Concepts of Chemistry for Engineering
Professor Debabrata Maiti
Indian Institute of Technology, Bombay
Lecture – 34
Introduction to Molecular Magnetism

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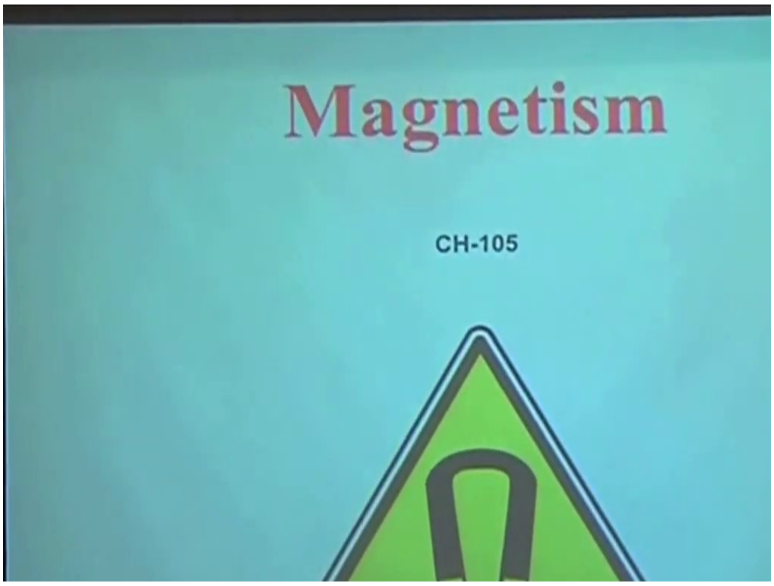

Magnetism

CH-105

Let us see magnetism. Magnetism, if you have, this is I guess chapter four, chapter four, chapter four for your syllabus magnetism. We will not finish the magnetism all of it today.

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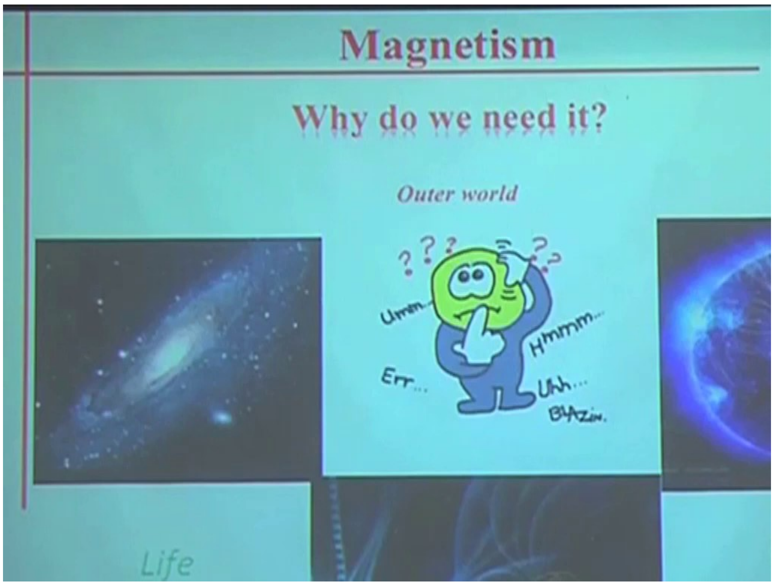
Magnetism

Why do we need it?

Familiar world



Magnetism

Why do we need it?

Outer world

So, magnet you are familiar with, I will give you some very simple, very simple pictorial representation. Magnet is basically, magnet is everywhere. How it is, it is really up to the universe also, it is what all we see is magnet. 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 say 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.

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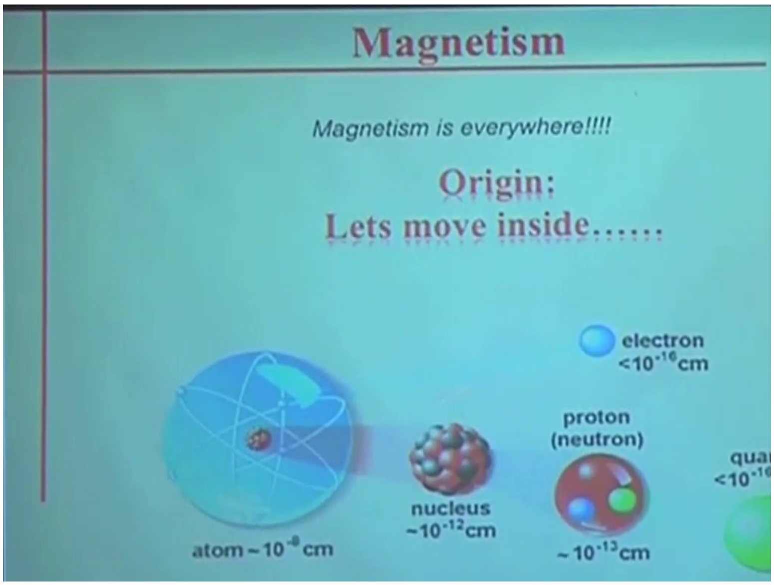

Magnetism

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. Two types of spinnings are possible. One is as you know, one is rotating around its own axis. And another is orbital, rotating, rotating, that is how the sun rotates, that is how the Earth rotates, that is how the moon rotates, you sorry. So, it rotates around its own axis that is the spinning, spin component, it rotates around the orbital that is the orbital component. And the total, these are two vectors, basically, you do the vector addition, you get that net magnetic moment.

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 (prop), 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 spinning behaviour or rotating behaviour the, and small as the molecule even you can go further in.

And 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 this ATM card to wherever you see that anything is has to do with the unpaired electrons, those are coming from the metal complexes.

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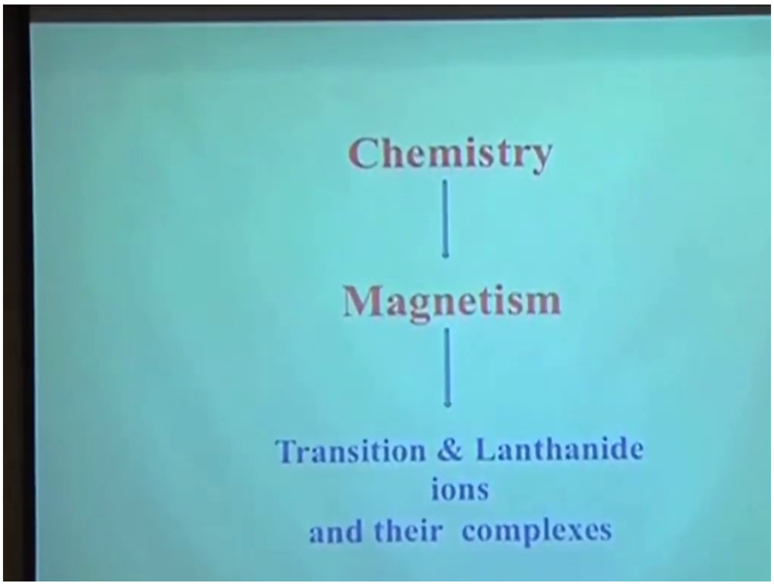
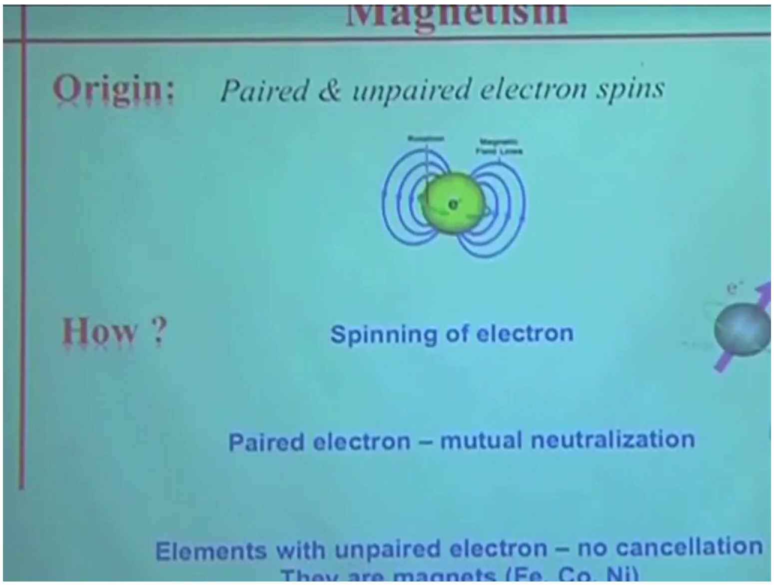


Chemistry

Magnetism

Transition & Lanthanide
ions
and their complexes



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)

Okay, let us, let me get into so we will discuss the magnetism of, of, of the metal complexes and then get into the lanthanide actinides or lanthanide specifically and then stop. So, I think we, I was discussing a moment ago, paired and unpaired electron pairs, unpaired electron pairs are the one which will be giving this magnetic behaviour because paired electrons will be cancelling out each other.

Spinning off electron as you can see spinning off 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 where paired electron will cancel each other out.

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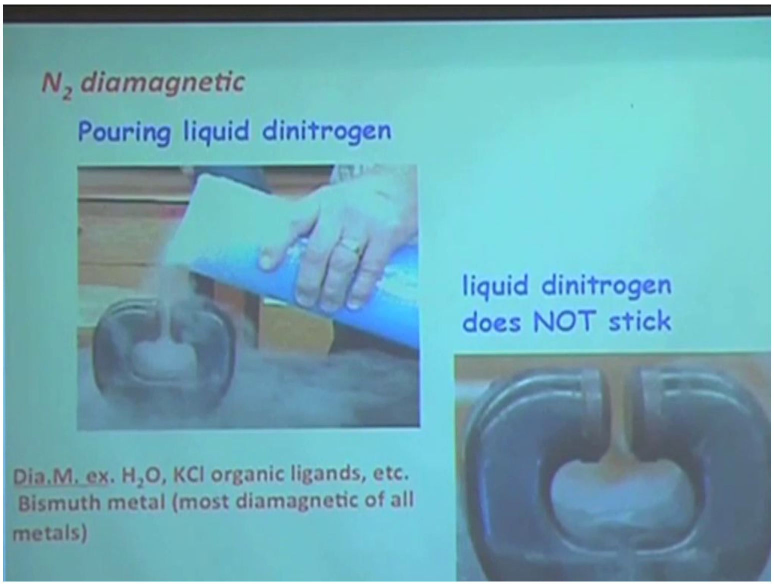

N_2 diamagnetic

Pouring liquid dinitrogen

liquid dinitrogen does NOT stick

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

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

Students: Diamagnetic.

Lecturer: Yes, how will you do these experiments? Simply, what you usually do, you pull it down, if you take even nitrogen gas, liquid nitrogen you have heard of, liquid nitrogen big tank goes down and funny, lot of funny experiments can be done. If you liquify 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.

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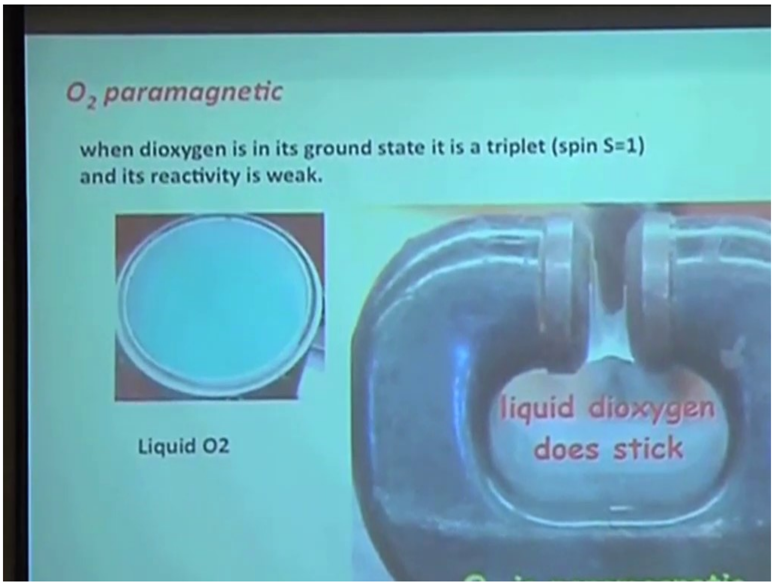

O_2 paramagnetic

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

Liquid O2

liquid dioxygen does stick

Same thing you do with oxygen, as you are correctly saying that it is paramagnetic, you can do the experiment you see it is sticking to the magnet, that is the simplest to all of the experiment you can do which can show you what the molecule is made of, oxygen, nitrogen it is amazing actually, if you think very simply. But do not try to liquify oxygen it can, it can be bad, do not do it, it could be a lot of bad things can happen afterwards if you do not know how to handle it.

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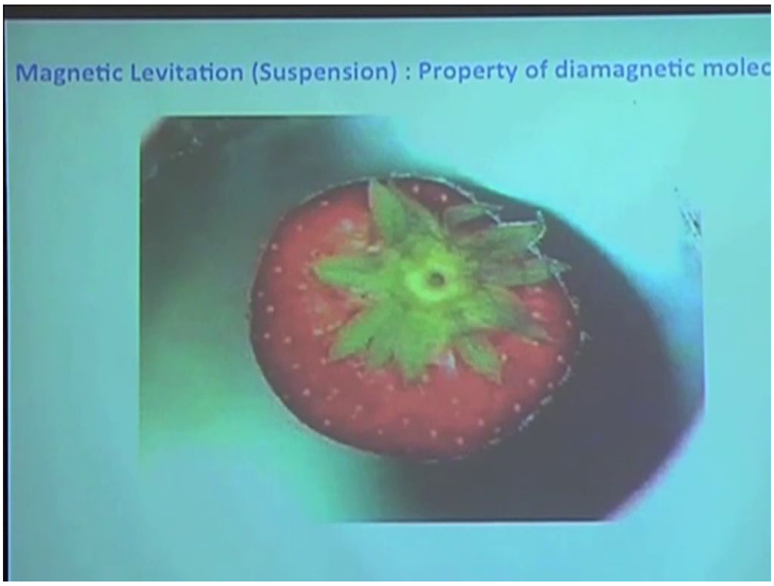

Magnetic Levitation (Suspension) : Property of diamagnetic molec

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

Students: (())(6:55)

Lecturer: Prestige, I like that. Lot of sometime body is floating, 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, some science behind it. So, you can make some object as, as big as like someone like us, a human being float in air.

Sometimes 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 things 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; I do not 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 what is this fruit?

Students: Strawberry.

Lecturer: Strawberry, yeah, I love it. So, strawberry can be floated. Well, of course, this is interesting, a magnet.

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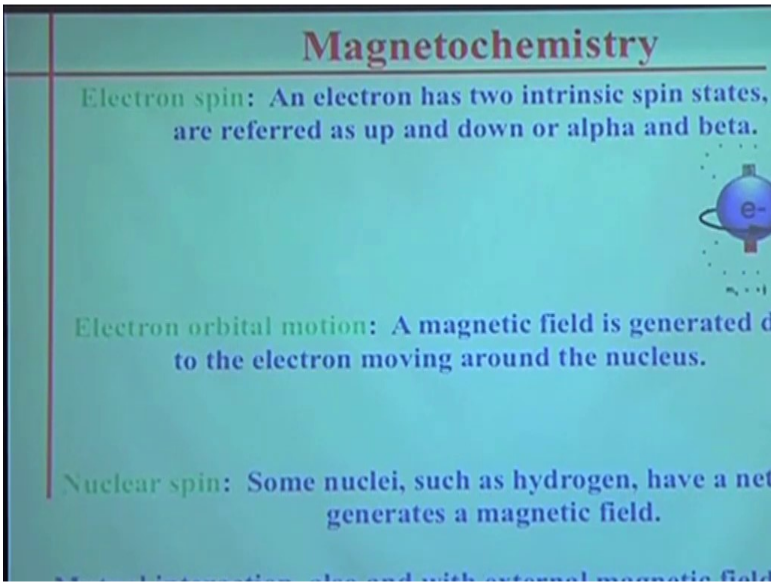

Magnetochemistry

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

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

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

Otherwise, I think Magnetochemistry if you are 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 we will show you the equations. So, an electron has two intrinsic spin states 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 that universe, centre is nucleus and electron is spinning. Now, nuclear spin of course, some nucleus are also having spin you just read, it becomes a little bit boring to teach because you know it.

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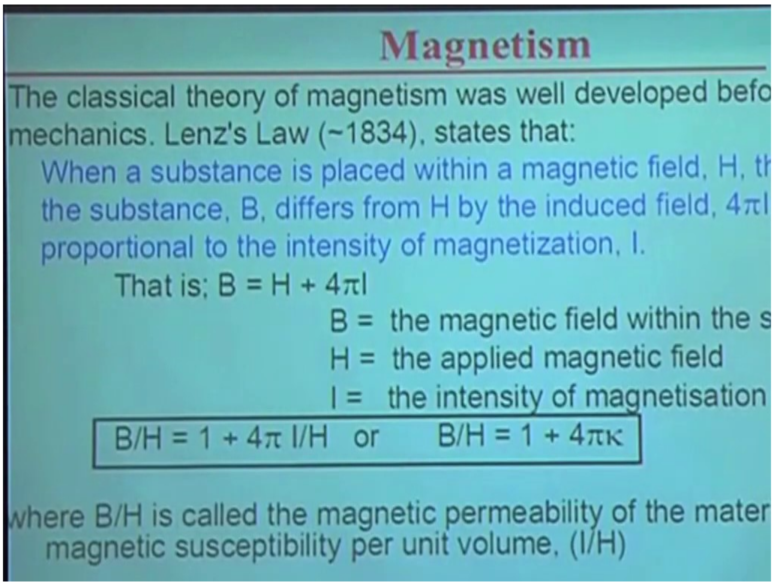


Magnetism

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

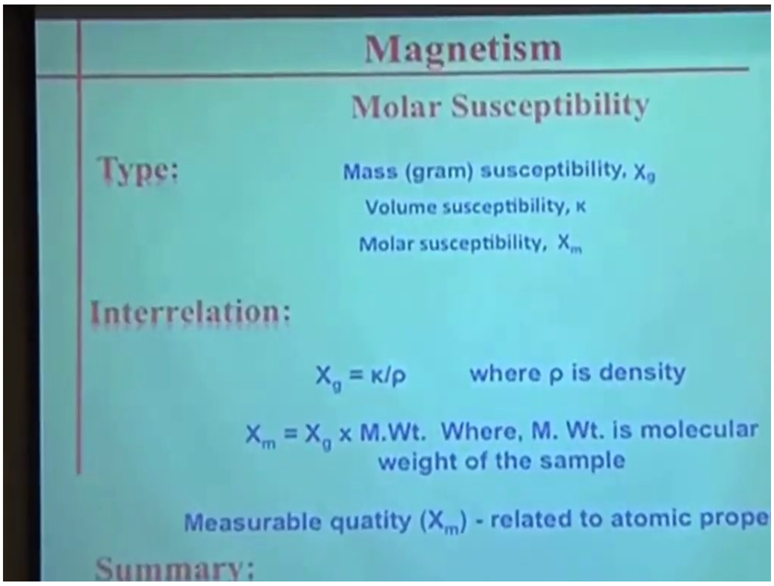
When a substance is placed within a magnetic field, H, th
the substance, B, differs from H by the induced field, $4\pi I$
proportional to the intensity of magnetization, I.

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

$B =$ the magnetic field within the s
$H =$ 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 mater
magnetic susceptibility per unit volume, (I/H)



Magnetism

Molar Susceptibility

Type:

Mass (gram) susceptibility, X_g

Volume susceptibility, κ

Molar susceptibility, X_m

Interrelation:

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

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

Measurable quatity (X_m) - related to atomic prope

Summary:

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 containing d orbital or any nonmagnetic molecule, whatever net effect it could be nonmagnetic, any molecule you can put, any object you put this one. The net magnetic behaviour 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 behaviour 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 (hype) hypnotised or magnetised it is going to get, that is the total, 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. All of you are in IIT, that 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, donate profusely, when you are donating "Jee khol ke donate karo", give back to IIT.

Really, I mean we need money, a lot of money, all of, a lot of you will be having as your start-up companies, some of them they will be bought out by some established company, you will be filthy rich, you have no idea what to do afterwards. Just think about me, for a moment. Wherever you are just think about me when you make money otherwise do not think really, or we cannot help.

So, all right, I think this is simple physics, you know what to do with it, you have studied it before in 12th standard, you studied again. 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. So that is, I will go to the another equation.

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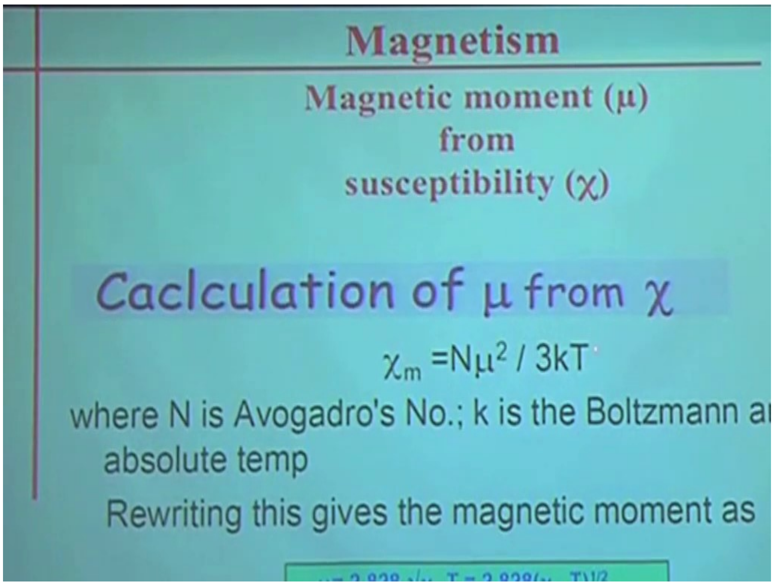

Magnetism

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 a
absolute temp

Rewriting this gives the magnetic moment as

So, the susceptibility and the magnetic moment, the susceptibility is related to magnetic moment and these are the two terms we are interested in. Remember, we will be discussing again in the next class. So, you study a little bit if you have any queries I can come back and discuss again.

Now, susceptibility, molar susceptibility you, molar, how do you get molar susceptibility, divided by, divided by total mole or average 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 equates with the magnetic susceptibility. Now all we need to care, sorry, we are coming back again.

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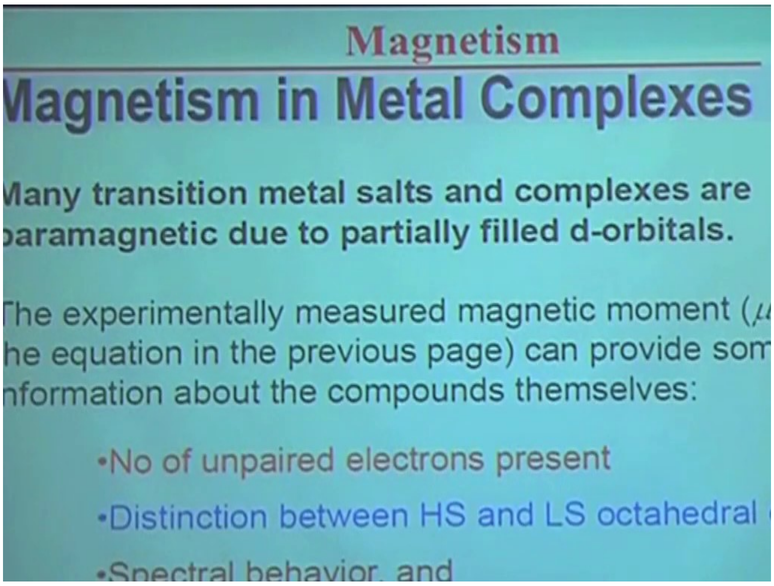

Magnetism

Magnetism in Metal Complexes

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

The experimentally measured magnetic moment (μ he equation in the previous page) can provide sor nformation about the compounds themselves:

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

All we need to care for this course, we are mainly trying to see the metal complexes with unpaired electrons, d electrons. 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. 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 electrons. And from there, we can of course, try to see the spectral behaviour and structure of the complex.

Now, many transition metal 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 two and try to explain what is the reason if experimental values are different.

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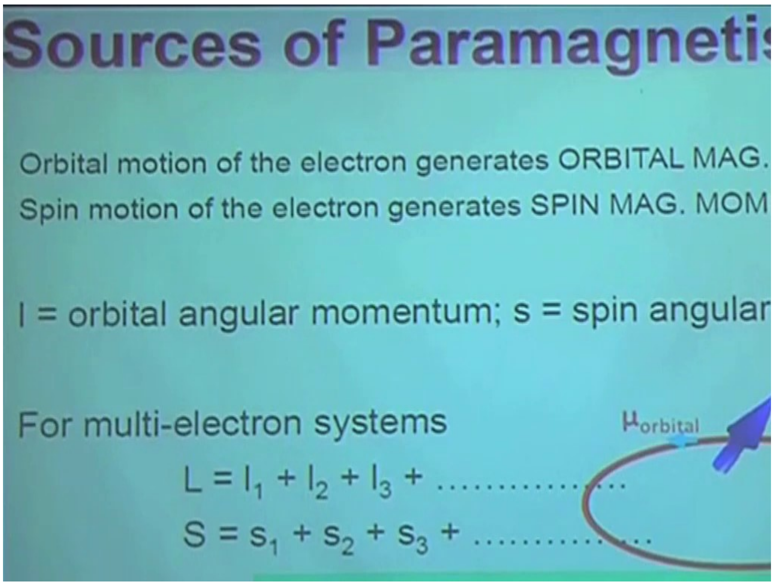

Sources of Paramagneti

Orbital motion of the electron generates ORBITAL MAG.

Spin motion of the electron generates SPIN MAG. MOM

l = orbital angular momentum; s = spin angular

For multi-electron systems

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

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

Let me get into it, you will be a little bit clearer. So, 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 two sorts of or two sources of creating magnetism. One is spinning around its own axis just and another is while spinning around its own axis, it is also rotating on the, along the orbital. So, two 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 its own axis or along its own axis, two 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 its orbital. So, the L component mu orbital component will be usually minimised, let us say zero, 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 its 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 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?

Two components are there, one component will be marginalised of course, I am not saying it is zero, it has, we will come back, that is what we will be seeing the orbital contribution and there is usually one or two questions are asked from orbital contribution which is a little bit exciting. But usually speaking, two components are there one is nullified and other is left, that is the spin only.

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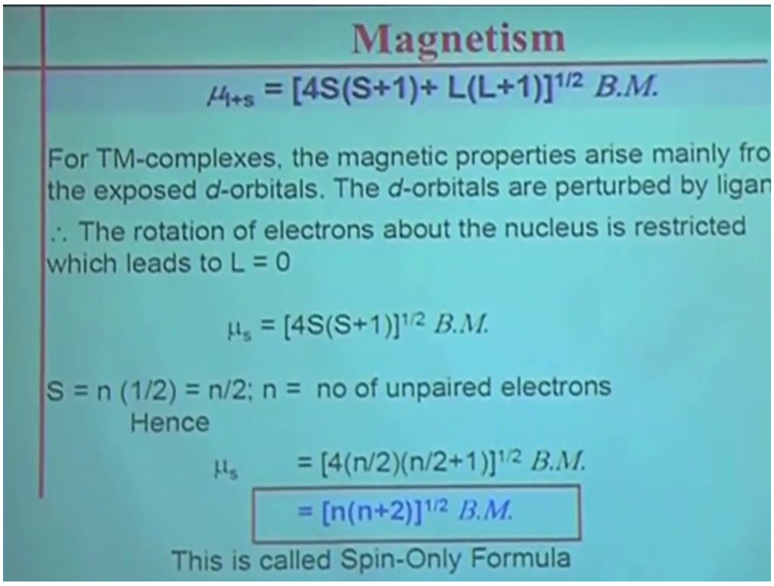

Magnetism

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

For TM-complexes, the magnetic properties arise mainly fro
the exposed *d*-orbitals. The *d*-orbitals are perturbed by ligan
∴ The rotation of electrons about the nucleus is restricted
which leads to L = 0

$\mu_s = [4S(S+1)]^{1/2}$ *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

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 electrons and those L values you have to know all of them, this is the theoretically calculated value.

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

Now, S is nothing but number of unpaired electron you are having. So, S equals total S equals number of unpaired electron divided by 2 or you can convert this equation by putting, putting the number of unpaired electrons, 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. So, if you have one unpaired electron, 1 multiplied by 1 plus 2 root of 3, 1.73, two unpaired electron, 2 plus 2 multiply by 2 root of 8, 2.83. So, one it is the easy way to remember it, 1, 1.73; 2, 2.83. So, one unpaired electron, 1 plus 0.73; two unpaired electron, 2 plus 0.83, three unpaired electron, 3 plus 0.8, four unpaired electron, 4 plus 0.9, I mean 0.7 let us say 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. Now, this is the spin only formula.

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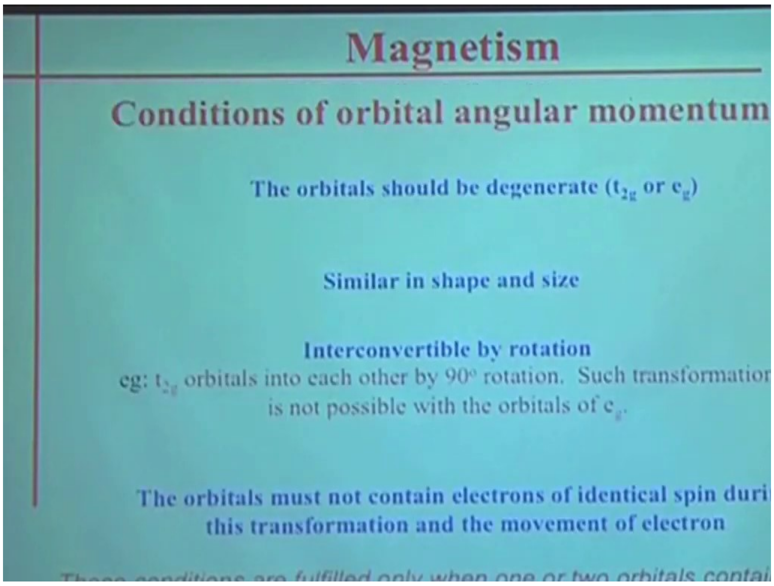


Magnetism

Conditions of orbital angular momentum

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

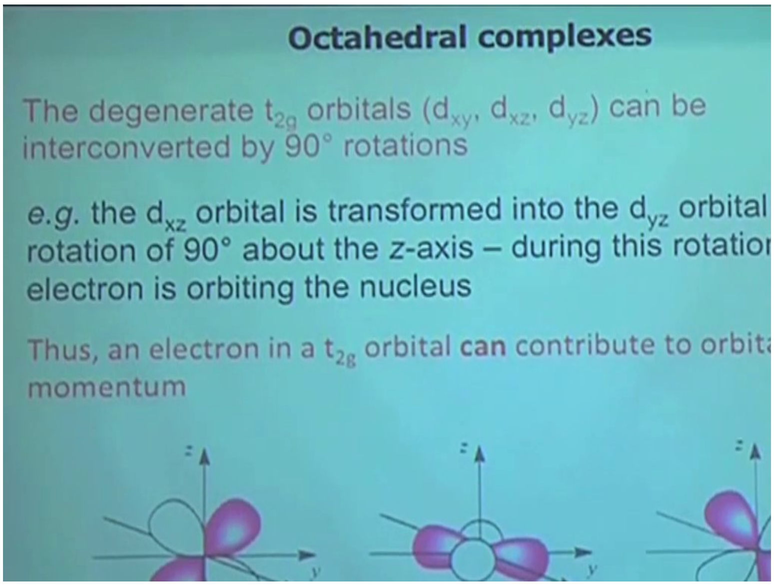
Similar in shape and size

Interconvertible by rotation

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

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

These conditions are fulfilled only when one or two orbitals contai



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 rotation of 90° about the *z*-axis – during this rotatior electron is orbiting the nucleus

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

Now we need to really get to see now whether the spin only formula is valid always, what we get experimentally when it deviates, how it deviates, that is what we are going to discuss, these are for the purist. Now we will discuss when we are going to get something like called orbital contribution, what is orbital contribution? Orbital contribution is nothing but orbital contribution. So, what is it? Orbital contribution. So, in addition to spin only values, if there is some rotation around the orbit specifically it comes when you have, again, again orbitals which are unsymmetrically fit, like t2g4.

So, there is some sort of transition from one orbital to another, when you can multiple, write down multiple electronic configuration t2g4 it could be dxy to dyz1, dxz1 or the other way around also, you can among the three degenerate orbitals you can write down differently.

So, this is when the orbital contribution comes because since the electrons can be delocalized or can be placed in different orbital and thereby you have the possibility of promoting some of the orbital, some sort of moment or some sort of magnetic moment can be generated due to these you can say the transition, due to this, due to this mobilisation of electron from one orbital to another dxy to dyz to dxz.

But can you do that? That is what the question. So, that is what we want to see, can we inter convert dxy into dyz or dx2 y2 into dyz, that is so, the orbital contribution is nothing but spin only values 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 value are little bit more then number of unpaired electron calculation.

How do you calculate number of unpaired electrons? That is by your crystal field theory. How many unpaired electrons are there t2g eg calculation you do. So, number of unpaired electron calculations should give you a very close idea what is going to be your magnetic moment, that is your theoretical calculation. Correct theoretical calculations 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 or 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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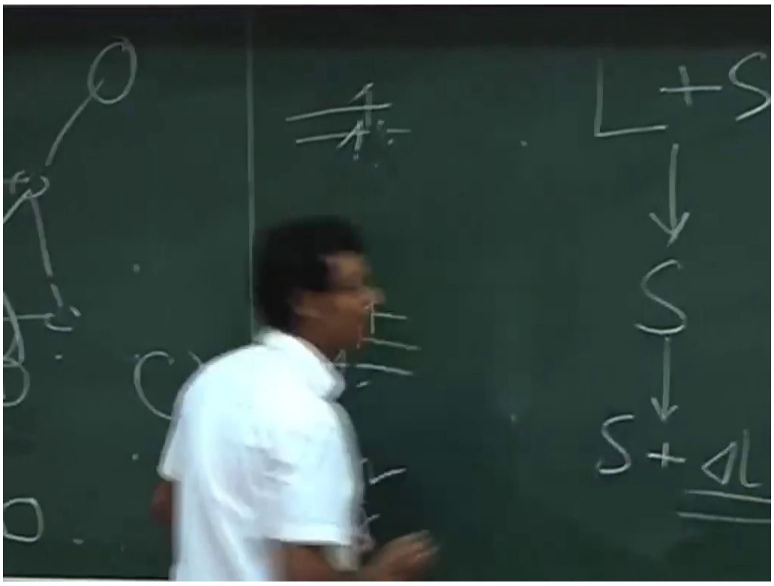

So, there is always L plus S contribution. But I am trying to say you just minimise it to S but in reality, S plus let us say delta L, very little contribution from L, when this comes, usually you see your experimental data and theoretically predicted data are the same. Some cases you have to worry about 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 OH, then only you can do that. Now, the degenerate t2g orbital dxy, dxz, dyz can be inter converted as in shown in here, you just rotate a little bit you can interconvert. Thus an electron in a t2g orbital can contribute to orbital angular momentum.

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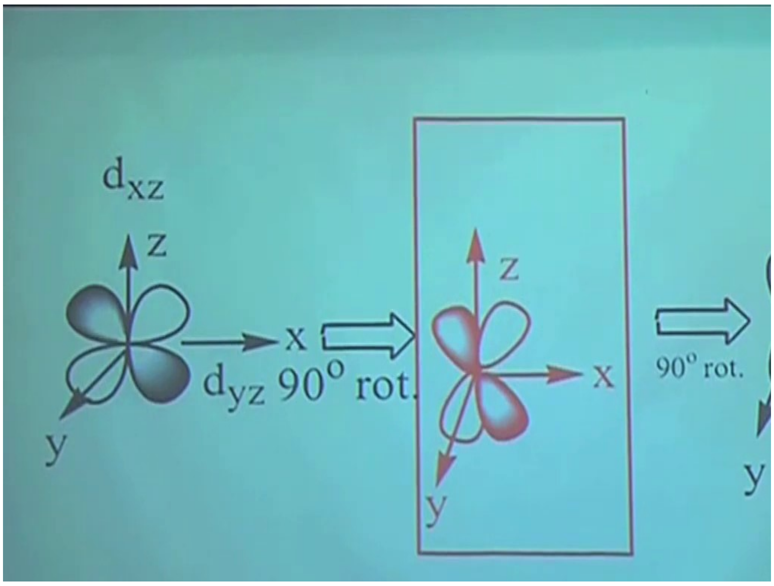

But what happened to eg, so this is the transition from dxz to dzx to dyz you just rotate the orbital, it is a plane, dxy plane let us say, you just rotate 90 degree, you get another one, if it is dxz you get initial and then finally you get dyz. You should be able to do that, you just take it, take a piece of paper and rotate how much angle you are rotating, you should be able to do.

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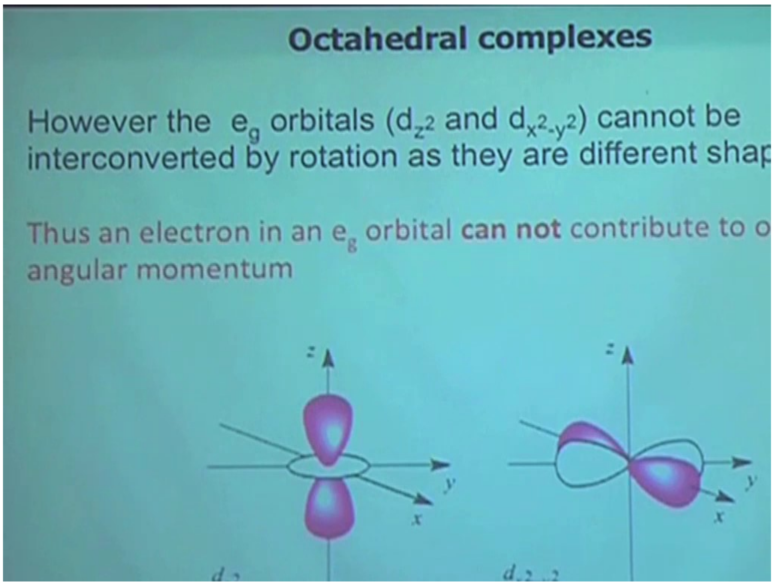

Octahedral complexes

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

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

Now, if you look at eg orbital, eg orbital you have dz square and dx2y2, any amount of rotation is it going to give you the interconversion? No, so eg orbital cannot give you the, cannot contribute for your orbital contribution. Now, eg orbital cannot contribute to orbital angular momentum.

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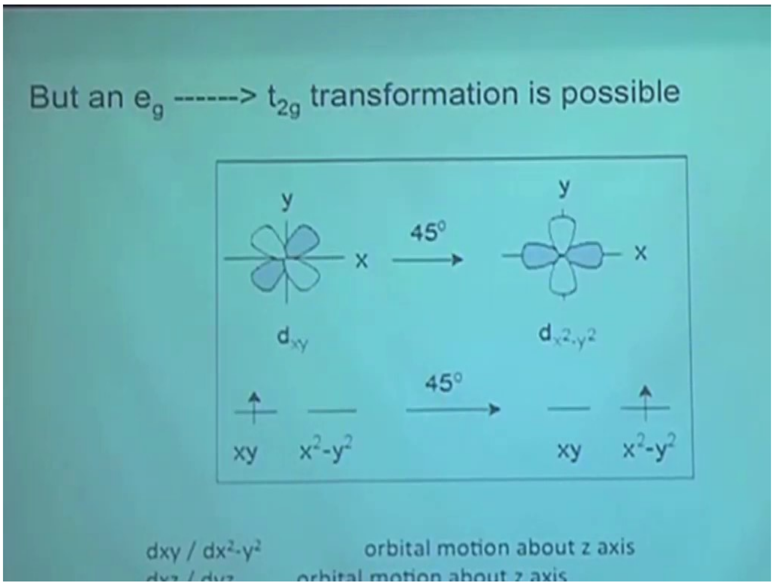

But an e_g ------> t_{2g} transformation is possible

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

So but there is a way to convert the eg into t2g, how it is? Dx2y2 or dxy can be converted to dx2y2 and vice versa. So, there is some way to do that and then you know that dx, once you get dxy, dxy can be converted into dyz, dxz. So, these are kind of interconvertible. So, what is not interconvertible orbital wise? So, dy dz square to anything else you cannot do but four of them can, rest four of them can be inter converted.

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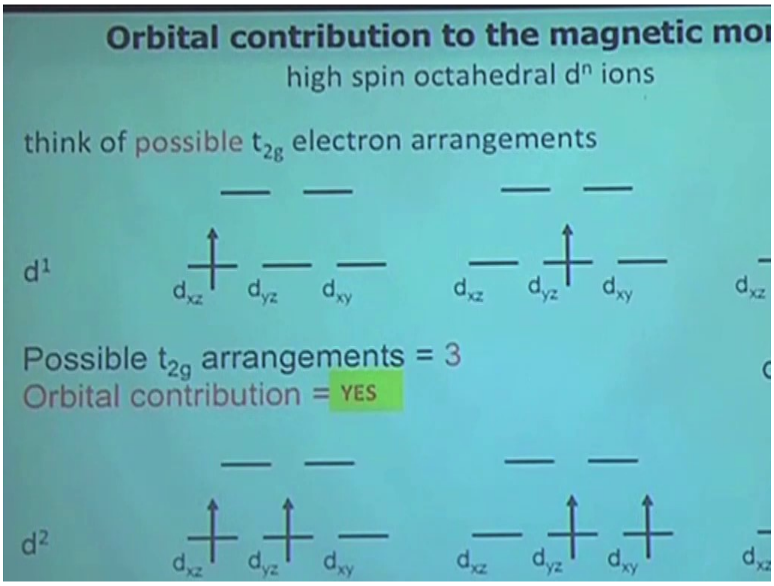

Orbital contribution to the magnetic mo

high spin octahedral d^n ions

think of possible t_{2g} electron arrangements

Possible t_{2g} arrangements = 3
Orbital contribution = YES

Now, orbital contribution to the magnetic moment, once again magnetic moment is spin plus orbital contribution should be there, orbital contribution is usually zero, orbital contribution can come when it is something like this, t2g electron arrangement, think of possibility t2g electron or arrangement it can be d1, d1 can be organised as is shown, dxz, dyz and dxy.

Possibility t2g arrangement is three, three different ways you can put the electrons, thereby orbital contribution is, yes, d1 in titanium 3 plus. So, if you calculate the angular, total magnetic moment for these, one 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. Because see if it is fixed on an orbital, if it is fixed in this orbital maybe your, of course, your ligand electrons and this elects, these ligand orbital overlap with the, with the d orbitals will be restricting the rotation. Since, if there is multiple orientation possible, then that can cause see anything that, 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, d orbitals that should allow you some sort of magnetic moment value.

I think, I should give you 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 somewhat to rotate around the orbital and thereby some contribution is coming, you are not allowing a free rotation thereby 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 makes some sense. If it is not 100 percent clear, I will try to look at more, I will come back to the magnetism in the next class.

Now, in the d2 orbital as you see three, again once again three different ways the electron can be distributed. And therefore, these degrees of freedom as you can see or as you can tell degrees of freedom should give some sort of, magnetic moment value and that is where you can get the orbital contribution, orbital contribution, of the experimental value once again will be a little bit more than what we see for the two unpaired electron.

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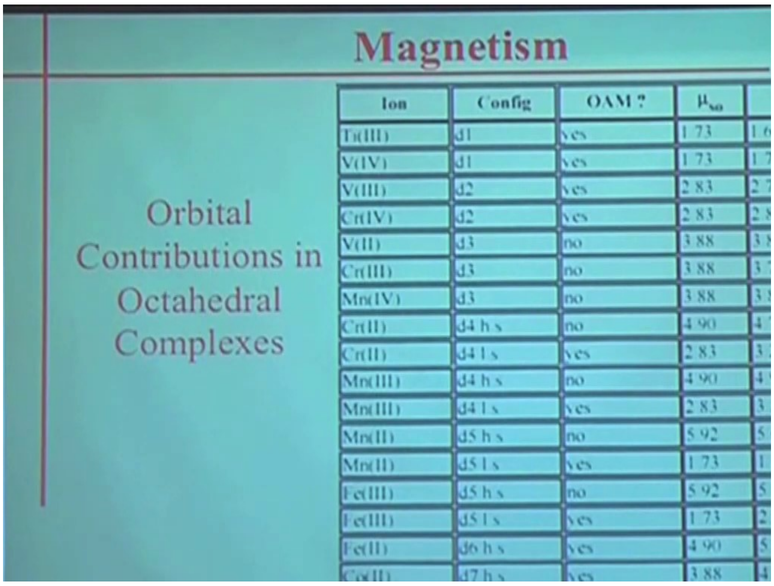

Magnetism

Orbital Contributions in Octahedral Complexes

Ion	Config	OAM ?	μ_{so}
Ti(III)	d1	yes	1.73
V(IV)	d1	yes	1.73
V(III)	d2	yes	2.83
Cr(IV)	d2	yes	2.83
V(II)	d3	no	3.88
Cr(III)	d3	no	3.88
Mn(IV)	d3	no	3.88
Cr(II)	d4 h s	no	4.90
Cr(II)	d4 l s	yes	2.83
Mn(III)	d4 h s	no	4.90
Mn(III)	d4 l s	yes	2.83
Mn(II)	d5 h s	no	5.92
Mn(II)	d5 l s	yes	1.73
Fe(III)	d5 h s	no	5.92
Fe(III)	d5 l s	yes	1.73
Fe(II)	d6 h s	yes	4.90
Co(II)	d7 h s	yes	3.88

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, look at it. I will stop it in here from here on I will discuss in the next class.