Introduction to Solid State Physics

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Lecture – 79
Diamagnetism in solids

So, far we have dealt with paramagnetic phenomena, in which the magnetic moment that is induced in the system is proportional to the applied field and in the same direction.

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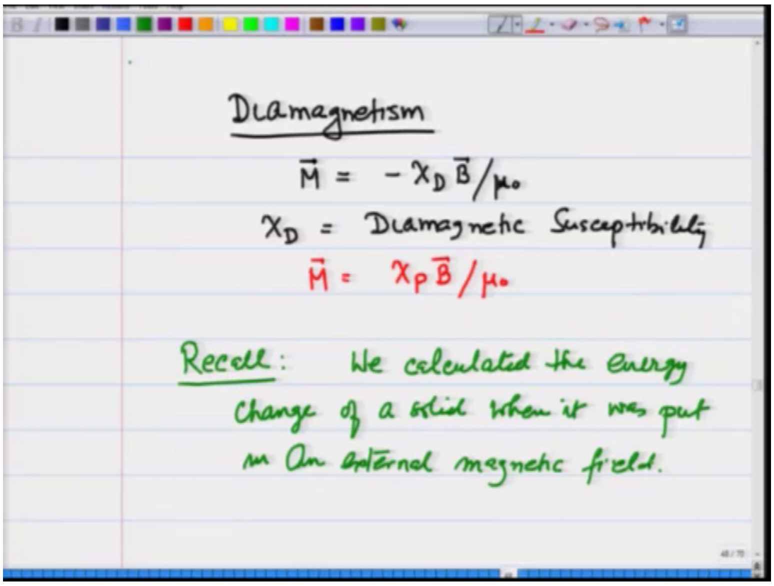

Diamagnetism

$\vec{M} = -\chi_D \vec{B}/\mu_0$

χ_D = Diamagnetic Susceptibility

$\vec{M} = \chi_P \vec{B}/\mu_0$

Recall: We calculated the energy change of a solid when it was put in an external magnetic field.

In this lecture I want to deal with diamagnetism. And diamagnetism is case where the applied field produces a magnetic moment in the direction opposite to the applied field.

So, the chi D is known as diamagnetic susceptibility. And it is meaning is the same as was the meaning for paramagnetic susceptibility where we had defined M to be equal to chi paramagnetic I had written M in the earlier lecture B divided by mu 0, I am writing for chi P to differentiated form the diamagnetic susceptibility. And we had calculated the paramagnetic susceptibility in the previous lectures.

In this lecture I want to focus on diamagnetism and see how we can calculate the susceptibility for diamagnetic materials. For this I want you to recall that to calculate the paramagnetic susceptibility, we calculated the energy change of a solid when it was put in an external magnetic field. Of course, when we did that when I took a system and put it in an external magnetic field, the levels are split and different levels were occupied differently and therefore, I got a temperature dependent paramagnetic susceptibility.

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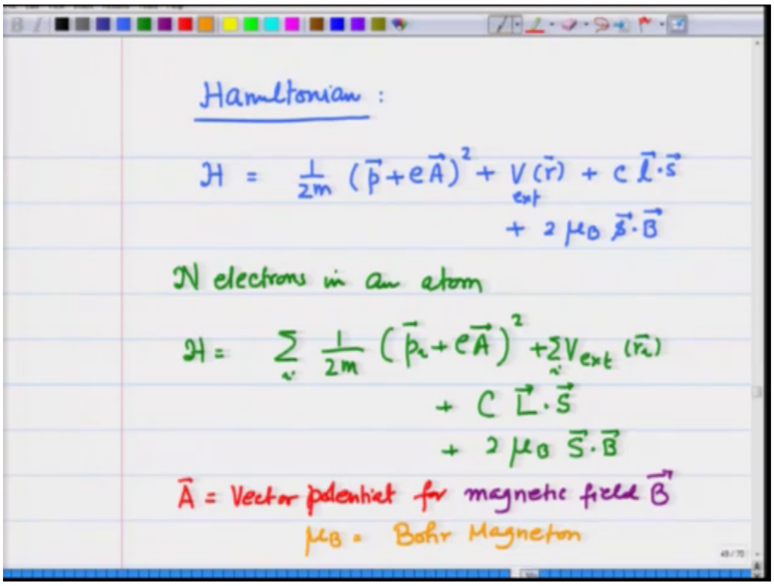

Hamiltonian :

$$\mathcal{H} = \frac{1}{2m}(\vec{p}+e\vec{A})^2 + V_{ext}(\vec{r}) + c\,\vec{l}\cdot\vec{s} + 2\mu_B\,\vec{s}\cdot\vec{B}$$

N electrons in an atom

$$\mathcal{H} = \sum_i \frac{1}{2m}(\vec{p}_i+e\vec{A})^2 + \sum_i V_{ext}(\vec{r}_i) + C\,\vec{L}\cdot\vec{S} + 2\mu_B\,\vec{S}\cdot\vec{B}$$

$\vec{A}$ = Vector potential for magnetic field $\vec{B}$

μ_B = Bohr Magneton

I want to look at this derivation of paramagnetic susceptibility from the Hamiltonian point of view by writing Hamiltonian explicitly. And recall that the Hamiltonian of an electron in a magnetic field is given as 1 over 2m p plus e A square plus V r external the potential in which the electron is moving plus there is spin orbit coupling L dot S and there is a interaction of the spin moment with the external field which I am going to write as plus 2 mu B s dot B this is the full Hamiltonian.

When we wrote it for N when I wrote it for N electrons in an atom this became H equals summation i 1 over 2m p i plus e A square plus v external ri summed over i plus some constant and then I write the spin orbit coupling as coupling between the total orbital angular momentum capital L and total spin capital S plus 2 mu B capital S dot B

In writing all this Hamiltonian my A is the vector potential for magnetic field that I have applied B and mu B is the Bohr magneton. This is the Hamiltonian. Now I will show you how from this we actually got the paramagnetic term and how I get from this the diamagnetic term also.

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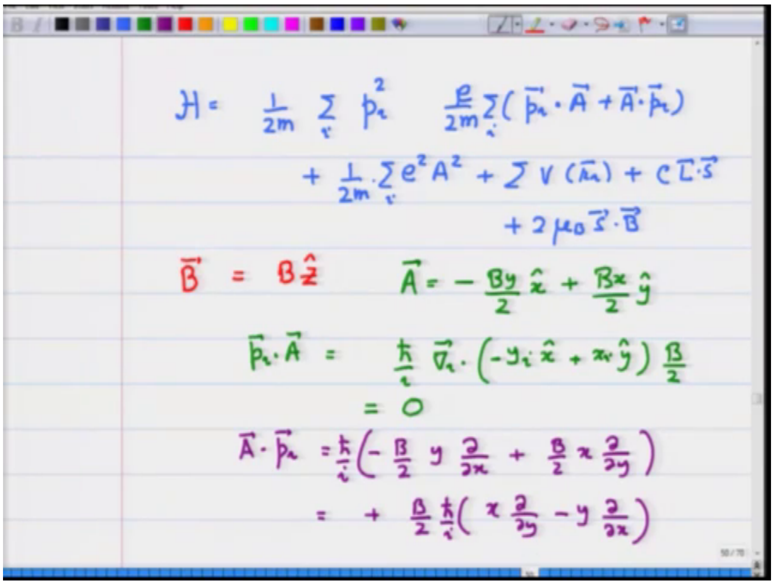

$$\mathcal{H} = \frac{1}{2m}\sum_i p_i^2 \quad \frac{e}{2m}\sum_i (\vec{p}_i\cdot\vec{A} + \vec{A}\cdot\vec{p}_i)$$

$$+ \frac{1}{2m}\sum_i e^2 A^2 + \sum V(\vec{r}_i) + c\,\vec{L}\cdot\vec{S}$$

$$+ 2\mu_0 \vec{S}\cdot\vec{B}$$

$$\vec{B} = B\hat{z} \qquad \vec{A} = -\frac{By}{2}\hat{x} + \frac{Bx}{2}\hat{y}$$

$$\vec{p}_i\cdot\vec{A} = \frac{\hbar}{i}\vec{\nabla}_i\cdot\left(-y_i\hat{x} + x_i\hat{y}\right)\frac{B}{2}$$

$$= 0$$

$$\vec{A}\cdot\vec{p}_i = \frac{\hbar}{i}\left(-\frac{B}{2}y\frac{\partial}{\partial x} + \frac{B}{2}x\frac{\partial}{\partial y}\right)$$

$$= +\frac{B}{2}\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

So, the Hamiltonian again when I write is going to be 1 over 2m summation when I expand the terms p i square plus 1 over 2m pi dot A plus A dot pi. This is also summed over and there is an e. So, that e will give me an e right here on top plus 1 over 2m e square A square summed over i plus summation V ri plus the spin orbit term L dot S plus 2 mu B S dot B.

Now, I take B field in the Z direction. And in that case you can easily show that the vector potential I can write in the form A equals minus B y by 2 in the x direction plus Bx by 2 in the y direction. There are other ways you can write it because a cannot be defined uniquely, but I choose this particular way of writing it. And in that case you see that p i dot A is going to be h cross over i del i for the ith electron dot a which will be y i in the x direction with a minus sign plus xi in the y direction and I get B by 2 outside and this is 0. This term becomes 0.

Then A dot pi is going to be equal to minus B by 2 y d by dx plus B by 2 x d by dy and I have h cross over i outside this is from the definition of momentum operator. Which I can write as minus B by 2 x d by dy minus y d by dx there should be plus and h cross over i.

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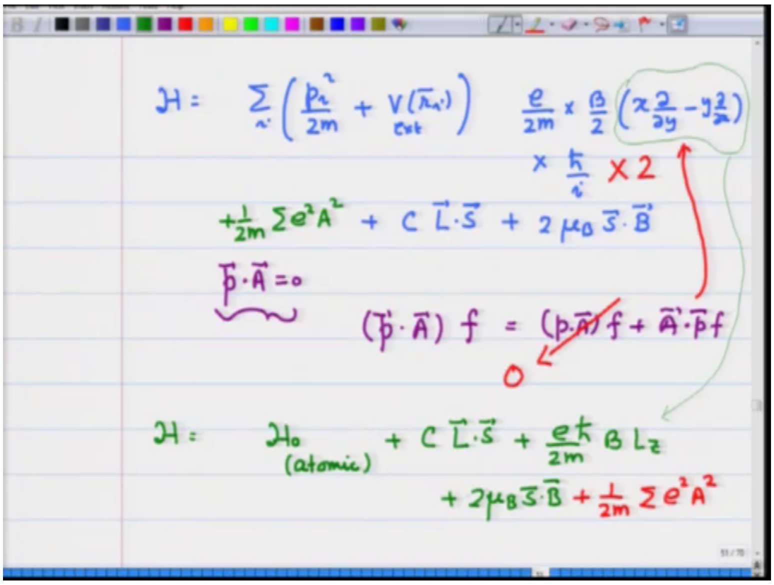

$$\mathcal{H} = \sum_i \left(\frac{p_i^2}{2m} + V_{ext}(\vec{r}_i) \right) \quad \frac{e}{2m} \times \frac{B}{2} \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \times \frac{\hbar}{i} \times 2$$

$$+ \frac{1}{2m}\sum e^2 A^2 + C\,\vec{L}\cdot\vec{S} + 2\mu_B \vec{S}\cdot\vec{B}$$

$$\underbrace{\vec{p}\cdot\vec{A} = 0}$$

$$(\vec{p}\cdot\vec{A})\,f = \cancel{(p\cdot\vec{A})}\,f + \vec{A}\cdot\vec{p}\,f$$

$$0$$

$$\mathcal{H} = \underset{(atomic)}{\mathcal{H}_0} + C\,\vec{L}\cdot\vec{S} + \frac{e\hbar}{2m} B L_z + 2\mu_B \vec{S}\cdot\vec{B} + \frac{1}{2m}\sum e^2 A^2$$

So, let us collect these terms together then I write the Hamiltonian again. So, if I write the Hamiltonian again, I have summation i pi square over 2m plus I will take this v external ri term with it plus e over 2m. And now you see that del dot a term got 0. And I have times B by 2 x d by dy minus y d by dx. And there is a term h cross over I here. Plus c L dot S term plus 2 mu B s dot B.

Now, slight correction here when I took p dot a equal to 0 in my previous calculation, what I should be doing is when I do this p in the operator form I have to write p dot A acting on whatever function f. So, this will give me p dot A f plus another A dot p f. So, what I had done there was taken this term to be 0. And I have another A dot p term here. So, I should be multiplying this whole thing by 2.

So, that the Hamiltonian now can be written as, the first term I am going to write H 0 or H atomic without any spin orbit coupling. Then I have the spin orbit coupling term C L dot S then I have plus e over 2m B Lz because the operator out here let me show that in green this operator corresponds to Lz along with h cross. So, that h cross I am going to write as I have been doing here and Lz will be only the differential operator. And plus 2 mu B s dot b. And the final term that we had earlier was plus 1 over 2m summation e square A square.

So, I should add this term here also, I had this term here also I had plus 1 over 2m summation e square A square. So, this is a Hamiltonian.

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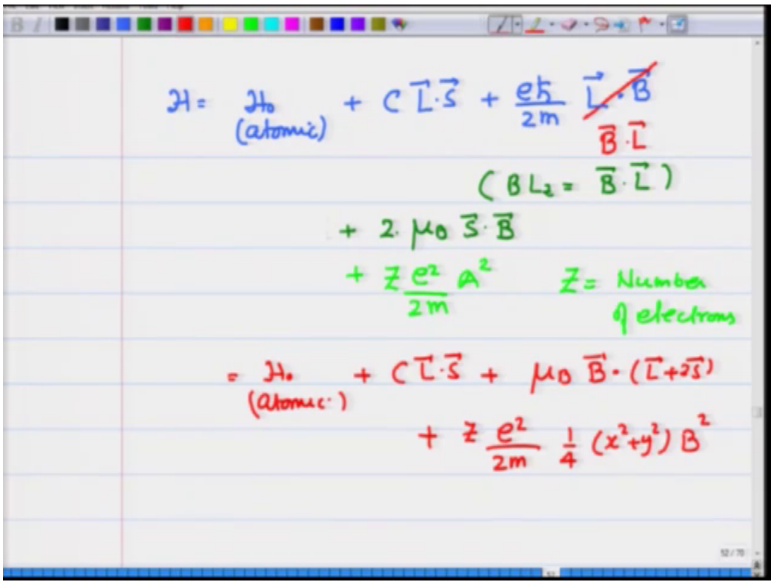

$$\mathcal{H} = \underset{(\text{atomic})}{\mathcal{H}_0} + C\vec{L}\cdot\vec{S} + \frac{e\hbar}{2m}\cancel{\vec{L}\cdot\vec{B}}$$

$$\vec{B}\cdot\vec{L}$$

$$(BL_z = \vec{B}\cdot\vec{L})$$

$$+ 2\mu_0\vec{S}\cdot\vec{B}$$

$$+ Z\frac{e^2}{2m}A^2$$

$Z =$ Number of electrons

$$= \underset{(\text{atomic})}{\mathcal{H}_0} + C\vec{L}\cdot\vec{S} + \mu_0\vec{B}\cdot(\vec{L}+2\vec{S})$$

$$+ Z\frac{e^2}{2m}\frac{1}{4}(x^2+y^2)B^2$$

Let me write it again. In the next page H is equal to H 0 which is atomic Hamiltonian without the ls coupling plus there is this C L dot S coupling. And then I have plus e h cross over 2m. Since I am summing over all i it becomes the capital L dot B I should actually write this as B dot L because L is operating on something on the right. And what I have done here let me explain is that I have written B Lz as equal to B dot L because B is in the Z direction.

And then I have plus 2 mu B s dot B and the final term plus e square over 2 M A square summed over and it is summed over all the electrons. So, I am going to write a Z out here Z is the number of electrons in the system. So, you have gotten all the terms in the Hamiltonian right.

So, I can again write this as equal to h 0 atomic plus C L dot S plus es cross by 2m is mu B. So, I can write this as mu B B dot L plus 2 S plus Z e square over 2m A square now I can write as 1 over 4 x square plus y square B square. These are all the terms in the Hamiltonian. Let us look at each term now.

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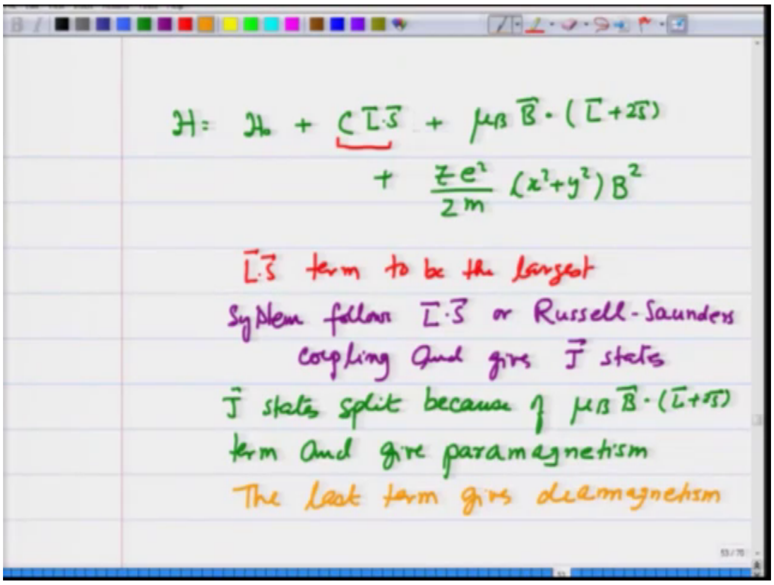

$$\mathcal{H} = \mathcal{H}_0 + \underline{C}\,\vec{L}\cdot\vec{S} + \mu_B \vec{B}\cdot(\vec{L}+2\vec{S})$$
$$+ \frac{Ze^2}{2m}(x^2+y^2)B^2$$

$\vec{L}\cdot\vec{S}$ term to be the largest

System follow $\vec{L}\cdot\vec{S}$ or Russell-Saunders coupling And gives $\vec{J}$ states

$\vec{J}$ states split because of $\mu_B \vec{B}\cdot(\vec{L}+2\vec{S})$ term And give paramagnetism

The last term gives diamagnetism

So, finally, I have reduced the Hamiltonian to the form H 0 plus C L dot S plus mu B B dot L plus 2 S plus Z e square over 2m x square plus y square B square. In calculating the paramagnetic susceptibility, what we had done was we had taken L dot S term, term to be the largest among these 3 terms.

So, that it dominates and because of this the system follows L dot S or Russell Saunders coupling and gives J states. And then those J states split, these J states split because of mu B B dot L plus 2 S term which is smaller than L dot S. So, it comes the next and give paramagnetism.

So, this is systematically how we are doing it. We are taking h 0 largest term and C L dot S gives you J states and then those J states are split and populated at a given temperature in a different way according to Boltzmann probability law, and gives paramagnetism and the last term gives diamagnetism.

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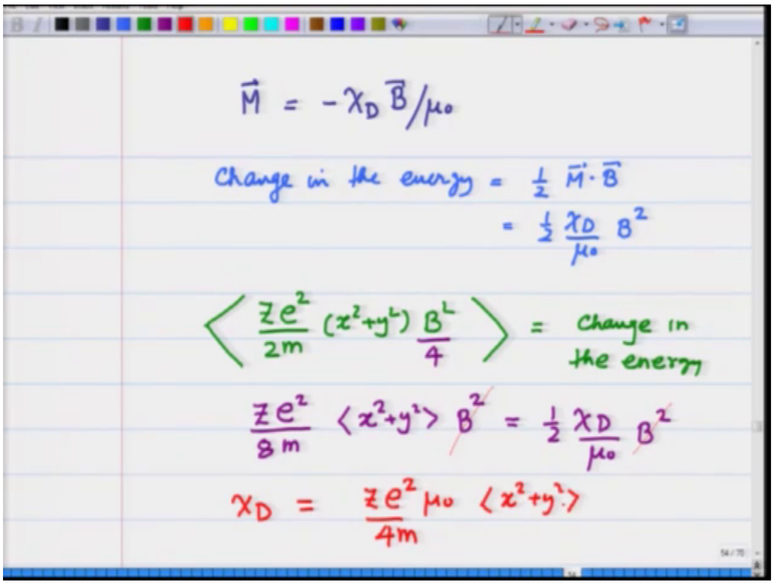

$$\vec{M} = -\chi_D \vec{B}/\mu_0$$

Change in the energy $= \frac{1}{2}\vec{M}\cdot\vec{B}$

$$= \frac{1}{2}\frac{\chi_D}{\mu_0}B^2$$

$$\left\langle \frac{Ze^2}{2m}(x^2+y^2)\frac{B^2}{4} \right\rangle = \text{Change in the energy}$$

$$\frac{Ze^2}{8m}\langle x^2+y^2\rangle \cancel{B^2} = \frac{1}{2}\frac{\chi_D}{\mu_0}\cancel{B^2}$$

$$\chi_D = \frac{Ze^2}{4m}\mu_0\langle x^2+y^2\rangle$$

Let us see how? If I develop a magnetic moment which is in the direction opposite to the applied field, then it will give me a positive energy contribution it will raise the energy of the system.

So, paramagnet lowers the energy of the system. And this raises the energy of the system and the change in the energy is going to be equal to one half M dot B, which is one half chi D over mu 0 B square. So, if I calculate the energy up to order B square from this term that we just saying I can calculate chi D. So, let us see what this is.

The last term that we saw in the Hamiltonian is Z e square over 2m x square plus y square B square. And it is expectation value will be equal to the change in the energy which I can write and there is a 1 over 4 also. So, I missed. So, which I can write as Z is a constant number e square is a constant number divided by 8 M. Expectation value of x square plus y square of the system times B square. That will be the change in energy. And this should be equal to one half chi diamagnetic over mu 0 times B square.

And this immediately gives me if I cancel B square this gives me chi D is equal to Z e square over 4 mu 0 expectation M expectation value of x square plus y square.

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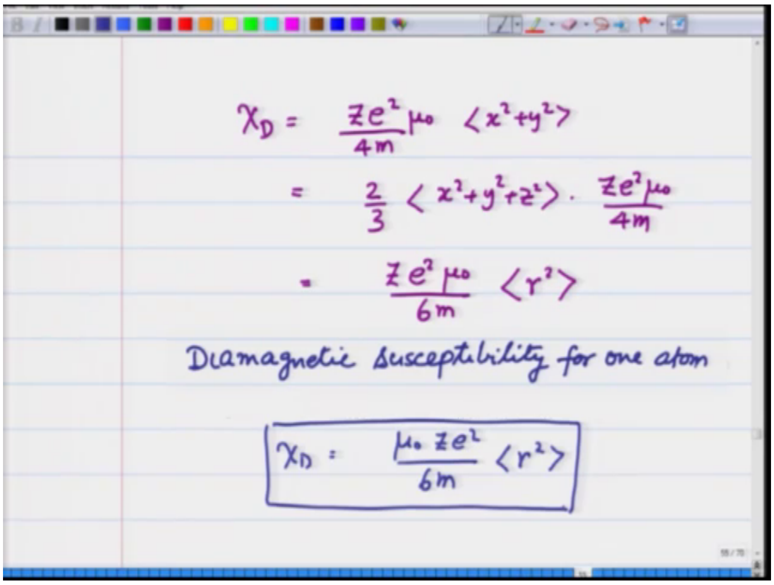

$$\chi_D = \frac{Ze^2}{4m}\mu_0 \langle x^2+y^2\rangle$$

$$= \frac{2}{3}\langle x^2+y^2+z^2\rangle \cdot \frac{Ze^2\mu_0}{4m}$$

$$= \frac{Ze^2\mu_0}{6m}\langle r^2\rangle$$

Diamagnetic susceptibility for one atom

$$\boxed{\chi_D = \frac{\mu_0 Ze^2}{6m}\langle r^2\rangle}$$

So, I can write the diamagnetic susceptibility chi D is equal to Z e square over 4 M mu 0 x square plus y square expectation value, which I can write as 2 thirds of x square plus y square plus z square expectation value because I am taking only 2 terms for a spherical system times z e square mu 0 over 4 m which then I can write as z e square mu 0 over 6 m expectation value of r square in a system.

So, this is the diamagnetic susceptibility for one atom which is given as chi D equals mu 0 let me bring in front z e square over 6 m the expectation value of r square. Let us now get a feel for the numbers.

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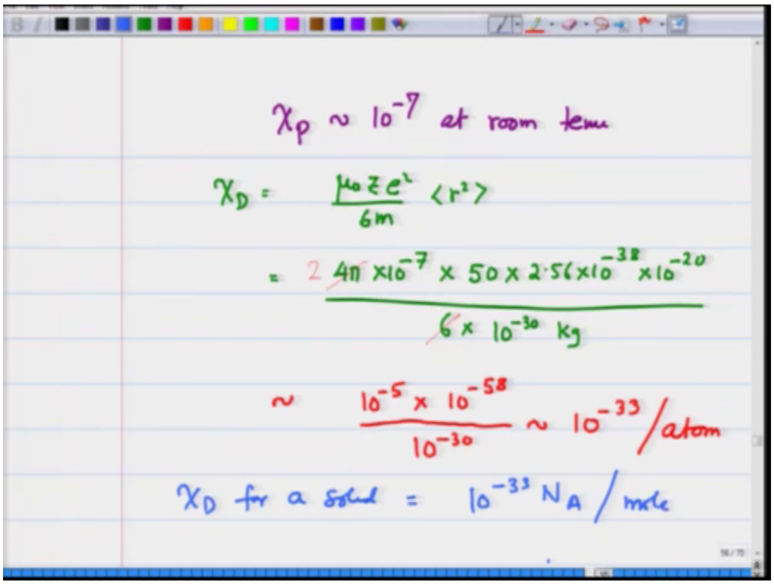

$\chi_P \sim 10^{-7}$ at room temp

$$\chi_D = \frac{\mu_0 Z e^2}{6m} \langle r^2 \rangle$$

$$= \frac{2\,\cancel{4\pi} \times 10^{-7} \times 50 \times 2.56 \times 10^{-38} \times 10^{-20}}{\cancel{6} \times 10^{-30}\ \text{kg}}$$

$$\sim \frac{10^{-5} \times 10^{-58}}{10^{-30}} \sim 10^{-33} / \text{atom}$$

χ_D for a solid $= 10^{-33} N_A$ / mole

Recall, that in the previous lecture I had calculated chi paramagnetic to be of the order of 10 raise to minus 7 at room temperature.

Now, let us see what chi is. So, chi D is equal to mu 0 z e square over 6 m r square. Mu 0 is 4 pi times 10 raise to minus 7. Then let us say we are taking a system of 50 electrons, e square is 2.56 times 10 raise to minus 38 r square I will take off the order of 1 angstrom square. So, that is 10 raise to minus 20 divided by 6 times m is of the order of 10 raise to minus 30 kilogram.

So, that is now cancel terms 6 and 4 pi I can just write this as 2. So, this becomes about 2 times 50 is 100 times 10 raise to minus 7 is 10 raise to minus 5 times 10 raise to minus 58 divided by 10 raise to minus 30 which comes out to be of the order of 10 raise to minus 33 per atom.

So, for a solid chi D for a solid will be equal to 10 raise to minus 33 times N Avogadro per mole.

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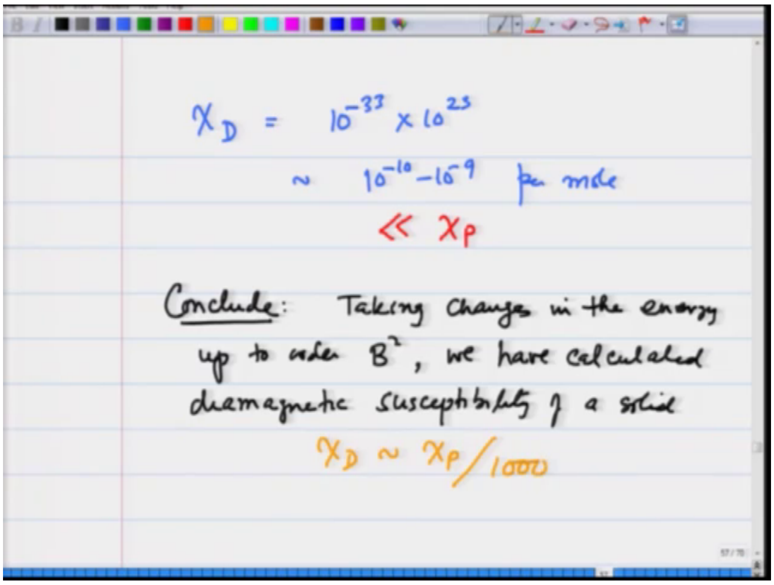

$$\chi_D = 10^{-33} \times 10^{23}$$

$$\sim 10^{-10} - 10^{-9} \text{ per mole}$$

$$\ll \chi_P$$

<u>Conclude</u>: Taking changes in the energy up to order B^2, we have calculated diamagnetic susceptibility of a solid

$$\chi_D \sim \chi_P/1000$$

And that number chi D will be equal to 10 raise to minus 33 times 10 raise to 23 of the order of 10 raise to minus 10, 10 into 10 raise to minus 9 per mole. And you can see that this is much less than chi paramagnetic.

So, diamagnetic effects are very small as we have shown just now compared to paramagnetic effects. So, to conclude this lecture taking changes in the energy up to order B square in first order. We have calculated diamagnetic susceptibility of a solid. And we found that chi D is roughly chi B over a 1000.