can be determined only from symmetry considerations. However, the symmetry should be broken by some other mechanism such as, a structure of the surface or by impurities. In such cases, the direction of the DM vector can be determined by the following rules. Consider the two spins at \( R_1 \) and \( R_2 \) and the middle is labeled as \( \tilde{R} = (R_1 + R_2)/2 \).[198]
2.8 Magnetic Interactions

- If the center of inversion is located at \( \hat{R} \), then \( D = 0 \)
- If a mirror plane is perpendicular to the \( (R_1 - R_2) \) and includes \( \hat{R} \), then \( D \perp (R_1 - R_2) \)
- If a mirror plane includes \( R_1 \) and \( R_2 \), then \( D \perp \) mirror plane
- If a two-fold rotation axis is \( \perp \) to \( (R_1 - R_2) \) and includes \( \hat{R} \), then \( D \perp \) two-fold axis
- If a \( n \)-fold rotation axis \( (n \geq 2) \) includes \( R_1 \) and \( R_2 \) then \( D \parallel (R_1 - R_2) \)

2.8.3 Magnetic Anisotropy

The magnetic moments of a material will prefer to lie along a certain direction, where the energy is minimum. The axis of such direction is called as the easy axis, where the energy is minimum. The easy axis is determined by the type of the crystal lattice, and it originates from two main contributions: the first one is due to spin-orbit coupling and another is due to dipole-dipole interaction.

The dipole-dipole interaction is treated classically, where the magnetostatic energy can be evaluated by considering the magnetic dipolar moments of the atoms instead of magnetization density. It affects the preferred real-space direction of the magnetic moments. The magnetostatic energy \( \varepsilon^d \) of a magnetic dipole at position \( r_0 \) with moment \( m_0 \) that is exposed to the fields of other dipoles at positions \( \{r_j\}_{j \neq 0} \) (shown in Fig. 2.9) is given as,

\[
\varepsilon^d = \frac{\mu_B^2}{2} \sum_{j \neq 0} \frac{(m_j \cdot m_0)(r_j - r_0)^2 - 3((r_j - r_0) \cdot m_j)(r_j - r_0) \cdot m_0}{|r_j - r_0|^5}
\] (2.186)

The above equation (Eq. 2.186) gives rise to magnetostatic anisotropic energy since \( \varepsilon^d \) depends on the orientation of the magnetic moments with respect to chemical lattice. In the bulk structures, the \( \varepsilon^d \) depends on the macroscopic shape of the magnetic sample (shape anisotropy), whereas in the materials with reduced dimensions e.g., magnetic films and wires, \( \varepsilon^d \) depends only on the local orientation of the magnetic moments. This can be understood from Eq. (2.186), that the sum converges if the lattice of the magnetic moments extends infinitely in less than 3 dimensions.

The contribution from spin-orbit coupling should be treated quantum mechanically, where the total energy is calculated with the magnetization direction along the high symmetry directions. For the calculation of the magneto-crystalline anisotropy energy (MCA), we have used the total energy difference method for different magnetization
directions, with the spin orbit coupling interaction included. We have defined \( E^1 = E^\hat{x} \), \( E^\hat{y} \), and \( E^2 = E^\hat{y} - E^\hat{z} \), where, \( \hat{x} \) is periodic wire direction, \( \hat{y} \) is the perpendicular direction in the plane of the wire and \( \hat{z} \) is perpendicular to both the wire axis and the wire plane. The spin-orbit contribution to the magnetic anisotropy energy is enhanced at surfaces and interfaces due to the broken symmetry.[243]

## 2.9 Ballistic Electronic Transport

In this thesis, we also investigate the electrical transport through a nanosized conductor such as nanowire. Each material exhibits a definite conductivity, so that, the conductance of a wire is inversely related to the length of the wire. However, if the length scale of the wire is reduced to the mean free path of the electrons the transport phenomenon changes from diffusive to ballistic as shown in Fig. 1.3. With the reduction in the length of the nanowire to the Fermi wavelength scale, the conductance in the nanowire is in quantized form.[12] In addition, the conductance no longer depends on the length of the wire. In such small size materials, the transport properties are ruled by quantization effects,[244] which requires problem to be treated quantum mechanically. We start to describe the problem using Landauer formalism within the framework of non-equilibrium Green’s function and its simplification using \textit{ab initio} methods.

### 2.9.1 Landauer-Büttiker’s formalism

In Landauer-Büttiker’s (LB) formalism,[245, 246] the electron transport is considered as a scattering process where the nanoscopic conductor acts as a quantum mechanical scatterer. The inelastic scattering i.e., scattering by phonons or by other electrons is neglected so the transport is coherent.\(^4\) Fig. 2.10 shows how a transport problem is modeled in LB formalism. The central scattering region (S) containing the nanoscopic conductor is connected by two semi infinite leads that are each in thermal equilibrium but at different chemical potentials \( \mu_L \) and \( \mu_R \). It can be assumed that, the conductor is narrow enough that the lowest of transverse eigenstates in the channel has its energy below the Fermi energy, this makes the channel essentially one-dimensional. At absolute temperature, suppose \( \mu_L > \mu_R \), then in the range between \( \mu_L \) and \( \mu_R \), we have fully occupied levels pouring from left to the right direction. The current is then given by

\[
I = - (\mu_L - \mu_R) e v (\frac{dn}{d\mu})
\]

\[\text{(2.187)}\]

\(^4\)The electron-phonon scattering plays a major role when the temperature of the system is raised up. In ballistic conductors, the mean square amplitude of vibration (\( u \)) of a bond at temperature \( T \) is

\[
\langle |\hat{u}|^2 \rangle = \langle n \rangle \hbar / 2 M \omega
\]

where, \( \omega \) is the frequency of vibration and \( M \) is the reduced mass. The temperature much below the melting point, should give the vibration amplitude much less than the equilibrium bond length.[247]
where, \((dn/d\mu)\) denotes the density of states including the degenerate spin states. The velocity is denoted by \(v\) and is along the tube (Fig. 2.10) at the Fermi surface. It can be written as, \((\mu_L - \mu_R) = -e(V_L - V_R)\), where \(V\) is the voltage and \(e\) is magnitude of charge.\(^5\) Also, \(dn/d\mu = 1/\pi \hbar v\). Therefore the current is given by,

\[
I = \left(\frac{e^2}{\pi \hbar}\right) (V_L - V_R) \tag{2.188}
\]

The conductance is then given as

\[
G = \frac{I}{V} = \frac{e^2}{\pi \hbar} \tag{2.189}
\]

This is the conductance for an ideal one dimensional conductor. In case of ideal one dimensional conductor, the electron population is controlled by reservoirs and the electrochemical potential \(1/2(\mu_L + \mu_R)\).

If we insert an obstacle into the channel, which transmits with probability \(T\), the current will be reduced accordingly and we find,

\[
G = \frac{e^2}{\pi \hbar} T \tag{2.190}
\]

The total current \(I\) due to applied voltage difference \((\mu_L - \mu_R)\) is given by

\[
I = \int_{\mu_L}^{\mu_R} dE I(E) = \frac{2e}{\hbar} T(E) \left[ f_L(E) - f_R(E) \right] \tag{2.191}
\]

where the Fermi function,

\[
f_L(E) = \frac{1}{e^{(E - \mu_L)/kT} + 1} \quad f_R(E) = \frac{1}{e^{(E - \mu_R)/kT} + 1}
\]

Now the problem is reduced to the calculation of transmission function \(T\) for the conductor. Using the scattering theory, the transmission function is evaluated as

\[
T(E) = Tr(t t^\dagger) \tag{2.192}
\]

where \(t\) is a transmission matrix of the scattering obstacle, utilizing the transverse eigenstates of the channel as a basis. For the calculation of the transmission function, we use the Fischer-Lee representation as,\(^[246]\)

\[
T(E) = Tr(\Gamma_L \Gamma_R G_C^{ret} G_C^{adv}), \tag{2.193}
\]

where, \(G_C^{adv/ret}\) represents the advanced and retarded Green’s functions of the conductor and \(\Gamma_L/R\) are the coupling between the conductor and semi-infinite leads, respectively. The analytic form of these quantities are give as,

\[
G_C^{adv/ret} = \left[ E \pm i\eta - H_C - \Sigma_L^{ret/adv}(E) - \Sigma_R^{ret/adv}(E) \right]^{-1} \tag{2.194}
\]

\(5\) The conduction depends on the availability of the energy states near the Fermi energy. For example, if the source and drain are in contact, the levels are matched depending on the positive voltage difference \(V_D\), at distinct electrochemical potential separated by \(eV_D\) as, \((\mu_L - \mu_R) = -eV_D\)
\[ \Gamma_{L/R}(E) = i \left[ \Sigma_{L/R}^{\text{ret}}(E) - \Sigma_{L/R}^{\text{adv}}(E) \right] \]  
(2.195)

Here, \( H_C \) is the Hamiltonian of the conductor and \( \Sigma_{L/R}^{\text{adv/ret}}(E) \) are advanced and retarded self energies due to the interaction with the leads. Intrinsic broadening due to scattering within the conductor is measured by the parameter \( \eta \) and \( \eta \rightarrow 0 \) in case of ballistic transport limit, that is considered in the present thesis.

Numerically, Eq. (2.193-2.195) are implemented in the real space. However, we follow the formulation proposed by B. Oetzel et al.,[248] where the calculations are performed in the \( k \)-space. This is much easier by means of modern \textit{ab initio} methods. For simplicity, we formulate the method for infinite length one dimensional wires where the conductor and the leads are of the same material. For such system, Eq. (2.193-2.195) can be simplified with the help of Fourier transform into a reciprocal space.

It is easy to calculate the band structure \( E_C(k) \) in the \( k \)-space using \textit{ab initio} methods, due to possible replacement \( H_C \rightarrow E_C(k) \). In addition, the periodicity of the structure is considered which requires that self energies for the left and right leads are identical. Hence we replace according to, \( \Sigma_{L/R}^{\text{adv}}(E) \rightarrow \pm \frac{1}{2} \gamma \). The quantity \( \gamma \) represents the level of broadening, e.g., band dispersion.[94] The equations (2.194 and 2.195) simplifies to,

\[ G_{C}^{\text{adv/ret}} = [E \pm i \eta - E_C(k) \mp i \gamma]^{-1} \quad \text{and} \quad \Gamma_{L/R}(E) = -\gamma \]  
(2.196)

The above matrix is diagonal and is represented with respect to wave vector \( k \). Hence trace of the matrix in Eq. (2.195) can be replaced by a sum over \( k \) and the transmission function for an infinite one dimensional chain within considered limit of \( \eta \rightarrow 0 \) for ballistic transport becomes

\[ T(E) = \sum_k \frac{\gamma^2}{[E - E_C(k)]^2 + \gamma^2} \]  
(2.197)

The level broadening in Eq. (2.197) is small in comparison with the energy scale of interest. Therefore, we simplify the notation and assume henceforth the limit \( \gamma \rightarrow 0 \).[94] Therefore above equation (Eq. 2.197) can be simplified into

\[ T(E) = \sum_k \delta_{E,E_C}(k) = N(E) \]  
(2.198)

This implies that, the transmission function at some particular energy can be obtained by calculating the number of states \( N(E) \) at this energy. Consequently, it can be directly obtained from the energy band structure performed in \( k \) space. This does not require any projections onto real space Hamiltonian using localized orbitals.

\subsection*{2.9.1.1 Simplification for Magnetic Wires}

In the thesis, we have also investigated the conductance for infinite length magnetic nanowires. The ballistic conductance in case of magnetic nanowires is calculated as

\[ G = \frac{e^2}{h} \left( \sum_{i=1}^{N_i} T_i + \sum_{j=1}^{N_j} T_j \right) \]  
(2.199)

where the sums over the occupied states \( T_i \) and \( T_j \) are the transmission function for the \( i^{th} \) channel of spin up and \( j^{th} \) channel of spin down electrons, respectively.
Unlike nonmagnetic case, the ferromagnetic nanowires show conductance in the quantized units of \((e^2/h)\), since spin up and spin down electrons contribute in the total conductance independently. The transmission coefficient of a periodic wire in one particular spin channel at a particular energy is calculated as

\[
T(E) = N(E)
\]

### 2.10 BALLISTIC ANISOTROPIC MAGNETORESISTANCE (BAMR)

The conductance in magnetic nanowires depends strongly upon the relative angle between the magnetization direction and the direction of electrical current.[249] This phenomenon is also observed in bulk materials and was called as anisotropic magnetoresistance. Ferromagnetic metals exhibiting a normal AMR effect show minimum conductivity when the current is parallel to the magnetization direction \((\rho_\parallel)\), and maximum conductivity when the current is perpendicular to the magnetization direction \((\rho_\perp)\). The ballistic anisotropic magnetoresistance for ferromagnetic nanowires is computed as,[249]

\[
\text{BAMR} = \frac{Q_\perp - Q_\parallel}{Q_\perp}
\]

where, \(Q_\perp\) is the total number of conducting channels, when the magnetization is perpendicular to the current direction (axial direction) and \(Q_\parallel\) is the number of conducting channels, when the magnetization is parallel to the axial direction.

At intermediate angles between the current and magnetization direction, \(\theta\), the \(\text{BAMR}\) is given as,

\[
Q(\theta) = Q_\perp + (Q_\parallel - Q_\perp) \cos^2(\theta)
\]

The physical origin of BAMR lies in the strong spin orbit interaction which produces the anisotropy of scattering. A stronger scattering is expected for electrons traveling parallel to the magnetization which leads to a large resistivity \(Q_\parallel\) in comparison with \(Q_\perp\).[249]

### 2.11 COMPUTATIONAL PARAMETERS USED TO SIMULATE NANOWIRES

In this thesis, we have investigated the electronic and magnetic properties of infinite length quasi-one dimensional nanowires of pure Au, Ni and alloys like Au-Ni, 3\(d\) – 5\(d\) nanowires (3\(d\): Fe, Co and 5\(d\): Ir, Pt, Au). The total energy calculations for Au, Ni and Au/Ni nanowires were performed using \textit{ab initio} density functional theory (DFT) as implemented in \textit{Vienna ab initio} Simulation Package (VASP). The magnetic calculations were performed using spin polarized density functional theory. [227, 250, 251] The noncollinear magnetic calculations of 3\(d\) – 5\(d\) nanowires were performed using full potential linearized augmented plane wave method (FLAPW) as implemented in Jülich FLEUR code.

**Ab initio calculations for Au, Ni and Au/Ni nanowires using VASP code:**

The pure Au, Ni and bimetallic Au/Ni nanowires were modeled in a periodically repeated unit cell, whose dimensions were chosen in such a way that the wires are infinite and periodic in one dimension and they do not interact with each other in other two directions as shown in Fig. 2.11. The Projector Augmented Wave method (PAW) and Generalized Gradient Approximation (GGA) have been used to describe electron-ion interaction and exchange correlation interaction respectively. The plane
Computational Parameters used to simulate Nanowires

Figure 2.11 – The simulation cell for modeling nanowires. Nanowire has periodicity in one dimension and enough vacuum in other two directions to avoid lateral interactions.

Figure 2.12 – Energy convergence with respect to \( k \)-points for infinite length gold nanowires.
wave cutoff energy for pure Au, pure Ni and Au-Ni nanowires used was 229.9 eV, 269.5 eV and 269.5 eV respectively. The energy convergence for linear nanowire was tested with respect to number of $k$-points used for integrating the Brillouin zone (Fig. 2.12). A $13 \times 1 \times 1$ mesh of $k$-points in the Monkhorst pack scheme gave reasonable convergence for Au and Ni nanowires as shown in Fig. 2.12.

Atomic relaxations were performed by preserving the cell shape and volume of the unit cell. The optimization algorithms used were Residual Minimization Method (RMM-DIIS) and Conjugate Gradient (CG) method. We have optimized the structures until the total forces on individual atoms were reduced below 0.01 eV/Å. The binding energy per atom was calculated as

$$E_B = \frac{[E_T - n_AE_A - n_BE_B]}{n_A + n_B}$$ (2.203)

where, $E_T$ is the total energy of the system, $E_A$ and $E_B$ are the single atom energies of atom of type A and B respectively. The number of atoms of type A and B are denoted by $n_A$ and $n_B$ respectively.

In order to understand the electronic and magnetic properties of the pure and bi-atomic nanowires, we have performed the band structure calculations. For linear nanowires, the Brillouin zone was integrated from $\Gamma(0,0,0)$ to $X(0.5,0,0)$ direction, whereas, for the two dimensional structures, the integration of the Brillouin zone was performed from $\Gamma(0,0,0)$ to $X(0.5,0.5,0)$ direction. In order to understand the contributions of the electrons in the $s$, $p$ and $d$ electrons, we have implemented fat band technique for VASP generated output, along the lines of TB-LMTO-ASA method (Appendix-D).[252].

**Noncollinear calculations using FLEUR code in 3d – 5d nanowires:**

The free standing zigzag bi-atomic $3d – 5d$ nanowires were modeled using the film version of the FLAPW method as implemented in Jülich FLEUR code.[236] For this nanowire, we choose a large unit cell with a vacuum of 20 a.u. in the $y$-direction. The lattice parameter is optimized using revised Perdew-Burke-Ernzerhof (rPBE)[253] exchange-correlation functional within the GGA. For noncollinear magnetic calculations, a dense mesh of $k$-points is required, hence the spin spiral calculations as well as DMI calculations are performed with 384 $k$-points. A plane wave cutoff of 3.8 a.u.$^{-1}$ was obtained by careful convergence in all nanowires. The spin spiral calculations were performed without inclusion of SOC but with the Generalized Bloch theorem, in a chemical unit cell. In this thesis, we consider only flat and homogeneous spin spirals along the periodic direction.

We considered the effects of spin orbit coupling viz., the magnetocrystalline anisotropy and the Dzyaloshinskii-Moriya interaction. We have investigated the DMI in $3d – 5d$ nanowires, with $D$ vector (Eq. 2.185), along the $z$-direction, due to symmetry arguments. The calculations performed within the single chemical unit cell. The total energy of the system is the addition of the spin spiral energy without SOC, and the energy due to the SOI calculated within the first order perturbation. The second energy contribution, that is magnetic anisotropy energy, has been computed for all $3d – 5d$ nanowires. We denoted $E^1$ as the energy difference between the easy axis and medium axis, whereas, $E^2$ is the difference between the easy axis and hard axis. We have computed the $\frac{1}{2}E^1$ and compared it against the energy due to DMI. The ground state of the system is noncollinear (spin spiral) only if, the energy due to DMI overcomes the MAE.

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