Introduction to Solid State Physics
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Lecture – 80
Understanding quenching of orbital angular momentum in transition metal ions

We had earlier considered both lanthanides and transition metals, where we considered, where we calculated the paramagnetic moment of these atoms.

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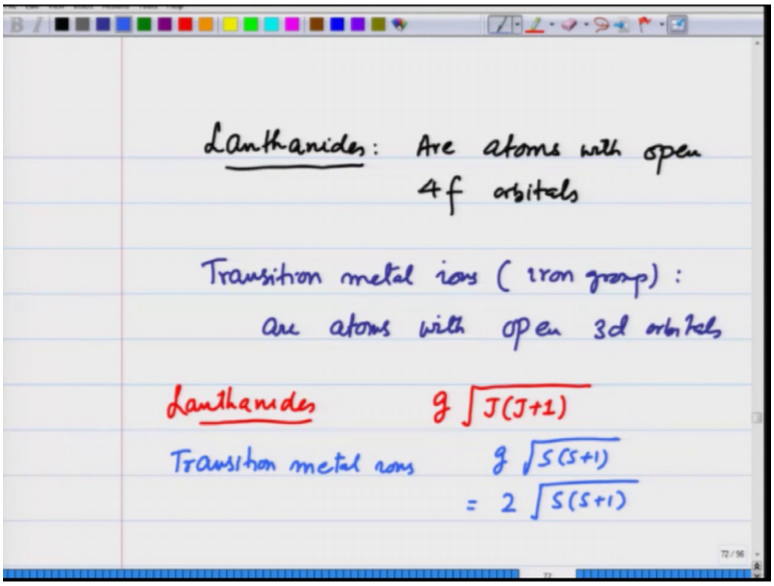

Lanthanides: Are atoms with open 4f orbitels

Transition metal ions (iron group): are atoms with open 3d orbitels

Lanthanides $g\sqrt{J(J+1)}$

Transition metal ions $g\sqrt{S(S+1)}$

$= 2\sqrt{S(S+1)}$

And let me just recall that lanthanides are atoms with open 4f orbitals and transition metal ions or transition metals and which is also the iron group are atoms with open 3d orbitals. And the difference between the two was that in lanthanides the effective Bohr magneton number was given by g square root of J J plus 1 whereas, in the transition metal ions it was given as g square root of S, S plus 1. And we said this is because the orbital angular momentum gets quenched and here the values of g therefore, becomes 2 square root of S, S plus 1.

So, in this lecture I want to come back to crystal field orbital angular momentum quenching and understand it from the point of view of Hamiltonian because we have already written it for the magnetic systems in the previous lecture.

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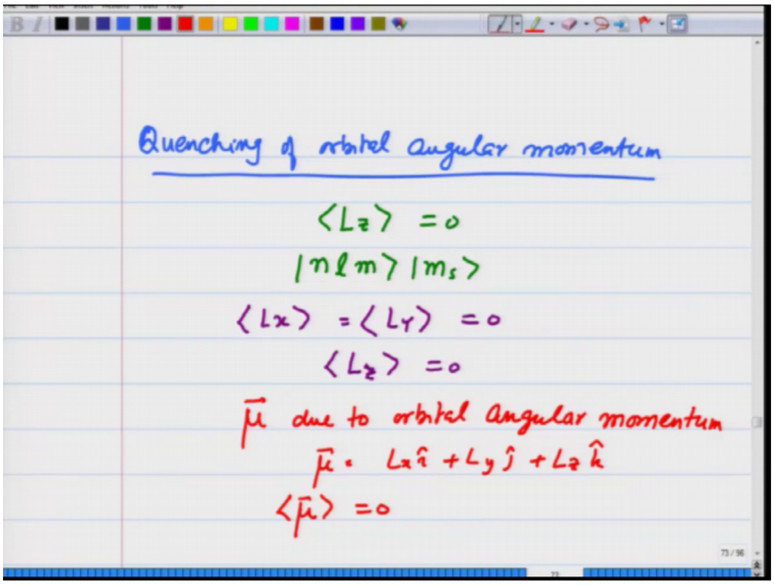

Quenching of orbital angular momentum

$\langle L_z \rangle = 0$

$|n l m\rangle |m_s\rangle$

$\langle L_x \rangle = \langle L_y \rangle = 0$

$\langle L_z \rangle = 0$

$\vec{\mu}$ due to orbital angular momentum

$\vec{\mu} = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}$

$\langle \vec{\mu} \rangle = 0$

So, the quenching of orbital angular momentum meant that L z expectation value is 0. Recall that in atoms, where I have the orbital n l m m s. We give the quantum numbers for the total angular momentum as L and the component in the z direction as m because the expectation value of L x and L y already is 0, in this basis the important point about quenching is that expectation value of L z also becomes 0. And therefore, in this case mu due to orbital motion which will be mu equals L x i plus L y J plus L z k. If I take its expectation value this will be 0 and therefore, it comes only from the spin of electrons.

Now, we want to understand where does this quenching arise from. I had indicated a bit in the lecture earlier on this topic, but now let us look at the Hamiltonian of the system.

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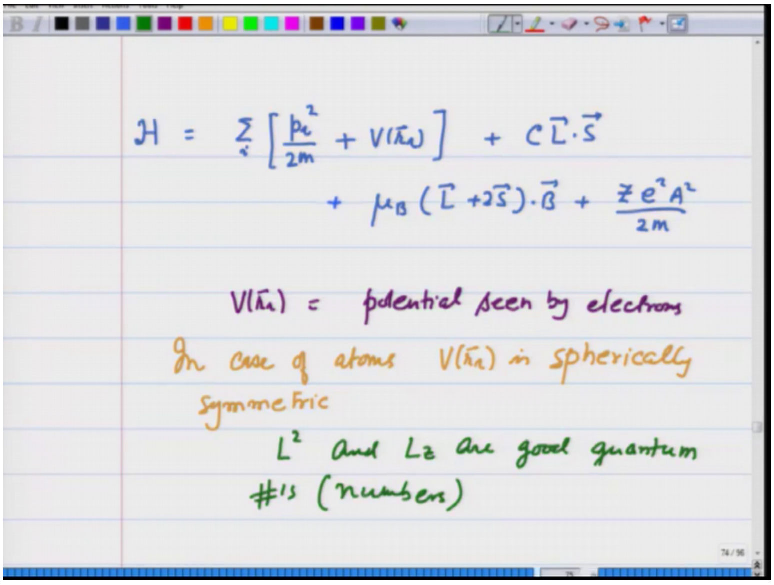

$$\mathcal{H} = \sum_i \left[\frac{p_i^2}{2m} + V(\vec{r}_i)\right] + C\vec{L}\cdot\vec{S} + \mu_B(\vec{L}+2\vec{S})\cdot\vec{B} + \frac{Ze^2A^2}{2m}$$

$V(\vec{r}_i)$ = potential seen by electrons

In case of atoms $V(\vec{r}_i)$ is spherically symmetric

L^2 and L_z are good quantum #'s (numbers)

When it is put in a magnetic field and this we had already derived there is nothing, but summation i, i sum over electrons p i square over 2 m plus V ri plus there is spin orbit coupling L dot S plus there is paramagnetic term L plus 2 S dot B and there is a diamagnetic term Z e square A square over 2 m.

V ri in this case is the potential seen by electrons. And in the case of atoms V ri is a spherically symmetric, and as a consequence the L square and L z are good quantum numbers this I mean numbers; that means, they can be specified to give an orbital.

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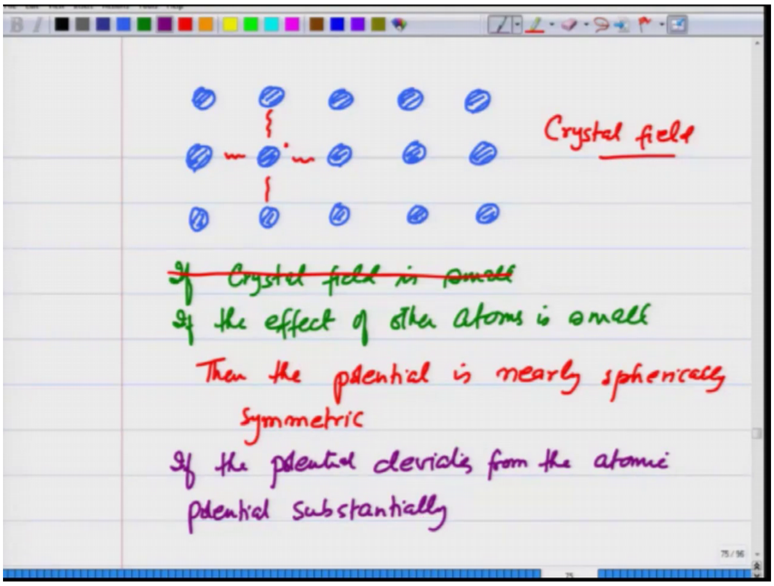

Crystal field

~~If Crystal field is small~~

If the effect of other atoms is small

Then the potential is nearly spherically symmetric

If the potential deviates from the atomic potential substantially

However, as I commented earlier if these atoms are sitting close together then for an electron in an atom say there is an electron which I show by this orange colour, the potential need not be severely symmetric. There is going to be influence due to potential of other atoms and the surrounding areas. And the net field that comes because of this I am going to call crystal field.

Now, if crystal field is small I mean the effect. So, I should not write crystal field I will cut it and write it again, if the effect of other atoms is small on this field then we can say that the potential is nearly spherically symmetric. Now, what do we mean by small that has to be specified? On the other hand, if the potential deviates from the atomic potential substantially then the quenching takes place and let me explain how that happens.

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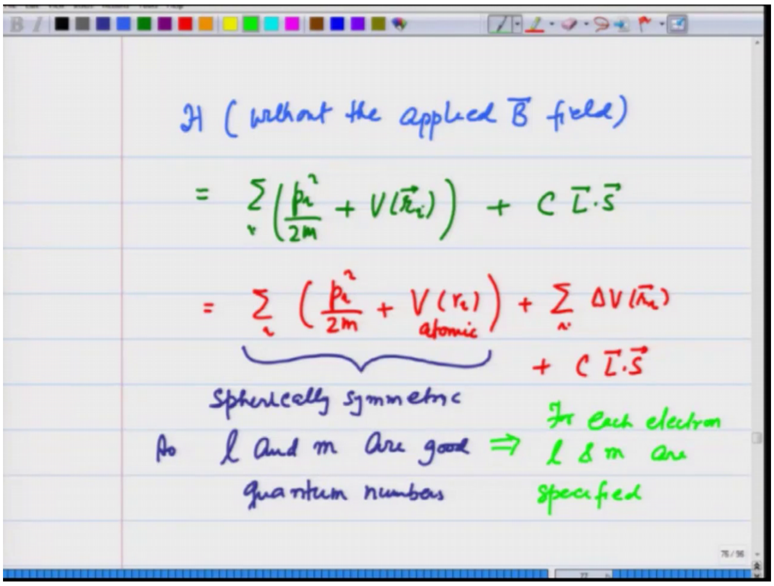

$\mathcal{H}$ (without the applied $\vec{B}$ field)

$$= \sum_i \left(\frac{p_i^2}{2m} + V(\vec{r}_i)\right) + C\,\vec{L}\cdot\vec{S}$$

$$= \underbrace{\sum_i \left(\frac{p_i^2}{2m} + \underset{\text{atomic}}{V(r_i)}\right)}_{\text{Spherically symmetric}} + \sum_i \Delta V(\vec{r}_i) + C\,\vec{L}\cdot\vec{S}$$

So l and m are good quantum numbers ⇒ For each electron l & m are specified

So, let me write this Hamiltonian without the applied B field because what I am really concerned with right now is the effect of crystal field and this was equal to summation p i square over 2 m plus V and I will put vector on top V ri plus C L dot S.

And let me decompose it further, as summation i pi square over 2 m plus V atomic. And let me write this as ri without the vector, so that it is fairly symmetric plus summation i, delta V ri and this all right as a vector plus C L dot S. And let us look at each term separately. When I look at this part of the Hamiltonian the one which is shown right now by this curly brackets, this is a spherically symmetric. So, l and m are good quantum numbers and what that means is that for each electron l and m are specified and they give you the corresponding angular momentum component.

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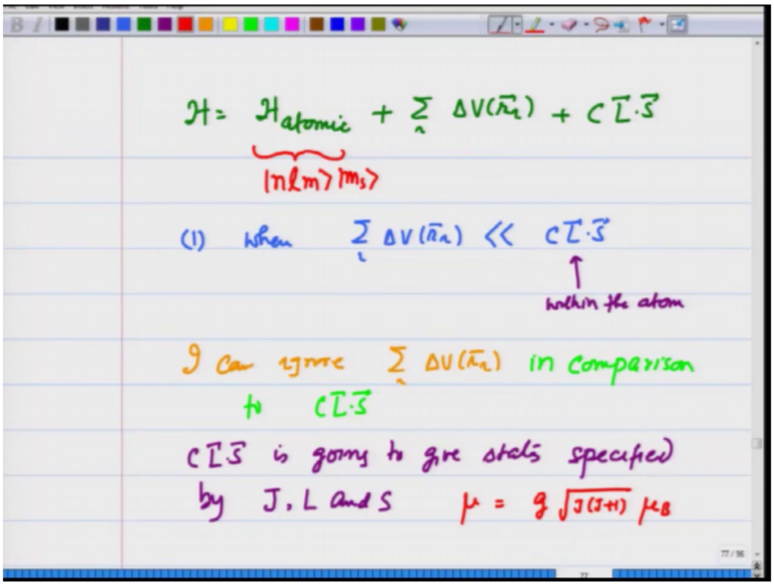

$$\mathcal{H} = \underbrace{\mathcal{H}_{atomic}}_{|n l m\rangle |m_s\rangle} + \sum_i \Delta V(\vec{r}_i) + C\vec{L}\cdot\vec{S}$$

(1) when $\sum_i \Delta V(\vec{r}_i) \ll C\vec{L}\cdot\vec{S}$

$\uparrow$ within the atom

I can ignore $\sum_i \Delta V(\vec{r}_i)$ in comparison to $C\vec{L}\cdot\vec{S}$

$C\vec{L}\vec{S}$ is going to give states specified by J, L and S $\mu = g\sqrt{J(J+1)}\,\mu_B$

So, let me go to the next slide and show H equals H atomic plus summation i delta V ri which is arising because of the crystal, the structure of the crystal because of the other atoms in it and plus C L dot S. So, this part we have already said that the state is n l m, m s.

Consider this scenario 1, when summation i delta V ri is much much smaller than C L dot S. That means, the effect of atoms other atoms in a crystal is much smaller than the spin orbit coupling within the atom. So, this part is within the atom. So, in the first instance I can ignore, right. So, I can ignore this term i delta V ri in comparison to C L dot S and therefore, what is going to happen is that C L dot S is going to give states which will be combination of l and s. So, specified by J L and S. So, they do not have J, L and S as good quantum numbers and in this case the magnetic moment mu will be g square root of J J plus 1 mu B. So, these are the lanthanides or systems with 4f electrons.

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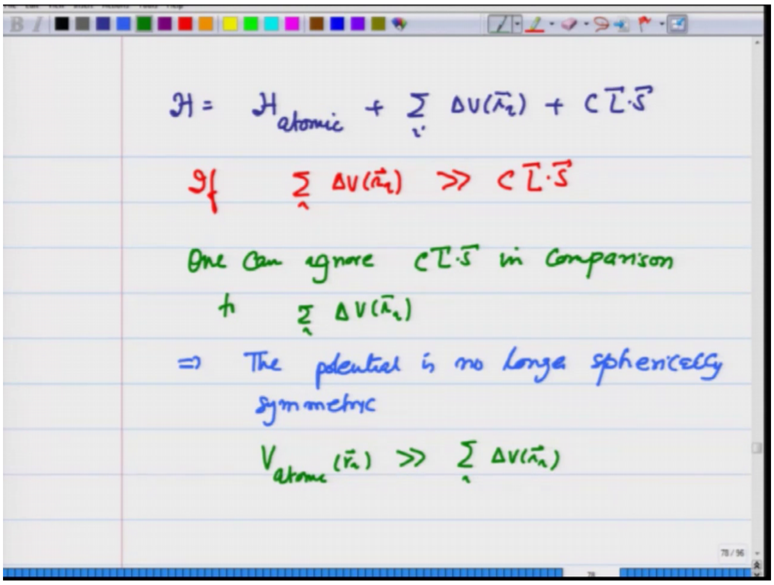

$$\mathcal{H} = \mathcal{H}_{atomic} + \sum_i \Delta V(\vec{r}_i) + C\,\vec{L}\cdot\vec{S}$$

If $\sum_i \Delta V(\vec{r}_i) \gg C\,\vec{L}\cdot\vec{S}$

One can ignore $C\,\vec{L}\cdot\vec{S}$ in comparison to $\sum_i \Delta V(\vec{r}_i)$

$\Rightarrow$ The potential is no longer spherically symmetric

$$V_{atomic}(\vec{r}_i) \gg \sum_i \Delta V(\vec{r}_i)$$

On the other hand, in this Hamiltonian H atomic plus summation i delta V ri plus C L dot S, if summation i delta V ri is much larger than C L dot S then in the first instance I have to take care of delta V ri, but I can ignore L dot S. So, one can ignore C L dot S in comparison to summation i delta V ri. So, this delta V ri summed over is called the crystal field and this is much larger than the spin orbit coupling.

So, electrons are not going to get coupled. Now, this is strong and therefore, the symmetry is broken. This means the potential is no longer is spherically symmetric. However, we are going to take this delta V ri still in the perturbative sense, in the sense that let us say that this V atomic ri still dominates this is much larger than summation i delta V ri. So, in the first instance I can say that each electron has an angular momentum. However, the effect of this delta V ri is going to be that is going to mix the states such that the components are not well defined. Let me explain that.

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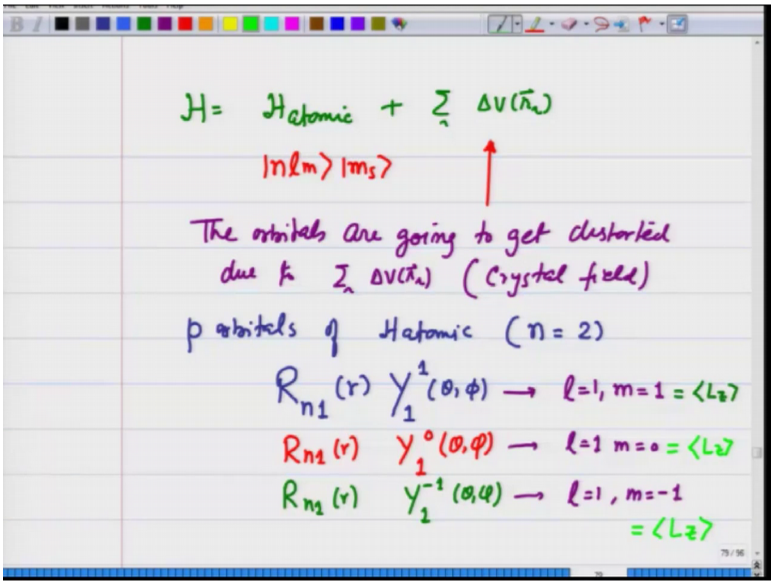

$$H = H_{atomic} + \sum_i \Delta V(\vec{r}_i)$$

$$|nlm\rangle |m_s\rangle$$

The orbitals are going to get distorted due to $\sum_i \Delta V(\vec{r}_i)$ (Crystal field)

p orbitals of H_{atomic} $(n = 2)$

$$R_{n1}(r)\, Y_1^1(\theta,\phi) \rightarrow l=1,\ m=1 = \langle L_z\rangle$$

$$R_{n1}(r)\, Y_1^0(\theta,\phi) \rightarrow l=1\ m=0 = \langle L_z\rangle$$

$$R_{n1}(r)\, Y_1^{-1}(\theta,\phi) \rightarrow l=1,\ m=-1 = \langle L_z\rangle$$

So, H I am going to write as H atomic plus this crystal field i delta V ri these are still specified by n l m and there is this spin component which I am not so much worried right now. And then when I include this something is going to happen. The orbitals are going to get distorted due to summation i delta V ri which is known as crystal field and therefore, they may not remain eigen functions of the angular momentum anymore.

For example, if I look at p orbitals and this is often given example in the book orbitals of H atomic. And let us say I take principal quantum number to be 2 then I have the orbitals of the form some R and L equals 1 which is a function of r alone, and then I have this spherical harmonic 1 1 which is a function of theta and phi. Then I am going to have the next orbital R n 1, r y 1 0 theta phi and then finally, I have the orbital R n 1 r y 1 minus 1 theta 5.

This orbital has l equals 1, m equals 1. This orbital has l equals 1, m equals 0. This orbital has l equals 1, m equals minus 1. And therefore, this is also equal to the expectation value of L z. It is an eigen value of L z and therefore, expectation value also, so this is expectation value of L z, this is expectation value of L z because this is an eigen values it has a well defined expectation value.

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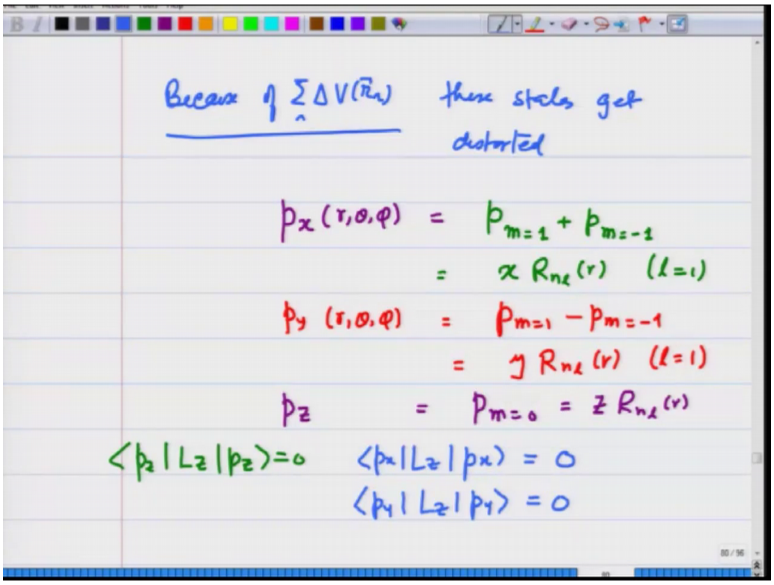

Because of $\sum_{i} \Delta V(\vec{r}_i)$ these states get distorted

$$p_x(r,\theta,\varphi) = p_{m=1} + p_{m=-1}$$
$$= x R_{nl}(r) \quad (l=1)$$
$$p_y(r,\theta,\varphi) = p_{m=1} - p_{m=-1}$$
$$= y R_{nl}(r) \quad (l=1)$$
$$p_z = p_{m=0} = z R_{nl}(r)$$
$$\langle p_z|L_z|p_z\rangle = 0 \qquad \langle p_x|L_z|p_x\rangle = 0$$
$$\langle p_y|L_z|p_y\rangle = 0$$

Now, because of delta V ri summed over i these states get distorted and the first approximation they are mixed with each other. So, I can have an orbital p x r theta phi which is given as a combination of p orbital with m equals 1 plus p orbital with m equals minus 1 and this comes out to be x R nl, where l equals 1.

Similarly, I have p y r theta phi which is also a combination of p m equals 1 and p m equals minus 1, and this is why R nl r, again l equals 1. And finally, of course, I have p z which anyway earlier also was equal to p m equals 0 which is nothing but z R nl r.

Now, it so happens that for p z, L z with respect to p z anyway was 0. The new thing is that when I take the expectation value of L z with respect to p x this also will come out to be 0 because it is a combination of equal probabilities of m equals 1 and m equals minus 1 and similarly p y L z p y comes out to be 0. Again, a linear combination of m equals minus 1.

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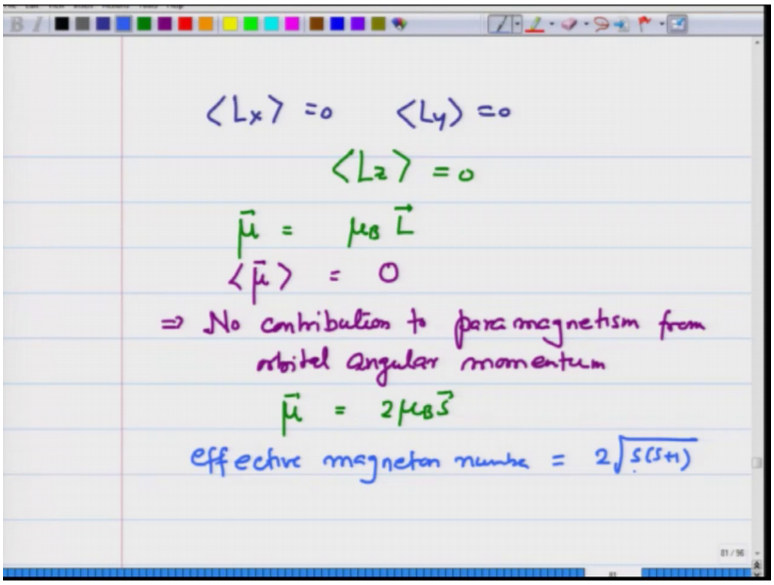

$\langle L_x \rangle = 0 \qquad \langle L_y \rangle = 0$

$\langle L_z \rangle = 0$

$\vec{\mu} = \mu_B \vec{L}$

$\langle \vec{\mu} \rangle = 0$

$\Rightarrow$ No contribution to paramagnetism from orbital angular momentum

$\vec{\mu} = 2\mu_B \vec{S}$

effective magneton number = $2\sqrt{S(S+1)}$

So, because of this crystal field what has happened is that I have L x anyway was 0 and y anyway expectation was 0, the new thing is that I also start getting L z expectation value to be 0 and that means, this can be no contribution of these 3 orbitals to the angular momentum. So, angular momentum mu which is mu B times L its expectation value will be 0 with respect to these states and therefore, no contribution to paramagnetism from orbital angular momentum.

If that is the case if there is no contribution to paramagnetism from orbital angular momentum the only place where mu comes from is S 2 mu B S and therefore, the effective magneton number becomes equal to 2 the square root of S S plus 1.

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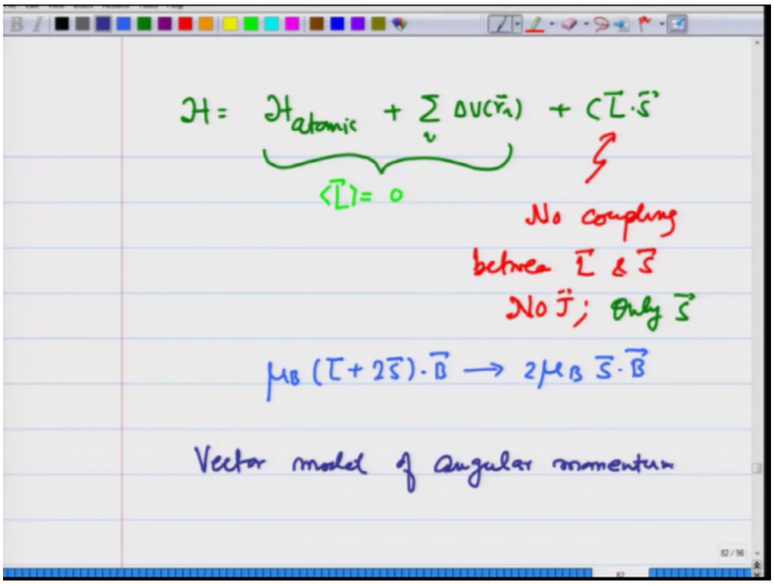

$$\mathcal{H} = \underbrace{\mathcal{H}_{atomic} + \sum_i \Delta V(\vec{r}_i)}_{\langle \vec{L} \rangle = 0} + C\vec{L}\cdot\vec{S}$$

No coupling between $\vec{L}$ & $\vec{S}$

No $\vec{J}$; Only $\vec{S}$

$$\mu_B (\vec{L} + 2\vec{S})\cdot\vec{B} \longrightarrow 2\mu_B \vec{S}\cdot\vec{B}$$

Vector model of angular momentum

If you again go back to the Hamiltonian picture, I had this Hamiltonian which is H atomic plus the crystal field delta V ri plus C L dot S. Now, these two together give you states with L vector expectation value equals 0 and therefore, there is going to be no coupling between L and S because there is no L, so no J, only S. So, you straightaway go from this to the paramagnetic term if you go there the paramagnetic term was mu B L plus 2 S dot B, this in this case goes over to mu B 2 S dot B and it explains everything.

Sometimes this is also given as a vector model. Now, the vector model of angular momentum is a sort of classical way of looking at the angular momentum of systems and the way it works is when we look at a state n l m ignoring spin right now and the capital L and L z are good quantum numbers.

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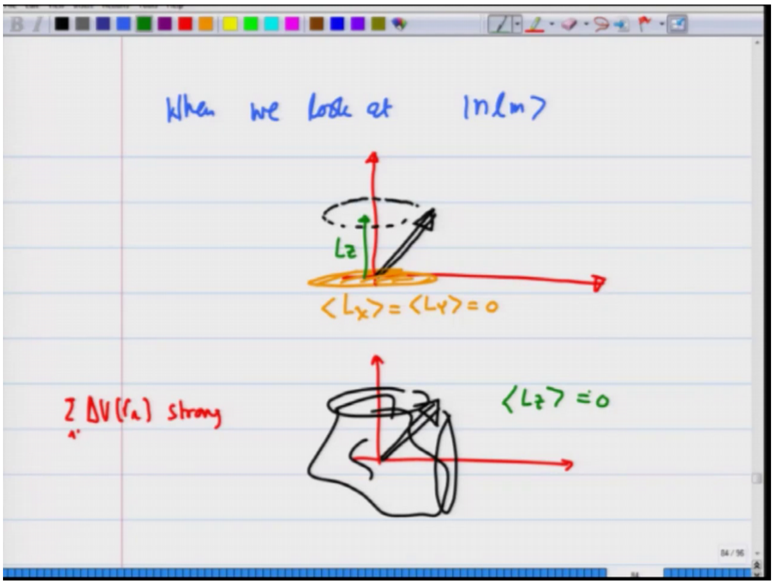

The model we make is that this, angular momentum vector possesses about the z axis. So, that is projection on the z axis, L z remains a constant and its projection on the x y plane averages out to 0 L x expectation value and L y expectation value comes out to be 0. What is happening when we include the crystal field is that this precession does not take place only about the z axis because of this crystal field, so delta V ri summed over i strong, because this crystal field this vector now starts moving all over the place. It may precise about this, it may precise about this, it may precise about the y axis.

So, it is going all over the place. With the result that L z also becomes 0 and that is the quenching of angular momentum. So, hopefully with this I have explained to you how the quenching arises, now the question is why quenching takes place in transition metals.

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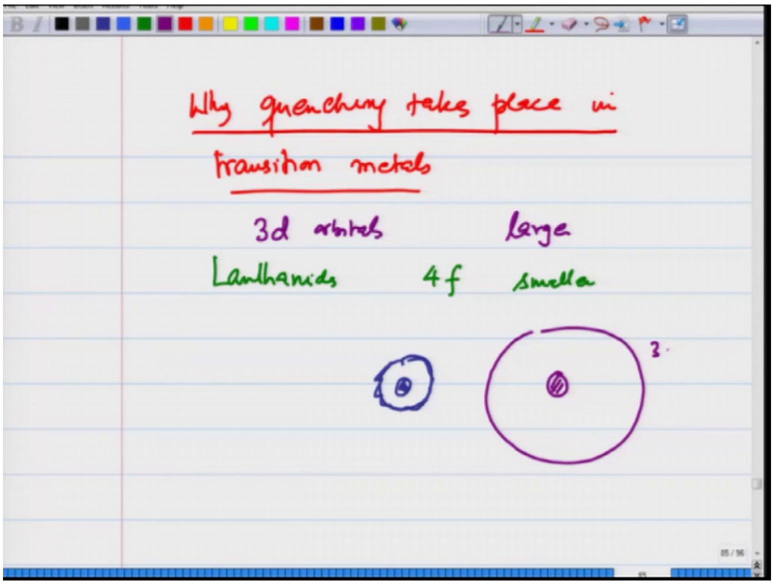

Why quenching takes place in transition metals

3d orbitals large

Lanthanides 4f smaller

And the reason is that the transition metals we have 3d orbitals and in lanthanides we have 4 of orbitals. Lanthanides have larger z, so 4 f orbitals are smaller they are smaller in comparison to 3d orbitals which I will write larger. So, you may kind of if you look at an atom with large z 4f maybe you know inside, but the with smaller z 3d for the transition metals could be larger this could be 3d. And larger orbital means it feels the potential of other atoms in the crystal and therefore, it gets affected much more and therefore, orbital angular momentum for these orbitals gets quenched.

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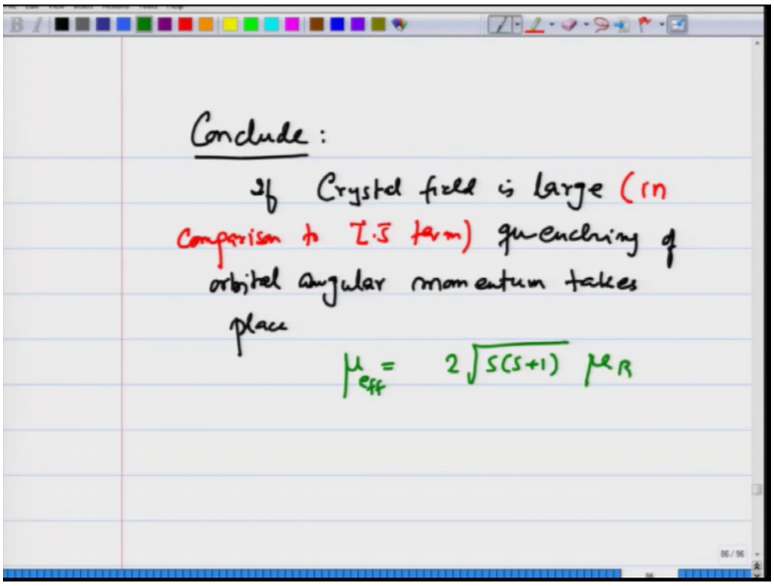

Conclude:

If Crystal field is large (in comparison to $L \cdot S$ term) quenching of orbital angular momentum takes place

$$\mu_{eff} = 2\sqrt{S(S+1)}\,\mu_B$$

So, to conclude what we have shown is if crystal field there is large and large and small is determined by the spin orbit coupling. So, I will let me write in comparison to L dot S term. Then, quenching of orbital angular momentum takes place and in this case mu effective becomes equals 2 square root of S S plus 1 mu B.

Thank you.