Electronic Theory of Solids
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Lecture - 40
Magnetic Order of different types & Heisenberg model

So, we start again at the point we left. We have been asking questions as to why should there be magnetic order, long range magnetic order and what sets its scale; scale of the say transition temperature?

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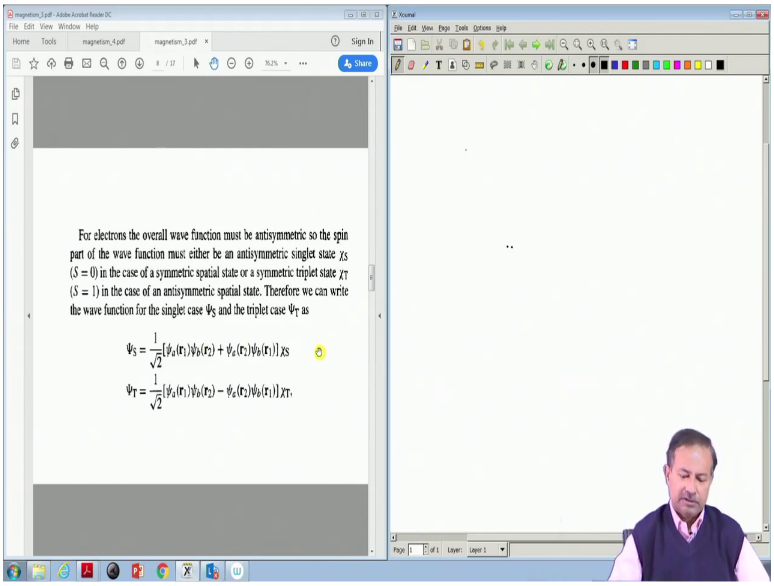

For electrons the overall wave function must be antisymmetric so the spin part of the wave function must either be an antisymmetric singlet state χ_S ($S = 0$) in the case of a symmetric spatial state or a symmetric triplet state χ_T ($S = 1$) in the case of an antisymmetric spatial state. Therefore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

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

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

So, that means; that we are basically asking the question, because starting from the microscopic interactions in the system and the quantum mechanical processes that go on when electrons or moments at when ions with moments come close together. And their electrons interact and then they there is an overlap of a function. And then can we find out a scale of temperature or interaction which distinguishes or selects out one magnetic state from the other.

For example, from parallel spin arrangement to anti parallel spin arrangements. So, this is the question that we are asking. And the second question is what is the scale of that energy. And what we found out was that, dipole interaction which is a very common interaction amongst two moments; anywhere does not do the job, because it is exceedingly small between even two atoms which is separated by say 2 angstrom, 2.5 angstrom is exceedingly small it is about 1 degree Kelvin.

Whereas, the insulating magnets where the moments are fixed at sites and they interact with each other the scale of temperature, which is defined by the by the either the ferromagnetic transition temperature or the anti ferromagnetic Neel temperature which is basically both are ordering temperature. That scale is between say 100 to few 100 and for certain materials like these are iron, cobalt, nickel for example, it is very high of course. They are not insulators. So, their magnetism is somewhat different.

Although, the scale that we are after is not electron volt which is the Fermi energy scale which is like 10000 degree, 20000 degree, 30000 degree. That is a huge scale, that is not what we are after. So, we have to generate a scale, which is around 100 degree to so 500 degree or 1000 degree. So, that is one thing and that energy that scale that interaction whose scale is that should also distinguish between spin states, the arrangements of spins as I said in the beginning.

And we found out that just by doing a quantum mechanical treatment of two electrons, when they come close by or two atoms when they come close by the electrons wave functions overlap and that requires to be anti symmetries.

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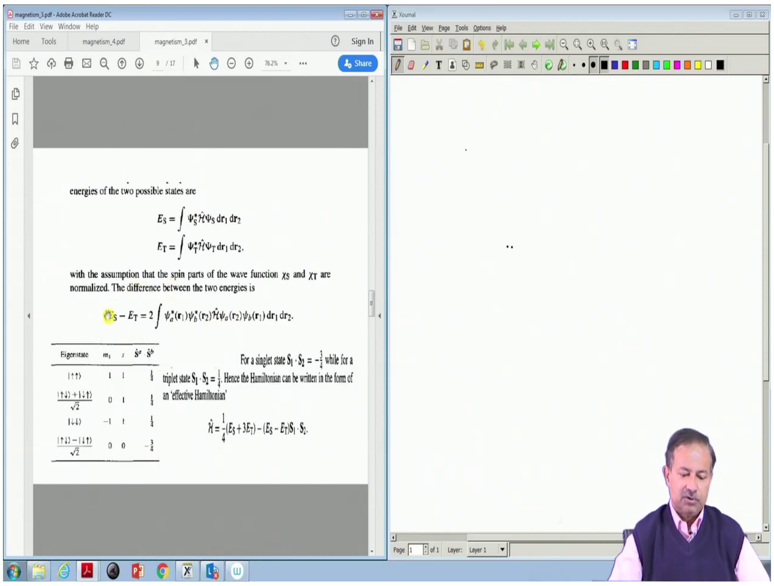

energies of the two possible states are

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

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

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

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

Eigenstate	m_s	s	$\hat{\mathbf{S}}^a \cdot \hat{\mathbf{S}}^b$
$\lvert\uparrow\uparrow\rangle$	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'

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

And that process, that quantum mechanical process gives rise to a energy which is a separation between two electronic energy scales ES and ET and that separation is of the order of the scale that we are asking for. And that is given that is what we defined as to be J.

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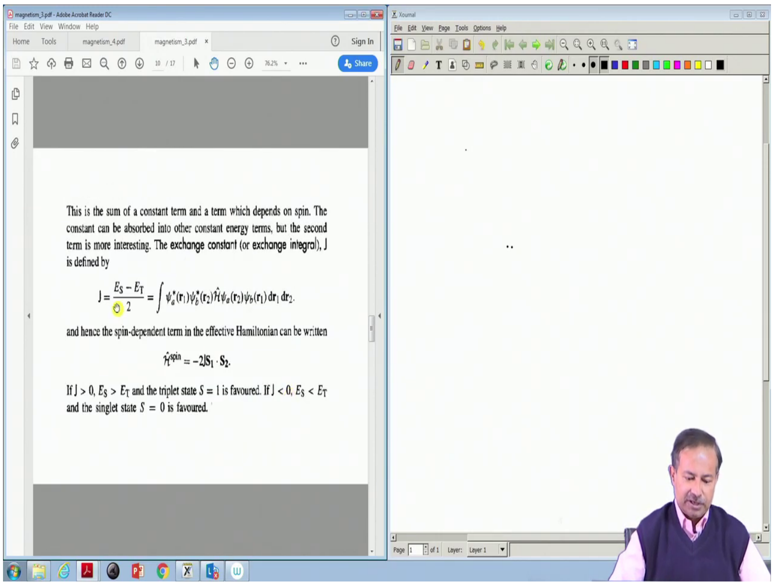

This is the sum of a constant term and a term which depends on spin. The constant can be absorbed into other constant energy terms, but the second term is more interesting. The **exchange constant** (or **exchange integral**), J is defined by

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

and hence the spin-dependent term in the effective Hamiltonian can be written

$$\hat{\mathcal{H}}^{\text{spin}} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2.$$

If $J > 0$, $E_S > E_T$ and the triplet state $S = 1$ is favoured. If $J < 0$, $E_S < E_T$ and the singlet state $S = 0$ is favoured.

So, that J is a difference between two electronic energy scales. So, it is a small scale and it is also not too small that we got from dipole interaction. And then, we could write a spin Hamiltonian which is given here which is say minus J S 1dot S 2 between two spins.

In that case, this Hamiltonian as you can see distinguishes between two spins parallel or two spins anti parallel depending on the sign of J ok. So, the purpose we started purpose with which we started the calculations is more or less served. Now we got Hamiltonian that Hamiltonian has a scale which is in the right ball park of energies and of course, that Hamiltonian can distinguish between states of different spins.

Now, we can do whatever we normally do with such Hamiltonians, these we can do ground state study ground state properties. We can study finite temperature properties ground state and excited state all that are now available to us, provided we can of course, solve these problems or do some approximation to get a solution.

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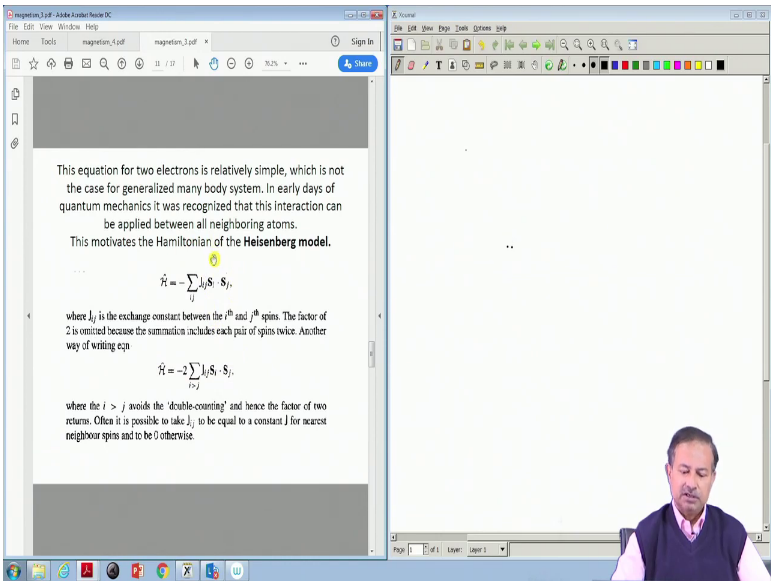

This equation for two electrons is relatively simple, which is not the case for generalized many body system. In early days of quantum mechanics it was recognized that this interaction can be applied between all neighboring atoms.

This motivates the Hamiltonian of the **Heisenberg model.**

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j,$$

where J_{ij} is the exchange constant between the i^{th} and j^{th} spins. The factor of 2 is omitted because the summation includes each pair of spins twice. Another way of writing eqn

$$\hat{\mathcal{H}} = -2\sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j,$$

where the $i > j$ avoids the 'double-counting' and hence the factor of two returns. Often it is possible to take J_{ij} to be equal to a constant J for nearest neighbour spins and to be 0 otherwise.

So, the main task now is to look at this Hamiltonian or its different versions because this J can be this is just between two spins. And here for example, in Heisenberg model we have taken long spin interaction between sites i and j which are could be far apart. In common practice, most of this most of the magnets that we study this J ij falls of very fast its small smaller as you go along in number of sites.

So, typically one keeps. So, 1 or 2 or maximum 3 nearest neighbors for J ij in the extreme case of course, the nearest neighbor the nearest neighbor Heisenberg model where J ij is 0 beyond nearest neighbor is the most standard model that one study. So, it is one of the models which is a celebrated model for spin systems.

So, that that input has to come from the experimental situation. And as I said the magnetic structure is also determined experimentally which is mostly neutron scattering experiments. So, given those inputs, one can start working with this Hamiltonian and try to fit the experimental results. The excitation spectrum can also be obtained from the neutron from neutron scattering experiments that an inelastic neutron scattering and that experiment is a very important experiment that tells us what is the excited what are the excitations of these of the ground state of a magnetic system.

So, all these can be tackled starting from a Hamiltonian which we have written down here, it is called the Heisenberg Hamiltonian. It is different versions, different dimensions, different incarnations are studied in most of the spin systems. J is called the exchange interaction.

So there are some techniques small technical issues where, if you make ij unrestricted sum then you have to you can take it out and then put it to here this the summation i greater than J is it takes care of the double counting of each bonds where J j is defined then you put this two match with the Hamiltonian ok. So, those are small technical issues that are not very relevant. Because once you start with a model you know what model you have started what are your conventions what are your J ij's and then you just continue.

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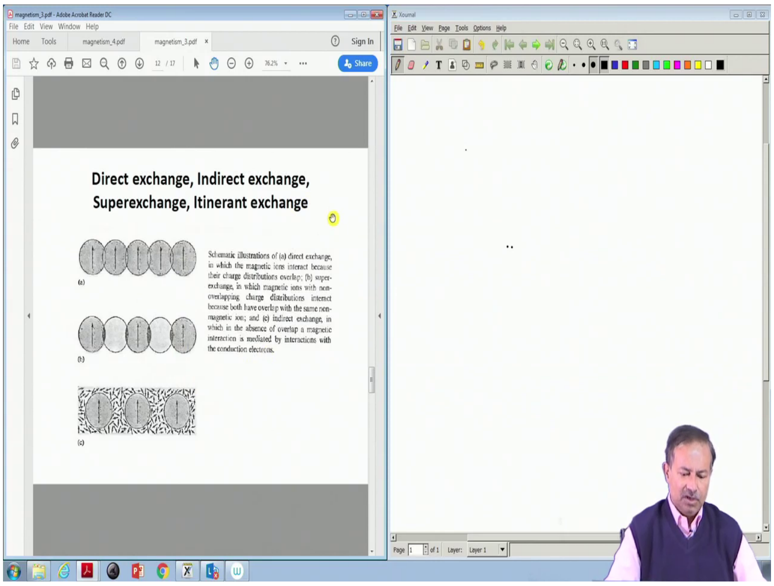

Direct exchange, Indirect exchange, Superexchange, Itinerant exchange

Schematic illustrations of (a) direct exchange, in which the magnetic ions interact because their charge distributions overlap; (b) superexchange, in which magnetic ions with non-overlapping charge distributions interact because both have overlap with the same non-magnetic ion; and (c) indirect exchange, in which in the absence of overlap a magnetic interaction is mediated by interactions with the conduction electrons.

Then, what we discussed was that there are these exchanges, which is what we are studying can be of various types; one is that there is a direct exchange where the ions containing the moments sit next to each other. But there is also a possibility that there is a non magnetic ion that separates the two ionic to moment carrying ions in a solid. And these the second case b gives a very famous exchange called super exchange depending on the angle between this the intervening one and this one.

So, the here for example, it is a straight line. So, the angles are 180 degree, but if the left atom is put at the top of this middle atom, then the angle will be this one, so it will be 90 degree. So, the depending on the angle the super exchange sign often changes and. So, these are minor these are issues that one deals with one when one does the calculation in a real system.

As of now I am just telling you that there are different kinds of exchange is possible, you have this direct exchange, you have the indirect exchange and there is and this is the super exchange and then there is an indirect exchange. And that indirect exchange is where say a deep lying 4f state is far separated. I am carrying and deep lying 4f state with a moment is separated from another which is which is also carrying a moment, but they are not close by, but there is a conduction band available.

So, this moment polarizes the conduction band locally and that polarization is carried through to the other ion carrying the moment. And so, therefore; these two moments can actually interact can talk to each other via this conduction band.

So, that is there is an indirect exchange that is very famous exchange mechanism called RKKY. We will if time permits we will discuss.

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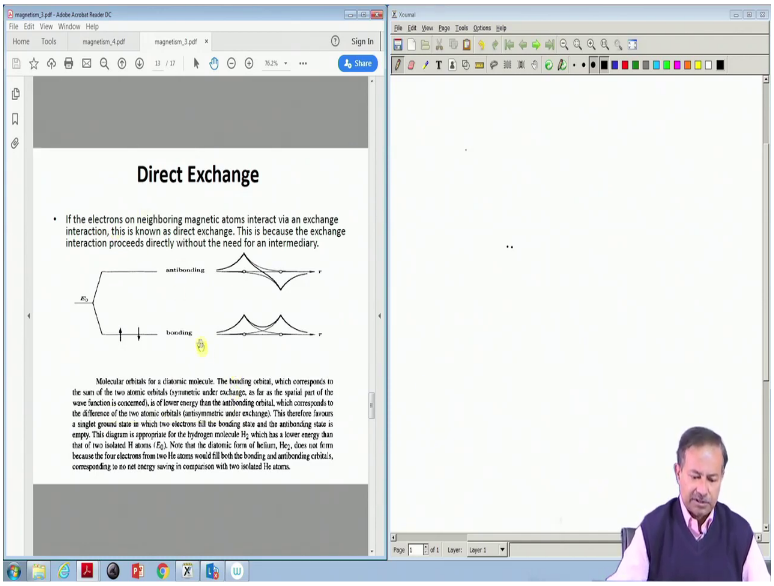

Direct Exchange

- If the electrons on neighboring magnetic atoms interact via an exchange interaction, this is known as direct exchange. This is because the exchange interaction proceeds directly without the need for an intermediary.

Molecular orbitals for a diatomic molecule. The bonding orbital, which corresponds to the sum of the two atomic orbitals (symmetric under exchange, as far as the spatial part of the wave function is concerned), is of lower energy than the antibonding orbital, which corresponds to the difference of the two atomic orbitals (antisymmetric under exchange). This therefore favours a singlet ground state in which two electrons fill the bonding state and the antibonding state is empty. This diagram is appropriate for the hydrogen molecule H_2 which has a lower energy than that of two isolated H atoms (E_0). Note that the diatomic form of helium, He_2, does not form because the four electrons from two He atoms would fill both the bonding and antibonding orbitals, corresponding to no net energy saving in comparison with two isolated He atoms.

Now, direct exchange as we said in we have studied in case of hydrogen molecule formation of hydrogen molecule where we had two electrons forming a singlet in and they go to the bonding orbital.

So, this is for example, a spin zero state. So, the interaction the exchange interaction is such that it selects out the spin singlet state as the lower energy state.

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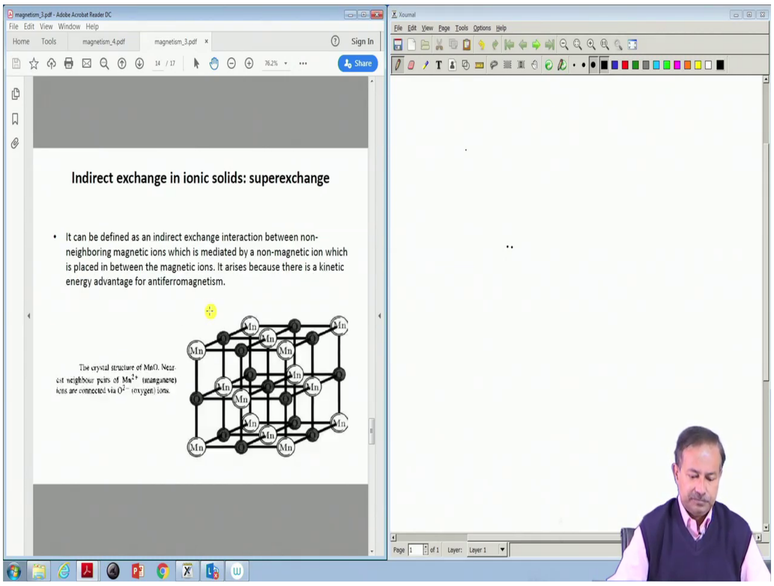

Indirect exchange in ionic solids: superexchange

- It can be defined as an indirect exchange interaction between non-neighboring magnetic ions which is mediated by a non-magnetic ion which is placed in between the magnetic ions. It arises because there is a kinetic energy advantage for antiferromagnetism.

The crystal structure of MnO. Nearest neighbour pairs of Mn^{2+} (manganese) ions are connected via O^{2-} (oxygen) ions.

As I said there is this super exchange which normally happens for example, in manganese, manganites and manganese oxide and so on. And this super exchange is the other oxides also copper cuprate, copper oxide, lanthanum copper oxide for example and so on. And this is a situation where an Mn atom for example, which carries the moment does not see the next Mn atom as a neighbor there is an intervening oxygen ion O2 minus and that O2 minus is a filled shell.

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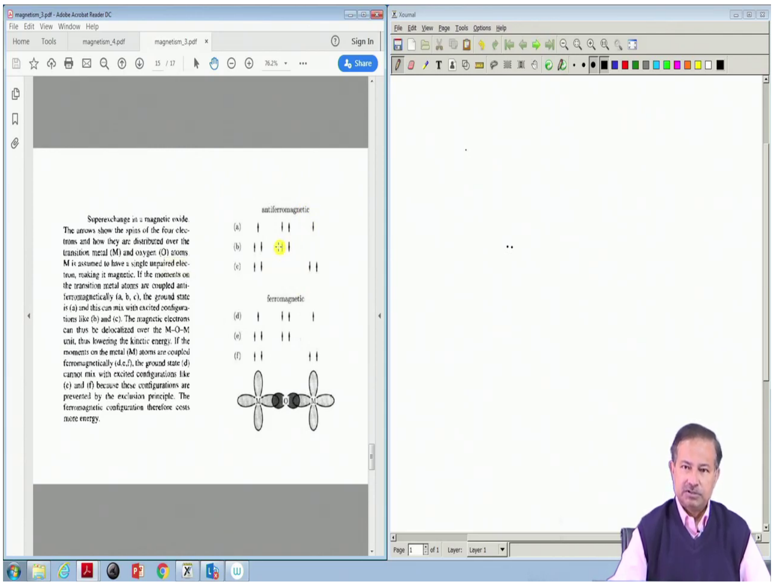

Superexchange in a magnetic oxide. The arrows show the spins of the four electrons and how they are distributed over the transition metal (M) and oxygen (O) atoms. M is assumed to have a single unpaired electron, making it magnetic. If the moments on the transition metal atoms are coupled antiferromagnetically (a, b, c), the ground state is (a) and this can mix with excited configurations like (b) and (c). The magnetic electrons can thus be delocalized over the M–O–M unit, thus lowering the kinetic energy. If the moments on the metal (M) atoms are coupled ferromagnetically (d,e,f), the ground state (d) cannot mix with excited configurations like (e) and (f) because these configurations are prevented by the exclusion principle. The ferromagnetic configuration therefore costs more energy.

And then we actually showed how the anti ferromagnetic configuration in this case leads to more delocalization energy than this one.

So, this state anti ferromagnetic state is has a lower energy because it allows the electrons to move about. So, the delocalization is allowed here whereas, here in the ferromagnetic configuration the extent of delocalization is far less compared to this one. So, therefore, the anti ferromagnetic state is favored it has a lower energy.

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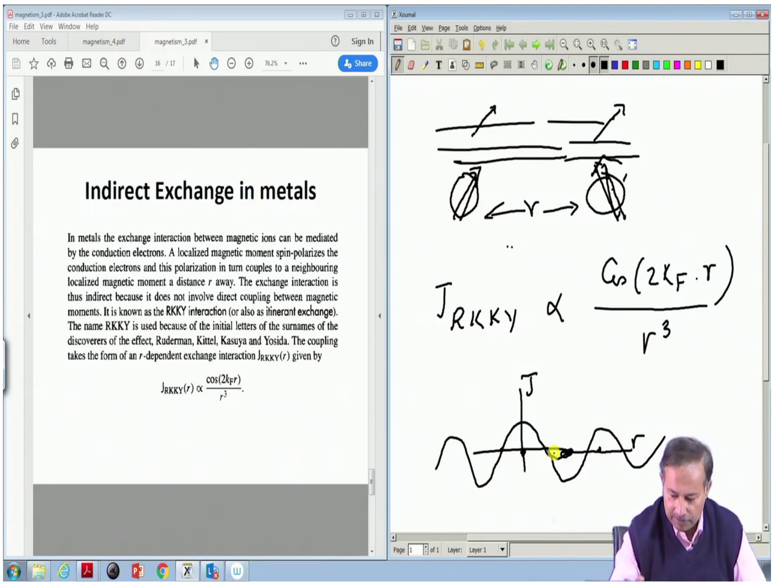

Indirect Exchange in metals

In metals the exchange interaction between magnetic ions can be mediated by the conduction electrons. A localized magnetic moment spin-polarizes the conduction electrons and this polarization in turn couples to a neighbouring localized magnetic moment a distance r away. The exchange interaction is thus indirect because it does not involve direct coupling between magnetic moments. It is known as the RKKY interaction (or also as itinerant exchange). The name RKKY is used because of the initial letters of the surnames of the discoverers of the effect, Ruderman, Kittel, Kasuya and Yosida. The coupling takes the form of an r-dependent exchange interaction $J_{RKKY}(r)$ given by

$$J_{RKKY}(r) \propto \frac{\cos(2k_F r)}{r^3}.$$

$$J_{RKKY} \propto \frac{Cos(2k_F \cdot r)}{r^3}$$

Of course, then we also as I mentioned, there is this indirect exchange in that happens in metals where there are impurities with spins sitting not impurity by impurity one means that these atoms with moments or ions with moments are separated, far separated from each other. They are not as dense as the atoms that carry the conduction electron.

So, in this or the moments I mean it can happen that the atoms are the ions are next to each other, but the moment carrying orbital's and deep lying orbital's. So, they do not see each other even if the atoms are ions are nearest neighbors. So, that can happen in rare earth systems where the 4f level carries the moment whereas, the conduction band is has comes from different orbitals and they these electrons move about freely. So, it is a metal, but it every ion has a deep lying 4 state which has a moment which is an unfilled shell.

So, that that is a situation that arises in certain rare earth materials and in these cases what can happen is that these moments that are said deep lying orbit in deep lying orbital's, they polarize the conduction band locally and that polarization then moves about it just the conduction bands move go just them they carry that information to the next ion carrying that moment and carrying a moment and then this kind of a situation, where the so, there is a 4f there is for example, a moment sitting here, there is a conduction band.

So, this moment for example, polarizes this conduction band locally into this direction for example, and that information comes here to the other spin and these spin has an exchange interaction with this conduction spins. So, this is for example, a large spin and they can now this conduction electrons spin can try can align this spin in a particular direction.

And that that interaction of course is has a oscillatory behavior depending on the distance r between these two ions. That was figured out by Ruderman, Kittel, Kasuya and Yosida and what so, this interaction is named after the their surnames the this is called J,RKKY.

And its proportional to cosine 2 k F, k F is the Fermi momentum into r divided by r cube ok so, Fermi momentum of the conduction electrons. So, now, you can see that since cosine function oscillates this will also oscillate. So, this will also oscillate right. And so depending on the distance between the ions, if one ion is at 0, the other ion is here, then the interaction is then J is positive whereas, if one ion is here, the other ion is here, then the interaction is negative.

So, it can oscillate depending on where the other ion is with respect to one ion the distance between them you can have either ferromagnetic interaction or an anti ferromagnetic interaction. And this is a very interesting situation, which is actually practically used in materials when you design materials. So, you choose your distances suitably as you want and change the sign of J by manipulating the distance between moments, moment carrying atoms in a metallic host.

So, that is one very important interaction, but we will not discuss in beyond this point because, that treatment is way beyond our scope.

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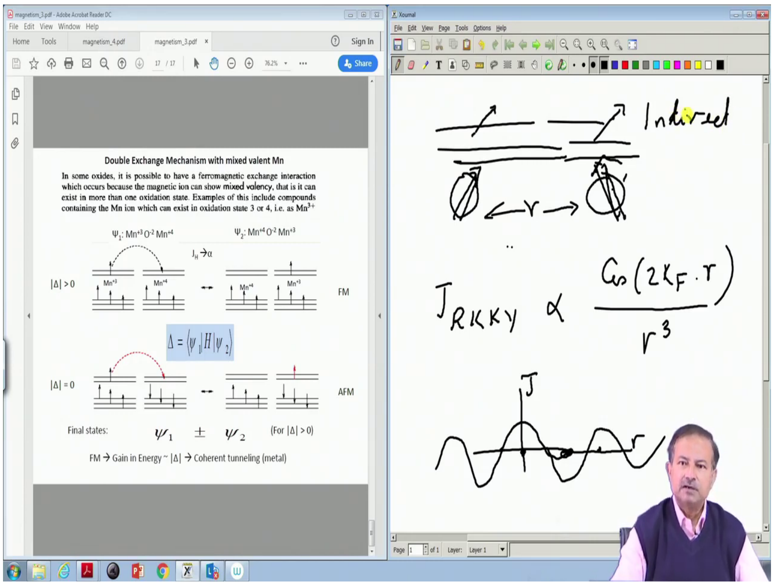

Double Exchange Mechanism with mixed valent Mn

In some oxides, it is possible to have a ferromagnetic exchange interaction which occurs because the magnetic ion can show mixed valency, that is it can exist in more than one oxidation state. Examples of this include compounds containing the Mn ion which can exist in oxidation state 3 or 4, i.e. as Mn^{3+}

Ψ_1: $Mn^{+3}O^{-2}Mn^{+4}$ Ψ_2: $Mn^{+4}O^{-2}Mn^{+3}$

$J_H \rightarrow \alpha$

$|\Delta| > 0$ FM

$\Delta = \langle \psi_1 | H | \psi_2 \rangle$

$|\Delta| = 0$ AFM

Final states: $\psi_1 \pm \psi_2$ (For $|\Delta| > 0$)

FM → Gain in Energy ~ $|\Delta|$ → Coherent tunneling (metal)

$$J_{RKKY} \propto \frac{\cos(2k_F \cdot r)}{r^3}$$

So, this is, this is a very interesting mechanism of exchange is called double exchange. So, what we are doing now is just we just showing you how many different ways exchange can appear in a system right. And so, you have discussed direct exchange, super exchange, this is indirect exchange RKKY. And now I am going to discuss something called double exchange ok. So, let me just show you what it is. This is a situation where which happens in for example, L a Mn O 3, when you dope it with strontium or something.

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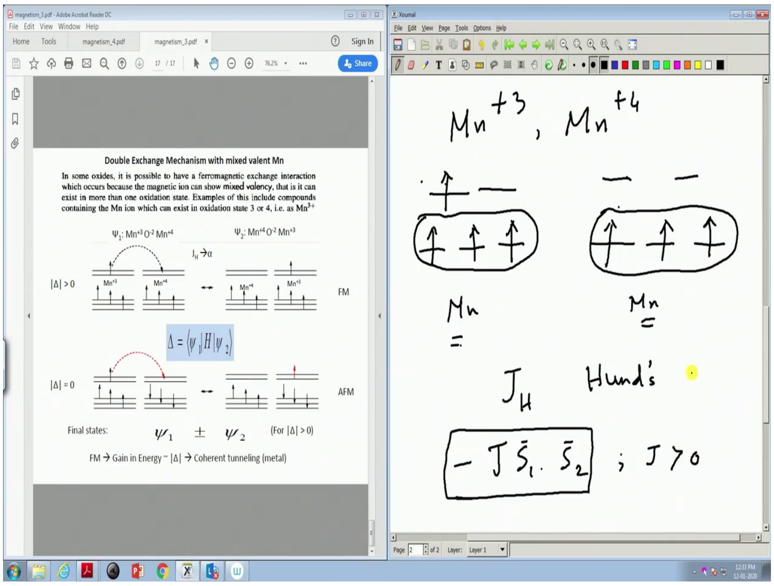

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FM → Gain in Energy ~ $|\Delta|$ → Coherent tunneling (metal)

Mn^{+3}, Mn^{+4}

J_H Hund's

$$\boxed{-J\,\bar{S}_1 \cdot \bar{S}_2} \; ; \; J > 0$$

Then M n has a mixed valence. So, Mn can be in plus 3 or plus 4. These two (Refer Time: 08:29) states. And the corresponding electronic structure atomic inside that ion, the electronic structure is such that the 3D level is it has 5 levels; which are where whose degeneracy is lifted and 3 levels are below and 2 are above. So, suppose you have 2 such manganese ions sitting next to each other, if it is in 3 plus state then it will have moments.

So, Hund's rule applies and moments will be like this. If it is 4 plus then one more electron has to go away and so, it is in this configuration for example. Now these pins, the suppose this is one Mn and it is the next Mn next to it in the solid. In these two cases the there is no electron here. So, this electron can move the top electron can move here that is being shown here, this M n 3 plus this electron can move here.

Now look at the configuration of these three spins below, these 3 spins here on the one atom, on this atom and this atom are now aligned. So, this is a ferromagnetic arrangement of spins of this cores these are called core spins. These spins do not move. They are stuck to the atom to the ion. The one that can move is this one ok.

So, in that case this can now move here and everything is fine because these are parallel with it, this is parallel with this one, so Hund's rule is satisfied, Hund's energy is satisfied.

But now, so this is allowed; that means, there is a finite matrix element between these two states. So, this matrix element is psi 1, this state we call psi 1 and this state we call psi 2 an then, so the other this state, this is the psi 1, where 1 both of them are ferromagnetically aligned. And the psi 2 is and the top electron is in this atom this psi 2 state is where this is same, but the top electron has moved to the other one. So, that is that is psi 2 for example.

And there is a matrix element therefore, between psi 1 and psi 2 of the Hamiltonian. So, Hamiltonian has a matrix element finite matrix element between these two states; that means, which basically means that an electron can move from one to the other. Whereas, in this case the arrangement is anti ferromagnetic the core spins which are these spins these which are not moving these three spins at the lower level, they are not moving. And they are not moving and they are anti ferromagnetically aligned.

And this in this case you can see that this top spin if I want to move this electron to the next site which is this red dashed arrow then you can move of course, you can bring it here. But look this is anti parallel to the spins at the bottom three levels the localized spins., That means; the Hund's rule is not satisfied you are going to pay a lot of energy. And the Hund's rule the energy corresponding to that J sub H which is called the Hund's energy J H the Hund's, Hund's rule this is the Hund's energy.

So, Hund's exchange between these electron, this and that is now dissatisfied, I mean they are not satisfied. So, the electron remains the system now becomes dissatisfied and it cost a lot of energy and that is the situation which is not tenable the system will not do it. So, that means; if I take J H to be very large going to infinity limit, for example, then this is not even allowed I mean this is cost infinite energy. Of course, quantum mechanically there are always these virtual transitions, but they will cost very large energy.

So, therefore, this matrix element in this case will be exceedingly small. So, that means; the in the ferromagnet, ferromagnetic configuration the electron can be delocalized and you gain the delocalization energy again. Whereas, if you have an anti ferromagnetic configuration of the core spins, then you cannot have this delocalization energy, it will cost you a lot of energy to move. And therefore, this state has a much higher energy than this one and this is the configuration that will be preferred by the system.

So, this look at this is a motion of an electron under the influence of an Hund's exchange Hund's rule basically and that drives an electron a system from an anti ferromagnetic to a ferromagnetic configuration; that chooses the ferromagnetic configuration from an anti ferromagnetic configuration.

So, this spin selectivity; that means, the spin order is dictated by the motion of the electrons that is exactly what happened in super exchange also. But here the exchange this exchange gives rise to a ferromagnetic configuration as opposed to the super exchange. And the super exchange is between in an insulating system, here this leads to metallicity of the electrons of the system. So, this leads to a metallic configuration, a ferromagnetic metallic system.

So, this is this was first proposed by Zener the famous person who whose name is associated with Zener diode and this one is called the double exchange. So, for historical reasons I will not get into that, but this leads to double exchange leads to a ferromagnetic metallic state ok. So, this is the, this is an interesting.

So, as you can see that there are just simple electronic processes obeying quantum mechanics can lead to various different exchange interaction between the. So, for example, now I can I can think of a Hamiltonian, where I will write the core spins as S 1 and S 2 and I know that it prefers a ferromagnetic configuration. So, in this case my J is, so they J will be greater than 0. So, both the spins are up the S 1 and S 2 are this 3 spins 3 these are 3 by 2 half plus half plus half.

So, that is that that is a model I can now write for the spins between the spins of the two manganese ions in say La Mn O3, doped La Mn O3. So, that is a beautiful example of how quantum mechanics plus microscopic descriptions lead to different kinds of interactions between different kinds of spin interaction driven by the motion of electrons their delocalization and so on in real systems.

What we will do now is to now start from the Heisenberg model and try to discuss how one goes about solving such models in some extreme cases, very simple cases. Heisenberg model is very difficult to solve and it is not been solved yet; except for some very special cases in the lower dimensions. So, what I will do is that, I will show you how this model is used and how one solves or makes approximations on such models to get physically relevant quantities.