Electronic Theory of Solids
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Lecture – 30
Hund's Rule

Hello, we have been discussing magnetism, particularly magnetism of an ion or an atom with its electrons inside. And so what one does is that one starts from the change in the Hamiltonian, see the electrons are the ones which are responding to the magnetic field. So, one actually writes down the Hamiltonian for the electron in the atom or the ion.

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And what we found out is that the there are three main terms in it, there is this term first term which is the para straightforward paramagnetic term, this term - the first term. Then there is a suppose this term vanishes, then we have to go we have to look for terms above it, beyond it which is the second order term. Remember, the as we discuss the susceptibility is a is it is a second derivative of the free energy. So, the second order contribution to energies you have to keep, and so the if the first order contribution some of vanishes, then of course, the second order becomes an important. And there is of course, a third order term.

So, these three terms basically come from the for example, the first order term and the second order term both come from the spin of the electron and the orbital angular momentum of the electron that couples to the field and the corresponding change in energy is given by the first two terms. So, the electronic configuration of the atom that we are discussing is extremely important, because all these terms L and S, their values are determined by the electronic configuration inside the atom or the ion. The other term the last term, its source is slightly different in that it is coming as you as you can see from the size of the orbital is important. So, it actually comes from the rotation of the orbital, the alignment of the orbital, plane of rotation shifts a bit when you put a magnetic field and so that shift in energy comes from that. And so this contribution is interesting, the last one in the sense that this is you will show as you as we will show this will give you a negative contribution to susceptibility.

Now, if you remember your school days magnetism, then the susceptibility is chi is positive, then we call it paramagnet; and if chi is negative, we call it diamagnet. See the diamagnetic materials as we learned in the school move away from the magnetic field and so on and so forth. So, that is basically reflected in the fact that the susceptibility is actually negative for so susceptibility is a response, response is negative.

Now, as I said these electrons are thought to electrons inside the atom, the ones which are contributing to magnetism. See the closed shell as we just show you that does not contribute to magnetic in at least not the first term, so the and this is the major contribution. So, that we will we actually look for contributions from the electrons which have beyond the closed shell.

So, for closed shell of course we will find that there is only term that will survive is this diamagnetic term which I will just come to. The other thing, I mentioned was that this term is the first term which is the first order contribution to energy coming from the paramagnetism of the of the atoms is a much higher term compared to the diamagnetic term.

The second term of course is also paramagnetic, but you see it has a denominator energy which is difference between two energy levels and these are electronic energy levels which are typically electron volts. So, this is actually way down compared to the first term as well. So, once the first term survives you know more or less magnetism of the material of the atoms, of the concerned atom is determined by the first term.

So, we estimated these to be at 10 to the power 4 gauss; the first term gives 10 minus 4 electron volt, the last term gives about 10 minus 9 electron volt and so on, so that is that is the ballpark figure one is considering. And as I said in a material, in a when you go to a solid or your collection of atoms and remember here the atoms, do not talk to each other at least this spins do not talk to each, the electrons do not talk to each other. Even inside the atom the electrons do not talk to each other, because the inside is closed shell and that does not contribute to magnetism whereas, the outermost orbital is the one which contributes.

So, these are considered completely independent and in such situation, this is the Hamiltonian. If they talk to each other of course, then we will have to add those terms and they involve much more work, we will come to it at a later stage; particularly when the moments sitting at the atoms at different atoms, talk to each other.

Now, the so the these typical for example, this picture of susceptibility that you got in your school days probably you have seen or you may not have may not have seen this, but this is what it is that you have paramagnetic susceptibility, this is chi and this is temperature T. So, paramagnetic susceptibilities are somewhere here, diamagnetic susceptibilities are here and free spin these are called Pauli paramagnetism and Van Vleck paramagnetism they are pretty close.

So, Pauli somewhere here is Van Vleck these are terms I am using, I will explain what they are as we go on. We will discuss Pauli paramagnetism so and Van Vleck comes from a term from the second term in this Hamiltonian. So, and then the free spin free moments will give you free atomic moments will give you the free moments on the atoms are they have this large much larger susceptibility and sort of diverges as T goes to as lower temperature; and the diamagnetic one is here, this is negative this is 0.

So, this is the typical graph that one sees in books and other places and all of these are explainable in terms of quantum mechanical calculations, as we are doing. See this Hamiltonian, this these have almost everything that you need to know for atomic magnetism. When as I said, we go to long range ordered systems atomic order, then one has to go beyond this that is a very different approach and that is where there you have to consider the moments on the atoms ah interacting with each other and different atoms ok.

So, so let us just go one more step this is Larmor diamagnetism this contribution from the last term ok, is typically called the Larmor diamagnetism. And because this has to corresponding susceptibility is the Larmor diamagnetic susceptibility. Now, this if you have a solid where the atoms are or ions; ions have all their electronic shells filled. For example, in this noble this argon neon, xenon this kind of system for example, they have completely filled shells right, so inert gases.

So, there of course they are inert, because they are completely filled shells. There you will have this situation that L is 0, S is 0; therefore J equal to L plus or minus S is 0. So, then so then everything you see if since L is 0, L is 0; if J and then J is 0, J is basically L plus S or L minus S as we will come to Hund's rule. Then this is this the there is absolutely no moment sitting at the atoms, so electrons have no moment total moment is 0.

Now, so this is a situation where your first term vanishes yours and remember the first term vanishes here, this term will also vanish second term, because L and S are 0, so then one has only the last term to contend with. This last term is proportional to H square already, so this will give me a with a minus sign and look at it all terms here are positive quadratic square terms right. So, there is no way this term, this term can give you a negative value.
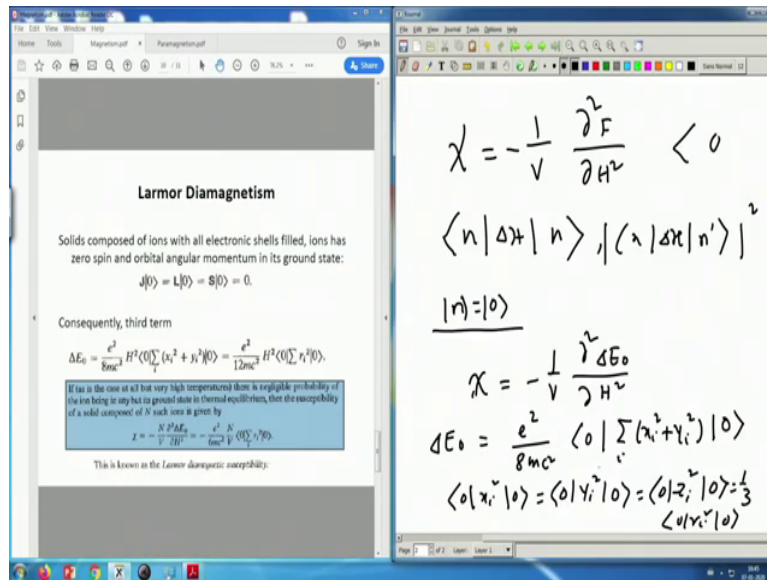
And then as we know that chi is minus 1 by V del 2 F at very low temperature this F is basically E. So, this will of necessity V less than 0 and this has to be diamagnetic because of this minus sign sitting there and this derivative being positive.

So, the other interesting thing that you have to remember is that although I have written the energy for the nth, so whatever I have put here is n or n so delta H n, n delta H n prime. So, this kind of things we have put in most of the times you will be dealing with n equal to 0, the ground state.

So, the ground state is all that you are concerned with simply, because the magnetic energies as we just found out are so small that they are smaller than the temperature scale typically, they are smaller than any other electronic scale. So, you are more or less confined to the ground state.

And so what one really does is to calculate the change in energy in the ground state, and in that case unless you are at finite temperature; where you the finite temperature contributions add up to free spin moments, free moments, so that we will come to ah, but for most atomic calculations you are you are looking at the change in energy of the ground state.
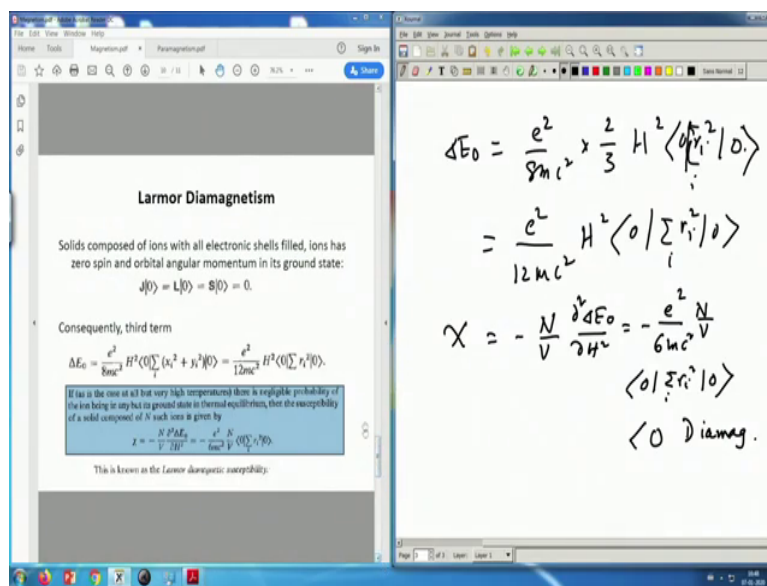
So, and so therefore you are as is done here, the ground state one has just taken the derivative here of the ground state change in the ground state energy. And in the see it is says that if all

but very high temperatures, there is negligible probability of the ion being ion or atom being in any but its ground state in thermal equilibrium.

So, your susceptibility is basically the two derivatives of the instead of F we can safely put del E 0 del H 2. Now, if you do that to that this term this delta E 0 as you can see is e square by 8 m c square into 0 sum over i x i square plus y i square 0. Now, if you have a closed shell atom, then the atom is its spherically symmetric the electronic distribution is spherically symmetric.

And then your 0 x i square 0 is the same as 0, y i square 0 equal to 0, z i square 0 and they, because they are three of them are same; so they should be equal to one-third 0 r i square 0 ok. So, if that is the case, then one can just replace this by two-third of r i square.

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And one gets delta E naught equal to e square by 8 m c square into two-third H square 0, r i square 0 sum over i, so that is the result that ok, so that is e square. Sorry, e square by 12 m c square, H square, 0 sum over i r i square 0.

Now, this sum over i r i square I can just replace by the average so they if there are by just the average r i for every atom, its it has to be the same for every atom. So, I can just replace it by this r square for that atom times N. So, then what I get is susceptibility two derivatives will

produce a two here is then going to be minus N by V del 2 E E 0 del H 2 equal to minus e square by 6 m c square N by V 0 r i square 0 for N such atoms, so that is the so this is the.

So, you all you have to do is to find out the r is of the ith electron in the atom and then sum over this squares, and then by and then so typically one actually replaces these by the average size of the atom in, and then you get a ball park figure which is fairly correct. So, that is what this treatment does and this is this is negative and you get a diamagnetic susceptibility, it is called the Larmor diamagnetic susceptibility ok. So, that that is the theory of diamagnetism that that comes out of these quantum mechanical calculations.

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Of course, as we are discussing the need is to know these values of this J, L, S and so on.

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So, the next task is to find the values of L, J and S; L, S, J these are quantities you need to find in an in an atom to do any calculation starting from this theory, so that is the next stage and that requires something called Hund's rule. So, which you probably have heard in your atomic physics courses that the how the electrons have to be distributed in a particular orbital.

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So, given an l value suppose you are doing with d orbital is l equal to 2, then you will you will you will find out the corresponding this distribution of atoms in the system. So, for example let us do the first understand what are these Hund's rules.

So, they tell us basically how to fill up the shells in an electron. So, suppose you are given an l value, then there are this 2 into 2l plus 1 right ah. So, there are 2l plus 1 given an l value leads 2l plus 1 choices right from minus l to plus l, from plus l to minus l. So, and in each of them you can put a spin either up or down. So, there is this 2 into 2l plus 1 levels.

So, the first rule says this is the rules are written first, second and third this order has to be maintained, because this is the first rule which is the most dominant rule. So, first rule is the is the most preeminent rule, then goes the second and then goes the third; you cannot first use the second rule and then the first, you have to first use the first rule.

So, it is like three laws of robotics in Asimov's books, you have to go by one which is the supreme, then 2, then 3 and so on. So, these n electrons are filled into a 2 into 2l plus 1 levels as I just showed. Then what you have to do is to first maximize S, what is the maximum value of S which is basically the largest projection of S along the direction of quantization which is the S z right. So, this S z maximum S z is what you have to first put sorry, maximum S z is where the S can take the maximum value. So, largest value of S z is the same as the maximum largest value of S, so you put the electron in that.

So, if n is less than or equal to 2l plus 1. So, let me just give you an example for example, in this case for example, this so l equal to 2 and you have 5 levels. So, then you have to maximize S, suppose you have 2l plus 1 electron which means 5 electrons. So, you have to start from the lowest and then just put all the spins up why is this so, well if a simple physical argument can tell you it has to be.

So, because of Pauli principle because Pauli principle prohibits 2 electrons of the same spin from coming to from sitting in the same orbital, sharing the same state. So, then of course you have to obey that and that gives you a lower energy and that is what this is done as long as you can do it, but of course if you have put 6 electrons, then you have to now put one of the orbit one of this these 5, you have to doubly occupy, so that you have to do.

So, up to 2l plus 1 S becomes its maximum. So, here for example its 5 by 2. So, so all 5 are up, so this is this is the value of maximum value of S is each S is plus half for an electron, so 5 of them. So, you will we will get this value.

So, after this you will have to reduce your maximum value by a half unit remember, so that is what it says that S has to reduce by half the next electron. If you have one more, you have to put it here that means, you reduce your total spin by half, because this one cancel this spin. So, instead of plus of you now have 0 there, so that is that cancels a half unit and so on and so forth you can keep on doing, so that is the first rule.

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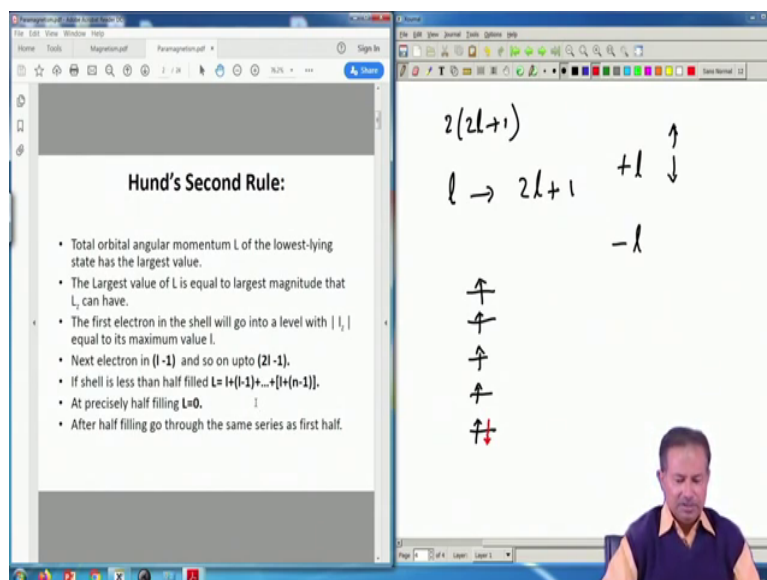
Second rule is the total orbital angular momentum L of the lowest-lying state has the largest value, this again is the same argument that orbital's which are rotating in the same direction in a classical way of thinking or to be excluded from each other as much as possible. So, you do not occupy those orbital's first, so you occupy one orbital, then look for another which is a different L and keep on maximizing your L value.

So, the first electron in the shell will go into the level with mod l z equal to its maximum value l, next we will go to l minus 1 and so on up to 2l minus 1. So, the shell is less than half filled, then this is your L value. At precisely half filling of course L will become zero, so I

will work out one example and then it will become pretty clear. After half filling go through the same series as the first one, so then again you put 2 electrons and so on.

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The third one comes from a completely different argument, it is it is called a spin-orbit coupling which basically couples particularly in higher atomic number atoms, there is a spin and orbit coupling that comes and that is given by this kind of a term. Lambda is a constant and L dot S is the typical Hamiltonian or the typical energy for these orbital's, these high atomic number elements. And then lambda also can have different values, depending on the filling of the total number of electrons in the in that atom, in that particular shell.

So, J; so J so this since L dot S, L and S are now coupled; L dot S is the energy, L and S are no longer good quantum numbers separately. So, what is a good quantum number is the total angular momentum J. So, you have to go to the basis with J and again if there are 2J plus 1 values, projections for J from plus J to minus J, J z takes these many values.

Now, the lambda is negative. So, lambda is negative if the shell is less than half filled. So, and in that case J and then L and S are parallel. As you can see L dot S is the energy, lambda being negative, they will try to align with each other.

If lambda is greater than 0, which happens when n is greater than or equal to 2l plus 1, then L and S are anti parallel which is again true if a lambda is greater than 0, then this term will be

negative if L and S are in opposite direction, so that lowers free energy. And correspondingly the J values are J equal to L minus S for up to half filling, and J equal to n plus L plus S for n greater than half filling. So, that is how you have to organize your atomic orbitals.

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The example is for example, d shell l equal to 2 which is which is a very important shell, which is which happens in the transition metal elements that is the outermost shell in transition metal elements, 3D transition metal elements, 4D transition metal elements, these are the levels that get filled out. And so from for example, from scandium to zinc these get in the 3D case these levels get filled up, the 3D level gets filled up and this is how you fill up.

So, what you do is that you put for example; you can choose to put start with the down spin, up and down does not matter you have to maximize S. So, which is the maximum value as it can take, so that is the so this you start filling up. If you have 1 electron, you put it in the largest l l as we the second rule tells us, so first rule tells us this will be up; I mean the first rule tells here the first rule does not tell anything, you can put up or down does not matter. Once you put a down for example if you have 2 electrons, the second one will go down go to down and it will go the first one will go to the largest l value which is 2 and l z equal to 2. And the next one will go to the next l value which is the next to the largest which is l z equal to 1.

So, and you see the third one will also have the same spin direction, up to 5 which is 2l plus 1 here. You will continue to do it right and starting from the largest l z, so that your l values are maximized, so that is exactly what one does. So, so your S keeps on increasing, at 5 you have 5 by 2 and your l z now all the l z's are filled up from minus from plus l equal to plus l to minus l so your L is 0 ok, so that is how it is done.

The so here we are not we will show you what J, L dot S termed as so up to this for we did not use the L S coupling or anything, but up to 5 by 2 you know the J value will have to be L minus S mod. So, to calculate the J value we have this L, J equal to L minus S, because you are less than half filled. So, beyond that you have to use J equal to L plus S and that determines the J value.

Remember the term symbol, so called the term symbol it is a it is a historically designed one and these are basically the x 2S plus 1 x J, so that is how you write the term symbol. So, 2[x] 2S plus 1 is 2 here, J equal to 3 by 2 and the L equal to 2 is d level and so on ok.

So, this is how the scheme works for 3D or 4D levels or any D level, l equal to 2 level for f f level it is you can accommodate 14 electrons, so it is a bit more complicated, but you can go ahead and do it.

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And as you can see that for f level which is l equal to 3 you can go ahead and do it. So, from minus 3 to plus 3 so 7 orbital's and the 7 into 2 that means, 14 electrons have to be put in. Again you see that S is maximized up to this, then you have 8 electrons now you have S reduces, and then it continues this way. And then corresponding J values are L minus S here and L plus S starting from here, so that is the that is this scheme of things by which J, S, L; a total S, total L and total J are determined, and these are the things that we need when we calculate those expectation values in the delta e sub n expression right.

And above the so suppose n equal to ground state, so we will find out the ground state electronic configuration and then put it on both sides and finally, calculate those expectation values. Just one small thing that is if these nth level is degenerate, then you have to diagonalize in that sector and that is how you do it in degenerate perturbation theory for example, and then use those levels that is not difficult. It is not an additional big complication, but that is the way the scheme works and this is what we are going to do in our next class.