Neutron Scattering for Condensed Matter Studies
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Week 6: Lecture 15 A

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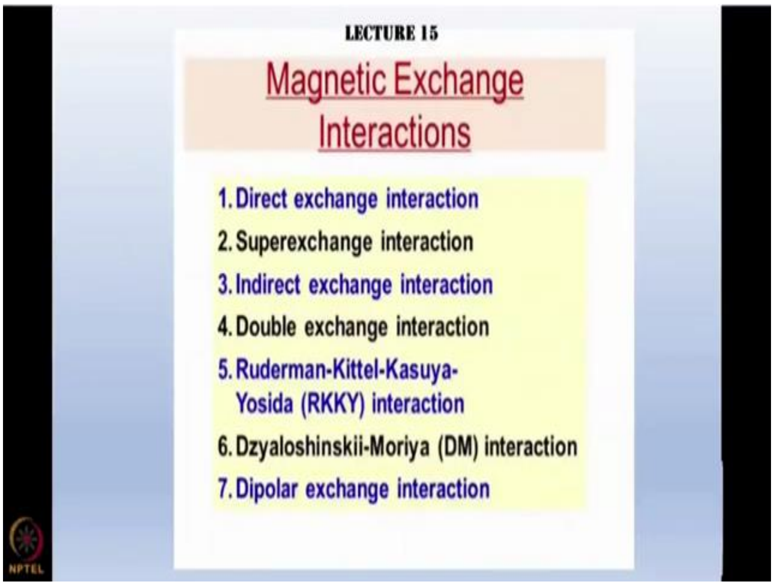

Last time I stopped before I could introduce you to various magnetic interactions in solids and I promised you that before we get into neutron diffraction for magnetic structures, I will give a brief introduction to at least some of the major magnetic interactions in solids.

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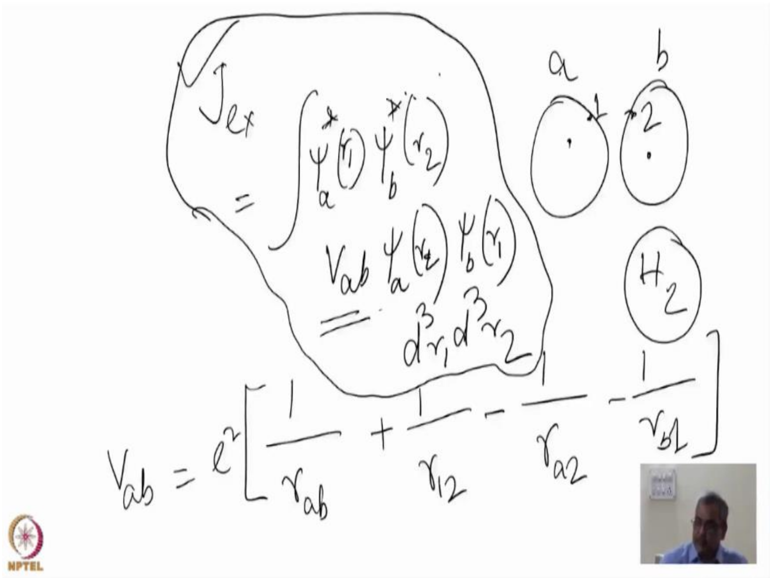

Direct exchange I discussed with you earlier. I discussed it with respect to hydrogen-like molecules. All I wanted to point out to you that the direct exchange comes when we exchange electron 1 (from atom *a*) with electron 2 (from atom *b*) based on Pauli exclusion principle. I get an exchange term (J_{ex}), which is given by,

$$J_{ex} = \int \psi_a^*(r_1)\psi_b^*(r_2)V_{ab}\psi_a(r_2)\psi_b(r_1)dv_1dv_2$$

Here, V_{ab} is an interaction potential and is given by,

$$V_{ab} = e^2 \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}}\right]$$

Here, r_{ab} is distance between the nuclei and r_{12} is distance between the two electrons. The interaction potential between electrons is purely coulombic in nature. But the exchange term, J_{ex} , comes due to Pauli Exclusion Principle where you can see that in the integration where I have kept V_{ab} as I wrote where the things are exchanged and where the things are not exchanged. This comes because two electrons are identical particles.

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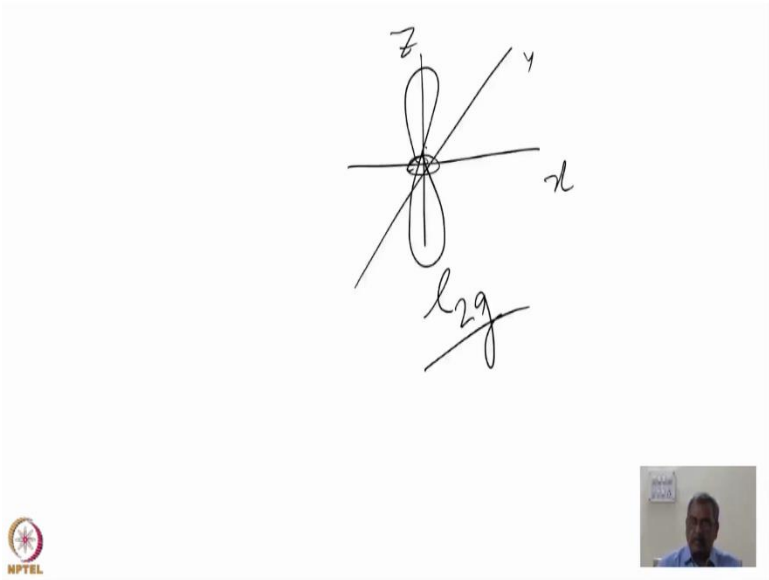

The direct exchange comes from overlap of electronic orbitals.

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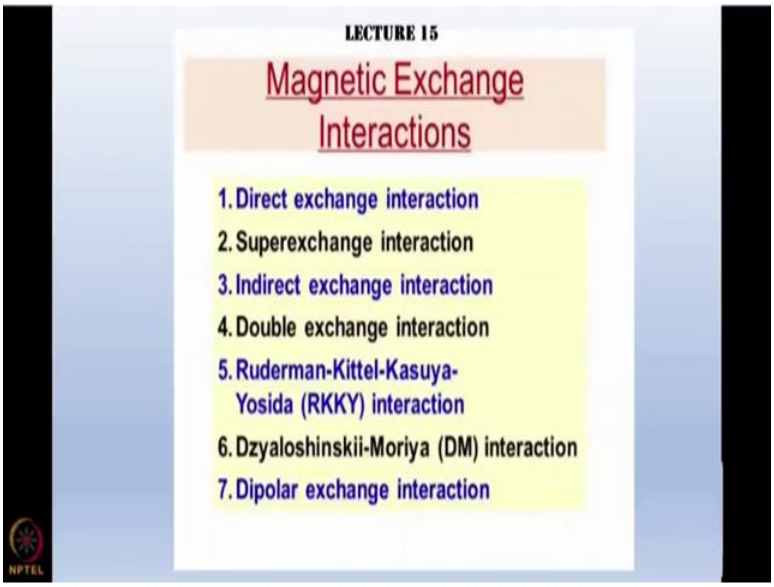

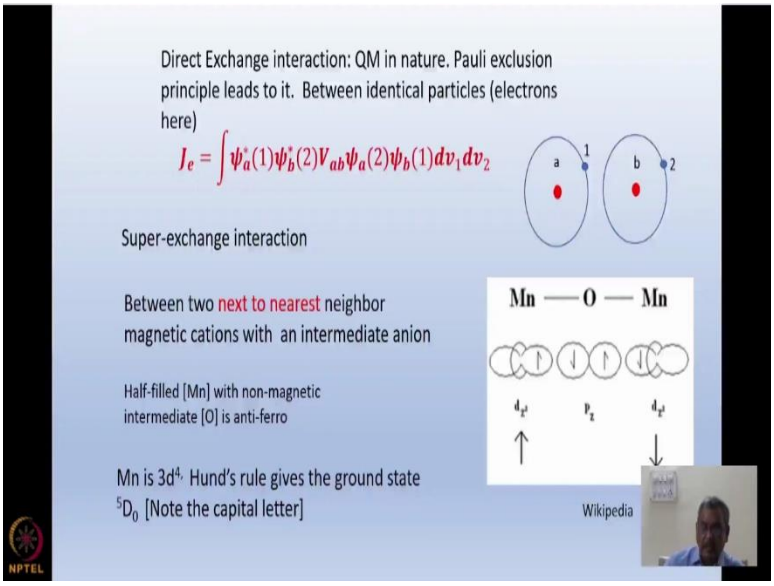

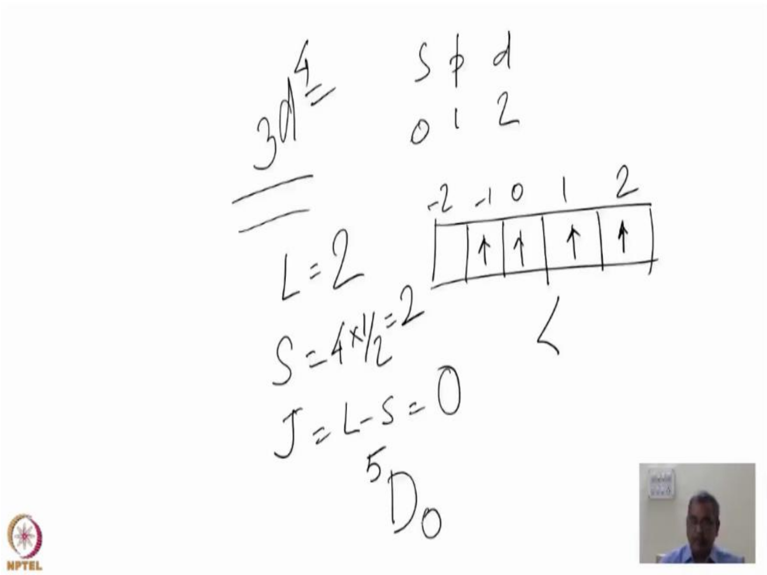

There are several other forms of exchange interactions. One of them is a super-exchange interaction. In this case, it is not the direct overlap of the wave functions of two neighbouring atoms but here you can see that this needs an intermediate atom. For example, in the picture, d_{z^2} orbitals of manganese are interacting through an intermediate oxygen p_z orbital. For example, manganese is a $3d^4$ element and let me quickly remind you how to calculate the ground state of manganese with $3d^4$ configuration. For d-orbit, there are 5 orbitals are possible,(-2,-1,0,1,2). Now, I have to put 4 electrons in them. These can be placed parallelly in 4 of them so that L = 2. As there are 4 parallel electrons, so, S = 4*1/2 = 2. The orbital is less than half-filled, so J = L - S = 0. So now you can see because S is equal to 2, there are five possible states but this is for the whole atom and not for one individual electron and then L = 2. So the state of atom is $^5D_0$. The d_{z^2} orbitals of manganese are interacting via oxygen 2p electrons. And through Pauli exclusion principle. It mostly favours anti-ferromagnetic order. In summary, this gives an anti-ferromagnetic interaction between two next to nearest neighbour manganese magnetic atoms.

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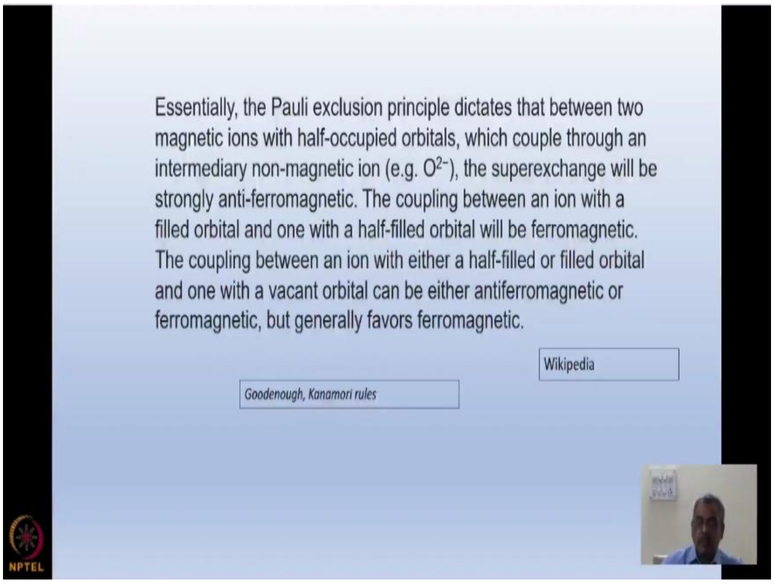

There are actually a set of rules named Goodenough-Kanamori-Anderson rules. This problem was first targeted by PW Anderson and later more successfully by Goodenough-Kanamori. It says that between two manganese magnetic ions (shown in previous slide), which coupled through an intermediate non-magnetic oxygen ion, the super-exchange will be strongly anti-ferromagnetic. But there are rules regarding others. For example, the coupling between ions with filled orbital and one with a half-filled orbital will be ferromagnetic. The coupling between ions with either a half-filled or filled orbital and one with a vacant orbital can be either ferromagnetic or anti-ferromagnetic but generally favours ferromagnetism.

These are known as Goodenough-Kanamori rules. The derivations are beyond the scope of this course but what I wanted to say that we discussed about direct exchange where two atomic orbitals overlap, there are other possibilities. Then, we talked about super-exchange where two magnetic ions are interacting through an intermediate non-magnetic ion which is oxygen.

Manganese oxide is a known anti-ferromagnetic atom. Anti-ferromagnetic means neighbours are anti-parallelly aligned.

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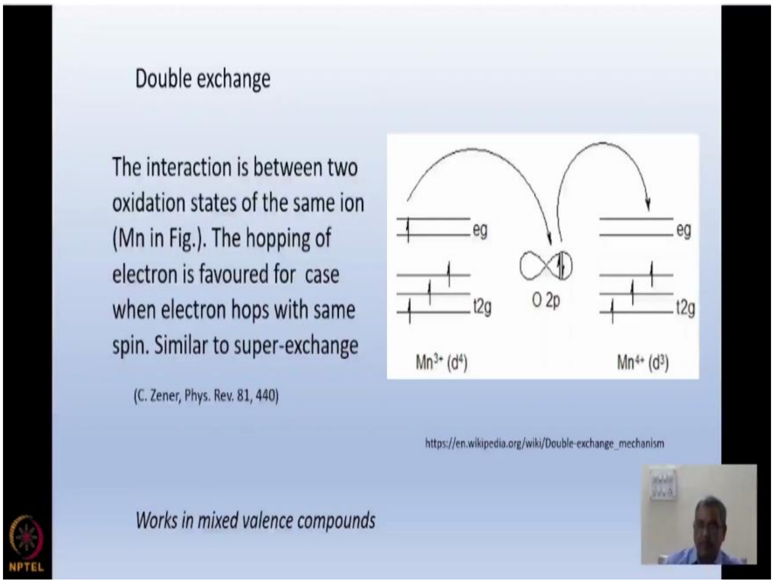

Then there is something known as the double exchange. Now, double exchange is similar to super-exchange but in a way, another form of super-exchange.. I request you to note the fact that here I am putting Mn^{3+} ion. That means three electrons have been taken out from the Mn and we have t_{2g} orbitals filled with 3 electrons and one more in the e_g orbital. Energy wise they are split in a crystal field. The other ion has a different valence state (Mn^{4+}) which has got 4 electrons taken out and hence e_g orbitals are vacant. Now, this electron can hop from here to oxygen 2p state and then hop to this vacant site and keep on hopping back and forth.

Now, by using quantum mechanical techniques, I can calculate this hopping parameter or the transfer integral and that will give rise to a double exchange. This was proposed by Zener in 1950s. This works especially in compounds (not in elemental magnets) with mixed valence because I need two interacting ions which will have different valency (here Mn^{3+} and Mn^{4+}).

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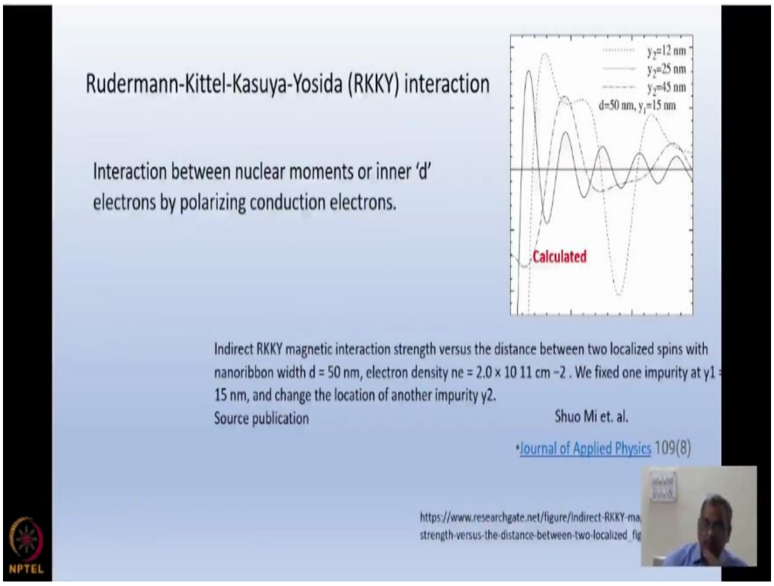

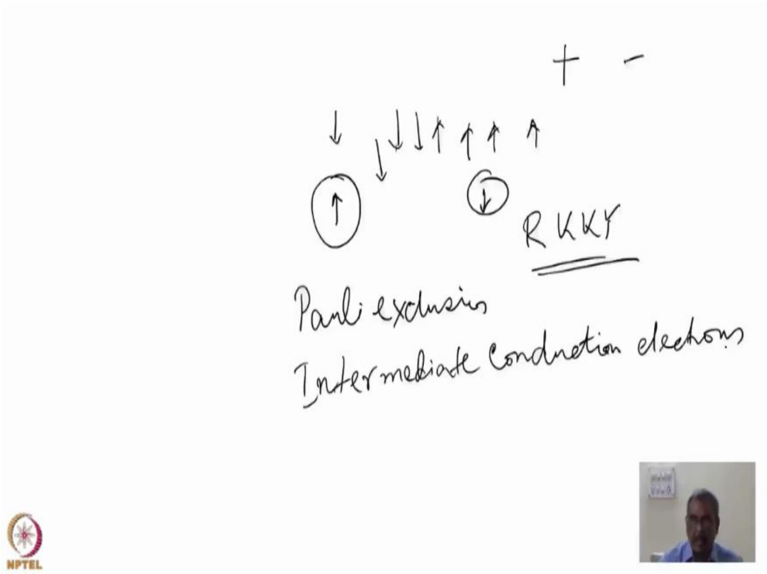

There is one more very interesting interaction known as Rudermann-Kittel-Kasuya-Yosida interaction or RKKY interaction. Here the interaction between two magnetic sites is by polarizing conduction electrons. This interaction was discovered when people discussed the nuclear lines. This is basically similar to the phenomena when one nuclear spin that can polarize the nearby conduction electrons which can further force another nuclear spin to align in some way.

Here, instead of nuclear spin, we are talking about *d* electrons. I will just try to give you a pictorial representation of this interaction. Let us say this in the context of spin magnetic moment of unfilled *d* electrons. Now, this 'd' moment will force the nearby conduction electrons to be oppositely aligned because of Pauli Exclusion Principle and then align another one magnetic ion.So, this will force it either parallel or anti-parallel, depending on the oscillation of the this spin density. I may say it will oscillate between plus and minus moments for the ‘d’ electrons. It will either give a positive alignment or these conduction electrons, near the next site are oppositely aligned to the first site , or will force them to anti-ferromagnetic ordering.

Actually, many times it is used to understand interaction between magnetic defects in an otherwise crystalline lattice and this interaction is known as RKKY interaction where the intermediate conduction electrons are responsible for the interaction. I will show you the RKKY ordering through a drawing. Here the indirect RKKY magnetic interactionbeen taken from the paper mentioned, where it is a long range interaction you can see. Here electron density of a system is given by 2×10^{11} cm^{-2} and one impurity is fixed at y1 = 15 nm. Change magnetic ordering in location of another impurity whose distance in nano-meters is 12, 25, 45, 50 etc, you can see. Basically, close to the first impurity, the electrons are polarized. Now, this polarization causes, as we go further, opposite polarization of the conduction electrons. Then this opposite polarization in the next distance will force the electron to be again polarized up. This is simply because of Pauli Exclusion Principle and now you can see the polarization of the electrons have an oscillatory behaviour. Depending on the polarization here, if a magnetic defect is situated at this point, then this will be polarized opposite to the polarization of the electron. And ultimately this defect or atomic or molecular site is forcing the alignment of another site which is quite far away. You can see this is the distance of the order of 12, 25, 45 nm, much larger than distance of crystallographic sites

This long-range magnetic interaction is known as RKKY interaction where the intermediaries are the conduction electrons. One may say that these are dynamic interaction using electron spins - close and away from one spin and then forcing the other spin to align ferromagnetically or anti-ferromagnetically with respect to the first spin. And often use for defects or impurities, magnetic impurities in solids.

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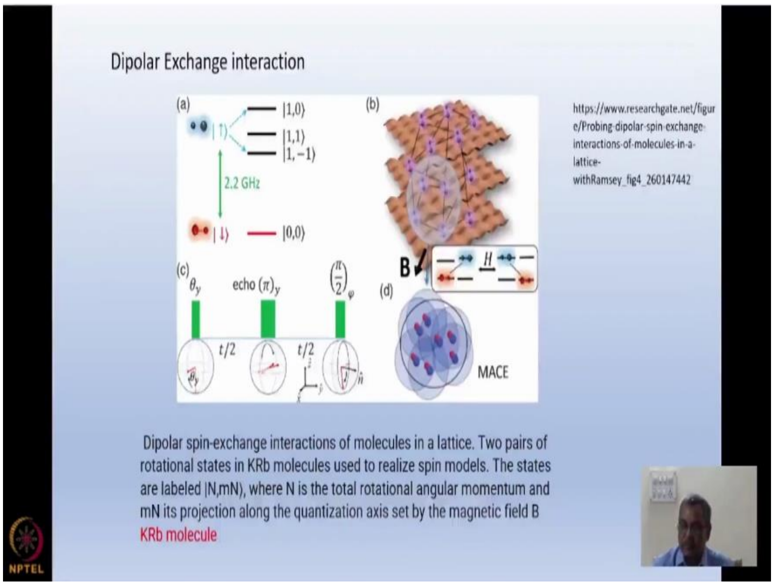

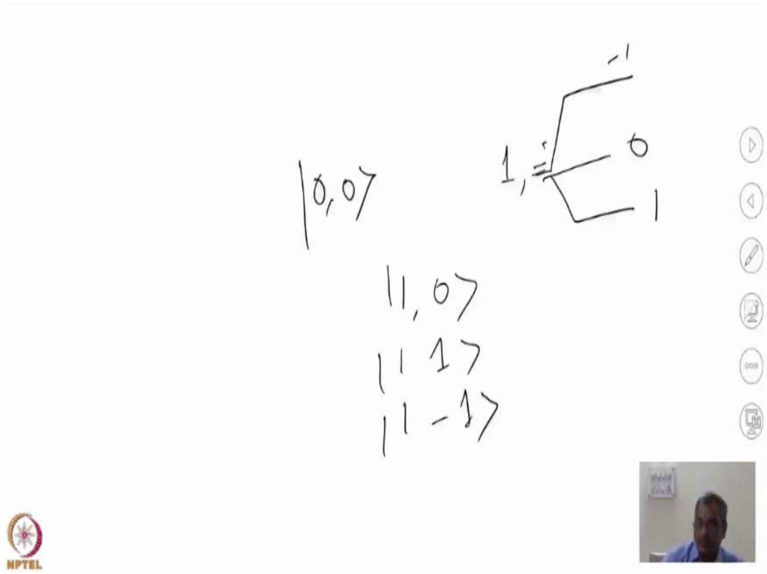

Dipolar exchange interaction is another type of interaction which I mentioned in my transparency earlier. It is basically the exchange interaction between two rotational states or a pair of rotation states of a molecule. Here,what I have shown here schematically,,is a potassium rubidium molecule. You can see thatif one state is $|11>$and the other is$|01>$ then there can be three possible spin projections: -1, 0, 1. This depends on the energy hierarchy of the spin 1 system. So primarily I am talking about exchange between the $|00>$and $|11>$ $|10>$ and $|1-1>$states of a molecule Again I can calculate the transfer integral and I can give you the energetics of this double exchange integral.

This is a dipolar spin exchange interaction of molecules. This figure has been taken from the source mentioned. In case anybody is interested, you can look up the article because it has been determined using some technique known as Ramsey optical scattering, because there is a difference of energy involved in this interaction which is 2.2 gigahertz unlike other exchange interactions where we do not mention any energy term between the two states we are considering for exchange.

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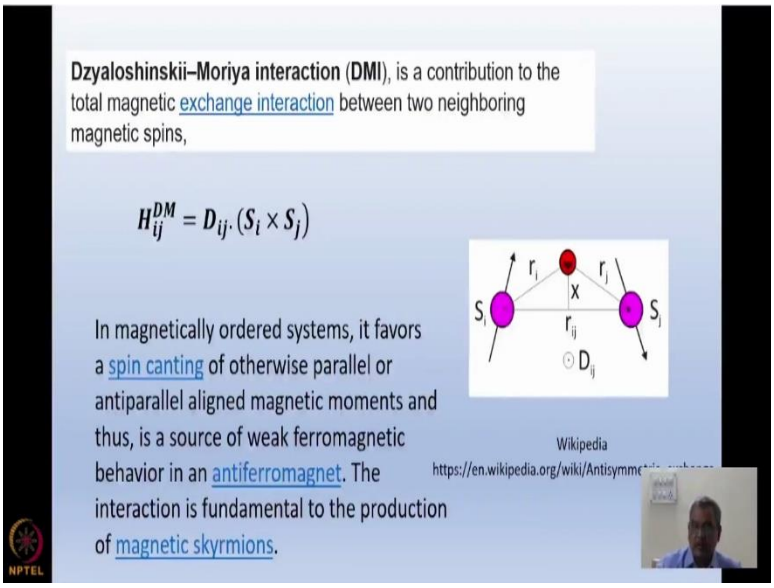

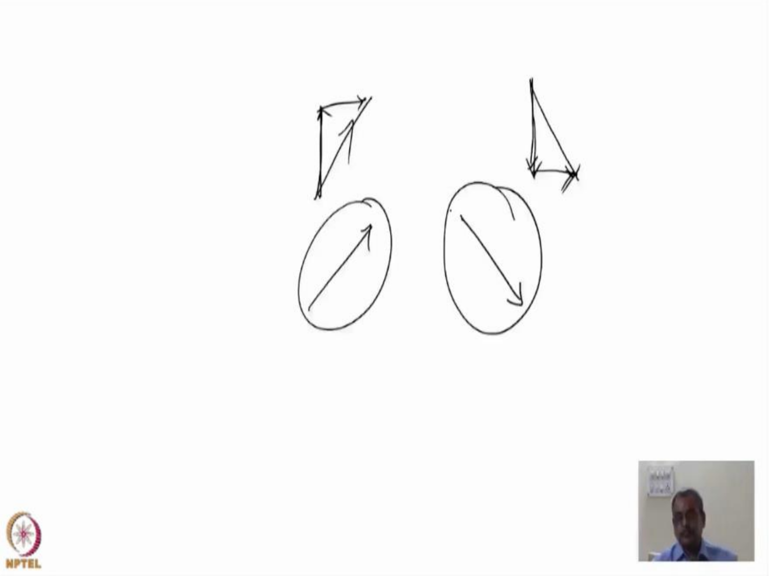

The Dyaloshinskii-Moriya interaction (DMI) is the last one I am discussing. So far in the exchange interaction I was writing $S_i.S_j$. It is $S_i \times S_j$ which means it is a cross product term and cross product term means you can see there is a component between the two which is normal to this plane of this figure and most interestingly it uses a weakly ferromagnetic behaviour in an otherwise anti-ferromagnetic material. I will try to give a vectorial picture for this.

Consider the material is an ideal anti-ferromagnetic. Now, if I can have some canting - that means if I add ferromagnetic term to these two; a small ferromagnetic component coming from that cross product, then it looks like this, as I showed you.. This is one spin and this is the other spin It gives a weak ferromagnetism due to the cross product term and it is a source of weak ferromagnetism in an otherwise antiferromagnetic material.

This was very difficult to determine experimentally. Without talking about this interaction, I cannot really bring you up to date with the list magnetic interactions because this interaction is important for generation of magnetic skyrmions. Now, some of you may be aware of this. It the latest ordered magnetic structures but at macroscopic length scale or mesoscopic length scale.

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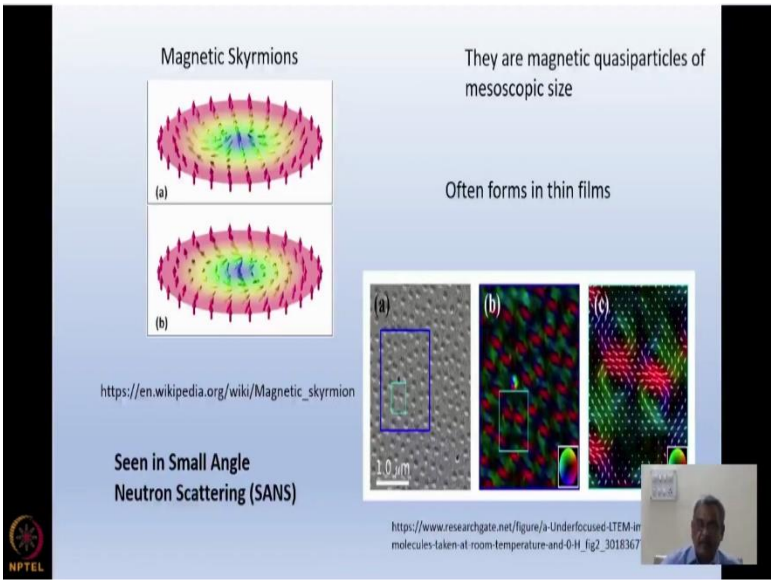

I just show you the schematic because I do not have the chance to give you the complete theory of skyrmions here. The fact is that this originates from the cross product and you see that this dimension is almost micron size. I am giving you a TEM image of a skyrmion. You can see this one-micron length.

Typically, this size can be fractions of a micron. It can go to 1000 Å also. Skyrmions are macroscopic to mesoscopic size objects and look at the spin canting. So here the spin canting is because of the crossproduct terms. You can see they keep turning and finally coming to parallel position at the boundary of this skyrmion. This is one skyrmion.

Well, I must mention to you that this is beyond neutron diffraction or crystallography neutron diffraction of a solid because the sizes are much larger but this can be investigated using small angle neutron scattering which will be a part of this module of diffraction. Small angle takes place at a much larger or mesoscopic length scale and skyrmions have been studied using small angle neutron scattering. If I have time along with other problems in small angle neutron scattering, I will try to introduce you to the studies on skyrmions.

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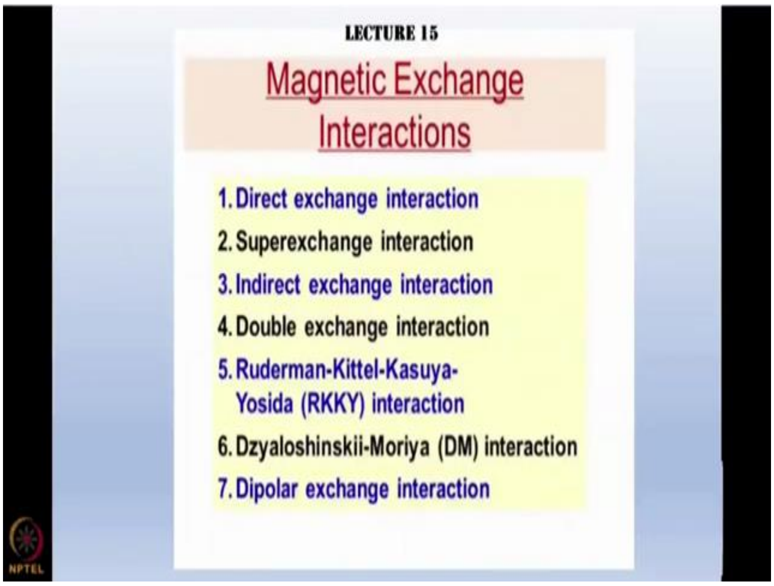

This completes my promise of introducing you to the major magnetic exchange interactions. I talked to you about direct exchange, super-exchange, through an intermediary. I did not talk about indirect exchange interaction. Double exchange happens where you take about talk about two different valances of the same magnetic ion.

Then RKKY interaction, where interaction between two magnetic defects in a solid are caused due to polarization of conduction electrons and then the Dzyaloshinskii-Moriya interaction which is due cross term of $S_i \times S_j$, between two interacting spins and this gives rise to skyrmions- mostly due to loss of inversion symmetry at the interfaces of thin films. You usually find skyrmions in thin films. I cannot give too much of theoretical details for all of them but I hope I have introduced you to most of the major magnetic exchange interaction. After this, I will go to magnetic neutron diffraction.