1 Magnetism

Magnetism in matter is a purely quantum phenomenon, arising from the interaction of electrons of atoms with other electrons or with external fields. Here, origins of magnetic interactions between electrons, and phenomenological types of magnetic behaviour will be discussed. We start by quick overview of neccessary knowledge.

1.1 Overview - Magnetic Field In Materials

Magnetic field induction $\vec{B}$ inside materials induces magnetisation $\vec{M}$ of the material, which corresponds to the magnetic dipole density. These are connected by

$$\vec{B} = \mu_0(\vec{M} + \vec{H}) \tag{1}$$

where $\mu_0 = 4\pi \times 10^{-7}$ H m^{-1} is the permeability of vacuum and $\vec{H}$ is the magnetic field strength imposed on the material (same as in vacuum surrounding the material). Specifically, in linear materials, we usually write constitutive relation

$$\vec{M} = \chi\vec{H} \tag{2}$$

where χ is the susceptibility of the material, and has no units. Depending on the phenomenology of the magnetic behaviour, χ can have vastly different values.

It follows from (1)-(2) that $\vec{B}$ inside the material can be expressed in terms of $\vec{B}_0$ outside the material as

$$\vec{B} = \mu_0(1 + \chi)\vec{H} = (1 + \chi)\vec{B}_0$$

where we used that in vacuum, $\vec{M} = \vec{0}$, and so

$$\vec{B}_0 = \mu_0\vec{H}$$

Usually, we write

$$\mu_r = 1 + \chi \tag{3}$$

as the relative permeability of the material.

1.2 Overview - Magnetic Phenomenologies

1.2.1 Diamagnetism

Diamagnetism occurs when no other magnetic order is present in the material. It arises as a reaction of individual, non-interacting atoms to the external magnetic field. For it to occur, the electron shell of the atoms must have no net magnetic moment due to unpaired electrons.

The susceptbility for diamagnetism is negative and small compared to 1, causing the magnetic field to be reduced slighlty in the material.

1.2.2 Paramagnetism

Paramagnetism occurs when the isolated itoms interact with the external field (as in diamagnetism), but the atomic shells have a net magnetic moment. This can occur due to mechanism of electron filling, which follows Hund's rules, which are now listed

1. First, try to fill the orbitals with electrons or electron pairs in the shell so that the spin of the shell is maximized.

2. After maximizing the spin, decide on which orbitals are occupied by electron or electron pairs so that the orbital angular momentum of the shell is maximized.

3. Determine the overall ground state angular momentum J of the shell, which is

   (a) $J = |L + S|$ for more than $\frac{1}{2}$ of the shell filled
   (b) $J = |L - S|$ for less than $\frac{1}{2}$ of the shell filled

if there are unpaired electrons left after the electron filling, the compound can be paramagnetic.
The susceptibility for paramagnets follows the Curie law

$$\chi = \frac{C}{T} \tag{4}$$

where C is a constant with temperature. This arises as the competition between the alignment of the atomic magnetic moments and the randomness of the finite temperature of the system.
Special case is for metalic paramagnetism, where the susceptibility is temperature independent. Susceptibilities for paramagnets are usually small and positive.
Curiosly, paramagnetism can sometimes occur even when we suspect that the shells of the atoms should have no unpaired electrons. This can arise from the interaction with crystal field of the compound, which causes orbital splitting and changes the quantum numers of the system. Then, the electrons fill the new orbitals differently, and can remain unpaired.

1.2.3 Ferromagnetism

Ferromagnetism occurs when the field produced by the alignment of the atoms can influence other atoms even in the absence of external field. The susceptibilities for ferromagnets are enormous, and the susceptibility as a concept stops being properly meaningful in many ferromagnets, as there is non-zero magnetisation in absence of the external field.

1.2.4 Anti-ferromagnetism

Anti-ferromagnetism is a peculiar ordering of the atoms, in which the neighbouring magnetic moments are anti-aligned with each other. The susceptibilities are positive, and there is zero magnetisation in the absence of external field.

1.3 Classical Magnetic Dipole Mechanics

Magnetic dipole moment $\vec{m}u$ is usually described as a current I running in a loop. Its magnitude is determined by integration over the loop area

$$\vec{\mu} = \iint_S I d\vec{S}$$

where $d\vec{S}$ is the oriented area element (oriented by the right hand rule with respect to the current direction). In this image, the current carriers also have a certain angular momentum. We relate the angular momentum to the magnetic momentum via the gyromagnetic ratio γ

$$\vec{\mu} = \gamma \vec{L}$$

where $\vec{L}$ is the angular momentum. For atoms, the magnetic moments are usually of the order of Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_E} = 9.274 \times 10^{-24} \text{ A m}^{-2} \tag{5}$$

Consider now such magnetic dipole placed in a $\vec{B}$ field at an angle θ to the field. The Lorentz force acting on the element of current $d\vec{I} = Id\vec{l}$, where $d\vec{l}$ is the step along the loop, is

$$d\vec{F} = Id\vec{l} \times \vec{B}$$

Let $\vec{l}$ be the vector from the centre of the loop to the edge. The element of torque on the loop is

$$d\vec{\tau} = \vec{l} \times d\vec{F} = I\vec{l} \times (d\vec{l} \times \vec{B}) = I(\vec{l} \cdot \vec{B}) - (\vec{l} \cdot d\vec{l})\vec{B}$$

For simplicity, consider an circular loop lying in the xy plane. Introducing cylindrical polar coordinates as

$$\vec{l} = r\hat{e}_r$$
$$d\vec{l} = r\hat{e}_\phi$$

Leads to

$$d\vec{\tau} = r^2 I(\vec{B} \cdot \hat{e}_r)\hat{e}_\phi$$

Integrating over the circle

$$\vec{\tau} = \int_0^{2\pi} r^2 I(\vec{B} \cdot \hat{e}_r)\hat{e}_\phi d\phi = Ir^2 \int_0^{2\pi} (B_x \cos\phi + B_y \sin\phi)(-\sin\phi\hat{i} + \cos\phi\hat{j})d\phi$$

where I expressed the unit vectors in terms of cartesian unit vector $\hat{i}$ and $\hat{j}$. Integrals over the sine-cosine cross-terms go to zero, and we are left with

$$\vec{\tau} = Ir^2 \int_0^{2\pi} (B_x \cos^2\phi\hat{j} - B_y \sin^2\phi\hat{i})d\phi = Ir^2 \int_0^{2\pi} \left[B_x \left(\frac{1 + \cos(2\phi)}{2} \right) - B_y \left(\frac{1 - \sin(2\phi)}{2} \right) \right] d\phi$$

Sine and cosine again integrate to zero, and therefore, we have

$$\vec{\tau} = Ir^2 \left(-B_y \pi\hat{i} + B_x \pi\hat{j} \right) = I\vec{S} \times \vec{B}$$

where $\vec{S}$ is the vector pointing in the z direction and with magnitude of the area of the loop πr^2.

Recognizing that the magnetic moment in this setup is $\vec{\mu} = I\vec{S}$, we can write the general result for the torque $\vec{\tau}$ acting on the magnetic moment

$$\vec{\tau} = \vec{\mu} \times \vec{B} \tag{6}$$

Now, we try to determine the energy of this setup. Suppose that we started from the magnetic moment aligned with the $\vec{B}$ field. Then, we rotate it towards angle θ away from the field. First, we should note that the torque $\vec{\tau}$ on the moment and the oriented angle $\vec{\theta}$ from the moment to the $\vec{B}$ vector point in the same direction. Therefore, the work done during this rotation of the magnetic vector is

$$W = \int_0^\theta \vec{\tau} \cdot d\vec{\theta} = \int_0^\theta |\vec{\tau}|d\theta = \int_0^\theta \mu B \sin\theta d\theta = \mu B(1 - \cos\theta)$$

Hence, the energy stored in the system is

$$E = -\mu B \cos\theta = -\vec{\mu} \cdot \vec{B} \tag{7}$$

where the arbitrary constant μB was substracted. Here, μ and B stand for magnitudes of $\vec{\mu}$ and $\vec{B}$ respectively.

1.4   Magnetic Interactions

The magnetic moments of different atoms can influence each other in different ways. Some of these are now described.

1.4.1   Magnetic Dipole Interaction

Magnetic dipole interaction is classical interaction of the two magnetic moments $\vec{\mu}_1$ and $\vec{\mu}_2$, with energy

$$E = \frac{\mu_0}{4\pi r^3} \left(\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r}) \right)$$

where $\hat{r}$ is the unit vector pointing between the moments and r is the distance between the moments. However, this interaction is not strong enough to explain magnetism at room temperatures, which is commonly observed. Quantum mechanisms have to be introduced to explain such behaviour.

1.4.2   Direct Exchange Interaction

More important interaction is the exchange interaction, which summarizes a couple of quantum based interactions. One such interaction is the direct exchange interaction. It can be explained by the tendency of the spins to have opposite/parallel direction to their neighbours. This tendency can occur because the electrons can or cannot (depending on the alignment) cross to the other orbital, depending on the sign.
More formaly, a pair of spins can form together a spin triplet or singlet, based on the addition of angular momentum in quantum mechanics. The electron state on the single atom can then be expressed as the combination of the triplet and singlet states, as these form an orthonormal basis. The energy of these mixed

states then determines the energy of the overall system, which can be written in terms of the Heisenberg hamiltonian

$$\hat{H} = -\sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j \tag{8}$$

where $\hat{S}_i$ is the vector spin operator for spin on site i and J_{ij} determines the energy for exchange between spins on site i and j, anywhere in the crystal.

1.4.3   Indirect Exchange Interaction

Indirect exchange interaction has the same essential mechanism as the direct exchange, but is mediated via other electrons. Example given in lectures is that of two spins connected by paired electrons in an p orbital of oxygen atom, which form the chemical bond. Each of the spins tries to anti-align with the electron on the oxygen, so that it can mix the orbitals with that of the oxygen. This leads to overall preference of anti-alignment of the two spins.

1.4.4   Double exchange

Double exchange interaction arises in systems with different valency on otherwise same atoms. The extra electron on one of such atoms can only propagate to the atoms of other type when specific orientation of other electrons is achieved. In example presented in lectures, the overall effect is the alignment of the electrons common for both atoms.

1.4.5   Anisotropic interaction - Dzyaloshinsky-Moriya interaction

Dzyaloshinsky-Moriya interaction tries to tilt the spins towards each other, and its Hamiltonian for a pair of spins $\hat{S}_1$ and $\hat{S}_2$ can be expressed as

$$\hat{H}_{12} = \vec{D}_{12} \cdot (\hat{S}_1 \times \hat{S}_2)$$

wherer $\vec{D}_{12}$ is a vector of constants and determines a direction from which the spins try to tilt away (in order to minimize energy).

1.4.6   Strong Anisotropy

In some cases, the anisotropy is so strong that the moments are effectively fixed to a certain direction, or two directions. This is introduced into the Hamiltonian by term

$$\hat{H}_i = D \sum_i (\hat{S}_i^k)^2$$

where $\hat{S}_i^k$ is the component k of the spin operator at site i. If $D > 0$, the k direction is unfavourable, and spins are restricted to the remaining two directions. If $D < 0$, the k direction is preffered and there is a single direction of alignment.
The effective Hamiltonian than only involves the effective spins. For $D > 0$ along z direction, it has form

$$H = -\sigma_{ij} J_{ij} (S_i^x S_j^x + S_i^y S_j^y)$$

and for $D < 0$ along z, it has form of the so called Ising Hamiltonian

$$H = -\sigma_{ij} J_{ij} S_i^z S_j^z$$

1.5   Magnetic Measurement Techniques

1.5.1   Magnetic Resonance

A sample placed inside an oscillating field. An external field is imposed on the sample, which causes splitting of the otherwise degenerate levels. The radiation form the oscillating field is then resonantly absorbed at frequencies corresponding to the splitting. The splitting is however also dependent on the local environment of the magnetic moment that is being investigated, and by deviations from predicted values of the splitting in the vacuum, a chemical shift can be determined.

1.5.2 Magnetisation and Susceptibility

Magnetisation is essentially measured by two techniques. Torque measurements try to extract the torque acting on the magnetised sample due to interaction of its magnetic dipole with an external imposed field. Usually, light interferometer is used to differentiate small deformations of a long rod with the sample on the end.

Other possibility is to measure the voltage induced by the moving magnetised sample. Classicaly, the sample has to vibrate at relatively high frequency to measure reasonable voltage amplitude (VSM). Other possibility is to used superconducting Josephson junction for the detection of small changes in the magnetic field (SQUID).

1.5.3 Calorimetry

The calorimetry measurements can be used to search for changes in entropy corresponding to phase transitions in the sample. Usually, the sample on a platform is heated slightly and the temperature relaxation is measured and fitted to determine the heat capacity of the sample.

1.5.4 Neutron Scattering

Neutrons have their own magnetic moment and interact with the magnetic moments in the material. And because they are neutral, they ignore the electronic structure in the material which is not magnetic. Neutron scattering can be both elastic or inelastic. The biggest problem for neutron diffraction is the steady source of neutrons at a specific energy, which is expensive, and so the neutron scattering experiments are only carried out at specialised facilities.

1.5.5 Mössbauer Spectroscopy

Mössbauer spectroscopy measures the shifts in nuclear spin states that are unaccessible by magnetic resonance. To achieve the high energies, an isotopy with gamma ray decay of energy similar to that of the transition that is measured is chosen. The sample is then moved at different velocities relative to the source of the gamma rays. When the Doppler shift matches the chemical shift, the gamma rays are resonantly absorbed, which is detected and thus the chemical shift is determined.

Because of the requirement on the transitions, this type of spectroscopy is restricted to a small number of nuclei, including iron, tin, iodine and few other elements.

1.5.6 Muon Spin Rotation

Muons can be produced at specific energy scale and therefore probe a specific type of magnetic moment interaction. However, a proton collider is usually neccessary to produce them from the decay of pions.

1.6 Paramagnetism

1.6.1 Classical Paramagnetism

Now, we move on to the discussion of magnetic phenomenologies in more detail, starting with a classical paramagnet. In a classical paramagnet, the magnetic moments on different sites have the same magnitude μ and do not interact. They form a simple canonical ensemble in an external magnetic field of magnitude B along certain direction (lets say z direction). The energy of a single paramagnet is given by

$$E = -\mu B \cos\theta = -\mu B z$$

where θ is the angle between the tilted magnetic moment, $\beta = \frac{1}{k_B T}$ and the field and z is the relative amount of μ that is projected onto the z axis.

The partition function can be then found as

$$Z = \frac{1}{N} \int_{-1}^{1} e^{-E(z)\beta} dz$$

where N is a normalization factor. Hence

$$Z = \frac{1}{N} \int_{-1}^{1} e^{\mu B \beta z} dz = \frac{1}{N} \left(\frac{1}{\beta \mu B} \right) \left(e^{\beta \mu B} - e^{-\beta \mu B} \right) = \frac{2}{N} \left(\frac{1}{\beta \mu B} \right) \sinh(\beta \mu B)$$

To find the normalization, we use the normality of the probability distribution $P(z)$ following from the partition function

$$P(z)dz = \frac{e^{\beta\mu Bz}dz}{Z}$$

$$\int_{-1}^{1} P(z)dz = 1 = \frac{1}{Z}\int_{-1}^{1} e^{\beta\mu Bz}dz = \frac{NZ}{Z} = N$$

Therefore, the partition function can be written as

$$Z = \frac{2}{\beta\mu B}\sinh(\beta\mu B) \tag{9}$$

Using the relation to the Helmholtz free energy

$$F = -k_B T \ln Z$$

we can recover the average magnetization in the z direction as

$$<\mu_z> = -\frac{\partial F}{\partial B} = k_B T \frac{1}{Z}\frac{\partial Z}{\partial B} = \frac{\mu B}{2\sinh(\beta\mu B)}\left(-\frac{2}{\beta\mu B^2}\sinh(\beta\mu B) + \frac{2}{\beta\mu B}\cosh(\beta\mu B)\beta\mu\right) =$$

$$= \mu\left(\coth(\beta\mu B) - \frac{1}{\beta\mu B}\right)$$

Defining the Langevin function $L(y) = \coth(y) - \frac{1}{y}$, we then have

$$<\mu_z> = \mu L(\beta\mu B) \tag{10}$$

The magnetization of the whole system is then simply $M = N<\mu_z> = N\mu L(\beta\mu B)$, where N is now the number of paramagnetic moments per unit volume.

Importantly, in the limit of small external field/high temperature (as only the B/T ratio determines the average magnetization of the system), we have $y = \beta\mu B \to 0$, and so

$$L(y) = \coth(y) - \frac{1}{y} = \frac{e^y + e^{-y}}{e^y - e^{-y}} - \frac{1}{y} \approx \frac{1 + y + \frac{y^2}{2} + \frac{y^3}{6} + 1 - y + \frac{y^2}{2} - \frac{y^3}{6}}{1 + y + \frac{y^2}{2} + \frac{y^3}{6} - 1 + y - \frac{y^2}{2} + \frac{y^3}{6}} - \frac{1}{y} =$$

$$= \frac{2 + y^2}{2y + \frac{y^3}{3}} - \frac{1}{y} = \frac{1}{y}\left(\frac{1 + \frac{y^2}{2}}{1 + \frac{y^2}{6}} - 1\right) \approx \frac{1}{y}\left(\left(1 + \frac{y^2}{2}\right)\left(1 - \frac{y^2}{6}\right) - 1\right) = \frac{1}{y}\left(\frac{y^2}{2} - \frac{y^2}{6} - \frac{y^4}{12}\right) \approx \frac{y}{3}$$

and so, the magnetization for small external field is

$$M = N<\mu_z> \approx N\mu\frac{\beta\mu B}{3}$$

and so the magnetic susceptibility can be determined at high temperature as

$$\chi = \frac{M}{H} = \frac{\mu_0 M}{B}$$

$$\chi = \frac{\mu_0 N\mu^2}{3k_B T} \tag{11}$$

this dependence is called the Curie's law (as seen in (4)), and is the important law we will see repeatedly at high temperature behaviour of magnets.

Note that in the expansion of the Langevin function, we have effectively shown that

$$\coth(y) = \frac{1}{y} + \frac{y}{3}$$

for small y.

1.6.2   Quantum Paramagnetism

Now, we quantise the possible magnetic moment positions by quantizing the angular momentum of the particles creating the magnetic moment. Suppose we have spin J particle, which has $2J + 1$ possible momentum states, differentiated by the projection of th angular momentum on the z axis. Using the gyromagnetic ratio, we can express the magnetic moment of the particle as

$$\mu_z = g\mu_B m_J \tag{12}$$

where $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton, g is the $g-$ratio and m_J is the magnetic quantum number, running from $-J$ to $+J$ in increments of 1. The energy of a state is still given by

$$E = -\mu_z B = -g\mu_B B m_J$$

and so the partition function is

$$Z = \sum_{m_J} e^{g\mu_B B\beta m_J} = \sum_{m_J=-J}^{J} e^{g\mu_B B\beta m_J} = e^{-g\mu_B B\beta J} \sum_{m_J=0}^{2J} e^{g\mu_B B\beta m_J}$$

This is a geometric series in powers of $e^{g\mu_B B\beta}$, and hence

$$Z = e^{-g\mu_B B\beta J} \frac{1 - e^{g\mu_B B\beta(2J+1)}}{1 - e^{g\mu_B B\beta}}$$

Hence, the average magnetic moment in the z direction is

$$<\mu_z> = -\frac{\partial F}{\partial B} = \frac{1}{\beta Z}\frac{\partial Z}{\partial B}$$

Here

$$\frac{\partial Z}{\partial B} = (-g\mu_B \beta J)e^{-g\mu_B B\beta J}\frac{1 - e^{g\mu_B B\beta(2J+1)}}{1 - e^{g\mu_B \beta B}} -$$

$$- e^{-g\mu_B B\beta J}\frac{g\mu_B \beta(2J+1)e^{g\mu_B B\beta(2J+1)}}{(1 - e^{g\mu_B B\beta})} + e^{-g\mu_B B\beta J}\frac{(1 - e^{g\mu_B B\beta(2J+1)})}{(1 - e^{g\mu_B B\beta})^2}g\mu_B \beta e^{g\mu_B B\beta}$$

Hence, letting $\alpha = g\mu_B B\beta$

$$<\mu_z> = (-g\mu_B J) - \frac{g\mu_B(2J+1)e^{\alpha(2J+1)}}{1 - e^{\alpha(2J+1)}} + \frac{g\mu_B e^\alpha}{1 - e^\alpha} =$$

$$= g\mu_B \frac{-J(1 - e^{\alpha(2J+1)})(1 - e^\alpha) - (2J+1)e^{\alpha(2J+1)}(1 - e^\alpha) + (1 - e^{\alpha(2J+1)})e^\alpha}{(1 - e^{\alpha(2J+1)})(1 - e^\alpha)} =$$

$$= g\mu_B \frac{-J(1 - e^\alpha - e^{\alpha(2J+1)} + e^{2\alpha(J+1)}) - (2J+1)(e^{\alpha(2J+1)} - e^{2\alpha(J+1)}) + e^\alpha - e^{2\alpha(J+1)}}{(1 - e^{\alpha(2J+1)})(1 - e^\alpha)} =$$

$$= g\mu_B \frac{-J + (J+1)e^\alpha + (J - (2J+1))e^{\alpha(2J+1)} + (2J+1 - J - 1)e^{2\alpha(J+1)}}{(1 - e^{\alpha(2J+1)})(1 - e^\alpha)} =$$

$$= g\mu_B \frac{-J + (J+1)e^\alpha - (J+1)e^{\alpha(2J+1)} + Je^{2\alpha(J+1)}}{(1 - e^{\alpha(2J+1)})(1 - e^\alpha)}$$

Factoring out $e^{\alpha(2J+1)/2}$ from the denominator, we have

$$<\mu_z> = g\mu_B \frac{-Je^{-\alpha(2J+1)/2} + (J+1)e^{-\alpha(2J-1)/2} - (J+1)e^{\alpha(2J+1)/2} + Je^{\alpha(2J+3)/2}}{(e^{-\alpha(2J+1)/2} - e^{\alpha(2J+1)/2})(1 - e^\alpha)} =$$

$$<\mu_z> = \frac{1}{2}g\mu_B \frac{Je^{-\alpha(2J+1)/2} - (J+1)e^{-\alpha(2J-1)/2} + (J+1)e^{\alpha(2J+1)/2} - Je^{\alpha(2J+3)/2}}{\sinh(\alpha(2J+1)/2)(1 - e^\alpha)}$$

Factoring $e^{\alpha/2}$ from the denominator

$$<\mu_z> = \frac{1}{4}g\mu_B \frac{-Je^{-2\alpha(J+1)/2} + (J+1)e^{-\alpha J} - (J+1)e^{\alpha J} + Je^{2\alpha(J+1)/2}}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)} =$$

$$= \frac{1}{4}g\mu_B \frac{-J\left(e^{-\alpha(J+1)} + e^{\alpha J}\right) + J\left(e^{\alpha(J+1)} + e^{-\alpha J}\right) + e^{-\alpha J} - e^{\alpha J}}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)} =$$

$$= \frac{1}{4}g\mu_B \frac{-Je^{-\alpha/2}\left(e^{\alpha(2J+1)/2} + e^{-\alpha(2J+1)/2}\right) + Je^{\alpha/2}\left(e^{\alpha(2J+1)/2} + e^{-\alpha(2J+1)/2}\right) + e^{-\alpha J} - e^{\alpha J}}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)} =$$

$$= \frac{1}{2}g\mu_B \frac{J\cosh(\alpha(2J+1)/2)\left(e^{\alpha/2} - e^{-\alpha/2}\right) - \frac{1}{2}\left(e^{\alpha J} - e^{-\alpha J}\right)}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)} =$$

$$= g\mu_B \frac{J\cosh(\alpha(2J+1)/2)\sinh(\alpha/2) - \frac{1}{2}\sinh(\alpha J)}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)}$$

Here

$$\sinh(\alpha J) = \sinh\left(\alpha(2J+1)/2 - \alpha/2\right) = \sinh(\alpha(2J+1)/2)\cosh(\alpha/2) - \sinh(\alpha/2)\cosh(\alpha(2J+1)/2)$$

Hence

$$< \mu_z > = g\mu_B \frac{\frac{2J+1}{2}\cosh(\alpha(2J+1)/2)\sinh(\alpha/2) - \frac{1}{2}\sinh(\alpha(2J+1)/2)\cosh(\alpha/2)}{\sinh(\alpha(2J+1)/2)\sinh(\alpha/2)} =$$

$$= g\mu_B J \left(\frac{2J+1}{2J}\coth(\alpha(2J+1)/2) - \frac{1}{2J}\coth(\alpha/2)\right)$$

Finally, changing variables to $y = g\mu_B \beta B J = \alpha J$, we can write, for the bulk magnetization

$$M = g\mu_B J N \left(\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}y\right)\right) = g\mu_B J N B_J(y) \tag{13}$$

where N is the paramagnetic moment density, and

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}y\right)$$

is the Brillouin function. The equation (13) gives the magnetization behaviour for quantized magnetic moment at finite temperature. To check the validity of our model, we should verify the correspondence principle. Letting quantum number $J \to \infty$ and setting $g\mu_B J = \mu$ as the magnitude of the magnetic moment (see (12)), we obtain

$$M \approx \mu N \left(\frac{2J}{2J}\coth(\frac{2J}{2J}y) - \frac{1}{2J}(\frac{1}{\frac{y}{2J}})\right) = \mu N \left(\coth(y) - \frac{1}{y}\right) = \mu N L(y)$$

and we recover classical analogue (10), as $y = \mu\beta B$.

Now, consider a high temperature/small field regime for a quantum paramagnet. The Brillouin function can be expanded as (using the expansion for $\coth(y)$ for small y)

$$B_J(y) \approx \frac{2J+1}{2J}\left(\frac{1}{\frac{2J+1}{2J}y} + \frac{2J+1}{6J}y\right) - \frac{1}{2J}\left(\frac{1}{\frac{1}{2J}y} + \frac{1}{6J}y\right) =$$

$$= \frac{(2J+1)^2 - 1}{12J^2}y = \frac{4J^2 + 4J + 1 - 1}{12J^2}y = \frac{J+1}{3J}y$$

Substituting in for y and going back to magnetization, we have

$$M = g\mu_B J N \frac{(J+1)g\mu_B B}{3k_B T}$$

and in terms of magnetic susceptibility

$$\chi = \frac{\mu_0 M}{B} = \frac{\mu_0 \mu_{eff}^2 N}{3k_B T} \tag{14}$$

with $\mu_{eff} = g\mu_B \sqrt{J(J+1)}$ as the effective magnetic moment of the paramagnetic particle. This is the quantum analogue of the Curie law, and it has the exact same form as the classical law.

1.6.3 Adiabatic Demagnetisation

The entropy of a paramagnet changes as the field is introduced or as the temperature is reduced, and again is only dependent on the ration of B/T. Hence, for a fixed B, entropy is a function of T and similarly, for a fixed T, entropy is a function of B. Since at $T \to 0$, entropy approaches 0 as well, we have only one topology of the entropy as a function of T possible, as seen in Fig. 1.
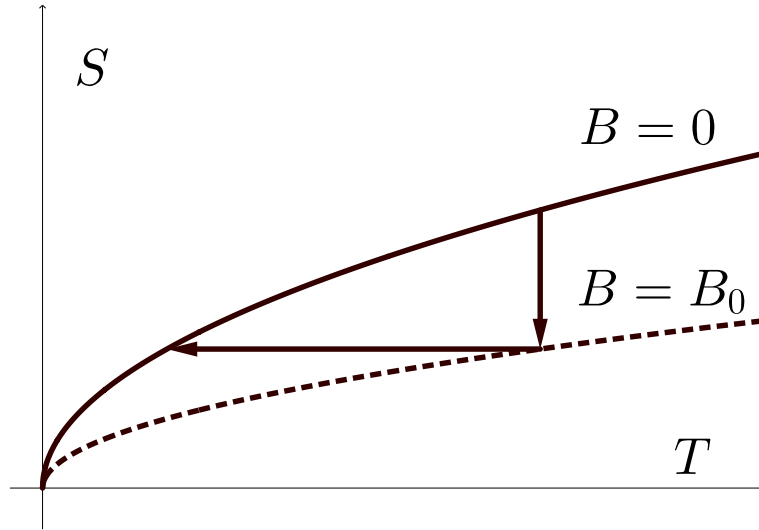

Figure 1: The lines of constant magnetic field induction leave $S = S(T)$. As in non-zero field, the paramagnet has more spins aligned with the field, the entropy as a whole is smaller in non-zero field case. The arrows show the steps taken during adiabatic demagnetisation cooling.

During adiabatic demagnetisation, the field is first slowly introduced to a sample in an isothermal bath. Then, the bath is extracted from the system, leaving the sample isolated. Then, the field is removed, which causes sample demagnetisation. But, since the sample is now isolated, the only way for it to demagnetise is adiabatically, and hence the entropy of the sample is conserved. Then, the temperature of the sample must reduce. This procedure can reduce the temperature of the sample significantly, down to order of mK.

1.7 Ferromagnetism

So far, we have explored paramagnets, which correspond to many body Hamiltonian of form

$$\hat{H} = g\mu_B \sum_i \hat{S}_i \cdot \vec{B}$$

where i indexes the paramagnetic particles. For ferromagnets, the interaction between the different particles takes place in terms of the Heisenberg Hamiltonian, as

$$\hat{H} = -\sum_{i,j} J_{ij}\hat{S}_i \cdot \hat{S}_j + g\mu_B \sum_j \hat{S}_j \cdot \vec{B}$$

where J_{ij} is the exchange constant and the second term is the Zeeman field interaction term, same as for the paramagnet. We can explicitly divide the sum as

$$\hat{H} = -\sum_j \hat{S}_j \cdot \left(\sum_i J_{ij}\hat{S}_i \right) + \sum_j g\mu_B \hat{S}_j \cdot \vec{B} = \sum_j \hat{S}_j \cdot \left(g\mu_B B - \sum_i J_{ij}\hat{S}_i \right) = g\mu_B \sum_j \hat{S}_j \left(\vec{B} + \vec{B}_{mf,j} \right)$$

where we defined the molecular field at site j as

$$\vec{B}_{mf,j} = -\frac{1}{g\mu_B} \sum_i J_{ij}\hat{S}_i$$

Sometimes, different definitions of the exchange constant are used, introducing the factor of 2 to the result for the molecular field. Nevertheless, we have effectively written the paramagnetic Hamiltonian again, but the field is offset by the molecular field.

1.7.1 Mean-Field Approach

Setting $\vec{B}_{mf,j} = \vec{B}_{mf}$ to be independent of the site in the material leads to the mean field approach to ferromagnetism. We usually write that the molecular field is proportional to the mean magnetisation of the sample as

$$\vec{B}_{mf} = \lambda \vec{M} \tag{15}$$

where parameter λ is possitive for ferromagnets.

Then, all results from paramagnetism hold, but the fields are now offset by the molecular fields, i.e. the magnetisation of the sample follows from (13)

$$M = g\mu_B J N B_J(g\mu_B \beta J(B + \lambda M)) \tag{16}$$

This is an equation of self-consistency. Consider the case when no external field is applied, i.e. $B = 0$. Then, we have

$$M = g\mu_B J N B_J(g\mu_B \beta J \lambda M)$$

The only way for this equation to have non-zero solutions is if the slope of $f(M) = g\mu_B J N B_J(g\mu_B \beta J \lambda M)$ as a function of M is bigger than one close to $M = 0$ point. Back in section about paramagnets, we have shown that

$$B_J(y) \approx \frac{J+1}{3J} y$$

for small y, and hence we can write that close to $M = 0$,

$$f(M) = g\mu_B J N \frac{J+1}{3J} g\mu_B \beta J \lambda M = \frac{(g\mu_B \sqrt{J(J+1)})^2 N}{3k_B T} \lambda M = \frac{\mu_{eff}^2 N}{3k_B T} \lambda M$$

Taking the derivative and applying the criterion for M to have a non-zero solution

$$\frac{df}{dM} = \frac{\mu_{eff}^2 N}{3k_B T} \lambda \geq 1$$

Hence, there exists a critical temperature T_C, below which there are always non-zero solutions for M, which statisfies

$$\frac{\mu_{eff}^2 N}{3k_B T_C} \lambda = 1$$

$$T_C = \frac{\mu_{eff}^2 N}{3k_B} \lambda \tag{17}$$

1.7.2 High Temperature Behaviour of Ferromagnets

Above the critical temperature $M = 0$ in the absence of external field. However, the sample can be magnetised by external field. Doing the expansion for high T leads to

$$M \approx g\mu_B J N \frac{J+1}{3J} g\mu_B J \beta(B + \lambda M) = \frac{\mu_{eff}^2 N}{3k_B T}(B + \lambda M) = \frac{\mu_{eff}^2 N}{3k_B T} B + \frac{T_C}{T} M$$

$$M(T - T_C) = \frac{\mu_{eff}^2 N}{3k_B} B$$

$$M = \frac{\mu_{eff}^2 N}{3k_B (T - T_C)} B$$

and in terms of susceptibility

$$\chi = \frac{\mu_0 M}{B} = \frac{\mu_0 \mu_{eff}^2 N}{3k_B (T - T_C)} \tag{18}$$

Note the similarity to the (14), with only difference being the offset in the temperature. This law is called the Curie-Weiss law. From fit of the susceptibility, the critical temperature can be measured, and hence the parameter λ can be determined. An estimate of the resultant molecular field

$$B_{mf} \approx \lambda M_{sat} = \frac{3k_B T_C}{\mu_{eff}^2 N} g\mu_B J N = \frac{3k_B T_C g\mu_B J}{\mu_{eff}^2}$$

For reasonable estimates on all variables and $T_C \approx 1000\,\mathrm{K}$, the molecular field comes out in thousands of Teslas, which is clearly unphysical. This result shows that even though some aspects of the ferromagnetism are explained by the mean field theory, it is mainly just an idealized model of the system.

1.7.3   Landau Theory of Ferromagnetism

In the framework of the Landau theory of phase transitions, magnetisation of the sample can be viewed as the order parameter, while temperature is the control parameter of the system. Then, close to the transition, we write the free energy of the system Φ as

$$\Phi = \Phi_0 + a(T)M^2 + b(T)M^4 \tag{19}$$

where $a(T) = a_0(T - T_C)$, $a_0 > 0$ changes signs once the critical temperature is crossed and $b(T) > 0$. To find the state of the system, we need to find the minimum of the free energy with respect to the order parameter M. The stationary points are at

$$\frac{d\Phi}{dM} = 0$$

$$2a_0(T - T_C)M + 4b(T)M^3 = 0$$

One solution is always at $M = 0$, other are at

$$a_0(T - T_C) + 2b(T)M^2 = 0$$

$$M = \pm\sqrt{\frac{a_0(T_C - T)}{2b(T)}} \tag{20}$$

Importantly, these solutions do not exist for $T > T_C$, and coincide with $M = 0$ at $T = T_C$. Now, we need to decide which of the stationary points are maxima and which are minima. Taking the second derivative

$$\frac{d^2\Phi}{dM^2} = 2a_O(T - T_C) + 12b(T)M^2$$

For stationary point at $M = 0$, $\frac{d^2\Phi}{dM^2} = 2a_0(T - T_C)$, so for $T > T_C$, the point is a minimum, but for $T < T_C$, the point is a local maximum of the free energy. The other two stationary points exist only if $T < T_C$, and for them

$$\frac{d^2\Phi}{dM^2} = 2a_O(T - T_C) + 6a_0(T_C - T) = 4a_O(T_C - T)$$

and for $T < T_C$, these are minima of the free energy. And hence, for $T < T_C$ the system spontaneously chooses a non-zero order parameter M.

From (20), it follows that $M \propto (T_C - T)^{\frac{1}{2}}$ close to the transition temperature T_C. In real systems, we observe more general dependence

$$M \propto (T_C - T)^\beta$$

where γ is called a critical exponent of the transition.
In terms of susceptibility

$$\chi \propto (T - T_C)^{-\gamma}$$

we observe a divergent behaviour as we approach the transiton, with other critical exponent γ.

1.7.4   Domain Walls

In a real magnetised sample, not all parts of the sample share the same direction of magnetisation. Instead, the sample granulates to smaller regions with distinct magnetisation directions, called domains. Domains arise essentially from the fact that the sample has finite volume. Outside of the volume, magnetisation does not exist, but since $\vec{B}$ field must be continuous in normal components across the boundaries, a so called demagnetization field $\vec{H}_d$ is created across the sample. The energy of the demagnetisation field can be expressed as

$$E_d = -\frac{\mu_0}{2}\int_V dV\,\vec{M}\cdot\vec{H}_D \tag{21}$$

where the integration is carried out over the volume of the sample. In a linearised regime, the demagnetisation field can be expressed in terms of the magnetisation of the sample as

$$\vec{H}_D = -N\vec{M}$$

where the minus sign is customary, but useful, as the field usually points in some sense opposite to the magnetisation. The N is called the demagnetisation factor, but generally it is a tensor with trace 1. For long cylindrical rod parallel to the direction of the external field/magnetisation, the influence of the boundary

is negligable and hence the demagnetising factor is 0. For sphere, it is $1/3$ and for flat plane perpendicular to external field, $N = 1$ (most demagnetisation).

The domains usually cause the magnetisation to not be perfectly perpendicular to the boundaries, and therefore reduce the demagnetisation field and the energy cost associated with it.

Now, we will discuss some types of the domain walls, which descibe how the magnetisation changes directions between two domains.

Néel Walls   Néel walls rotate the spins on individual atoms in direction perpendicular to the domain wall plane. Suppose that the energy between two spins can be expressed as $E = -2J\vec{S}_1 \cdot \vec{S}_2$, where $\vec{S}_i$ is the direction of the ith spin. Then, for small angle θ between the spins, the energy is

$$E = -2J|\vec{S}|^2 \cos\theta \approx -2J|\vec{S}|^2 \left(1 - \frac{\theta^2}{2}\right)$$

Hence the price for rotating the spin through angle θ is

$$\Delta E = J|\vec{S}|^2 \theta^2$$

For a domain wall consisting of N spins, the total energy is

$$\Delta E_N = JN|\vec{S}|^2 \theta^2$$

Suppose now that the total angle through which the spins rotate is $\alpha = N\theta$. Then

$$\Delta E = \frac{JN|\vec{S}|^2 \alpha^2}{N^2} = \frac{J|\vec{S}|^2 \alpha^2}{N}$$

This would suggest that it is reasonable to make the domain wall arbitrarily long, but this is not observed. Instead, the magnetic anisotropy introduces another energy that has to be taken into account. Suppose that for spin at angle ϕ to the easy direction the extra energy from deviation from the easy axis is

$$\Delta E_D = D\sin^2\phi$$

Then, if $\phi(i) = \frac{\alpha}{N}i$ is the angle of the ith spin to the easy axis, we have the total energy due to anisotropy

$$\Delta E_{D,N} = \sum_i D\sin^2(\frac{\alpha}{N}i) \approx DL \int_0^\alpha \sin^2(\phi)d\phi$$

where L is the length of the domain wall. Writing $L = Na$ where N is the number of spins in the wall and a is the distance between two spins and assuming that $\alpha = \pi = N\theta$, we can write the total cost of the domain wall (in energy per unit area) as

$$\Delta E_T = \frac{JS^2\pi^2}{Na^2} + \frac{NDa}{2} \tag{22}$$

as the integral evaluates to 2.

The energy per unit area has minimum

$$\frac{\partial \Delta E_T}{\partial N} = -\frac{JS^2\pi^2}{N^2 a^2} + \frac{Da}{2} = 0$$

$$N^2 = \frac{2}{Da}\frac{JS^2\pi^2}{a^2}$$

$$N = \frac{\pi S}{a}\sqrt{\frac{2J}{Da}}$$

Leading to domain wall length

$$L = Na = \pi S\sqrt{\frac{2J}{Da}} \tag{23}$$

which leads to optimal domain wall energy density

$$\sigma = \frac{JS^2\pi^2}{aL} + \frac{LD}{2} = S\pi\sqrt{\frac{JD}{2a}} + S\pi\sqrt{\frac{JD}{2a}} = S\pi\sqrt{\frac{2JD}{a}} \tag{24}$$

Bloch Walls   Bloch walls follow the same equations as Néel walls, but the spins in them rotate in plane parallel to the plane of the wall.

Domains in Fields   In fields, the domains resize and the domain walls move so that the overall magnetisation of the material is achieved. Depending on the material and direction of magnetisation, two extreme behaviours can be extracted. The material can behave like a soft magnet, where the domains resize, but upon cancellation of the external field return to their original shape. On the other hand, hard magnets have domains that reshape and merge upon introduction of the external field, which leads to retention of some overall magnetisation. The fact that the magnetisation is retained is called the hysteresis of the magnet.

1.8   Antiferromagnetism

Antiferromagnetic systems have the same Hamiltonian as ferromagnetic systems, but the exchange constant has opposite sign, and therefore, instead of all spins preffering alignment in one direction, spins prefer to align with opposite directions to each other. If the most important interaction is between neighbouring spins, then a Néel state, when neighbouring spins point in opposite directions, is preffered.

This leads to overall magnetisation of an antiferromagnet to be zero even in the ordered state, and therefore different order parameter has to be used. Typically, the spins are divided into two sub-lattices with twice the length of the unit cell, and the difference in magnetisation of these two sublattices

$$\vec{M}_S = \vec{M}_+ + \vec{M}_-$$

is taken as the order parameter. Magnetisation $\vec{M}_S$ is also called the staggered magnetisation.

The doubling of the unit cell size leads to Bragg peaks in neutron diffraction two reduce twice, and hence the antiferromagnetic transition has a very recognizable signature.

1.8.1   Mean Field Approach

In the mean field, we again express the molecular field, but this time, the molecular field acting on one sublattice is due to spins on the other lattice, i.e.

$$\vec{B}_{mf,+} = -|\lambda|\vec{M}_-$$

$$\vec{B}_{mf,-} = -|\lambda|\vec{M}_+$$

where the minus sign signifies the opposite alignment of the spins.

The magnetisation on either lattice than follows the same law as for ferromagnets

$$M_{\pm} = g\mu_B J \frac{N}{2} B_J(g\mu_B \beta J(B - |\lambda|M_{\mp}))$$

where the density of the spins N is reduced by half as we are taking only one sublattice into account. The overall magnetisation is then

$$M_T = M_+ - M_- = g\mu_B J \frac{N}{2} \left(B_J(g\mu_B \beta J(B - |\lambda|M_-)) - B_J\left(g\mu_B \beta J(B - |\lambda|M_+)\right)\right) \tag{25}$$

Consider now the Néel state in the zero field. For Néel state, $M_+ = -M_-$, and since $B_J(y) = -B_J(-y)$

$$M_T = g\mu_B J \frac{N}{2} \left(B_J(g\mu_B \beta J|\lambda|M_+) - B_J(-g\mu_B \beta J|\lambda|M_+)\right) = g\mu_B J N B_J(g\mu_B \beta J|\lambda|M_+)$$

Again, we can determine the high temperature limit

$$M_T \approx g\mu_B J N \frac{J+1}{3J} g\mu_B \beta J|\lambda|M_+ = \frac{\mu_{eff}^2 N|\lambda|}{3k_B T} M_+$$

Taking $M_T \approx M_+ = M$ in this limit (the $-$ sublattice remains free to move - does not get influenced by small field B), we have the same behaviour as for ferromagnets, where

$$\chi = \frac{\mu_0 \mu_{eff}^2 N}{3k_B(T + T_N)}$$

where T_N is called the Néel temperature

$$T_N = \frac{\mu_{eff}^2 N}{3k_B}|\lambda|$$

But, this rarely matches the experimental observation. The reason behind it is that the next-nearest interaction can shift the Néel temperature quite dramatically. Under next-nearest neighbour interaction which creates molecular field like

$$B_{mf,\pm} = -|\lambda|M_{mp} + \Gamma M_{\pm}$$

the Néel temperature changes as

$$T_N = \frac{\mu_{eff}^2 N}{3k_B}(|\lambda| - \Gamma)$$

Hence, we generally write the Curie-Weiss law as

$$\chi = \frac{C}{T - \theta}$$

where θ can be both positive or negative.

1.8.2 Susceptibility in the Ordered State

Consider now the two sublattices of the antiferromagnet in the ordered state. Suppose that we apply field $\vec{B}$ perpendicular to the directions of magnetisation of the lattices. Then, we can imagine the response of the magnet in the classical limit as rotation of magnetisation of each sublattice by some small amount. Suppose that the interaction between lattices is characterised by energy $U\vec{M}_+ \cdot \vec{M}_-$. Both latices also interact with the external field by term $-\vec{B} \cdot (\vec{M}_+ + \vec{M}_-)$. Hence, for conserved magnetisation magnitude and small rotation of each sublattice by angle ϕ towards $\vec{B}$, the energy of the system can be written as

$$E = U\vec{M}_+ \cdot \vec{M}_- - \vec{B} \cdot (\vec{M}_+ + \vec{M}_-) = -UM^2\cos(2\phi) - 2BM\sin\phi \approx -UM^2 - 2BM\phi + 2UM^2\phi^2$$

The chosen small angle will be such that the energy is minimised, i.e.

$$\frac{\partial E}{\partial \phi} = 0 = -2BM + 4UM^2\phi$$

$$\phi = \frac{B}{2UM}$$

The resultant total magnetisation is therefore

$$M_T = 2M\sin\phi \approx 2M\phi = \frac{B}{U}$$

and therefore the susceptibility can be expressed as

$$\chi_\perp = \frac{\mu_0}{U} \tag{26}$$

and is independent of temperature.
For field applied in the direction parallel to the magnetisation direction, $\chi_\parallel$ is usually dependent on temperature via a power law, i.e. $\chi_\parallel \propto T^a$ where a is some exponent. Overall, it applies that for a powder, the susceptibility is a combination of perpendicular and parallel components in ratio 2:1, respectively.

1.8.3 Spin Flop Transition

In the presence of small magnetic anisotropy, the behaviour in parallel direction can change. At some point, it becomes energetically favourable to reorient the spins so that they can tilt towards the external field, even if they predominantly point perpendicular to the easy direction. We will investigate this.
Let $M_+^\parallel$ and $M_-^\parallel$ be the components of the sublattice magnetisation along the easy axis. The field points along the easy axis of the magnetisation. Then, the energy of the system in parallel configuration is

$$E_\parallel = U\vec{M}_+ \cdot \vec{M}_- - \vec{B} \cdot (\vec{M}_1 + \vec{M}_2) - D((M_+^\parallel)^2 + (M_-^\parallel)^2) = -UM^2 - 2DM^2$$

In perpendicular configuration, the energy is

$$E_\perp = -UM^2\cos(2\phi) - 2BM\sin\phi - 2DM^2\sin^2\phi \approx -UM^2 - 2BM\phi + (2UM^2 - 2DM^2)\phi^2$$

the energy will be minimised in the perpendicular configuration, i.e.

$$\frac{\partial E_\perp}{\partial \phi} = 0 = -2BM + 4(U - D)M^2\phi$$

$$\phi = \frac{B}{2(U - D)M}$$

and therefore

$$E_\perp = -UM^2 - 2\frac{B^2}{2(U - D)} + \frac{B^2}{2(U - D)} = -UM^2 - \frac{B^2}{2(U - D)}$$

At the spin flop transition, these two energies have to be equal

$$E_\parallel = E_\perp$$

$$-UM^2 - 2DM^2 = -UM^2 - \frac{B_{sf}^2}{2(U - D)}$$

$$B_{sf} = 2M\sqrt{D(U - D)} \tag{27}$$

where B_{sf} is the critical spin flop field.

1.9   Alternative Magnetic Orders

Besides ferromagnets and antiferromagnets, many other forms of magnetic order can exist in materials. For example, **ferrimagnets** occur when antiferromagnetic order takes place but the value of moments on the two sublattices are different. As a result, there is a net magnetisation in zero applied field, as long as we are below a certain compensation temperature. Typical example is the structure of Fe_3O_4.

Other known order is the **helical** order, where spins are rotated by some angle θ in the plane perpendicular to the line connecting the spins with $\theta \neq \pi$. Helical order can take place as a optimalization between nearest-neighbour and next-nearest-neighbour interaction. In this sense, it is in the middle between ferromagnets and anti-ferromagnets.

Because the helical order arises from optimalization of energies, the resultant order can be incommensurate, meaning that there is no finite sized unit cell that could describe the whole material (the material lacks periodicity).

Another type is the **spin-density wave** order, where the magnetic moments align with alternating magnitude along certain axis, with no net magnetisation.

1.10   Spin Waves

We will now briefly discuss the excitations in magnetic systems.

1.10.1   Classical Spin Waves

Consider a ferromagnetic chain of spins with nearest-neighbour interaction, so that the Hamiltonian can be expressed as

$$\hat{H} = -2J\sum_{i=0}^{N} \hat{S}_i \cdot \hat{S}_{i+1}$$

Magnetic moment on each site can be expressed as $\vec{\mu}_i = -g\mu_B\hat{S}_i$, and hence the Hamiltonian can be rewritten as

$$\hat{H} = -\sum_i \vec{\mu}_i \cdot \vec{B}_i$$

where $\vec{B}_i = \frac{-2J}{g\mu_B}(\hat{S}_{i-1} + \hat{S}_{i+1})$ is the local field acting on the ith moment. We can then determine the torque acting on the spin as

$$\tau_i = \vec{\mu}_i \times \vec{B}_i$$

Relating torque to the change in angular momentum, which can be related to spin as $\hbar\vec{S}_i$, we obtain vector differential equation (now writing vectors instead of operators)

$$\hbar\frac{d\vec{S}_i}{dt} = 2J(\vec{S}_i \times \vec{S}_{i-1} + \vec{S}_i \times \vec{S}_{i+1})$$

Assuming that the spins have nearly constant term in the z direction $S_i^z = S = const.$, we can write three linearized equations

$$\frac{dS_i^x}{dt} = \frac{2J}{\hbar}\left(S_i^y S - SS_{i-1}^y + S_i^y S - SS_{i+1}^y\right) = \frac{2JS}{\hbar}\left(2S_i^y - S_{i-1}^y - S_{i+1}^y\right)$$

$$\frac{dS_i^y}{dt} = \frac{2J}{\hbar}\left(SS_{i-1}^x - S_i^x S + SS_{i-1}^x - S_i^x S\right) = \frac{2JS}{\hbar}\left(-2S_i^x + S_{i-1}^x + S_{i+1}^x\right)$$

Substituting in a wave-like solution

$$S_i^x = ue^{i(kx_i - \omega t)}$$
$$S_i^y = ve^{i(kx_i - \omega t)}$$

leads to equations

$$-iu\omega e^{i(kx_i - \omega t)} = \frac{2JS}{\hbar}\left(2ve^{i(kx_i - \omega t)} - ve^{i(k(x_i - a) - \omega t)} - ve^{i(k(x_i + a) - \omega t)}\right)$$

$$-iv\omega e^{i(kx_i - \omega t)} = -\frac{2JS}{\hbar}\left(2ue^{i(kx_i - \omega t)} - ue^{i(k(x_i - a) - \omega t)} - ue^{i(k(x_i + a) - \omega t)}\right)$$

Dividing by the common phase, we obtain

$$-iu\omega = \frac{2JS}{\hbar}v\left(2 - (e^{ika} + e^{-ika})\right) = \frac{4JS}{\hbar}v(1 - \cos(ka))$$

$$-iv\omega = -\frac{4JS}{\hbar}u\left(1 - \cos(ka)\right)$$

These equations can be written in matrix form as

$$\begin{pmatrix} i\omega & \frac{4JS}{\hbar}(1 - \cos(ka)) \\ -\frac{4JS}{\hbar}(1 - \cos(ka)) & i\omega \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

In order for this to be a true wave solution, the solution needs to apply independent of the wave amplitudes u and v. This can only be true when the system of equations above does have a non-zero kernel, which implies that the determinant of the matrix must be zero, which gives us a dispersion relation

$$-\omega^2 + \left[\frac{4JS}{\hbar}(1 - \cos(ka))\right]^2 = 0$$

$$\hbar\omega = 4JS(1 - \cos(ka)) \tag{28}$$

For small wavenumbers, the spin wave dispersion is quadratic

$$\hbar\omega \approx 2JSk^2 a^2$$

which is significantly different from phonons, which are linear for small wavenumbers.

1.10.2   Magnons

We quantize spin waves with the dispersion relation (28) by assuming a ladder of energies analogous for simple harmonic oscillator (i.e. free boson spectrum). These boson particles have spin 1 and are called magnons. They follow Bose-Einstain statistics, with occupancy

$$n(\omega) = \frac{1}{e^{\hbar\omega/(k_B T)} - 1}$$

The total number of magnons in the system can be then determined as

$$N = \int_0^\infty g(\omega)n(\omega)d\omega \propto \int_0^\infty \frac{\sqrt{\omega}}{e^{\hbar\omega/(k_B T)} - 1}d\omega = \left(\frac{k_B T}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{x}}{e^x - 1}dx$$

and so

$$N \propto T^{\frac{3}{2}}$$

The more magnons are in the systems, the less ordered the system is, until it reaches disordered state. Suppose that there is some magnon number N_0 at which the transition to disorder occurs. Then, the order parameter is reduced in state with higher temperature by relative value $N(T)/N_0$, and hence the relative order parameter follows $1 - aT^{\frac{3}{2}}$ dependence, where a is some constant. This dependence is observed in nearly ordered states, while for mostly disordered states, the Landau-type critical emergence of the order parameter is observed.

2 Superconductivity

2.1 Introduction to Superconductivity

First, we do an overview of basic properties of superconductors, so that we know what behaviour does a potential theory of superconductivity need to encompass.

The basic property is zero electrical resistance under certain critical temperature. This requires also zero electric field in the bulk of the superconductor, as any field in the bulk is imediately compensated for by charge transfer.

Another property is no magnetic field in the bulk of the superconductor, i.e. the superconductors form ideal diamagnets with magnetic susceptibility of $\chi = -1$.

Besides critical temperature, there is a critical field, above which the superconducting transition does not occur. The transition line between resistive and superconducting state follows

$$B_C(T) = B_C(0)\left(1 - \left(\frac{T}{T_C}\right)^2\right) \tag{29}$$

where T_C is the critical temperature of the superconducting transition at zero field.

There is however another type of superconductors (so called type II superconductors), which do not loose all the superconducting properties when above a critical field - instead, they form a mixed state with vortex lines of superconducting regions, which only vanish above higher second critical field B_{c2}. For both types, the superconductivity completly disappears above T_C. It is the type II superconductors that are the most useful ones, as they retain superconductivity even in high field situations, when most of the measurements can be done.

Because $\vec{B}$ is zero in the bulk of the material, Ampere's law implies that the current density is also zero in the bulk of the material, leaving all the current to be transported by the boundary region of superconductors. The current that is carried by the boundary can then create magnetic field, and if the magnetic field crosses the critical field line, the superconductor can loose its properties again. Hence, there is a corresponding critical current for superconductors.

Finally, from the more general properties, superconductors are poor thermal conductors.

2.1.1 Flux Trapping

Consider now a loop of superconducting wire. The magnetic flux Φ through the centre of the wire is defined as

$$\Phi = \iint_S \vec{B} \cdot d\vec{S}$$

and its time derivative follows

$$\frac{\partial \Phi}{\partial t} = \iint_S \frac{\partial \vec{B}}{\partial t} \cdot d\vec{S} = -\iint_S (\nabla \times \vec{E}) \cdot d\vec{S} = \oint_{\partial S} \vec{E} \cdot d\vec{l} = 0$$

where the last integrand involves only $\vec{E}$ in the bulk of the superconductor, where $\vec{E} = 0$. Hence, if there is a flux going through the middle of the superconducting wire, the flux cannot change its value - it is trapped. This setups a persistent currents which create such flux, and basically never dissipate, due to zero resistance of the superconductor.

2.1.2 Thermodynamics

The Gibbs Free energy for a magnetic system can be expressed as

$$G = -SdT - mdB$$

where m is the magnetic moment of the system in the direction of the field B. For superconductor with magnetisation M,

$$m = MV = \chi HV = -\frac{BV}{\mu_0}$$

where $\chi = -1$ for the ideal diamagnet. Hence, the energy of the superconductor in a finite field at constant temperature is

$$G_S(B) - G_S(0) = \int_0^B -mdB = \int_0^B \frac{BV}{\mu_0}dB = \frac{VB^2}{2\mu_0}$$

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Importantly, this change in energy depends only on the magnetic field applied to the superconductor, and for non-magnetic material it can represent the energy of the phase transition. If we write G_N as the Gibbs free energy of the normal state of the material and G_S as the energy of the superconducting state, than close to the phase transition

$$G_N - G_S = \frac{V B_c^2}{2\mu_0}$$

where B_c is the critical field. Then, we can find the difference in entropies of the two states

$$S_N - S_S = \frac{\partial G_S}{\partial T} - \frac{\partial G_N}{\partial T} = -\frac{\partial}{\partial T}\left(\frac{V B_c^2}{2\mu_0}\right) = -\frac{V B_c}{\mu_0}\frac{\partial B_c}{\partial T}$$

Using $B_C = B_C(0)\left(1 - \left(\frac{T}{T_C}\right)\right)$, we then have

$$S_N - S_S = \frac{V B_C}{\mu_0}B_C(0)\frac{2T}{T_C^2}$$

We can see that the entropy of the normal state is therefore higher than the entropy of the superconducting state, showing that the superconducting state is an ordered state. Furthermore, at zero applied field, the transition occurs exactly at $T = T_C$, where $B_C = 0$, and hence it is a second order phase transition, as in this case, $S_N - S_S = 0$.

Finally, we could determine the thermal capacity difference as

$$C_N - C_S = T\frac{\partial}{\partial T}\left(S_N - S_S\right) = \frac{B_C(0)V}{\mu_0}\left(-B_C(0)\frac{2T}{T_C^2}\frac{2T}{T_C^2} + B_C\frac{2}{T_C^2}\right)$$

which is non-zero even at the transition with zero field, and hence the superconducting transition can be viewed as a second order phase transition.

2.2 London Equations

London equations describe the macroscopic properties of superconductors based on several observations. First, it is assumed that the charge carriers are not electrons. Second, it is assumed that the particles are in a state with zero canonical momentum (i.e. in the ground state).

Canonical momentum for a particle moving in magnetic field follows from the particle Lagrangian

$$L = \frac{1}{2}mv^2 - qV + q\vec{v}\cdot\vec{A}$$

where $\vec{v}$ is the particle velocity, q is the particle charge, V is the scalar potential and $\vec{A}$ is the vector potential. The canonical momentum is given as

$$p_i = \frac{\partial L}{\partial v_i} = mv_i + qA_i$$

$$\vec{p} = m\vec{v} + q\vec{A}$$

Setting the canonical momentum to zero leads to

$$m\vec{v} = -q\vec{A}$$

Hence, the current density can be expressed as

$$\vec{J} = nq\vec{v} = -\frac{n}{m}q^2\vec{A} \tag{30}$$

This expression is called the London equation.

2.2.1 Poisson Equation

Now, from Maxwell equations, we know that $\vec{B} = \nabla \times \vec{A}$ and for zero electric field inside of the superconductor, it also applies that $\nabla \times \vec{B} = \mu_0\vec{J}$. Hence, taking the curl of the London equation leads to

$$\nabla \times \vec{J} = -\frac{n}{m}q^2\nabla \times \vec{A}$$

$$\nabla \times (\nabla \times \vec{B}) = -\frac{\mu_0 nq^2}{m}\vec{B}$$

Here,

$$\nabla \times (\nabla \times \vec{B}) = \nabla(\nabla \cdot \vec{B}) - \nabla^2\vec{B} = \nabla^2\vec{B}$$

and therefore

$$\nabla^2\vec{B} = \frac{\mu_0 nq^2}{m}\vec{B} \tag{31}$$

This is Poisson equation for $\vec{B}$, which is well studied equation with known solutions. Consider now 1D solution to this equation close to a boundary of contant $\vec{B} = B_0\hat{x}$. The 1D formulation of the equation is

$$\frac{d^2 B_x}{dx^2} = \frac{\mu_0 nq^2}{m}B_x$$

$$B_x = Ae^{x/\lambda} + Be^{-x/lambda}$$

where $\lambda = \sqrt{\frac{m}{\mu_0 nq^2}}$. From observations, we know that infinitely far into the bulk from the boundary, the $\vec{B}$ field should go to zero, and hence, we can say the solution has form

$$B_x = B_0 e^{-x/\lambda}$$

and the field exponentially decreases with penetration depth of λ. Hence, we can explain why there is no mangetic field in the material, and also that the current density is concentrated in the boundary region of size $\approx \lambda$. It can infact be shown that the size of the boundary region is also a parameter that changes with the temperature and close to the phase transition, it diverges. This corresponds to the fact that the superconducting charge carrier density n goes to zero at the phase transition.

2.2.2   Flux Quantisation

Consider now taking the current density in terms of the wavefunction

$$\vec{J} = \text{Re}\left(\Psi^* q\vec{v}\Psi\right)$$

where $\vec{v} = \frac{1}{m}\left(\vec{p} - q\vec{A}\right)$ is the velocity, which can be determined from the canonical momentum, for which we know the explicit operator form. Then

$$\vec{J} = \text{Re}\left(\Psi^*\frac{q}{m}\left(-i\hbar\nabla - q\vec{A}\right)\Psi\right)$$

Now, assume that the wavefunction corresponds to free particle wavefunctions, i.e. $\Psi = \Psi_0 e^{i\theta(x)}$, where Ψ_0 is constant. Then

$$\vec{J} = \text{Re}\left(\frac{q}{m}|\Psi_0|^2\left(-i\hbar(i\nabla\theta) - q\vec{A}\right)\right) = \left(\frac{q}{m}|\Psi_0|^2\left(\hbar\nabla\theta - q\vec{A}\right)\right)$$

For the free particles, $|\Psi_0|^2$ corresponds to the particle density n, and hence we can write

$$\vec{J} = \frac{qn}{m}(\hbar\nabla\theta - q\vec{A})$$

Suppose that we now integrate along a closed loop in the bulk of the superconducting material

$$\oint_C \vec{J} \cdot d\vec{s} = \frac{qn}{m}\left(\hbar\oint_C (\nabla\theta) \cdot d\vec{s} - q\oint_C \vec{A} \cdot d\vec{s}\right)$$

In the bulk of the superconductor, $\vec{J} = 0$ in the steady state. Using Stokes' theorem

$$\hbar\oint_C (\nabla\theta) \cdot d\vec{s} = q\iint_S (\nabla \times \vec{A}) \cdot d\vec{S} = q\iint_S \vec{B} \cdot d\vec{S} = q\Phi$$

where Φ is the magnetic flux through the loop. Suppose that θ is not a single valued function, but the wavefunction Ψ is. Then, we require

$$\oint_C (\nabla\theta) \cdot d\vec{s} = 2\pi k$$

where k is an integer. Hence, we can write that the flux enclosed by a loop that is entirely in the bulk of the supreconductor follows

$$\Phi = \frac{\hbar}{q}2\pi k = \frac{h}{q}k \tag{32}$$

and hence it is quantised in increments of $\frac{h}{q}$. Hence, we could determine the superconducting particle charge, if we measure these increments.

2.3   Ginzburg-Landau Theory of Superconductivity

As we talked about the superconducting phase transition as a second order phase transition, it is only natural to incorporate it in the Ginzburg-Landau formalism for phase transitions.

We can take the superconducting wavefunction as the order parameter and temperature of the system as the control parameter, taking $\Psi = \Psi_0(\vec{r})e^{i\theta(\vec{r})}$ for the wavefunction components, with Ψ_0 real. In the bulk of the material, where we can assume free movement of the superconducting carriers, we have $\Psi_0 = const.$ and it makes sense to write the general second-order transition free energy as

$$F = F_0 + a_0(T - T_C)|\Psi|^2 + b_0|\Psi|^4 \tag{33}$$

where a_0 and b_0 are positive constants. The extremum points are located at order parameter values for which

$$\frac{\partial F}{\partial|\Psi|} = 0 = |\Psi|\left(2a_0(T - T_C) + 4b_0|\Psi|^2\right)$$

Hence, we have solutions $|\Psi| = 0$ (unordered solution) and $|\Psi| = \pm\sqrt{\frac{a_0(T_C - T)}{2b_0}}$, but from the nature of absolute value, only the positive root makes sense. Also, the second solution only exist for $T < T_C$. Taking second derivative will let us determine which solutions are maxima and which are minima

$$\frac{\partial^2 F}{\partial|\Psi|^2} = 2a_0(T - T_C) + 12b_0|\Psi|^2$$

Hence, for $|\Psi| = 0$, $\frac{\partial^2 F}{\partial|\Psi|^2} = 2a_0(T - T_C)$, and the point is a minimum for $T > T_C$ and maximum for $T < T_C$. For $|\Psi| = \sqrt{\frac{a_0(T_C - T)}{2b_0}}$, $\frac{\partial^2 F}{\partial|\Psi|^2} = 4a_0(T_C - T)$ and the point is a minimum for $T < T_C$. Hence, the system below the critical temperature chooses the ordered state with order parameter

$$|\Psi| = \sqrt{\frac{a_0(T_C - T)}{2b_0}}$$

Recalling that we can interpret the square of magnitude of the wavefunction as the density of the superconducting particles n, we can write

$$n = |\Psi|^2 = \frac{a_0(T_C - T)}{2b_0}$$

and so the penetration length of the magnetic field into the superconductor is

$$\lambda \propto \frac{1}{\sqrt{n}} \propto \frac{1}{\sqrt{T_C - T}}$$

and we have the divergence with critical exponent of $\frac{1}{2}$.

2.3.1   Behaviour close to the boundary

Close to the boundary of the superconductor, we expect that the superconducting wavefunction is dependent on the position in the medium. Hence, instead of taking average values for the free energy, we need to explicitly integrate over the region of the boundary. Furhtermore, close to the boundary, the magnetic field can be present in the material, and its energy has to be considered, together with the energy of movement of the superconducting particles. Hence, the overall expression for the total free energy can be written as

$$F = \int_V d^3r \left(a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{|i\hbar\nabla - q\vec{A}|^2}{2m}\Psi + \frac{(B(\vec{r}) - B_0)^2}{2\mu_0}\Psi\right) \tag{34}$$

where the $\frac{1}{2}$ factor in front of b occurs so that after integration, we obtain similar expression as (33). Variations in both $\vec{A}$ and Φ lead to two Euler-Lagrange equations for the minimum of the free energy.

$$\frac{\hbar^2}{2m}(-i\nabla + \frac{q}{\hbar}\vec{A})^2\Psi + (a + b|\Psi|^2)\Psi = 0 \tag{35}$$

$$\frac{\nabla \times \vec{B}}{\mu_0} = \vec{J} = \frac{-iq\hbar}{2m}\left(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\right) - \frac{|\Psi|^2q^2}{m}\vec{A} \tag{36}$$

Notice that in the bulk in the absence of field, first equation becomes the equation for the location of minimum of the free energy. Furthermore, in bulk, where Ψ does not depend on the position, the second equation becomes the London equation. Hence, Ginzburg-Landau theory creates a functional that encompasses all macroscopic thermodynamic behaviour of the superconductor.

The solutions of this pair of equations can be characterized into two classes, based on two numbers, λ, which is the penetration depth as seen before, and ξ, which is called the coherence length. In terms of the parameters above, these can be expressed as

$$\lambda = \sqrt{\frac{mb}{\mu_0 q^2 |a|}}$$

$$\xi = \sqrt{\frac{\hbar^2}{2m|a|}}$$

Their ratio then predicts the type of the solution/superconductor.

$$\frac{\lambda}{\xi} = \kappa = \sqrt{\frac{2m^2 b}{\mu_0 \hbar^2 q^2}}$$

For $\kappa < \frac{1}{\sqrt{2}}$, the superconductors are the Type I superconductors, and the boundary regions for them are highly unfavourable. For $\kappa > \frac{1}{\sqrt{2}}$, the Type II superconductors are the solution and boundary regions are not so unfavourable, and hence the superconducting vertex regions can exist in otherwise normal material. For the type II, the second critical field value $B_{c2} = \frac{\Phi_0}{2\pi \xi^2}$, where Φ_0 is the magnetic flux through the material.

Interestingly, the vortices formed in the material repel each other, and so they form a lattice of normal states vortices, which can be observed and from which the values of different parameters can be determined. As seen before, the phase can become a multivalued function depending on the position in the material, and therefore the symmetry broken by this phase transition is the phase invariance. We can also see from (36) that gradients in the phase in the bulk of the material can lead to superconducting current density.

2.4   BCS Theory of Superconductivity

We have discussed macroscopic properties of superconductors, but have not stated a microscopic reasoning behind the occurance of the superconducting state. Indeed, superconductivity has evaded proper understanding for a long time, with first hints about its nature coming from the observation of so called isotope effect.

When the transition temperature was measured for different isotopes of the same element, it was observed that

$$T_C \propto M^{-\alpha}$$

where M is the mass of the isotope, T_C is its transition temperature of superconducting transition and $\alpha \approx \frac{1}{2}$. The suggestion how to explain that the mass of the atoms has significance was to assume that the electronic interaction with phonons has some importance. This lead to the development of the Cooper pair concept.

2.4.1   Cooper Pairs

Cooper pairs are bound pairs of electrons, where the attractive interacion is mediated by the phonons of lattice vibrations. The attraction has potential which is fairly long ranged, and therefore the electrons can be bound at great distances, where the Coulomb repulsion is not so strong. The interaction requires mediation of the force with non-zero momentum transfer, and therefore only the electrons close to the Fermi surface interact. Usually, electrons within $\pm \hbar \omega_D$, where ω_D is the Debye frequency, interact and form Cooper pairs.

Putting this all together, we can express the wavefunction of the Cooper pair as

$$\Psi_C = e^{i\vec{k}_T \cdot \vec{R}} \psi(\vec{r}_1 - \vec{r}_2) \phi(\sigma_1, \sigma_2)$$

where $\vec{k}_T$ is the total wavenumber of the pair, $\vec{R}$ is the position of the midpoint of the pair, $\vec{r}_i$ is the position of the ith electron, σ_i is its spin and ψ and ϕ are the orbital and spin parts of the wavefunction, respectively. Cooper suggested that ψ corresponds to a $L = 0$ (s-state) spherical harmonic, which requires

the spin part ϕ to be anti-symmetric under the electron exchange. The energy of the Cooper pair could then be calculated as

$$E = -2\hbar\omega_D e^{-1/(|g_{eff}|^2 g(E_f))}$$

where g_{eff} is the coupling constant for electron-phonon scattering and $g(E_f)$ is the electron density of states at the Fermi energy E_f. Interestingly, for good metals, which have low g_{eff}, energy of the Cooper pairs is higher than for worse metals, which corresponds to the experimental observation that metals such as gold or platinum do not superconduct.

2.4.2   Coherent States

To make further progress, we introduce the concept of coherent states. Coherent states are eigenstates of the so called annihilation operator $\hat{a}$, which is an operator that removes one quantum of certain particle from the system. Let $|n>$ be a state containing n particles of some kind, and let $\hat{a}$ be the annihilation operator of these particles. Then, annihilation operator is defined to follow these rules

$$\forall n > 0 : \hat{a}|n> = \sqrt{n}|n-1>$$

$$\hat{a}|0> = 0$$

Now, lets write state $|\alpha>$, which will be our coherent state

$$|\alpha> = \sum_{i=0}^{\infty} \frac{\alpha^i}{\sqrt{i!}}|i>$$

acting with annihilation operator on such state leads to

$$\hat{a}|\alpha> = \hat{a}|0> + \sum_{i=1}^{\infty} \frac{\alpha^i}{\sqrt{i!}}\hat{a}|i> = \sum_{i=1}^{\infty} \frac{\alpha^i}{\sqrt{i!}}\sqrt{i}|i-1> = \alpha\sum_{i=1}^{\infty} \frac{\alpha^{i-1}}{\sqrt{(i-1)!}}|i-1>$$

Reindexing the sum, we are left with

$$\hat{a}|\alpha> = \alpha\sum_{i=0}^{\infty} \frac{\alpha^i}{\sqrt{i!}}|i> = \alpha|\alpha> \tag{37}$$

and hence the coherent state satisfies our definition.
Now, as well as an annihilation operator, we can define a creation operator as its Hermitian conjugate $\hat{a}^{\dagger}$, which is defined by properties

$$\hat{a}^{\dagger}|n-1> = \sqrt{n}|n>$$

and so we can write

$$|n> = \frac{1}{\sqrt{n}}\hat{a}^{\dagger}|n-1> = \frac{1}{\sqrt{n(n-1)}}(\hat{a}^{\dagger})^2|n-2> = ... = \frac{1}{\sqrt{n!}}(\hat{a}^{\dagger})^n|0>$$

Therefore, we can define the coherent state as

$$|\alpha> = \sum_{i=0}^{\infty} \frac{\alpha^i}{\sqrt{i!}}|i> = \sum_{i=0}^{\infty} \frac{\alpha^i(\hat{a}^{\dagger})^i}{i!}|0> = e^{\alpha\hat{a}^{\dagger}}|0>$$

where we identified the Taylor series of an exponential.

2.4.3   BCS Wavefunction

The state that is described by the most advanced theory of superconductivity (which is the BCS theory), is a coherent state of Cooper pairs. Lets label a creation operator of Cooper pair with wavenumber k as $\hat{P}_k^{\dagger}$. The BCS state is defined as

$$|\Psi_{BCS}> = c\prod_{\vec{k}} e^{\alpha_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger}}|0>$$

where c is a normalization constant. This can in fact be simplified, if we notice that the pair creation as creation of two electrons, i.e.

$$\hat{P}_{\vec{k}}^{\dagger} = \hat{c}_{\vec{k},\uparrow}^{\dagger}\hat{c}_{-\vec{k},\downarrow}^{\dagger}$$

where the arrows show two possibilities for the spin of the electrons. Hence, from the Pauli exclusion principle,

$$\hat{P}_{\vec{k}}^{\dagger}\hat{P}_{\vec{k}}^{\dagger} = (\hat{c}_{\vec{k},\uparrow}^{\dagger})^2(\hat{c}_{-\vec{k},\downarrow}^{\dagger})^2 = 0$$

as application of two identical fermionic creation operators consecutively leads to impossible state, and hence the state collapses to 0. Therefore, only the first two terms of the exponential remain non-zero, and so we write

$$|\Psi_{BCS}> = c\prod_{\vec{k}}(1 + \alpha_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger})|0> \tag{38}$$

Importantly, even though $\hat{P}_{\vec{k}}^{\dagger}$ has some properties similar to bosonic creation operator, it does not obey the same commutator relations, and therefore the Cooper pairs cannot be viewed as bosons (even though they are often portrayed as such).

Finally, we require the state to be normalized, and therefore

$$< \Psi_{BCS}|\Psi_{BCS}> = 1$$

$$< \Psi_{BCS}|\Psi_{BCS}> = < 0|c^*c\left(\prod_{\vec{k}}(1 + \alpha_{\vec{k}}^*\hat{P}_{\vec{k}})\right)\left(\prod_{\vec{j}}(1 + \alpha_{\vec{j}}\hat{P}_{\vec{j}}^{\dagger})\right)|0> = 1$$

For $\vec{k} \neq \vec{j}$, the creation and anihilation operators of the electrons and hence of the Cooper pairs are commuting, and therefore

$$< \Psi_{BCS}|\Psi_{BCS}> = c^*c < 0|\left(\prod_{\vec{k}}(1 + \alpha_{\vec{k}}^*\hat{P}_{\vec{k}})(1 + \alpha_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger})\right)|0> =$$

$$= c^*c < 0|\prod_{\vec{k}}\left(1 + \alpha_{\vec{k}}^*\hat{P}_{\vec{k}} + \alpha_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger} + |\alpha_{\vec{k}}|^2\hat{P}_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger}\right)|0>$$

Again, we can move the bracket for a specific $\vec{k}$ through the other operators and take it to apply directly to the vacuum state $|0>$

$$(1 + \alpha_{\vec{k}}^*\hat{P}_{\vec{k}} + \alpha_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger} + |\alpha_{\vec{k}}|^2\hat{P}_{\vec{k}}\hat{P}_{\vec{k}}^{\dagger})|0> = |0> + \alpha_{\vec{k}}|1_{\vec{k}}> + |\alpha_{\vec{k}}|^2|0>$$

where $|1_{\vec{k}}>$ represents the state with one Cooper pair with $\vec{k}$. However, no other operator in the product can create/annihilate the state with the same $\vec{k}$, and since $< 0|1_{\vec{k}}> = 0$ by orthonormality, only the vacuum states remain. Therefore

$$< Psi_{BCS}|\Psi_{BCS}> = c^*c < 0|\prod_{\vec{k}}(1 + |\alpha_{\vec{k}}|^2)|0> = c^*c\prod_{\vec{k}}(1 + |\alpha_{\vec{k}}|^2) = 1$$

and so we conclude that

$$|c| = \frac{1}{\sqrt{\prod_{\vec{k}}(1 + |\alpha_{\vec{k}}|^2)}}$$

Therefore, the normalized BCS state can be written as (choosing c to be real)

$$|\Psi_{BCS}> = \frac{1}{\sqrt{\prod_{\vec{k}}(1 + |\alpha_{\vec{k}}|^2)}}\prod_{\vec{j}}(1 + \alpha_{\vec{j}}\hat{P}_{\vec{j}}^{\dagger})|0>$$

We can move the normalization factors from the first product and distribute them to appropriate terms in the second product to obtain

$$|\Psi_{BCS}> = \prod_{\vec{k}}\left(\frac{1}{\sqrt{1 + |\alpha_{\vec{k}}|^2}} + \frac{\alpha_{\vec{k}}}{\sqrt{1 + |\alpha_{\vec{k}}|^2}}\right)|0>$$

Labeling

$$u_{\vec{k}}^* = \frac{1}{\sqrt{1 + |\alpha_{\vec{k}}|^2}}$$

and

$$v_{\vec{k}}^* = \frac{\alpha_{\vec{k}}}{\sqrt{1 + |\alpha_{\vec{k}}|^2}}$$

leaves us with

$$|\Psi_{BCS}> = \prod_{\vec{k}} (u_{\vec{k}}^* + v_{\vec{k}}^* \hat{P}_{\vec{k}}^\dagger)|0> \tag{39}$$

for the normalized BCS state. We should note that here, $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$, and hence we can interpret $|u_{\vec{k}}|^2$ and $|v_{\vec{k}}|^2$ as the probabilities of the Cooper pair state with $\vec{k}$ to be unoccupied/occupied, respectively.

2.4.4   BCS Hamiltonian

The energy of the BCS state is calculated via the BCS Hamiltonian, which has form

$$\hat{H}_{BCS} = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} \hat{c}_{\vec{k},\sigma}^\dagger \hat{c}_{\vec{k},\sigma} - |g_{eff}|^2 \sum_{\vec{j},\vec{j}'} \hat{P}_{\vec{j}}^\dagger \hat{P}_{\vec{j}'} \tag{40}$$

It is not explicitly done here, but by applying this Hamiltonian to the BCS state and minimizing the resultant energy with respect to parameters $u_{\vec{k}}$ and $v_{\vec{k}}$ under the constraint that $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$ leads to following solution for the parameters

$$|u_{\vec{k}}|^2 = \frac{1}{2} \left(1 + \frac{\epsilon_{\vec{k}} - \mu}{E_{\vec{k}}} \right) \tag{41}$$

$$|v_{\vec{k}}|^2 = \frac{1}{2} \left(1 - \frac{\epsilon_{\vec{k}} - \mu}{E_{\vec{k}}} \right) \tag{42}$$

where

$$E_{\vec{k}} = \sqrt{(\epsilon_{\vec{k}} - \mu)^2 + \Delta_{\vec{k}}^2}$$

and

$$\Delta_{\vec{k}} = |g_{eff}|^2 \sum_{\vec{k}} u_{\vec{k}} v_{\vec{k}}^*$$

Here, $\Delta_{\vec{k}}$ can be associated with the band gap that forms during the superconducting transition and that protects the Cooper pairs from disjoining back to free electrons. Furthermore, any other scattering of electrons have to be accompanied by opposite scattering of the other electron in pair (since there is usually not enough energy to destroy the whole pair) and hence the scattering cannot decrease the momentum/energy of the pair overall. This is the reasoning behind zero electrical resistance of the superconductors.

For a BCS theory, we can go further and have some approximate predictions on value of $\Delta_{\vec{k}}$. It turns out that the band gap is k independent and at $T = 0$ has value

$$\Delta \approx 2\hbar\omega_D e^{-1/\lambda}$$

where $\lambda = |g_{eff}^2|g(E_f)$ is the previously mentioned coupling parameter (it approximately takes the value of single Cooper pair, as seen before). For $T \neq 0$, the dependence is more complicated, and comes up from solution of normalization condition

$$1 = \lambda \int_0^{\hbar\omega_D} d\epsilon \frac{1}{\sqrt{\epsilon^2 + \Delta^2}} \tanh\left(\frac{\sqrt{\epsilon^2 + \Delta^2}}{k_B T} \right)$$

For temperature close to the transition temperature T_C, we expect the band-gap to be small. Then, the integral can be approximately solved to give

$$k_B T_C = 1.13\hbar\omega_D e^{-1/\lambda} \tag{43}$$

which gives prediction on the BCS transition temperature.

2.4.5   Evidence For Presence of the Band Gap

There are several experimental observations that support the existence of the band gap. These are now briefly discussed.

Heat Capacity   Close to the transition temperature, the pairs can be destroyed by scattering, and the destruction of the pairs adds to the thermal capacity of the sample by factor $e^{-\Delta/(k_B T)}$. This can be observed directly.

Optical Absorption   Photons with energy lower than twice the band gap energy cannot excite the pairs of electron accross the band gap and hence cannot propagate by absorption and reemission through the material. Therefore, they are almost perfectly reflected from the material. The position of the absorption edge can be measured and the band gap can be measured from it.

Electron Tunneling   The tunneling of electrons under certain applied voltage cannot occur for voltages corresponding to energies lower than the band gap. The tunneling offset again corresponds to the band gap and it can be measured.

2.5   Josephson Junction

One of the most useful superconducting devices is called the Josephson junction. We will now explain briefly what is the principle behind its function and describe the three operation modes - DC and AC and inverse AC.

The Josephson junction consists of two superconducting materials, joined by a layer of insulating (SIS) or non-superconducting (normal, SNS) material. There can be a phase difference between the phases of the wavefunctions in the two superconducting materials

$$\phi = \theta_1 - \theta_2$$

which leads to non-zero value of the tunneling current through the junction. The current from 1 to 2 is proportional to

$$I_1 \propto e^{i\phi}$$

while the opposite current is only proportional to

$$I_2 \propto e^{-i\phi}$$

Hence the total current is proportional to

$$I \propto I_1 - I_2$$

and so we can write

$$I = I_S \sin \phi \tag{44}$$

where I_S is some amplitude of the current.

Next, we can determine the energy the current is transported through, in order to find the voltage the current is transported through. We can determine the energy of the carriers from their wavefunction as

$$\epsilon \Psi = i\hbar \frac{\partial}{\partial t} \Psi = i\hbar \frac{\partial}{\partial t} (\Psi_0 e^{i\theta}) = -\hbar \frac{\partial \theta}{\partial t} \Psi$$

and therefore energy difference between 1 and 2 is

$$\epsilon_1 - \epsilon_2 = -\hbar \frac{\partial (\theta_1 - \theta_2)}{\partial t} = -\hbar \frac{\partial \phi}{\partial t}$$

The energy difference is related to the voltage across the junction by $\epsilon_1 - \epsilon_2 = qV$ where q is the charge of the superconducting charge carriers, in our case the Cooper pairs with $q = -2e$. Therefore

$$V = \frac{\hbar}{2e} \frac{\partial \phi}{\partial t} \tag{45}$$

Now, the phase difference can be influenced by the magnetic field applied to the junction, if the junction is part of a loop of superconducting material. Hence, for the DC effect, when $\frac{\partial \phi}{\partial t} = 0$, there is a current, which periodically increases and decreases with increasing magnetic field applied to the junction.

In the AC effect, constant voltage is applied to the junction. Then, from (45)

$$\phi = \frac{2eV}{\hbar} t + \phi_0$$

Marking $\omega = \frac{2eV}{\hbar}$, we can write

$$I = I_S \sin(\omega t + \phi_0)$$

and hence we have AC current through element with DC voltage applied to it.

In the inverse AC effect, besides a constant voltage, an high frequency oscillating voltage is applied on top of it, so that

$$V = V_0 + V_{rf} \cos(\omega_{rf} t)$$

Hence

$$\phi = \frac{2eV_0}{\hbar} t + \frac{2eV_{rf}}{\hbar \omega_{rf}} \sin(\omega_{rf} t) + \phi_0$$

and so the current through the junction is

$$I = I_S \sin\left(\omega t + \frac{V_{rf}}{V_0} \frac{\omega}{\omega_{rf}} \sin(\omega_r f t) + \phi_0\right) \tag{46}$$

This can be written as series expansion

$$I = I_S \sum_{n=-\infty}^{\infty} (-1)^n J_n \left(\frac{2eV_{rf}}{\hbar \omega_{rf}}\right) \sin\left[(\omega - n\omega_{rf})t + \phi_0\right]$$

where J_n are the Bessel functions. Noticable, whenever $\omega = n\omega_{rf}$, i.e. when

$$V_0 = \frac{\hbar \omega_{rf}}{2e} n$$

the current is purely DC. This causes a peaks in the IV characteristic of the junction, which can be observed and hence the voltage across the junction can be well determined.

2.5.1   Real Josephson Junction

In a real junction, the normal current and capacitance effects have to be taken into effect. Simulating these by a resistor and capacitor connected in parallel to the ideal Josephson junction leads to equation

$$I = I_S \sin\phi + \frac{V}{R} + C\frac{dV}{dt}$$

and in terms of the phase difference

$$I = I_s \sin\phi + \frac{\hbar}{2eR} \frac{d\phi}{dt} + \frac{\hbar C}{2e} \frac{d^2\phi}{dt^2}$$

which can be recast as

$$\frac{\hbar C}{2e} \frac{d^2\phi}{dt^2} = -\frac{\hbar}{2eR} \frac{d\phi}{dt} - \frac{d}{d\phi}\left(-I\phi - I_S \cos\phi\right)$$

which can be viewed as en equation of motion for particle at position ϕ with mass $m = \frac{\hbar C}{2e}$ in potential $u = -I\phi - I_S \cos\phi$ with drag force $-\frac{\hbar}{2eR} \frac{d\phi}{dt}$. There are then 2 cases. In the case when $I_S < I$, the potential is that of downward slope with no stable minima, leading to continuous increase in the value of the phase over time. On the other hand, for $I_S \geq I$, the potential has local minima where the phase stops increasing, and DC Josephson effect is observed.

The Josephson junction can be used to measure magnetic fields to great accuracy, and it is used in the SQUID interferometers, which are the commonly used to analyze small variations in magnetic fields.

2.6   Unconventional Superconductors and Applications

Throughout this module, we were only able to theoretically describe the type I superconductors, which have critical temperatures always below $30 - 40$K. However, most useful type of superconductors are unexplained superconductors such as cuprates with critical temperatures up to 150K, so up to temperatures of liquid nitrogen. Besides cuprates, organic, iron based or heavy fermion based superconductors are also being researched.

From what can be measured, we know that the charge carriers are still electron pairs, the Meissner effect (perfect diamagnetism) still takes place and the materials still have zero electrical resistance. However, the coupling is different from classical BCS theory. Some ideas for the differences include possible different

symmetries for the Cooper pairs, i.e. the pairs in these materials might form other than $L = 0$ s-states. Some clues also lie in the very common anti-ferromagnetism present in these materials.

So far, the highest temperature superconductor was metallic hydrogen ant $T_C = 203K$ and $100 - 200GPa$. Problem with the high temperature superconductors is that they are usually ceramics, and hence much less viable for any form of manufacturing.

However, some applications for superconductors are viable. The SQUIDs are used for magnetisation measurements, MRI scanners use superconducting coils to produce high, steady magnetic field, and some advanced electrical power management (spike protection, flywheel and superconducting energy storage) is carried out using superconductors. Also, maglev trains use superconductors.

3 Optical Properties of Materials

During the last section of the module, we will explore some of the optical properties of the materials. Since we are able to produce electromagnetic radiation (light) at very different energy scales, the physics of light in materials at different frequencies varies greatly as well. For low energy, big wavelength light, it usually suffices to use classical physics to describe the material response. However, for higher energy, quantum physics has to be applied in order to obtain accurate results. We will start with the classical physics approach.

3.1 Classical Optics

Classical optics follow from the Maxwell equations in material

$$\nabla \cdot \vec{D} = \rho \tag{47}$$

$$\nabla \cdot \vec{B} = 0 \tag{48}$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{49}$$

$$\nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t} \tag{50}$$

where $\vec{D}$ is the electric displacement field, $\vec{B}$ is the magnetic induction, $\vec{E}$ is the electric field, $\vec{H}$ is the magnetic field, ρ is the free charge density and $\vec{j}$ is the free current density. Furthermore, in linear materials, we write the following constitutive relations

$$\vec{D} = \epsilon \vec{E} \tag{51}$$

$$\vec{B} = \mu \vec{H} \tag{52}$$

$$\vec{j} = g \vec{E} \tag{53}$$

where ϵ is the permitivity of the medium, μ is the permeability of the medium and g is the conductivity of the medium, all of which we take as material constants.

Taking curl of (49) leads to

$$\nabla \times (\nabla \times \vec{E}) = \nabla(\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\frac{\partial}{\partial t}(\nabla \times \vec{B}) = -\mu \frac{\partial}{\partial t}\left(\vec{j} + \frac{\partial \vec{D}}{\partial t}\right)$$

where I used (50) and (52). Using (51) and (47)

$$\nabla\left(\frac{\rho}{\epsilon}\right) - \nabla^2 \vec{E} = -\mu \frac{\partial}{\partial t}\left(\vec{j} + \epsilon \frac{\partial \vec{E}}{\partial t}\right)$$

Assuming that the material is overall neutral ($\rho = 0$) and applying (53), we finally arrive to expression

$$\nabla^2 \vec{E} = \mu g \frac{\partial \vec{E}}{\partial t} + \mu \epsilon \frac{\partial^2 \vec{E}}{\partial t^2} \tag{54}$$

which is a damped wave equation for $\vec{E}$. We can try to find 1D wave-solution of form

$$\vec{E} = \vec{E}_0 e^{i(kx - \omega t)}$$

which leads to dispersion relation

$$-k^2 = -i\mu g\omega - \mu\epsilon\omega^2$$

$$k^2 = \mu\epsilon\left(\omega^2 + i\frac{g\omega}{\epsilon}\right) \tag{55}$$

and we see that k will have an imaginary part, leading to presence of exponential decay of the wave while in the material, as long as it has non-zero conductivity g. We can also use the refraction index to express the same information, with refraction index defined as

$$n = \frac{ck}{\omega}$$

Separating the real and imaginary component of the refraction index as $n = n_r + i\kappa$ leads to wave

$$\vec{E} = \vec{E}_0 e^{i(\omega n x/c - \omega t)} = \vec{E}_0 e^{-\kappa\omega x/c} e^{i(n_r\omega x/c - \omega t)}$$

The intensity of the light, which corresponds to the energy transferred per unit area by the light, is proportional to the square of the magnitude of the electric field, and so

$$I \propto |\vec{E}|^2 \propto e^{-2\kappa\omega x/c}$$

and we have a intensity decay $I \propto e^{-\alpha x}$ with $\alpha = 2\kappa\omega/c$.

3.1.1 Dipole Oscillator Model

A density of electric dipole moment in the material can be expressed by the polarization field $\vec{P}$, which in linear materials follows

$$\vec{P} = \chi\vec{E}$$

where χ is the susceptibility of the material, and $\epsilon_0(1 + \chi) = \epsilon$. A dipole can be present in the material for various reasons, and under the action of external wave-like electric field, it responds by harmonic oscillations. Suppose that we have dipole moment due to electron oscillating around some equilibrium position with frequency ω_0. Also assume there is damping of the motion present, with damping constant γ, so that the equation of motion of the position of the electron $\vec{x}$ away from the equilibrium is

$$m\frac{d^2\vec{x}}{dt^2} = -m\gamma\frac{d\vec{x}}{dt} - e\vec{E} - m\omega_0^2\vec{x} \tag{56}$$

Suppose that the driving field $\vec{E}$ is wave-like, i.e. $\vec{E} = \vec{E}_0 e^{-i\omega t}$. The steady-state response of the oscillator will be wave-like with the same frequency, so that $\vec{x} = \vec{x}_0 e^{-i\omega t}$, and hence

$$-m\omega^2\vec{x} = m\gamma i\omega\vec{x} - e\vec{E} - m\omega_0^2\vec{x}$$

Hence $\vec{x} \parallel \vec{E}$ and so we can work with magnitudes $x_0 = |\vec{x}_0|$ and $E_0 = |\vec{E}_0|$

$$m(\omega_0 - \omega^2)x_0 - mi\gamma\omega x_0 = -eE_0$$

$$x_0 = \frac{\frac{-eE}{m}}{(\omega_0^2 - \omega^2) - i\gamma\omega}$$

The induced dipole moment can be written as $p = qx_0 = -ex_0$ (it is parallel to $\vec{E}$ again) and the polarization field can be written as dipole moment density, which is obtained by multiplying dipole moment per electron p by the density of electrons N, and so we have

$$P = Np = -eNx_0 = \frac{\frac{e^2 N E_0}{m}}{\omega_0^2 - \omega^2 - i\gamma\omega} = \frac{Ne^2 E_0}{m}\left(\frac{(\omega_0^2 - \omega^2) + i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right)$$

Hence, the susceptibility is obtained by $\chi = \frac{P}{E_0}$ and the permitivity is obtained as

$$\epsilon = \epsilon_0(1 + \chi) = \epsilon_0 + \frac{\epsilon_0 Ne^2}{m}\left(\frac{(\omega_0^2 - \omega^2) + i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{57}$$

During the resonance ($\omega = \omega_0$), the permitivity becomes highly imaginary, which corresponds to high absorption of the waves.

Sometimes, we can add an additional term ϵ' to the expression for ϵ, which describes the behaviour of the permitivity on scales different from the oscillator resonance scale.

3.1.2 Free Electron Model

Consider now a material where the electrons are relatively free, but there is a finite conductance of the material, and so the electrons have a certain maximum velocity at which they can travel. This is a good model for interactions such as intraband absorption, where electrons in half-filled band (such as in metals) interact with incident radiation.

Let the electron have a momentum $\vec{p}$ and let it be under the force $\vec{f}$. Also, let there be an average scattering time τ in which the momentum of the electron is reset. Then, Newton's second law can be written as

$$\frac{d\vec{p}}{dt} = \vec{f} - \frac{\vec{p}}{\tau}$$

This can be integrated using the integrating factor method.

$$\frac{d\vec{p}}{dt} + \frac{\vec{p}}{\tau} = \vec{f}$$

Suppose that this is a result of a differentiation of product of functions p and g

$$\frac{d(pg)}{dt} = h$$

$$\frac{dp}{dt}g + \frac{dg}{dt}p = h$$

$$\frac{dp}{dt} + \frac{1}{g}\frac{dg}{dt}p = h$$

In our case

$$\frac{1}{g}\frac{dg}{dt} = \frac{1}{\tau}$$

So that

$$g = e^{\frac{t}{\tau}}$$

And hence

$$e^{\frac{t}{\tau}}\frac{d\vec{p}}{dt} + \frac{1}{\tau}e^{\frac{t}{\tau}}\vec{p} = e^{\frac{t}{\tau}}\vec{f}$$

$$\frac{d}{dt}\left(e^{\frac{t}{\tau}}\vec{p}\right) = e^{\frac{t}{\tau}}\vec{f}$$

$$\vec{p} = e^{-\frac{t}{\tau}}\int^{t} e^{\frac{t'}{\tau}}\vec{f}(t')dt'$$

For an oscillating field

$$\vec{f} = -e\vec{E}_0 e^{-i\omega t}$$

so

$$\vec{p} = -e\vec{E}_0 e^{-\frac{t}{\tau}}\int^{t} e^{\left(\frac{1}{\tau}-i\omega\right)t'}dt'$$

$$\vec{p} = -e\vec{E}_0 e^{-\frac{t}{\tau}}\frac{1}{\frac{1}{\tau}-i\omega}e^{\frac{t}{\tau}-i\omega t}$$

and so we recover oscillations of the momentum

$$\vec{p} = \frac{-e\vec{E}_0\tau}{1-i\omega\tau}e^{-i\omega t} \tag{58}$$

The velocity of the electrons is given as

$$\vec{v} = \frac{\vec{p}}{m^*}$$

where m^* is the effective mass of the electrons (see later). Then, the current density can be expressed as

$$\vec{j} = N(-e)\vec{v} = \frac{Ne^2\vec{E}_0\tau}{m^*(1-\omega\tau)}e^{-i\omega t} = \frac{g_D}{1-i\omega\tau}\vec{E}_0 e^{-i\omega t}$$

where g_D is the so called Drude conductivity. We can then recast this as a standard Ohm's law with imaginary conductivity g_ω

$$\vec{j} = g_\omega\vec{E}$$

where $\vec{E} = \vec{E}_0 e^{-i\omega t}$ is the applied field and

$$g_\omega = \frac{g_D}{1 - i\omega t} \tag{59}$$

Using (55), we can obtain

$$\epsilon_r = \epsilon_{r,\infty} + i\frac{g_\omega}{\omega\epsilon_0}$$

where $\epsilon_{r,\infty}$ is the limit of the relative permittivity at high frequency. Then

$$\epsilon_r \approx \epsilon_{r,\infty} + i\frac{g_D}{(1 - i\omega\tau)(\omega\epsilon_0)} = \epsilon_{r,\infty} - \epsilon_{r,\infty}\frac{\omega_p^2}{\omega^2 + i\frac{\omega}{\tau}}$$

where

$$\omega_p = \frac{Ne^2}{\epsilon_{r,\infty}\epsilon_0 m^*}$$

is called the plasma frequency, and corresponds to the electron-plasma oscillations.
For good metals, the scattering time is very long, and hence

$$\epsilon_r \approx \epsilon_{r,\infty}\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

Also, for good metals ω_p is big, and so the refractive index

$$n \approx \sqrt{\epsilon_r}$$

is pure imaginary, and we have a strong reflection, as expected for metals.

3.2   Tight Binding Model

Many optical properties of materials arise from their quantum nature. In this part, we will explore the tight binding structure of crystals and its implications for the optical properties of crystals.

3.2.1   Bloch's Theorem

Suppose that we have a lattice and a wavefunction $\Psi(\vec{r})$ defined on this lattice. Let $\hat{T}_{\vec{n}}$ be a translation operator, defined by

$$\hat{T}_{\vec{n}}\Psi(\vec{r}) = \Psi(\vec{r} + \vec{R}_{\vec{n}})$$

where $\vec{R}_{\vec{n}} = n_1\hat{e}_1 + n_2\hat{e}_2 + n_3\hat{e}_3$ is a displacement vector on the lattice. Suppose that the Hamiltonian for the system has periodic potential $V(\vec{r})$, such that

$$V(\vec{r} + \vec{R}_{\vec{n}}) = V(\vec{r})$$

and Hamiltonian is written as

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r})$$

Then

$$\hat{T}_{\vec{n}}\hat{H}\Psi(\vec{r}) = \hat{T}_{\vec{n}}\left[\left(\frac{\hat{p}^2}{2m} + V(\vec{r})\right)\Psi(\vec{r})\right] = \left(\frac{\hat{p}^2}{2m} + V(\vec{r} + \vec{R}_{\vec{n}})\right)\Psi(\vec{r} + \vec{R}_{\vec{n}}) =$$

$$= \left(\frac{\hat{p}^2}{2m} + V(\vec{r})\right)\Psi(\vec{r} + \vec{R}_{\vec{n}}) = \hat{H}\hat{T}_{\vec{n}}\Psi(\vec{r})$$

Hence, $\hat{T}_{\vec{n}}$ and $\hat{H}$ commute and share the same eigenstates. We should therefore try to define the properties of these eigenstates. Assume that the system as a whole has the lattice translation symmetry. The action of the translation operator can be expressed as

$$\Psi(\vec{r} + \vec{R}_{\vec{n}}) = \hat{T}_{\vec{n}}\Psi(\vec{r}) = c_{\vec{n}}\Psi(\vec{r})$$

For observables to be unchanged by the translation, we require

$$|\Psi(\vec{r} + \vec{R}_{\vec{n}})|^2 = |\Psi(\vec{r})|^2$$

$$|c_{\vec{n}}|^2 |\Psi(\vec{r})|^2 = |\Psi(\vec{r})|^2$$

$$|c_{\vec{n}}|^2 = 1$$

$$c_{\vec{n}} = e^{i\theta_{\vec{n}}}$$

Since $\vec{n}$ variables form a vector space on the lattice, we need $\theta_{\vec{n}}$ to be linear in $\vec{R}_n$ or $\vec{n}$, and we usually write

$$c_{\vec{n}} = e^{i\vec{k}\cdot\vec{R}_{\vec{n}}}$$

Hence, the action of the translation operator multiplies the wavefunction by a certain phase, but otherwise leaves it unchanged. Suppose that we now define

$$u(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\Psi(\vec{r})$$

Which satisfies

$$u(\vec{r} + \vec{R}_{\vec{n}}) = e^{-i\vec{k}\cdot\vec{r}}e^{-i\vec{k}\cdot\vec{R}_{\vec{n}}}\Psi(\vec{r} + \vec{R}_{\vec{n}}) = e^{-i\vec{k}\cdot\vec{r}}e^{-i\vec{k}\cdot\vec{R}_{\vec{n}}}e^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\Psi(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\Psi(\vec{r}) = u(\vec{r})$$

Hence, $u(\vec{r})$ has the periodicity of the lattice, and we can define

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) \tag{60}$$

as the eigenstate of both energy and translation operator. The basis of the eigenstates is given by the different $\vec{k}$ vectors.

3.2.2   Tight-Binding State

Suppose now that electron exist in the lattice, but are mostly localized around the lattice sites. Then, an accurate description of the electron state is

$$|\Psi(\vec{r})> = \sum_{\vec{n}} e^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\frac{1}{\sqrt{N}}|\phi(\vec{r} - \vec{R}_{\vec{n}}) > \tag{61}$$

where $\frac{1}{\sqrt{N}}$ factor is due to normalization and $\phi(\vec{r})$ is a atomic orbital wavefunction (of some kind, i.e. 1s or 2p) for atom centered on the origin. We can check that

$$|\Psi(\vec{r} + \vec{R}_{\vec{m}}) > = \sum_{\vec{n}} e^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\frac{1}{\sqrt{N}}|\phi(\vec{r} + \vec{R}_{\vec{m}} - \vec{R}_{\vec{n}}) > =$$

$$= \sum_{\vec{n}} e^{i\vec{k}\cdot\vec{R}_{\vec{m}}}e^{i\vec{k}\cdot(\vec{R}_{\vec{n}} - \vec{R}_{\vec{m}})}\frac{1}{\sqrt{N}}|\phi(\vec{r} - (\vec{R}_{\vec{n}} - \vec{R}_{\vec{m}})) >$$

Reindexing the sum $\vec{R}_{\vec{n}} - \vec{R}_{\vec{m}} = \vec{R}_{\vec{p}}$ (for infinite lattice) and factoring out the exponential factor leads to

$$|\Psi(\vec{r} + \vec{R}_{\vec{m}})| = e^{i\vec{k}\cdot\vec{R}_{\vec{m}}}\sum_{\vec{p}} e^{i\vec{k}\cdot\vec{R}_{\vec{p}}}\frac{1}{\sqrt{N}}|\phi(\vec{r} - \vec{R}_{\vec{p}}) > = e^{i\vec{k}\cdot\vec{R}_{\vec{m}}}|\Psi(\vec{r}) >$$

so this state is a valid Bloch state. Now, suppose that the Hamiltonian for the system is given by

$$< \phi(\vec{r})|\hat{H}|\phi(\vec{r}) > = E_0$$

$$\vec{R}_{\vec{m}} \neq 0 : < \phi(\vec{r})|\hat{H}|\phi(\vec{r} + \vec{R}_{\vec{m}}) > = < \phi(\vec{r})|\hat{H}|\phi(\vec{r} - \vec{R}_{\vec{m}}) > = -t\delta_{\vec{m},\pm\vec{a}}$$

where $\vec{a}$ is the vector pointing to the nearest neighbour. This encapsulates the idea that there is only a small overlap of nearest neighbour orbitals that leads to potential electron transport/band formation. Acting with such Hamiltonian on the tight binding state, as defined in (61) leads to

$$E_{\vec{k}} = < \Psi(\vec{r})|\hat{H}|\Psi(\vec{r}) > = \frac{1}{N}\sum_{\vec{m},\vec{n}} < \phi(\vec{r} - \vec{R}_{\vec{n}})|e^{-i\vec{k}\cdot\vec{R}_{\vec{n}}}e^{i\vec{k}\cdot\vec{R}_{\vec{m}}}\hat{H}|\phi(\vec{r} - \vec{R}_{\vec{m}}) > =$$

$$= \frac{1}{N}\sum_{\vec{n},\vec{m}} e^{i\vec{k}\cdot(\vec{R}_{\vec{m}} - \vec{R}_{\vec{n}})} < \phi(\vec{r} - \vec{R}_{\vec{n}})|\hat{H}|\phi(\vec{r} - \vec{R}_{\vec{m}}) > = \frac{1}{N}\sum_{\vec{n},\vec{m}} e^{i\vec{k}\cdot(\vec{R}_{\vec{m}} - \vec{R}_{\vec{n}})}\left(E_0\delta_{\vec{n},\vec{m}} - t\delta_{\vec{n},\vec{m}\pm\vec{a}}\right) =$$

$$= \frac{1}{N} \sum_{\vec{n}} E_0 - t \left(e^{i\vec{k}\cdot\vec{a}} + e^{-i\vec{k}\cdot\vec{a}} \right) = E_0 - 2t\cos(\vec{k}\cdot\vec{a}) \qquad (62)$$

Hence, we have a dispersion relation for the electrons in the tight binding model. This dispersion relation characterizes one band of electrons present in the material. The bandwidth of this band is $\Delta E = 4t$ and the band is centered around E_0.

3.2.3 Effective Mass

For free electron, the mass can be established from the free energy of the electron $E_f = \frac{\hbar^2 k^2}{2m}$ by derivative with respect to the wavenumber

$$m = \frac{\hbar^2}{\frac{\partial^2 E_f}{\partial k^2}} = \frac{\hbar^2}{\frac{\partial^2 \left(\frac{\hbar^2 k^2}{2m} \right)}{\partial k^2}}$$

In tight binding model, the effective mass of the electron is derived analogously, but E_k is used instead of E_f, so that

$$m^* = \frac{\hbar^2}{\frac{\partial^2 E_k}{\partial k^2}} = \frac{\hbar^2}{2ta^2 \cos(ka)}$$

For small wavenumber k, this can be approximated to the first order in k as

$$m^* \approx \frac{\hbar^2}{2ta^2}$$

which is constant. To the second order of accuracy, we could write

$$m^* \approx \frac{\hbar^2}{2ta^2 \left(1 - \frac{k^2 a^2}{2} \right)} \approx \frac{\hbar^2}{2ta^2} \left(1 + \frac{k^2 a^2}{2} \right)$$

and hence we see that the effective mass tends to increase for small k.

3.2.4 Band Character

The sign of the overlap integral $t = - <\phi(\vec{r})|\hat{H}|\phi(\vec{r}\pm\vec{a})>$ depends on the character of the atomic orbital $\phi(\vec{r})$. For s type orbitals, which are symmetrical under parity exchange, t is positive. But for p type orbitals, t comes out as negative, and hence the dispersion relation is different and the effective mass of the electrons in these orbitals is negative. Also, the base energy E_0 will be different for different orbitals, giving the rise to the band structure of the materials and possibly a band gap, depending on the filling of the bands.

Usually, the overlap of the atomic orbitals converts half of the atomic orbitals into bonding and half to anti-bonding orbitals, with energy of the anti-bonding orbitals higher than that of the bonding orbitals.

3.3 Transition Rates

3.3.1 Fermi's Golden Rule

Consider a time evolving system with Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{V}$ is some small perturbation. Suppose that a state of the system can be expanded as

$$|\Psi(t)> = \sum_n c_n(t)|\phi_n(t)> = \sum_{n,j} c_n^j(t)|\phi_n(t)>$$

where $|\phi_n(t)>$ are the eigenstates of $\hat{H}_0$ with energies E_n and $c_n = \sum_j c_n^j(t)$ are the expansion coefficients, with $c_n^j(t)$ forming a convergent series in j in orders similar to order difference between $\hat{V}$ and $\hat{H}_0$. The Schrödinger equation is

$$i\hbar \frac{\partial}{\partial t} \left(\sum_{n,j} c_n^j(t)|\phi_n(t)> \right) = (\hat{H}_0 + \hat{V}) \sum_{n,j} c_n^j(t)|\phi_n(t)>$$

To the zeroth order in j and $\hat{V}$, we obtain equation

$$i\hbar \frac{\partial}{\partial t} \left(\sum_n c_n^0(t) |\phi_n(t) > \right) = \hat{H}_0 \sum_n c_n^0 |\phi_n(t) >$$

Distributing the derivative leads to

$$i\hbar \sum_n \frac{\partial c_n^0}{\partial t} |\phi_n(t) > + \sum_n c_n^0(t) i\hbar \frac{\partial}{\partial t} |\phi_n(t) > = \sum_n c_n^0 \hat{H}_0 |\phi_n(t) >$$

Recognizing that the action of the time derivative on the state $|\phi_n(t) >$ is the same as action of $\hat{H}_0$ on the state $|\phi_n(t) >$, we are left with

$$i\hbar \sum_n \frac{\partial c_n^0}{\partial t} |\phi_n(t) > = 0$$

Taking inner product with $< \phi_m(t)|$ leads to

$$\forall m : \frac{\partial c_m^0}{\partial t} = 0$$

and therefore, to the zeroth order, the components of the state of the system remain the same. We should note that the eigenstates themselves evolve in the Schrödinger representation as

$$i\hbar \frac{\partial}{\partial t} |\phi_n(t) > = \hat{H}_0 |\phi_n(t) > = E_n |\phi_n(t) >$$

$$|\phi_n(t) > = e^{-\frac{i}{\hbar} E_n t} |\phi_n(0) >$$

For the first order in j and $\hat{V}$, we get

$$i\hbar \frac{\partial}{\partial t} \sum_n c_n^1(t) |\phi_n(t) > = \hat{H}_0 \sum_n c_n^1(t) |\phi_n(t) > + \hat{V} \sum_n c_n^0 |\phi_n(t) >$$

where I dropped the time dependence of c_n^0, since we have already shown it is time independent. Distributing the time derivative leads to

$$i\hbar \sum_n \frac{\partial c_n^1}{\partial t} |\phi_n(t) > + \sum_n c_n^1(t) E_n |\phi_n(t) > = \sum_n c_n^1(t) E_n |\phi_n(t) > + \sum_n c_n^0 \hat{V} |\phi_n(t) >$$

$$i\hbar \sum_n \frac{\partial c_n^1}{\partial t} |\phi_n(t) > = \sum_n c_n^0 \hat{V} |\phi_n(t) >$$

Taking inner product with $< \phi_m(t)|$ leads to

$$i\hbar \frac{\partial c_m^1}{\partial t} = \sum_n c_n^0 < \phi_m(t) |\hat{V}| \phi_n(t) >$$

Hence, we can write

$$c_m^1(t) = \frac{-i}{\hbar} \int_0^t \sum_n c_n^0 < \phi_m(t') |\hat{V}| \phi_n(t') > dt'$$

Plugging in for the eigenstate evolution

$$c_m^1(t) = \frac{-i}{\hbar} \int_0^t \sum_n c_n^0 e^{-\frac{i}{\hbar}(E_n - E_m)t'} < \phi_m(0) |\hat{V}| \phi_n(0) >$$

Now suppose that the system starts in one concrete eigenstate $|\phi_n(0) >$, so that $c_m^0 = \delta_{n,m}$, and hence, we can write

$$c_m^1(t) = \frac{-i}{\hbar} \int_0^t e^{-\frac{i}{\hbar}(E_n - E_m)t'} M_{nm}$$

where $M_{nm} = <\phi_m(0)|\hat{V}|\phi_n(0)>$ is called the matrix element of the $n \to m$ transition. This can be integrated to

$$c_m^1(t) = \frac{-i}{\hbar}M_{nm}\frac{i\hbar}{(E_n - E_m)}\left(e^{-\frac{i}{\hbar}(E_n - E_m)t} - 1\right) =$$

$$= M_{nm}\frac{1}{(E_n - E_m)}e^{-\frac{i}{2\hbar}(E_n - E_m)t}\left(e^{-\frac{i}{2\hbar}(E_n - E_m)} - e^{\frac{i}{2\hbar}(E_n - E_m)t}\right) =$$

$$= M_{nm}\frac{2}{(E_n - E_m)}(-i)e^{-\frac{i}{2\hbar}(E_n - E_m)t}\sin\left(\frac{(E_n - E_m)}{2\hbar}t\right)$$

Hence, the probability of the transition to state m from state n is given by

$$|c_m^1|^2 = |M_{nm}|^2\frac{4}{(E_n - E_m)^2}\sin^2\left(\frac{(E_n - E_m)}{2\hbar}t\right)$$

Now, suppose that we are interested in some narrow band of states centred around E_f with bandwidth of $2\Delta E$. The probability of transition from initial state i to the narrow band is

$$P_{i \to f} = \int_{E_f - \Delta E}^{E_f + \Delta E} g(E_f)4|M_{if}|^2\frac{\sin^2\left(\frac{E' - E_i}{2\hbar}\right)}{(E' - E_i)^2}dE'$$

where $g(E_f)$ is the density of states. Both the density of states and matrix element are taken as approximately constant and equal to the value in the middle of the band. Changing variables to $\alpha = \frac{E' - E_i}{2\hbar}t$, we get

$$P_{i \to f} = \frac{2}{\hbar}g(E_f)|M_{if}|^2t\int_{\frac{E_f - \Delta E - E_i}{2\hbar}t}^{\frac{E_f + \Delta E - E_i}{2\hbar}t}\frac{\sin^2\alpha}{\alpha^2}d\alpha$$

Assuming that the bandwidth is significantly larger than the energy difference, we can approximate the result as

$$P_{i \to f} = \frac{2}{\hbar}g(E_f)|M_{if}|^2t\int_{-\infty}^{\infty}\frac{\sin^2\alpha}{\alpha^2}d\alpha$$

It can be shown that the integral approaches to π, and so we get

$$P_{i \to f} = \frac{2\pi}{\hbar}g(E_f)|M_{if}|^2t$$

And the rate of the transition is

$$W_{i \to f} = \frac{P_{i \to f}}{t} = \frac{2\pi}{\hbar}g(E_f)|M_{if}|^2$$

which is called the Fermi's golden rule.

3.3.2   Band Selection Rules

Fermi's golden rule states that the transition rate $W_{i \to f}$ between bands of states is

$$W_{i \to f}\frac{2\pi}{\hbar}g(E_f)|M_{if}|^2 \tag{63}$$

where the matrix element is

$$M_{if} = <\phi_f|\hat{V}|\phi_i>$$

where $\hat{V}$ is the perturbing potential and $\phi_{i/f}$ is the initial/final state. For interaction with light, we will use dipole approximation, where

$$\hat{V} = \vec{p}_d \cdot \vec{E} = q\vec{r} \cdot \vec{E}_0 e^{\pm i\vec{k} \cdot \vec{r}}$$

where $\vec{p}_d$ is the dipole moment operator, $\vec{r}$ is a position operator, $\vec{E}$ is the electric field, q is the charge of the carriers, $\vec{k}$ is the wavenumber of the electric field and $\vec{E}_0$ is the amplitude of the electric field. Suppose that the field oscillates in y direction, so that we have

$$\hat{V} = qyE_0e^{\pm i\vec{k} \cdot \vec{r}}$$

In crystals, we expect $\phi_{i/f}$ to be Bloch waves, so that

$$\phi_{i/f} = \frac{e^{i\vec{k}_{i/f}\cdot\vec{r}}}{\sqrt{V}} u_{i/f}(\vec{r})$$

where the $\sqrt{V}$ factor ensures normalization. Hence, the matrix element can be expressed as

$$M_{if} \int_V \frac{q}{V} u_f^*(\vec{r}) u_i(\vec{r}) y e^{i(\vec{k}_i - \vec{k}_f \pm \vec{k})\cdot\vec{r}} E_0 dV$$

where the integration runs over the whole volume of the crystal. Importantly, we should note that for $\vec{k}_f - \vec{k}_i \neq \pm\vec{k}$ the integral goes to zero, and therefore we require that

$$\vec{k}_f - \vec{k}_i = \pm\vec{k}$$

i.e. we require the conservation of momentum. Also, the integral can be reduced to a integral over the unit cell, multiplied by some constant. Then

$$M_{if} \propto \int_{cell} u_f^* u_i y dV$$

Now, we should note that y is an odd function, and the integral is only non-zero in case where product $u_f^* u_i$ is an odd function as well. This occurs for transitions from s-type to p-type orbital, but for example s to s or p to p transitions are forbidden in the dipole approximation.

3.3.3 Transitions Close to Band Edge

Close to the band edge for a material with direct band gap (band gap such that the smallest energy difference between the bands is at point of zero wavevector difference), the band dispersions can be approximated as parabolic, with energies $E_{c/v}$ for conductance/valence band following

$$E_c = E_g + \frac{\hbar^2 k^2}{2m_c^*}$$

$$E_v = -\frac{\hbar^2 k^2}{2m_v^*}$$

By conservation of energy, we require that a photon of energy $\hbar\omega$ causes transition between energies E_c and E_v following

$$\hbar\omega = E_c - E_v = E_g + \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right) = E_g + \frac{\hbar^2 k^2}{2\mu} \tag{64}$$

where we defined the reduced mass μ by $\frac{1}{\mu} = \frac{1}{m_c^*} + \frac{1}{m_v^*}$. We can approximate the density of states for the transition by free density of states for electrons with mass μ. For wavenumber k, free density of states for electrons is given as

$$g(k)dk = 2\frac{4\pi k^2 dk}{\left(\frac{2\pi}{a}\right)^3} = \frac{k^2}{\pi^2}V dk$$

where a is the size of the unit cell (cubic), V is the volume of unit cell and the factor of 2 accounts for the spin degeneracy. Often, we use the density of states per unit volume, which is obtained by simply dividing by V, and leaves us with

$$g(k)dk = \frac{k^2}{\pi^2}dk \tag{65}$$

To transfer the density in terms of the energy, we write

$$g(k)dk = g(k(E))\frac{dk}{dE}dE$$

From (64)

$$k = \sqrt{\frac{2\mu}{\hbar}(\hbar\omega - E_g)}$$

What will be variable in our case will be the photon energy, so we will use $E = \hbar\omega$. Hence

$$\frac{dk}{dE} = \sqrt{\frac{2\mu}{\hbar}}\frac{1}{2\sqrt{\hbar\omega - E_g}}$$

and therefore

$$g(E)dE = \frac{1}{2\pi^2\sqrt{\hbar\omega - E_g}}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}(\hbar\omega - E_g)dE$$

and after simplification

$$g(E)dE = \frac{1}{2\pi^2}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\hbar\omega - E_g} \tag{66}$$

From (63), we then obtain the rate of transitions close to the band edge

$$W_{i\to f} \propto |M_{if}|^2\sqrt{\hbar\omega - E_g}$$

which can be experimentally verified through the absorption coefficient $\alpha \propto W_{i\to f}$.

3.4 Excitons

Excitons are bound states of electrons and holes which have energy spectrum analogous to hydrogen atom. They can form across the band gap and and there are two basic types.

Wannier-Mott excitons   These excitons form over long distances in real space and have relatively low energy (i.e. 10 meV)

Frenkel excitons   These are more tightly bound pairs of electrons and holes, with higher binding energies (i.e. 100 meV)

Importantly, excitons only form under certain temperature T, for which $k_B T \approx E_b$, where E_b is the binding energy of the excitons. For higher temperatures, the random fluctuations destroy the excitons.

In hydrogen atom, the electronic spectrum follows

$$E_n = -\frac{R_H}{n^2}$$

where $R_H \approx 13.6 eV$ is the Rydberg energy unit. However, the dynamics inside a crystal are different, as the medium has different permittivity and the electrons have an effective mass. Since this is a bound state of electron and hole, we need to use the reduced mass as well. This means that for exciton, the energy spectrum follows

$$E_{x,n} = -\frac{\mu}{m_e\epsilon_r^2}\frac{R_H}{n^2} = -\frac{R_X}{n^2} \tag{67}$$

where μ is the reduced mass, m_e is the vacuum electron mass and ϵ_r is the relative permittivity of the medium. Also, we defined the specific Rydberg constant $R_x = \frac{\mu}{m_e\epsilon_r^2}$. Since ϵ_r is usually of order of 10, the energy scale is greatly reduced, and the excitonic effects are seen as peaks close to the band gap absorption edge.

3.5 Quantum Confinement

3.5.1 Spectrum of Quantum Wells

Consider a 1D quantum system which is restricted to the region of length L, where it is free to move. The boundary conditions and Schrödinger equation lead to energy spectrum

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2 \tag{68}$$

In 2 independent dimensions, this generalizes to

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2) \tag{69}$$

and similarly for 3 dimensions. Here, n_x and n_y are two independent quantum numbers.

3.5.2 Absorption of Quantum Wells

In real materials, doping can create confinement in all dimensions. Quantum wells create confinement in one direction, quantum wires confine in two dimensions and quantum dots confine in all three directions. In the unconfined directions, the electrons still form a continuum of states, but in confined direction, the states are discretized.
The state of the electrons can be written as product of the Bloch state and of the discretized wavefunction

$$\Psi = \frac{1}{\sqrt{A}} u(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \phi_n(z)$$

where I assumed the confinement in the z direction, $\phi_n(z)$ is the quantum confined wavefunction and A is the area of the quantum well. There is an important consequence in the selection rules for transitions between two quantum wells. Suppose that the initial state is

$$\Psi_i = \frac{1}{\sqrt{A}} e^{i\vec{k}_i\cdot\vec{r}} u_i(\vec{r}) \phi_{h,n}(z)$$

where h signifies hole index (electron starts in the valence band, where it will leave hole behind, confined). and the final state is

$$\Psi_f = \frac{1}{\sqrt{A}} e^{i\vec{k}_f\cdot\vec{r}} u_f(\vec{r}) \phi_{e,n'}(z)$$

Hence

$$M_{if} \propto <u_i|\vec{E}\cdot\vec{r}|u_f><\phi_{e,n'}|\phi_{h,n}>$$

Hence, we have a 2D version of previous selection rules, but we have additional selection rule for transition between the levels of the confined spectrum. Since all the levels are mutually orthogonal, the only transition can occur when $n = n'$, i.e. between corresponding levels of the quantum well.

3.5.3 Confined Density of States and Transition Rate

Since the continuum of states is only in reduced number of dimensions, the density of states is also significantly different for confined systems.
For two-dimensional systems, the density of states is

$$g(k)dk = 2\frac{2\pi k dk}{(2\pi)^2} = \frac{k}{\pi} dk$$

The energy of the two dimensional system absorption can be written as

$$E = E_g + \frac{\hbar^2 k^2}{2\mu} + \frac{\hbar^2\pi^2}{2\mu L^2}n^2$$

where k is in 2 dimensions only. The dispersion is still quadratic, so

$$k = \sqrt{E - E_g - \frac{\hbar^2\pi^2}{2\mu L^2}n^2}\sqrt{\frac{2\mu}{\hbar^2}}$$

$$\frac{dk}{dE} = \frac{\sqrt{\frac{2\mu}{\hbar^2}}}{2\sqrt{E - E_g - \frac{\hbar^2\pi^2}{2\mu L^2}n^2}}$$

and

$$g(E)dE = g(k(E))\frac{dk}{dE}dE = \frac{\mu}{\pi\hbar^2}$$

which is independent of the energy. Hence, in absorption coefficient, we see plateaus of constant absorption, followed by quick steps, which correspond to available jump between levels of quantum well. Importantly, before we reach energy to jump between 1st confined level, nearly no absorption occurs.
For 2D confinement and 1D continuum, the situation is similar, but $g(E) \propto \frac{1}{\sqrt{E-c}}$, and so the absorption decreases after each jump.
One interesting effect of the confinement is that the excitons become confined aswell, leading to altered spectrum (in this case for 1D confinement)

$$E_n = -\frac{R_x}{\left(n - \frac{1}{2}\right)^2}$$

which is much stronger than no confinement for small n.

3.6   Luminescence

Luminescence occurs when the electrons decay from the conduction band to the valence band across the band gap, producing a photon of visible light in the process. Depending on how the electron got into the conduction band, we differentiate between photoluminescence (when the electron was excited to the conductance band from valence band by photon of light) and electroluminescence (when the electron was injected by electric current).

In the band, the electrons decay through the continuum of states, and only produce very low energy, thermal photons. Once the electrons gets to the band edge, it can further only decay across the band gap, and this will be of interest to us.

3.6.1   Luminescence Intensity

While for absorption of light, we could be fairly certain that there is a electron in a valence band and a free state in the conduction band, we can never be sure that there is an electron in the conductance band and free state in the valence band for it to decay to and emit light. Therefore, besides the rate from Fermi's golden rule, we need to include the probability of occupation of conductance state by electron and valence state by hole. Both hole and electron are fermions, and so we use the Fermi-Dirac distribution for the occupation probability, leading to proportionality

$$I \propto W_{i \to f} f_h f_e g(\hbar\omega) \propto |M_{if}|^2 \frac{1}{\left(e^{(E_e - \mu)/(k_B T)} + 1\right)\left(e^{(E_h - \mu)/(k_B T)} + 1\right)} \tag{70}$$

where $f_{e/h}$ is the electron/hole Fermi-Dirac distribution, μ is the chemical potential of the system, $E_{e/h}$ is the relative energy of the electron/hole, taken from the bottom/top of the conductance/valence band, respectively, and g is the joint density of states.

We will further assume that the carried concentrations are low, and therefore both f_v and f_h are small, which corresponds to $E_e - \mu$ and $E_h - \mu$ being relatively big compared to $k_B T$. Then, we can approximate the expression as

$$I \propto |M_{if}|^2 g(\hbar\omega) e^{-(E_e - \mu)/(k_B T)} e^{-(E_h - \mu)/(k_B T)} \propto |M_{if}|^2 g(\hbar\omega) e^{-(E_e + E_h)/(k_B T)}$$

By conservation of energy

$$\hbar\omega = E_g + E_e + E_h$$

and so

$$I \propto |M_{if}|^2 g(\hbar\omega) e^{-(\hbar\omega - E_g)/(k_B T)}$$

as shown in (66), $g(\hbar\omega) \propto \sqrt{\hbar\omega - E_g}$, and hence

$$I \propto |M_{if}|^2 \sqrt{\hbar\omega - E_g} e^{-(\hbar\omega - E_g)/(k_B T)} \tag{71}$$

The main difference to the absorption is in the exponential factor, that occurs due to sparse population of the conduction band by the electrons. In absorption, this is not a problem, and hence the absorption spectrum is much wider, compared to the luminescence emission spectrum.

3.6.2   Monolayers

In monolayers, the band structure depends on the size of the layer, as there is no pure bulk region of the crystal. This significantly influences the structure of the bands and density of states, and in turn the optical properties are changed and can be tuned to serve specific purposes.

3.7   Polaritons

Consider now the oscillations of the ions in the lattice of the crystal. For transverse optical modes, the oscillations can be driven by an electric field of a photon. In turn, the oscilliations can create a photon, and when a resonant frequency is hit, the photon-oscillation(phonon) system can become quasi-stable. This quasi-stable particle is called polariton.

3.7.1   Photon-Polariton Interaction

The interaction between photon and a polariton can be modelled just as interaction between classical dipole moment and photon, as in (57). As the natural frequency of the oscillator, we use the frequency of the phonon transverse optical mode, and as the mass, we use the reduced mass of the ions in the optical mode. Then, the permittivity of the medium can be estimated as

$$\epsilon = \epsilon_0 + \epsilon' + \frac{\epsilon_0 N e^2}{\mu}\left(\frac{1}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}\right)$$

It is sometimes useful to reparametrize this expression in terms of the limits for static DC field ($\omega \to 0$) and for high frequency $\omega \to \infty$. For high frequency

$$\epsilon \to \epsilon_\infty \approx \epsilon_0 + \epsilon'$$

For low frequency

$$\epsilon \to \epsilon_s \approx \epsilon_0 + \epsilon' + \frac{\epsilon_0 N e^2}{\mu}\frac{1}{\omega_{T0}^2} = \epsilon_\infty + \frac{\epsilon_0 N e^2}{\mu\omega_{TO}^2}$$

Therefore, we can express

$$\frac{\epsilon_0 N e^2}{\mu} = (\epsilon_s - \epsilon_\infty)\omega_{TO}^2 \tag{72}$$

Hence, the permittivity dependence can be expressed entirely in terms of well measurable quantities

$$\epsilon = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} \tag{73}$$