CHAPTER 2

FUNDAMENTAL CONCEPTS AND METHOLOGY

2.1. Introduction

It is known that the spontaneous ordering of electronic spin in ferromagnetic and antiferromagnetic materials cannot be understood on the basis of dipolar magnetic field. It is proposed that there might exist a strong exchange force in ferromagnetic and antiferromagnetic materials given by well known Heisenberg Hamiltonian for explaining the spontaneous ordering. The origin of the exchange energy is considered as due to the difference between the energies of two-electrons system for which the space parts of the wave functions are symmetric and antisymmetric respectively. The symmetries of the space part of the electrons depend on the spin configuration. Consequently, the spin of the electrons are aligned in such a way for which the energy of the system is minimum. As the spins of the electrons are coupled *via* exchange energy in these materials, any spin deviations may be shared by the entire network of spins which may propagate in a wave like form. This is known as spin wave and quantum of exchange particle is termed as magnon. The dispersion relation of magnon can be deduced using Holstein-Primakoff transformations followed by Fourier transformations.

Some substances are found to show zero dc resistance below a critical temperature. This phenomenon is known as superconductivity. The comprehensive theory of superconductivity was presented by Bardeen, Cooper and Schrieffer, known as BCS theory of superconductivity. The BCS theory provides an expression for the computation of the critical temperature of superconductivity.

The most common electronic structure method known as Density functional theory (DFT) is discussed in concise in this chapter. Instead of using the many-body wave function, as used in Hartree-Fock theory, the electron density is taken as the fundamental property in Density functional theory (DFT). In DFT, all the energies like the kinetic, the potential, the exchange and the correlation energies are expressed in terms of density of electrons. In the ground state of the system, the density of the electrons is configured in such a way that the total energy of the system is minimized.

2.2. Magnetic materials

Depending on the behaviour of the materials in the presence of an external magnetic field, they are divided into two main categories namely, diamagnetic and paramagnetic. In diamagnetic substances, the elementary magnetic moments of atoms are found zero without application of external field. On the other, the elementary magnetic moments of atoms of paramagnets are found nonzero even without application of any external magnetic field. When a paramagnet is subjected to an external magnetic field, these magnetic moments are aligned along the field direction and consequently, the magnetic ordering arises. Now, if the temperature of a paramagnetic substance is decreased below a certain critical value, a spontaneous magnetization is built due to interaction between the individual atoms even in the absence of the external magnetic field. Depending on the nature of this interaction of the atoms, different types of ordered states are built. The main types of the magnetically ordered materials are ferromagnets and antiferromagnets.

2.2.1. Ferromagnets

In ferromagnetic materials, there may exist a bulk magnetic moment and the magnetization is large even if external field is removed. A ferromagnetic substance consists of small magnetized regions which are called magnetic domains. The total magnetic moment of a sample of the substance is the vector sum of the magnetic moments of the domains. The electronic spins of the atoms within a particular domain are parallel to each other. In the presence of an external magnetic field, the domains are oriented along the direction of the field. When the external field is removed, the magnetization still continues to exist due the internal molecular field. If the temperature of a ferromagnetic substance is enhanced beyond a certain temperature, known as Curie temperature or Curie point, the ferromagnetic substance is transformed into a paramagnetic one.

Ferromagnetism is the one of the strongest forms of magnetism and it is liable for most of the magnetic behaviour encountered in our everyday life, and is the basis for all permanent magnets. Metals like Fe, Ni, Co, Dy and insulators like EuO and EuS are some examples of ferromagnets.

2.2.2. Antiferromagnets

It has been observed that, in some magnetic materials, there may exist an antiparallel alignment of magnetic moments at the nearest neighbours which makes the total bulk spontaneous magnetization zero. These materials are known as antiferromagnetic material. In such materials, the spins of the electrons align in a regular pattern such that neighbouring spins points in opposite directions. Generally, antiferromagnetic materials show antiferromagnetism property at low temperatures which become disordered above a certain temperature. The transition temperature is known as the Neel temperature. Above the Neel temperature, the antiferromagnetic materials usually turn into a paramagnetic one. An antiferromagnetic crystal may be considered as consist of two inter penetrating sub lattices with spin opposite to each other such that the resultant magnetization of a unit cell is equal to zero. However, materials with more than two magnetic sublattices may also exist in nature. Antiferromagnetic ordering is observed in some oxides such as MnO, FeO, CoO and in some fluorides such as MnF_2, CoF_2, FeF_2 *etc.*

2.3. Exchange Energy

In physics, the exchange interaction is a quantum effect between identical particles which cannot be explained from the view point of classical mechanics. The effect arises due to fact that the wave function of indistinguishable particles is subjected to exchange symmetry, *i.e.*, either symmetric or antisymmetric. In the case of symmetric wave function, it remains unchanged on exchange of two particles and but in the case of antisymmetric wave function it changes sign on exchange of two particles. Both bosons and fermions can experience such exchange interaction. The exchange interaction alters the expectation value of the distance between two indistinguishable particles. In the case of fermions, the expectation value of distance increases whereas in the case of bosons it decreases.

The exchange interaction is found to be liable for the spontaneous ordering in ferromagnetic and antiferromagnetic materials. The effective internal magnetic field in a ferromagnetic material is of ~100 T which cannot be described as arising from the interaction of the atomic magnetic dipoles. The internal field arises from the exchange interactions of the electrons. There is an energy difference between parallel and antiparallel spin configurations of the two electrons at neighbouring sites. The spin configuration for which the energy is minimum is favoured. The Inter-atomic exchange is weaker than the intra-atomic exchange which leads to Hund's first rule. The Pauli principle requires that the total wave function of two electrons is antisymmetric on exchange of two electrons numbered 1 and 2, *i.e.,*

$$\varphi(1,2) = -\varphi(2,1) \tag{2.1}$$

The total wave function of two electrons may be considered as the product of two functions $\psi(\boldsymbol{r_1},\boldsymbol{r_2})$ and $\chi(s_1,s_2)$ which depends on the space and spin coordinates respectively, each of which may be either symmetric or antisymmetric. For parallel spin configuration, the spin part of the wave function is symmetric and consequently, the space part is antisymmetric. For antiparallel spin orientation, the spin part is antisymmetric and consequently the space part is symmetric. The total energy of the system can be written as

$$E = \int \psi^*(\boldsymbol{r_1},\boldsymbol{r_2}) H(\boldsymbol{r_1},\boldsymbol{r_2}) \psi(\boldsymbol{r_1},\boldsymbol{r_2}). \tag{2.2}$$

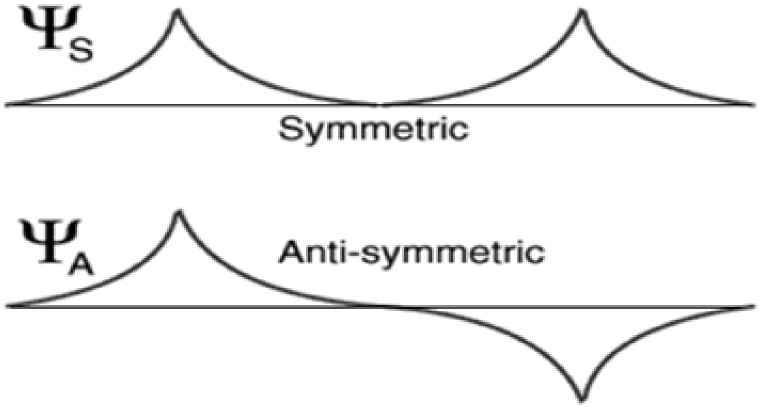

Figure 2.1. Symmetric and antisymmetric wave functions of electrons.

In the above, $H(\boldsymbol{r_1},\boldsymbol{r_2})$ is Hamiltonian of two electrons system. The symmetric and antisymmetric forms of the space part of wave function may be written as

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_1(\boldsymbol{r_1})\psi_2(\boldsymbol{r_2}) + \psi_1(\boldsymbol{r_2})\psi_2(\boldsymbol{r_1})\right), \tag{2.3}$$

and

$$\psi_A = \frac{1}{\sqrt{2}}\left(\psi_1(\boldsymbol{r_1})\psi_2(\boldsymbol{r_2}) - \psi_1(\boldsymbol{r_2})\psi_2(\boldsymbol{r_1})\right). \tag{2.4}$$

The energies evaluated with these two functions are in general not the same. The difference between these two energy levels is called exchange energy. Heisenberg generalized this exchange interaction to many-electron atomic spins $\boldsymbol{S_i}$ and $\boldsymbol{S_j}$ and expressed in terms of his famous Hamiltonian [1],

$$\hat{H}_{exch} = -2J\ \boldsymbol{S}_i \bullet \boldsymbol{S}_j \,. \tag{2.5}$$

In some substances, the value of exchange coupling is found positive which favours parallel spin orientation exhibiting ferromagnetism. On the other hand, in some substances, the negative exchange coupling favours antiparallel spin orientation exhibiting antiferromagnetism.

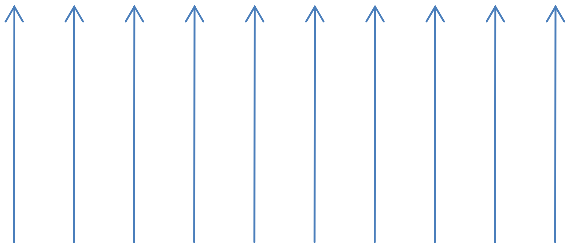

Figure 2.2. Positive *J* favours parallel spin orientation in ferromagnetic materials.

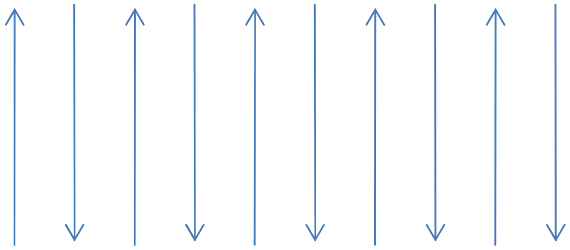

Figure 2.3. Negative *J* favours antiparallel spin orientation in antiferromagnetic materials.

2.4 Spin wave

The concept of spin waves was first brought in physics by Bloch [2].According to Bloch, the dynamic excitations of the spin system of a magnetic crystal results in collective precession of individual spins which can be represented as a propagating wave [3]. In both, ferromagnetic and antiferromagnetic materials, the spins at nearest neighbouring sites are coupled to each other *via* exchange interaction. If the spin at a particular site of a spin system is inverted, then the spin inversion may not be localized to that particular site, but is be shared by the total network of the spins and the precessional motion will propagate in a form of wave, which is known as spin wave. The corresponding quasiparticles that come out as a result of quantization of spin waves are known as magnons. The magnons are very similar to the phonons. Like phonons they are bosons and can be described by Bose-Einstein distribution function. The spin of a magnon, as a magnetic quasiparticle, is equal to one in the unit of reduced Planck's constant. For temperatures far below the Curie temperature for a ferromagnetic substance and Neel temperature for a antiferromagnetic substance, the ordered magnetic moments in the crystal may be described well as a gas of magnons on the top of the ground state. Such description is found to be successful to determine thermodynamic characteristics of ferromagnets such as temperature dependence of the magnetization and contribution to heat capacity and thermal conductivity *etc.* [4].

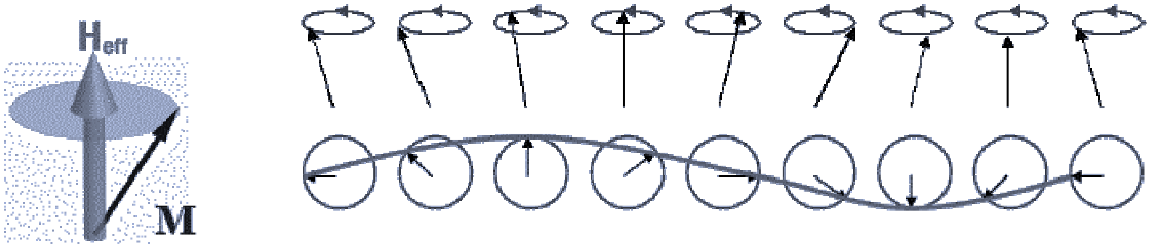

Figure 2.4. Propagation of spin wave.

2.4. Holstein-Primakoff description of ferromagnetic spin waves

To find the magnon dispersion relation of ferromagnetic magnons, consider a ferromagnetic material magnetized to saturation by strong static magnetic field H_0 taken along z-axis. Taking the exchange, dipolar and Zeeman energies into account, the Hamiltonian of the system can be written as [5]

$$\hat{H}_0 = -J\sum_{j\delta} \boldsymbol{S}_j.\boldsymbol{S}_{j+\delta} - g\mu_B H \sum_j S_{jz} + \frac{1}{2} g^2\mu_B^2 \sum_{i,j}\left[\frac{\boldsymbol{S}_i.\boldsymbol{S}_j}{r_{ij}^3} - \frac{3(\boldsymbol{S}_i.\boldsymbol{r}_{ij})(\boldsymbol{S}_j.\boldsymbol{r}_{ij})}{r_{ij}^5}\right] \tag{2.6}$$

where the vector $\boldsymbol{\delta}$ connects jth atom with its nearest neighbours on the lattice , $\boldsymbol{S_i}$*'s* are the spin at the ith site, $\boldsymbol{r_{ij}}$ is the displacement vector between the ith and jth site and H is the effective magnetic field compromising of external field, demagnetizing field and anisotropy field *etc.*. To frame the boson formalism, Holstein-Primakoff introduced the following transformation which converts the spin operators to magnon operators [4-6]

$$\left.\begin{aligned} S_j^+ &= S_{jx} + iS_{jx} = (2S)^{1/2}\left(1 - a_j^\dagger a_j/2S\right)^{1/2} a_j, \\ S_j^- &= S_{jx} - iS_{jx} = (2S)^{1/2} a_j^\dagger\left(1 - a_j^\dagger a_j/2S\right)^{1/2}, \\ S_{jz} &= S - a_j^\dagger a_j. \end{aligned}\right\} \tag{2.7}$$

With the help of the transformation and taking the Fourier transformations of the magnon creation and annihilation operators $a_j^\dagger$ and a_j one can find the Hamiltonian of the magnon system as

$$\hat{H}_0 = \sum\left\{A_k a_k^\dagger a_k + \frac{1}{2}B_k\left[exp(-2i\varphi_k\ )a_k a_{-k} + h.c.\right]\right\}, \tag{2.8}$$

where h.c. denotes the Hermitian conjugate of the expression preceding it, and

$$A_k = g\mu_B(H + Dk^2 + 2\pi M\sin^2\theta_k\ ), \tag{2.9}$$

$$B_k = g\mu_B 2\pi M\sin^2\theta_k\,. \tag{2.10}$$

In the above, $\theta_{\boldsymbol{k}}$ and $\varphi_{\boldsymbol{k}}$ are the polar angles that characterize the wave vector $\boldsymbol{k}$, $D = 2JSa^2/\hbar\gamma$, with γ the gyromagnetic ratio, is the phenomenological exchange constant and M is saturation magnetization. After diagonalization, using Bogoliubov linear transformation, the Hamiltonian becomes

$$\hat{H}_0 = \sum_{\boldsymbol{k}} \hbar\omega_{\boldsymbol{k}} c_{\boldsymbol{k}}^{\dagger} c_{\boldsymbol{k}}, \tag{2.11}$$

with the dispersion relation of magnons given by the following relation,

$$\left.\begin{aligned} \omega_{\boldsymbol{k}} &= \gamma\left[\left(H_0 - N_z M + Dk^2\right)\left(H_0 - N_z M + Dk^2 + 4\pi M \sin^2\theta_{\boldsymbol{k}}\right)\right]^{1/2}, for\ k \neq 0\ modes \\ &= \gamma\left[H_0 - \left(N_z - N_x\right)M\right]^{1/2}\left[H_0 - \left(N_z - N_y\right)M\right]^{1/2}, \qquad for\ k = 0\ mode \end{aligned}\right\} \quad 2.12)$$

In the above, N_x, N_y and N_z are the demagnetizing factors along *x, y* and *z*-axes respectively. From the dispersion relation it is apparent that magnon frequency is a quadratic function of wave vector.

2.5. Holstein-Primakoff description of antiferromagnetic spin waves

In the case of antiferromagnetic materials, the spin structure of the crystal may be divided into two interpenetrating sub lattices, named *a* and *b,* such that all nearest neighbours of an atom on *a* lie on *b* and *vice versa.* The model Hamiltonian of the system can be written as[4,5]

$$\hat{H} = J\sum_{j\delta} \boldsymbol{S}_i . \boldsymbol{S}_{j+\delta} - g\mu_B H \sum_j S_{jz}^a + g\mu_B H \sum_j S_{jz}^b . \tag{2.13}$$

where *J* is the nearest neighbour exchange coupling constant with the new choice of sign is positive for antiferromagnet and *H* is the applied magnetic field taken along *z*-axis. To get the magnon picture, the following Holstein-Primakoff transformations are introduced [4-6],

$$\left.\begin{aligned} S_{aj}^{+} &= S_{ajx} + iS_{ajy} = (2S)^{1/2}\left(1 - a_j^{\dagger}a_j/2S\right)^{1/2} a_j, \\ S_{aj}^{-} &= S_{ajx} - iS_{ajy} = (2S)^{1/2} a_j^{\dagger}\left(1 - a_j^{\dagger}a_j/2S\right)^{1/2} \end{aligned}\right\}, \tag{2.14}$$

and

$$\left.\begin{aligned} S_{bl}^{+} &= S_{blx} + iS_{bly} = (2S)^{1/2} b_l\left(1 - b_l^{\dagger}b_l/2S\right)^{1/2}, \\ S_{bl}^{-} &= S_{blx} - iS_{bly} = (2S)^{1/2}\left(1 - b_l^{\dagger}b_l/2S\right)^{1/2} b_l^{\dagger} \end{aligned}\right\}. \tag{2.15}$$

One can introduce spin wave variables as [4,5]

$$\left.\begin{aligned} c_{\boldsymbol{k}} &= N^{-1/2}\sum_j e^{i\boldsymbol{k}.\boldsymbol{x}_j} a_j \\ c_{\boldsymbol{k}}^{\dagger} &= N^{-1/2}\sum_j e^{i\boldsymbol{k}.\boldsymbol{x}_j} a_j^{\dagger} \end{aligned}\right\} \quad (2.16) \qquad \left.\begin{aligned} d_{\boldsymbol{k}} &= N^{-1/2}\sum_j e^{i\boldsymbol{k}.\boldsymbol{x}_j} b_j \\ d_{\boldsymbol{k}}^{\dagger} &= N^{-1/2}\sum_j e^{i\boldsymbol{k}.\boldsymbol{x}_j} b_j^{\dagger} \end{aligned}\right\} \quad (2.17)$$

The Hamiltonian of the system can be written in terms of magnon variable as follows

$$\hat{H} = -2NzJS^2 - 2Ng\mu_B HS + \hat{H}_0 + \hat{H}_1, \tag{2.18}$$

where z is number of nearest neighbour and $\hat{H}_0$ is part of the Hamiltonian that contains only the quadratic terms in magnon variables and $\hat{H}_1$ is the part that contains higher order term in magnon variables. The part of the Hamiltonian containing only the quadratic term is given by

$$\hat{H}_0 = 2JzS\sum_{\boldsymbol{k}}\left[\gamma_{\boldsymbol{k}}\left(c_{\boldsymbol{k}}^{\dagger}d_{\boldsymbol{k}}^{\dagger} + c_{\boldsymbol{k}}d_{\boldsymbol{k}}\right) + \left(c_{\boldsymbol{k}}^{\dagger}c_{\boldsymbol{k}} + d_{\boldsymbol{k}}^{\dagger}d_{\boldsymbol{k}}\right)\right] + g\mu_B H\sum_{\boldsymbol{k}}\left(c_{\boldsymbol{k}}^{\dagger}c_{\boldsymbol{k}} + d_{\boldsymbol{k}}^{\dagger}d_{\boldsymbol{k}}\right), \tag{2.19}$$

with $\gamma_{\boldsymbol{k}} = z^{-1}\sum_{\boldsymbol{\delta}} e^{i\boldsymbol{k}.\boldsymbol{\delta}} = \gamma_{-\boldsymbol{k}}$. To diagonalize the above Hamiltonian, the following Bogoliubov transformations are used

$$\left.\begin{aligned} \alpha_{\boldsymbol{k}} &= u_{\boldsymbol{k}}c_{\boldsymbol{k}} - v_{\boldsymbol{k}}d_{\boldsymbol{k}}^{\dagger} \\ \beta_{\boldsymbol{k}} &= u_{\boldsymbol{k}}d_{\boldsymbol{k}} - v_{\boldsymbol{k}}c_{\boldsymbol{k}}^{\dagger} \end{aligned}\right\} \tag{2.20}$$

with $u_k^2 - v_k^2 = 1$. These transformations provide the diagonalized form of the quadratic term of the Hamiltonian as given by the following expression

$$\hat{H}_0 = \sum_k \omega_k \left(\alpha_k^\dagger \alpha_k + \beta_k^\dagger \beta_k + 1 \right). \tag{2.21}$$

The magnon eigen frequencies ω_k are given by,

$$\omega_k^2 = \left(\omega_e + \omega_A \right)^2 - \omega_e^2 \gamma_k^2 . \tag{2.22}$$

with $\omega_e = 2JzS$ and $\omega_A = 2\mu_0 H$. The above equation is the dispersion relation for antiferromagnetic magnons. The higher order term $\hat{H}_I$ gives the interaction between magnons.

2.6. Interaction of magnons

The inclusion of the terms higher in order of magnon variables gives the interaction between magnons of different modes [7]. First in its kind are two magnon processes, where one magnon is destroyed and another is created [8]

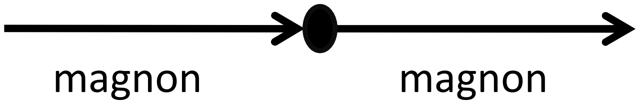

Figure 2.5 Two magnon processes

The term of order three in magnons variables gives two distinct processes, known as three magnon processes. The first kind of processes is called three magnon confluence process, where two magnon are combined to give one magnon , and the second kind is called three magnon splitting process, where one magnon is destroyed and two magnon are created

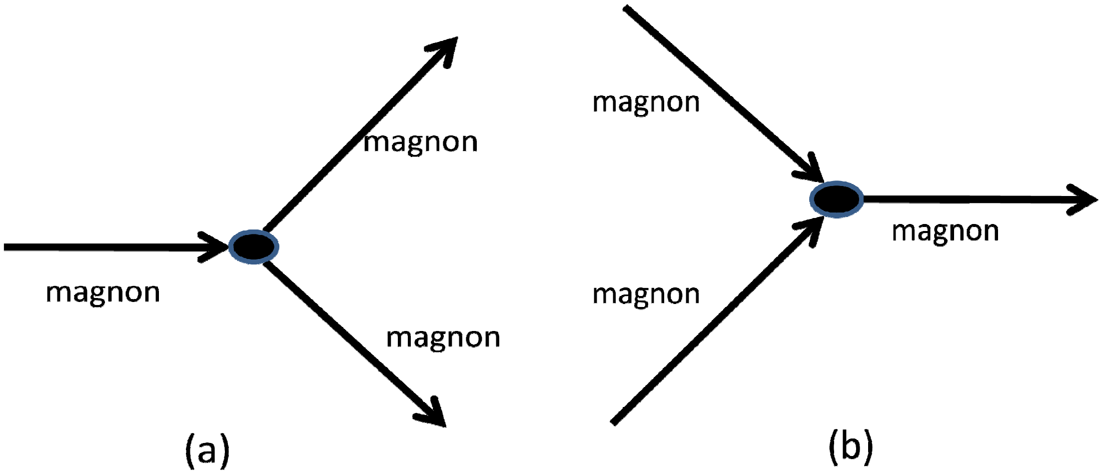

Figure 2.6 Three magnon a) splitting and b) confluence processes

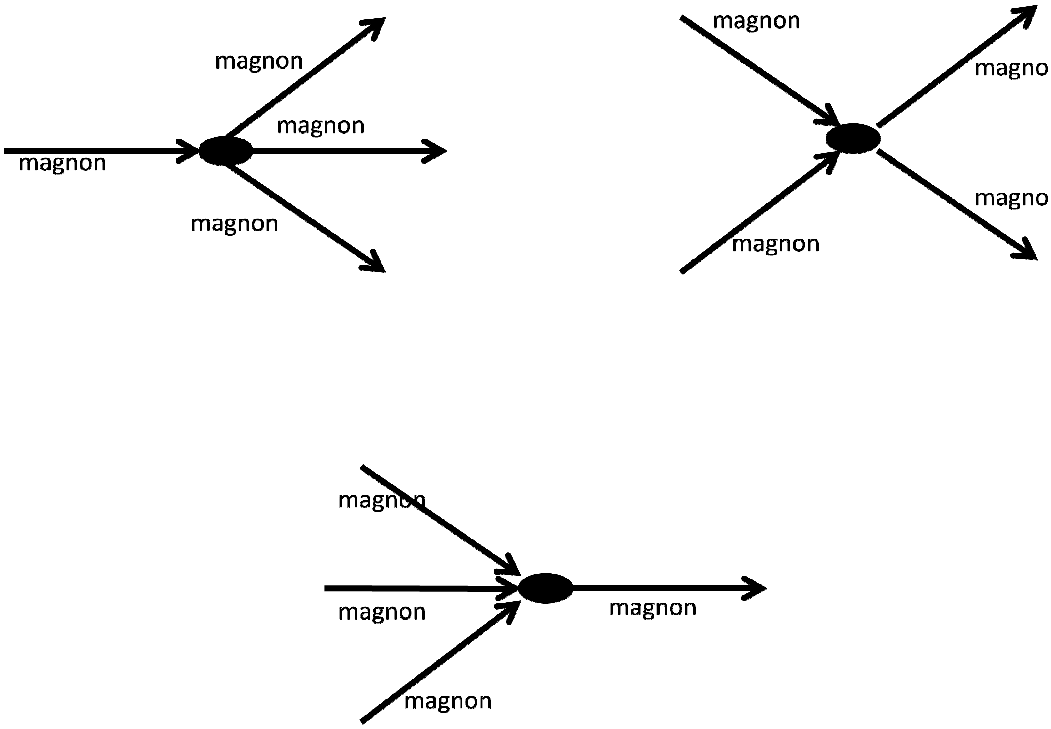

Figure 2.7 Four magnon processes

[9-11]. The processes are illustrated in Figure (2.6). The terms having four orders in magnons variables gives the different kinds of four magnon processes as shown in Figure (2.7) [12,13].

If a particular mode of magnon is enhanced above the thermal level, the different interaction processes lead to a state of thermal equilibrium.

2.7. Superconductivity

The phenomenon of superconductivity continues to be an important area of solid state physics with continuing surprises. It has been observed that some substances show zero dc resistance when cooled down a critical temperature. This phenomenon, discovered by H. Kamerlingh Onnes in 1911, is known as superconductivity [15]. In some metals, the superconducting state occurs due to the presence of a very small fraction of abnormal electrons, while the other free electrons remain absolutely normal. The correlated behaviour of the small fraction of the abnormal electrons dominates over the large fraction of the normal electrons. The presence of these abnormal electrons is responsible for a metal to become a superconductor which cannot resist a small-magnitude electrical dc current.

Nonetheless, the superconductivity being a state of matters is not a property of isolated atoms, but is a collective effect determined by the structure of the sample. The superconducting state is a quantum mechanical state that occurs on a macroscopic scale and makes a connection between the microworld and the macroworld. This connection allows us to study the physics of the microworld directly and has attracted the attention of so many scientists. Between 1911 and 1957, so many scientists have tried to describe such mysterious state of maters caused by only about 0.01 % of conduction electrons.

In 1933, W. Meissner and R. Ochsenfeld discovered a important property of superconductors that the superconductors are perfect diamagnet [15]. They found that when the sample is cooled below its critical temperature of superconductivity in a weak external magnetic field, the magnetic flux is expelled out of the sample. This makes the net magnetic field zero inside a metal when it becomes superconducting. This phenomenon is known as the Meissner effect.

To explain the phenomenon of superconductivity, Dutch physicists C. J. Gorter and H. B. G. Casimir introduced in 1934 the two-fluid model to describe phenomenon of superconductivity[16]. According to them, in the superconducting state, there are two types of the conduction electrons termed as normal and superconducting electrons. The properties of normal electrons are similar to those of the electrons in a normal metal, and the superconducting electrons are responsible for the anomalous properties. In the superconducting state, these two components of electrons coexist as interpenetrating liquids. The two-fluid model was found to be a useful concept for analysis of the different properties of superconductors. The brothers F. London and H. London together provided two equations to describe the microscopic electric and magnetic fields [17]. These two equations describe well the anomalous diamagnetic property of the superconductors in a weak external field. In the framework of the two-fluid model, the London equations and the Maxwell equations describe the behaviour of the superconducting electrons. The London equations provided an expression for the first characteristic length of superconductivity which is known as the London penetration depth λ_L.

On the other hand, L. V. Shubnikov and coworkers in 1937, observed an unusual property of some superconductors in external magnetic fields. They found that there may exist two critical magnetic fields for some superconductors which are termed as type-II superconductors. The state of superconductors between two critical field is known as the mixed state or the Shubnikov phase [18].

Fröhlich proposed that there may exist a relation between superconductivity and vibration atoms of the material[19]. According to Fröhlich, such relation may be established by discovering an isotope effect in superconductors. Following this scheme, E. Maxwell indeed discovered the isotope effect and confirmed the proposal of Fröhlich[20]. The study on different superconducting isotopes of mercury established that the critical temperature Tc depends on the isotope mass M given by the relation $T_c M^{1/2}$= constant. The discovery of isotope effect played a crucial role in finding the accurate theory of superconductivity.

V. Ginzburg and L. Landau put forwarded a phenomenological theory of superconductivity in 1950 [21]. The theory involves the general theory of the second-order phase transition that was developed by L. Landau. The equations derived from the theory was confirmed on the basis of the microscopic theory. The Ginzburg-Landau theory played an crucial role in describing the superconducting state. This theory describes well the behaviour of superconductors in strong magnetic fields. The Ginzburg-Landau theory gives the expression for the penetration depth as which is same as derived from the London equations.

Moreover, the theory also provides an expression for the second characteristic length ξ_{GL}, which is known as the coherence length. Using the Ginzburg-Landau theory, A. A. Abrikosov theoretically confirmed the existence of vortix state and explained the result of Shubnikov's experiments [22]. In 1956, Leon Cooper established that two conduction electrons can form a stable paired state due to the electron phonon interaction. This was a breakthrough which leads to formulation of the accurate theory of superconductivity. This paired state is now known as the Cooper pair. The comprehensive microscopic theory of superconductivity in metals was formulated by J. Bardeen, L. Cooper and R. Schrieffer in 1957, which is known as the BCS theory [23]. According to the BCS theory, a weak electron-phonon interaction can lead to the existence of an attractive potential between two electrons. The superconducting state occurs when this attractive interaction dominates over the coulomb repulsive interaction. The electrons may form Cooper pairs due to the overall attractive force.

2.8. BCS theory of Superconductivity

The indirect interaction between electrons *via* phonon may be attractive in certain cases. When an electron interacts with the crystal and it deforms the crystal. Another electron finds the deformed crystal and adjusts itself to take advantage of the deformation to lower its energy. In the BCS theory, it is assumed that the formation of Cooper pairs may occur when the indirect attractive interaction between electrons dominates over the repulsive Coulomb force. An attractive indirect interaction between electrons *via* phonon can lead to a ground state separated by an energy gap. The critical field, the thermal properties, and the electromagnetic properties of the superconductors depends on the energy gap. A Cooper pair is a weak electron-electron bound pair mediated by a phonon interaction.

The model Hamiltonian is taken to be of the form

$$\hat{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}\boldsymbol{\sigma}} + \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \, . \tag{2.23}$$

The first term is the sum of the kinetic energies of the electrons where $c^{\dagger}_{\boldsymbol{k}'\sigma}$ and $c_{\boldsymbol{k}'\sigma}$ are the electron creation and annihilation operators of wave vector ***k*** and spin σ. The second term is the phonon mediated electron-electron interaction translated into the suitable form. Writing $b_k = \langle c_{-k\downarrow} c_{k\uparrow} \rangle_{avg}$, the Hamiltonian can be written as

$$\hat{H} = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{kl} V_{kl} (c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} b_l + b^{\dagger}_k c_{-l\downarrow} c_{l\uparrow}) . \tag{2.24}$$

To obtain the solution of the above equation the following function, known as gap function, has been introduced,

$$\Delta_k = -\sum_{l} V_{kl} b_l = -\sum_{l} V_{kl} \langle c_{-l\uparrow} c_{l\downarrow} \rangle . \tag{2.25}$$

In terms of the gap function, the model Hamiltonian becomes

$$\hat{H} = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k'\sigma} c_{k\sigma} + \sum_{kl} V(\Delta_k \, c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} + \Delta^{\dagger}_k \, c_{-l\downarrow} c_{l\uparrow} - \Delta_k \, b^{\dagger}_k) . \tag{2.26}$$

This Hamiltonian can be diagonalized using Bogoliubov transformation given by,

$$\left. \begin{aligned} c_{k\uparrow} &= u^{\dagger}_k \gamma_{k0} + v_k \gamma^{\dagger}_{k1} \\ c^{\dagger}_{-k\downarrow} &= -v^{\dagger}_k \gamma_{k0} + u_k \gamma^{\dagger}_{k1} \end{aligned} \right\} , \tag{2.27}$$

where u_k and v_k satisfy the relation $|u_k|^2 + |v_k|^2 = 1$, with γ_{k0} and γ_{k1} are new Fermi operators. Substituting these new operators into the model Hamiltonian one obtains the diagonalized form of the Hamiltonian as given below

$$\hat{H} = \sum_{k} \left(\varepsilon_k - E_k + \Delta_k \, b_k \right) + \sum_{k} E_k \left(\gamma^{\dagger}_{k0} \gamma_{k0} + \gamma^{\dagger}_{k1} \gamma_{k1} \right) , \tag{2.28}$$

under the choice $|v_k|^2 = 1 - |u_k|^2 = \frac{1}{2}\left(1 - \frac{\varepsilon_k}{E_k} \right)$, with $E_k = \left(\varepsilon_k^2 + |\Delta_k|^2 \right)^{1/2}$. In the above Hamiltonian the first term is a constant, which differs from the corresponding sum for the normal state at *T=0* by exactly the condensation energy. The second sum gives the increase in energy above the ground state in terms of numbers operators $\gamma_{k0}^{\dagger}\gamma_{k0}$ and $\gamma_{k1}^{\dagger}\gamma_{k1}$. These Fermi operators γ_k describe the elementary quasiparticle excitations of the system having energies E_k. Now, the gap function can be written as

$$\Delta_k = -\sum_l V_{kl}\left\langle c_{-l\uparrow}c_{l\downarrow}\right\rangle = -\sum_l V_{kl}u_l^{\dagger}v_l\left(1-\gamma_{l0}^{\dagger}\gamma_{l0}-\gamma_{l1}^{\dagger}\gamma_{l1}\right). \tag{2.29}$$

Using Fermi Dirac statistics, the above function can be written as

$$\Delta_k = -\sum_l V_{kl}u_l^{\dagger}v_l\left(1-2f\left(E_l\right)\right) = -\sum_l V_{kl}\frac{\Delta_l}{2E_l}\tanh\frac{\beta E_l}{2} \quad , \tag{2.30}$$

where $f\left(E_l\right)=\left(e^{\beta E_l}+1\right)^{-1}$, with $\beta = 1/k_B T$. Making use of approximation $V_{kl}=-V$ within a very narrow range of electronic energy and consequently writing $\Delta_k=\Delta_l=\Delta$, one can write the following relation

$$\frac{1}{V}=\frac{1}{2}\sum_k\frac{\tanh\left(\beta E_k/2\right)}{E_k}. \tag{2.31}$$

After changing the sum to an integral, using the symmetry of $\left|\varepsilon_k\right|$ about the Fermi level, one can obtain the condition as

$$\frac{1}{N(0)V}=\int_0^{\beta_C\hbar\omega_C/2}\frac{\tanh x}{x}dx\,, \tag{2.32}$$

where $N(0)$ is the density of states of electrons with spin of one kind. Evaluating the integral, one can find the following expression for the critical temperature of superconductivity as

$$k_B T_C = 1.14\hbar\omega_C e^{-1/\lambda}\,, \tag{2.33}$$

with $\lambda = N(0)V$ is called coupling constant and ω_C is the Debye cut off frequency of magnons. If one takes the repulsive coulomb interactions between electrons the above expression transformed to

$$k_B T_C = 1.14\hbar\omega_C e^{-1/(\lambda-\mu)}, \tag{2.34}$$

where the μ is an empirical parameter introduced to account for the coulomb interaction between electrons. If the coupling constant becomes large then effect of mass renormalization should be taken into account which modifies the expression as

$$k_B T_C = 1.14\hbar\omega_C e^{-(1+\lambda)/(\lambda-\mu)}. \tag{2.35}$$

The above equation determines the critical temperature of superconductivity in metals. This equation computed correctly the critical temperature of the superconductors discovered then.

2.9. Density functional theory

It is well-known that the physical and chemical properties of matters can be recognized from electronic structure calculations through density functional theory. With the introduction of band theory and numerical analysis, the density functional theory (DFT) has become widespread application in material science in the modern era.

The quantum mechanical wave function contains all the information about a given system. For the simplest case of a hydrogen atom, one can solve exactly the Schrödinger equation to get the wave function of the system and then the allowed states of energies of the system can be determined. But, it is not possible to solve exactly the Schrödinger equation for a many body system. As a consequence, one must involve in some approximations to simplify the problem to a form that is easily solvable. First of all, the Born-Oppenheimer approximation reduces the number of degrees of freedom of the system as far as possible [24]. Due to their large masses, the nuclei move much slower than the electrons and hence, one can consider the electrons as moving in the field of fixed nuclei. In Born-Oppenheimer approximation, the nuclear kinetic energy is neglected and their potential energy is taken as a constant. Thus, the effective Hamiltonian of the electronic system is transformed to the form given below

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{M}\frac{1}{r_{ij}} = T + V_{Ne} + V_{ee}\,. \tag{2.36}$$

In the above, the first term is the total kinetic energy of electrons, the second term is the sum of coulomb potential energies between nuclei and electrons and the third one is the sum of coulomb potential energies between electrons. The Hamiltonian operator consists of operators that involve on the coordinates of one or two electrons only. To compute the total energy of the system one may not need to know the 3N dimensional wave function. The energy states of a system may be determined from the information of the two-particle probability density, *i.e.*, the probability of finding simultaneously an electron at $\mathbf{r}_1$ and an electron at $\mathbf{r}_2$.

DFT is the most common electronic structure method of today which was first developed by Hohenberg & Kohn and Kohn & Sham [25,26]. A functional is a function of a function. In DFT, the functional is the electron density which is a function of space and time. In DFT, the electron density is taken as the fundamental property, unlike Hartree-Fock theory which deals directly with the many-body wave function. The electron density is defined as the following integral over the spin coordinates and the spatial coordinates $\boldsymbol{x} \equiv \boldsymbol{r}, \boldsymbol{s}$ except one spatial coordinates

$$\rho(r) = N\int \ldots\ldots\int |\psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots\boldsymbol{x}_N)|^2 ds_1 d\boldsymbol{x}_2 \ldots\ldots d\boldsymbol{x}_N\,, \tag{2.37}$$

The density $\rho(\boldsymbol{r})$ determine probability of finding any of the *N* electrons within the volume element. Hohenburg and Kohn introduced the two important theorems [25]. The first theorem states that the electron density determines the external potential. Consequently, it follows that the electron density uniquely determines the Hamiltonian operator. Thus, for a given the charge density, the Hamiltonian operator and wave functions may be uniquely determined that describe all the properties of the material.

The second theorem is the variational principle which states that for any positive definite trial density ρ_t such that $\int \rho_t d\boldsymbol{r} = N$, the condition $E[\rho_t] \geq E_0$ is satisfied, with E_0 being the ground state energy.

From the Hamiltonian given in Equation (2.36), one can find that the energy functional comprise of three terms namely the kinetic energy, the interaction with the external potential and the electron-electron interaction and so one may write the functional as

$$E(\rho) = T(\rho) + V_{ext}(\rho) + V_{ee}(\rho). \tag{2.38}$$

The interaction with the external potential is given by following expression

$$V(\rho) = \int \hat{V}\rho(r)dr. \tag{2.39}$$

The kinetic and electron-electron interaction functionals are unknown. If one can approximate these functional then direct minimization of the energy may be possible. To approximate the kinetic and electron-electron interaction functional, Kohn and Sham[26] introduced a fictitious system of N non interacting electrons to be described by a single determinant wave function in N orbitals ϕ_i. In such a system the kinetic energy and electron density are known exactly from the orbitals as follows

$$T = -\frac{1}{2}\sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle. \tag{2.40}$$

Here the suffix implies that this is not the true kinetic energy but is that of a system of non-interacting electrons, which reproduce the true ground state density given by

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} \varphi_i^2. \tag{2.41}$$

The major component of the electron-electron interaction is potential energy due to the classical Coulomb interaction, known as Hartree energy, and is given by,

$$V_H(\rho) = \frac{1}{2}\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \,. \qquad (2.42)$$

The energy functional may be reorganized as follows

$$E(\rho) = T(\rho) + V_{ext}(\rho) + V_H(\rho) + E_{XC}(\rho), \qquad (2.43)$$

where the exchange-correlation functional is introduced which is given by,

$$E_{XC}(\rho) = [T(\rho) - T_S(\rho)] + [V_{ee}(\rho) - V_H(\rho)] \,. \qquad (2.44)$$

In the above, $E_{XC}(\rho)$ is simply the sum of the error made in using a non-interacting kinetic energy and the error made in treating the electron-electron interaction classically. Writing the functional explicitly in terms of the density built from noninteracting orbitals and applying the variational theorem one can find the orbitals, which minimise the energy.

2.9.1. The local density approximation (LDA)

The local density approximation (LDA) is the basis of all approximation to compute the exchange-correlation functionals. In this approximation $\varepsilon_{XC}(\boldsymbol{r})$ is taken as the exchange and correlation energy density of the uniform electron gas. Thus in this approximation, $\varepsilon_{XC}(\boldsymbol{r})$ is a function of only the local value of the density.

$$E_{XC}^{LDA} = \int \rho(r)\varepsilon_{XC}(\rho(r))dr \,. \qquad (2.45)$$

In the above, ε_{XC} is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(\boldsymbol{r})$. The quantity can be further divided into exchange and correlation contributions as follows

$$\varepsilon_{XC}(\rho(\boldsymbol{r})) = \varepsilon_X(\rho(\boldsymbol{r})) + \varepsilon_C(\rho(\boldsymbol{r})) \,. \qquad (2.46)$$

The first part represents the exchange energy of an electron in a uniform electron gas of a particular density. Bloch and Dirac derived the expression for the exchange part as given by the following expression

$$\varepsilon_X = -\frac{3}{4}\left(\frac{3\rho(\boldsymbol{r})}{\pi}\right)^{1/3} . \tag{2.47}$$

In the case of correlation part, no such explicit expression is found. However, numerical quantum Monte-Carlo simulations of the homogeneous electron gas with high level of accuracy are available

2.9.2. The generalized gradient approximation (GGA)

The generalized gradient approximation (GGA) is the logical step to improve LDA. In this approximation, beside the density $\rho(\boldsymbol{r})$ at a particular point ***r,*** the gradient of the charge density ($\rho(\boldsymbol{r})$) is also taken into account for the non-homogeneity of the true electron density. Thus, one can write the exchange-correlation energy in the following form

$$E_{XC}^{GGA} = \int \rho(\boldsymbol{r})\varepsilon_{XC}(\rho,\nabla\rho)d\boldsymbol{r} . \tag{2.48}$$

The GGA describes the binding energy of molecules significantly better than the LDA which lead to the very wide spread acceptance of DFT in the chemistry community. A number of functionals within the GGA family have been developed.

In the thesis, these methodologies are used to compute the parameters of the substances to understand the theory of unconventional superconductivity.