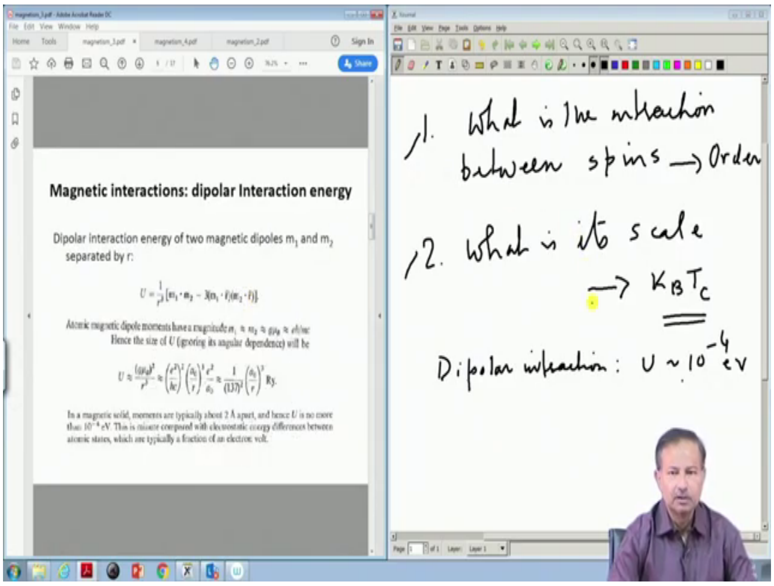
Electronic Theory of Solids
Prof. Arghya Taraphder
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture – 38
Exchange interactions of different types

(Refer Slide Time: 00:29)



Magnetic interactions: dipolar Interaction energy

Dipolar interaction energy of two magnetic dipoles m_1 and m_2 separated by r:

$$U = \frac{1}{r^3}[\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\mathbf{m}_1 \cdot \hat{\mathbf{r}})(\mathbf{m}_2 \cdot \hat{\mathbf{r}})]$$

Atomic magnetic dipole moments have a magnitude $m_1 \approx m_2 \approx g\mu_B \approx e\hbar/mc$. Hence the size of U (ignoring its angular dependence) will be

$$U \approx \frac{(g\mu_B)^2}{r^3} \approx \left(\frac{e^2}{\hbar c}\right)^2 \left(\frac{a_0}{r}\right)^3 \frac{e^2}{a_0} \approx \frac{1}{(137)^2}\left(\frac{a_0}{r}\right)^3 \text{Ry}.$$

In a magnetic solid, moments are typically about 2 Å apart, and hence U is no more than 10^{-4} eV. This is minute compared with electrostatic energy differences between atomic states, which are typically a fraction of an electron volt.

/1. What is the interaction between spins $\rightarrow$ Order

/2. What is its scale

$\rightarrow \underline{\underline{K_B T_c}}$

Dipolar interaction : $U \sim 10^{-4}$ eV

Hello, we are posing ourselves to questions and as you see these are the 2 questions I posed for us to understand. And if we can understand these 2 questions our part of the job is done. And it is of course, not given that once you understand this questions you have solved the problem which we will come back to when we write down models microscopic models and start understanding those models.

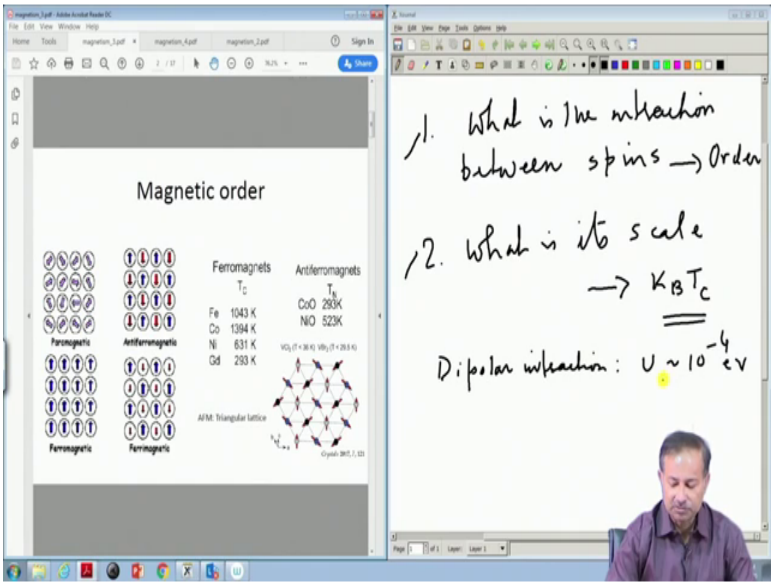
But of course, these are the first 2 steps you have to take to get an understanding of the magnetic interactions that lead to spontaneous magnetization and long range order. Now, one source of interaction between moments is this dipole dipole interaction right. So, that is something we have done in our electrodynamics electromagnetism courses and we know how to moments interact.

And this form on the left gives you the potential between dipoles and m 1 and m 2 m 1 dot m 2 minus 3 m 1 dot r like r r hat m 2 dot r hat divided by r cube. So, it goes as 1 over r cube and one can estimate in an atom typical atoms have atomic separations moments are separated by above 2 angstrom which is the atomic separation say 2 to 2 between 2 and 3 angstrom at most.

And then you can calculate this scale of this energy. See this is this the, so we are trying to understand number 2 first where what are the interactions available to us? And what are their scales? So, one available interaction between moments is this dipole interaction and let us estimate this scale of that.

So, like it is like a simple back of the envelope calculation and you can do this take this m 1 and m 2 to be g mu b which is h cross by m c. And you can easily work it out and you will see that dipole-dipole, dipolar interaction gives an energy scale U is of the order of 10 minus 4 e V. Now, this is of course, a minute scale compared to the electrostatic energy difference between atomic states which are typically of the order electron volts or a fraction of that ok.

(Refer Slide Time: 03:32)



Magnetic order

Ferromagnets	T_C
Fe	1043 K
Co	1394 K
Ni	631 K
Gd	293 K

Antiferromagnets	T_N
CoO	293K
NiO	523K

AFM: Triangular lattice

Crystals 2017, 7, 121

1. What is the interaction between spins → Order

2. What is its scale → $k_B T_c$

Dipolar interaction : $U \sim 10^{-4}$ eV

And the other thing that you remember is that in iron for example we have already mentioned that the ferromagnetic transition temperature is a 100 degree Kelvin. And if you convert this energy to in into temperature scale this will give you over 1 degree Kelvin. So, this dipolar interaction cannot produce an energy scale which is 1000 degree which is 1000 times more than this energy scale.

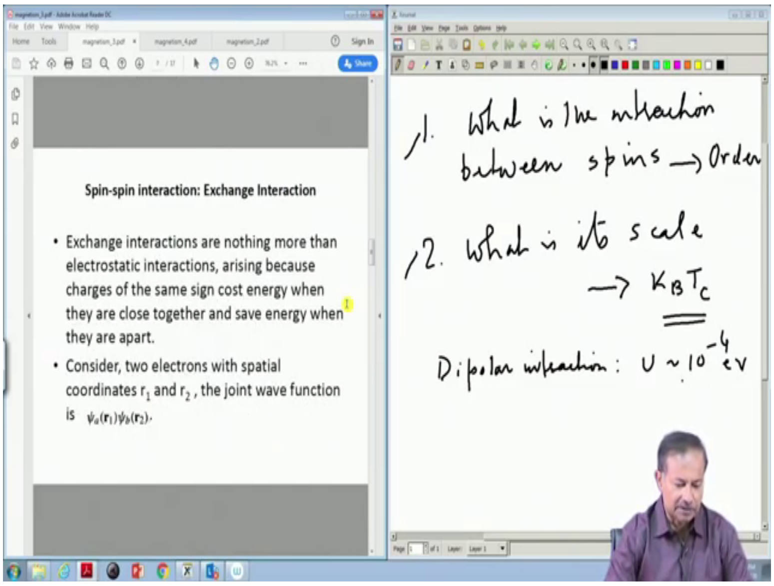
So, the ordering interaction from for iron for example, or even cobalt which is even more between the 2 moments nearest near nearby moments is about 1000 degree or 1400 degree. Whereas, this interaction if it is the cause this dipolar interaction where the cause for this ordering then it would give me a transition temperature about 1 degree.

Because this scale is 1 degree temperature of 1 degree will already make the system disorder. So, this certainly is not the origin of this ordering interaction in the spontaneous magnets that we just discussed ok. Now, the trouble is that in inside the solid in the in at in amongst the moments and everywhere the only interaction is we have is electromagnetic.

See the in a the interesting thing is that the world we live in unless you go to atomic scale or below atomic scales sub nucleus as subatomic scales the only interactions that govern most of the phenomena that we have are gravity. And electromagnetic interactions and gravity is very weak and that acts uniformly on every mass, so that is very different.

So, the only interaction that is left with us is the electrostatic or electromagnetic interactions. And we have to find out the cause of this interaction starting from that. So, coulomb interaction is what we have and we will try to find out what is this possible source of this interaction which orders these moments between moments. How do the moments talk and what is its scale ok, so we have to go one more step.

(Refer Slide Time: 06:01)



Spin-spin interaction: Exchange Interaction

- Exchange interactions are nothing more than electrostatic interactions, arising because charges of the same sign cost energy when they are close together and save energy when they are apart.
- Consider, two electrons with spatial coordinates r_1 and r_2, the joint wave function is $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$.

/1. What is the interaction between spins → Order

/2. What is its scale

$\rightarrow K_B T_c$

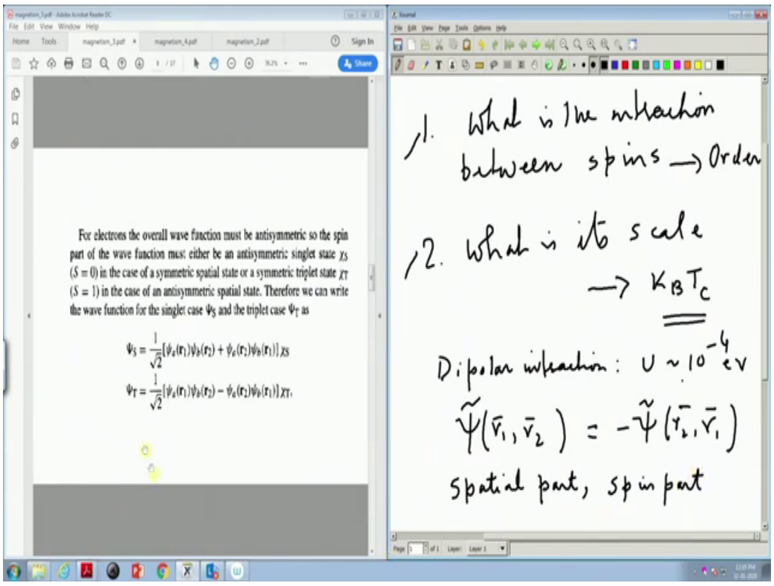
Dipolar interaction : $U \sim 10^{-4}$ eV

Remember that these electrons are of course, quantum mechanical objects and their mechanics is governed by quantum mechanics. So, the way we are our classical thinking should not be the right way to go about. And so, we have to find out what are the possible we have to find out the possible sources starting from a quantum mechanical description. How two electrons which are which carry the moment talk to each other that has to be figured out starting from quantum mechanics.

So, that is the spin interaction and it is called the exchange interaction, I will explain why it is called exchange interaction. So, these are nothing more than electrostatic interactions arising because charges of the same sign caused energy when they are close together and save energy when they are away from it. So, so far no quantum mechanics is discussed here, it is just saying that the two electrons will try to stay apart. Because they are sorry they are have the same sign of charge, so they will repel and they will stay away.

Now, comes the quantum mechanical description in point two bullet two. So, we are now we have to write down the wave function for 2 electrons interacting with each other through coulomb interaction. So, we have to write a joint wave function starting from say two single particle wave functions size of a and size of b. One way of writing is psi a r 1 into psi be r 1 where r 1 and r 2 are the special coordinates of the two electrons.

(Refer Slide Time: 07:54)



For electrons the overall wave function must be antisymmetric so the spin part of the wave function must either be an antisymmetric singlet state χ_S $(S = 0)$ in the case of a symmetric spatial state or a symmetric triplet state χ_T $(S = 1)$ in the case of an antisymmetric spatial state. Therefore we can write the wave function for the singlet case Ψ_S and the triplet case Ψ_T as

$$\Psi_S = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_S$$

$$\Psi_T = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_T.$$

/1. What is the interaction between spins → Order

/2. What is its scale $\rightarrow K_B T_c$

Dipolar interaction : $U \sim 10^{-4}$ eV

$$\tilde{\Psi}(\bar{r}_1, \bar{r}_2) = -\tilde{\Psi}(\bar{r}_2, \bar{r}_1)$$

spatial part, spin part

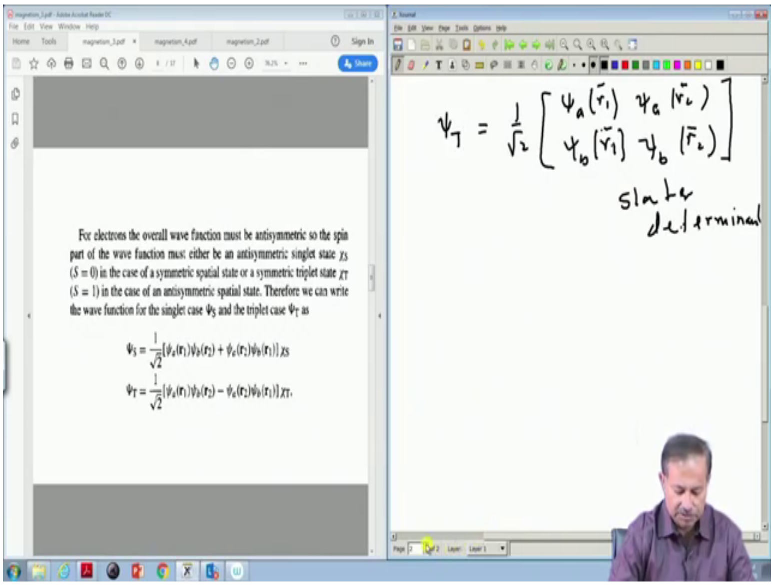
But then that is not the correct description because electrons are fermions and we know that their wave functions have to be joint wave function has to be antisymmetrize. So, if I write psi r 1 r 2 sum psi say psi tilde r 1 r 2 then this has to be equal to minus i tilde r 2 r 1. So, that is because the electrons obey Fermi statistics and, so we know that their wave functions have to be anti symmetriced.

So, there are two ways you can do it; one is that a wave function also has a spatial part which is what is written in terms of psi a and psi b those were functions and there is a spin part. So, let us see what are these two. So, this spatial part one can one can write in two fashions one is this one by root 2 psi a r 1 psi b r 2 plus psi a r 2 psi b r 1.

Now, in this case for example, if you interchange r 1 and r 2 you do not change the sign. So, then the spin part has to accommodate the sign change and that is called the singlet. I will show you the state you already know it it’s basically up down minus down up. Whereas, there is the other way of writing it which is psi a r 1 psi b r 2 minus psi a r 2 psi b r 2 r 1.

Now, if you interchange r 1 and r 2 you can easily see that this size of T; T orbital the special part of it changes sign when you interchange r 1 and r 2. Therefore, the spin part will have to remain symmetry. So, that overall wave function is still anti symmetric. So, these are two cases chi sub S gives you S equal to 0 and chi sub T gives you S equal to 1 state. I will enumerate I will show you the state there is a maybe you know already, but there is a way to write this anti symmetrised wave function for example, by a determinant.

(Refer Slide Time: 10:33)



For electrons the overall wave function must be antisymmetric so the spin part of the wave function must either be an antisymmetric singlet state χ_S ($S = 0$) in the case of a symmetric spatial state or a symmetric triplet state χ_T ($S = 1$) in the case of an antisymmetric spatial state. Therefore we can write the wave function for the singlet case Ψ_S and the triplet case Ψ_T as

$$\Psi_S = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_S$$
$$\Psi_T = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_T.$$

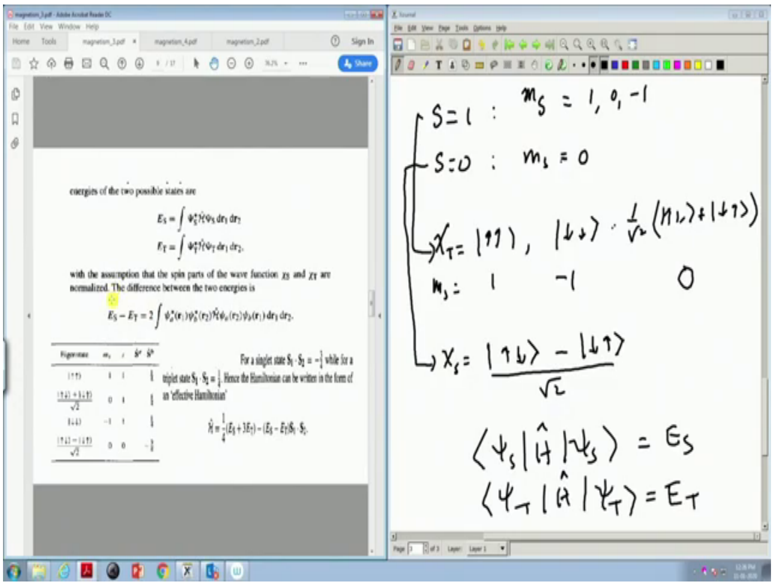
$$\psi_T = \frac{1}{\sqrt{2}}\begin{bmatrix} \psi_a(\bar{r}_1) & \psi_a(\bar{r}_2) \\ \psi_b(\bar{r}_1) & \psi_b(\bar{r}_2) \end{bmatrix}$$

Slater determinant

For example I can write psi of the special part of psi triplet for example, the special part I can write as 1 by root 2 psi a, psi a, psi b, psi b, r 1, r 2, r 1, r 2. And these determinants this is a determinant I have written you have to determinant of this matrix gives you this wave function. For exams psi a r 1 psi b r 2 minus psi r 2 psi b r 1. So, this is called a Slater determinant which we might use later on, so I just introduce it.

This is cute way, nice way of writing is an anti symmetries wave function if you have more than one more than two electrons you can carry on this procedure with psi c for example, r 1 r 2 r 3 and so on. And this is a beautiful scheme by which you can write an anti symmetric wave function. Now, address this is not relevant at this point, but we have written the wave function. So, what are these wave functions?

(Refer Slide Time: 12:05)



energies of the two possible states are

$$E_S = \int \Psi_S^* \hat{\mathcal{H}} \Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$E_T = \int \Psi_T^* \hat{\mathcal{H}} \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2,$$

with the assumption that the spin parts of the wave function χ_S and χ_T are normalized. The difference between the two energies is

$$E_S - E_T = 2 \int \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \, d\mathbf{r}_1 \, d\mathbf{r}_2.$$

Eigenstate	m_s	s	$\hat{S}^a \cdot \hat{S}^b$
$\lvert\uparrow\uparrow\rangle$	1	1	$\frac{1}{4}$
$\frac{\lvert\uparrow\downarrow\rangle + \lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
$\lvert\downarrow\downarrow\rangle$	-1	1	$\frac{1}{4}$
$\frac{\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

For a singlet state $\mathbf{S}_1 \cdot \mathbf{S}_2 = -\frac{3}{4}$ while for a triplet state $\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{4}$. Hence the Hamiltonian can be written in the form of an 'effective Hamiltonian'

$$\hat{\mathcal{H}} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S}_1 \cdot \mathbf{S}_2.$$

$S = 1 \; : \; m_S = 1, 0, -1$

$S = 0 \; : \; m_s = 0$

$\chi_T = |\uparrow\uparrow\rangle, \; |\downarrow\downarrow\rangle \; \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$

$m_s : \; 1 \quad -1 \quad 0$

$\chi_s = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$

$\langle \psi_s | \hat{H} | \psi_s \rangle = E_S$

$\langle \psi_T | \hat{H} | \psi_T \rangle = E_T$

So, here are these states are given the spin states. So, if you look at these states on the lower bottom that S equal to 1 has 3 states. So, S equal to 1 which is the triplet has 3 projections of S z which is written as m sub S here. So, m sub S equal to 1 0 minus 1 right 3 states 2 S plus 1 states.

For S equal to 0 2 S plus 1 gives me just 1 state I have just this m S equal to 0. And the states these S equal to 1 states the 3 states are given here, so these are up down, down up. So, this is plus 1 m S equal to 1 this is a.

So, this is a up sorry up, so I mean the triplet. So, my m S value has to be here it is up then here it is down. So, m S is minus 1 sorry m S is minus 1 and the other one is the one the last one is 1 by root 2 up down minus down up ok.

And that is m S equal to 0 m m S equal to 0 state plus m S this is m S this is the triplet 1. So, here I will have plus, but still the m s is 0. Now, for S equal to 0 I have only one state which is up down minus down up. So, here remember that this is these are chi Ts and this is chi S by root 2. Now, the reason chi T have this form is that you can interchange the 2 spins here also and you will see that you do not pick up a minus sign.

Whereas here you interchange the 2 spins you will pick up a minus sign. So, this is called triplet because there are 3 states out of it this is called singlet because there is only 1 state. So, more than that the arrangement of spins in a triplet and singlet are different that is important. Triplets can have these states where both spins are up both spins are down like a Ferromagnet or it can also have a component which is where spins are up down and down up linear combination of the two.

So, whereas, in singlet you have no choice you only can have up and down. So, that is that is a major difference between, so the magnetic structure is different. So, now, let me just go back and tell you one interesting thing that we are dealing with the coulomb interaction still. Coulomb interaction does not bother about what spin your charge has right. So, as far as the in a classical if you look at it classically then two charges we have let them have their moments then these charges interact through coulomb interaction.

Coulomb interaction will not bother about what is the direction of moment in one vis a vis the other one. So, coulomb interaction is just blind to the moment that these charges are carrying. Whereas, when you do quantum mechanics now you have to separate your state space in such a way that there are 2 different kinds of spin arrangements; one is the triplet one is the singlet.

So, now, the coulomb interaction when you calculate the matrix element which with respect to these wave functions; the wave functions. The quantum mechanics itself brings in the spins in the orientation of the spins in the problem. So, that is the difference ah, so it is a very important difference between treating things classically and treating things quantum mechanically.

In quantum mechanics you have to bother about the symmetries of the wave function and corresponding and which comes from the statistics. And the for fermions you have to anti symmetrized and the anti symmetrisation means that you are now working with pairs of wave function which differ in their spin arrangements.

And although coulomb interaction does not care about what spins these have the Pauli exclusion principle makes it contingent upon us that we bother about what the spins are. If the spins are in the same direction, remember Pauli exclusion principle prohibit them from coming to the same state or come nearby for example, two in the same orbital same quantum state.

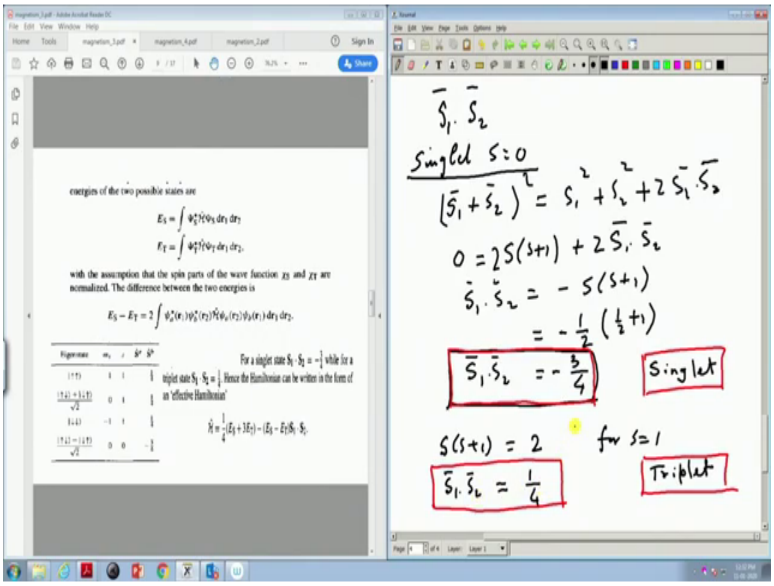
So, this is where the quantum mechanics plays a major role in selecting out these spin states. So, coulomb interaction does not select out the spin state, it does not filter the spins whereas, quantum mechanics does. And it is just that this anti symmetrization that leads to this as I will show that will lead to a difference between the energy of singlet and the triplet configuration. Which means, that two different spin configurations are different in energy. So; that means, this can lead to a preferential spin orientation.

And this is shown here you can calculate the energies of the two possible states with the Hamilton Nina between two electrons sitting next to each other in with in their parent atoms. You can actually go through this calculation and you will see that the this is straightforward. If you write the Hamiltonian and take the matrix element of psi sub S and with respect to that that will give you.So, h, so psi S h psi S is E S and psi T H psi T equal to E T, so this is these are 2 energies and they are not equal. So, they differ and the difference is this and this difference is nonzero and it has this.

Look at the matrix element the way this difference comes about, it is on the from the left to the right there is just an exchange of r 1 and r 2. See this is psi a r 1 psi b r 2 with the stars, so whereas, the complex conjugate of psi a and psi b, but r 1 and r 2. Whereas, here psi a carries r 2 and psi b carries r 1 on the right. So, it is a matrix element between 2 states which are just exchange with the where the coordinates are exchanged with 2 electrons coordinates are just exchanged that is why it is called an exchange interaction.

This is an exchange term and this is the separation in energy. So, now, what I will do is a small problem for you, you can do it yourself, but let me just ask this question. And then justify this way of writing things for example, for a, so it is say this says that S 1 dot S 2.

(Refer Slide Time: 21:05)



energies of the two possible states are

$$E_S = \int \Psi_S^* \hat{\mathcal{H}} \Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$E_T = \int \Psi_T^* \hat{\mathcal{H}} \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2,$$

with the assumption that the spin parts of the wave function χ_S and χ_T are normalized. The difference between the two energies is

$$E_S - E_T = 2 \int \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\, d\mathbf{r}_1 \, d\mathbf{r}_2.$$

Eigenstate	m_s	s	$\hat{S}^a \cdot \hat{S}^b$
$\lvert\uparrow\uparrow\rangle$	1	1	$\frac{1}{4}$
$\frac{\lvert\uparrow\downarrow\rangle+\lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
$\lvert\downarrow\downarrow\rangle$	−1	1	$\frac{1}{4}$
$\frac{\lvert\uparrow\downarrow\rangle-\lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

For a singlet state $\mathbf{S}_1 \cdot \mathbf{S}_2 = -\frac{3}{4}$ while for a triplet state $\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{4}$. Hence the Hamiltonian can be written in the form of an 'effective Hamiltonian'

$$\hat{\mathcal{H}} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S}_1 \cdot \mathbf{S}_2.$$

$\bar{S}_1 \cdot \bar{S}_2$

Singlet $S=0$

$(\bar{S}_1 + \bar{S}_2)^2 = S_1^2 + S_2^2 + 2\bar{S}_1 \cdot \bar{S}_2$

$0 = 2S(S+1) + 2\bar{S}_1 \cdot \bar{S}_2$

$\bar{S}_1 \cdot \bar{S}_2 = -S(S+1)$

$= -\frac{1}{2}\left(\frac{1}{2}+1\right)$

$\boxed{\bar{S}_1 \cdot \bar{S}_2 = -\frac{3}{4}}$ Singlet

$S(S+1) = 2$ for $S=1$

$\boxed{\bar{S}_1 \cdot \bar{S}_2 = \frac{1}{4}}$ Triplet

Suppose you have 2 spins S 1 and S 2, and these are spin S for example. So, you want to calculate this dot product. Now, of course; these are quantum mechanical objects you cannot just take a S 1 S 2 sin of theta you cannot do that that is not allowed. So, what do you do these are spin operators with their dot product you want to calculate.

So, how do you do it ok? So, the way to do it is for example, let me do it for singlet first in this example singlet S equal to 0. So, this means that S 1 plus S 2 is giving me S equal to 0 and that is. Let me just start from here S 1 plus S 2 square equal to S 1 square plus S 2 square plus 2 S 1 dot S 2 this is just a identity.

Now, S 1 plus S 2 is 0, so this left hand side is 0 and the right hand side is now look at this S 1 square what is the eigen value is S into S plus 1. This is again S into S plus 1, so 2 of that plus 2 S 1 dot S 2 this is the quantity I want. So, so; that means, S 1 dot S 2 equal to minus S into S plus 1 for spin half for spin half I can calculate it for any spin I can calculate it.

So, for S I will now put spin half, so that is minus half into half plus 1 equal to minus 3 by 4. So, S 1 dot S 2 is this when S 1 equal to S 2 equal to half and S 1 plus S 2 which is total S is 0, so that is the singlet, so that is what is written here. So, for a single state this is the result. For triplet state you can just all you have to do is to just change this S 1 plus S 2 equal to 1.

So, you will have 1 plus, so this will be S into S plus 1 S equal to, so this left hand side for triplet this will be the total S right. So, this will be how much? S 1 plus S 2 is 2, and so, S into S plus 1 will give you the. So, on the left hand side you will have to put S into S plus 1 with S equal to 1 which is 2 for S equal to 1.

So, you do that, then you will get instead of 0 here you will get 2 and the result is S 1 dot S 2 S 1 dot S 2 for spin S equal to 1 is one fourth. So, that is the result that we have for S equal to 1, so this is for sing triplet. So, let me again tell you the difference.

So, we have found out that the product S 1 dot S 2 is different for a singlet state and a triplet state. And that difference is that S 1 dot S 2 is minus three fourth for singlet, and S 1 dot S 2 is one fourth for a triplet state and that is what we are going to use now.

Now, let us look at this formula and we will come back to write down a Hamiltonian for the spins and that is what we are after. So, once we have a Hamiltonian microscopically obtained we know the energy scale and we know how to work with it, so that is the next step that we are going to take.