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5.112 Principles of Chemical Science, Fall 2005
Transcript – Lecture 31

Let's get started.

We have a lot more chemistry to learn today. And, as you are probably becoming aware, the octahedron plays a very important role in the coordination chemistry of the d-block elements.

So we are going to begin today also with the octahedron.

And I just want to remind you of the approach that we were taking on Monday to understand how d-orbitals split under the influence of the presence of a set of ligands. And this splitting I am referring to is an energy splitting.

We are talking once again about how we can use energy level diagrams to understand and interpret the properties of molecules.

And today in particular we are going to be thinking about how we can go from the angular properties of the d-orbitals all the way to some of the magnetic and spectroscopic or color properties of ions that contain these d-block transition elements.

And so, you will remember last time on Monday, we looked at placing ligands at positions one through six on the octahedron in reference to our coordinate system that we had chosen x, y and z here, as specified.

And what we were doing was, at each of these positions that corresponds to a ligand atom, evaluating each of the d-orbitals for the value of theta and phi that is found at that ligand position.

And so, I am going to put up part of the table that we generated last time.

And that part will correspond to ligand position where we have ligands one, two, three, four, five and six. Those six ligand positions.

And two of the d-orbitals here, d_{x^2} and $d_{x^2 - y^2}$ were found to give non-zero values at these six ligand positions that correspond to an octahedral complex.

The other three d-orbitals gave zero at those positions because all six of these ligands lie on nodal planes of xz , yz and xy .

And what we are doing is just writing down, in tabular form, the relative magnitude of what you get if you evaluate the orbital at those ligand positions. We had one in positions one and six, which are on the big lobes of d_{x^2} along the z-axis.

And we set that to one because that is the largest value that we get when we evaluate any of the orbitals.

And then, relative to that, these ligands two through five that are in the xy plane and which interact with the torus of the d_{z^2} orbital in the xy plane have a value of one-quarter of what it is along the z-axis.

And then $d_{x^2 - y^2}$ evaluated at positions one and six gave us a zero.

And that is because positions one and six fall on the z-axis, which is actually an intersection of two nodal planes for the $d_{x^2 - y^2}$ orbital. And then here we have at positions two through five three-quarters.

And if you are having trouble understanding what these numbers mean, remember that we started out with a sphere, so we are interested in seeing essentially what the probability is in finding that electron in that particular d-orbital at that point on the surface of the sphere.

And so what this is saying is that, if you will, the radial probability of finding an electron in d_{z^2} at the torus at some distance from the center is one-quarter what it is along the z-axis at the same distance from the center.

And then, at that same distance, if we are in the xy plane along x or along y , because that is where the lobes of $d_{x^2 - y^2}$ extend, that probability drops to three-quarters relative to the two big lobes of d_{z^2} along z .

You can think of it as telling you about the size of the lobes.

And, accordingly, the way that these lobes of the d-orbitals can interact with the ligands at these positions on the surface of the sphere coming right out of evaluating the angular parts of the wavefunction.

And then there are other important coordination geometries that we have to consider.

Because coordination number six, which corresponds to the octahedron, is relatively common. But coordination number four is also quite common.

And one of the important coordination geometries for coordination number four is a tetrahedral coordination geometry. The tetrahedron is not limited to being important in organic chemistry. It is also important for coordination chemistry.

And you will recall that when we look at a tetrahedron we talk about ligands at alternating corners of a cube.

And I will call these ligand positions seven, eight, nine and ten. And, if we have a tetrahedral metal complex with four ligands, be they water ligands or chloride ligands and be the central metal ions, something like cobalt 2 or nickel 2, a tetrahedral array like this is produced.

And we can go ahead and evaluate the d-orbital wavefunctions at theta and phi values that correspond to these positions, seven, eight, nine and ten, all at the same distance from the center.

And then we can generate a similar table where we have our ligand position and our set of d-orbitals.

And I will start here with dxz , dyz and dxy , and over here dz^2 and $dx^2 - y^2$. And we need our ligands positioned at seven, eight, nine and ten, which are these alternating corners of the cube, which is the tetrahedral geometry.

And what we find, when we go through and evaluate for those theta and phi values that correspond to these ligand positions using our polar coordinate system and then scaling it the same way that we do over here for the octahedron, is that all of these values come out to be one-third.

Notice that, in the case of the octahedron, we are interacting with some of the lobes.

Like the lobes of d_{z^2} , the large ones, directly along the axis that makes it a pure sigma interaction, a cylindrically symmetric interaction. A big lobe of d_{z^2} and a ligand coming in along the z-axis.

But if you think of the positions of the lobes of the xz , yz and xy orbitals relative to these ligand positions, seven, eight, nine and ten, the interaction is kind of oblique.

It is not zero. We are not on a node, but it is pretty small.

The overlap is not going to be as good. And it evaluates to one-third for all of those positions. What we find is that while xz , yz and xy were all zero over here for the octahedral case, over here, for the tetrahedral case, they are all the same again but they are not at zero.

They are at one-third. And then, for $x^2 - y^2$, remember $x^2 - y^2$ has its lobes along x and y . What that means is that ligands seven, eight, nine and ten actually lie on a nodal surface of the $d_{x^2 - y^2}$ orbital.

And that means that this is zero, this is zero, this is zero and this is zero.

And the amazing thing about the math of the tetrahedral geometry is that these ligands, seven, eight, nine and ten also lie on the nodal surface of d_{z^2} .

Remember that d_{z^2} looks like this and has our opposite phase torus in the middle and then has a conical nodal surface. We actually went ahead and --

If you set the equation for d_{z^2} equal to zero and solved for it, we found this angle here.

We found that angle. And you will remember that that was the arch cosine of root three over three. It turns out that that value is exactly half of the tetrahedral angle, which is the angle between seven, the center and eight.

And, because of this, all ligands, seven, eight, nine and ten lie on the conical nodal surface of d_{z^2} such that we get zeros here, too.

One thing that relates very nicely, the orbital picture for the tetrahedral case for the octahedral case, is that z^2 has the same energy as $x^2 - y^2$. When you sum over all the ligand positions, we are going to get three here and we are going to get three here.

And xz , yz and xy all have zero.

And over here xz , yz and xy all have four-thirds. And z^2 and $x^2 - y^2$ both have zero. And so I will redraw that over here.

What we are doing is drawing up d-orbital splitting diagrams for two different possible coordination geometries for a coordination complex.

Let me just make that very clear.

And I have my energy units here, zero, one, two, three. And this energy level diagram looks like this for the octahedral. And we symbolize the octahedral geometry with this O_h for octahedral.

And we have here an energy splitting.

We have a triply degenerate set of orbitals which we recognize as xz , yz and xy . And the name that we give to that triply degenerate set is t_{2g} . This t_{2g} triply degenerate set, for this whole set, is the t_{2g} set.

If I use that label t_{2g} you should remember the specific d-orbitals that contribute to the t_{2g} set and make up the t_{2g} set.

Up here we have the d_{z^2} and the $d_{x^2 - y^2}$ at the same energy, which are three relative energy units here. And those two together constitute the e_g set. And I will often write that with a star because we are going to find out later, when we do the molecular orbital theory of coordination complexes, that these are antibonding.

And the reason they are antibonding is because, if you go over here and look at it, if you have a ligand that wants to act as a Lewis base with respect to d_{z^2} then putting an electron in d_{z^2} leads to repulsion of that ligand generating antibonding characters.

You want your Lewis acid to have empty orbitals to receive lone pairs of electrons.

And, if instead they are populated, that corresponds to antibonding character, much like we have talked about for other types of molecular orbital diagrams.

This d-orbital splitting diagram for O_h is really a simplified molecular orbital diagram for the molecule in which we just look at those orbitals that derive from the set of five d-orbitals on that metal ion.

Because these are the orbitals.

And, together with the electrons that occupy them, they control the properties of color and magnetism that we will be talking about for the rest of today. And let me remind you here that we have a name for the magnitude of this splitting which is called ΔO for octahedral.

And then we also have the tetrahedral case. And how do we get the diagram from this?

We just sum over the contributions from each of the ligand positions. In tetrahedral, there are only four ligands.

For xz , yz and zy we have to sum up four times one-third, and that gives us, for that set of three orbitals using the same energy scale as over there, three orbitals at a value of four-thirds and two orbitals down here at our zero of energy.

And these will be d_{z^2} located on that node and $x^2 - y^2$. Whereas, up here we have xz , yz and zy . And these get the names e and t_2 in the tetrahedral geometry. And the splitting between the levels, the doubly degenerate and the triply degenerate pair of energy levels, is here referred to as Δt .

And from the math of these two tables and the magnitude of this splitting being three relative to this one being four-thirds, you can easily derive the relation that Δt is equal to four-ninths of ΔO .

One of the neat things about this result qualitatively is that if you have more ligands, six versus four, you have a larger splitting of the energy levels.

And that corresponds to putting more Lewis bases, more negative charges around that sphere that we talked about in the coordination sphere.

And also if you have interactions between ligands and metal d-orbitals that are end on sigma symmetry directed at each other you get bigger splitting because that leads to better overlap than the type of oblique overlap that you get if you have a ligand at a position such as seven relative to an orbital like dxz .

You can now see that to fully appreciate this you really have to have a very good grasp of the nodal properties of the d-orbitals.

This is why I am going to re-emphasize that you should spend some time on the computer visualizing these things and rotating them around and seeing where these ligand positions for these different coordination geometries are with respect to each of the five d-orbitals.

That is quite important.

Also you are going to see that you could consider other possible coordination geometries that involve ligands at these positions or at other positions. For coordination number five, you could have a trigonal bipyramid coordination geometry.

And you could go ahead and evaluate the d-orbitals at the relevant positions. You would already have three of them here because in a trigonal bipyramid you would have ligands at positions one and six and two.

And then two more back here at 120 degrees to two but in the xy plane.

So you can do a trigonal bipyramid the same way and generate the d-orbital splitting diagram for it. You can also go ahead and do a d-orbital splitting diagram for a different geometry corresponding to coordination number four, which would be the square planar coordination geometry.

If you just took ligand positions two, three, four and five you could generate a diagram.

And that diagram would be relevant for systems that do have square planar coordination around a metal center, and these are actually fairly common.

Those are the four coordination geometries, octahedral, tetrahedral, trigonal bipyramid and square planar that are all pretty commonly

encountered and that you can actually interpret pretty nicely using the d-orbital splitting diagrams.

Now, one of the properties that we are going to want to interpret will be the magnetism.

And, in talking about the magnetism of coordination complexes, we are going to start by mentioning two terms that you have probably heard but I would like to define explicitly today.

One is paramagnetic. That term is given to substances that are attracted into a magnetic field. It is somehow a bulk phenomenon that we are going to relate to properties of d-orbital splitting diagrams.

And systems can also be described as diamagnetic.

And there are many other types of magnetic behavior that we won't be discussing.

And that means that the substance is repelled out of or away from a magnetic field. And one thing that you should keep in mind is that the magnitude of paramagnetism is usually orders of magnitude greater than the magnitude of diamagnetism.

So, this is much larger.

And what this means is if a substance behaves as a paramagnet you can often neglect its diamagnetism that also may be present, also must be present. The substances that are paramagnetic are also diamagnetic, but the paramagnetism is much larger in terms of its order of magnitude and wins out.

If you want to measure one of these quantities for a system that which is far more difficult to measure is the diamagnetism because it is a much smaller number.

And then I want to bring up this quantity S .

This is the spin quantum number.

And you can readily calculate S from looking at a populated d-orbital splitting diagram because it will be the total number of electrons multiplied by one-half which is the spin per electron.

If you are confronted with a particular coordination complex, the kind of thought process you will need to go through is what is the coordination number, what is the coordination geometry, what does the d-orbital splitting diagram look like, how many electrons do I have with which to populate the d-orbital splitting diagram? After I have figured out how to populate the d-orbital splitting diagram, how many of those electrons are unpaired? That gives me this.

I can then calculate S . And, if I have S , I can make a prediction about the value of something called the spin-only magnetic moment.

Let me mention one more thing back here, and that would be the units.

When we talk about magnetism, we are going to be using units.

This is called the Bohr magneton. It is sometimes written as μ_B . It is also sometimes written as capital B , capital M . That is the Bohr magneton.

And it is equal to 9.2741×10^{-24} joules per tesla.

This is the value of the Bohr magneton. And the Bohr magneton is the unit also of our magnetic moment.

And, in particular today, I am going to be talking about the spin-only value of the magnetic moment.

So we are going to be making predictions using spin-only considerations. And for those considerations, we need to be able to calculate S .

And we can do that pretty quickly after we have it correctly populated, correctly chosen d-orbital splitting diagram for the system.

And so the spin-only value for the magnetic moment is given by this formula, which is μ is equal to 2.00 times the square root of S times S plus one.

And, in this formula, this part, this square root of S times S plus one from the quantum mechanics is the value of the angular momentum, the electron spin angular momentum.

And this value 2.00 , I am calling it 2.00 .

It is actually a number that differs only very slightly from two. So we can, for most purposes, use 2.00. This is called the gyromagnetic ratio of the electron.

And, as its name implies, it is the ratio of the angular momentum to the magnetic moment for the electron.

This is our conversion factor to go back and forth between angular momentum and magnetic moment. And that factor is the gyromagnetic ratio for the electron. You will see this as gamma sometimes. And, for the free electron value, it is a number very close to two.

And so, if you think about different ions that could be at the center of a coordination complex, you wonder, well, what are my possible values for the spin-only magnetic moment as given by this formula? Well, we can make a table for that.

We have the number of electrons that are unpaired, remember. And then we will be able to calculate S.

And then we will want to get mu, which is this spin-only value calculated according to that formula.

And ions from the part of the Periodic Table that we may consider working with can have one, two, three, four, five, six, up to seven unpaired electrons.

These numbers, like six and seven, are more important for the lanthanide ions in systems with f-electrons than for systems with d electrons.

But, nonetheless, we can easily make these predictions the same way. And so S would be one-half for one electron, one, then three-halves, then two for four unpaired electrons, then five-halves for five unpaired electrons, then three and then seven-halves finally for seven unpaired electrons.

And if you put this into this formula, you would see that for one unpaired electron it would be one-half times one-half plus one square root times two.

That would be square root of three, so this would be a spin-only magnetic moment of 1.73. And then for S equals one, we actually have a value of about 2.83.

And then for three unpaired electrons we have a value of let's say 3.87.

And then for S equals two, or four unpaired electrons, we have a value of 4.90.

For the spin-only magnetic moment, if you go through with these values of S, these numbers of "unpaired electrons". Let's just make sure we are very clear on that.

And then 5.92, 6.93, 7.94 approximately. You can check those numbers, but they are approximately right.

And in each case what you are seeing is the spin-only prediction for the magnetic moment is always, in units of Bohr magnetons, a little less than one plus the number of unpaired electrons.

It is not like you have four unpaired electrons so your spin-only magnetic moment is around four.

It is actually a little less than five. And that is because of the quantum mechanics of the electron spin angular momentum.

And this kind of consideration here leads you into thinking about what happens with different DN counts for a particular type of metal complex.

This means that we are going to attack and address the high spin/low spin problem.

These systems are not so terribly difficult, but let's face it.

Once you have been presented with a particular coordination complex and you think you know the geometry and you think you know the d-orbital splitting diagram that corresponds to that geometry and you think you know how many d electrons go into that diagram there is one more thing.

And that is sometimes you have to figure out if it is high spin or if it is low spin.

And what that means is for a particular d end count there might be two possible choices over here, depending on how the electrons occupy the orbitals.

And so let's look at an example of this. Again, we are really focusing a lot on energy level diagrams. Sometimes we focus on molecular orbital diagrams. Right now we are using these d-orbital splitting diagrams.

And I will give you an example that is octahedral.

And this is a species that we looked at in a recent demonstration in class, which is hexaquo meaning six waters around an iron two plus in an octahedral array. This will be our metal complex for which we will draw the d-orbital splitting diagram.

It is an octahedral complex so we draw our diagram like this.

And of course we have t_{2g} and e_g^* levels that we can populate with our d electrons. And we are going to need to figure out how many d electrons we have to put into this diagram for the octahedral system.

The oxidation state of the iron here is plus two.

And you can tell that because the way you tell oxidation state is to take into account both the charge on the ligands. Chlorides, for example, are minus one. Because water is a neutral molecule it is simply neutral.

And then you have to also take into account the charge on the whole ion.

So this is iron two plus. The iron and the plus two oxidation state with six neutral ligands. If I had six NH_3 ligands in the same charge on the ion then it would still be iron plus two.

And you are going to get some practice figuring out oxidation state, because if you cannot do that correctly you cannot identify the number of d electrons to put into the diagram correctly. And this is iron plus two.

You need to know that iron is in Group 8 of the Periodic Table.

The equation for number of d electrons here is eight minus two equals six. If it is in Group 8 that means that an iron atom has eight valence electrons, the same way that carbon has four valence electrons or oxygen has six valence electrons.

And in Group 8 of the Periodic Table we are subtracting two from the eight valence electrons because there is a two plus charge on the system.

That leaves six valence electrons on the iron. And that means this is what we call a d^6 system. By convention, we are considering all the valence electrons that remain after the metal has been oxidized to plus two as d electrons meaning they are going to go into our d-orbital splitting diagram.

Now, the reason we do this, in fact, is because in ions like this, the d-orbitals are the orbitals on the metal, on the iron that are the lowest in energy.

After, in the case of iron, iron has principle quantum number three. There is also a 4S and a 4P set of orbitals available to iron, but they are much higher in energy.

We are simplifying the system and just looking at what happens with the five d-orbitals which are the lowest valence energy orbitals available to the iron.

Just like a carbon has a 2S and a set of three 2p orbitals, an iron has a set of five 3d orbitals, a 4s and three 4p orbitals. But those S and P one are higher.

We are just focusing on our d-orbitals here using our d-orbital only splitting diagrams with which we have six electrons for population of a diagram.

And so what you see immediately is you will identify with the notion that there are two ways to populate this diagram with six electrons.

Because we can do this.

Here we are following Hund's rule of maximum multiplicity trying not to pair up any electrons until we run out of spots for them and so we have to.

There is one way to populate the diagram. Two electrons in eg^* . Four electrons in t_{2g} .

One of them has been inverted relative to the other five because you cannot put two electrons in the same orbital unless they have different spins.

And, finally, we could populate the diagram this way. The case on the left is what we call high spin.

The case on the right is what we call low spin.

And, as you think about it, you will realize that the high spin/low spin problem only arises for certain DN counts.

It doesn't arise, for example, for d_1 because we would just put one electron down here in t_{2g} and that is not a problem.

And you will see that, as you run through the d_1 all the way up to the d_{10} .

DN counts can go from d_0 to d_{10} , and that is the limit of the possibilities here. Zero, one, two, three, four, five, six, seven, eight, nine and ten. Here I have chosen a d_6 case to illustrate the high spin versus low spin dichotomy.

And you might wonder when do you --

Well, let me get back to that in a moment. And let me just say here that we have four unpaired electrons in d_6 high spin. We have one, two, three, four. That makes this an S equals two case.

And, over here, we have S equals zero. And so this one on the right, this low spin case is S equals zero. We would say that this is not paramagnetic.

It is going to be only diamagnetic. It has no unpaired electrons to give it a magnetic moment according to the spin only formula that we looked at over here.

On the other hand, over here we have an S equals two state that predicts a magnetic moment of 4.90 Bohr magnetons. And experimentally μ is found for this system to be 5.1 Bohr magnetons.

So we say this one turned out to be high spin.

And in a little while we will be talking more about what are the physical factors that determine whether a system is low spin or high spin. Remember, we have this ΔO here.

And there is not one value for ΔO , and this is something I am going to emphasize again in a moment.

ΔO varies according to a number of factors, and these factors include the specific nature of the ligands. It includes the charge on the metal center. It includes the specific metal that you are using.

And at some point if ΔO gets bigger and bigger and bigger and exceeds what we call the pairing energy --

This pairing energy is something I will talk more about later, but it is the energy required to put two electrons in the same d-orbital.

If you get to a condition where ΔO is greater than this pairing energy, in other words, there is a big splitting between t_{2g} and e_g^* then the electrons will prefer to pair up down here in the t_{2g} .

Whereas, if you think of it going to the limit of an infinitely small ΔO they would have S equals two.

Because the gap between t_{2g} and e_g^* in the limit of vanishing ΔO , for example, when ligands go to an infinite distance away from the metal center they would then, in that limit, have all five the same energy.

And so your S would naturally equal two.

If ΔO is much greater than the pairing energy giving a large value of ΔO then that favors low spin. Factors that give rise to large values of ΔO favor low spin, and I will talk about a few more factors like that in a moment.

Here is a brief introduction to the magnetic properties of coordination complexes.

And I want to show that we can use the same types of diagrams to talk about the colors of transition metal complexes. We looked at the color change in that demonstration I showed you.

And one of the really fascinating aspects of transition metal chemistry is the colors that arise because of absorption of a photon coincident with promotion of an electron from t_{2g} to e_g^* .

And so we will talk briefly now about electronic / absorption spectroscopy.

And the most important thing I want to impart to you here is a selection rule wherein ΔS is equal to zero.

This is the spin selection rule.

And this means that when a photon comes in and interacts with d electrons, in a system of the type we are discussing, that photon can be absorbed coincident with promotion of an electron from t_{2g} to e_g^* , as long as it doesn't violate this spin selection rule.

And that means that the number of unpaired electrons should be the same in the system before the photon is taken up, as it is after.

And so here is an example of that, a simple example. Here is an octahedral system, titanium with six waters and a three plus charge. Titanium is in Group 4 of the Periodic Table.

Our water ligands are neutral with three plus charges to be subtracted from four.

We have a d^1 system. This is one of the simplest cases for talking about electronic absorption spectroscopy and is the first thing that you encounter in your textbook. By the way, let me just remind you that right now you should be reading Chapter 16 in your textbook that deals with coordination chemistry, electronic structure of d-block elements, colors and magnetism and so forth.

And the ground state here is one in which t_{2g} has a single electron in it for this d^1 ion and e_g^* is vacant.

And, if that system, in the case of titanium three aquo and aqueous solution, is a pale blue color, a pretty pale blue --

If a photon comes in of the appropriate energy ΔO to promote the electron into e_g^* then that transforms this system into an excited state as follows with a configuration $(t_{2g})^0$ and $(e_g^*)^1$.

These diagrams, just like the molecular orbital diagrams we developed for diatomic molecules, can be associated with configurations.

And this transition can be written as $(t_{2g})^1 (e_g^*)^0$, photon in, electron promoted into e_g^* $(t_{2g})^0$ and $(e_g^*)^1$ now corresponding to the excited state.

And this excited state is produced in a vibrationally excited manner.

And it and the ground state interact with the environment in different ways such that the absorption spectrum for a system of this type gives rise to not a sharp but a broad peak.

And, in fact, the spectrum would look something like this. Going from 200 to 700 nanometers in wavelength, you would see a profile like this with one broad peak somewhere in the red such that we would be behind the pale blue color of these solutions of aqueous titanium three.

So this would be an absorption spectrum and this is wavelength down here.

And this is the peak for what we call this d-d transition from t_{2g} to e_g^* . There are a lot more subtleties on this, which is where I will begin on Monday. Have a great weekend.