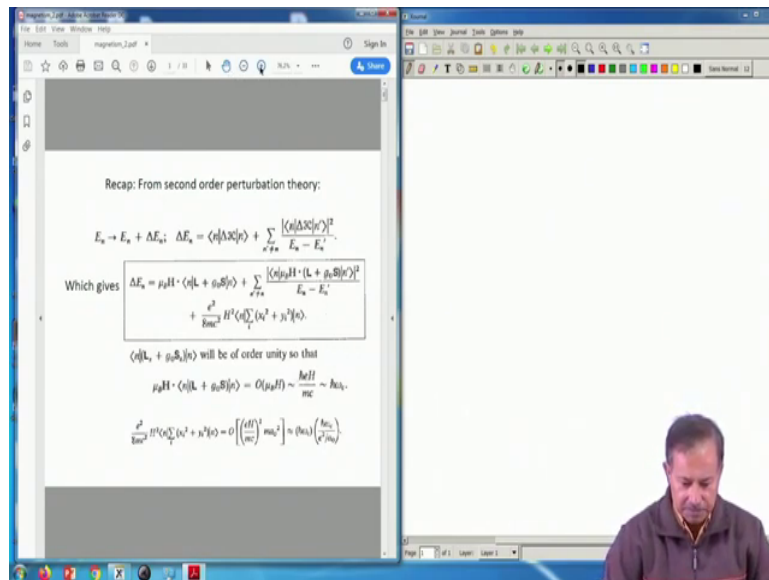**Electronic Theory of Solids**
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Lecture – 31
Curie's Law and Van Vleck Paramagnetism

Hello we are dealing with the magnetic system. So, magnetism is what our concern is at the moment.

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So, let us just recap a bit quickly what we did is that we took a magnetic ion or an atom, and tried to calculate its magnetic behavior. And for that we took in the electrons in the ion or the atom. And assume that they are independent; they independently respond to the magnetic field, and their magnetic energies are calculated. These energy being extremely small, one can treat them the corrections due to magnetic field as a perturbation, and so then one basically sums up the contribution from an ion. And then finally, I have just multiply that by the number of ions to get the total magnetization.

And so that is the procedure we followed. In that procedure what we did was that we encountered three terms up to second order in perturbation theory. The first two terms come from the first order and second order, and they look at them they are this one is proportional

to L plus g S. So, L and S are explicitly inside. This also has L and s; that means, a magnetic ion an ion which has nonzero L and S, that means, it has moment contributes these two terms. Whereas, this term the last term the third term in this does not require the atom or the ion to possess a magnetic moment. It is the response of the electronic orbits against the magnetic field like Lenz law that the back emf we have generate in Lenz law in a circulating current.

So, excuse me. So, this term is different, the last term compared to the first term. The first two require you to have the presence of magnetic moment in the system already whereas, the last term is just the magnetic response of the orbits you know of the electrons in an ion. This, this basically a contribution from Lenz law that we have studied in electrodynamics.

So, the then of course, there are situations where if you do not have L and S like in a closed shell system, then you do not have any contribution you from the first two terms, and then that is what we called Larmor diamagnetism which comes from the last term ok. Such situations remember this happens in every atom whether it is close shell or its open shell or whatever. So, this contribution will always be there the third one in the diamagnetic contribution.

Whereas, the first term being overwhelmingly large when you have a magnitude when you have this non zero, and so generally one neglects these higher these terms, the second and the third term if the first term is present and that is that is called the paramagnetic contribution as its shown here that this is much larger. So, this we discussed in earlier slides.

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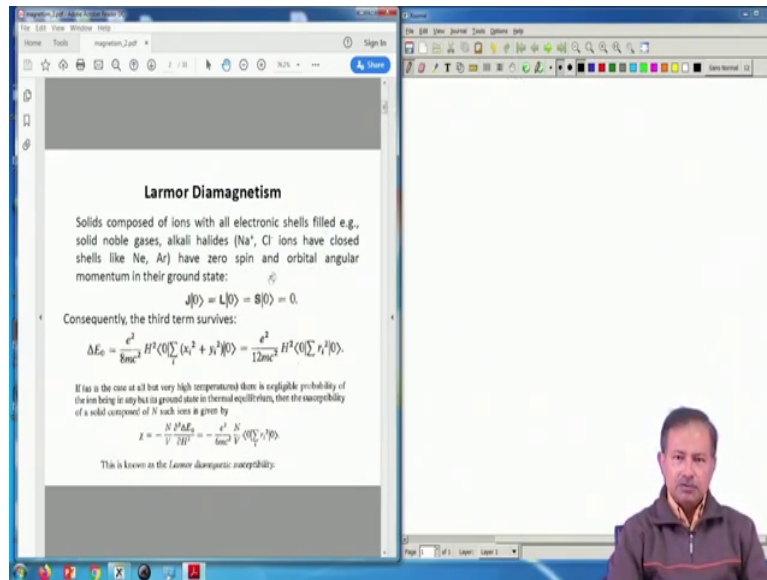
So, the Larmor diamagnetism as I said comes from the last term, and it is it is to be calculated, it is there in every atom every ion and it is to be calculated when L, J, S are all zeros, then there is no contribution from the first two terms ok. So, these when does one encounter such a situation, I will give you a list of such atoms, but look at the noble gas, near all the noble gases for in solid state, they will contribute only to diamagnetic part, Larmor diamagnetism because they have a completely closed shell. ah

Similarly, sodium and chlorine atoms do not have well closed shell, but Na plus and Cl minus are closed shells, so like neon and argon. So, they will also contribute to; that means, the sodium chloride crystal will also contribute to sodium chloride salt will also contribute to this diamagnetic term, and they are these terms are relevant. So, the in the ground state that is that contribution is important.

Ah So, this generally the r square that appears here this x square plus y square is two-third of r square in a symmetric atom, the close shell atom is more or less symmetric. So, in that case you can write this by just the replace it by its average I mean this is generally done in almost in many cases, because these does not bring in too much of an error. So, this, so, so over all the electrons you sum these r is and then just divide by the Z i the atomic number, and then you can write a molar susceptibility by this formula. It is just that this part is the diamagnetic susceptibility this part that we calculated, Larmor diamagnetism times these factors. So, it is typically of this order for example.
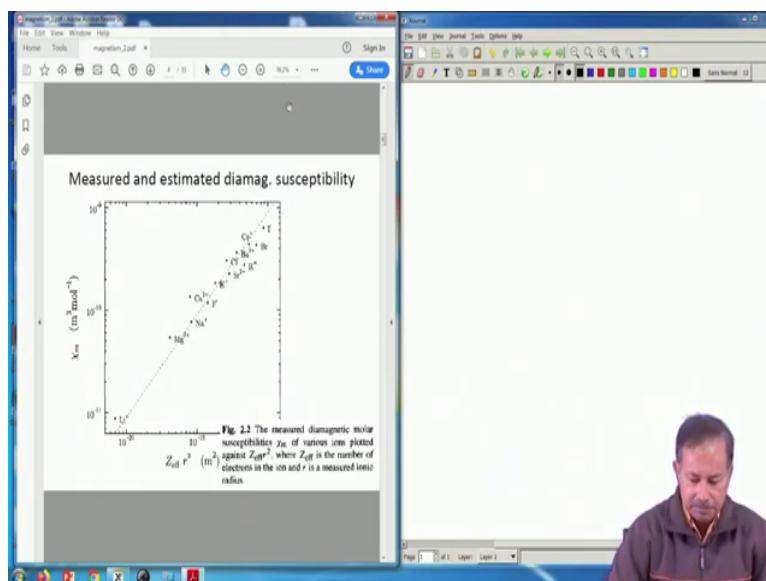
So, these are some comparison of the measured and estimated diamagnetic susceptibilities. And as you can see that the comparison is not too bad, some molar susceptibilities are versus there Z effective that quantity that average quantity for example, you can think of as Z effective, I mean it is just it is an effective number of electrons in the ion; and so these quantities on the x-axis, and then you have chi m on the y-axis.

So, this look at these the values these dotted line is the theoretical estimated diamagnetism, and the dot the dashed line the dotted line, and these dots these larger circles small circles are the measured values. And you can see that there is fairly good comparison. This is iodine at the top. The comparison is not bad, I mean the agreement is fairly good and this kind of theory quantum theory of magnetism is fairly successful in predicting their diamagnetic susceptibilities.

But the magnitudes you can see are exceedingly small and that is what we mentioned right in the beginning. So, sodium ion and chlorine minus are all in this, fluorine minus, and basically alkali halides are more or less they have this as I said these Na plus and Cl minus are both closed shells. So, these they fit into the bill.
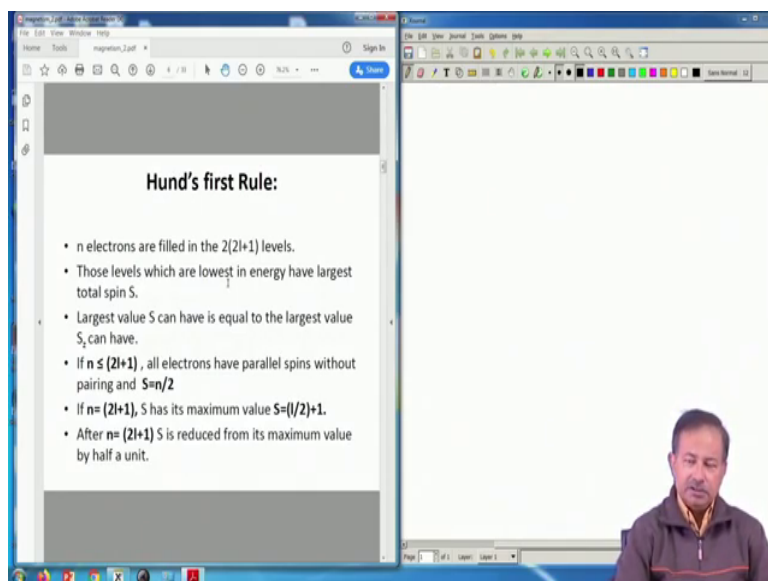
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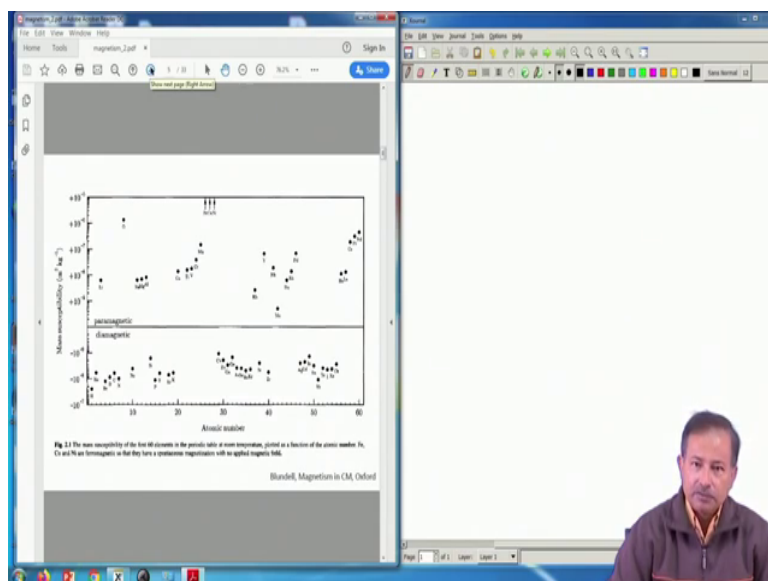
This is the susceptibility of this is total susceptibility of first 60 elements in the periodic table at room temperature plotted as a function of the atomic number ok. So, look at this, these are the upper side of course, above zero is paramagnet, below zero are diamagnets, and there are fairly large number of diamagnetic materials, and of course, there is a fairly large number of paramagnetic materials as well.

The interesting thing is of course, these three – iron, cobalt, nickel, and they are spontaneously magnetized their magnetism requires a different treatment and understanding, where the actually the ionic ions the moments on the ions interact with their neighboring ions. So, this is a completely different ballgame, these are spontaneously magnetized system, and they are much higher magnetic susceptibility.

But this is a very nice graph chart which tells you that there are many systems where these the as I said these are 60 system, 60 elements in the periodic table whose magnetic susceptibility mass susceptibility is plotted. And in many of cases as I said theory agrees fairly well with the experiment.
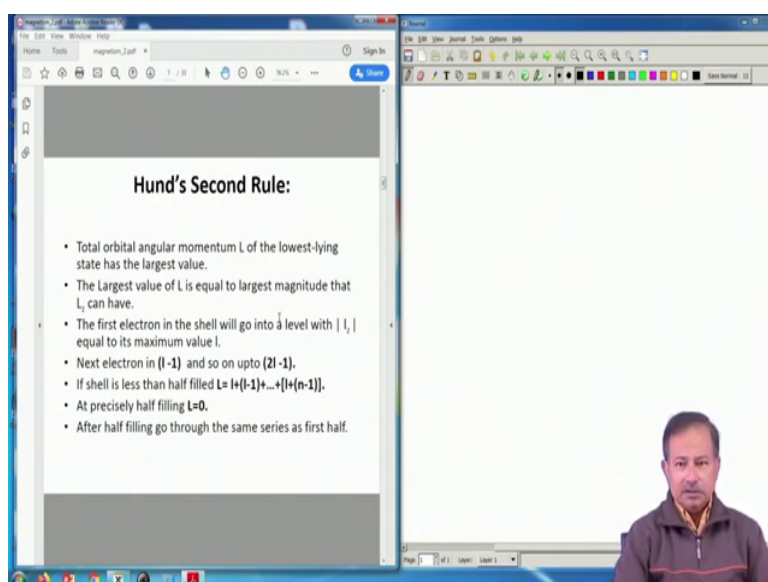
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Then we went ahead and did Hund's rule this is required because we need to know L and S, and of course J. So, then these are the three rules 1, 2 and 3 in that order. You have to first apply rule 1, then apply rule 2 consistent with rule 1, and then apply rule 3 if the spin orbit coupling is strong enough then consistent with rule 1 and 2.

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So, that is the that is the scheme.

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In that scheme, we showed how the d-shells for example, L equal to 2, are organized d d-shell electrons are organized, their L values, S values and the corresponding J values are calculated. This term symbols you need not bother too much, because but this is the historical way of writing these configurations. ah

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This is more elaborate in L equal to 3, where you can put 14 electrons; these are f-shells and as you can see. I would like to draw your attention to one case of course, this completely filled shell as I said has everything 0, S, L and J are 0 ok. Whereas, there is one which is 1 electron less than half filling, so this for example, is d-shell it can take 10 electrons, so half filling is 5. Look at 4, 1 less than half filling, this as L and S same. So, L minus S is 0, which is J. Similarly, this is f shell it can accommodate 14 electrons. So, take 7 is the half minus 1 is 6. Look at 6, L and S are same, and J is 0. This J equal to 0 has consequences which I will come to.
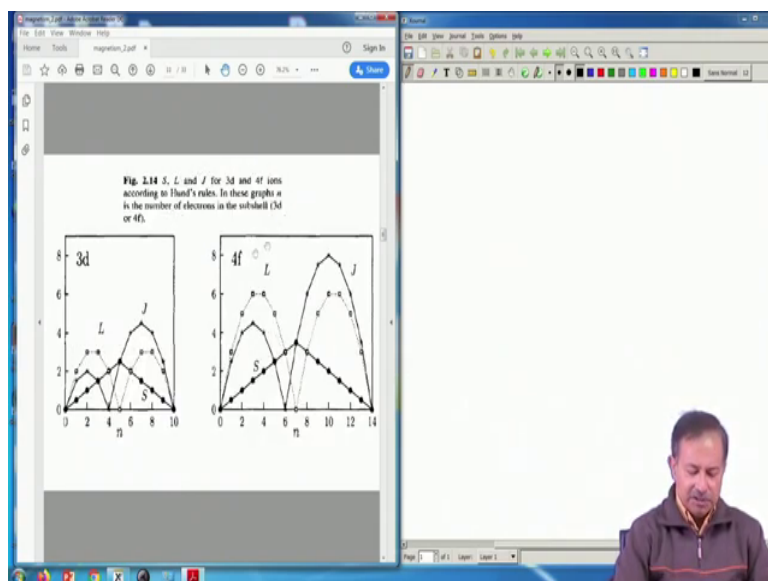
So, these are the standard values of S, L and J from atomic data, they are consistent with Hund's rule for 3d and 4f ions ok. So, 3ds like scandium to zinc, and 4 f is this lanthanide series. So, if you look at this, this is L, this is S, the solid line is S, this dotted line is L, and this solid line with stars is the J. And as you as I showed that just one less than half filling, you have this J turning out to be 0, similarly here also at 6, here at 4. So, so this is this is basically the atomic that table being plotted here.

Now, this is the magnetic ground state for 4f ions which is whose scheme is given on the right hand side here, configuration scheme. So, using Hund's rule again for each ion the shell configuration, and the predicted value of L, S, J for the ground state are listed which we already did. The additional thing is that calculated value of something called mu effective by mu b which has this form g sub j into J into J plus 1 to the power half this will come from a calculation which we will do next.

So, so just take this as an effective value of the moment that is sitting and the in that ion or the atom from the Hund's rule predictions. And the next column shows you what the experiment tells us. So, this has to be the column last but one column p has to be compared with p x x e x p. And the first three are just the first four at first the shell S, L and J are from Hund's rule. So, there is no nothing in that.

The columns to be compared at this last and the last but one. So, you can see that for this series 4 f series cerium to lutenium, lutetium there is this agreement is not bad initially. The initial agreement is not bad, but then suddenly here the agreement became terrible. This is 4 f 5, 4 f 6,and the somehow these two did not match. And why did not match, requires some, some work, but the rest of it more or less match matches fairly well. So, there is a lot of truth in the theoretical calculation that has is being done, and experiment is peering it out ok.

Why is why are these two not so good, it is because the next J multiplied is pretty close here and that is not accounted for in this calculation when this is x p calculation was done theoretically, so that that brings in additional complication. So, that is not what we are going to study, but it is just to remember that it the agreement is fairly well; when there is no agreement then there is also an understanding as to why the agreement is not good. And if you incorporate those, the agreement actually becomes much better.
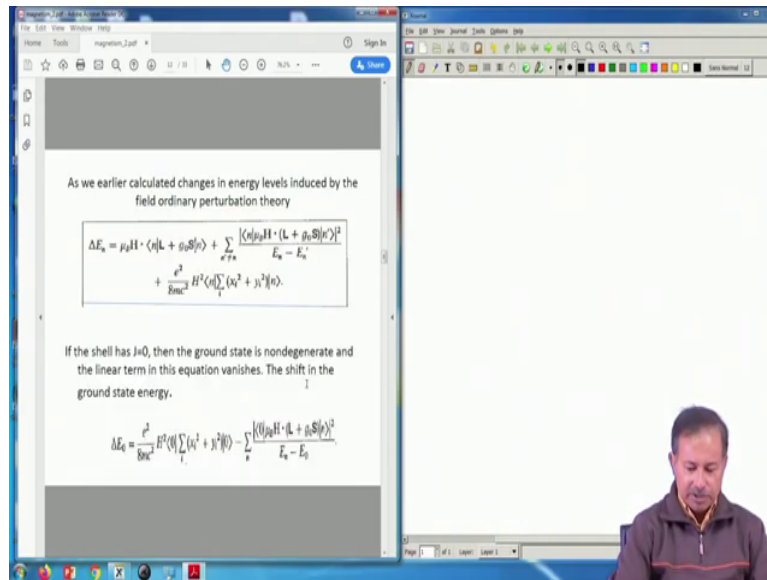
So, this was something that we have been showing many times, this is the this is all that we got from the second order perturbation. These are the terms. Now, the thing that I mentioned that a shell has suppose J equal to 0, but then the ground state is non-degenerate of course, and the linear term in this equation will vanish. This can be shown that L plus g 0 S this, this whole thing is the expectation value in the ground state vanishes if you have you actually because this can be replaced by something proportional to J. So, the expectation value actually dependent is proportional to J, and that gives rise to if J equal to 0 then this term vanishes. So, this will then vanish for the closed shell as well as for the n equal to half minus 1 situation ok. So, ok, so these are the two cases we have to be we are being alerted by this ok.

So, if J equal to 0, then we have these the next two terms. Remember here n and n prime if n is the ground state for example, n prime is different. And in this case, this will not vanish, and this has consequences. What is the consequences, look at this the signs of these two terms. These term as we say as we find it gives an energy which is positive, that means, this it contribution to energy is positive, that means, free the susceptibility will become negative. Whereas this one has a contribution which is negative and look at how it is written it is negative because now we have changed the denominator from E here the denominator was E

0 minus E n, whereas we just took the minus sign here and wrote E n minus E 0, so because E n is almost is always greater than E 0, so that in that case in the non-degenerate system.

So, in that case, this situation tells us that there is a negative contribution to energy, and this term will provide a positive susceptibility to the system. So, this will be Larmor diamagnetic contribution – the first one, and the second one will be a paramagnetic contribution coming from J equal to 0 shells in the second order.

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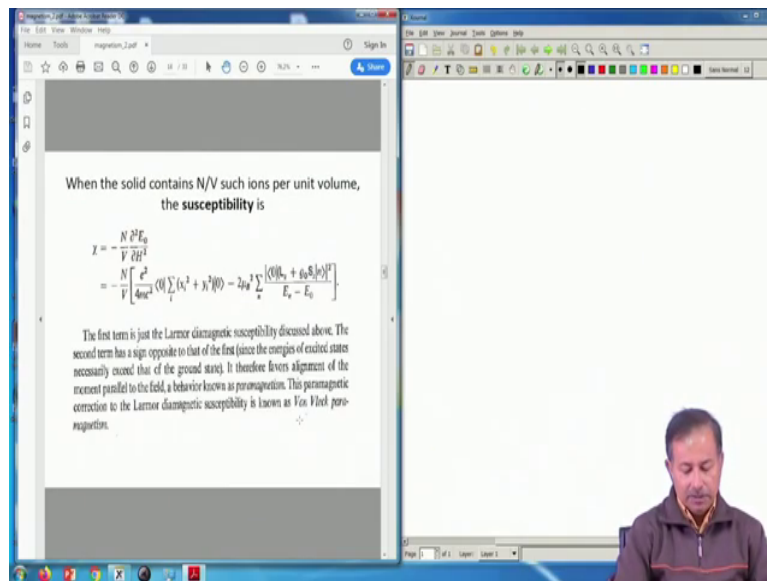
And this is actually called the this was shown by Van Vleck. And he in his name after his name this is named a Van Vleck paramagnetism. So, the point is that this term favors in alignment the first term then is diamagnetic it favors alignment of magnetic moment opposite to the field, whereas this will favor an alignment in the direction of the field as a paramagnetic contribution. And so the total magnetic moment and the susceptibility contribution will have to be sum of the two ok.

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So, this is again the if J equal to 0, the first order perturbation contribution is 0 as I said, and therefore, you are only left with for the paramagnetic contribution second in second order perturbation, this is the only term that is left plus the Larmor diamagnetism term. So, that then so this term gives a contribution as you see to chi which is positive ok. Remember E n is greater than E 0. So, this term is negative exactly as I said in the previous slide. So, the susceptibility becomes positive. So, the you add to this the Larmor term and get the total susceptibility. So, it is a subtraction between the two.

So, this is so far we have been doing magnetic behavior of ions and then just multiplying it by the number total number of ions in the in that in a system and dividing by volume to get the magnetization density. Now, and these question now is that what happens at finite temperature, and suppose you have a system with a give given J and at finite temperature, how would you find its magnetization and susceptibility as a function of temperature.

Here again we will assume that these moments are just free moments. So, now, we forget the ion. We just have a moment coming from those ions or atoms. And these moments are now the solid consist of these moments they are randomly arranged of course, and then that is what a paramagnet is, there is no net magnetization that you get unless you put in a field.

So, the question then is what will happen if I put a field in this paramagnet at a finite temperature. And for that we have to do statistical mechanics and that is exactly what we will do. In many books, you will find a classical treatment of this thing. And that classical treatment as we said in the beginning has his own hazards Bohr, remember again I mentioned Bohr Van Leeuwen this spelling is always, I think it is correct is it is complicated, but it is of course, this is her name and Bohr Van Leeuwen had, Bohr and Van Leeuwen had shown that you do not have in equilibrium any magnetic moment coming from classical description of the system, so that we must keep in the background.

So, whenever you see a classical treatment you must have seen in many books that a draw a sphere and then an annulus, and there is a field in this direction. And one calculates the number of then this mu b cos theta and so on, I mean this treatment gives you correct results. And it is in the J equal to infinity limit of course the spins can be treated classically the moments can be treated classically, but nevertheless I will avoid doing any classical treatment because inherently they have there problem due to Bohr Van Leeuwen theorem.

So, ok, so this is this is the theta. And now so I will not go through this kind of a classical calculation, although you will find it in many books and they give more or less they give correct results in at least in a at high temperatures and for J equal to infinity, they are correct. They give right results.

So, energies will be then this is something we know from Stern-Gerlach experiments that minus mu B into magnetic field is H, actually I am using H, this is written B sorry about it, but this is minus mu B H and plus mu B H.

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Ok. So, then of course, you can do a very this is a two-level system only two energy states to be considered and you can calculate the partition function easily. So, from the partition, you can do it in many ways. Here for example, you can straight away calculate the expectation value of m J by multiplying the m Js with their corresponding probabilities or that will give

you this mu B times tan hyperbolic mu B H by k B T. So, that gives my the saturation magnetization is of course, where all spins are saturated. So, in, so if you divide by that then you get a tan hyperbolic function where y is mu B H by k B T.

Now, what is interesting is that why is this factor inside that is coming you see it is always coming as mu B H by k B T. So, this is a dimensionless quantity, it is a ratio between two energies. So, it is basically H by T, and corresponding dimension full quantities to the dimension for making to energy dimension you multiply by k B and here by mu B.

Now, it is H by T at finite temperature, for example, tells us a story. What does it say suppose I put a magnetic field and these free moments are there, they will start aligning towards the magnetic field. So, what stops them from completely aligning immediately, because that will minimize the energy, well, it they then there is a temperature at any finite temperature the alignment will not be complete because of the randomness the energies that are coming from the temperature from finite temperature. So, the temperature tries to randomize them, set the moments, some of the moments will become then 0 if you temperature dominates because temperature will completely randomize the these moments, they will fluctuate and they will have their a directions in all possible ways.

Whereas, the magnetic field is trying to align it, so the ratio see look at it the h is in the numerator it is trying to align, whereas T is in the denominator is trying to randomize, so that is the ratio that you will have to have to when you calculate this in this way of doing things. Of course, if you take interactions, if you take other relevant term in terms which are which will come into play particularly at low temperatures for example, then of course, this description is not entirely correct. But till very fairly low temperature and this H by T ratio will dictate everything. And this is physically very obvious that this is how it has to be.

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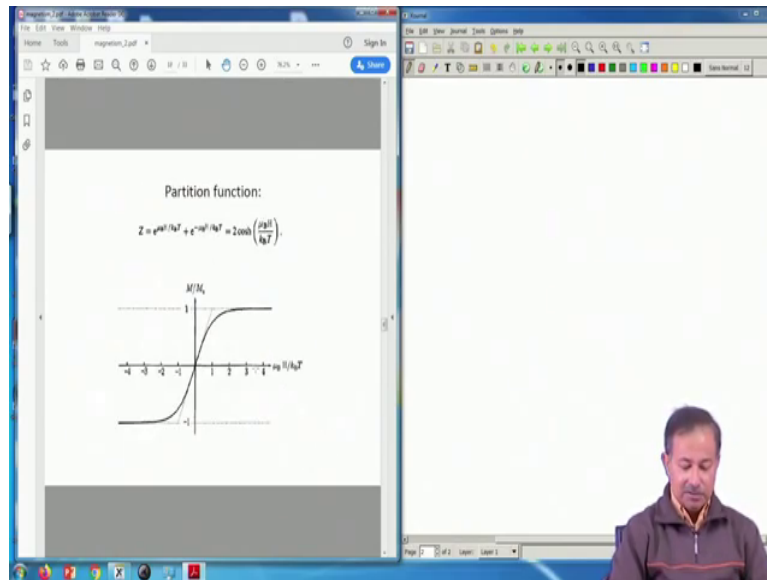
So, this gives a chi which is n, n is the density mu B square by k B T. So, it is inverse in temperature ok. There is a very famous law Curies law, for example, that says the susceptibility this is one law of named after Pierre curie. And this is so this tells us that the susceptibility will go inversely as temperature. So, it has a divergence as you go down to zero temperature, so that is something we will not bother here about too much, but there is a lurking divergence at as t goes to 0.

The other way to do it is just blindly do statistical mechanics. So, that is where you I mean that is what we learned that we just calculate the partition function and just go ahead, and calculate all relevant physical thermodynamic quantities that you want to calculate.

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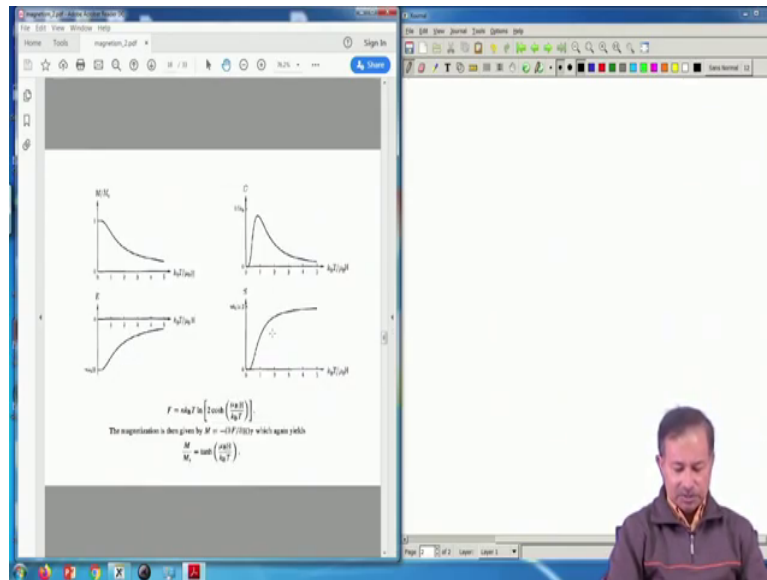
And so I will just show you that this. So, once you get a partition function, then of course life becomes very simple in statistical mechanics and that is what we will continue discussing in the next lecture.

So, thank you.