Basics in Inorganic Chemistry
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Lecture - 14
Magnetism

Hi. I will start on Magnetism, ok. Before going to magnetism, I think one or two application what we were discussing for you know coordination chemistry I will show in here, ok.

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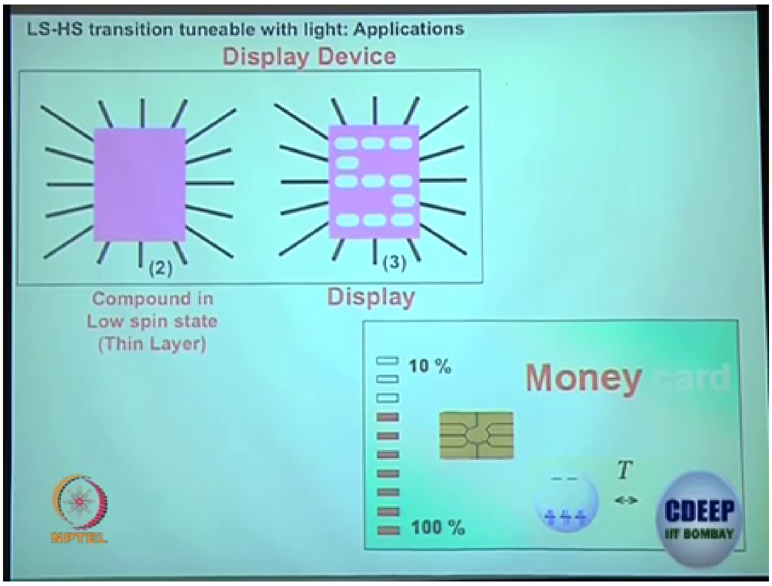

LS-HS transition tuneable with light: Applications

Display Device

Compound in
Low spin state
(Thin Layer)

Display

Money card

Sometimes we do not realize that the simple high spin low spin configuration can give you something very very important. For example, let us say you have a complex which is low spin, it has one color. Low spin you know what sort of transition you do expect it can vary depending on the compound. Let us say you have a given compound the compound is low spin.

If you give the temperature, if you heat the complex what you can have is you can convert the low spin compound into high spin. Because low spin means what? Those spin cannot go in the e g orbital let us say, t 2 g to e g orbital.

Now, as soon as you put heat or let us say laser light some of the spin, some of those electron will be now traveling to the e g orbital t 2 g to e g. Now, the color of that compound will be different. It could be white to red, red to white or whatever it is, right. So, by changing these something like display you see lot of these color display you know in big audience or big auditorium or even display in the on road side somewhere else.

So, basically let us say it is one color, the moment laser light is you know signing on this display what happens, it may be showing a particular thing, particular let us say name written whatever you want to happy, but they wish that something you have wished me that can be written over here on the board just by signing those laser lights. That is nothing but changing the high spin to low spin configuration, lot of things can be done and it has been done, without realizing we are seeing those, ok

Other form of these sort of high spin, low spin configuration can be used in your money card or ATM. Let us say you have a debit card, you have 10,000 rupees. Every time you pick up money let us say first time you pick up 2,000 rupees from ATM machine, right.

Now, so what can happen is a selected amount of laser light can be eradicated on your card because 2,000 rupees will let us say be selecting by default how much laser light to sign, thereby some of the complex will go from high spin to low spin or low spin to high spin let us say low spin to high spin, specifically you are putting light, so low spin to high spin will be going.

Next time when you are punching the card again the machine can read how much money you have left. Let us say after 10,000 minus 2,000, 8,000. These show a let us say at the end you have 1,000 rupees you want to draw 5,000 rupees from that instrument will not allow.

So, these are also technique, these are different ways to take advantage of this complex. This is something one paper has already come and only problem is so far this technique is little bit expensive that is why we do not see it in the market right now, but soon enough it will be make hopefully made cheaper then you can you know the technology itself is coming expensive that is why it is not in the market, but in principle it can be done.

So, lot of the practical application just by signing lights, since just by signing light you can change the electronic configuration of a compound. Of course, you have to choose the right compound, right wavelength, right everything let us say, but once you have that right combination you can do wonder, something like this, right.

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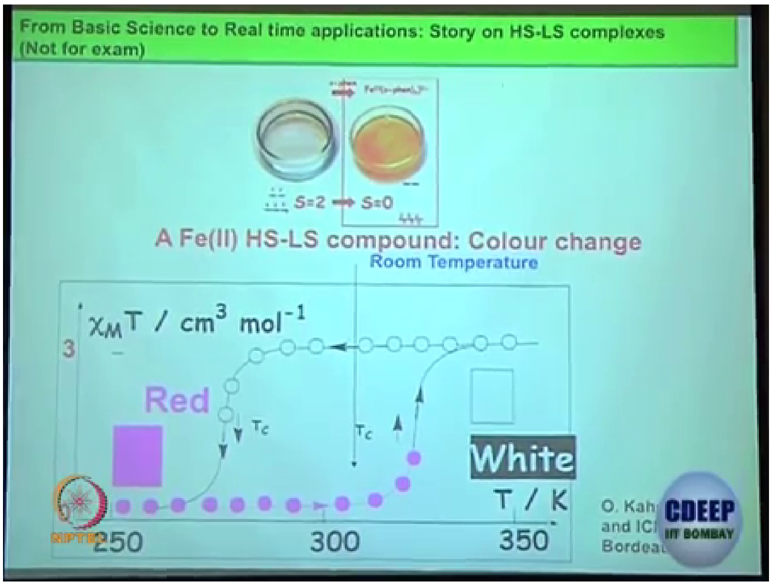

From Basic Science to Real time applications: Story on HS-LS complexes (Not for exam)

A Fe(II) HS-LS compound: Colour change

Also other things of course, you will know that you have a colourless compound, you add something high spin to let us say low spin complex form or low spin to high spin complex form, something like you cannot read here, this is a iron aqua complex which is colourless, you the moment you add phenanthrol into it high spin complex becomes low spin complex color changes, ok. Another, so this is of course, some time you can use it for magic lot of other application you can have simple color change.

Other things, for example, if you have let us say this red complex, red complex is due to the low spin complex, red complex is due to the low spin complex for example, you starting with that. You are heating it, ok. So, this is the temperature initially it was 250 Kelvin, that is almost like room temperature let us say, ok.

You start from there, you keep on heating nothing happening, nothing happening select at a selected temperature now these low spin to high spin transition is going on. Then what you will see all of a sudden at a particular temperature this red compound is becoming white, ok. So, at that let us say this is 325 this is becoming white.

Now, that white compound you can try to pull down, it will not follow exactly same pathway because the relaxation of the spin, like spin was up, spin has to go down that relaxes and need not be necessarily following the same path. You have excited something, the relaxation means coming back from the you know that e g level to t 2 g level need not follow the same temperature profile, what it can happen is at after reaching this white color it will take quite some time to come back to the red color.

So, that even if you are decreasing the temperature still it stays white and at a particular temperature cooling down at a particular temperature can bring you red. So, these are nothing this is like a very good I mean you know some these sort of you know behaviour you can apply to something which may be let us say, I mean it could be let us say what I said for money card, your ATM card it could be for other display device lot of other things you can do.

So, display device for example, it is here you just sign the light, so it is getting heated they are by some red color or let us say purple color it is coming white color, even if you cooled down significantly these white color may not go back to red very quickly. But then again there are different materials which can relax faster; that means, high spin to low spin it can come down faster. So, you sign the light the whatever we says whatever writing is there you see it, you take off the light, it goes back to the white or red or blue sorry this purple again.

So, you can basically dictate the term you can tell what you want thereby which complex to pick, you want to sign the light from let us say violet color or red color, you want to go to white color and you want to stay in white that is one of the mode or if you want to go back right after switching off the laser that can be also possible. So, these are nothing, but application in different display which you can have based on the synthetic chemistry knowledge.

Of course, lot of start-up companies and lot of other related application material science has already come up. These are something of course, you can in future if you are looking for a start-up companies, ok. Something that this knowledge, it not necessarily this knowledge it is some other knowledge you read in let us say in 4th year, 5th year or sorry 4th year. So, you can take it off and try to set up a company from these simple ideas if there is non-existing.

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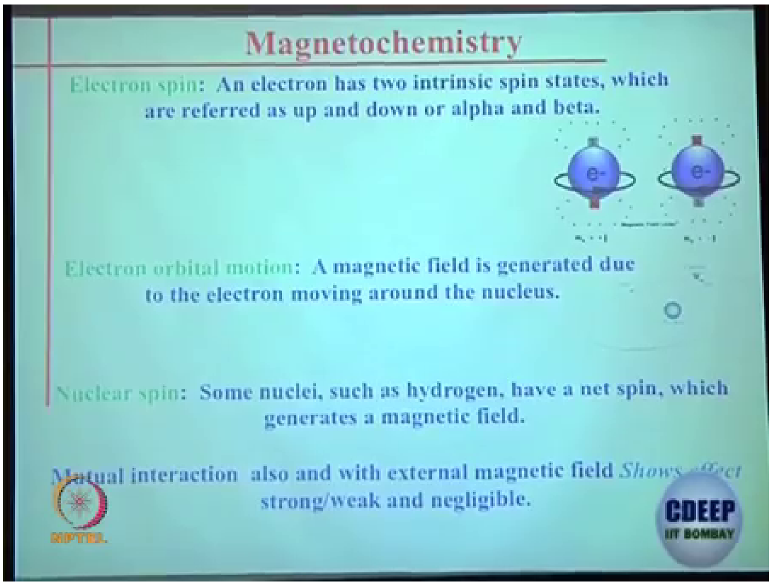

Magnetochemistry

Electron spin: An electron has two intrinsic spin states, which are referred as up and down or alpha and beta.

Electron orbital motion: A magnetic field is generated due to the electron moving around the nucleus.

Nuclear spin: Some nuclei, such as hydrogen, have a net spin, which generates a magnetic field.

Mutual interaction also and with external magnetic field *Shows effect* strong/weak and negligible.

So, that is I guess that is that knowledge sharing and today we will discuss mainly magnets, ok. We were discussing magnets in the last class. Simply magnets are nothing, but having or magnetic compounds are nothing, but having unpaired electrons that is what we were discussing. More than unpaired electron better the magnetic moment or higher the magnetic, moment magnetic values will be high, ok.

If you have paired up all the spin paired up, if you have unpaired electron, but those unpaired electron are not unpaired they are pairing it up then you are losing the magnetic values, right magnetic moment value. So, all the complexes can potentially therefore, give you magnetic moment because all of them are having electrons.

Now, the electron as we were saying electrons are rotating around its own axis that is the spin value its spinning that is why it can give you one type of momentum, or spin or spin angular momentum or sorry it is called spin only values for magnetic moment or it can rotate around the orbital, ok. There is a nucleus surrounding it the electrons are rotating.

So, these are the two types of motion that can give you magnetic moment, but what we are saying usually you do not have to worry about the orbital component, only the spin only value good enough because ligands are restricting the electrons because they are overlapping effectively, restricting the electrons to rotate around the orbital. So, therefore, since the electrons cannot really balanced electron mind you, not the inner electron, balanced electron not effectively able to rotate around its own orbit or rotate along its orbit you would end up getting only spin component, only spin magnetic moment value you get, ok.

Now, also we were trying to tell you that some cases you have to have spin value plus some orbital contribution. Why is that? That is simply because those whenever one orbital to another orbital transition is possible, I guess last class we were trying to discuss. So, let us say d xy to d yz to d xz these transitions are allowed transition because by rotating just 90 degree you can interconvert these orbital. Therefore, you can see there is a magnetic component let us say from xy direction to a xz direction, so thereby there is a some sort of magnetic contribution on those z direction..

It is not necessarily ligand is holding the electron completely, it is retarding it, it is preventing it, but not 100 percent. The moment electron can transfer from one orbital to another orbital; that means, the direction changes xy direction to xz direction z direction some component will be arriving that is the one going to give you the orbital contribution, ok. I will come back to that again, ok.

Let me tell you again simply electron can spin therefore, magnetic moment values can come out of it, but opposite spin can cancel each other as we were trying to say, ok.

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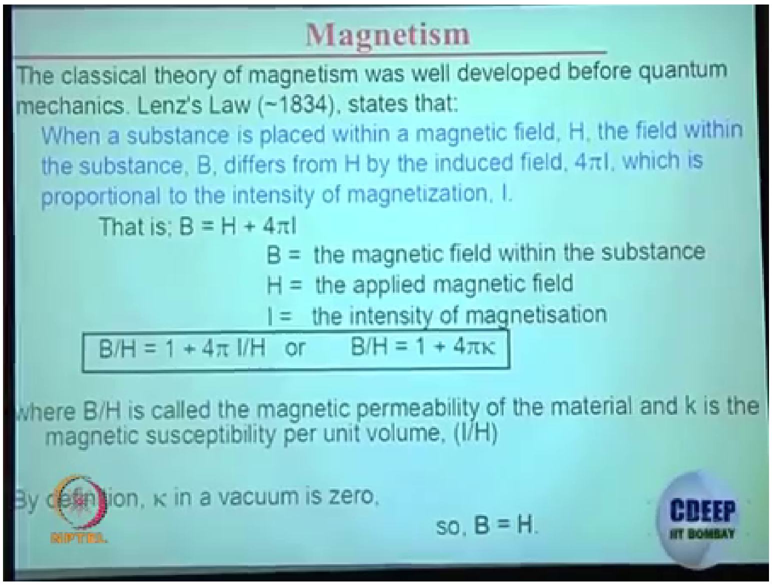

Magnetism

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law (~1834), states that:

When a substance is placed within a magnetic field, H, the field within the substance, B, differs from H by the induced field, $4\pi I$, which is proportional to the intensity of magnetization, I.

That is; $B = H + 4\pi I$

B = the magnetic field within the substance
H = the applied magnetic field
I = the intensity of magnetisation

$$\boxed{B/H = 1 + 4\pi\, I/H \quad \text{or} \quad B/H = 1 + 4\pi\kappa}$$

where B/H is called the magnetic permeability of the material and k is the magnetic susceptibility per unit volume, (I/H)

By definition, κ in a vacuum is zero,

so, B = H.

Overall, I guess overall we in terms of mathematical calculation. We can have this equation where essentially you are keeping your molecules in a magnetic field and that that magnetic field is going to be your H. So, in let say this is the magnetic field of H here you are keeping the compound, right.

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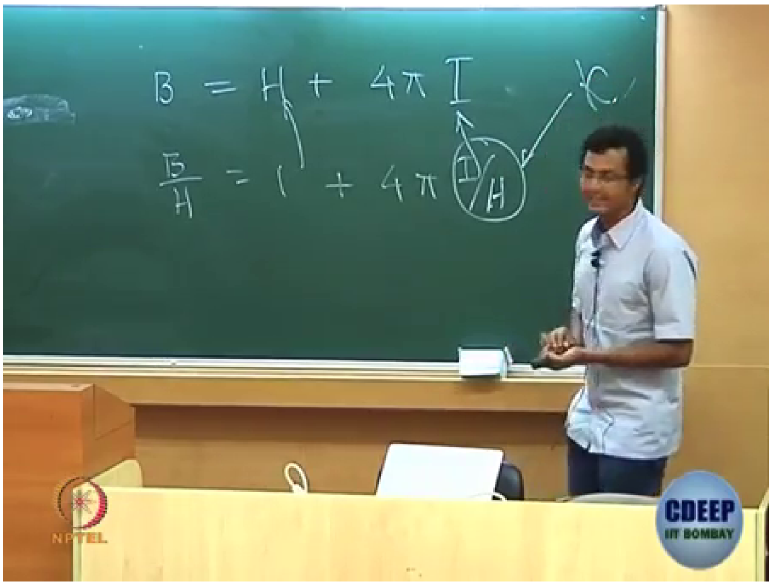

So, how much magnetization or how much effect this molecule is going to fill that is dependent on the magnetic field that H plus its characteristics, its nature what can it be magnetized pretty easily that is the term called I, ok. So, any pieces kept in a magnetic field is going to fill the field itself plus its inherent behaviour that will try to make it magnetized. So, that is the I component.

Now, so intensity of magnetization how quickly it can or how greatly it can orient with respect to that magnetic field, ok. Now, if you do the math, so B by H if you divided by H, B by H will be 4 pi, I by H, right this term is called this kappa or the magnetic susceptibility, ok. So, this is the term kappa is the magnetic susceptibility.

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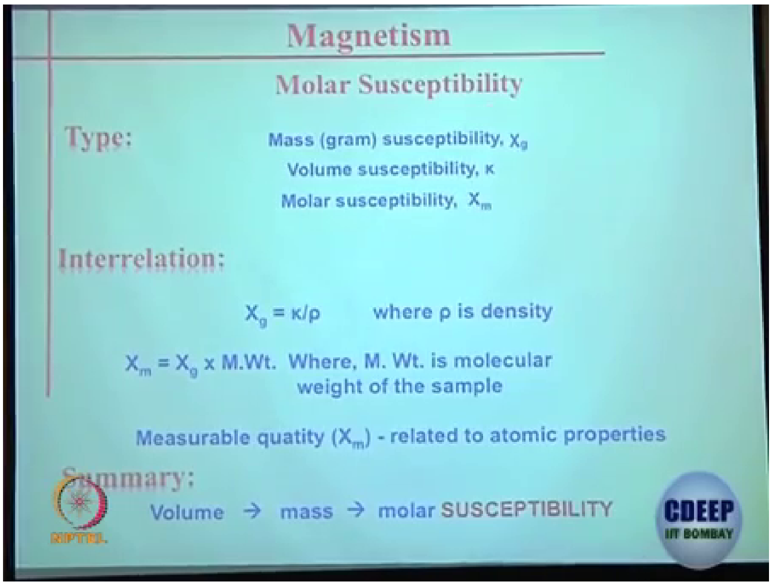

Magnetism

Molar Susceptibility

Type:

Mass (gram) susceptibility, χ_g
Volume susceptibility, κ
Molar susceptibility, X_m

Interrelation:

$X_g = \kappa/\rho$ where ρ is density

$X_m = X_g$ x M.Wt. Where, M. Wt. is molecular weight of the sample

Measurable quatity (X_m) - related to atomic properties

Summary:

Volume → mass → molar SUSCEPTIBILITY

Now, from there you can do the following math simply there is kappa by rho which is the density of the species, density of the molecule that will be the gram molars grams of magnetic susceptibility, multiply that with molecular weight that will be molar susceptibility. So, this I by H term is divided by row simple its density of the molecule you get chi g or X.

This magnetic susceptibility gram magnetic susceptibility this term you will multiply by molecular weight you get molecular or I am sorry these molar susceptibility, ok. This is just simple math you have this equation divide by H, you get I by H which is kappa divide kappa by rho that is going to be your gram susceptibility or mass susceptibility. Mass susceptibility multiply by molecular weight you are going to get this molar susceptibility. It is something I think you have studied before.

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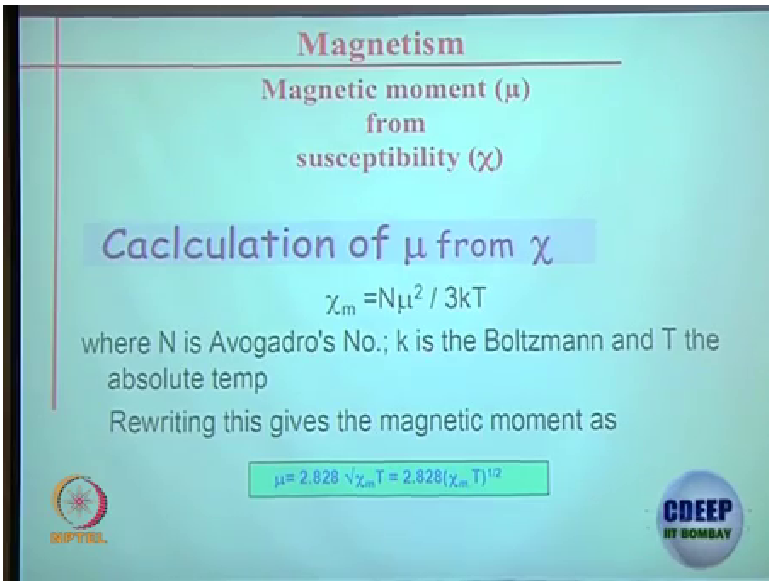

Magnetism

Magnetic moment (μ)
from
susceptibility (χ)

Caclculation of μ from χ

$$\chi_m = N\mu^2 / 3kT$$

where N is Avogadro's No.; k is the Boltzmann and T the absolute temp

Rewriting this gives the magnetic moment as

$$\mu = 2.828 \sqrt{\chi_m T} = 2.828(\chi_m T)^{1/2}$$

Now, once you have that molar susceptibility that is corresponded with the magnetic moment value. This is the simple equation. Now, from there you can get the magnetic moment value of a compound, right. Of course, mu we you can calculate what it is coming, it has a temperature component. So, what it tells you is the temperature is going to affect your magnetic moment value. We are going to see how it is affecting.

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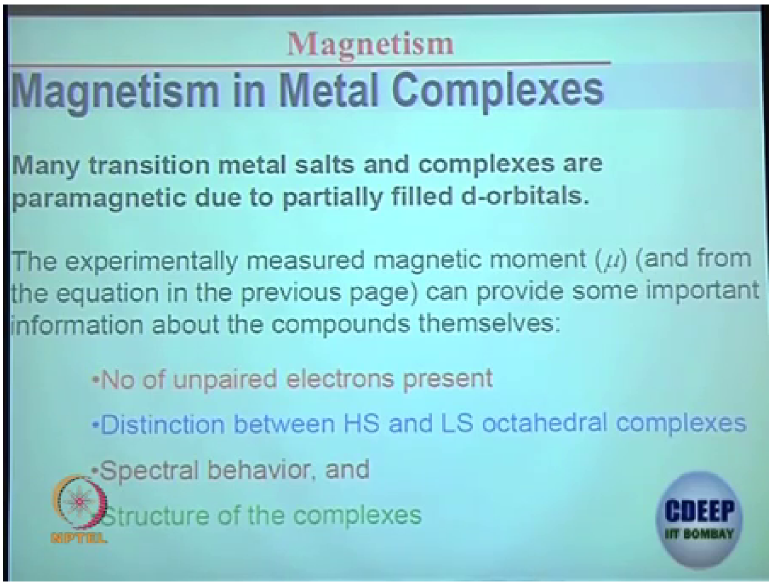

Magnetism

Magnetism in Metal Complexes

Many transition metal salts and complexes are paramagnetic due to partially filled d-orbitals.

The experimentally measured magnetic moment (μ) (and from the equation in the previous page) can provide some important information about the compounds themselves:

- No of unpaired electrons present
- Distinction between HS and LS octahedral complexes
- Spectral behavior, and
- Structure of the complexes

The magnetic moment value is the one we were talking, it has two component, ok, that spin component and the orbital component, ok. Now, this magnetic moment value can give you the idea about the complex itself, what it is made of, how many unpaired electron it has. This is a experimentally measurable quantity. You can measure the magnetic moment value and thereby you can get crucial information about your let us say unknown compound, ok.

It can give you number of unpaired electrons present, high spin, low spin it can give you the spectral behaviour you can it can also tell you something about the structure of the complex. So, what all we are saying is if you have an unknown complex, you can measure the magnetic moment value of it and thereby you can try to tell what that compound is made of, right. How the equation equations are? We have seen in here. These are two different equation one is this one, another is this one.

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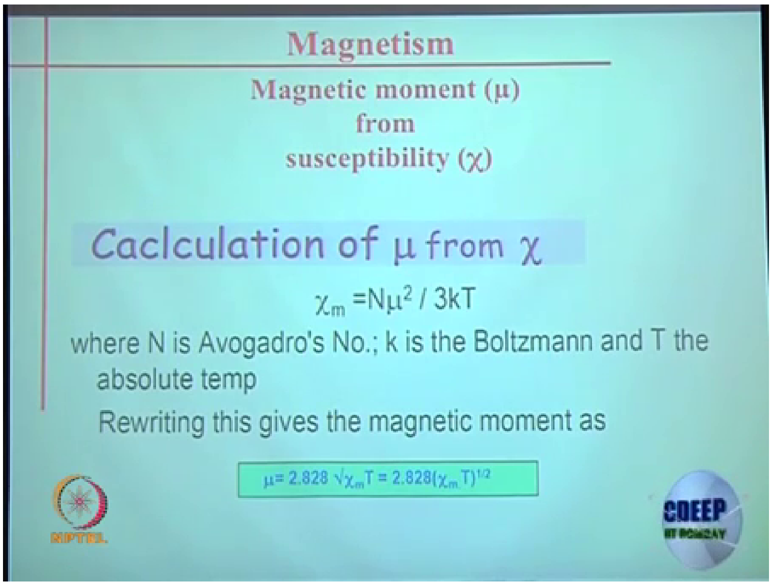

Magnetism

Magnetic moment (μ)
from
susceptibility (χ)

Caclculation of μ from χ

$$\chi_m = N\mu^2 / 3kT$$

where N is Avogadro's No.; k is the Boltzmann and T the absolute temp

Rewriting this gives the magnetic moment as

$$\boxed{\mu = 2.828 \sqrt{\chi_m T} = 2.828(\chi_m T)^{1/2}}$$

As long as you know the relationship between these two equations, you are good to go. This is simple connection between them you just figure it out between these two equation these equation and that equation, ok. They are connected by this kappa I by H and then kappa divided by your density will give you molar susceptibility and then multiply by molecular weight you just look 2 minutes it should be clear, right

So, based on these equation it is expected usually one of the math is given, usually we get one question at least based on these two equation. They are inter relation some value will be given and thereby you have to calculate the magnetic moment let us say, ok. Usually, also in I think maybe it is in the tutorial question as well, I forgot, ok, fine.

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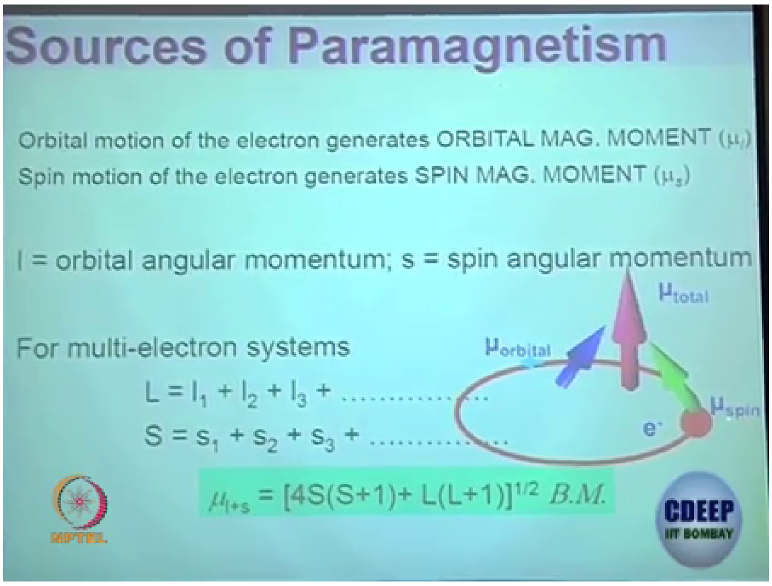

Sources of Paramagnetism

Orbital motion of the electron generates ORBITAL MAG. MOMENT (μ_l)
Spin motion of the electron generates SPIN MAG. MOMENT (μ_s)

l = orbital angular momentum; s = spin angular momentum

For multi-electron systems

$L = l_1 + l_2 + l_3 + \ldots\ldots\ldots\ldots\ldots$

$S = s_1 + s_2 + s_3 + \ldots\ldots\ldots\ldots\ldots$

$\mu_{l+s} = [4S(S+1)+ L(L+1)]^{1/2}$ *B.M.*

Now, we were talking in the last class as well and today itself also, we have two component orbital component and spin component. The resultant one is going to be the know total, right. But this orbital component is going to be nullified or it will be diminished decreased not necessarily you can prevent it 100 percent, that is the orbital contribution. Usually, we do not have to worry about orbital contribution, you can calculate just new spin only.

The equation for calculating this mu total by taking this orbital and spin contribution is this one, all, right. Now, what happens? So, the capital S, this S is number of unpaired electrons they are spin, if it is 3 unpaired electron half plus half plus half, 3 by 2. L, L that we will come for the lanthanide section it is the summation of usually m l, right.

So, for the orbital it is let us say plus 2, plus 1 0 minus 1, minus 2 will come for the lanthanide from there well discuss. Anyway, you do not have to calculate for d block element you usually do not have to calculate the L values. You can only plug this equation for the S value ok, all right.

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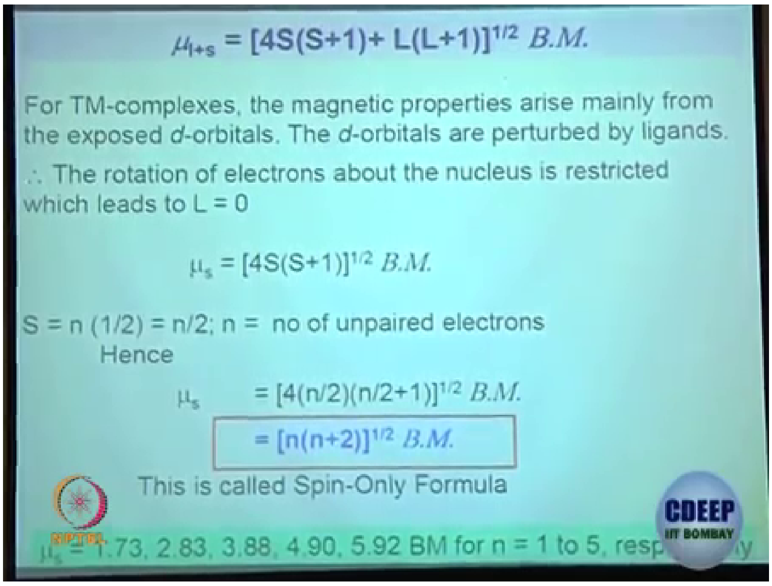

μ_{l+s} = [4S(S+1)+ L(L+1)]$^{1/2}$ *B.M.*

For TM-complexes, the magnetic properties arise mainly from the exposed *d*-orbitals. The *d*-orbitals are perturbed by ligands.

∴ The rotation of electrons about the nucleus is restricted which leads to L = 0

μ_s = [4S(S+1)]$^{1/2}$ *B.M.*

S = n (1/2) = n/2; n = no of unpaired electrons

Hence

μ_s = [4(n/2)(n/2+1)]$^{1/2}$ *B.M.*

$\boxed{= [n(n+2)]^{1/2} \text{ B.M.}}$

This is called Spin-Only Formula

μ_s = 1.73, 2.83, 3.88, 4.90, 5.92 BM for n = 1 to 5, resp y

So, we have two component once again only spin value is good enough. What you nail it down further is root of n multiplied by n plus 2, n times n plus 2 root of that; that gives you for one unpaired electron, two unpaired electrons, three unpaired electrons, 4 and 5 and so on what would be the magnetic moment value. So, by knowing how many unpaired electron is there pretty much you can be confident what will be the experimental or experimentally observed magnetic moment for pretty much a lot of cases.

Now, so that is the magnetic moment value. But often what you see is at the end of it, the experimentally observed magnetic moment value is slightly higher some time lot higher how those are coming from or where they are coming from that is due to the assumption that this component does not exist, ok. We bring them back to explain it, ok.

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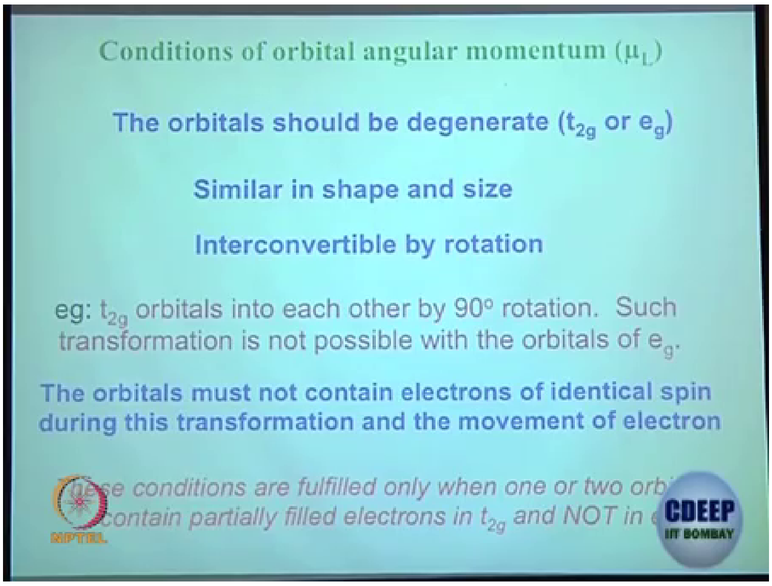

Conditions of orbital angular momentum (μ_L)

The orbitals should be degenerate (t_{2g} or e_g)

Similar in shape and size

Interconvertible by rotation

eg: t_{2g} orbitals into each other by 90° rotation. Such transformation is not possible with the orbitals of e_g.

The orbitals must not contain electrons of identical spin during this transformation and the movement of electron

These conditions are fulfilled only when one or two orb
contain partially filled electrons in t_{2g} and NOT in e

So, when you need to when the orbital angular momentum that mu L part comes in, ok. It comes in when you have degenerate orbital. We have degenerate into orbital if d orbital was not splitted then this component would have been high, if 5 d orbitals were degenerate then inter conversation would have been possible much easier or 5 of the or 5 of the orbital it can interconvert. So, electron can interconvert between 1 2 3 4 5. So, therefore, the orbital so sorry orbital angular momentum value would have been higher.

Since in octahedral field for example, or tetrahedral field it is splitted into t 2g, e g or et 2 we are going to get little less orbital angular momentum value, compared to unsplitted d orbital, right. Now, of course, inter conversion leads to some sort of new directionality xy to xz z is new, xz to yz y is new, right. So, that is the one contributing for your little bit more momentum, right. Now, just degeneracy is not good enough. Why? Because you should be able to interconvert also. For example, d x 2 y 2, ok.

This is the last warning, ok. It is a big class, if it was a small class I would not have mind too much because I know what exactly goes on, ok. Please have some respect, ok. So, what we are trying to have is T 2 g, e g, e g dx 2 y 2 and dz 2 by no way you can inter convert, therefore, in e g you from e g you cannot get any orbital angular momentum value only possibility is t 2g because the d xy, d yz, d xz are inter convertible, ok. Of course, if they are having same spin you cannot interconvert, right.

So, let us say t 2g 3, 1 1 1, all 3 of them are having same spin, you cannot interconvert fair enough. So, inter there they should be similar shape in size d xy, d yz, d xz are the same shape in size they are should, they should be interconvertible and the orbital must not contain electrons of identical spin that is the criteria for getting some orbital angular momentum. Is it clear?

So, t 2g 1 you can get orbital angular momentum because t 2g 1 that one unpaired electron can be either in d xy, d yz or d xz 3 different orientations are possible. t 2g 2 is possible, t 2g 3 is not possible, t 2g 4 once again is possible, t 2g 5 is possible, t 2g 6 is not possible, ok.

Student: (Refer Time: 24:24).

Ah?

Student: (Refer Time: 24:25).

T 2g 3, all 3 are having same spin from where to where you will interconvert. See t 2g 1 means d xy 2, d yz you can go. Interconvert means one one means they have to exchange. If there is no scope for exchanging how will you exchange, same spin t 2g 3 means 3 unpaired spin in the same direction spin multiplicity same direction they will be having. So, only so far as we see only t 2g 3 will not be able to give you.

Student: Sir.

Yeah?

Student: (Refer Time: 24:03).

That I am coming, next slide. So, that inter conversation will be having some contribution not as great as let us say t 2g to t 2g configuration. So, t 2g to t 2g I mean interchange will give you little bit more orbital angular momentum value compared to e g to t 2g conversion that is what the next slides (Refer Time: 24:31) know.

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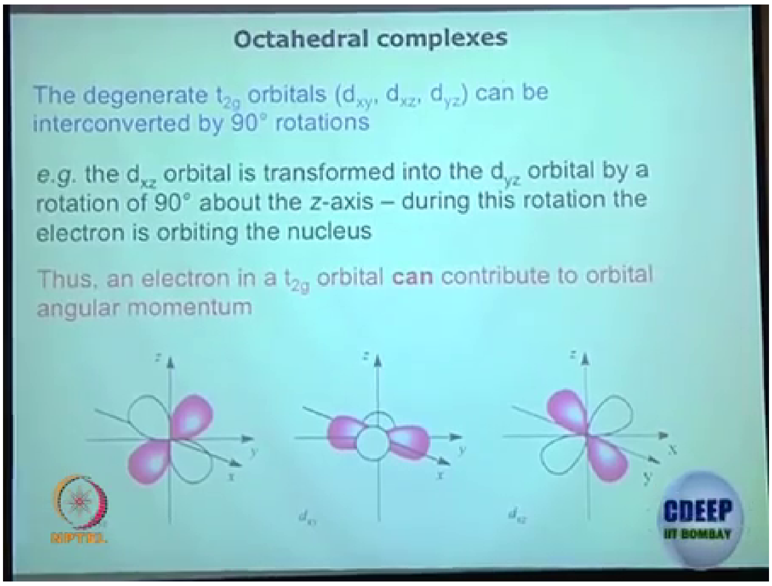

Octahedral complexes

The degenerate t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) can be interconverted by 90° rotations

e.g. the d_{xz} orbital is transformed into the d_{yz} orbital by a rotation of 90° about the *z*-axis – during this rotation the electron is orbiting the nucleus

Thus, an electron in a t_{2g} orbital **can** contribute to orbital angular momentum

So, d yz, d xy and d xz these 3 orbitals are interconvertible, no problem, ok.

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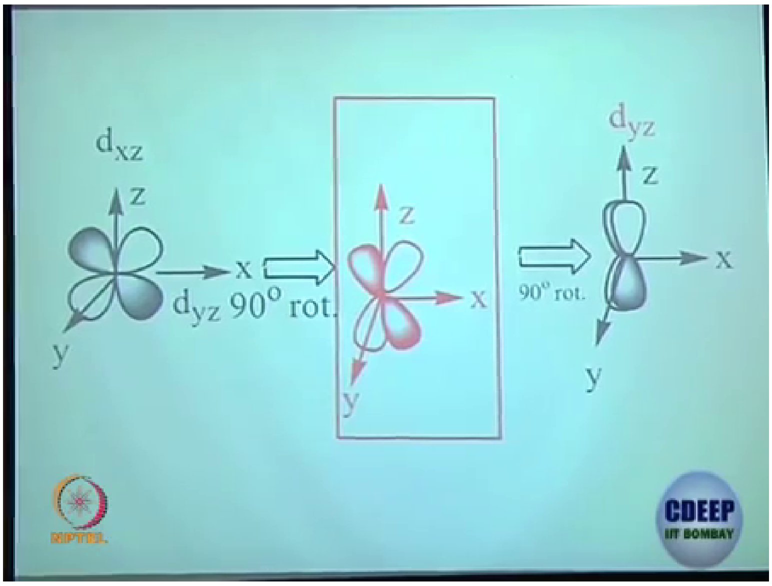

Over here that is the inter conversion is shown. So, you just, so you just rotate by 90 degree you will be able to rotate d xy. So, this plane to that plane to that or whatever these 3 different plane you can see.

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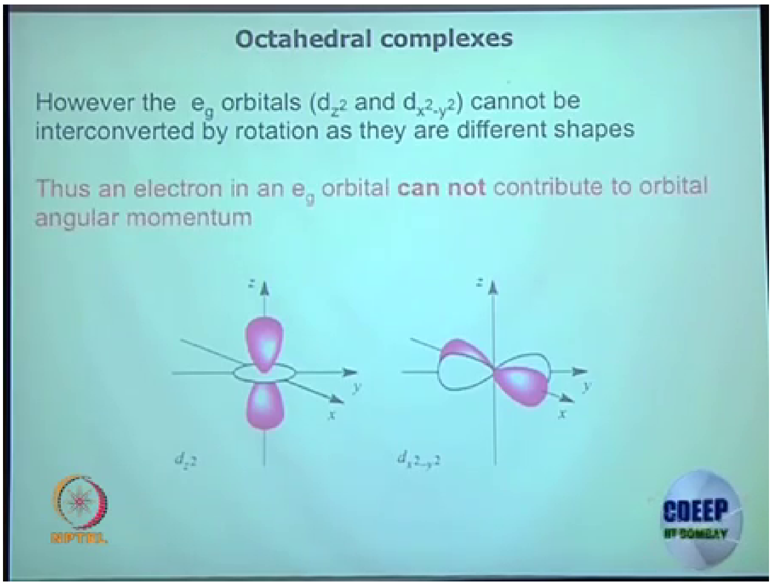

Octahedral complexes

However the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation as they are different shapes

Thus an electron in an e_g orbital **can not** contribute to orbital angular momentum

Now, as you see d z 2 and d x 2 y 2 are not interconvertible. So, from purely from e g orbital, just e g orbital itself cannot give you any orbital angular momentum value. So, you know the spin only value is only considered, ok.

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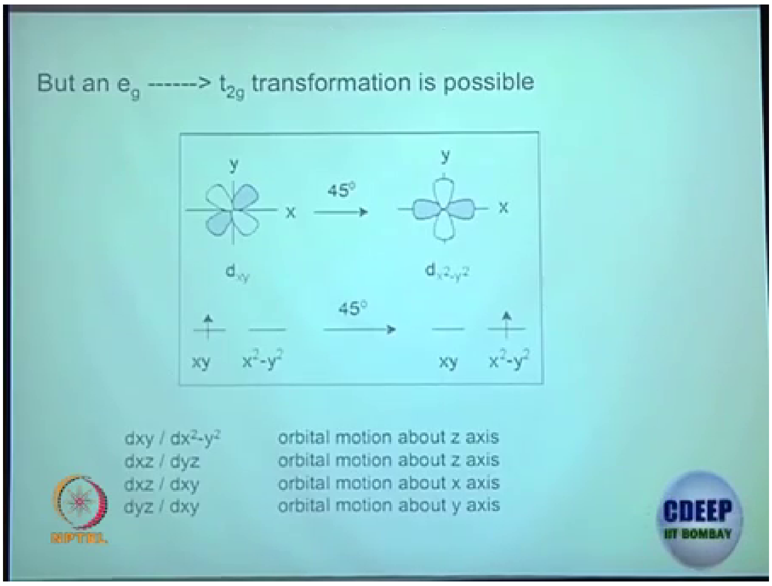

But an e_g ------> t_{2g} transformation is possible

dxy / dx^2-y^2	orbital motion about z axis
dxz / dyz	orbital motion about z axis
dxz / dxy	orbital motion about x axis
dyz / dxy	orbital motion about y axis

Now, of course, what your friend trying to say is d xy is convert can be converted to d x 2 y 2. Yes and thereby once you can convert d x 2 y 2 into d xy then you can interconvert d xy to d xz, d yz and so on So, t 2g e g mixing if you can have then you will be able to get better orbital angular momentum value, but usually for mixing those energy has to be close enough. If the gap is very high that mixing is not going to be possible, right, ok.

So, we all hopefully by now understand that it is angular momentum or these orbital angular momentum and spin momentum value are important. Usually, spin only value is good enough, but in some cases you have to talk about orbital angular momentum. Actually, that is makes it you know little bit important or interesting otherwise whatever unpaired electron is there you will just end up calculating based on your calculator, right that is not fun.

Of course, the exam questions are asked at least one two or so on orbital angular momentum, ok. When orbital angular momentum is there?.

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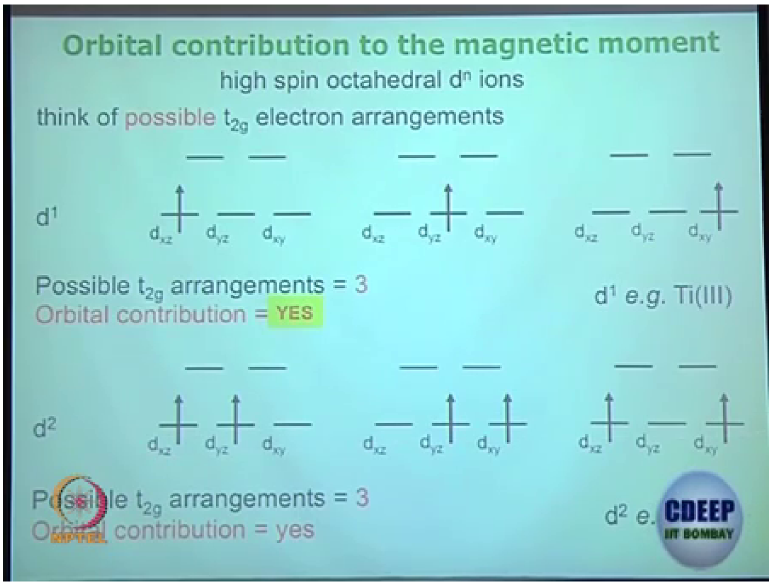

Orbital contribution to the magnetic moment

high spin octahedral d^n ions

think of possible t_{2g} electron arrangements

Possible t_{2g} arrangements = 3

Orbital contribution = YES

d^1 e.g. Ti(III)

Possible t_{2g} arrangements = 3

Orbital contribution = yes

d^2 e.

Now, so this is the same thing what I was trying to say d 1 can have these 3 different contribution for example, titanium 3 plus is having d 1 electronic configuration and therefore, orbital contribution will be there for example, d 2 vanadium 7 plus. So, how the question would be let us say a complex is given where vanadium is sorry the vanadium 3 plus, vanadium 3 plus and you are asked whether it will have any orbital angular momentum or not or in some other form it will be asked indirectly.

But mostly definitely I can assure you at least one question will be there on orbital angular momentum at least if not two, ok. So, they are there you can have two different or three different configuration orbital contribution possible. Yes, ok.

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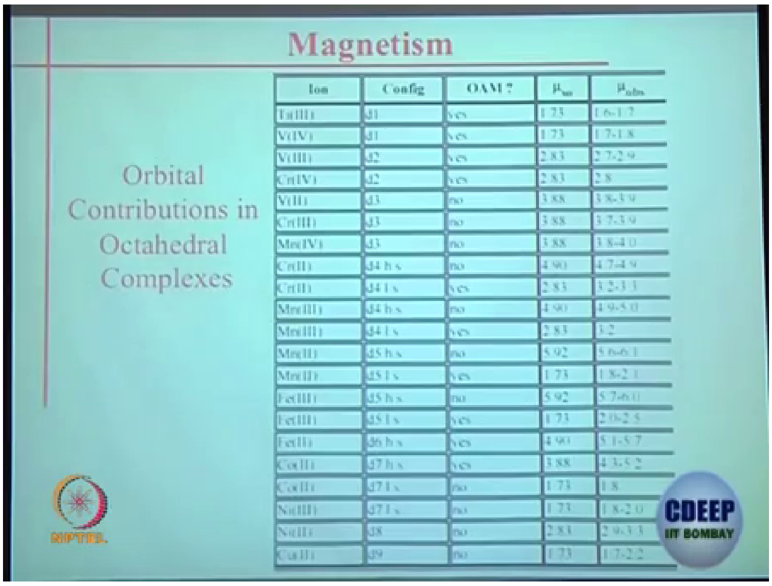

Magnetism

Orbital Contributions in Octahedral Complexes

Ion	Config	OAM ?	μ_{so}	μ_{obs}
Ti(III)	d1	yes	1.73	1.6-1.7
V(IV)	d1	yes	1.73	1.7-1.8
V(III)	d2	yes	2.83	2.7-2.9
Cr(IV)	d2	yes	2.83	2.8
V(II)	d3	no	3.88	3.8-3.9
Cr(III)	d3	no	3.88	3.7-3.9
Mn(IV)	d3	no	3.88	3.8-4.0
Cr(II)	d4 h.s.	no	4.90	4.7-4.9
Cr(II)	d4 l.s.	yes	2.83	3.2-3.3
Mn(III)	d4 h.s.	no	4.90	4.9-5.0
Mn(III)	d4 l.s.	yes	2.83	3.2
Mn(II)	d5 h.s.	no	5.92	5.6-6.1
Mn(II)	d5 l.s.	yes	1.73	1.8-2.1
Fe(III)	d5 h.s.	no	5.92	5.7-6.0
Fe(III)	d5 l.s.	yes	1.73	2.0-2.5
Fe(II)	d6 h.s.	yes	4.90	5.1-5.7
Co(II)	d7 h.s.	yes	3.88	4.3-5.2
Co(II)	d7 l.s.	no	1.73	1.8
Ni(III)	d7 l.s.	no	1.73	1.8-2.0
Ni(II)	d8	no	2.83	2.9-3.3
Cu(II)	d9	no	1.73	1.7-2.2

Now, this is something you do not have to remember, but you can justify. You can go through each of those one by one, so d 1 orbital angular momentum possible. Yes, you can perhaps not read from here that is ok. So, what we have tried to do here is given you the complex, different complex and their electronic configuration d 1, d 2, d 3, d 4 up to d 10 and then you have to write down t 2g, e g electronic configuration.