ELEMENTS OF MODERN PHYSICS

Prof. Saurabh Basu
Department of Physics
IIT Guwahati

Lec 26: Magnetism and Magnetic Materials

Welcome to this last module of solid-state physics, in which we will cover magnetism and superconductivity back to back. And because, you know, the whole of solid-state physics is merged into one week or one module, we will have to be quick and will only give you the bare minimum description of both magnetism and superconductivity. But nevertheless, these are very important topics, and one should learn them more rigorously than what will be presented in this course. We will try to give you a bird's-eye view, and you can build upon that. So we will start with magnetism and we talk about different types of magnetic ordering which you all are familiar with and in particular we will talk about dia, para and ferromagnets.

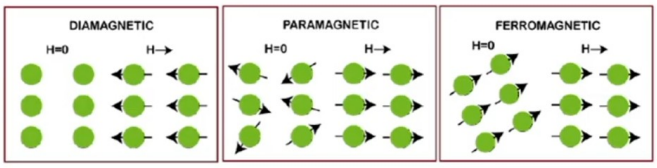
There are also antiferromagnets and ferrimagnets and so all those things we will not talk about here. So we will give examples of magnetic materials. And the main part of this discussion will form out of these elementary treaties of magnetic ordering, which means that we'll talk about dia, para and ferromagnets to the extent we can in this course. So starting with a bit of history of the magnetic phenomena, the magnetic phenomena was discovered a long time back. In lodestone, and lodestone is actually a naturally magnetized piece of mineral.

It's a magnetite, rather an iron oxide, which is one of the main iron ores. And you see the picture that it actually catches a lot of nails there. It attracts and holds all these nails there. The Greek philosophers have discussed magnetism between 625 before Christ to about 545 before Christ. And the ancient Indian medical text, Sushruta Samhita, it also has mentioned about usage of these magnetites in removing metallic objects embedded in a person's body.

And in ancient China, the earliest mention of a lodestone attracting a needle is found in the first century work there. So the different types of magnetism that we are going to talk about here is diamagnetism. Diamagnetism is the tendency of a material to oppose an applied field, magnetic field. And therefore, it's repelled by a magnetic field or rather the ordering takes place in a direction which is opposite to the field. And diamagnetic materials have no unpaired electrons.

Different types of magnetism

- Diamagnetism: Diamagnetism is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. In a diamagnetic material, there are **no unpaired electrons**.
- Paramagnetism: In a paramagnetic material there is a tendency to enhance an external magnetic field inside the material. A paramagnetic material **has unpaired electrons**.
- Ferromagnetism: Ferromagnetic materials possess intrinsic magnetic moments that tends to be parallel to an applied field and enhance the external field. Has **unpaired electrons too**.

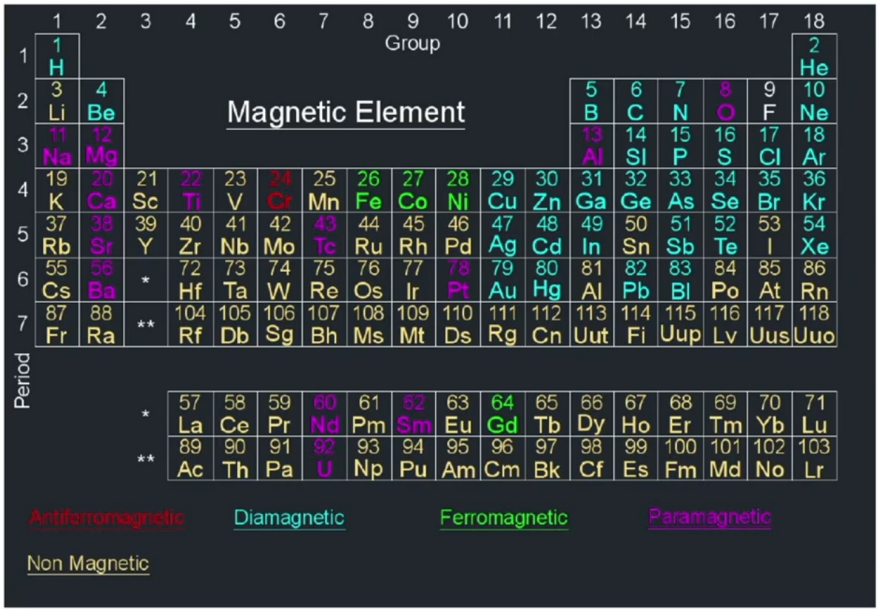


And this puts them in direct contrast with paramagnetism where there are a lot of unpaired electrons there. And this paramagnetic material may not have a magnetization of their own. But when it is put in a magnetic field, they develop magnetic moments. And ferromagnetic materials, they possess intrinsic magnetic moments and they tend to align parallel to the applied field and enhance the external field in the way. It has also unpaired electrons.

And this picture that you see there is a schematic representation. All these green dots are the particles carrying the spin like the electrons. At H equal to 0, you have these neutral particles. They do not do anything. If you put an H pointing in the rightward direction, then the magnetization develops in the leftward direction as shown.

So paramagnet in no magnetic field that is H equal to 0. So here we denote the magnetic field intensity or the magnetic field by H. And when you put them in a magnetic field, there is a development of the magnetic moment along the direction of the field. So, these are paramagnetic materials and as said earlier that they have a lot of unpaired electrons and same goes with ferromagnetic material in the absence of a field. They have the magnetic moment pointing in a certain direction. If you expose them to an external field, then of course, the magnetization takes place in a direction of the external field.

This is a periodic table that's known to everybody and we are simply showing the different magnetic elements there. So the red are the antiferromagnetic elements which are chromium as you can see here. There are a lot of diamagnetic materials which are copper, zinc, silver, cadmium and so on which are here in this region. Let me use a color maybe. So this is in this region and so on.



And then, of course, there are a lot of them here. And that's the diamagnetic materials. And we have ferromagnetic. These are the well-known ferromagnets, that is, iron, cobalt, nickel. and also gadolinium here.

These are well-known ferromagnets with a large sort of magnetic susceptibility. We'll talk about that in a while. And there are paramagnetic materials, which means they do not have magnetic properties of their own. but they show magnetism when they are exposed to external magnetic fields and these are these pink colors like aluminium that you see here, oxygen, samarium, neodymium, TC and uranium and all that and then something that is here. They are also paramagnetic and these are the rest of them which are shown here by a dull yellow color that those are all non-magnetic materials. All right. So we'll sort of go on to discuss some quantitative aspects of this magnetism. And we start with the molar susceptibility. So we define magnetization M, which we have defined earlier—that magnetization appears in a magnetic material when there is an applied magnetic field.

Molar susceptibility

- Molar susceptibility: When a magnetization $\boldsymbol{M}$ appears in a magnetic material due to an applied magnetic field $\boldsymbol{H}$,

$$\boldsymbol{M} = \kappa \boldsymbol{H} \tag{1}$$

we can define molar susceptibility χ_m as,

$$\chi_m = \kappa V_m = \kappa \frac{M}{\rho}$$

κ volume susceptibility
V_m: molar volume,
M: Molar mass,
ρ: mass density

And we write these linear relations. These are called linear magnets. because M is proportional to single power of H. There could be a non-linearity there at large fields, but we don't talk about them here. And these M equal to kappa H and these molar susceptibility chi M is defined as this kappa into V M, where V M is the molar volume and H equal to kappa into M over rho. M is the molar mass and mass density, and so on and so forth.

So these are the quantitative way of, you know, describing a magnetic system. Very large number of elements are presented here and you see that there are these ferromagnets which are here and there are these nickel is a ferromagnet, manganese is also a ferromagnet and so on. And there are a varied degree of, you know, this values of chi m expressed in 10 to the power minus 6 centimeter cube per mole. And this sort of tells you that essentially gives you the same information that the periodic table gives. And here these values are presented, numerical values are presented.

Magnetic susceptibility of some magnetic elements

Element	χ_m ($\times 10^{-6} cm^3/mol$)	Element	χ_m ($\times 10^{-6} cm^3/mol$)
Aluminum (Al)	+16.5	Nickel (Ni)	Ferro
Bismuth (Bi)	-280.1	Molybdenum (Mo)	+72.0
Boron (B)	-6.7	Phosphorus, Black (P)	-26.6
Calcium (Ca)	+40.0	Platinum (Pt)	+201.9
Carbon (C)	-6.0	Potassium (K)	+20.8
Cesium (Cs)	+29.0	Silicon (Si)	-3.9
Chromium (Cr)	+16.7	Silver (Ag)	-19.5
Copper (Cu)	-5.46	Strontium (Sr)	+92.0
Cobalt (Co)	Ferro	Sulfur α (S)	-15.5
Gallium (Ga)	-21.6	Sodium (Na)	+16.0
Gold (Au)	-28	Tantalum (Ta)	+154.0
Indium (In)	-64.0	Thorium (Th)	+132.0
Iron (Fe)	Ferro	Thallium (Tl)	-50.0
Lanthanum (La)	+118.0	Tin Gray (Sn)	-37.0
Lead (Pb)	-23.0	Titanium (Ti)	+151.5
Lithium (Li)	+14.2	Tungsten (W)	+59.0
Manganese-α (Mn)	+529.0	Zinc (Zn)	-11.4

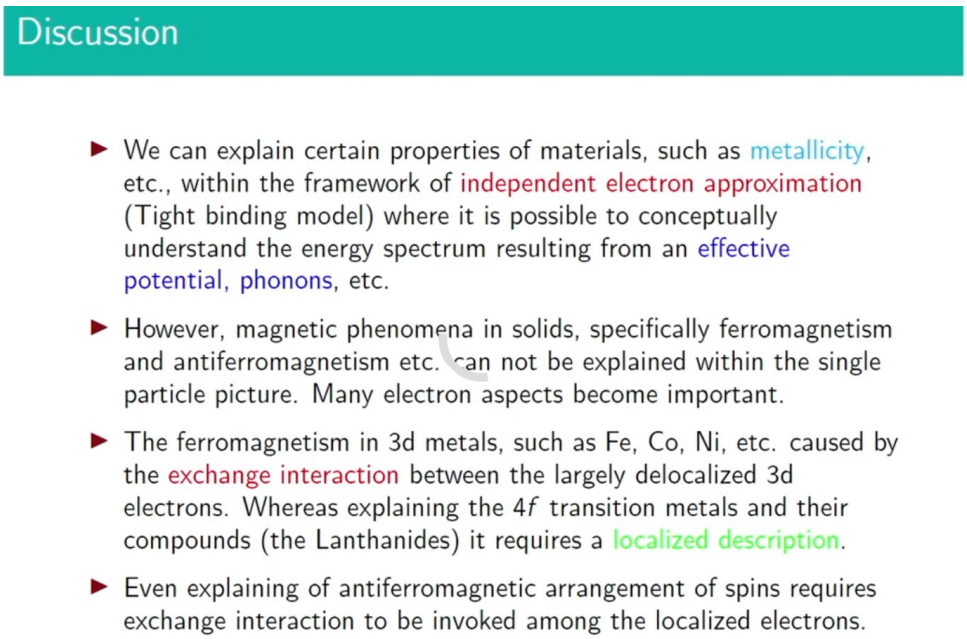
Okay. So, so let us see what how we can understand magnetism and we will as said earlier that we will try to do it in the simplest way or without doing too much of calculations because this magnetism is a topic by its own which could take you know even one full course and these applications of magnets etc. which we do not do it here. So we start by saying that there are certain properties such as metallicity, etc., which we know the metals can be explained within the framework of independent electron approximation, for example, a tight-binding model. A tight-binding model means that we are really talking about the band theory—that is, when an electron passes through a periodic or crystalline solid, there are gaps that form in the spectrum.

And the wave function is, of course, given by what are known as the Bloch equations or Bloch theorem. But the energies, to get the energies in such periodic system or exact form of these energies is, In certain crystal lattices, one needs to resort to certain approximation, and one of them is tight binding approximation, which says that the electron, while moving through the periodic solid, it gets tightly bound to the ionic cores or the ionic locations, and the wave function only has a very small overlap with the neighboring ions. And it does not extend beyond that in the lowest-order approximation. This is called the tight-binding model.

And with this, we can conceptually understand the energy spectrum resulting from an effective potential. We have also looked at phonons, how phonons are described as quantized lattice vibrations. However, magnetic phenomena, specifically ferromagnetism and antiferromagnetism, cannot be explained within this independent electron picture or

the single-particle picture. And many-electron aspects, meaning the interaction between electrons, become important, and you cannot describe these magnetic orderings, such as ferromagnets and antiferromagnets, without invoking electron-electron interaction. This ferromagnetism in 3D metals includes specific examples such as iron, cobalt, and nickel.

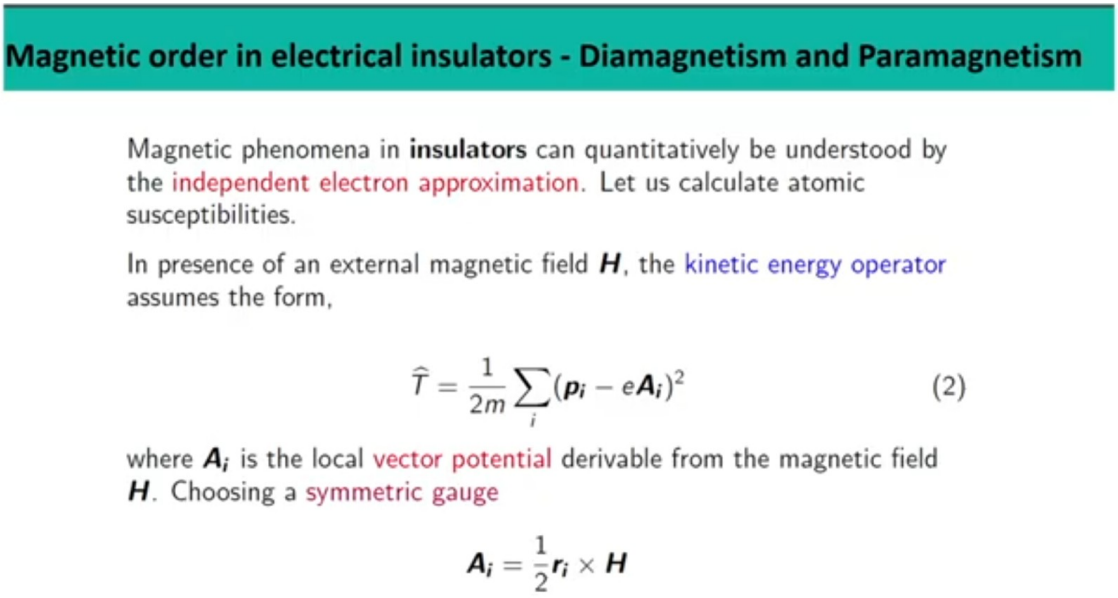
They are caused by exchange interaction between the largely delocalized 3D electrons. Okay. However, some of the lanthanide series, which are 4F transition metals, require a more localized description. These are ferromagnets, and they require, as we have said, that interacting description. And so, explaining antiferromagnetic arrangement of spins also requires one to invoke the exchange interaction between the spins.



So the spins are, you know, they interact, the neighboring spins interact via localized interaction. However, the actual interaction is not between the magnetic moments. It's actually between the electrons. The Coulomb interaction is responsible for inducing these exchange interaction between the spins. So we start with elementary treaties of diamagnetism and paramagnetism.

So, these are magnetic orderings present in electrical insulators. Insulators mean that they do not have any charge conduction properties. So, they are electrically neutral, and we need to study diamagnetism and paramagnetism in them. So, they can be largely understood, as I said, by using the independent electron approximation. However, for

ferromagnets and antiferromagnets, we have to go beyond that and invoke electron-electron interactions.



So, to start doing that, let us calculate the atomic susceptibilities. And how do we do that? Let us start with this kinetic energy operator, which takes a form in the presence of a magnetic field. Here, the momentum is replaced by this term eA, where e is the electronic charge and A is the vector potential. And this vector potential is defined by the magnetic field.

into curl A. It is true that we have talked about magnetic field as H and now we are talking about B, but they really mean the same thing. Here we have of course talked about H and so if you really stick to H, let us not try to write this equation, but A is the vector potential and the magnetic induction vector has a relation which is what we have written there. And one can fix a gauge, and usually, it is more sensible to talk about a symmetric gauge. A symmetric gauge means if H is in the Z direction, A will have components both in the X and Y directions. That's called a symmetric gauge.

one gets

$$\hat{T} = \frac{1}{2m}\sum_i (\boldsymbol{p}_i - \frac{e}{2}\boldsymbol{r}_i \times \boldsymbol{H})^2 \cdot$$
$$= \frac{1}{2m}\sum_i \left[\boldsymbol{p}_i^2 + \frac{e^2}{4}(\boldsymbol{r}_i \times \boldsymbol{H})^2 - \frac{e}{2}\{\boldsymbol{p}_i \cdot (\boldsymbol{r}_i \times \boldsymbol{H}) + (\boldsymbol{r}_i \times \boldsymbol{H}) \cdot \boldsymbol{p}_i\}\right] \quad (3)$$

Since the last two terms can be combined,

$$\hat{T} = \hat{T}_0 + \frac{e^2}{8m}H^2 \sum_i [r_i^2 - \frac{e\boldsymbol{p}_i}{2m} \cdot (\boldsymbol{r}_i \times \boldsymbol{H})] \quad (4)$$

Using the vector identity,

$$\boldsymbol{a} \cdot (\boldsymbol{b} \times \boldsymbol{c}) = \boldsymbol{b} \cdot (\boldsymbol{c} \times \boldsymbol{a}) = \boldsymbol{c} \cdot (\boldsymbol{a} \times \boldsymbol{b}) \quad (5)$$

And symmetric gauge for a constant H is represented by this half R cross H, where R and I, all of them are vectors. And what we do is that we put in this in this equation, equation number two, we put this A I there. And what we get is that we get this resultant equation and in which case we can solve it or rather we can expand this square and get this term, which is R I P I dot R I cross H and R I cross H dot P I. These are the cross terms. This is the 0th order term pi squared and this is coming because of the magnetic field being present there. So now you see that we can choose actually a gauge in which we can combine these two terms and really can write it like a single term and that gauge is you know divergence if a equal to 0.

So you may actually want to work out this term which is not difficult. And what we have finally is that we have these T0, which is nothing but pi square over 2m, which is the kinetic energy of the electrons without the magnetic field. This is the correction that's coming from this term that you see up there. And then these cross terms are put in here where now we can use a vector identity with A dot B cross C, which is P is A and R is B and H is C and can use this identity to write this equation as A. Pi dot Ri cross H equal to H dot Ri cross Pi and Ri cross Pi is nothing but L which is the angular momentum or the orbital angular momentum.

So, that is a total orbital angular momentum and this is H dot L and this is like there is a sum over I of course and there is a Li there. So, it is H dot L it is a total angular

momentum and And so, in absence of any interaction, the Hamiltonian can be written as T equal to T0, which is due to the non-interacting term that is without any magnetic field, sorry, not non-interacting, it is without a magnetic field. And then you have a term like that and then H squared term coming from this term. the term that you see there.

on the second term, that is,

$$\sum_i \boldsymbol{p_i} \cdot (\boldsymbol{r_i} \times \boldsymbol{H}) = \sum_i \boldsymbol{H} \cdot (\boldsymbol{r_i} \times \boldsymbol{p_i}) = \sum_i \boldsymbol{H} \cdot \boldsymbol{L_i} = \boldsymbol{H} \cdot \boldsymbol{L} \qquad (6)$$

where $\boldsymbol{L}$ is the total electronic orbital angular momentum. Thus the kinetic energy (and also the Hamiltonian $\hat{H}$) becomes,

$$\hat{H} = \hat{T} = \hat{T}_0 + \mu_B \boldsymbol{L} \cdot \boldsymbol{H} + \frac{e^2}{8m} H^2 \sum_i (x_i^2 + y_i^2) \qquad (7)$$

Treating the last two terms on the RHS as perturbation, that is, treating

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

So, we can put a laser pointer here. It is because of this term that you see an H squared term. Now, the whole idea is that you will use a perturbation theory with this as the, you know, the perturbation term. And in order to do that, we have to necessarily use second-order perturbation theory because we have a term which is quadratic in H squared. And there is a term which is linear in H. So, if you have to treat both these terms together, then there is no other way but to go into perturbation.

You know, the second order, and we'll do exactly that and write this term as so there's an H0 here and then there's H prime. So these will be our H prime. And we'll do perturbation theory with that. So this is your H prime. You can write S, which is large.

we have for $\hat{H}'$,

$$\hat{H}' = \mu_B(\boldsymbol{L} + g\boldsymbol{s}) \cdot \boldsymbol{H} + \frac{e^2}{8m} H^2 \sum_i (x_i^2 + y_i^2) \tag{8}$$

Where $\mu_B = \frac{eh}{2m}$ is the Bohr magneton having a value 0.579×10^{-8} eV/G and the Lande'g factor $g \approx 2$.

The energy correction can be computed via a **perturbation theory** using the unperturbed states of the Hamiltonian $\hat{H}_0$.

The magnetization M is defined as the first derivative of the free energy F with respect to the field H. That is,

$$M = -\frac{1}{V}\frac{\partial F}{\partial H} \tag{9}$$

So that's the total spin and the total orbital angular momentum. And then these are XI square and YI square are nothing but the coordinates of this individual atoms or, you know, they are involved in the magnetism. I mean, these are the coordinates of those atoms. Then mu B is equal to E H over 2 M. And so this has a value which is 5.58 times 10 to the power minus 8 electron volt per Gauss. And the Lande g-factor that you see here is approximately equal to 2.

There is some correction to that. Let us not worry about it now. So the energy correction can be computed using a perturbation theory. and using the unperturbed states of this Hamiltonian, which is the Hamiltonian without the magnetic field that is H0. And this is the basics of perturbation theory that you do not know what the eigenfunction of the total Hamiltonian is.

And if you can identify a term which can be used as a perturbation because of its smallness, then you can use or rather employ the eigenfunctions of H0 to compute the correction in energy and even the correction in wave function. We just talk about correction in energy because that is what we need. And after that, we can take this magnetization will be defined by the, you know, the derivative of the free energy with respect to H, the magnetic field H. So, it is del F del H. Now, here, of course, we have written out a scalar equation where M and H, etc., all are taken as scalar quantities. That is because you cannot divide by a vector, take a derivative with respect to the vector.

So, what you do is that you take the derivative with respect to the magnitude of h. So, the susceptibility is defined as del M del H. Now, it is very clear that you have a double derivative. So, this is actually a del 2 F del H 2. And so, you need the free energy to survive up to a second order in H. And that is why you need to evaluate this H prime up to H square. This is magnetic field.

Thus the susceptibility χ is obtained from the magnetization as,

$$\chi = \frac{\partial M}{\partial H} \qquad \frac{\partial^2 F}{\partial H^2} \tag{10}$$

thereby implying that the susceptibility as the second derivative of the free energy with respect to H.

perturbation term ↓ ↓ magnetic field

Thus we need to evaluate both terms in H' up to H^2. Since the last term needs an evaluation using a second order perturbation theory.
Hence,

$$\Delta E_n = \sum_{n \neq m} \underbrace{\frac{|\langle \phi_n | \mu_B \boldsymbol{H} \cdot (\boldsymbol{L} + g\boldsymbol{S}) | \phi_m \rangle|^2}{E_n - E_m}}_{2^{nd}\ order} + \underbrace{\frac{e^2}{8m} H^2 \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle}_{1^{st}\ order} \tag{11}$$

Remember that and these other things that we talked about earlier. Are these other H? You know, you can make it a curly H if you wish. And these are nothing but the perturbation term in the Hamiltonian. Alright, so this is the formula for the second order perturbation theory which involves an energy correction and then the terms that are written there and you see that each term is of the order of H square where H is a magnetic field, H square here because the second order term. However, if you note that this, we have used a first-order perturbation theory, so this is second-order.

Because we are interested in getting H square, and this is first-order. And this is OK because we want delta E n up to second-order in H square. OK, so we treated first term in up to second order and the first term, the second term up to first order so that our, correction up to order h square is obtained. And why do we want H square? It's just what we have written here in equation 10.

So, we need the free energy or the energy to be, you know, take a double derivative with respect to magnetic field so that we need these correction to be of the order of h square. And so, if you have all the if you really talk about an insulating material, then the total orbital and the spin angular momentum quantum number is 0, which means l equal to s equal to 0 total l s equal to 0. So, we have only corrections coming from the second term or the last term, and that will give us a correction if you do it carefully. Then you have to calculate this expectation value of this XI square plus YI square, which are nothing but the planar coordinates of these atoms. And in an isotropic crystal, your X square plus Y square plus Z square is equal to R square.

So if X, Y, and Z are treated on the same footing, then X square plus Y square is, is really, you know, two-thirds of R square. And that is what is written. You see a factor of two-thirds coming out, and that is, you have to calculate these, the coordinate square of those, you know, the atoms which are involved in this process or in this calculation. So, this phi 0 is nothing but the ground state wave function. Alright, so we will calculate the susceptibility using this minus N by V and this del 2 del E 0, that is the correction to the ground state energy by h square.

The insulating materials have all the **valence electronic shells filled**. Hence the total orbital and spin angular momentum is zero, that is the only surviving term is $L=S=0$

$$\Delta E_n = \frac{e^2}{8m} H^2 \langle \phi_n | \sum_i (x_i^2 + y_i^2) | \phi_n \rangle \qquad (12)$$

Let us evaluate the change in ground state energy

$$\begin{aligned} \Delta E_0 &= \frac{e^2}{8m} H^2 \langle \phi_0 | \sum_i (x_i^2 + y_i^2) | \phi_0 \rangle \\ &= \left(\frac{2}{3}\right) \frac{e^2}{8m} H^2 \langle \phi_0 | \sum_i (r_i^2) | \phi_0 \rangle \\ &= \frac{e^2}{12m} H^2 \langle \phi_0 | \sum_i (r_i^2) | \phi_0 \rangle \end{aligned} \qquad (13)$$

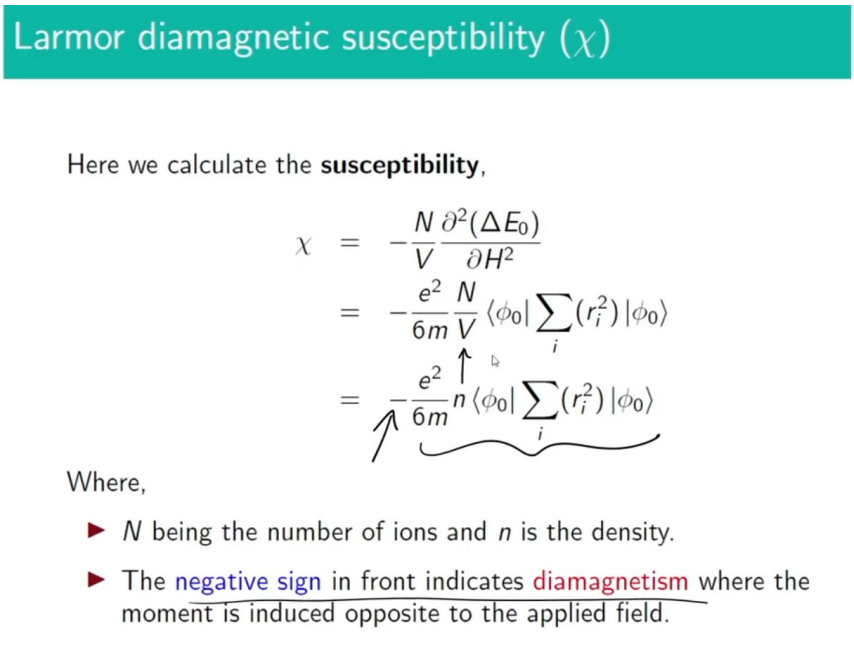
$x^2+y^2+z^2 = r^2$

$x^2+y^2 = \frac{2}{3} r^2$

The ground state wave function is $|\phi_0\rangle$.

You have these, it is second order in H, so you take a double derivative and what you land up with is this expression. And this is, of course, an expression for the magnetic insulators, the diamagnetic susceptibility. Because of this negative sign, you see that

there's a negative sign that indicates diamagnetism. And n is basically nothing but the small n is nothing but n over V. That's the number of, or rather the density of, these ions that are involved here. So, this is an expression for the susceptibility, magnetic susceptibility, that we get, and these are for the insulators.



Now, we keep talking about these filled shell materials or the insulating materials, and so, this equation, let us see, this equation is really, let us call this as equation 1. So, we want to actually refer to this equation 13. So, we will make this correction here. Sorry about that. So, it is equation 13.

So, electron in the outermost shells will contribute maximum because of the large mean square distance because ri square is the mean square distance from some chosen origin. So, the origin is presumably in the nucleus or inside the atom, and you measure ri square with respect to the origin, which can be obtained by, you know— So, ri square is maximum. So, this contribution to this diamagnetic susceptibility is maximum for the ones that are in the outermost shell. So, we simply replace this, you know, this sum or rather the expectation value.

by this Rout square and multiply it by the number of, you know, Z out, which is like the atomic number. And so, we simply replace this expectation value by these ri squares. And that ri square would be maximum. So, that corresponds to the r out, which is in the

outermost shell. And then you have this expression, which is the diamagnetic susceptibility.

Susceptibility of completely filled shell materials

- One may note that in the sum Eq.(13), electron in the outermost shells contribute maximum owing to their large mean square distance from the nucleus.
- Consider Z_{out} be the number of outermost electrons and r_{out} be the corresponding distances, then the largest term in the sum yields

$$\chi \sim -\frac{e^2}{6m} n Z_{out} r_{out}^2$$

The above formula Eq.(6) correctly explains the magnetic behavior of the alkali halides, inert elements He, Ne, Ar, Kr, Xe etc.

And these correctly explain the magnetic behavior of these halides, alkali halides, such as helium, neon, argon, krypton, xenon, etc. All right, so let us now talk about partially filled shell materials. And we now do not have this Li sum over Li or sum over Si not equal to 0. So, Li is not equal to 0, and Si is not equal to 0 either. So, we now have identical non-interacting spin particles in the presence of an external magnetic field.

Susceptibility of partially filled shell materials

Consider N identical non-interacting spin-S particles in presence of an external magnetic field H.

The corresponding **Zeeman Hamiltonian** can be written as,

$$\mathcal{H} = -\mu_B \boldsymbol{S} \cdot \boldsymbol{H}$$

It may be noted that electronic degrees of freedom are not important for this discussion.

The canonical partition function is defined as,

$$\mathcal{Z} = \sum_{\{S\}} e^{-\beta \mathcal{H}\{S\}} = \sum_{|\boldsymbol{S}|=-S}^{+S} e^{-\beta \mu_B S H} \quad [\beta = \frac{1}{k_B T}]$$

Where it is assumed that lowest $2S+1$ states ($-S$ to $+S$ through 0) are thermally excited at a temperature, T with appreciable probability.

The Zeeman term is represented by this minus mu B S dot H. And what we do is that we'll follow a statistical route in order to calculate the partition function. And this partition function can be calculated for all orientation of S from minus S to plus S corresponding to the Zeeman Hamiltonian that's written up there, which is minus mu B S dot H. Now we have made a distinction. This H is basically the, uh, Hamiltonian and this H is basically the magnetic field and beta is equal to 1 over KT. So, this sum actually goes over to S plus 1 states from minus S to plus S and at a given temperature T and all these states are thermally excited at temperature T with appreciable probability. So, one can calculate these partition function in a closed form, which will be obtained by, you know, summing up a GP series. And then you take this F is equal to minus KT log Z. and then calculate M with this formula using minus del F del H, and one gets a Brillouin function, which is nothing but this thing, where X is equal to mu B H over KT. This magnetization is obtained in terms of some spin, and spin is a general spin.

You can set it equal to half, but S is a general spin. And this is the Brillouin function. And this Brillouin function, when you plot it for different S values, they look like this. The ones that's for smallest S, which is that blue curve, which is outward. And the red one, which is the largest spin that is considered here, is the innermost curve.

The above sum Eq.(8) is computed in the form of a geometric progression (GP) series,

$$\mathcal{Z} = \frac{e^{\beta\mu_B H(S+\frac{1}{2})} - e^{-\beta\mu_B H(S+\frac{1}{2})}}{e^{\beta\mu_B H/2} - e^{-\beta\mu_B H/2}}$$

$F = -k_B T \ln Z$

As earlier the magnetization, M can be calculated using,

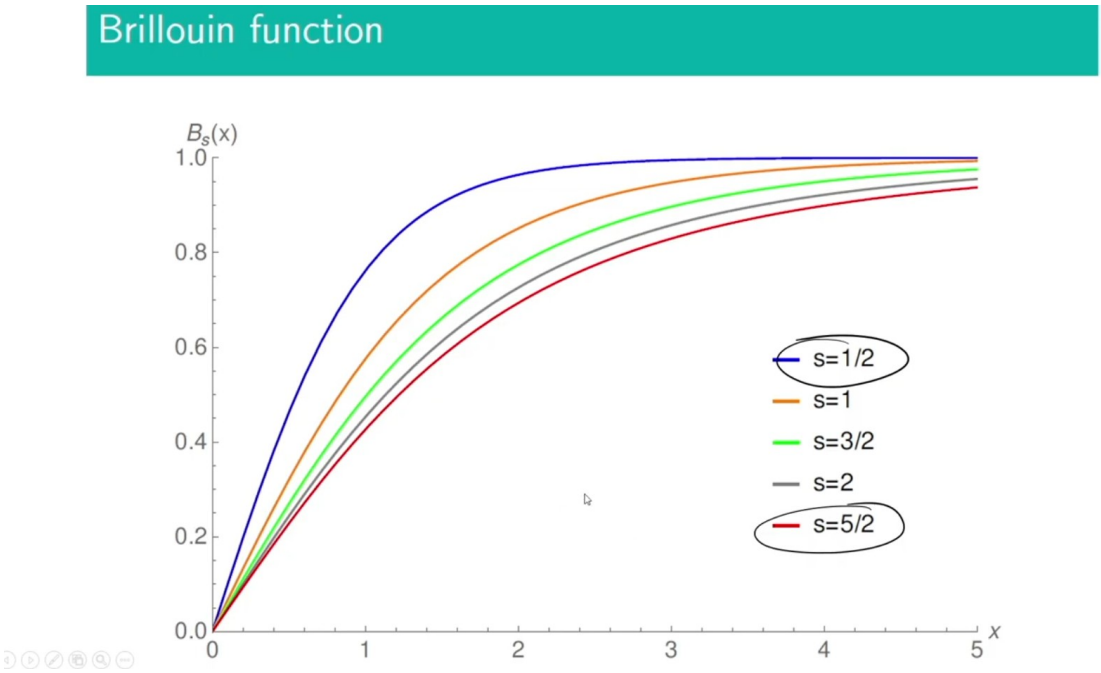
$$M = -\frac{\partial F}{\partial H} = \mu_B S B_S(\beta\mu_B SH)$$

$B_S(x)$ is called as the Brillouin function and is defined by

$$B_S(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}x\right)$$

where $x = \mu_B H/k_B T$.

So that's the, you know, just to show you how the Brillouin function look like as a function of X, where X is defined as mu BH by KT. So let us look at various limits of this behavior of either the magnetization or susceptibility. So let us just talk about X much greater than 1, which means that the mu B H is much greater than K T. So which means that this magnetic energy or the associated magnetic energy is much larger than the temperature, which means temperature is small. So at low temperature, the magnetization appears saturation value because this Bs, which is this Brillouin function that tends to be 1, which is what you see here. So that is the behavior for large X. And so that is your X large and you get Bs equal to 1.



So the saturation, the magnetization attains the saturation. In the other limit, when you have, you know, the temperature is low, rather temperature is high, the magnetic energy is much lower compared to the temperature. We can do a small x expansion of this Brillouin function, which yields the Brillouin function to have a form, which is s plus 1 divided by 3s into x. That gives you what is known as the Curie susceptibility. So when you put it back into this equation for the chi, which is nothing but, so the chi is defined as del M del H. So then we have this M is equal to minus del F del H and chi is equal to del M del H.

Curie's law

- For $x >> 1$, that is $\mu_B H >> k_B T$, $B_S(x) \to 1$. Thus, at lower temperature and large external fields, the magnetization acquires its saturation value.
- In the other limit, that is $\mu_B H << k_B T$, we do a small x-expansion which yields,

$$\coth(x) \approx \frac{1}{x} + \frac{1}{3}x + \mathcal{O}(x^3).$$

Thus,

$$B_S(x) \approx \underbrace{\frac{S+1}{3S}}x + \mathcal{O}(x^3)$$

Hence the susceptibility is computed as,

$$\chi_{\text{Curie}} = \frac{\mu_B^2}{3}\frac{S(S+1)}{k_B T}$$

that acquires a form which goes as 1 over T for a spin S. So this goes as 1 over T. And so remember that the susceptibility of these paramagnets, which are, you know, for the electrons which are attached to atoms or ions, the susceptibility is Curie-like, which goes as 1 over T. Whereas there is another susceptibility, which is what we are going to talk about just in a while, So, this is called as Curie's law. So, the susceptibility behaving inversely with temperature and it is a feature of paramagnetic solids, all solids, paramagnetic solids. And the law is found to be valid at large temperatures even when there is magnetic, considerable magnetic interactions exist as well. Among the magnetic moments, the magnetic properties of the rare earth materials such as LA, LU, that is lanthanum, lotatium, nidenium, cerium, dysprosium, etc.

Discussion

- **Curie's law**: The susceptibility behaving inversely with temperature is a feature of 'paramagnetic solid'

$$\chi_{\text{Curie}} \propto \frac{1}{T}$$

  The law is found to be valid at large temperatures even when considerable magnetic interactions exist among the magnetic moments.
- The magnetic properties of the rare earth materials (such as, La, Lu, Nd, Ce, Dy, etc.) are adequately described by Curie's law.
- In the next lecture we will look at Pauli Paramagnetism and Diamagnetism.

They are adequately described by Curie's law. And, well, I mean, in the next lecture means in the next slide, actually. So this is really the slide that you have. So we'll talk about Pauli paramagnetism and also we'll talk about diamagnetism. So, we have discussed Curie's law and one should be aware at this moment that there is another type of paramagnetic phenomena that is applicable for metals or where there are a lot of free electrons.

Having discussed Curie's law, one should be aware that there is another type of paramagnetic phenomenon applicable for metals, namely, Pauli paramagnetism which refers to the magnetic moments of conduction electrons. These electrons behave in a way that is distinct with respect to the localized electrons in partially filled ionic shells. Standard techniques of statistical mechanics can be applied (for example, see Pathria) to obtain the magnetic susceptibility, χ_{Pauli} which is a constant (as opposed to having an inverse temperature dependence as that in χ_{Curie}). In fact the expression is,

$$\chi_{\text{Pauli}} = \mu_B^2 N(\varepsilon_F)$$

where $N(\varepsilon_F)$ refers to the density of states at the Fermi level. Thus the susceptibility, χ of free electrons (Pauli) is a constant (independent of temperature), while for electrons bound to atoms, χ depends inversely on temperature (Curie).

These are called Pauli paramagnetism and you can get a nice description of this in this book of statistical mechanics by Patria and which obtains the magnetic susceptibility, you know, which is called as Chi-Pauli. And the result is that the chi Pauli is equal to mu B square into N, this density of states at the Fermi level. There is another course of mine, statistical mechanics, where you would find the derivation of all these things. These are for free electrons, that is metallic susceptibility or where there are a lot of free electrons. but the electrons that are bound to atoms, you get a Curie susceptibility, which is 1 over T. See, Chi, Pauli, that is, Pauli susceptibility is independent of temperature, only depends on the density of states at the Fermi level.

So, they are distinct susceptibilities. One is Pauli, one is Curie. Now, to study ferromagnetism, it is shown by Heisenberg that for ferromagnetic ordering, or ferromagnetic ordering can be only explained if you invoke electronic interactions. Even though it has a structure of a spin-spin interaction in the Hamiltonian, the origin is purely electronic in nature.

An exact treatment of the interaction is not possible. It will be long you know kind of derivation rather if you are interested in some you know some exact solution for a 1D chain spin chain then again you can look at this statistical mechanics course and so we will do quickly this mean field theory and skip all the rest of the things but there are you know method of solutions of the Heisenberg model which for a ferromagnet using these methods as well. So, coming to the mean field theory, let us try to see what the structure of the Hamiltonian is.

And to begin with, let us start with a two-spin system. It has just two spins. And there are four states because there are these two spins, meaning two spin-half particles. So, there are up and down particles, and one can actually form these up-up, up-down, down-up, and down-down, okay. And we can take a linear combination of that and can form these as S equal to 0 states, which are called the singlet states.

And these are the three triplet states formed out of up-up, up-down plus down-up, and down-down. And these have certain properties. And if you just take an S square of the total S, basically, it's S1 plus S2 whole square. And then I can do an S1 square plus S2 square. Now, these S1 and S2, of course, commute.

That is why we can write that 2s1 dot s2. Now, s1 square is for the spin half; it is s1 into s1 plus 1. And similarly, for s2 square, it is s2 into s2 plus 1. Both are 3 by 4 h cross square if you take s equal to half h cross. So, S square gives you a value which is this 3

by 2 h cross square plus 2 S1 dot S2, which means that you know, if you operate it on its eigenfunction of S or S square, you get these as eigenvalue and of course, you get an operator here which whose eigenvalue you do not know and this is interesting to us because these operator we can now these operator S1 dot S2 has eigenvalue which is 3 by 4 h cross square or 1 by 4 h cross square because this total S is equal to either 0 or 1. So these are total S.

Two-spin system ($S = \frac{1}{2}$) $\uparrow, \downarrow$ $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$

$$\chi_{00} = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \quad : \quad s = 0 \quad \text{singlet}$$

$$\left.\begin{aligned} \chi_{11} &= \tfrac{1}{\sqrt{2}}[|\uparrow\uparrow\rangle] \\ \chi_{10} &= \tfrac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] \\ \chi_{1-1} &= \tfrac{1}{\sqrt{2}}[|\downarrow\downarrow\rangle] \end{aligned}\right\} \quad : \quad \mathrm{s} = 1 \quad \text{triplets .}$$

$s_1(s_1+1)$
$s_2(s_2+1)$

$$\begin{aligned} S^2 = (S_1 + S_2)^2 &= S_1^2 + S_2^2 + 2S_1 \cdot S_2 \\ &= \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2S_1 \cdot S_2 \\ &= \frac{3}{2}\hbar^2 + 2S_1 \cdot S_2. \end{aligned}$$

This is actually the capital S. So this for S equal to 0 is 0 and for S equal to 1 is 2, 2 or 2 h cross square. So, we know the eigenvalues of these S1 dot S2 on for these singlet and triplet state and we can now construct a spin only Hamiltonian which are these ES is the energy of the singlet state and ET is the energy of the triplet state. There is a constant term and then there is a term which is S1 dot S2. So we can write down if we neglect this constant term in the Hamiltonian, we can write a Hamiltonian involving the two spins with a minus J term, which is the coupling between the two spins.

Thus, for the singlet state, the operator $S_1 \cdot S_2$ has an eigenvalue $-\frac{3}{4}\hbar^2$, and $\frac{1}{4}\hbar^2$ for the triplet states. Denoting these eigenvalues by E_s and E_t respectively, we can write down a spin-only Hamiltonian, namely,

$$\mathcal{H} = \frac{1}{4}(E_s + 3E_t) - (E_s - E_t)S_1 \cdot S_2.$$

$$\mathcal{H} = -JS_1 \cdot S_2 \qquad \text{where } J = E_s - E_t.$$

$$\mathcal{H} = -J \sum_{i,\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta}$$

And this case is nothing but ES minus ET, which is the difference between the singlet and the triplet energies. So, for a chain comprising n spins and interacting via nearest-neighbor interaction, we can write this Hamiltonian as minus j SI dot SI plus delta, which is similar-looking to S1 dot S2 but now generalized to n spins. How can we do a mean field theory? We can do a sort of decoupling of the spins so that each spin is an effective field due to the presence of all other spins. So that each spin feels a magnetic field like this and say there is also an external magnetic field.

Mean Field Theory

$$\mathcal{H}_{MF}(i) = \mathbf{S}_i \cdot \left(J \sum \mathbf{S}_{i+\delta} \right) - \mu_i \cdot \mathbf{B}_{ext}$$

$$\mathcal{H}_{MF}(i) = -\mu_i \cdot \mathbf{B}_{eff}$$

where $\mathbf{B}_{eff} = \mathbf{B}_{ext} - \frac{J}{g\mu_B} \sum_\delta \mathbf{S}_{i+\delta}$. Here g is the landé g factor, and μ_B denotes the Bohr magneton. In fact $\mathbf{S}_{i+\delta}$ can be replaced by its thermal average $\langle \mathbf{S}_{i+\delta} \rangle$, so that

$$\begin{aligned} \mathbf{B}_{eff} &= \mathbf{B}_{ext} - \frac{J}{g\mu_B} \sum_\delta \langle \mathbf{S}_{i+\delta} \rangle \\ &= \mathbf{B}_{ext} - z\frac{J}{g\mu_B} M \end{aligned}$$

where $M = \langle \mathbf{S}_{i+\delta} \rangle$ is the magnetization and z denotes the coordination num-

And we can combine them and write down a one-particle equation or one-spin equation in an effective magnetic field given by this term, okay, this term and so on. Where these M is nothing but the average value of this spin, that is a psi plus delta, and Z denotes, of course, the coordination number. So, in 1D, the coordination number is 2; in 2D, it is 4, and so on. Again, we take a statistical route, and we can calculate the partition function. Now, it became a one particle problem or a one spin problem, that one spin.

So, you go to any spin and consider the effect of all other spins due to that is as if the spin is in an effective field. And we also have an external field, but this effective field due to all other spins is modifies or renormalizes the external field and we get this everything in terms of this B effective. And again we get a Brillouin function as we have seen there. So by taking this del F del B effective we know the partition function so we can get F by taking a KT log Z and then we can get this magnetization which has this form in terms of the Brillouin function.

So, in the limit, this H going to 0, one can actually take this expansion of the Brillouin function, very similar to what we have done. So, the magnetization really looks like this. And we can extract out the transition temperature, which is Tc equal to S into S plus 1 by 3 into Zj. Z is the coordination number. And what we get is this, that the M versus temperature, that means as you are increasing temperature, initially these magnetic ordering, it is resilient to temperature.

$$\mathcal{Z} = \sum e_{MF}^{-\beta\mathcal{H}} = \sum e^{-\beta\mu_i\mathcal{H}_{eff}} = \mathcal{Z} = \sum e^{-\beta\gamma SB_{eff}}$$

$$= \frac{e^{\beta\gamma B_{eff}(S+\frac{1}{2})} - e^{-\beta\gamma B_{eff}(S+\frac{1}{2})}}{e^{\beta\gamma B_{eff}/2} - e^{-\beta\gamma B_{eff}/2}} \qquad \text{where } \gamma = g\mu_B.$$

using $M = \frac{\partial F}{\partial B_{eff}}$ $\qquad M = \gamma SB_S(S\beta\gamma B_{eff}) = \gamma SB_S\left(S\beta\gamma(B - \frac{zJ^2}{\gamma}M)\right)$

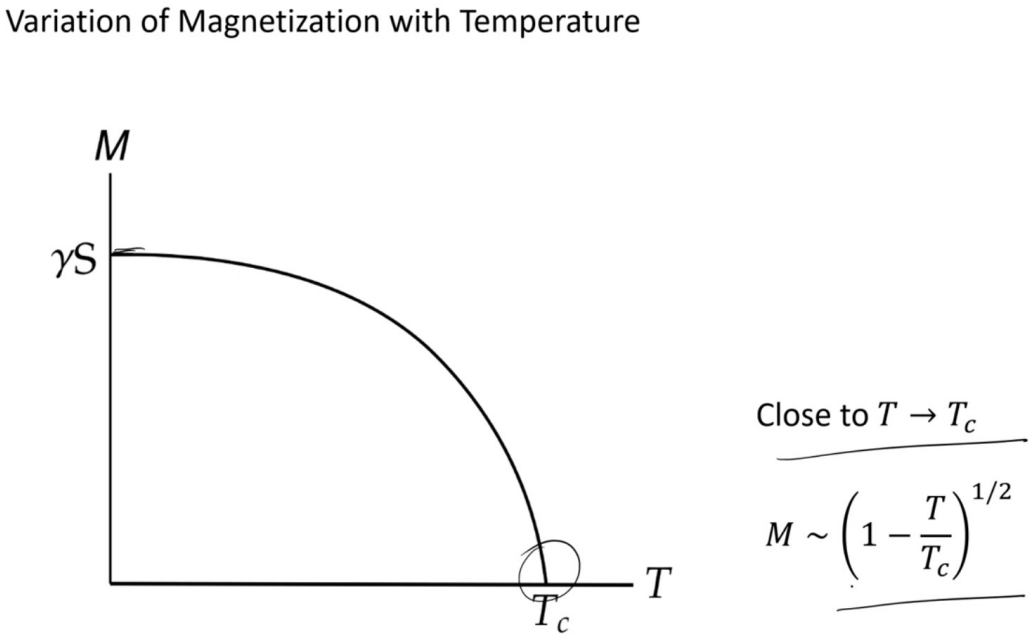
limit $H \to 0$, $B_S(x)$ can be expanded for small x,

$$M \simeq -\gamma S\left(\frac{S+1}{3S}\right)\frac{zJ}{\gamma k_B T_c}M.$$

Solving for the transition temperature, T_c,

$$T_c = \frac{S(S+1)}{3}zJ.$$

So it's sort of slow here. It's kind of, you know, flattish here. But as you keep increasing the temperature, the thermal, these effects or the thermal energy will randomize the, you know, the alignment of the spins. And you'll keep getting these magnetic moments or the magnetization destroyed. And it will go to zero as T goes to Tc.



And, this behavior is important that close to T equal to Tc, this goes as 1 minus T by Tc to the power half and this is the hallmark of mean field theory being, you know, put in action is basically this T to the power half or 1 minus T by Tc to the power half is the feature for this, magnetization or the behavior of magnetization. And at T equal to 0, it has a value which is gamma s and, that is, you know, all these things are, mentioned here, and so on. Gamma is equal to g, uh, the Landé g factor into the Bohr magneton. So that is all we do for magnetism.

It is a very brief discussion of magnetism, but I hope that you got a feel for what these different magnetic orderings are and that the diamagnetism and the paramagnetism are still treatable within the independent electron approximation, which is what we have done. We have started from the kinetic energy term, modified the momentum to P minus Ea, and have done these calculations. We got these these you know QD susceptibility for the paramagnets and we also got a diamagnetic susceptibility and these we have done it for you know diamagnetic susceptibilities for the insulators and the ones that are you

know partially filled systems which have some metallic properties they are characterized by the

This QD susceptibility, but then we have also distinguished it from another kind of susceptibility, which is the Pauli susceptibility. Then, we have done an elementary treatment of ferromagnetism where there are spins that are arranged. And we are not talking about the dimension because, as soon as you do a mean field theory, the dimensional information goes away. And it only sort of enters through the coordination number, the coordination number Z, or the number of nearest neighbors. And we found that the magnetization of the system as a function of temperature, it falls off. like this that is shown on your screen and the characteristic behavior as T goes to Tc is 1 minus T by Tc to the power half.

We will stop here. Thank you.