

good morning everybody

so far we are talking about the coordination equilibria

so there we see that how a particular metallion center is important of certain oxidation state whether it is present in a catalytic site or in some biochemical reactions and we are talking about the binding of

so many ligand centers

so if the center is present in a octahedral geometry and if we can block all the positions through the corresponding equilibria and if 5 positions are occupied already

so we have 5 k values such as k_1 k_2 k_3 k_4 and k_5 and last one we will be talking about is very important in terms of the corresponding form in the biology what we get as in deoxymyoglobin another form is the corresponding oxy-myoglobin where we can consider simply the binding of the dioxygen molecule to that iron center

so all these things are very important in terms of the corresponding coordination bonding and the interaction to the metal ion center with these ligands

so what we find in case of myoglobin this particular part is a very important ligand system which we all know as a macrocyclic ligand which is a porphyrin ligand and this part is coming from the protein chain which is the globin chain

so situation is much more complex with respect to the corresponding metal ion coordination when we finally talk about this oo coordination to this particular one and apart from that if we go from myoglobin to hemoglobin which itself is a tetramer

so four such o two binding we have to consider and there lies the importance or the complexity in the biochemical reactions where in the protein chain

so we can have a corresponding tetrameric form of myoglobin which is hemoglobin and you still have available one coordinate site to each iron center and the binding of this O_2 is again dependent on several equilibria and that equilibria will again controlled by the different values like k_1 k_2 k_3 k_4

so these knowledge are important and we find that if we have some k value the formation constant value how this can be energetically favored for the formation of this particular one that means the binding of the corresponding protein chain or the perforin ring to the metal ion center is again will be controlled by these k values and in the simplest form what we are just considering that if we take a metal ions a nickel 2 plus in a test tube in a solution it is bound by the water molecules then we add the sufficient drops of ammonia across ammonia will see the color change and then if we add ethylene diamine

so what are the steps which are going on or taking place during this particular transformation is again controlled by the different k values because if we consider that replacement of all six water molecules which were originally surrounding the nickel two plus center in octahedral geometry will now be substituted by three ethylenediamine molecules because these ethylenediamine molecules are bidentate in nature

so we need three of them

so from this reaction from the left hand side we have one cationic species which is the hexamine nickel two plus ion which is binding with three ethylene diamine molecules altogether we are considering four species but on the right hand side we have one the complex species and the six ammonia molecules are coming out

so this is the main idea if a polydentate ligand such as a ah polydentate ligand or a multidentate ligand like edta we know that it is a hexadentate ligand if we give edt over here

so edta will also bind over there and remove all these groups but for edta on

the left hand side will be having that particular cationic complex and the ligand as the edta

so two species going to seven species

so the number of species which is coming out from the reaction is more

so that must have some contribution to the K value the equilibrium constant value depending upon the number of species which is reacting if it is ethylene diamine we require three in the denominator and if it is edta we require one

so this K value is basically is changing and this change is very important when we consider that one ligand is replaced by the other such that initially we have the water molecules bound to the nickel and then we add ammonia

so ammonia is replacing all the water molecules now ethylene diamine or any other chelating ligand will be replacing this particular group and its important contribution in terms of the thermodynamic parameter is that the ΔH values will also contribute and as well as the entropy function will also contribute in terms of the number of molecules removing over there

so the entropy is increasing from left to right

so that will have the contribution for the formation of this particular metal killer

so then we just switch on to a particular theory which will consider about the valence bond theory and this valence bond theory what we consider because when we have this particular complex and we try to consider what are the orbitals available and the number of unpaired electrons that means we are focusing our attention not only to the number of unpaired electrons but also the color

so color we all know that how these can be achieved if we have two energy levels one is e_1 and another is e_2 and there is an electronic transition from one particular level to other level due to the absorption of $h\nu$ and that $h\nu$ will have some relationship with the corresponding λ value

so the one λ will be absorbed

so we will have the absorbed λ and we see the corresponding complementary color this is the very simplest form or the simplest idea to have the color for this coordination compound

so this coordination compounds how they look like that means the corresponding geometry we are talking now how the different number of electrons will be there in the different orbitals if we now consider the d orbitals and their arrangement in space will find that one particular theory which is talking about the valence and the structure and this valence band theory which considers that the overlapping of atomic orbitals why we are talking about this atomic orbitals of the participating atoms form a chemical bond because they form a particular chemical bond

so the orbitals available from the metal ion as well as the orbitals available from the ligand system is basically coming for the corresponding picture where we get that the participating atoms that means the metal ion and the ligand is responsible for the formation of the coordinate bond but this particular theory this balance band theory will be talking about something where the field orbital of the ligand will now talk not in terms of the corresponding covalent bond but the formation of the coordinate bond

so the overlap is important

so the balance of this particular or the valence electron configuration of the complex is important if we consider the overlap between a field orbital and an empty orbital on the metal ion

so this picture will propose something about the geometry of the complex and we can have the corresponding hybridization scheme

so it's a very simple idea that how we consider the corresponding hybridization scheme for the methane formation or any organic molecule formation we know that

the four how we can propose that for the formation of that CH_4 molecule in terms of the hybridization of that particular carbon center similarly that very basic idea will be introduced for hybridization using the metal ion

so metal ion will have now large number of orbitals mostly the d orbitals if we talk in terms of the corresponding d electrons in all the available d orbitals

so we must have some suitable hybridization scheme to understand the structure because all these hybridizing schemes we know that they will provide to ultimately that corresponding structure

so as for the methane molecule where we see that the hybridization scheme is sp^3 and it gives rise to the corresponding tetrahedral geometry which is centered around the carbon center or the carbon atom

so now if we just extend that idea to any other metal ion and metal ion is considering for the corresponding tetrahedral geometry

so we can have the similar type of arrangement of the orbitals and the hybridization

so what are the positioning of the different hybrid orbitals when they undergo overlap

so this particular one

so atomic orbitals we can have and if they have some proper character for bonding is called the hybridization

so same hybridization scheme will be utilized for the bonding between metal and the ligand that means the metal ion and the ligand

so if we have a very simple thing that means the tetrahedral geometry and that tetrahedral geometry will give us a corresponding compound which is $CoCl_4^{2-}$ where we can have three unpaired electrons and whether that particular arrangement can give rise to a paramagnetic system or not and is known that if you have a corresponding $CoCl_4^{2-}$ for two minus species it will definitely have unpaired electrons it will be paramagnetic and will be attracted by the magnet

so what we see there that this particular arrangement as well as we will see immediately some other species

so one is the corresponding $CoCl_4$ and we can also go like species like CoF_3 three three minus and $Co(CN)_6^{3-}$ six three minus

so in all these cases what we see we are talking about some interaction where the cobalt center is present it can be two plus or three plus and the ligands are chloride fluoride and cyanide

so what we find that this particular one since we are talking about the four chloride groups surrounding this cobalt center

so the arrangement of this will be definitely a tetrahedral one

so that tetrahedral geometry will give us something where we find that the cobalt is at the center of the tetrahedron and four chlorides surrounding this particular cobalt center

so we will have this though we have to give certain hybridization scheme or allow certain hybridization scheme such that in a tetrahedral arrangement we have this corresponding hybridized orbital

so these are the hybridized orbitals

so the bigger lobes which are pointed towards the corner of a regular tetrahedron

so that is the basic idea

so these are the typical sp^3 hybrid orbitals but when we talk about in terms of the corresponding unpaired electron on the cobalt center what you see that we are not involving any hybridization involving the d orbitals that means the d orbitals will be untouched

so untouched d orbitals will have the same magnetic moment pattern what we can have if we have five d levels which are there and which are degenerate in nature

that means all of them have the same energy

so the n number of electrons which is present on cobalt two plus can be distributed on the five levels or the five orbitals which are d in character but the situation is not

so simple because we can have five different d orbitals and which will be interacting differently with those ligands for this particular metal ion center so if we have something

so the hybridization scheme is telling us that this is there and the ligand will come and ligand will overlap with all these orbital but the middle ion will have the corresponding d orbitals available

so the magnetic moment or the color of this thing can be explained in terms of the only the number of d electrons present in it

so like that of our methane molecule we consider as a sp^3 hybridized orbital which will be tetrahedral in nature and the number of electrons available for its magnetic moment will be present in the d orbitals in cobalt two plus in case of nickel two plus will consider something else because we have to arrange four cyanide groups and we just now try to understand something where we find that changing from a ligand which is Cl^- to CN^- is different that we are seeing in this particular example that if we can have a chloride fluoride and cyanide

so if we just consider the corresponding relative strength that means how strongly they are interacting when we talk the corresponding interaction between the metal ion Mn^{2+} with that of our ligand lone pairs

so if the interaction is different we can have a situation where the cobalt two center this is cobalt two

so cobalt two center is interacting with four chloride ions giving a particular magnetic moment when we go to particular thing where we can have the Co^{3+} six three minus and if we just see that the number of unpaired electrons if we get some indication what we get directly by measuring the magnetic moment

so the magnetic moment will be therefore something where we get the corresponding moment of the total number of unpaired electrons available in this particular species

so here if the indication is that we can have four unpaired electrons and those four unpaired electrons will give rise to a corresponding magnetic moment and that magnetic moment will be considering for this particular arrangement and this is octahedral in nature

so the geometry for this will definitely because an octahedron because we can have the arrangement of six fluoride groups around the cobalt three plus center so this is covalent three

so if this is sp^3 for the tetrahedral arrangement what we can have we just include two of the orbitals which are of d character

so two d we can take

so four plus two that means there we have the four hybrid orbitals four plus two will give you the six hybrid orbitals

so those six hybrid orbitals will be considering for the d_2 and the other type of d_2

so there will be two d_2 type things

so one will be sp^3 and another d_2

so we simply write something where $sp^3 d_2$

so this is you can have and this d_2 we are what we are getting we consider as the d_2 is coming from other type which is not outer orbital hybridization and we can have four unpaired electrons

so is a different type of arrangement but if we can go for $d_2 sp^3$ that means d from the three d level but these d rs are from the four d level there is

on the right hand side and those two will be on the left hand side
 so the situation will be different and that we get for the next compound where
 we do not have any unpaired electron
 so unpaired electron number is zero the species is diamagnetic and this will
 give rise to d^2sp^3 hybridization
 so that immediately tells us the nature of this ligand and this ligand is
 completely different because we are unable to explain the magnetic property of
 these two cases in one case the number of unpaired electron is zero and another
 case number of unpaired electron will be four
 so in this particular case we can have the four electrons are coming for these
 five d levels
 so these d levels which are three d in nature because we are not touching these
 d levels from this hybridization scheme
 so this will be there
 so we all know that it has 6 unpaired electrons trivalent cobalt is a $3d^6$
 system
 so we put 6 electrons in all over these available orbitals
 so these available orbitals will give us four unpaired electrons
 so that's why we get a four unpaired electron for this particular species but
 in case of this particular arrangement where the d two
 so two of these d two will not be available over there
 so we will have available only three d two and two will go there s and three p
 so three of them will be available for these two and this d two sp^3 will be
 there
 so this sp^3
 so this is 1d
 so you will have these six electrons will now be arranged in this fashion and
 these are the corresponding one where we can have this is not there
 so d two s p three
 so one d this is the second d this is s p sorry this is there
 so sp^3
 so this orbital
 so will be therefore $d^2 sp^3$
 so this diamagnetic behavior can also be explained
 so this is a very simplest arrangement for where you can get that the magnetic
 property and will also try to explain in some cases what will be the color if we
 add chloride ligand fluoride ligand or cyanide ligand to the cobalt solution and
 what are the different colors we can get and whether an electronic transition is
 possible from these levels
 so similarly what you find for another example which is bivalent nickel which
 is diamagnetic
 so how we can explain the diamagnetic behavior of this tetra cyano nickel head
 species that we have to consider that we take out one d out of this
 configuration which is three d eight that means we have eight electrons to
 occupy the four available d levels on nickel
 so the all will be paired
 so definitely this compound will be diamagnetic in nature
 so the hybridization scheme will typically will be dsp^2 similarly for this
 one that this particular ag one we have like that of acetylene we know acetylene
 we have which is C_2H_2 the acetylene carbon will give rise to the corresponding
 hybridization is sp hybridization and this particular one is a linear one
 so the linear arrangement for this will give rise to an situation where silver
 is at the center and on the left we have one ammonia
 so nitrogen is bound to the silver and another nitrogen will be bound on the

right hand side and the nitrogen silver nitrogen bond angle will be 180 degree
so this is the linear arrangement

so the linear ligand arrangement will be like this

so silver will be here and ammonia this ammonia will be here and the second ammonia will be here which will be for sp hybridized scheme

so sp as well as sp³ hybridization scheme will be little bit simple because we are not touching the corresponding arrangement of d electrons in the hybridized orbitals whether it is same or different from the unhybridized electronic configuration of the corresponding metal ion such as this can also happen if we just simply go for the zinc we know that zinc in the bivalent state this is zinc in the bivalent state where all the d orbitals are filled we know that the electronic configuration is 3d¹⁰ and that electron configuration will give rise to some arrangement where we get that we all know that when we add gradually the hydroxide ion to a zinc two plus solution initially there is a turbidity and then zinc hydroxide will be precipitated like aluminium hydroxide but if we add more zinc ah sorry more hydroxide ion to this solution

so the precipitated zinc hydroxide will now be dissolved as more and more hydroxides will be bound to the same zinc center giving ultimately to zinc o h whole for two minus iron and definitely this is a tetrahedral arrangement because we cannot have the corresponding hybridizing scheme what we just learnt for the nickel as dsp² hybridization because the d orbitals will not be available for bonding for in the hybridization scheme

so that hybridization will not be allowed to ask for a typical arrangement where we get four ligand

so this is one ligand

so this is one h this is one h and this is one h and these are the hybridized orbitals on the corresponding zinc center and these lone pairs are coming from the hydroxide ion

so this will be typically a tetrahedral arrangement

so what we are trying to compare that is whether we write in a circular form or the red arrow that means we are not touching the corresponding electronic configuration of the free ion that means the free zinc ion while we get the corresponding complex pc

so nothing is changing we are unable to change the color also because these are all colorless and we are not able to change the magnetic property but here is no such clue for measuring the magnetic moment because the zinc is filled but whether this model is valid for zinc also the valence bond picture is valid for the zinc also that we can see

so what are there that means these levels are not filled

so the we have the empty orbital

so we require empty orbitals for the formation of the coordinate bond on the zinc two plus

so this s and p orbitals will give rise to four hybridized orbitals on the four corners of a regular tetrahedron and that regular tetrahedron will now be available for accepting the lone pair electron density from the four hydroxide ions

so those four hydroxide ions will now give the corresponding electron density to the orbitals which are sp³ hybridized orbitals associated to the zinc center that means these are basically connecting to the zinc center and as a result we have the zinc o bond

so what we get ultimately will be getting a zinc o bond

so there will be four such zinc o bonds on the four corners of a regular tetrahedron

so the valence bond picture we must have

so which is also valid for a corresponding element which do not have any unpaired electron in the d levels

so this we have seen just now that the square planar arrangement will give you a corresponding hybridized arrangement where we get a corresponding coordination which is d_{sp^2}

so d_{sp^2} hybridization is important for an ion hole for two minus ion

so will be definitely a square planar arrangement

so this particular arrangement what we get is the d for that particular arrangement is for the 3d level

so out of these 5 or d orbitals

so we will see very shortly that what are the shapes of the different d orbitals which are also very important

so that will also tell you that which particular d orbital will be available for this particular type of bonding

so if this particular square plane is in the x y plane

so the those orbitals which are concentrated on the x y plane will be available for this particular type of bonding

so what we do we have two unpaired electron in the free ion situation that means where we have the nickel 2 plus is present

so this electron this unpaired electron of the nickel will be pushed back to the orbital of the nickel which is 3d in character pure 3d in character making this orbital vacant for this hybridization which is d_{sp^2}

so this orbital will be vacant and this vacant orbital will now accept the electron density from the cyanide ion

so not only this

so we'll have one d one s and two p now not three p unlike we have the d two s p three hybridization in this particular case we have one d one s and two p orbitals

so they will hybridize together since we are talking about the orbitals which will again see that what are the p orbitals also will be there

so in this particular situations the d_{sp^2} hybridization will be there and one p will be vacant and that view will not take part in this particular hybridization scheme

so what we see there that this particular hybridization what we are considering as d_{sp^2} hybridization and we all see that the equi energetic five d orbitals

so these five d orbitals what we have and if they can have some level we just will talk about the corresponding shapes and all these things

so the shapes of these will be there

so we will start from here

so it can have one orbital which is labeled as $d_{x^2 - y^2}$

so the electron density will be available for the orbital which centered on the nickel 2 plus will be in the x y plane then we can have another is d_{z^2} square and then d_{xy} d_{xz} and d_{yz}

so these are the possibilities basically likewise what we know that the for the p orbitals we can have the p x we can have the p y and we can have the t

so what are the possibilities for this d_{sp^2} hybridization which is leveled or tagged for a square panel arrangement

so a square panel arrangement is there and we just take the corresponding plane which is the x y plane

so if we just consider the x y plane

so we have the hybridized orbitals available over there and these hybridized orbitals will be pointing towards the four corners of the regular square plane

so they are all d_{sp^2} hybridized or vital

so this is along the pz direction

so these two are x and y and z will be the perpendicular direction
 so we just immediately for this
 so one of the p will not be there
 so this is out
 so this p z will not take part in this particular hybridization scheme and the corresponding one which will basically there
 so there will be two types of these orbitals in the x y plane for the d level one is d x y and another is d x square minus y square one will be pointing directly towards x and y and another will be in between
 so if our axis this is the x axis and if this is the y axis
 so is not this particular one
 so this perpendicular to
 so this is if this is the x axis and this is the y axis
 so definitely this particular orbital will be d x square minus y square
 so we will take this orbital
 so out of these five orbitals we take one of the d orbital one s obviously one s will be and two p's will be p x and p y giving rise to a corresponding dsp to hybridization which will be square planar in nature
 so that in detail the hybridization scheme will be 3 d x square minus y square then 4 s and 4 p 2 which is x and y
 so if we take all these like this
 so we will get
 so the corresponding valence bond picture or the valence bond electronic configuration will be like this
 so these are the hybridized orbitals
 so definitely we will have the four ligands coming over here to accommodate the four lone pair of electrons on these hybridized orbital this hybridized orbitals will be empty and we will have the four other orbitals available for accommodating the electrons the four electrons which are for the nickel two plus
 so if we just take those electrons
 so these will be filled over here
 so all four will be filled
 so we do not have any unpaired electrons
 so the unpaired electron will be equal to zero and will have a diamagnetic situation
 so this we basically get
 so that picture is if we just elaborate that way
 so that will give rise to this particular arrangement
 so this is the corresponding hybrid orbital
 so the hybrid orbitals pointing towards all the coordinates of the four regular tetrahedron
 so this is the typical geometry and the perspective what you can have it is available everywhere
 so in ah this type of arrangement
 so these are the hybrid orbitals
 so these what are the shapes of this hybrid orbital that will tell us that why the tetracyanonically is diamagnetic and you do not have any magnetic moment for this
 so next we take another example where we take or where we add ammonia molecules as ligands to chromium three plus and we are going towards the left that is the lower side of the corresponding d series where we have the ah chromium
 so titanium vanadium and chromium
 so we all know that the d1 d2 and d3 system
 so chromium which you get that corresponding one

so ah the number of unpaired electrons what we can is a d^3 system
 so we have now if we can
 so electrons available
 so three orbitals if we reserve or to preserve they are for accommodating the
 electrons which are the chromium electrons and we can take these two
 so these two electrons again like that 2 will be the corresponding one for the
 $d^2 s p^3$ hybridization we have the $d_{x^2 - y^2}$ already we have seen
 just now and other one will be d_{z^2} because it is a three dimensional
 structure
 so the ligands will be approaching in all three direction all three cartesian
 axis x y and z
 so we have to take the $d_{x^2 - y^2}$ orbital as well as the d_{z^2}
 square orbital for this hybridizing scheme
 so these two orbitals we reserve for this hybridization scheme
 so these two will be there and then we have the s and the p orbitals
 so p orbitals will definitely be x and y we are not touching the z orbital as
 the p_z in the case of $d s p^2$ but here we have all three
 so all three p we are taking
 so these three p orbitals we are taking for this particular arrangement
 so will be having the $d^2 s p^3$ configuration and your magnetic moment what we
 expect for the free electron con free ion configuration which is the nickel 3
 plus sorry chromium 3 plus that we have three electrons available on three
 orbitals three available orbitals which is not changing due to complexation
 so we get that for this and how we just consider this for the magnetic
 properties
 so because in all these cases we are just considering the corresponding
 magnetic moment what we determine the corresponding μ_B value the bohr magneton
 values will be considering now and we are talking about the number of unpaired
 electron whether you have a hybridization scheme of sp^3 or a corresponding one
 just now we have seen as a $d^2 sp^2$ and another one which is also of same type that
 dsp^2 we see that the corresponding four coordinate
 so so four coordinate that means the coordination number is equal to four
 so another one we immediately write the hybridization scheme for the $s p^3$
 which is tetrahedral
 so you have the tetrahedral as whether the square planar arrangement for these
 but we can have that another arrangement for the coordination number of five if
 you have the coordination number of five we know that the two regular geometry
 one is the trigonal by pyramidal geometry and another is the square pyramidal
 geometry
 so depending upon the shape of these thing
 so this trigonal bipyramid is that you have a trigonal plane and a
 perpendicular one
 so what we take we just basically take one more d orbital
 so one more d orbital we take over here for this trigonal bipyramidal
 arrangement ah sorry square pyramidal arrangement but for the trigonal
 bipyramidal arrangement if we move from here that dsp^2 what we can do we just
 do here we have four hybrid orbitals
 so we can have one more hybrid orbital
 so what we do if we just consider that it can be $d sp^2$ obviously this is
 corresponding square planar one but we are moving from a square panel one but we
 are going to a trigonal planar one which is we all know that we have a sp^2 ah two
 arrangements
 so this sp^2 arrangement we can have
 so this sp^2 arrangement is the corresponding one for a regular trigonal plane

so this regular trigonal plane we have now we have to have some hybrid orbital which will be and this two perpendicular direction

so these two perpendicular directions we can have

so these two perpendicular direction 1 one 1 third 1 fourth 1 and the fifth 1

so this one perpendicular direction we can have this s p two we put what we just we have we can put another p over there that we all know that the p z was lying over there

so we take all three p

so the hybridization will be d s p three which will be for your trigonal by pyramidal geometry

so so instead of taking the corresponding orbital which is the other one that means the d z square because we have taken we have not taken this one

so this one will be the other one that means since we are taking the p g orbital this will not be x square minus y square like the case of dsp 2 this will be dz square

so this orbital is also different

so this dz square will be there and the p z

so we are focusing on attention on the z direction because we are having two ligands on the z direction and for square pyramidal arrangement

so you will have more d because we have a square planar arrangement that means the d s p two arrangement the square planar arrangement

so this square plane arrangement plus one d

so this will be d s p two for this square planar one plus 1 d we put and we get the hybridization scheme as d2 sp 2

so that is again this another second d will be what we are adding is our dz square now

so these are the arrangements

so this is typically all will be the corresponding mental model how we look at the geometry and what are the shapes of the different orbitals and how these different orbitals will now take pair

so as we move from here to up to the other two that means the d2 sp3 and sp3 d2 the available orbitals that means the orbitals which are available for the unpaired electron occupying the unpaired electron will be different

so that will change the corresponding behavior of the magnetic moment and this we measure experimentally

so we do experiment

so we use some balance which is known as the gub balance and if your sample that means the most of the compound the coordination compounds are solid in nature

so the solid compounds we can put that balance and we measure the corresponding magnetic moment to understand about the corresponding magnetic moment

so what we see this magnetic property is that the magnetic moment of the corresponding coordination compounds by measuring the corresponding magnetic susceptibility that means we have the key the gram susceptibility the gram magnetic susceptibility we can have then we can convert it to molar magnetic susceptibility and ultimately we can consider it as the corresponding magnetic moment but the μ_b what we report earlier also we have seen that the μ_b we can report in terms of the number of unpaired electron

so whatever number of unpaired electron we can have on the d orbitals available we will only focus our attention to those unpaired electrons which will contribute to the overall magnetic moment of those compounds

so again like that of fluoride and cyanide because most of these cases we are just trying to compare we are trying to see the corresponding strength of those ligands whether your fluoride ligand is a stronger ligand than cyanide or the

reverse is true

so what we see here simply by measuring the magnetic moment whether your valence bond picture can give us some idea but we are not getting right picture from the valence bond electron configuration

so that's why you have to go from some other theory and this is the corresponding limitation if we are not able to predict the corresponding right magnetic moment which is experimentally determined quantity for all these compounds

so in case of this efficient whole six three minus it has a magnetic moment corresponding to one unpaired electron while Fe^{3+} has a paramagnetic moment of five unpaired electron that means the typical arrangement though we are having the similar type of octahedral arrangement around the iron center but our magnetic moments are different that means our hybridizing scheme should be different one will support the corresponding low spin arrangement and another will support the corresponding high spin arrangement and we already seen that in one case the hybridization for the low spin will be d^2sp^3 less number of d orbitals will be available for occupying those electrons and for the high spin one more number of d levels will be available for those electrons

so as a result what we get that the corresponding deficiencies we can now jot down the deficiencies for this particular valence bond approach because we will be having some other theory which is known as the crystal field theory because the interaction we cannot explain in terms of the simple hybridization model like that of our formation of the methane molecule

so that hybridization scheme is not applicable for all this particular complexes because it assumes that all the d orbitals are of equal energy which is not true will see now that due to the interaction with the ligands the energy of the d orbitals will change and will have two different groups of those d orbitals and admittedly we are using when we require we use and when is not required we use the other one that means the use of these 3d and 4d orbitals of bonding is not so helpful because the energy difference is pretty high and this particular consideration of the energy difference between the 3d and 4d levels we are not considering

so we are just having a model mental model where we are considering together for the outer orbital hybridization like that of our sp^3d^2 where we are considering these as the 4d levels but the 4d levels energetically pretty high so though we are able to explain in terms of the corresponding magnetic moment but it is not right to include the 4d levels for the hybridization

so we will unable to explain the electronic and magnetic properties of these complexes nicely because we are unable to predict the corresponding color of these complexes also

so as we use for the main group elements starting from carbon to silicon that transition metal chemistry will now be dominated by another theory what will be known as the corresponding crystal field theory and when the crystal field theory will have some limitation will go beyond that and will be considering the molecular orbitals where the individual orbitals or the atomic orbitals of the metalloid and the ligand will not give us all the explanations we must consider the corresponding molecular orbitals and this particular molecular orbital theory the one we called is the molecular orbital theory can sometime be known as also the corresponding ligand field theory because the ligand like that of our crystal field

so we are going slowly moving from crystal to ligand

so is the interaction is like a crystal field interaction will be like the interaction of the sodium ion and the chloride and what we will be considering

in this crystal field theory but in case of the ligand field theory will be considering the interaction as the ligand field is responsible for the corresponding observation for the overall molecular orbitals for the metal and the ligand that means the complexes

so what do you see that quantitative interpretation of the magnetic data is not possible to get the color of the compounds are not precisely explained

so these colors are very crucial sometime that how we record these colors when we go for the corresponding sphere spectrophotometric measurements also the λ_{max} values and the ϵ_{max} values then unable to also give the quantitative interpretation of the thermodynamic and the kinetic stabilities in terms of the corresponding valence bond picture and is not possible for the exact prediction whether the complex will be a tetrahedral one or a square planar one in terms of only the magnetic moment and lastly it cannot distinguish the corresponding strength of the ligands whether we have a weak field ligand or a strong field ligand until and unless we use the weak field ligand for a type of complexes will be knowing as the high spin complexes and the strong field ligands will be for the low spin complexes that will discuss the the corresponding strength of this ligand in terms of the corresponding d orbitals and how they look like along the different axis

so if we just consider these orbitals in all these directions and will be considering these as just now we are leveling these but now we see how they look like how the $d_{x^2 - y^2}$ is different from the corresponding d_{xy} because the corresponding lobe the availability of the electron density will be there in between the x and y axis

so these two are in the plane but they are somehow shifted towards ah say 90 degree on this particular plane similarly in the same way that if we take other two cartesian axis x and z and y z we get these orbitals

so we basically from the picture basically we just have some classification or the differences between the positioning of these when we place the ligand suppose we have a octahedral field

so the crystal field or the ligand field is octahedral in geometry

so which is very important

so those ligands will be considering as point charges or point dipoles if it is anionic we consider as a point charge if it is a dipole like water or ammonia we have the corresponding point dipole and we are not considering anything like that of our valence bond picture that means we are not considering any overlap

so we just simply place these orbitals ah that charges are the dipoles on x on y and on z on the positive side of x and y similarly on the negative side of x and y and z will have

so 3 plus 3 6 will be there now you see that those orbitals will be facing directly to those ligands are these two only that $d_{x^2 - y^2}$ and d_{z^2} because x y z they are facing this ligand

so they will interact differently with that of our ligand system compared to d_{xy} d_{xz} and d_{yz}

so basically we will be getting two groups of d orbitals in a octahedral crystal field

so similarly in any other crystal field we have to critically consider the geometry even we can also think of the placing of s orbital and placing of p orbital within that particular octahedral field

so placement of those orbital field and the shape of these particular orbitals whether it is s simply s or p x p y and p z and as of the five d orbital we can have the different types of interactions

so how the four lobes are interacting with the different orbitals

so in case of d_{xz} and d_{yz} the four lobes are concentrated in between

the coordinate axes

so they will not be face to face there

so they will not interact strongly as the lobes of $d_{x^2 - y^2}$ and d_{z^2} which are along the x y axis and they will face they will be facing the orbitals directly

so what we get that the combination of these

so this basically what we see that why this is different from that of our $d_{x^2 - y^2}$ because these are all some amount of linear combinations so linear combinations of some of the orbitals

so this is basically a hybrid of d_{z^2} minus $d_{x^2 - y^2}$ and $d_{x^2 - y^2}$

so these are the corresponding combination of these that's why we get this particular one as d_{z^2} only because we are omitting minus $d_{x^2 - y^2}$ and minus $d_{y^2 - x^2}$

so that is why this concentric lobe is there and is available in the x y plane

so this particular one truly speaking it has to be written in this form that means $d_{z^2} - x^2 - y^2$ but in the simplest way we are writing only d_{z^2}

so if we place them in a typical octahedral field and the placement of these

so this will be there

so they will basically of different types

so we will have

so five orbitals will be there and those five orbitals when they are placed in presence of six ligands

so will be placing six ligands over there and this is for the free ion

so in this case the energy of the five d orbitals will be raised

so the overall energy overall energy means that is there is no such splitting or anything but the overall energy of these orbitals will be raised but afterwards what will happen we will have two groups of these orbitals

so one of these will be of two and another set will be of three

so they will be lowered in energy and will have the corresponding very center because of the placement of these orbitals they will not remain degenerate and this degeneracy will be lost and the orbitals which are face to face that means $d_{x^2 - y^2}$ and d_{z^2} orbitals will be raised in energy compared to the unsplit energy level this is the unsplit energy level will be considering if for all the electrons will having this particular splitting will consider this splitting as x and the other splitting will be therefore the y

so this will be the lowering in energy and this will be the elevation in the energy compared to the unsplit level which we get by raising the energy in the from the free ion situation

so there will be the splitting

so this particular one since we have three d orbitals we consider it as labeling as the t which is a triplet one and these are basically the symmetry level dont worry about these and the other level will be the e level which is the doublet because will be having two orbitals

so in a sense what we are thinking over here is that we are able to develop something that means splitting is there that means one energy level we have created and another energy level

so the color magnetic moment everything can be explained nicely in terms of that that means it is little bit superior compared to our balance bond picture

so the crystal field picture or the crystal field theory which will apply will be little bit superior compared to our valence band picture in identifying these

so this particular e g level and the t two g levels

so each set will be these two orbitals and that two g set will be these

so this can give rise to this particular one

so we will just basically raise the thing

so metalline in an octahedral complex we are simply talking about the field which is octahedral field and that octahedral field will give rise to this particular splitting

so one will be up by x from the corresponding free metal ion then somewhere it is there the metal ion plus six ligands

so it will be not directly from the free metal ion but you will have the ligand just now what we have shown you that it will be there from there this particular splitting will take place

so this particular ones from there will just get the corresponding fitting and this x plus y the whole splitting what we get as x plus y will be termed as the corresponding Δ and sometimes denote as the Δ_o or oct that means o subscript is for the octahedral symmetry

so this is the corresponding crystal field splitting

so since they are pointing directly towards the ligand

so their energy will be raised

so this energy gap this Δ which is very much useful and the Δ is very useful in considering the number of unpaired electrons and the energy transitions for the pushing the electron from the lower level to another other

so this Δ is the crystal field splitting the Δ_o the subscript o will be for the octahedral crystal field splitting

so when we talk the corresponding absorption spectra what color we should get the absorption spectra will tell us that the crystal field splitting energy is dependent on the ligands nature that means the magnitude of this Δ how this Δ is changing

so definitely in all these cases because we are bringing all the six ligands whether it is a fluoride or chloride or cyanide but we are bringing three different types of ligands surrounding a central metal ion but the interaction will all be different depending upon the nature of the fluoride or the chloride or the cyanide

so what we see that the Δ will be changing just now what we have discussed in the very beginning of this class that you have certain thing for the corresponding K values the equilibria the coordination equilibria now the magnitude of that particular coordination equilibria will also be changing for the splitting that means the magnetic moment and the electron transition for electronic spectra will also be changing and terms of this Δ value will immediately say a particular type of ligand can give you higher Δ value compared to the other

so when we have water molecule when we have nickel two plus in solution which will be replaced by ammonia in the first step and those six ammonia what we have seen for the K values also the thermodynamic parameters for that substitution also we have seen but Δ is a very simple parameter which can say that since we are able to replace water by ammonia and ammonia by ethylene diamine

so the Δ value for en will be higher than that of ammonia and will be higher than that of your water molecule and that we simply visually observe if we go to chemistry laboratory and we dissolve nickel two plus salt in a test tube and which is the corresponding hexaco complex immediately we see the color which is green then we add one drop or two drops of ammonia you never know whether all the water molecules you are substituted but if you add little bit excess of ammonia only little bit will be getting something which is blue in color

so that blue color is due to the corresponding hexamine complex and if we add now the ethylene diamine which is the liquid

so ethylenediamine solution also drop by drop which can be diluted one also you will just see a blue to a color change blue to violet coloration that means your ethylene diamine complex is pretty strong and the colour is changing from green to blue to violet that Δ will also tell you how these different colors are changing and the k values are saying that no it will go from left to right because the k value for ethylene dime is much more compared to your corresponding k value for the hexa etho or hexa amine complex formation

so this is the thing that is the pictorial representation for these things that means what we get we are having here

so what is that is the your Δ value

so your splitting we'd all know now that the placement of six water molecules surrounding this nickel two plus center is something and we have two unpaired electrons

so definitely is a paramagnetic compound and we can have this particular situation that the energy values now we can start thinking how we get the color

so what particular λ value is absorbing and how this color is changing from green to blue and to violet because your Δ value is changing it is small it is medium it end is higher

so when the separation is higher we have the violet coloration

so what violet coloration we get for the corresponding λ value because the λ for the corresponding complementary color

so we should have the corresponding absorption

so the absorption will be in the higher energy values that means the shorter wavelength

so the shorter wavelength absorption will take place in case of trees ethylenediamine complex compared to the corresponding hexaammine 2 complex

so that's why we get

so we should be able to justify this particular color change in terms of the corresponding Δ values why the color is changing from green to blue to violet if we know the order that means Δ_{en} is greater than Δ_{NH_3} Δ_{NH_3} will be greater than water in terms of the corresponding Δ values and if we just talk in terms of the corresponding Δ_1 Δ_2 and Δ_3

so Δ_3 will be higher than Δ_2 and Δ_2 will be higher than Δ_1

so from this we how we can apply these values and what will be the magnitude in terms of the pairing energy will all discuss this in our next class ok thank you you