Basics in Inorganic Chemistry
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Lecture - 12
Introduction to Molecular Magnetism

Let us see Magnetism ok, magnetism if you have this is I guess chapter 4; chapter 4 right chapter 4 for your syllabus magnetism ok.

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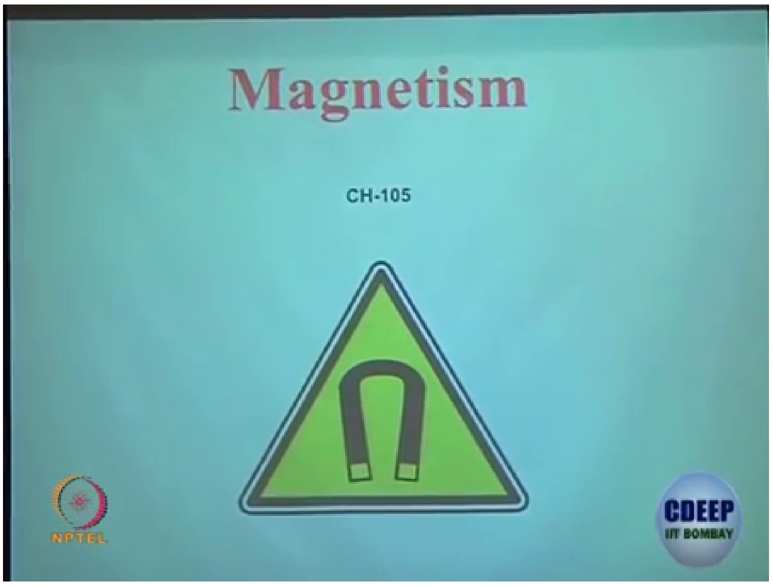

Magnetism

CH-105

We will not finish the magnetism all of it today. So, magnet you are familiar with ok.

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Magnetism

Why do we need it?

Familiar world

How does it work???

I will give you some very simple pictorial representation magnet is basically magnet is everywhere ok.

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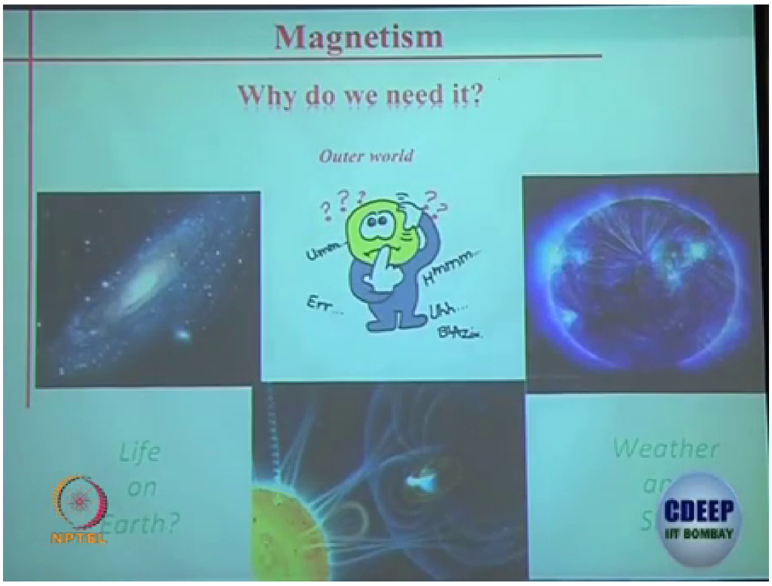

Magnetism

Why do we need it?

Outer world

Life on Earth?

Weather ar S

How it is really up to the universal. So, it is what all we see is magnet ok. What is magnet? Anything I think the simple definition is or how the magnet is created, anything that has a rotation moment or some rotational behaviour it can create some field around it. See electron, proton, neutron, every object that can rotate can create some sort of field that is what I will come into I think magnet is everywhere you can trace back to the origin of life ok.

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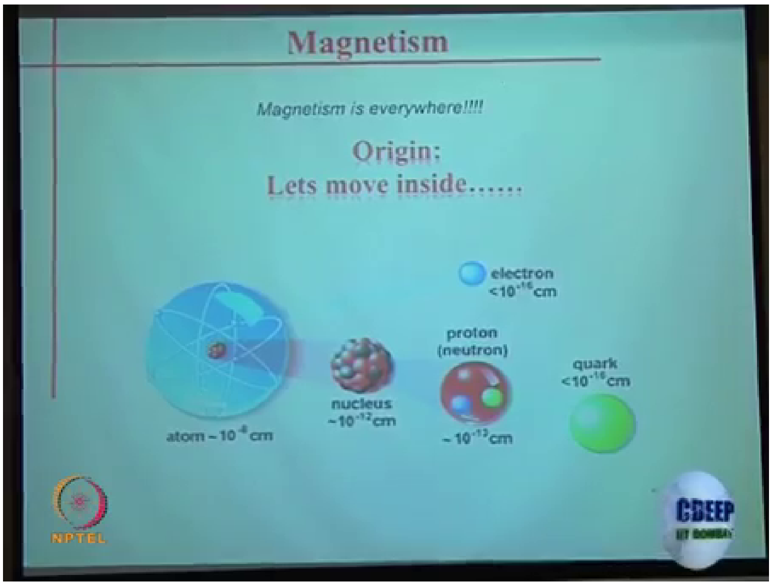

Magnetism

Magnetism is everywhere!!!!

Origin:
Lets move inside……

Now, what is next you can basically from universe to your atom level if you go all of them are having some sort of spinning behaviour ok, 2 types of spinnings are possible one is as you know one is rotating around it is own axis and another is orbital rotating that is how the sun rotates that is how the earth rotates that is how the moon rotates you.

Student: (Refer Time: 02:13).

Sorry. So, it rotates around it is own axis that is the spinning spin component it rotates around the orbital that is the orbital component and the total these are 2 vectors basically you do the vector addition you get done net magnetic moment ok. We will come to that, that is what is this chapter about, but to speak you very clearly the unpaired electrons are the one which causes most of the magnetic I mean which induces the magnetic properties into the molecule.

So, not only the bigger thing like earth, sun, moon, we see the magnetic behaviour due to their you know spinning behaviour or rotating behaviour the as small as the molecule even you can go further in as I think we are trying to discuss the complex.

Complex means metal complex, metal ligand is there, metal d orbitals are there, those d orbital electrons are the one which are essentially giving us the magnetic behaviour in different application what we are using nowadays, different whatever electronic devices even for our you know this ATM card to wherever you see that anything is has to do with the unpaired electron those are coming from the metal complexes ok.

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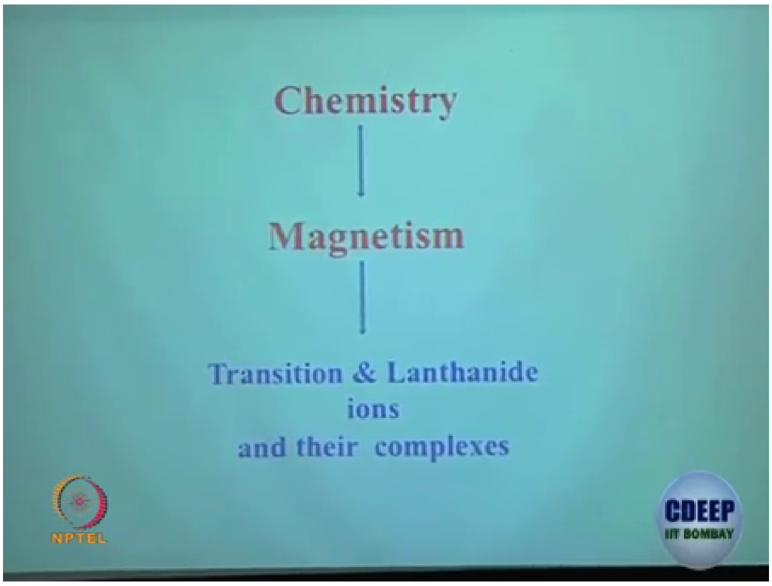

Chemistry

Magnetism

Transition & Lanthanide
ions
and their complexes

Let us let me get into. So, we will discuss the magnetism of the metal complexes and then get into the lanthanide actinides or lanthanide specifically and then stop.

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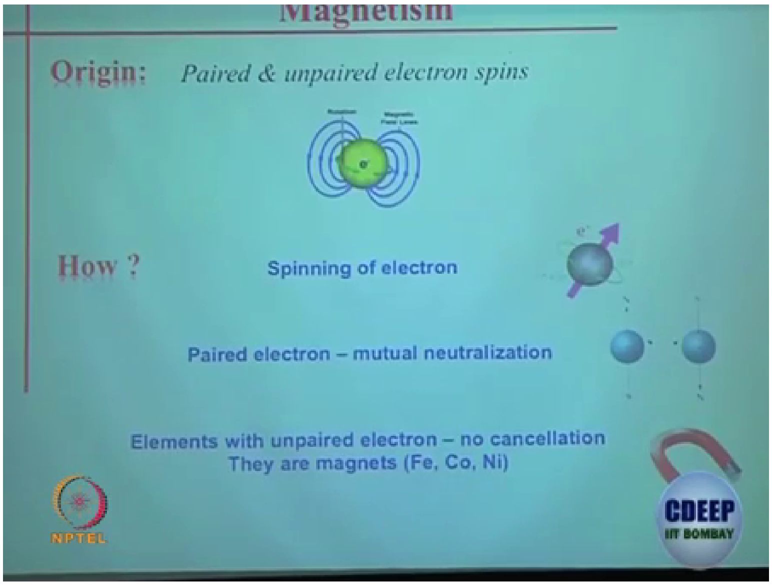

Magnetism

Origin: *Paired & unpaired electron spins*

How ? Spinning of electron

Paired electron – mutual neutralization

Elements with unpaired electron – no cancellation
They are magnets (Fe, Co, Ni)

So, I think we I was discussing moment ago paired and unpaired electron pairs, unpaired electron pairs are the one which will be giving these magnetic behaviour, because paired electrons will be cancelling out each other. Spinning of electron as you can see spinning of electron and this is the pairing of electron. So, spinning this un what is that called I mean unpaired electron will be giving you the magnetic behaviour, paired electron will cancel each other out.

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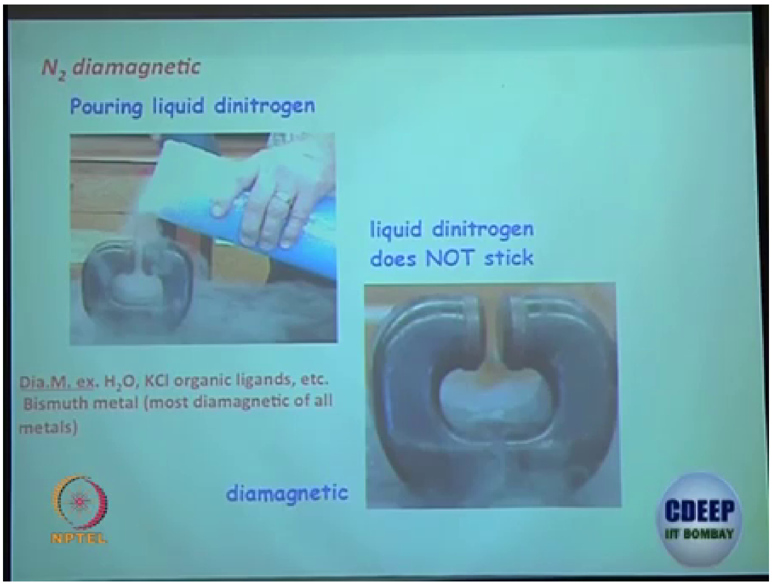

N_2 diamagnetic

Pouring liquid dinitrogen

liquid dinitrogen does NOT stick

Dia.M. ex. H_2O, KCl organic ligands, etc. Bismuth metal (most diamagnetic of all metals)

diamagnetic

Now, can you see this behavior, can you just from simple experiment, can you determine the magnetic behavior of any compound such as oxygen, nitrogen, oxygen is a gas, nitrogen is a gas, are they paramagnetic or diamagnetic?

Student: (Refer Time: 04:58).

Sorry.

Student: Diamagnetic.

Yes, how will you do this experiment, simply what do you usually do you pull it down, if you take even nitrogen gas liquid nitrogen you have heard of liquid nitrogen big tank goes on and you know funny lot of funny experiments can be done. If you liquefy the nitrogen gas it becomes liquid nitrogen now that liquid nitrogen we want to see whether that nitrogen is going to be diamagnetic or paramagnetic.

Simply if you take a magnet this is a magnet it is a big magnet and you pour liquid nitrogen through it, you will see that I mean magnet opposite direction should attract each other, you will see there is no attraction. So, this is what a simple experiment can tell you that liquid nitrogen is going to be diamagnetic in nature, same thing you do with oxygen as you are correctly saying that it is paramagnetic.

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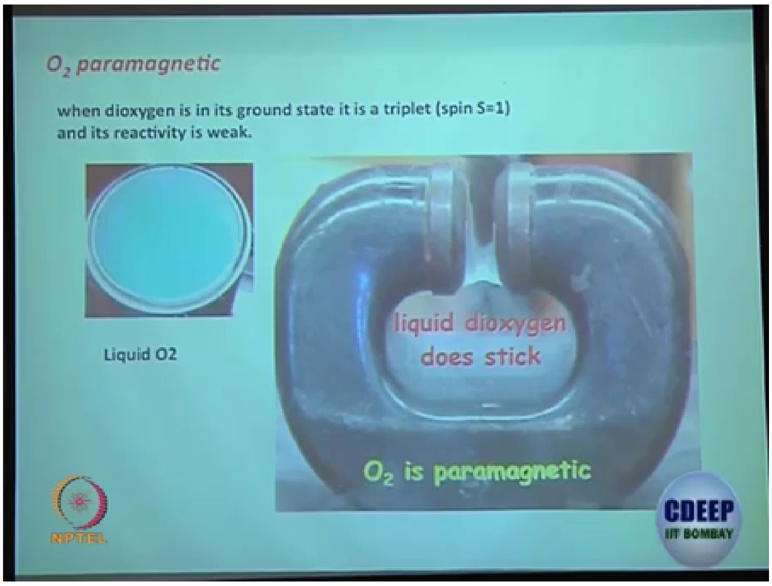

O_2 paramagnetic

when dioxygen is in its ground state it is a triplet (spin S=1) and its reactivity is weak.

You can do the experiment you see it is sticking to the magnet that is the simplest one of the experiment you can do which can show you what the molecule is made off. Oxygen nitrogen it is amazing actually if you think very simply, but do not try to liquefy oxygen it can be bad do not do this it is it could be a lot of bad things can happen afterwards if you do not know how to handle it right.

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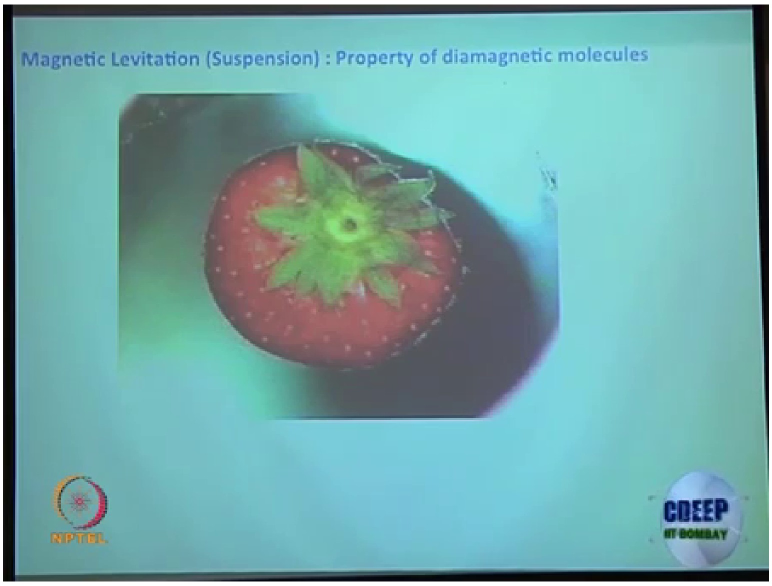

Magnetic Levitation (Suspension) : Property of diamagnetic molecules

Of course there are a lot of other things you see magnetic levitation like suspension you see the magic P C Sarkar or whoever big magician you know of you see they are showing some time you see this movie and one of them Hollywood movie what was that?

Student: (Refer Time: 06:57).

Prestige I like that see the lot of sometime bodies floating right you know that of course, if you look at the movie if you go to the movie theatre or in of course, you can watch today tonight if you want there is some science behind it. So, you can make some object as big as like someone like us a human being float in here sometime that also of course, can give you the thought sometime in the ancient history, Indian history we see that people are walking on the water.

I do not I mean I do not know whether other supernatural things are there or some extra thing are there, but something like this you can explain perhaps scientifically as well that there is opportunity for science to contribute I do not know you know I do not know want to caught into some sort of controversy here. So, something can be floated you can float something like I think movie is not working even a you know what is this fruit?

Student: Strawberry.

Strawberry I would I love it sure strawberry can be floated right well of course, this is interesting a magnet right.

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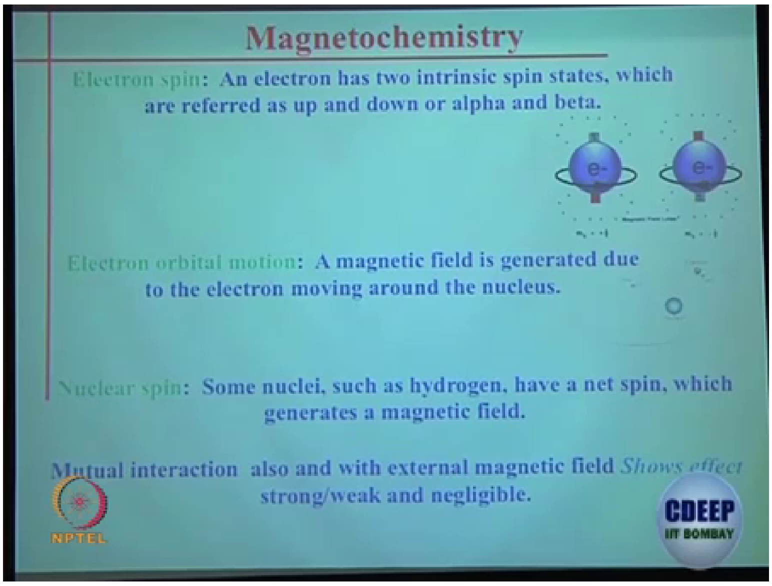

Magnetochemistry

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.

Otherwise I think magneto chemistry if you want to discuss you have to understand electron spin, see this is little bit physics in there I will try to skip it because you have studied it already it is all will show you the equations. So, an electron has two intrinsic spin state which are preferred, referred as up and down or alpha and beta spin alpha and beta spin.

Electron orbital motion is nothing, but what you see in the universe you know center is nucleus and electron is spinning. Now nuclear spin of course, some nucleus are also having spin you just read it becomes little bit boring to teach because you know it ok.

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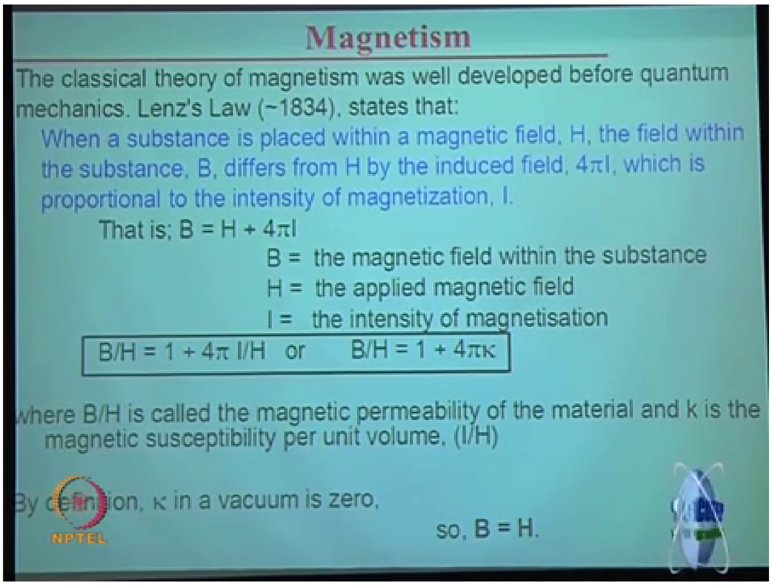

Magnetism

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, $B = H$.

Now, magnetism this is an equation, what we are trying to say we have a magnetic field you put an object into the magnetic field. A molecule d orbital contenting d orbital or any non magnetic molecule whatever net effect it could be non magnetic any molecule you can put any object you put this one.

The net magnetic behavior or magnetism you are going to get is the magnetic field plus whatever it can induce on it the magnetic field can induce some magnetic behavior inside it or in it. So, this is what the equation is the magnetic field what gets generated or total magnetic field you get is equal to the applied magnetic field H and the intensity of magnetization how much magnetization it is going to have or how much high hypnotize or magnetized it is going to get that is the total magnetic field within the substance.

What is the field? Not only the field you create what is the material made of that makes a difference the type of material you have that makes a difference ok, all of you are in IIT they are, all of you are attending the same class, some of you will be millionaire, trillionaire and you will give me some money I will be very happy right.

Donate profusely when you are donating [FL] donate [FL] give back to IIT really I mean we need money lot of money all of lot of you will be having and see your start up companies some of them will be bought out by some established company you will be fill the region you have no idea what to do afterwards just think about me ok.

Student: [laughter].

For a moment wherever I you are just think about me when you make money otherwise do not think really how we cannot help so.

Student: (Refer Time: 11:35).

All right I think this is simple physics you know what to do with it you have studied it before in 12 standard you study it again ok. Now what are the things we are interested in for this class, we are interested in few parameters like you know B by H and this kappa value right.

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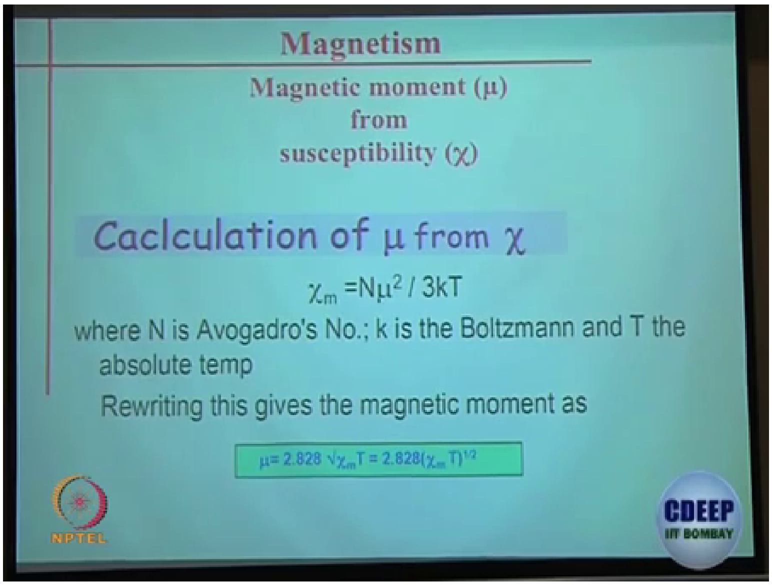

Magnetism

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

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

So, that is I will go to the another equation. So, the susceptibility and the magnetic moment ok, the susceptibility is related to magnetic moment and these are the 2 terms we are interested in remember we will be discussing again in the next class. So, you study little bit if you have any queries I can come back and discuss again.

Now, susceptibility molar susceptibility you how do you get molar susceptibility divided by total mole right or Avogadro number. Now from there on you get the molar susceptibility and mu these two are related like that and you get a equation to calculate magnetic moment how it equate with the magnetic susceptibility.

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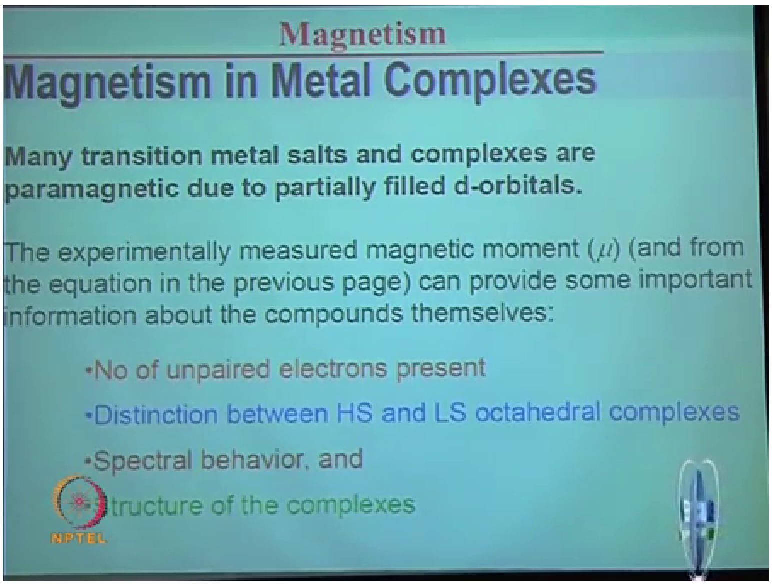

Magnetism

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

Now, all we need to care sorry we are coming back again all we need to care for this course we are mainly trying to see the metal complexes with unpaired electrons d electrons right. So, number of unpaired electrons is going to matter to us because the unpaired electrons are the one which are going to give you the magnetic moment ok.

Of course, we need to worry about high spin and low spin because that will also determine indirectly what is going to be the number of unpaired electron and from there we can of course, try to see the spectral behaviour and structure of the complex. Now, many transition metals salts and complexes are paramagnetic of course, due to their partially filled d orbitals, the moment everything gets filled you do not get much of a magnetic moment.

The experimentally major magnetic moment and of course, the equation I was talking can provide some important information about the compound themselves. So, what we do? We have a compound we try to measure the magnetic moment and we have an equation from where we can calculate the magnetic moment. Now we try to see the difference between the 2 and try to explain what is the region if experimental values are different ok.

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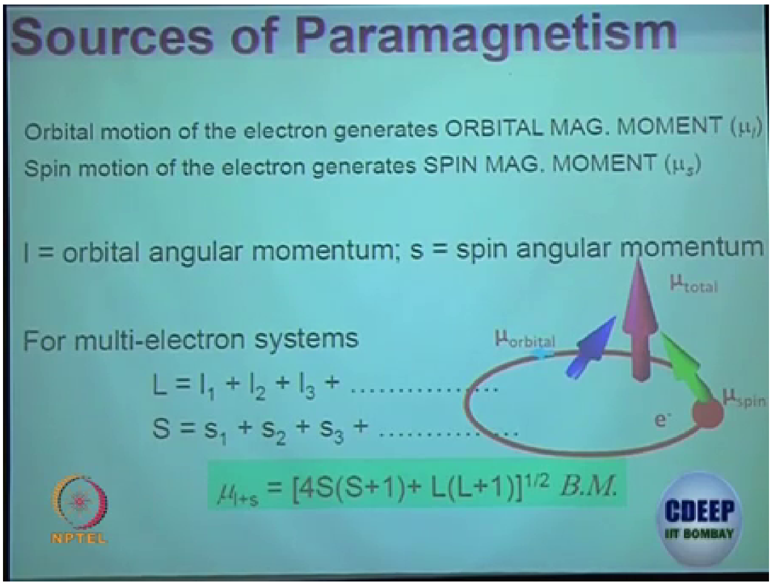

Sources of Paramagnetism

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

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

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

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

Let me get into it will be little bit clearer. So, as I was saying the source of magnetism in the molecule is going to be your unpaired electron that is all. Now the unpaired electron can have 2 shots of or 2 sources of creating magnetism, one is spinning around it is own axis just and another is while spinning around it is own axis it is also rotating on the along the orbital right.

So, 2 components the ml or l component angular sorry orbital component for which it is rotating around the orbital and the other component is the spin spinning around it is own axis or along it is own axis 2 components, but the d orbitals are the one which are getting affected mostly by the ligand metal d orbitals are getting affected by the ligands.

So, the ligand will not allow too much to spin around it is orbital. So, the l component mu orbital component will be usually minimized let us say 0, leave the metal electrons will only be able to give you spin only values spinning they are spinning they are not able to freely rotate around it is orbital because ligand electrons are overlapping and ligand electrons are restricting them.

So, essentially what you need to understand is the magnetic or mu total is ending up to be what spin only value, but in reality you have to have the spin only value and the mu orbital value coupled together or you it is a vector addition you can do and that is what the mu total is going to be, in reality it is going to be the mu spin only value clear. 2 components are there one component will be marginalized of course, I am not saying it is 0 it has we will come back that is what we will be seeing the orbital contribution and there is usually 1 or 2 questions are asked from orbital contribution which is little bit exciting, but usually speaking 2 components are there one is nullified, another is left that is the spin only ok.

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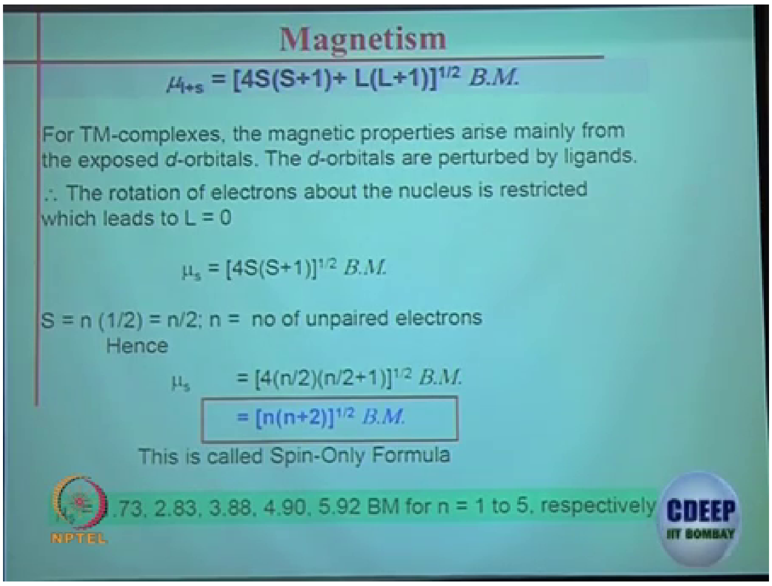

Magnetism

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

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

$\therefore$ The rotation of electrons about the nucleus is restricted which leads to $L = 0$

$$\mu_S = [4S(S+1)]^{1/2} \text{ B.M.}$$

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

Hence

$$\mu_S = [4(n/2)(n/2+1)]^{1/2} \text{ B.M.}$$

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

This is called Spin-Only Formula

.73, 2.83, 3.88, 4.90, 5.92 BM for n = 1 to 5, respectively

Now, what is the equation over here? This is the mu L plus S both orbital and spin this is the equation this is the correct equation, this is the incorrect or partially true equation, but this is the one which we do care. What is the correct equation? It has total number of unpaired electron and those L values you have to know all of them this is the theoretically calculated value ok

Now, in reality this is the spin only formula where you get rid of the L value it is 1 root over 1 by root over or sorry root over this spin component and L component right, but if you get rid off that component it becomes 4 S into S plus 1 root of that right if you get rid off that component orbital component.

Now, S is nothing, but number of unpaired electron you are having ok. So, S equals total S equals number of unpaired electron divide by 2 or you can convert this equation by putting the number of unpaired electron it becomes n into n plus 2 n times n plus 2 root of that simple that is what you need to remember, I think you have studied it before n multiplied by n plus 2 the root of that ok.

So, if you have 1 unpaired electron you know 1 multiply by 1 plus 2 root of 3 1.73, 2 unpaired electron 2 plus 2 multiply by 2 root of 8 2.83. So, one it is a there is a easy way to remember it 1 1.73, 2 2.83. So, 1 unpaired electron 1 plus 0.73, 2 unpaired electron 2 plus 0.83, 3 unpaired electron 3 plus 0.8, 4 unpaired electron 4 plus 0.9 I mean 0.7. Let us say 1 1.7, 2.7, 3.7, 4.7 and 5.7 it is close anyway that is how we you do not have to every time do use your calculator ok.

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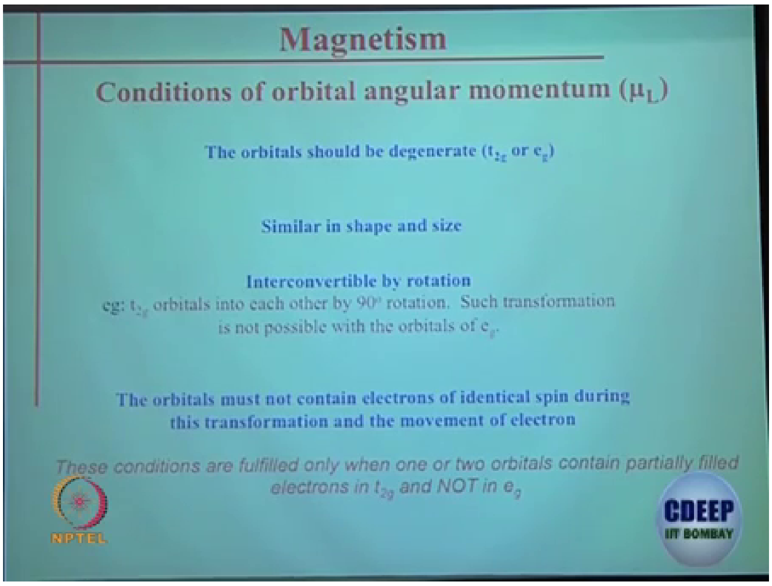

Magnetism

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 orbitals contain partially filled electrons in t_{2g} and NOT in e_g

Now, this is the spin only formula, now we need to really get to see now whether the spin only formula is valid always, what we get experimentally when it delegates, how it delegates that is what we are going to discuss these are for the purist ok. Now, we will we will discuss when we are going to get something light called orbital contribution, what is orbital contribution? Orbital contribution is nothing, but orbital contribution right. So, what is it?

Student: Orbital contribution.

Orbital contribution so, in addition to spin only values if there is some rotation around the orbit specifically it comes when you have again orbitals which are unsymmetrically filled like t 2 g 4. So, there is some sort of transition from one orbital to other, when you can write down multiple electronic configuration t 2 g 4 it could be d xy 2 d yz 1 d xz 1 or other way around also you can among the 3 degenerate orbitals you can write down differently right.

So, this is when the orbital contribution comes because since the electrons can be you know delocalized or can be placed in different orbital and thereby you have the possibility of promoting some of the orbital you know some sort of movement or some sort of magnetic moment can be generated due to these you can say that transition due to this; due to this mobilization of electron from one orbital to another d xy to d yz to d xz, but can you do that is what the question.

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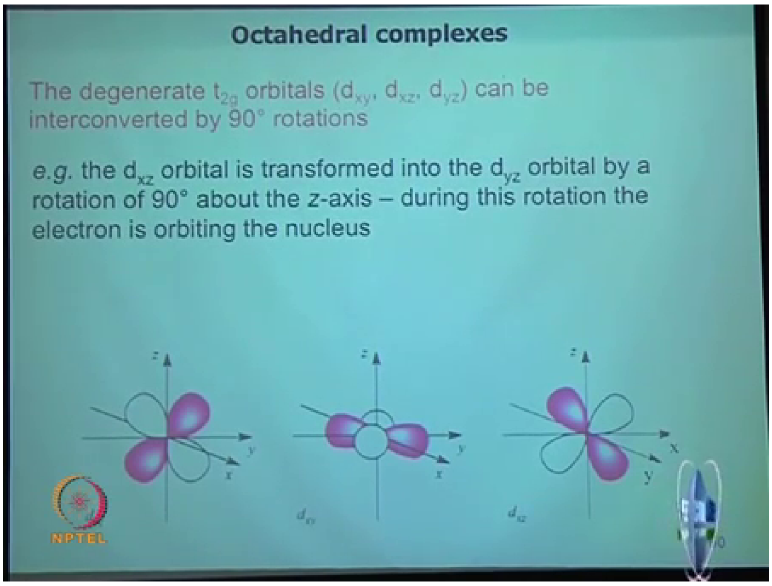

Octahedral complexes

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

So, that is what we want to see can we interconvert d xy into d yz or d x 2 y 2 into d yz that is. So, the orbital contribution is nothing, but spin only value plus something extra you get, usually speaking spin only value should be good enough and our calculated number of unpaired electron should give us the exact value the experiment is going to give us, often what we see that experimental values are little bit more than number of unpaired electron calculation.

How do you calculate number of unpaired electron? That is by your crystal filled theory how many unpaired electrons are there t 2 g easy calculation you do. So, number of unpaired electron calculation should give you a very close idea what is going to be your magnetic moment that is your theoretical calculation.

Correct theoretical calculation should include the L plus S orbital moment also, but orbital moment calculation is or that much value we do not get the value what experimentally we get is usually close to the spin only value, but on top of that spin only value itself is not going to be sufficient some are very little amount of orbital momentum value comes when it comes, this is the scenario we are going to discuss. So, I will just briefly I think little bit confusing maybe I have made it.

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So, there is always L plus S contribution, but I am trying to say you just minimize it to S, but in reality S plus let us say delta L very little contribution from L when this comes usually you see your experimental data and theoretically predicted data are same some cases you have to worry about the orbital angular momentum.

When you have to worry about orbital angular momentum, when you can convert one orbital to another thereby you have the possibility of distributing the electron in different different ways then only you can do that. Now the degenerate t 2 g orbital d xy, d xz, d yz can be interconverted as it shown in here you just rotate little bit you can interconvert right. Thus an electron in a t 2 g orbital can contribute to orbital angular momentum.

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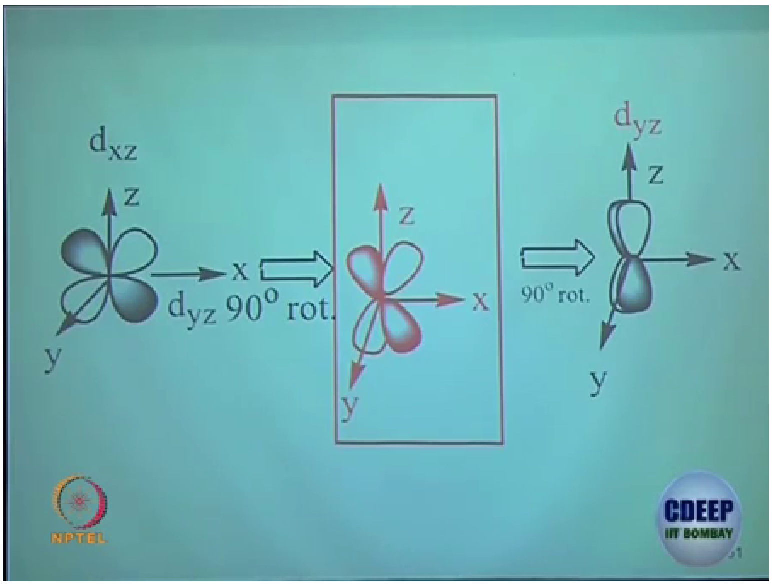

But what happened to e g. So, this is the transition from d xz to d zx to d yz you just rotate the orbital it is a plane d xy plane let us say you just rotate 90 degree you get another one if it is d xz you get initial and then finally, you get d yz right.

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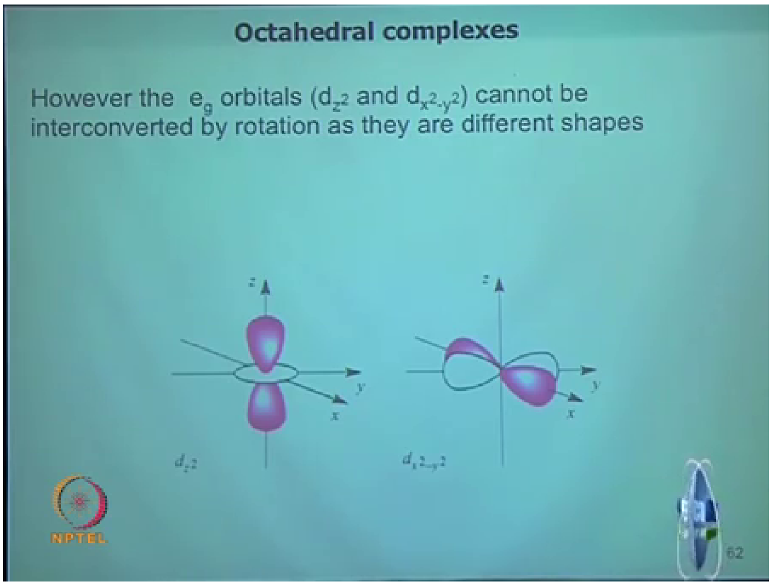

Octahedral complexes

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

You should be able to do that you just take it take a piece of paper and rotate how much angle you are rotating you should be able to do. Now, if you look at e g orbital, e g orbital you have d z square and d x 2 y 2 any amount of rotation is it going to give you the inter conversion no. So, e g orbital cannot give you the you know the cannot contribute for your orbital contribution right. Now, e g orbital cannot contribute to orbital angular momentum right.

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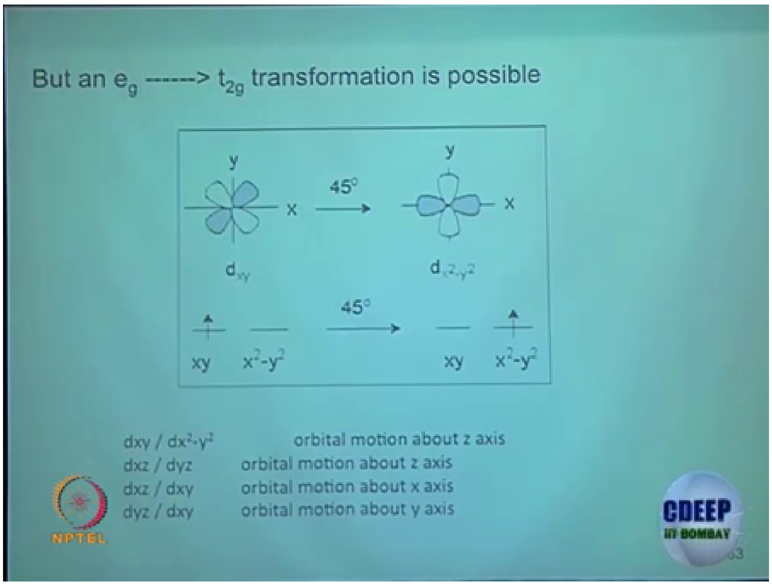

But an e_g ------> t_{2g} transformation is possible

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

So, but there is a way to convert the e g into t 2 g, how it is d x 2 y 2 or d xy can be converted to d x 2 y 2 and vice versa right. So, there is some way to do that and then you know that d d once you get d xy d xy can be converted into d yz d xz. So, these are kind of inter convertible. So, what is not inter convertible orbital wise? So, dy d dz square to anything else you cannot do, but 4 of them can rest 4 of them can be inter converted.

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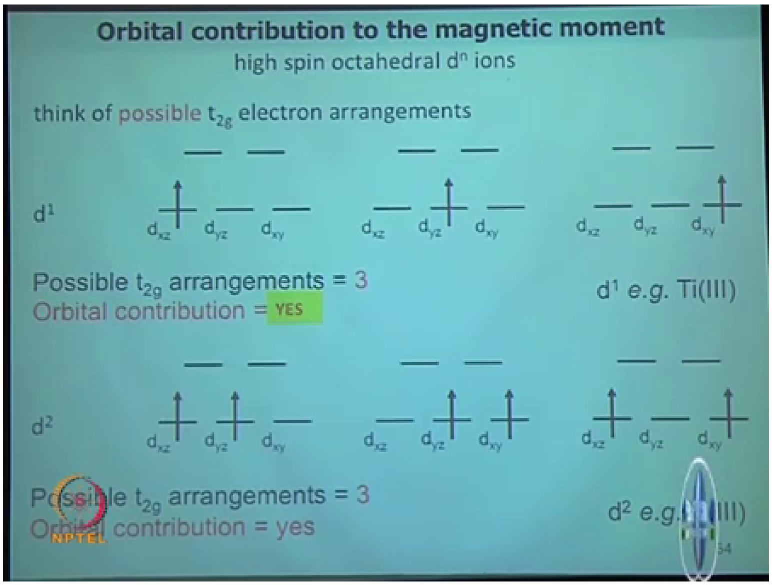


Orbital contribution to the magnetic moment

high spin octahedral d^n ions

think of possible t_{2g} electron arrangements

d^1

Possible t_{2g} arrangements = 3

Orbital contribution = YES

d^1 *e.g.* Ti(III)

d^2

Possible t_{2g} arrangements = 3

Orbital contribution = yes

d^2 *e.g.* [illegible](III)

Now, orbital contribution to the magnetic moment, once again magnetic moment is spin plus orbital contribution should be there orbital contribution is usually 0 orbital contribution can come when it is something like this. T 2 g electron arrangement right think of possibility t 2 g electron arrangement it can be d 1, d 1 can be organized as it is shown d xz d yz and d xy.

Possibility t 2 g arrangement is 3 3 different ways you can put the electrons they are by orbital contribution is yes d 1 in titanium 3 plus. So, if you calculate the angular total magnetic moment for these 1 electron should give you what 1.73 it will be a little bit more than that, let us say experimentally found value is 1.83 instead of 1.73 why it is that because it is coming from here.

Student: (Refer Time: 28:07)

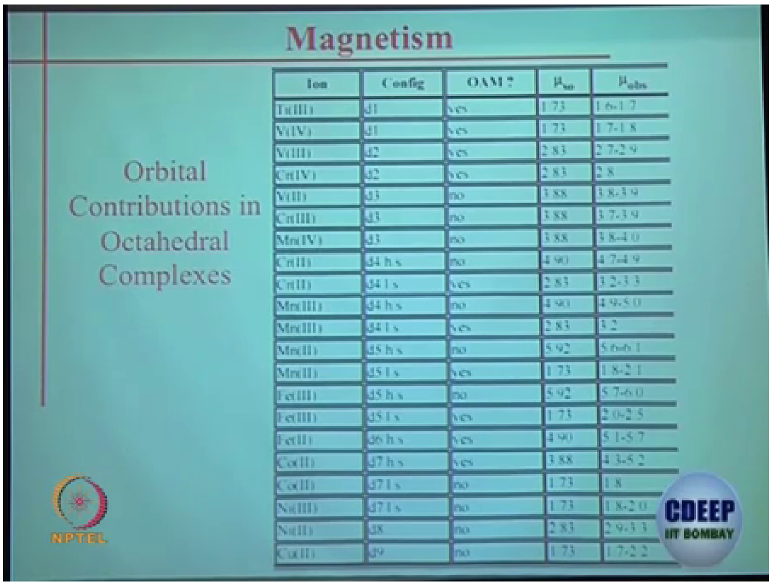
Because see if it is fixed on an orbital if it is fixed in this orbital maybe you are of course, your ligand electrons and this ligand orbital overlap with the d orbitals will be I mean restricting the rotation.

Since if there is multiple orientation possible then that can cause say anything that is allowed to rotate allowed to spin allowed to rotate will give you the some magnetic moment value, you are able to rotate among these orbitals the orbitals that should allow you some sort of magnetic moment value ok. I think I should give a better explanation I will have to look at that, but that is I think the moment you are freezing something you are not going to get it.

If d orbital if this d orbital is going to overlap with the ligand d orbital, then complete overlap means you are going to restrict the orbital motion. The moment you are giving it is multiple possibilities then you are allowing some sort to rotate around the orbital and thereby some contribution is coming, you are not allowing a free rotation there by the component will not be huge, but since it can interconvert between or among all these orbitals it gives you some possibility to give some contribution for the magnetic moment.

I think that make some sense if it is not 100 percent clear I will try to look at more I will come back from the magnetism in the next class as well. Now, in the d 2 orbital as you see 3 again once again 3 different ways the electron can be distributed and therefore, this degrees of freedom as you can see or as you can tell degrees of freedom should give some sort of you know magnetic moment value and that is where you can get the orbital contribution orbital contribution. So, the experimental value once again will be little bit more than what we see for the 2 unpaired electron ok.

(Refer Slide Time 30:42)



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

So, the spin only plus some value should be there I think it is not readable from there, but it should be in the slide. So, orbital angular momentum that orbital motion we are able to see in these cases ok, look at it I will stop it in here from here on I will discuss in the next class.