Condensed Matter Physics

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Lecture - 21
Quenching of Orbital Angular Momentum; Ferromagnetism

In the last lecture, we saw that even though both the 3 d and 4 f electron systems namely the iron-group and the rarest group of paramagnetic ions both have similar outer electron structure, still there is a big difference in their magnetic behavior. For example, if you measure the magnetic susceptibility and try to relate it to the ((Refer Time: 00:49)) function expression for the paramagnetic susceptibility or the magnetization, you find that there is very good agreement between the calculated values and the theoretical values in the cases there are rarest ions the 4 f ion. Whereas, the agreement is rather poor in the case that the 3 d electrons. Now we would like to spend some time trying to understand this reason for this difference in behavior between 4 f and 3 d electrons in the unfiled shelves.

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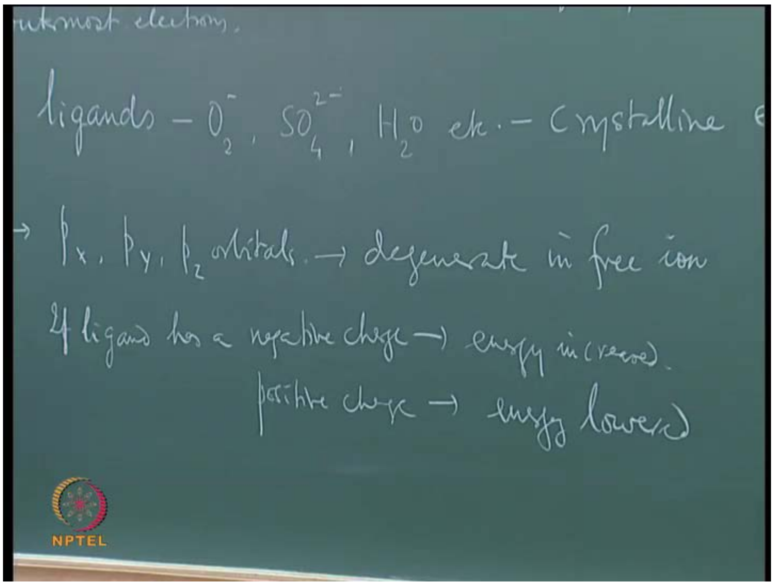

utmost electrons.

ligands – O_2^-, SO_4^{2-}, H_2O etc. – Crystalline

→ p_x, p_y, p_z orbitals → degenerate in free ion

If ligand has a negative charge → energy increased.

positive charge → energy lowered

We know that in the case of the rare earth ions the 4 f electrons have outer 5 s and 5 p electrons 4 f electrons surrounded by whereas in the case of the 3 d electrons, there are no electrons outside and they are the outer most electrons. So, this is the rare earth group and this is the ion group. So, the 3 d electrons lie outer most whereas, the 4 f electrons are protected from outside influence, relative isolated because of the presence of the outer 5 s and f 5 p electrons. Therefore, they shield the 4 f electron from the influence of debarring electric charges, whereas in the ion group compounds this 3 d electrons are outermost one and they are considerably affected by the presence of neighboring electric charges. And usually in all these compounds, the paramagnetic ions is surrounded by what are known as ligands such as O 2 minus or S O 4 2 minus or and so on H 2 O etcetera.

These are the ligands, which are present which surround the paramagnetic ions and because such electric charges are present, they produced crystalline electric fields at the site of the paramagnetic ion. So, the paramagnetic ion, the behavior that we saw regarding the ground state of this is affected to a large extent by the presence of this crystalline electric fields, and this results in a stark spitting of the ground state. As we know that the magnetic behaviors is profoundly affected by the ground state of the paramagnetic ion, because for statistical reasons it is the ground states which is mostly occupied by an which is occupied by most of the ions, and therefore the magnetic behaviors is completely almost completely determined by the nature of the ground state.

And since this ground state is fit by the stark effect due to the crystalline electric fields produced by ligands, therefore, the nature of the paramagnetic ground state is different and therefore, the magnetic behaviors is also considerably different in the case of the ions group ion. To see this effect, let us consider for simplicity a P state ion. This is a little complicated solid is just a an ion which has P electrons, in the electrons in the P s, P shell which consists of 3 orbital’s which are known as the P x, P y, P z orbital which are shown in the next figure.

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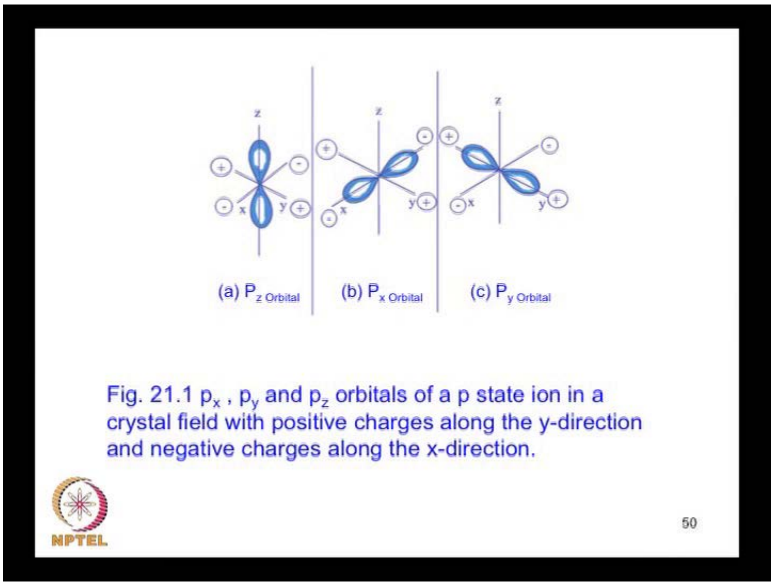

(a) $P_{z\ \text{Orbital}}$ (b) $P_{x\ \text{Orbital}}$ (c) $P_{y\ \text{Orbital}}$

Fig. 21.1 p_x , p_y and p_z orbitals of a p state ion in a crystal field with positive charges along the y-direction and negative charges along the x-direction.

So, the lower observes these orbital’s are directed along the x, y and z axis. These are shown in the figure. Now you see also in this figure charges or the ligands being shown. These ligands surround this ion, and some of them are positive and some of them are negative.

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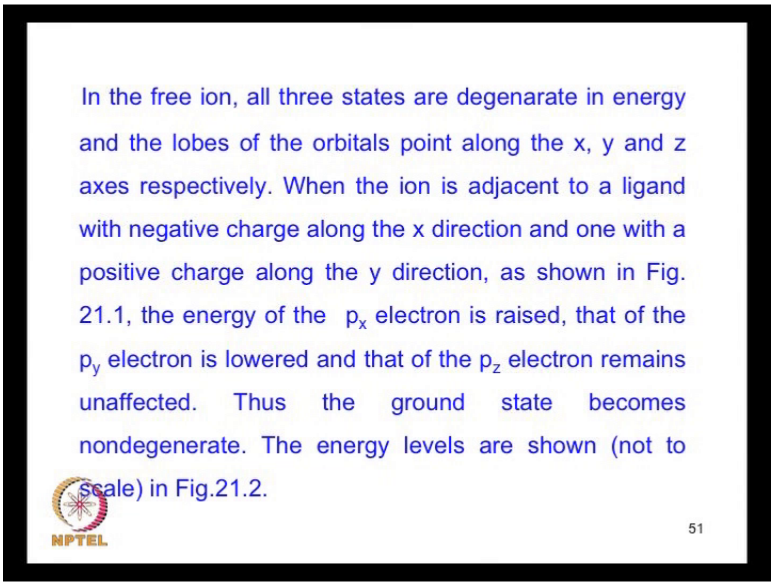

In the free ion, all three states are degenarate in energy and the lobes of the orbitals point along the x, y and z axes respectively. When the ion is adjacent to a ligand with negative charge along the x direction and one with a positive charge along the y direction, as shown in Fig. 21.1, the energy of the p_x electron is raised, that of the p_y electron is lowered and that of the p_z electron remains unaffected. Thus the ground state becomes nondegenerate. The energy levels are shown (not to scale) in Fig.21.2.

So, in the free ion, all these three are degenerate, but now we have an ion which is not free, but it is subject to the crystal electric fields. So, because if this ligands has a negative charge, next to the electronic cloud that the electron cloud will be repulsed by the negative charge. And therefore, the negative energy of this particular state will go up, it will be increased, whereas, if it is then energies is increased. Obviously, if it is a positive charge, the energy will be lower; and if there is no charge and it is neutral, then nothing will happen to the energy. So, if you see the p x electron, if you consider the orbital shown in the figures one finds that the p y orbital have positive charges, so p y orbital will get lower.

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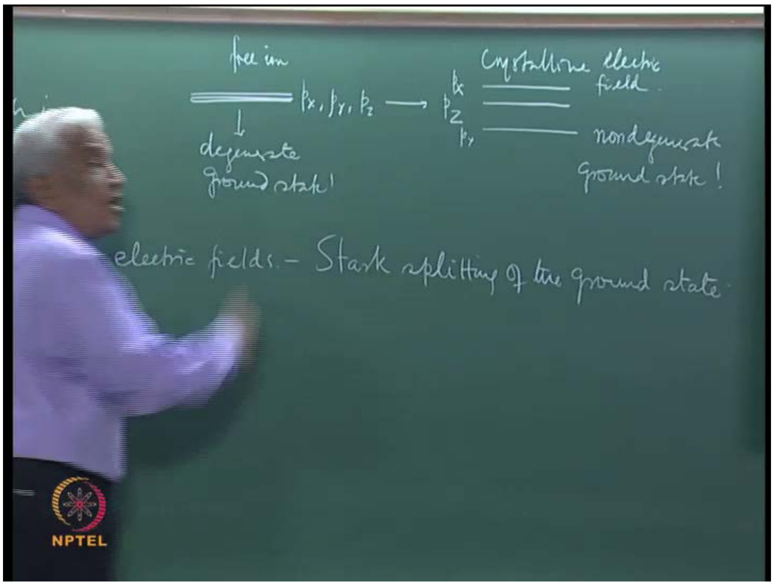

So, start with the p x, p y and the p z are all together in the free ion. Now this degeneracy is the lifted by the free ion. The crystalline electric field lift this degeneracy due to the ligand, and therefore, the p y gets lower, the p x get increased and the p z remains the same for the configuration that is shown in the figure. So, the presence of the ligand, lifts this degeneracy, and makes all these three energy levels separate and therefore, the ground state has become non-degenerate ground state, whereas this is a degenerate ground state.

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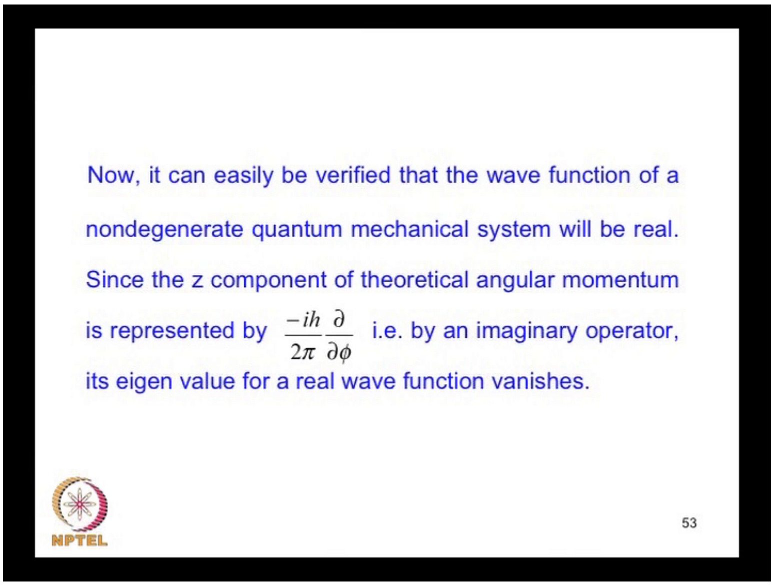

Now, it can easily be verified that the wave function of a nondegenerate quantum mechanical system will be real. Since the z component of theoretical angular momentum is represented by $\frac{-ih}{2\pi}\frac{\partial}{\partial\phi}$ i.e. by an imaginary operator, its eigen value for a real wave function vanishes.

The consequence of having a non-degenerate ground state can be readily seen from the Schrodinger equation that a non-degenerate ground state.

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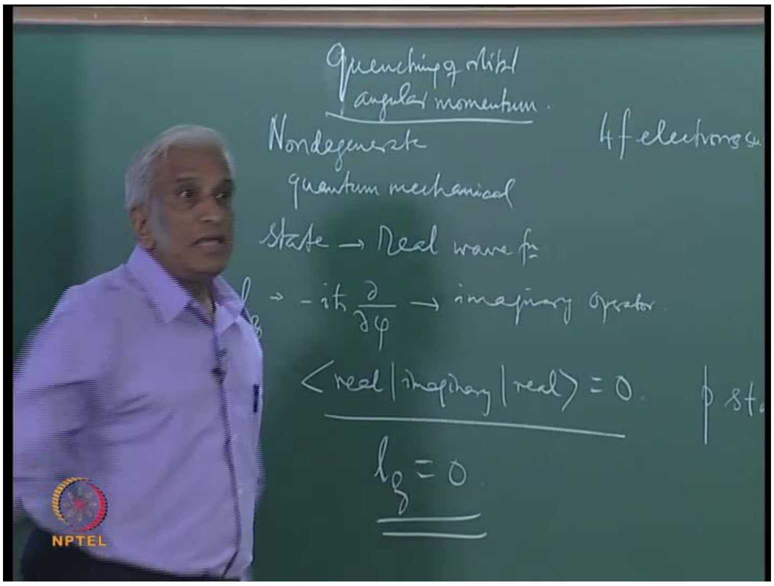

Any non-degenerate quantum mechanical state is represented by a real wave function. If the wave function is real then the z component of the angular momentum is represented by minus i h cross d by d pi in a spherically symmetric atom. So, this is l z, and therefore, this is an imaginary operator. So, if you have an imaginary operator with a real function, this will be 0, so the Eigen value will be 0. So, the Eigen value of l z vanishes for such a system, and therefore the paramagnetic moment is identically equal to 0. So, the orbital angular momentum for such a state is set to be quenched. So, this is an very famous phenomenon namely that are the quenching of the orbital angular momentum by the crystal field, crystalline a electric field of the ligands.

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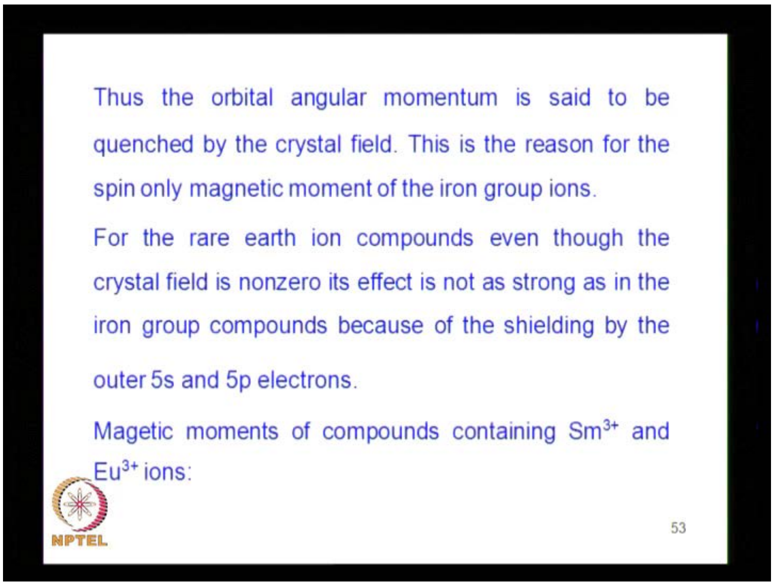

Thus the orbital angular momentum is said to be quenched by the crystal field. This is the reason for the spin only magnetic moment of the iron group ions.

For the rare earth ion compounds even though the crystal field is nonzero its effect is not as strong as in the iron group compounds because of the shielding by the outer 5s and 5p electrons.

Magetic moments of compounds containing Sm^{3+} and Eu^{3+} ions:

So, when the orbital angular momentum is quench, it does not any longer contribute to the magnetic moment and we have only a spin and the magnetic moment. We have already seen that the magnetic moment arises from two contributions, one due to the orbital angular momentum, another due to the spin angular momentum. Because the orbital angular momentum is quench, physically this means that the crystal electric field keeps the paramagnetic around locked and therefore, it is unable to reorient in the applied magnetic field. So, there is no contribution to the magnetic moment from the orbital state. Therefore, it is only the spins which contribute to the magnetic moment; where as in the case of the rare earth compound even though the crystal field is not zero, but its affect on the ion is not as strong as in the case of the ion group. Because of the shielding of the 4 f electrons by the outer 5 s and 5 p electrons.

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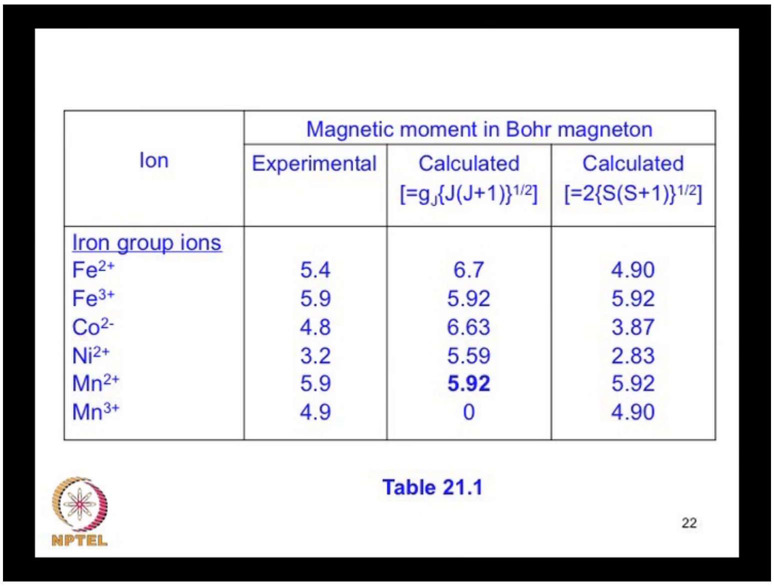

Ion	Magnetic moment in Bohr magneton		
	Experimental	Calculated $[=g_J\{J(J+1)\}^{1/2}]$	Calculated $[=2\{S(S+1)\}^{1/2}]$
Iron group ions			
Fe^{2+}	5.4	6.7	4.90
Fe^{3+}	5.9	5.92	5.92
Co^{2-}	4.8	6.63	3.87
Ni^{2+}	3.2	5.59	2.83
Mn^{2+}	5.9	**5.92**	5.92
Mn^{3+}	4.9	0	4.90

Table 21.1

So, this is the reason why the paramagnetic behavior of the ion group ions is only due to spin, if we went to the table which showed the magnetic moments calculated and experimental values of the magnetic moments of the rarer earth and the ion group ions. We will see in this table that for example, if we consider an ion like M N 3 plus, you see that the experimental value of the magnetic moment is 4.9 Bohr magnetons; whereas, the value calculated from assuming that the total angular momentum is J is exactly 0. So, is no comparison between the experimental and theoretical value. Whereas, if you consider this spin only contribution then the magnetic moment is equal to 2 twice S into S plus 1 to the power half. Therefore, that calculated value comes to be exactly the same as the experimental value for Bohr magnetons.

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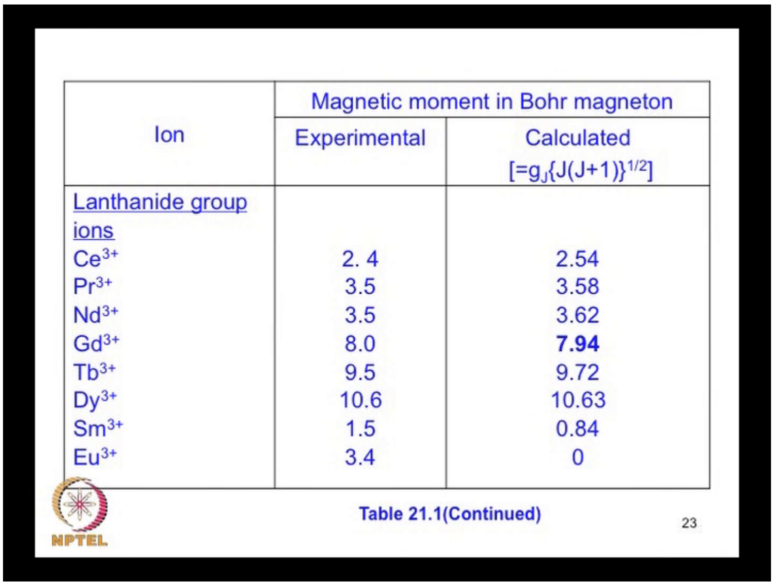

Ion	Magnetic moment in Bohr magneton	
	Experimental	Calculated $[=g_J\{J(J+1)\}^{1/2}]$
Lanthanide group ions		
Ce^{3+}	2. 4	2.54
Pr^{3+}	3.5	3.58
Nd^{3+}	3.5	3.62
Gd^{3+}	8.0	**7.94**
Tb^{3+}	9.5	9.72
Dy^{3+}	10.6	10.63
Sm^{3+}	1.5	0.84
Eu^{3+}	3.4	0

Table 21.1(Continued)

Whereas in the case of rare earth ion that is very good agreement between the experimental and calculated values on the basis the assumption that the total angular momentum J is the resultant of l and s that is both orbital and spin contributions exist. So, this is the main difference between the rare earth ions and the ion group ion.

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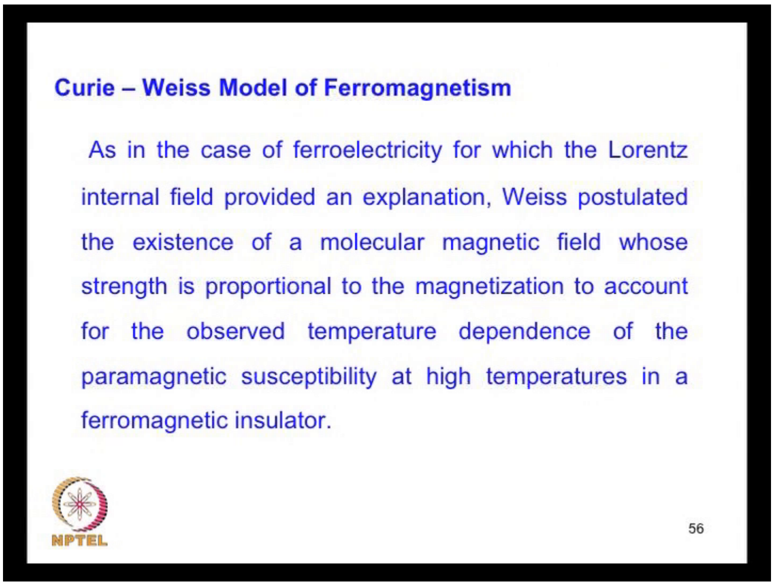

Curie – Weiss Model of Ferromagnetism

As in the case of ferroelectricity for which the Lorentz internal field provided an explanation, Weiss postulated the existence of a molecular magnetic field whose strength is proportional to the magnetization to account for the observed temperature dependence of the paramagnetic susceptibility at high temperatures in a ferromagnetic insulator.

Next we pass on to very important topic, the entire problem of magnetism is of interest for practical reasons only because of the existence of phenomenon ferromagnetism. Paramagnetic moments as well as diamagnetic moment are extremely weak, and they are badly perceptible in ordinary experiments. It is only because of existence of ferromagnetic materials such as cobalt, iron and nickel that there is a lot of current interest in magnetism as the phenomena with respect to practical applications as well as theoretical explanations.

So, what is ferromagnetism, in the case of ferromagnetism, we recall what happened in the case of the dielectric materials, we had noted that the under with the presence of the Lawrence internal field in a dipolar solid, let to the phenomenon of a raw electricity under certain conditions. Very similar to that a ferroelectric phenomenon meant that there existed at spontaneous polarization. In other words, the dielectric get polarized even in the absence of an applied electric field, in the case of a ferroelectric material. Similarly, in the case of the ferromagnetic material, the magnetic material flows magnetism even in or a magnetization even in the absence of an applied magnetic field. Even if you have a piece of iron which has been magnetized then even then you do not have an applied magnetic field, even if you keep it like this get a piece of iron, it will attract another bar magnet showing the magnetic effect. So, you do not add up apply a magnetic field in order to produce this.

So, there already a spontaneous magnetism present in such a ferromagnetic material. This is not there in the case of diamagnetism. In the case the diamagnetic, the magnetization is percent only as long as the field is apply, it vanishes when the field is removed. In the case of the paramagnetic moment, this is not the case there is a net magnetic moment in the presence of the field which is proportionate which increases with the up magnets strength of the applied electric field, until the you reach saturation. But still the bad magnitude at this effect is very weak, in comparison to a ferromagnetic. So, wise postulated that the existence of a molecular magnetic field whose strength is proportionate to the magnetization in order to account for the observed temperature-dependent of the paramagnetic susceptibility at high temperature in a ferromagnetic insulator. So, this is what we are going to consider now.

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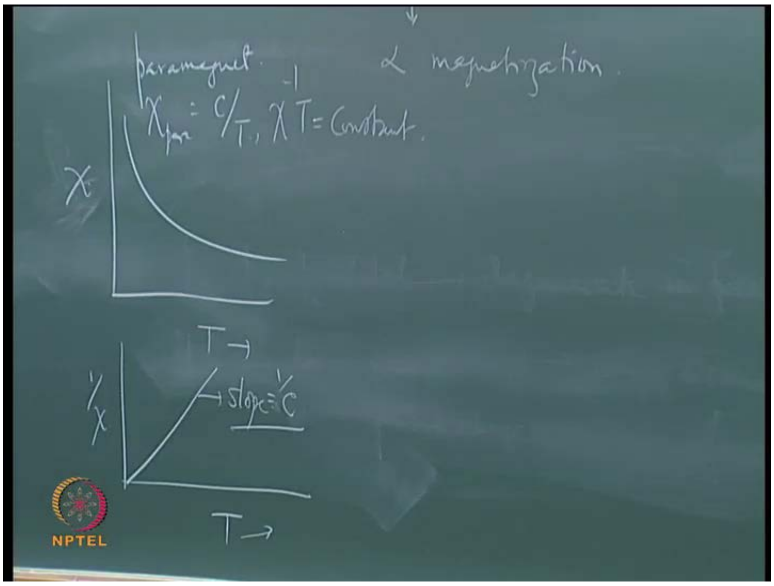

So, Weiss molecular field hypothesis, this molecular field is very similar to the Lorentz internal field in a dielectric. So, this is hypothesize, and this molecule field this strength of this proportional to the magnetization. This is the hypothesis by Weiss in order to account for the observed temperature dependent for the paramagnetic susceptibility of such a material at high temperature. Now how does the paramagnetic susceptibility of such a ferromagnetic insulate depend on the temperature. We have already seen that in the case of a paramagnet, this paramagnetic susceptibility equal C by T where, C is the Curie constant.

So, if I plot be 1 by chi versus T e, this product is a constant. So, we are going to get a if I plot chi versus T is going to be at hyperbola rectangular hyperbola, but if I plot one by chi against temperature then this is going to be a straight line, because 1 by chi is proportion to T, it is T by C. So, this is a straight line through the origin with the slope equal to C or 1 by C, 1 by the curie the reciprocal as a curie constant. So, this is the behavior in the case of the high real paramagnet, but this is a rarely observed in practice, because there is no material which remains the paramagnetic down to the lowest temperatures. At some low temperature, which is low enough, there is a ferromagnetic order, as you will see ferromagnetism is because of an ordering of the magnetic moments.

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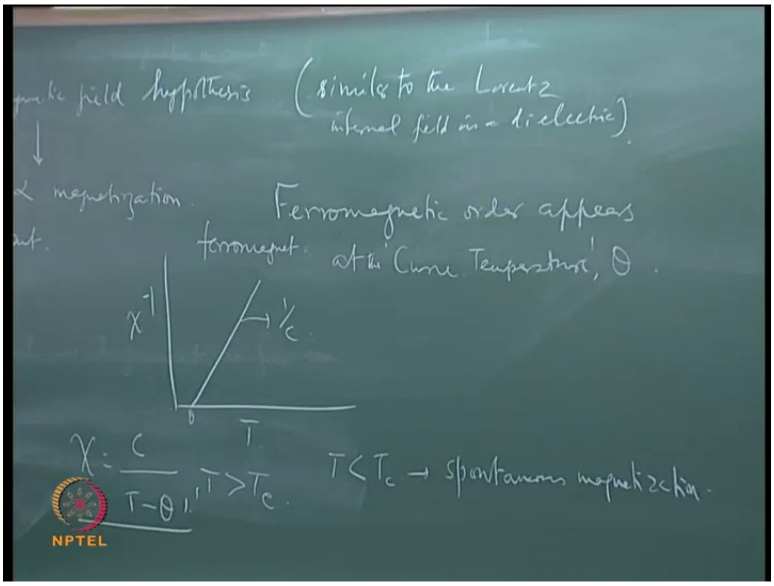

field hypothesis (similar to the Lorentz internal field in a dielectric)

$\propto$ magnetization

ferromagnet.

Ferromagnetic order appears at the 'Curie Temperature', θ.

$\chi = \frac{C}{T-\theta}$, $T > T_c$.

$T < T_c \rightarrow$ spontaneous magnetization.

So, the ferromagnetic order sets in at some temperature known as the Curie, it temperature appear at what is known as the curry temperature being be indicated by theta.

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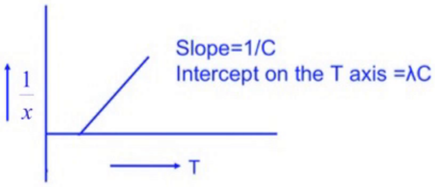

Fig.21.2 Plot of reciprocal of susceptibility with temperature for a ferromagnet

In which case the xi versus T behavior such a ferromagnetic rather the k involves versus T is not a straight line through the origin, but it is a straight line with an intercept on the T the axis and this intercept is as the value theta its slope is still 1 by C. In other words, chi is C by T minus theta. So, this is the for the temperatures greater than the d ferromagnetic transition temperature are critical temperature T c. So, the paramagnetic susceptibility obeys.

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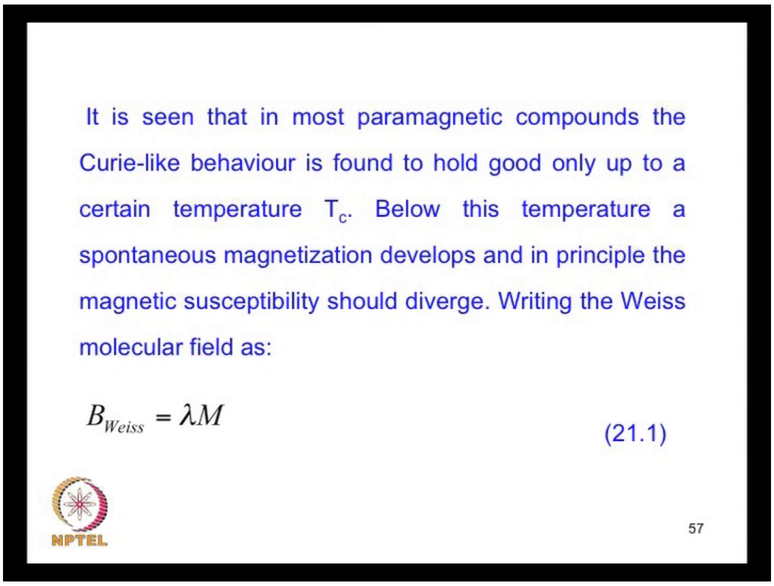

It is seen that in most paramagnetic compounds the Curie-like behaviour is found to hold good only up to a certain temperature T_c. Below this temperature a spontaneous magnetization develops and in principle the magnetic susceptibility should diverge. Writing the Weiss molecular field as:

$$B_{Weiss} = \lambda M \qquad (21.1)$$

Variation of the chi C by T minus theta, and below this temperature at for T less than T C as we have already seen ferromagnetism sets N and we have a spontaneous magnetization that is we have a magnetization, non-zero magnetization below T C even when there is no applied magnetic field. Therefore, in principle the magnetic susceptibility which is the ratio of these two, the magnetization to the applied field for diverge. So, this is very similar to the polarization catastrophe in the case of a ferroelectric.

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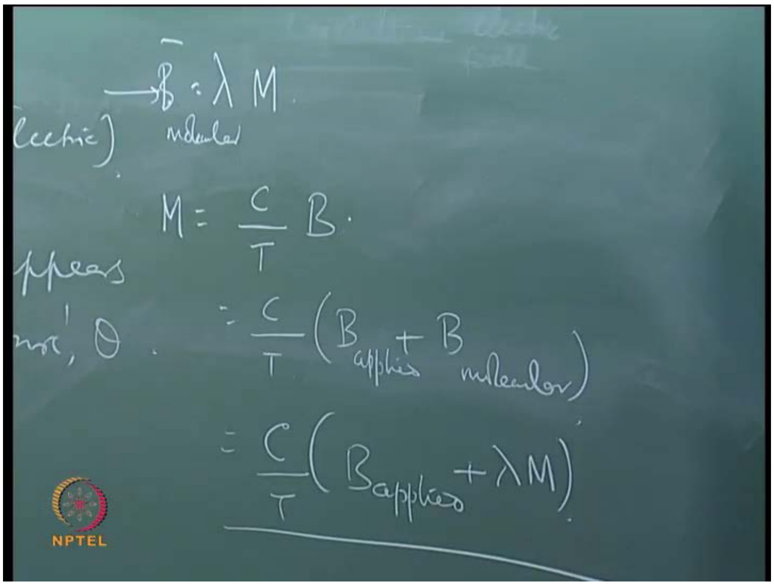

$$B_{molecular} = \lambda M$$

$$M = \frac{C}{T} B$$

$$= \frac{C}{T}\left(B_{applied} + B_{molecular}\right)$$

$$= \frac{C}{T}\left(B_{applied} + \lambda M\right)$$

So, we can write this molecular magnetic field, since it is proportional to the magnetization, we can write it as B molecular equals lambda M, where lambda is a constant known as the molecular field concept. So, now we have M equal to C by T times B that is the well known behavior of the magnetization.

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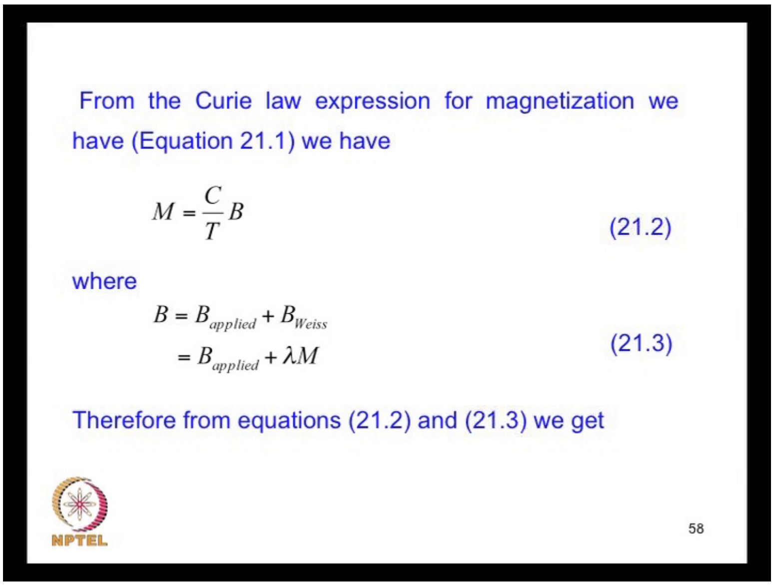

From the Curie law expression for magnetization we have (Equation 21.1) we have

$$M = \frac{C}{T} B \qquad (21.2)$$

where

$$\begin{aligned} B &= B_{applied} + B_{Weiss} \\ &= B_{applied} + \lambda M \end{aligned} \qquad (21.3)$$

Therefore from equations (21.2) and (21.3) we get

Now the B is not what you have applied, but it is the sum of the B applied plus the B molecular. Therefore, this is C by T into B applied plus lambda M. Since I have terms involving the magnetization M on both the left and right sides of this is equation, we will bring it together and write M into 1 minus C by T into lambda equals C by T in to B applied.

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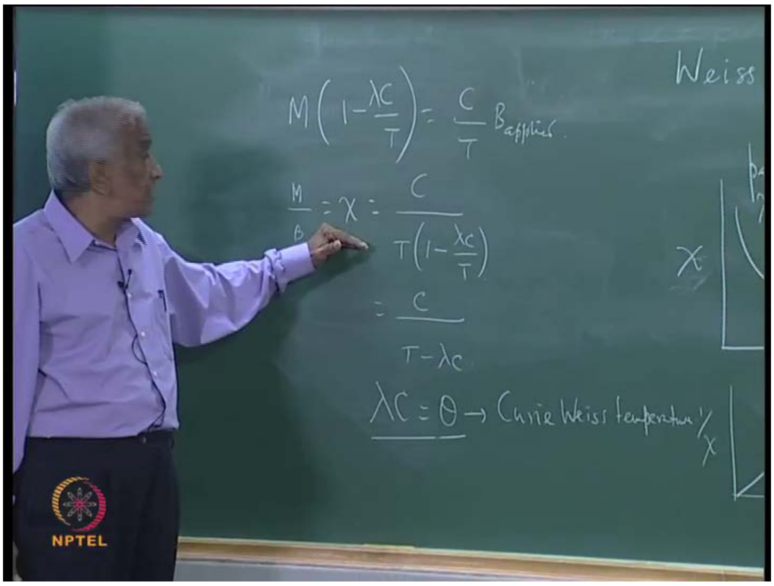

So, M by B which is chi in the linear region of the response is C by T in to 1 minus lambda C by T and that is equal to C by T minus lambda C, so lambda C equal theta. So, we are able account for using the molecular field hypothesis of Weiss, we are able to account in a very simple way to the for the existence of the Curie-Weiss temperature theta is known as a Curie-Weiss temperature. So, the molecule field hypothesis accounting for rather simple way straightforward manner, go for the variation experimentally observed temperature variation of the paramagnetic susceptibility at temperatures about the ferromagnetic Curie point, our transition temperature. So, this is what we have seen and now we would like to use this molecular field hypothesis to developed a criterion for the existence of ferromagnetism, using the theory that we have used already.

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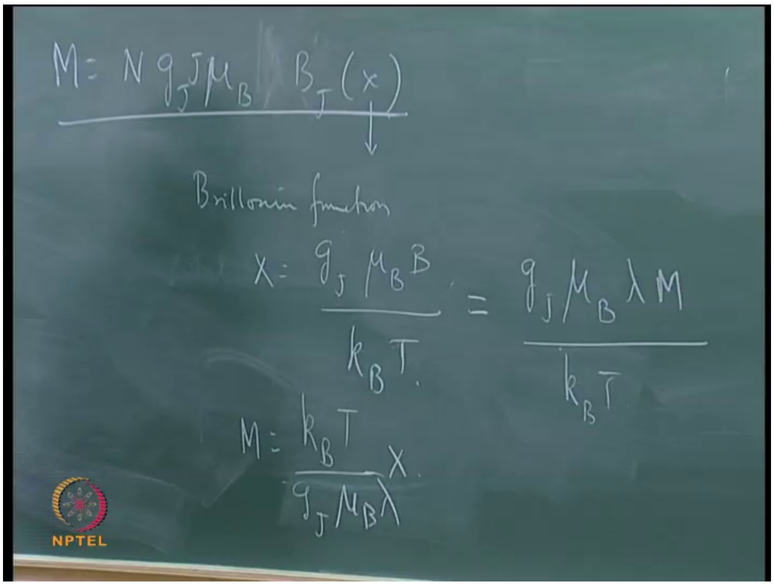

$$\underline{M = N g_J J \mu_B B_J(x)}$$

$\downarrow$ Brillouin function

$$x = \frac{g_J \mu_B B}{k_B T} = \frac{g_J \mu_B \lambda M}{k_B T}$$

$$M = \frac{k_B T}{g_J \mu_B \lambda} x$$

So, let us do this now. So, we have according to the theory M is N g J mu B B J into B J of x, N g J into J mu B into B J of x. Where B J of x is the Brillouin function and X is g J mu B by k B T. And since we know that in the absence of an applied magnetic field this will simply be g J mu B lambda M, which s the Weiss molecular field by k B t.

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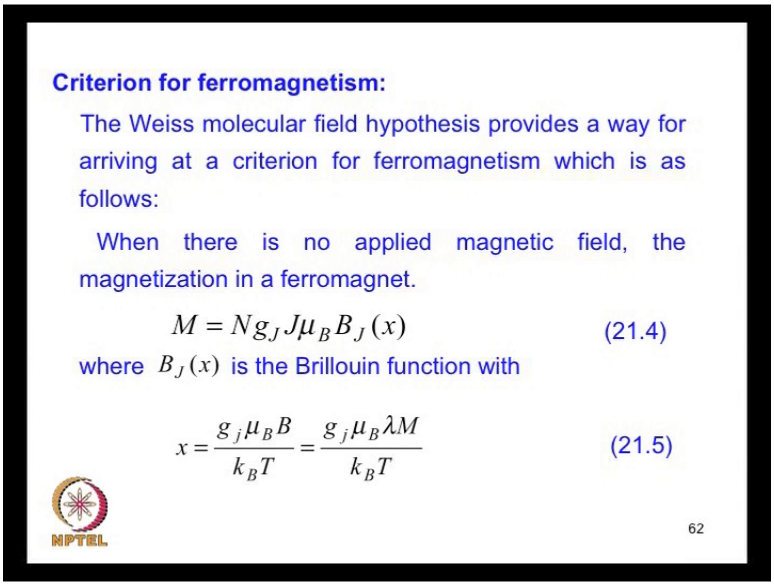

Criterion for ferromagnetism:

The Weiss molecular field hypothesis provides a way for arriving at a criterion for ferromagnetism which is as follows:

When there is no applied magnetic field, the magnetization in a ferromagnet.

$$M = N g_J J \mu_B B_J(x) \qquad (21.4)$$

where $B_J(x)$ is the Brillouin function with

$$x = \frac{g_j \mu_B B}{k_B T} = \frac{g_j \mu_B \lambda M}{k_B T} \qquad (21.5)$$

So, we have already one equation governing the magnetization and now this gives me another equation for the magnetization by inverting this. So, this is going to be k B T by g J mu B times X lambda.

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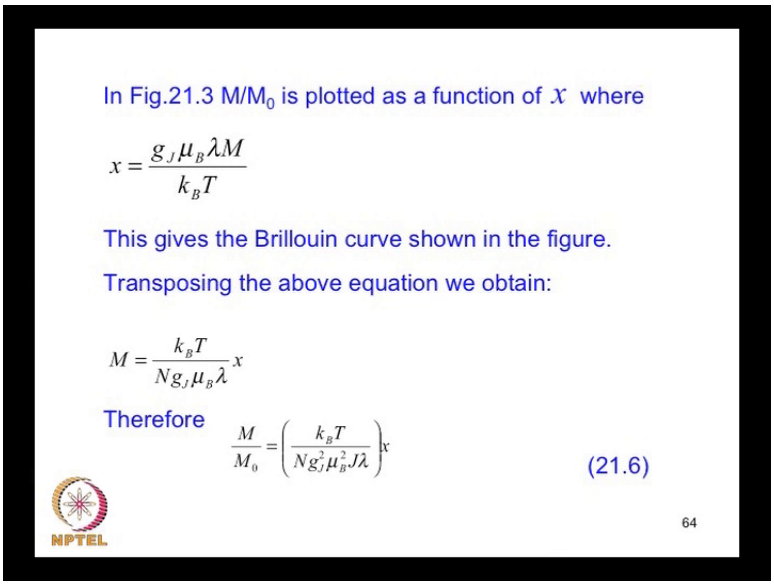

In Fig.21.3 M/M$_0$ is plotted as a function of x where

$$x = \frac{g_J \mu_B \lambda M}{k_B T}$$

This gives the Brillouin curve shown in the figure.

Transposing the above equation we obtain:

$$M = \frac{k_B T}{N g_J \mu_B \lambda} x$$

Therefore $$\frac{M}{M_0} = \left(\frac{k_B T}{N g_J^2 \mu_B^2 J \lambda} \right) x \qquad (21.6)$$

So, I have two equations now for the magnetization in this case one according to the well known below in function independent which we are derived earlier in the last time and we also have another relation for the magnetization by at the molecular field. So, both of this have to be satisfied then there is such a vise molecular presence a field percent. So, we have solve both this equation simultaneously in order to applying a solution for the magnetization. So, we do this graphically by means of a graphical method.

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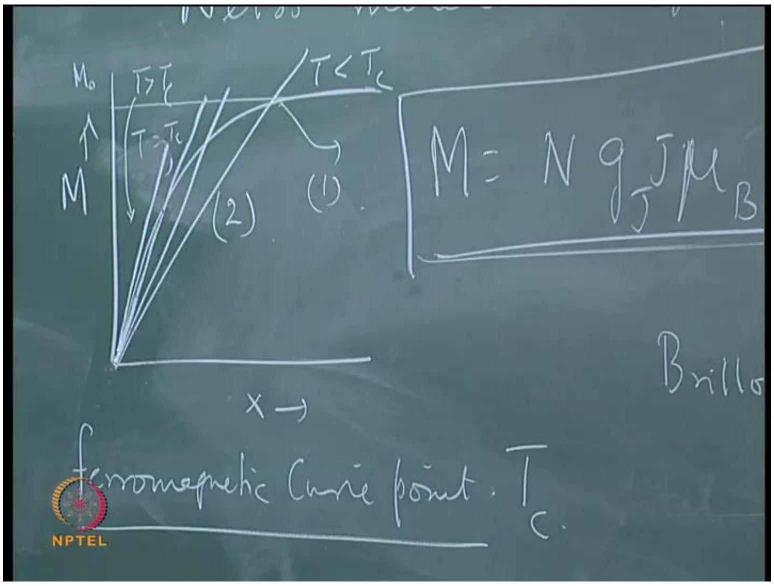

So, if we plot this below in function we are going to get M versus x is going to be the believing function dependence which we have seen already.

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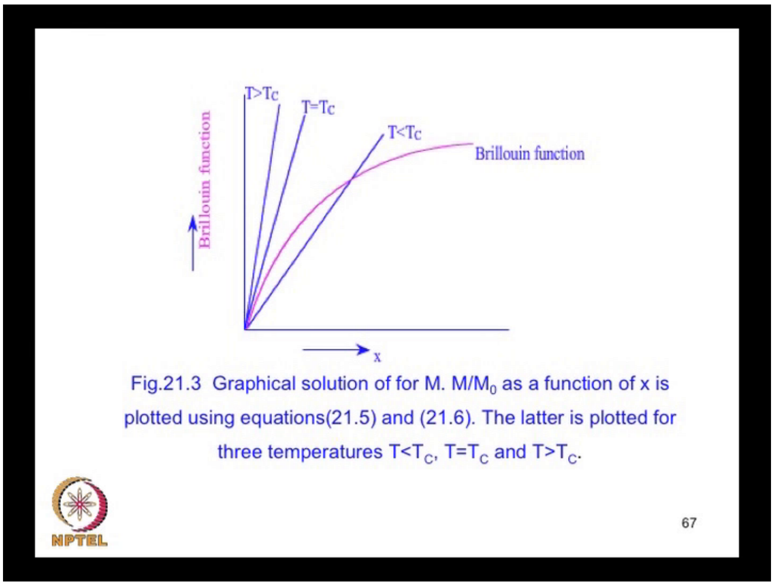

Fig.21.3 Graphical solution of for M. M/M_0 as a function of x is plotted using equations(21.5) and (21.6). The latter is plotted for three temperatures $T<T_C$, $T=T_C$ and $T>T_C$.

So, this is M naught in addition we also have a linear relation between M and x given by this equation by equation two. So, this is going to be a linear relation. So, this is one this is to. So, the graphical method involves the simultaneous presence of this two. So, the graphically the intersection of these two show this graphically the intersection of these two graphs gives you the magnetization. So, this is the situation, but as I see as to be vary the field r the temperature in this case we see that slope of these graph change here and. So, we have successively straight lines like this. So, eventually a situation is reached when this straight line touches this below in function graph idea at the origin.

So, a simultaneous solution of one and two is not possibly for values of the temperature which are which is that it goes beyond this saw there the straight-line is just conjunction at the origin to the bellowing function graph at to the transition temperature this point is defined as the point at which the transition takes place. So, above this when there is a simultaneous solution for these equation then you say that that is a spontaneous magnetization. And there is a ferromagnetic order presence for temperatures below the this, this point that for for these the slope is that that is all you have situation like this is the greater than T C and this is p less than a T C and this corresponds to T equals to T c.

So, the ferromagnetic curie point is defined by the simultaneous solution as the point that which the linear graph is tangential to the following function. Since we know the slope of the bellowing function expression at the origin, we can equate the slope of the straight line and the slope at the below in function in order to obtain this ferromagnetic curie point.

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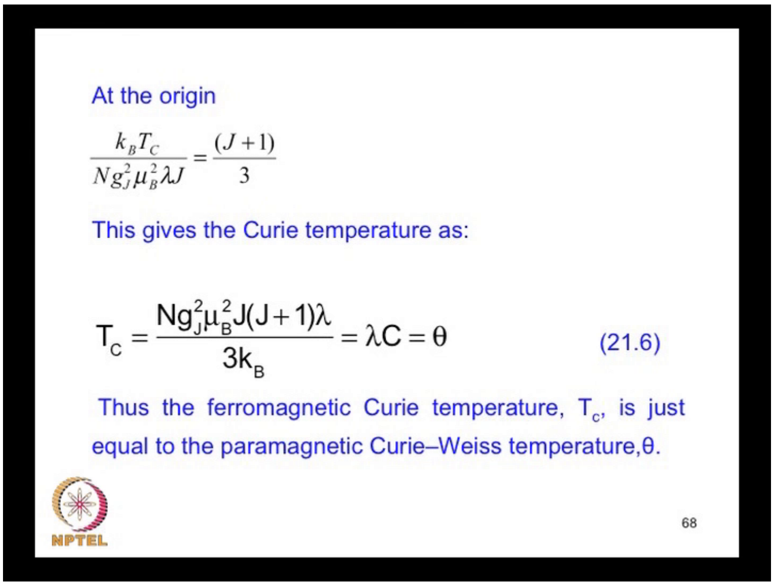

At the origin

$$\frac{k_B T_C}{N g_J^2 \mu_B^2 \lambda J} = \frac{(J+1)}{3}$$

This gives the Curie temperature as:

$$T_C = \frac{N g_J^2 \mu_B^2 J(J+1)\lambda}{3k_B} = \lambda C = \theta \qquad (21.6)$$

Thus the ferromagnetic Curie temperature, T_c, is just equal to the paramagnetic Curie–Weiss temperature, θ.

So, this is what we do. So, at the origin this slope a is J plus 1 by 3 that is the sloop at the origin and that will be equal to this k B T C by g J nu B lambda. So, that gives the expression for T c. So, we get T C as T C equal g J mu b J plus 1 into lambda by 3 k B T, this is really J into J plus 1 by 3. And we know g J mu B into J into J plus 1 by 3 k B is our effective magnetic moment, and therefore, this is if this ferromagnetic curie temperature is the same as the curie wise temperature then this is lambda C equal to theta. So, this tells me since curie constant is just this therefore, this is just lambda C.

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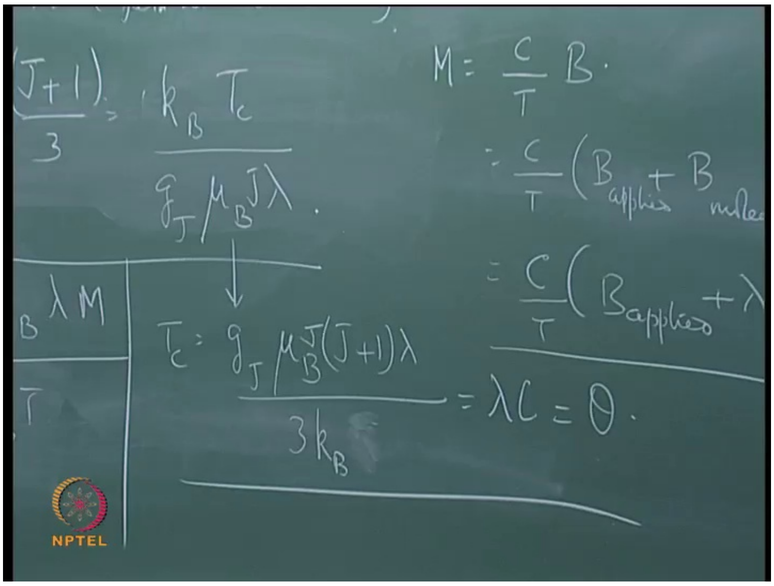

$$\frac{J+1)}{3} = \frac{k_B T_c}{g_J \mu_B J \lambda}.$$

$$\frac{{}_B \lambda M}{T}$$

$$T_c = \frac{g_J \mu_B J(J+1)\lambda}{3k_B} = \lambda C = \theta.$$

$$M = \frac{C}{T} B.$$

$$= \frac{C}{T}(B_{applies} + B_{molec}$$

$$= \frac{C}{T}(B_{applies} + \lambda$$

So, this just say the T c the ferromagnetic curing temperature is the same as the curie wise temperature according to the molecular field theory of a ferromagnetic. Of course, all this is very nice phenomenon logically, it gives a very nice explanation for all the at the effects enough paramagnetism and special ferromagnetic material. But still we are left with the basic question of what is a responsible for the existence of such a molecular magnetic field wise hypothesis remains the hypothesis is it does not address this question because monocular field as will see is basically of a quantum-mechanical origin. So, it needs a quantum-mechanical explanation to understand, why this molecular feel arises in the case of a is a order ferromagnetic material made he this quantum mechanical molecular field is known as the exchange field by reasons you will see. So, this is arises from what is known as the exchange interaction.

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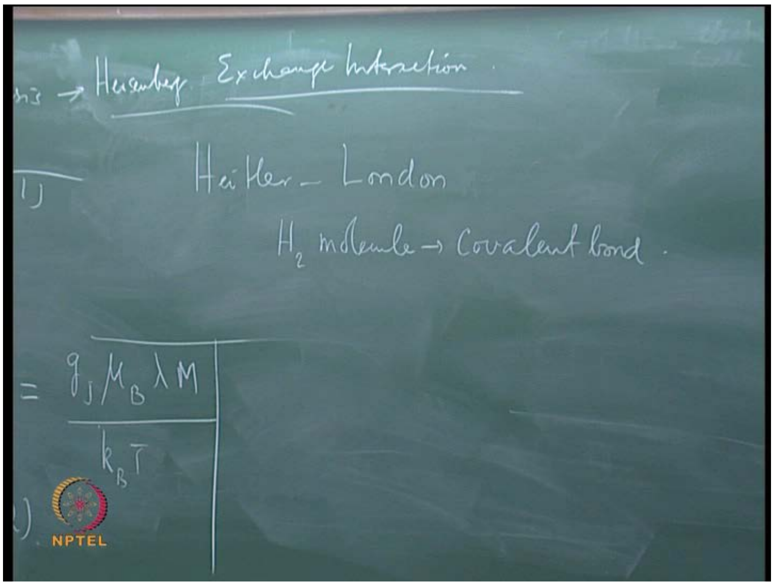

So, next we will deal with the exchange interaction. So, the exchange interaction was proposed that the theory this was proposed by Heisenberg. So, it is known as the Heisenberg exchange interaction. So, this is the one this interaction is responsible for this molecular field theory in order to understand the origin of this exchange material mechanism you have to consider the theory of covalent bonding of a homo nuclear diatomic molecule such as I hydrogen which was originally proposed Heitler and London. So, if you take hydrogen molecule which consists of two hydrogen atoms which are bonded together. And the nature of the bonding is that they sadly electrons and farm what is known as the covalent bond Heitler and London considered this model of a diatomic molecule homo nuclear diatomic molecule by hydrogen and stated that the electron shared between the two bonded atoms. So, that a given the electron belongs to the equal probability to either of the two atoms.

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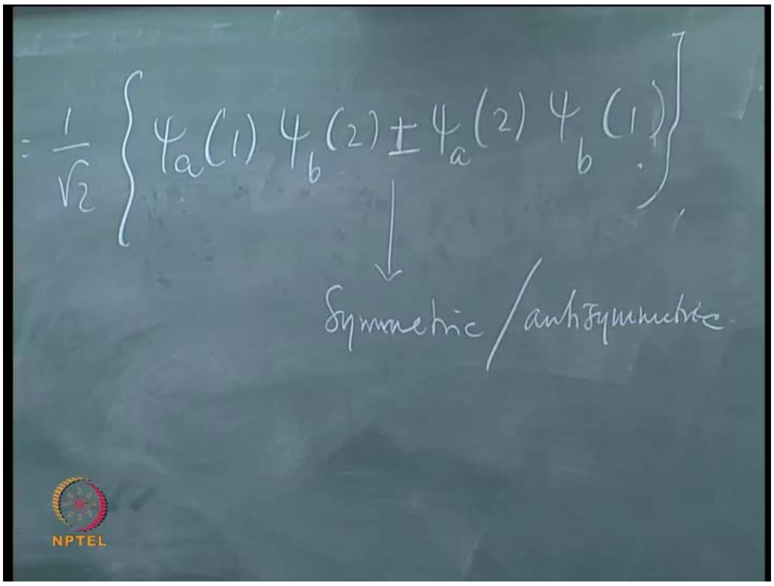

$$= \frac{1}{\sqrt{2}} \left\{ \psi_a(1)\, \psi_b(2) \pm \psi_a(2)\, \psi_b(1) \right\}$$

$\downarrow$

Symmetric / antisymmetric

So, we can write the two electron way function of such a state as the two-electron wave function is written as since it involves two electron let me write electron one, electron two. So, this will be one by root 2 psi a 1 psi b 2 plus psi a 2 psi b 1, what is the meaning of this when a write it can be plus or minus. In other words, you have two combinations linear combinations of the individual atomic wave functions. They are known as psi a and psi b 2, psi a 1 means electron one is belongs to atom a in the hydrogen molecule we have to atoms two hydrogen atoms one is called a, another is called b. So, we can have the electron one sitting with atom a and then the electron two sitting with atom b. So, such a state is called psi a 1 for the electron one and phi b 2 for the for the electron two. So, the total electron way two electron way function is a simple product of these two. So, it is psi a 1 psi b two, but as the model says a two electrons can be shared by the two atoms and therefore, a given an electron can belong with equal probability to either of the two atoms.

So, it is not necessary that the electron one should be that nuclear a instead electron one can also belong to nuclease B p and the electron two will then belong nucleus a. So, in this case, the two-electron wave function product wave function will have the form psi a 2 psi B. And the model say both these wave functions psi a 1 psi b 2 and psi a 2 psi b 1 are equally probable. Since it is only the mode of the sigh square which is which is related to the probability and therefore, as the real significant.

So, we can have these equal probability represented by either a symmetric linear combination of these two functions corresponding to the plus sign here or an anti symmetric. So, you have a symmetric linear combination or anti-symmetric linear. The anti symmetric combination corresponds to the negative sigh, because if you are interacting done it changes a sign. So, it is anti symmetric with respect to exchange that is why you call it an anti-symmetric linear combination- negative sign. If it is a plus sign it is symmetric if you exchange nothing happens the sign remains the same. So, it is symmetric with respect to exchange. So, you have a symmetric linear combination as well as on anti symmetric linear combination both are equally valid wave function for the two electron system.

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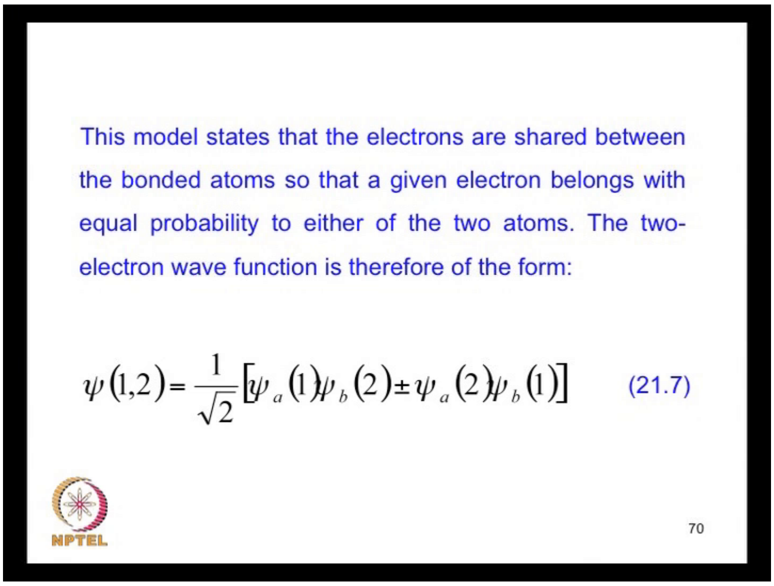

This model states that the electrons are shared between the bonded atoms so that a given electron belongs with equal probability to either of the two atoms. The two-electron wave function is therefore of the form:

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right] \qquad (21.7)$$

This is what you have you use in the Schrodinger equation for hydrogen molecule. So, next step in writing this Schrodinger equation is to write the Hamiltonian.

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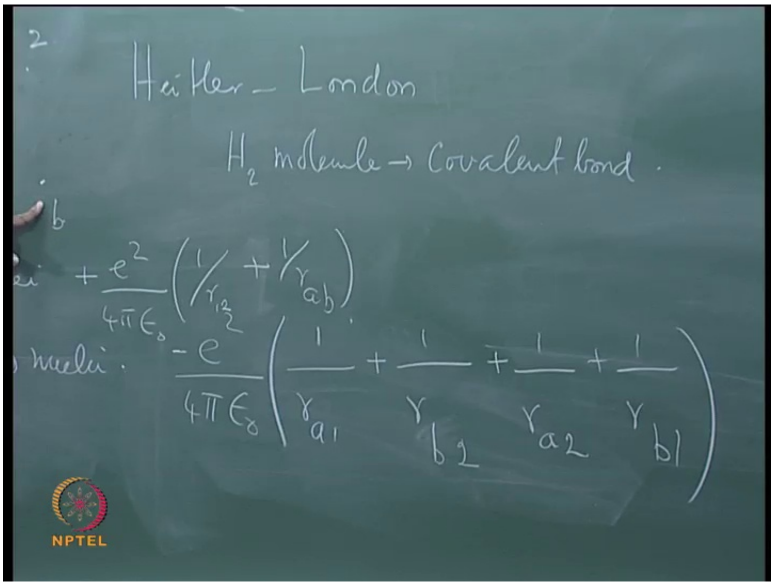

Heitler – London

H_2 molecule → Covalent bond.

$$+\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{ab}}\right)$$

nuclei : $$\frac{-e}{4\pi\epsilon_0}\left(\frac{1}{r_{a1}}+\frac{1}{r_{b2}}+\frac{1}{r_{a2}}+\frac{1}{r_{b1}}\right)$$

So, that we have eights sigh equal e site as the Schrodinger equation that gives you the this is the Hamiltonian operator operating on this wave function giving rise to the energy Eigen value in which what we are interested. We are interested in the basic question why is the ground state of this molecule lower in energy, why the energies lowered by the bonding by the formation of the molecule instead of being two separate atoms, why it has the two atoms system prefer to form a molecule? The answer is that it is because the molecular configuration is lowering energy and therefore, has greater stability. So, we have to find the energy which mean that we have to solve the Schrodinger equation which involves a Hamiltonian operator.

So, we have to next consider the Hamiltonian of these two electron system. So, the various term are P 1 square plus by 2 M plus P 2 square by 2 M which is the which are the kinetic energies of the two electrons. So, I have two nucleate and two electrons. So, what is the energy? Now these are electrons and these are positive nuclei charges. So, there are electron repulsion terms. Now this can be by this is one possibility another, so you have various interactions possible now. So, the nuclear repel as well as the electrons repel. So, you have various distances which will determined this repulsion energy plus column repulsion of electrons and nuclei as well as the nuclei plus column attraction terms between electrons and nuclei. The attractive terms are negative and the repulsive terms are positive. So, the attractive term are example, half minus e square by for phi epsilon naught. Since it is a hydrogen atom, you have one-electron; and the nucleus of charge equal to the electronic charge.

So, I have minus into one by r a 1 - that is the distance between a and 1. And then, so these are all attractive, because it is between nucleus a and electron one, and then nucleus b and electron two, and nucleus a and electron two, nucleus b and electron one all of which are attractive terms. So, you have 4 such terms. Whereas, the repulsive terms which are positive in sign are plus e square by 4 by epsilon naught times 1 by r 1 2 plus 1 by r a b. So, these are the distances between the two nuclei r a b and the two-electron r 1 2 both of each are equals. So, all these terms enter into the Hamiltonian and we use this Hamiltonian and these two electron wave function to solve for the Eigen values at the molecular state, ground state. And that will give us a clue for the presence of the exchange interaction. We will consider the solution in the next lecture.

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