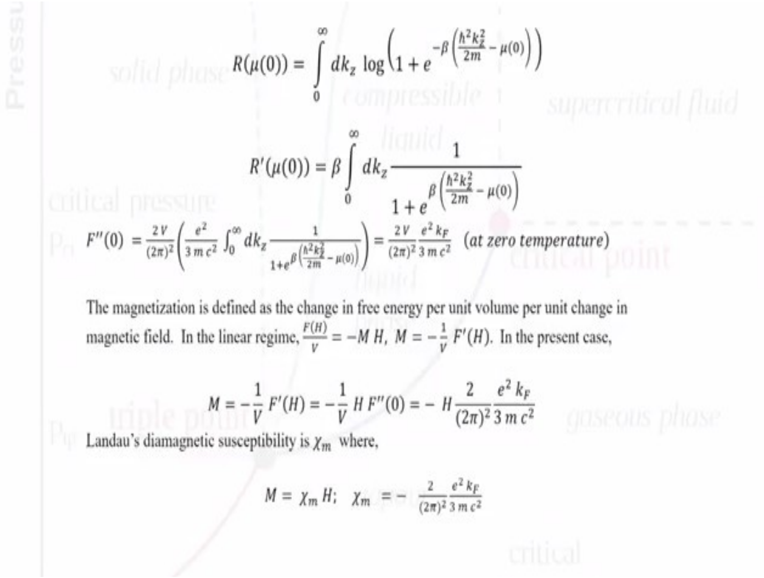
Introduction to Statistical Mechanics
Girish S Setlur
Department of Physics
Indian Institute of Technology, Guwahati

Lecture no. #15
Pauli's Paramagnetism

Ok, so now before we start a new topic. So remember that we finished off with the Landau diamagnetism, where we derived the diamagnetic susceptibility.

(Refer Slide Time 00:47)



$$R(\mu(0)) = \int_0^\infty dk_z \, \log\left(1 + e^{-\beta\left(\frac{\hbar^2 k_z^2}{2m} - \mu(0)\right)}\right)$$

$$R'(\mu(0)) = \beta \int_0^\infty dk_z \frac{1}{1 + e^{\beta\left(\frac{\hbar^2 k_z^2}{2m} - \mu(0)\right)}}$$

$$F''(0) = \frac{2V}{(2\pi)^2}\left(\frac{e^2}{3\,m\,c^2}\int_0^\infty dk_z \frac{1}{1+e^{\beta\left(\frac{\hbar^2 k_z^2}{2m} - \mu(0)\right)}}\right) = \frac{2V}{(2\pi)^2}\frac{e^2\,k_F}{3\,m\,c^2} \quad (at\ zero\ temperature)$$

The magnetization is defined as the change in free energy per unit volume per unit change in magnetic field. In the linear regime, $\frac{F(H)}{V} = -M\,H$, $M = -\frac{1}{V}\,F'(H)$. In the present case,

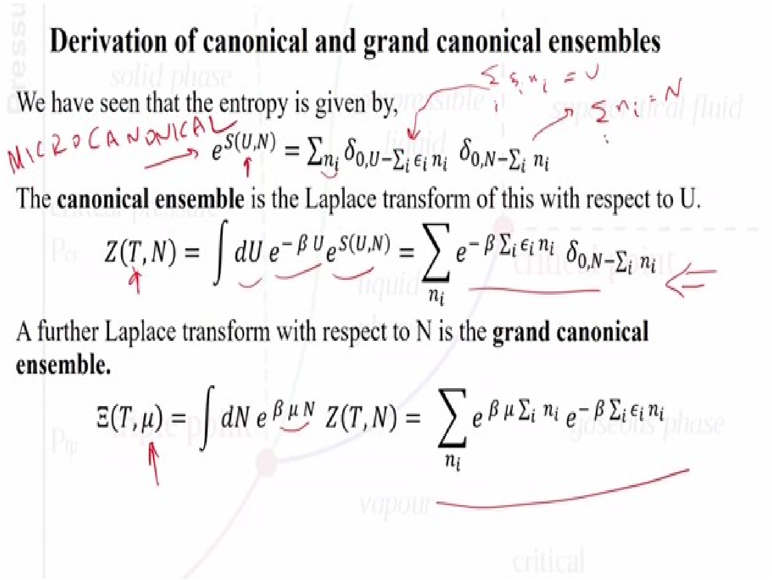
$$M = -\frac{1}{V}\,F'(H) = -\frac{1}{V}\,H\,F''(0) = -\,H\frac{2}{(2\pi)^2}\frac{e^2\,k_F}{3\,m\,c^2}$$

Landau's diamagnetic susceptibility is χ_m where,

$$M = \chi_m\,H; \quad \chi_m = -\,\frac{2}{(2\pi)^2}\frac{e^2\,k_F}{3\,m\,c^2}$$

To be given by this formula.

(Refer Slide Time 00:50)



Derivation of canonical and grand canonical ensembles

We have seen that the entropy is given by,

MICROCANONICAL

$\Sigma \epsilon_i n_i = U$

$\Sigma n_i = N$

$$e^{S(U,N)} = \sum_{n_i} \delta_{0,U-\sum_i \epsilon_i n_i}\ \delta_{0,N-\sum_i n_i}$$

The **canonical ensemble** is the Laplace transform of this with respect to U.

$$Z(T,N) = \int dU\, e^{-\beta U} e^{S(U,N)} = \sum_{n_i} e^{-\beta \sum_i \epsilon_i n_i}\ \delta_{0,N-\sum_i n_i}$$

A further Laplace transform with respect to N is the **grand canonical ensemble.**

$$\Xi(T,\mu) = \int dN\, e^{\beta \mu N}\ Z(T,N) = \sum_{n_i} e^{\beta \mu \sum_i n_i}\, e^{-\beta \sum_i \epsilon_i n_i}$$

So before I jump into a new topic, I thought it is important for me to explain very explicitly how to shuttle between the micro canonical canonical and grand canonical partition functions? So notice that in this course, I have purposely focused on the micro canonical ensemble. That means I have always gravitated towards calculated entropy first.

That is typically not what many other people other authors and speakers do, they kind of depending upon the situation, they directly use the canonical ensemble or the grand canonical ensemble. So I wanted to purposely not do that, because I wanted to emphasize the central role played by entropy in the subject of statistical mechanics. But it is also important to understand, you know, in order to minimize the amount of effort you are going to put in.

In practical calculations, how to start with the canonical ensemble directly if you wish to. So the way you do that is, you start off recall that the entropy function, basically the number of microstates is exponential of entropy. And that is given by just this combinatorial formula, which tells us just the number of ways in which you can arrange your micro states such that the total energy which is $\Sigma_i\ \varepsilon_i n_i$, is constrained to be U.

And also you constrain the number of particles to be N but otherwise there is no constraint, well, depends upon whether nature is described by in the particles in question are bosons or fermions. So classical particles, but otherwise, there is no further constraint. So, this is how you count the number of microstates. So it is a very combinatorial, discreet way of counting. And that is the essence of that goes to the heart of the notion of entropy.

The fact that it is a combinatorial quantity. Now that we know what combinatorial is, I mean, how to define entropy from a combinatorial perspective. And so this is known as the micro canonical perspective. So, it is possible to think of the canonical perspective. Which you if you recall that I had described the canonical ensemble by saying that you have a system where the system is allowed to exchange energy with the surroundings, which was a huge reservoir.

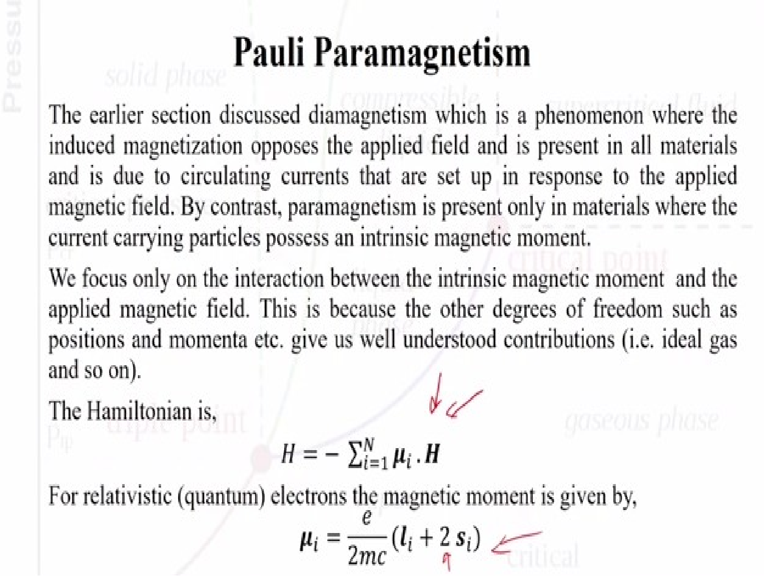
And that is how I defined canonical ensemble they come to an equilibrium and the temperature equalizes. So, it so happens that you can also think of it more mathematically. You can think of the canonical partition function more mathematically as the Laplace transform of the micro canonical partition function. So this is the number of microstates. And you just multiply by e raised to β by U and you some over all of U's.

And what you get is directly the canonical partition function. So you trade the energy for temperature. So basically, you do a Laplace transform of the energy and replace it. Basically would trade it for temperature. And again, so this would be a valid description of the canonical ensemble of the system. Now, you can do a further Laplace transformation, where you exchange the number of particles for quantity known as chemical potential.

So when you do that, when you do this further Laplace transform, what you end up doing is you get a quantity known as the grand canonical, or the grand potential, or the grand partition function specifically. So the grand partition function is easy to calculate, as you can see from this formula, there are no kronecker deltas anymore, it is just a bunch of exponential and sum over all ends. So you can expect this to be a simple geometric series, for the most part.

It is easy to calculate. So that is the reason why most people directly calculate the grand canonical partition function, they work with a grand canonical picture. And that is how we did it for the fermi, and Bose gases if you recall, so we work with chemical potential and temperature. That is because it is easy to do. Then, for large systems, we have convinced ourselves that fluctuations are suppressed, and that they are equivalent, In the sense that they are, they contain the same amount of information.

And you can shuttle back and forth between the various pictures. alright,
(Refer Slide Time 06:14)



Pauli Paramagnetism

The earlier section discussed diamagnetism which is a phenomenon where the induced magnetization opposes the applied field and is present in all materials and is due to circulating currents that are set up in response to the applied magnetic field. By contrast, paramagnetism is present only in materials where the current carrying particles possess an intrinsic magnetic moment.

We focus only on the interaction between the intrinsic magnetic moment and the applied magnetic field. This is because the other degrees of freedom such as positions and momenta etc. give us well understood contributions (i.e. ideal gas and so on).

The Hamiltonian is,

$$H = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \boldsymbol{H}$$

For relativistic (quantum) electrons the magnetic moment is given by,

$$\boldsymbol{\mu}_i = \frac{e}{2mc}(\boldsymbol{l}_i + 2\,\boldsymbol{s}_i)$$

so now that is out of the way. Let us get on with describing paramagnetism. So if you recall, we stopped with Landau diamagnetism. Here the induce the magnetic moment opposes the applied field. But here, what happens is that there is no induced magnetic moment, there is already a magnetic moment even before the field is applied, it is just that they do not all point in the same direction.

So in other words, every molecule has its own intrinsic magnetic moment, but they are all pointing in random directions. So what a field does is basically tries to align all the moments along the direction of the field. Well, then there is a competition to that from what is called temperature. So basically, there is a temperature which tries to randomize the spins, which tries to misalign the spins and make it isotropic.

So temperature tries to make the spins, isotropic, whereas the magnetic field tries to align them, and there is a competition. So the end result is some kind of a compromise between full alignment and full isotropy and you get what is called Pauli's paramagnetic susceptibility. Which tells you how strong the magnetization is, as a function of temperature and as a function of the applied field and so on.

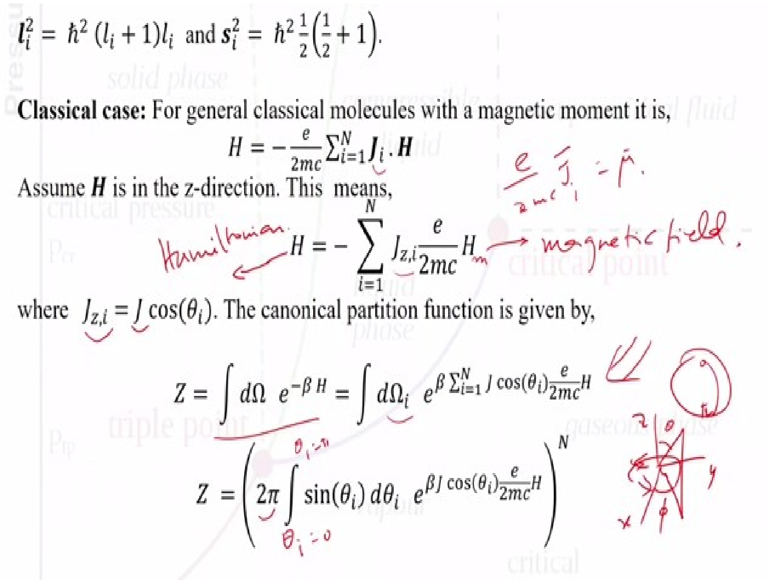
So the goal is to calculate this Pauli's paramagnetic susceptibility. Alright, so in order to do this, I am going to start with an obvious starting point, which is that if you have molecules or atoms with the intrinsic magnetic moment, So we are at liberty to denote it with a symbol for μ_i, which is a vector for the i’th item. So this i’th item experiences a magnetic field called edge and energy that the magnetic moment interacts with the magnetic field and there is interaction energy of this form.

So the magnetic moment, as you very well know, is given by this formula, which is kind of easy to convince yourself of its validity. So we know that the magnetic moment is basically proportional to the angular momentum of the supposed electrons in the outermost shell. So the magnetic moment is going to be proportionate to the angular momentum. So the proportionality is going to be e / 2mc. So this is derived in various atomic physics or source quantum mechanics courses. But then for spin, because the magnetic moment due to spin basically, spin itself is not as a result of something going round and round. So it is not orbital see, orbital angular momentum is because the charged particles going round and round. And if it is going round and round, you can actually derive this using classical arguments. And the magnetic moment comes out as e / 2mc times the angular momentum.

But then the spin is an intrinsic property of the electron, for example, which is not because it is going around and around or anything. So it is like charge and mass, it is intrinsic to the particle. And so special relativity gives this additional factor of two, which is not explainable using Newtonian ideas. And you have to just live with it. So that is how it is. So so the magnetic moment of an electron in an atom is given by this formula

$$\mu_i = (e/2mc)(l_i+2\ s_i)$$

(Refer Slide Time 10:15)



$$l_i^2 = \hbar^2 (l_i + 1) l_i \text{ and } s_i^2 = \hbar^2 \frac{1}{2}\left(\frac{1}{2} + 1\right).$$

Classical case: For general classical molecules with a magnetic moment it is,

$$H = -\frac{e}{2mc} \sum_{i=1}^{N} \boldsymbol{J}_i \cdot \boldsymbol{H}$$

$$\frac{e}{2mc} \vec{J}_i = \vec{\mu}.$$

Assume $\boldsymbol{H}$ is in the z-direction. This means,

$$\text{Hamiltonian} \leftarrow H = -\sum_{i=1}^{N} J_{z,i} \frac{e}{2mc} H_m \rightarrow \text{magnetic field.}$$

where $J_{z,i} = J \cos(\theta_i)$. The canonical partition function is given by,

$$Z = \int d\Omega \; e^{-\beta H} = \int d\Omega_i \; e^{\beta \sum_{i=1}^{N} J \cos(\theta_i) \frac{e}{2mc} H}$$

$$Z = \left(2\pi \int_{\theta_i = 0}^{\theta_i = \pi} \sin(\theta_i)\, d\theta_i \; e^{\beta J \cos(\theta_i) \frac{e}{2mc} H} \right)^N$$

Now, because of quantum mechanics, you know that the square of the orbital angular momentum is in orbital quantum number is l(l +1), and the spin is being it is 1/2. So its 1/2×(1/2+1). So now before we jump into the classical quantum picture, rather, so this was the quantum description, i am going to start with something simpler, which is the classical picture. So now imagine there is a classical molecule with an intrinsic magnetic moment.

Well, j_i is rather, your (e /mc) j_i is my intrinsic magnetic moment and j_z is a classical vector, it is not a quantum object, not an operator, it is just a normal vector and assume that the magnetic field is in the z direction. So in which case, the Hamiltonian so I have to apologize for this being both the magnetic field and the Hamiltonian. So I am going to put a subscript m there signifying is the magnetic field is the Hamiltonian okay. That is the magnetic field alright.

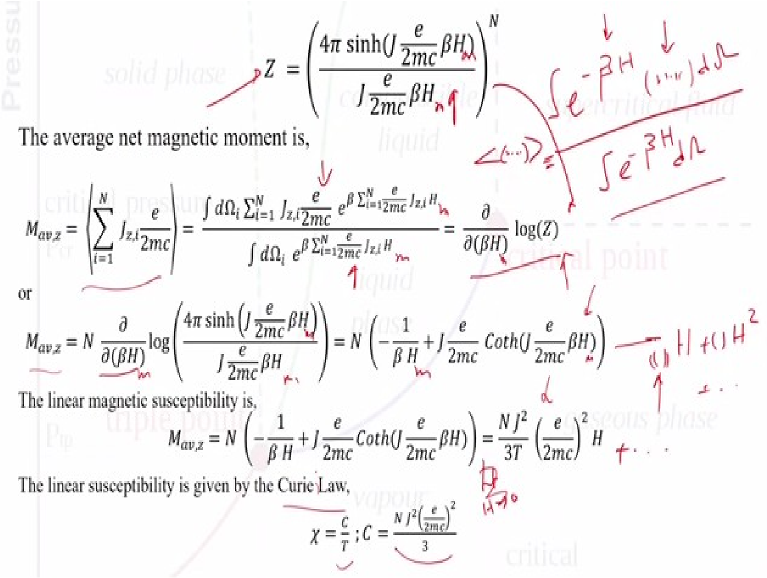
So now notice that because J and Jz are all classical quantities that basically and the magnetic field is in the same direction, The only component that is relevant, as Jz, and $Jz_{,i}$ = j cos(θ_i), were θ is angle made by the magnetic moment with the z axis. Now in order to calculate the grand partition, I mean, the canonical partition function allowed to integrate over all the angles. So the way to integrate all the angles is this way.

So I am going to integrate over the angles by using this solid angle as the so basically the density of states is one if you use the solid angle as your measure of integration, And this is how it works.

So this is how the canonical partition function is this 2π is because of integration or the angle Φ, and the integral over θ is from 0 to θ=π this remember what that is. So This is your θ, this is your φ, the φ goes all the way from 0 to 2π.

And θ goes from 0 to π like, you will be covering the entire sphere. So 0 to 2π over whole sphere. So, so that is what you are going to be integrating. And when you do that integration, you get this answer. Now you can go ahead and calculate the average magnetic moment. So the average magnetic moment is the so remember that if you want to calculate the average of anything,

(Refer Slide Time 13:31)



$$Z = \left(\frac{4\pi \sinh(J\frac{e}{2mc}\beta H)}{J\frac{e}{2mc}\beta H}\right)^N$$

$$\langle(\dots)\rangle = \frac{\int e^{-\beta H}(\dots)\,d\Omega}{\int e^{-\beta H}\,d\Omega}$$

The average net magnetic moment is,

$$M_{av,z} = \left\langle \sum_{i=1}^{N} J_{z,i}\frac{e}{2mc}\right\rangle = \frac{\int d\Omega_i \sum_{i=1}^{N} J_{z,i}\frac{e}{2mc}\, e^{\beta \sum_{i=1}^{N}\frac{e}{2mc}J_{z,i}H}}{\int d\Omega_i\, e^{\beta \sum_{i=1}^{N}\frac{e}{2mc}J_{z,i}H}} = \frac{\partial}{\partial(\beta H)}\log(Z)$$

or

$$M_{av,z} = N\frac{\partial}{\partial(\beta H)}\log\left(\frac{4\pi \sinh\left(J\frac{e}{2mc}\beta H\right)}{J\frac{e}{2mc}\beta H}\right) = N\left(-\frac{1}{\beta H} + J\frac{e}{2mc}\,Coth(J\frac{e}{2mc}\beta H)\right) \rightarrow (\,)H + (\,)H^2 + \dots$$

The linear magnetic susceptibility is,

$$M_{av,z} = N\left(-\frac{1}{\beta H} + J\frac{e}{2mc}\,Coth(J\frac{e}{2mc}\beta H)\right) = \frac{NJ^2}{3T}\left(\frac{e}{2mc}\right)^2 H + \dots$$

$H \to 0$

The linear susceptibility is given by the Curie Law,

$$\chi = \frac{C}{T}\,; C = \frac{NJ^2\left(\frac{e}{2mc}\right)^2}{3}$$

It is basically this one H times whatever average you want to calculate, divided by. So this is the average of that whatever you wanted to calculate. So the average of something is the phase space. So you put the Boltzmann weight, it is called here is called the Boltzmann weight and multiply with that thing, yours was average you want to calculate and then you divide by the total, weight. So that is what I have done here.

So, this happens to be also equal to the surface you can easily verify because So the log of so if I take the log (z) and I differentiate with respect to βH means magnetic, okay. So, this is the

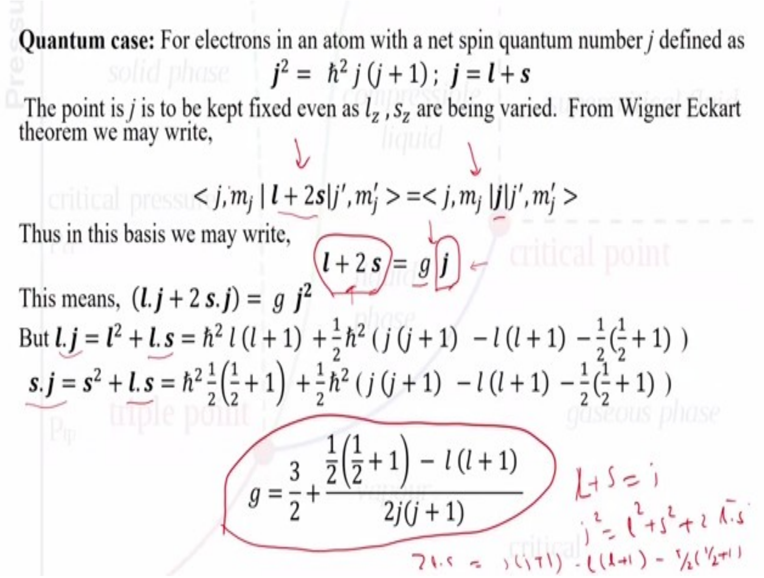
Hamiltonian, this is the magnetic moment. This is magnetic field rather not magnetic moment. So this is magnetic field. magnetic field magnetic field magnetic field. So If I differentiate with respect to magnetic field.

Take the log (z) differentiate with respect to magnetic field and multiply by temperature, which is 1/β, I get the average magnetization of the system, okay, as you can easily convince yourself because, because of this alright, so now, because I know what z is, now, I have just calculated it. I substitute that here and do the relevant differentiation. And I end up with this result, which tells me that the average magnetization is related to temperature and magnetic field in this fashion. And the magnetic susceptibility is basically defined as the linear. So if I Taylor expand this in powers of H, so I will get something into $H+H^2$ over ... This something is called the linear magnetic susceptibility. So this is limit as $x \rightarrow 0$ or the linear term, basically the linear term. So there will be other terms squared. So the linear term has this feature that it is inversely proportional to temperature, the proportionality constant is this.

So this is called Curie's law. So after Pierre Curie theory, so it just basically tells you that the paramagnetic susceptibility falls off inversely with temperature. So that is the linear paramagnetic susceptibility. So now, that was the classical description. So if your magnetic moments are classical, that is how it is going to look like. But now the question is, what if the magnetic moments are quantum so that I remember, that is how we started off.

We started off this way, when we started off discussing electrons. But then we said, let us do the classical case first. And we got this result which is Curie’s law.

(Refer Slide Time 16:44)



Quantum case: For electrons in an atom with a net spin quantum number j defined as

$$\boldsymbol{j}^2 = \hbar^2 j(j+1)\,;\ \boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$$

The point is j is to be kept fixed even as l_z, s_z are being varied. From Wigner Eckart theorem we may write,

$$< j, m_j \,|\, \boldsymbol{l} + 2\boldsymbol{s} | j', m_j' > = < j, m_j \,|\boldsymbol{j}| j', m_j' >$$

Thus in this basis we may write,

$$\boxed{\boldsymbol{l} + 2\,\boldsymbol{s}} = g \boxed{\boldsymbol{j}}$$

This means, $(\boldsymbol{l}.\boldsymbol{j} + 2\,\boldsymbol{s}.\boldsymbol{j}) = g\ \boldsymbol{j}^2$

But $\boldsymbol{l}.\boldsymbol{j} = \boldsymbol{l}^2 + \boldsymbol{l}.\boldsymbol{s} = \hbar^2\, l\,(l+1) + \frac{1}{2}\hbar^2\,(j\,(j+1)\ - l\,(l+1)\ - \frac{1}{2}(\frac{1}{2}+1)\ )$

$\boldsymbol{s}.\boldsymbol{j} = \boldsymbol{s}^2 + \boldsymbol{l}.\boldsymbol{s} = \hbar^2 \frac{1}{2}\left(\frac{1}{2}+1\right) + \frac{1}{2}\hbar^2\,(j\,(j+1)\ - l\,(l+1)\ - \frac{1}{2}(\frac{1}{2}+1)\ )$

$$\boxed{g = \frac{3}{2} + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) - l\,(l+1)}{2j(j+1)}}$$

$l + s = j$

$j^2 = l^2 + s^2 + 2\, l.s$

$2l.s = j(j+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1)$

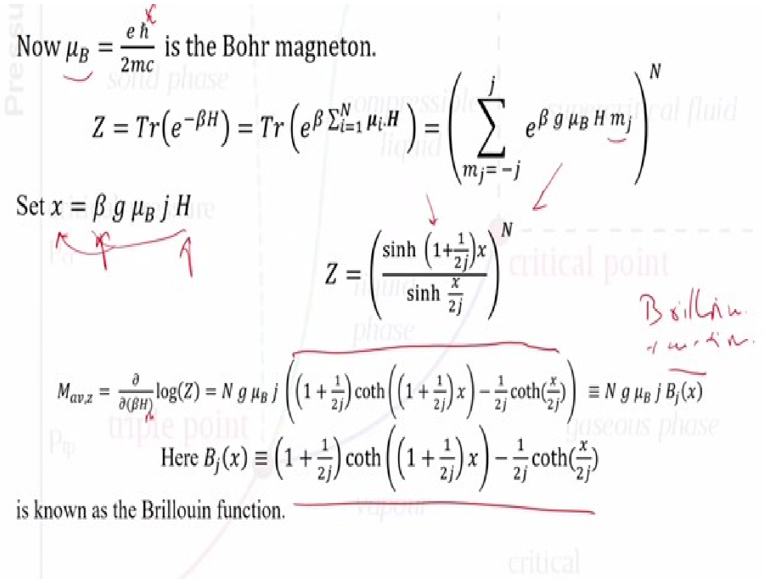
Now let us go ahead and do the quantum case where basically the electrons are now because they have both orbital angular momentum and spin angular momentum. Their states are now labeled by the total net angular momentum.

So which is l+s. So then, you have both jz, and J, which is the the quantum number corresponding to j^2, as being the good quantum numbers. Now, it so happens that you can kind of use what is called Wigner Eckart theorem, which guarantees that l plus two s is basically points in the direction of j, so long as you are interested in matrix elements between eigenstates of j square and jz. So this proportionality constant is called Lande g factor.

And this can be computed in the following sense. That to take the dot product with respect to j on both sides, And then you work out s, sj is this lj is this an ls. Remember that l + s is J. So basically, $j^2 = l^2 + s^2 + 2l.s$. So $j^2 = j(j+1)$. And $l^2 = l(l+1)$, and $s^2 = 1/2\times(1/2+1)$. And that is basically your 2l.s. So 2l.s is just a number. So I am going to use that and then I derive this formula this formula for the Lande g factor.

The proportionality constant, it so happens that see, the thing is that all my good quantum numbers are related to j, l+2s is neither L nor s nor j. So I want to be able to write it in terms of j. So fortunately, Wigner Eckart theorem allows me to do this. And it says that l+2s is guaranteed to find the long j, so long as you are only interested in the matrix elements with respect to the eigenstates of j square and jz. Alright, so and that proportionality is going to be this so this is called Lande g factor.

(Refer Slide Time 19:03)



Now $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton.

$$Z = Tr\left(e^{-\beta H}\right) = Tr\left(e^{\beta \sum_{i=1}^{N} \mu_i . H}\right) = \left(\sum_{m_j=-j}^{j} e^{\beta\, g\, \mu_B\, H\, m_j}\right)^N$$

Set $x = \beta\, g\, \mu_B\, j\, H$

$$Z = \left(\frac{\sinh\left(1+\frac{1}{2j}\right)x}{\sinh\frac{x}{2j}}\right)^N$$

Brillin. funtin.

$$M_{av,z} = \frac{\partial}{\partial(\beta H)}\log(Z) = N\, g\, \mu_B\, j\left(\left(1+\frac{1}{2j}\right)\coth\left(\left(1+\frac{1}{2j}\right)x\right) - \frac{1}{2j}\coth\left(\frac{x}{2j}\right)\right) \equiv N\, g\, \mu_B\, j\, B_j(x)$$

Here $B_j(x) \equiv \left(1+\frac{1}{2j}\right)\coth\left(\left(1+\frac{1}{2j}\right)x\right) - \frac{1}{2j}\coth\left(\frac{x}{2j}\right)$

is known as the Brillouin function.

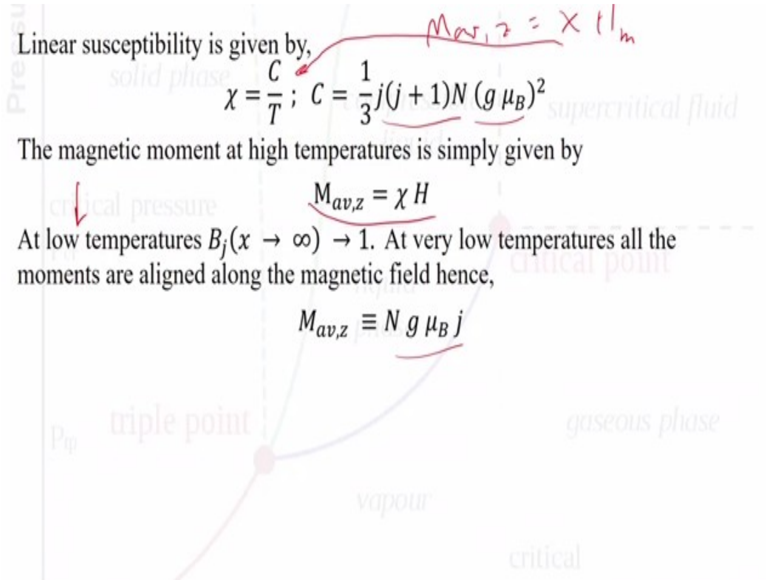
So I am going to use this Lande g factor and then substitute instead of l+2 instead of l+2 i am going to write g× j vector then j vector dotted with H is basically Jz. which is, you know, M, the magnetic quantum m_j ħ. So that is the reason why there is an ħ here. So it is a e /2 mc times h bar, which is already put into this, this becomes the Bohr magneton. And so I am gonna have this nj because jz, then I will be forced to some over all m_j N.

Remember what what the values of Mj are restricted to be, they are restricted to go from - j to +j. So I am going to be summing over all the values of MJ from - j to j. And then in order to facilitate this, i am going to make a re definition of this quantity as x. So when I do that, I can do the summation, just a simple, you know, geometric progression, geometric series, a finite geometric series, which you can do yourself. So I had this answer in terms of this x.

Now as usual, I am going to go ahead and differentiate log z at with respect to β times the magnetic field, And I get my average magnetization, the z direction. And that is related to this function, which is known as the Brillouin function. So this is called function Brillouin function. So now it is worthwhile to understand how this thing behaves for small and large values of x. Because after all small values of x correspond to, on the one hand, small magnetic field,on the other hand, large temperature, so you can either look at small values of x as being because of large temperature, or because of small magnetic fields. So that is the linear, classical regime. But then, conversely, if x is very large, it could be either because the temperature is very small, or your magnetic field is large. So, so you can suspect that if the magnetic field is large all the moments are going to be aligned.

So it is nice to know that that is synonymous with low temperature. So that is telling you that when the is temperature is low, also, it is similar to the magnetic field being large.

(Refer Slide Time 21:37)



Linear susceptibility is given by,

$M_{av,z} = \chi H_m$

$$\chi = \frac{C}{T}\;;\; C = \frac{1}{3}\underbrace{j(j+1)}N\,\underbrace{(g\,\mu_B)}^2$$

The magnetic moment at high temperatures is simply given by

$$\underbrace{M_{av,z} = \chi\, H}$$

At low temperatures $B_j(x \to \infty) \to 1$. At very low temperatures all the moments are aligned along the magnetic field hence,

$$M_{av,z} \equiv N\, g\, \underbrace{\mu_B\, j}$$

Alright, so so let us work out the first case, where the temperature is large, or the magnetic field is small, in which case, the average magnetization, is going to be proportional to the applied magnetic field. And the proportionality constant is called the magnetic susceptibility. So In this case, this is paramagnetism. So we have a susceptibility that is inversely proportional to temperature and proportionality constant is derivable in this fashion.

So however, at for low temperatures, or high magnetic field, x, very large, and when x is very large. What is going to happen is that this cotangent hyperbolic, basically becomes unity. And because it is, like, you know, cosh / sinh, and they are both equal, arguments are large. And then this becomes approximately 1+1/2j-1/2j=1. So then when x is very large, this Brillouin function is one. And because this one.

The average magnetization is, just independent of temperature at low temperatures, and it kind of saturates to the maximum value, which is given by the maximum magnetization, that is possible when all the magnetic moments are aligned with the magnetic field. So that is the story of para magnetism and Landau diamagnetism. So The next topic we are going to discuss is what is known as Ferromagnetism naturally.

And the prototype or the simplest model that exhibit ferromagnetism is known as Ising model. So i am going to first describe Ising model in one dimension, mainly because it is solvable Exactly. But downside, unfortunately, is that it does not exhibit ferromagnetism, except at absolute 0. So that is really puts a damper on things. So fortunately, things brighten up in higher dimensions, like two dimensional Ising model has non trivial ferromagnetism at finite temperature.

But of course, is much harder to solve. So let us see if I get around to it. I will discuss it, but I am certainly going to discuss one dimensional Ising model. And some approximate methods to handle Ising model in two and three dimensions. Alright, so I am going to stop here. In the next lecture, I am going to discuss the Ising model.