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5.112 Principles of Chemical Science, Fall 2005
Transcript – Lecture 30

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Some of you will recognize this molecule that I have rotating up on the screen because it is one of the coordination complexes of Werner that we talked about last time. And Werner, of course, was well-known. And some of you probably read his biography over the last few days on the Nobel Prize website. Well-known for his theory that broke down the preconceived notions that had been prevailing at that time concerning the structure of systems that have unusual salt-like behavior in some cases but that contain the 3D elements.

I am focusing on 3D, but this is also true of 4D and 5D elements, the transition metals. Elements like titanium, vanadium, chromium, iron, cobalt, nickel, etc. This molecule here, that you see spinning up on the screen, is being represented here on the screen in one of these kind of arbitrary forms wherein the cobalt center at the middle of the molecule is just a round ball of an arbitrary size.

And then this particular molecule that contains a cobalt three ion is surrounded by a complement of six ligands. We have three chloride ligands that because this program chose to do so colored those chlorides the same as the cobalt, not what I would do, and put the three ammonia ligands, colored the ammonia nitrogens in dark blue and the ammonia hydrogens in white.

And we talked about the fact that these transition elements, in fact, these three plus ions of metals like cobalt can behave simultaneously as Lewis acids toward a multitude of Lewis bases, here six. This is a time six Lewis acid in the middle and six Lewis bases, which are three chloride ions and three ammonia molecules oriented around it, in an arrangement that is quasi-octahedral.

Because the positions of the three nitrogens of the ammonias that are interacting with the cobalt center and the three chloride ions are located near the vertices of a regular octahedron. So we will be taking

use of the geometry of molecules like this in discussing electronic structure properties of these molecules today.

We will be doing that beginning today. And that will be important to understanding the magnetism and the color and also the reactions of molecules like this. Now, one other arbitrary thing that this program did is it chose not to draw lines between the cobalt and any of the six ligands. But normally, when you see these molecules drawn in textbooks, you will see that the lines drawn are the same as the lines between the nitrogens and these hydrogens.

So we would have to add six more lines to this drawing to get the typical textbook representation of a molecule like this. But, still, that would be a somewhat arbitrary representation. And so, I would like to show you a less arbitrary representation. And we will do that forthwith. And this one has to do with looking at the same molecule but represented as an electron density isosurface. And that isosurface will be colored according to this function that tells us about the propensity to pair electrons in 3D space. And so you will recall that when we talk about coloring electron density isosurfaces in this way, so this now is a physically important kind of representation of this coordination complex, this color scale will run from red all the way to blue.

And at blue is where you find regions in space where you are most likely to find pairs of electrons mapped onto the value here, colored mapped onto the value of an electron density isosurface. Here the value of the electron density that is present for every point represented on this surface is 0.11 electrons per unit volume. And so what you see here is that, in fact, the electron density does become low as you move from the cobalt in the direction of any one of the ligands.

But the lone pair on each ammonia is certainly polarized in the direction of the cobalt center. And the cobalt center is not uniform in terms of the way that electron density is organized around it. You will see that right on the metal center we see red. And then sort of at the corners of a cube you see this yellow or green color on the cobalt, and that is very significant.

And what we are going to be today is we are going to try to understand what happens when you put a set of ligands into an octahedral array around a central metal ion that has d-electrons and d-orbitals to play with. And, in fact, what you will see is that the oxidation state of the cobalt center here is plus three. That is why I am

referring to it as a cobalt plus three ion. And because cobalt is in group nine of the Periodic Table you then know that there are six valence electrons on the cobalt center that you have to put into orbitals.

And so what we are really seeking to know is how can we get an energy-level diagram for a system like this so we will know how to put those six electrons into that diagram, the ones that are mostly localized on the cobalt, and make predictions on whether the electrons should be paired up or not, for example. We saw with homonuclear diatomics, like the dioxygen molecule, that electrons are not all paired up.

Two of the electrons are unpaired. And, when we have six electrons to put into an energy-level diagram for the cobalt ion, we are going to wonder just what the case is. How many energy levels are there and where do we put the electrons? And so we are going to need to very briefly review what I did at end of lecture last time. And that has to do with the properties of the five d-orbitals.

Because, in order to answer the kinds of questions that we are posing about energy levels of metal ions that are transition metals, we are going to really need to know very well the nodal properties of these d-orbitals. And so remember the m quantum number here can be zero for the d_{z^2} . It can be plus one for the d_{xz} .

And plus two for the $d_{x^2 - y^2}$. Minus one for the d_{yz} orbital. And minus two for the d_{xy} orbital. And let's draw those. d_{z^2} is an interesting one.

And, because it is distinct from the other four d-orbitals, we are going to be spending more time on it today than the others. What it has, these are the x , let's say y and z axes here, is a positive lobe along both plus and minus z . So it looks like a p-orbital so far, except that we have the same sign both in plus or minus z .

And then what we have is a very interesting toroidal shape that goes around in the xy plane all the way around in a cylindrically symmetric manner. And so if you were to look down z onto this orbital it might look something like this.

Like that. It would be cylindrically symmetric about z . And that was another feature that I didn't get to add to this diagram at the end of last hour, which is that because of this property, this m equals zero that means this is a sigma orbital with respect to the z -axis.

Cylindrically symmetric about z . And then let's go to the xz , since I am making this x , y and z over here. The dxz has four lobes and they are in between the x and z axes, as I am trying to represent here.

These two are kind of coming out in front here and these two back behind. And then the phases go as follows. Unshaded is again plus. And then we have the x^2 minus y^2 orbital, which has four lobes.

In fact, the shape of xz , x^2 minus y^2 , yz and xy are all the same. It's just that they point in different directions in space with respect to the Cartesian coordinate axes. x^2 minus y^2 , like dz^2 , is an orbital whose lobes point along the coordinate axes like this. And it is minus along y , as the name suggests, and plus along x , as the name suggests.

That is our dx^2 minus y^2 orbital. And then yz is like xz , but let me finish this part here. If dz^2 is sigma with respect to z , and you imagine looking down z onto dxz , what would that be with respect to z ?

Anyone. Pi. Thank you. That would be pi with respect to z , because the yz plane is a nodal surface for this d-orbital, as is the xy plane. And that is what we are trying to do here, is become familiar with these orbital surfaces. And, accordingly, now, if you look down z onto the dx^2 minus y^2 orbital, you are now going to see two nodal surfaces when you look down it that way.

Because you are going to see that there is one located over here. That is a plane that contains the z -axis, but it bisects the x and y axes. And then there is another one over here, but that is 90 degrees to the first one. And that makes this one delta with respect to z .

Delta is when you have two nodes that contain the z -axis and if we are looking down that z -axis. And then over here the dyz orbital has its four lobes between y and z like that. And it is positive between y and z and negative over here, as I am shading.

And this one, like dxz , is pi with respect to z . And then over here we have a dxy orbital as our final orbital. And what you might be able to guess, we have a sigma with respect to z , we have a pair of pi with respect to z for m equals plus and minus one. We also must have a pair of delta with respect to z for m equals plus and minus two.

And that means that the dxy orbital, like dx^2 minus y^2 , must lie in the xy plane. And, in order to be orthogonal to dx^2 minus y^2 , we are going

to have to rotate it such that its four lobes point now between the x and y Cartesian coordinate axes like this, although I am trying to improve on that with my coloration. That is like that.

Again, this is an orbital perpendicular to z and which has delta symmetry. And now the two nodes are, in fact, the xz and yz coordinate axes. Indicating those nodal planes there. This is certainly the basics for what you need to know about the d-orbitals. And just briefly I would like to switch to Athena terminal here to show you that there are ways for you to go ahead and visualize the orbitals.

And I am going to make this information available to you so that you can go ahead and do this yourself in order to visualize these in a way to take you right from the equations for the orbitals to their graphical representation. I think that is important to get a good understanding of orbitals.

Let's zoom this a little bit so that you can begin to see it.

This is a worksheet put together that, in fact, contains all the functional forms for the d-orbitals. Let me see. Where is that? Here we go.

And you can look at this with Maple on Athena. And then you can look at the equation that represents the angular part of the wavefunction for the orbital that you are interested in. And then you can go ahead and plot it. And you can plot it in such a way that the function is animated. And, rather than just seeing it projected on a board as well as I can draw, you will be able to see it drawn up graphically. In fact, these come from the solution for the Schrödinger equation for the hydrogen atom. And the angular part of these wavefunctions that is going to be oh so important to us is something known as the set of spherical harmonic equations. And that should reference you to this issue of standing waves that we have discussed. Let's just see what we can do here.

Sometimes I am not so good at using Maple up in front of the class.

What you are seeing is we are getting representations for d_{z^2} . Right here is a way of writing d_{z^2} . You are going to see an important term here, three cosine squared theta minus one. And we will come back to that in a moment. That is the angular part of the d_{z^2} wavefunction.

And then we can look at some of these other ones. You will see that some of the d-orbitals come as combinations of real and imaginary functions that are the solutions to the differential form of the Schrödinger equation. And then we take linear combinations of these to get real forms so that we can get plots that we can look at. And let's see if we can get d_{z^2} here.

There it is. There is a picture of d_{z^2} . And you see, if you are using this Maple worksheet, that you can actually rotate that around and animate it a little bit. You see that we have this torus that is in the xy plane. And you have the two large lobes that extend up along plus and minus z. And so I am going to encourage you to go ahead and look at that worksheet, which will be available from our website.

Go ahead and look at some of the functions. And if some of you are interested in higher orbitals, the f-orbitals are also available in this worksheet. So you can visualize the f-orbitals that are important for understanding the chemistry of elements like, for example, uranium which is a little bit beyond the scope of 5.112. Now let's switch to the document camera.

And, if you could, I would like you to make this part big. This is a table in your textbook that has the angular part of the wavefunctions for various hydrogen-like orbitals. And this is the part that I am most interested in here. If you could just focus in on the d-orbitals over here.

When I was talking about the d_{z^2} orbital a moment ago, I was focusing on this term here, this cosine squared theta minus one term. And here are the other d-orbitals. These are the descriptors for the d-orbitals, zy , yz , xz , $x^2 - y^2$ and z^2 . And I will need to refer to this in a moment, so we will leave this up.

The reason why I have this arrow written into my book here is because these are backwards in the text. This one is actually $x^2 - y^2$ and this one is actually the xy orbital. We figured that out last year when we were doing this lecture. And so your book isn't always right. You should make sure you check. The same is certainly true of your instructor, but we will try not to mislead you. And so now here is the approach that we are going to take.

Let's say that we have our coordinate system, and we want to know how to evaluate one of these d-orbital wavefunctions for a particular point in space. Actually, we are going to want to evaluate the square

of the wavefunction. And so we are going to make use of a Cartesian coordinate system. And we are going to express things in terms of polar coordinates.

Here is a sphere projected onto our Cartesian coordinate system. And some of you will be very familiar with this. We are going to say if you are at a point here in space then we can describe that point in space by a set of variables which will be R , θ and ϕ .

And here is our angle θ . And if we drop down to a perpendicular on the xy plane from our point then we are going to define ϕ as being from the x -axis and going over in the direction of y .

And so, when you look at the d -orbital wavefunctions, you see that they are all written here in terms of just θ and ϕ . And not in terms of R , which is this distance here from the nucleus, from the center of this metal ion that we are talking about. This would be the R .

And what we are going to do is if this point on the surface of our sphere represents one of our ligand atoms, so think back to that complex we were describing a few moments ago, cobalt with three ammonia ligands and three chloride ligands, we are going to approximate each of those six ligands by a point on the surface of our sphere. And then we are going to say if there is a metal at the center, that cobalt ion in particular, what is the probability of finding a d -electron where that ligand atom is?

And, in order to do that, we are going to need to be able to evaluate the wavefunction. And we are making the assumption, for simplicity, that this is a perfect sphere, and also that our coordination geometry is a perfect octahedron. And so we are not going to consider R , because R is going to be the same everywhere. It is just a perfect sphere with one value of R , no matter which ligand position we are looking at.

And so that means we can focus in just on these which are the angular part of the wavefunction for the molecule in question. And so let's see what this means with respect to d_{z^2} .

The probability of finding an electron at some point in space in a particular atomic orbital is proportional to the square of that atomic orbital at that point in space.

That is our probability density. And we encountered that very early in the semester. Now we are going to make use of that to make a plot. We are going to plot this probability density of finding electron in dz^2 as a function of theta. Why can I do that ignoring phi? Well, that is because if you look at dz^2 there is no phi in that equation.

Why is that? That is because dz^2 is cylindrically symmetric about z. And look at how we defined phi. It is as you go in the xy plane around starting from x. Because of the sigma symmetry of dz^2 with respect to z there is no phi dependence of this wavefunction. And that should appear here in the angular form of the description of the dz^2 orbital.

But we do know that dz^2 does depend on theta, because theta starts out somewhere here along, let's say initially theta equals zero would be right on the positive z-axis. And then, as we keep a constant R and we sweep down here toward the xy plane, the dz^2 probability density is dropping off.

And then at some point, when we get to the node here, and we are going to be interested in that, it goes to zero, because that is what happens on nodes, as we continue down toward the xy plane past that node it is going to be nonzero again and rise up as we approach this smaller torus in the xy plane. Smaller than the big lobes that extend up along z and down along minus z. Let's represent that graphically.

Coming down in theta from theta equals zero to some value here, we are going to be interested in just what that value is. And then rising up again to theta is equal to pi over two. Do you see that? This is another way of displaying this property. This is at constant R --

-- and varying theta.

First of all, how can we find out at what value theta goes to zero? Well, we look up here at the function form of the dz^2 . We get nodal properties of dz^2 .

We can pretty quickly see that in each of these we have a factor leading out in front, which is a normalization factor that assures us that the sum integrated over all space of this wavefunction will come out to be one.

If there is an electron in that orbital somewhere, the probability of finding that electron somewhere in space will be one. We have these

normalizing constants out in front that allow for that and ensure that that is the case. But where we actually find the angular dependence is in that second term. Here it is three cosine squared theta minus one.

And what we want to do is say when does this function go to zero? Because when that goes to zero we will have this angle here. If we say let this equal zero, we are looking for the value of the angle theta which corresponds to the node of the dz² orbital.

Remember, we mentioned this last time, because of this cylindrical symmetry of the dz² orbital this really is a conical nodal surface that is above and below the plane here. If you are anywhere on that cone, either in plus or minus z, the value of that dz² orbital is zero. And so we are setting it equal to zero to find the angle theta.

And we can rearrange this and say that cosine squared theta is equal to one over three. And, if we go ahead and solve that, this comes out to the arccosine of root three over three. And the other possibility that satisfies that relation is pi minus the arccosine of root three over three.

And so what that means is that this relation here gives us the angle for that cone in the plus z axis. And then this one down here, pi minus arch cosine root three over three, gives us the angle for that cone down in the minus z axis. And what is this? This is, in degrees, something like 54.476 dot dot dot degrees approximately. That is just how far down you are from the z-axis when you hit that nodal surface of z.

And that number, you are going to see, is kind of a magical number in chemistry. And it will hearken back to some of the things that we have been taking about recently. And, in order to get to that point, I am going to need to now talk about our ligands again with respect to dz².

We are considering now an octahedral metal complex.

This is the type of Werner-esque complex that we talked about last time. You are going to see that we are going to have ligands. We are not really specifying them. We are numbering them and locating them at positions one, two, three, four, five and six relative to our metal center at the middle. And what you might begin to realize is that in order to find out what our energy-level diagram will be that refers only to the five d-orbitals on the cobalt center, or whatever metal center is

at the middle of this ion, is evaluate the square of the wavefunction at each of these ligand positions.

And we are assuming that all the ligands are equivalent. If you think of the ligand as an electron or as a point charge in space then you can imagine that if we have an electron in d_{z^2} up here that it is going to interact strongly and very repulsively with a point charge that would be located at position one.

Whereas, if we instead had a point charge located at that theta angle of 54 point whatever over there that we solved for then, since that is on the node of d_{z^2} , that would be the least possible repulsive interaction that you could get between an electron and an electron in d_{z^2} because it is on the node. And so what we would like to do is to go ahead and solve for some of these things. Essentially, what we seek --

-- is an energy-level diagram.

And so let's write this up here. This is five over 16π . This is d_{z^2} that I am writing up. Three cosine squared theta minus one. And because we are talking about the probability density of finding an electron at a particular point in space, which will mean a particular theta value in our case for d_{z^2} , we are talking about that wavefunction squared.

What we need to do is evaluate it. We have already evaluated it where the node is, but we would like to evaluate it at position one. Because we have a ligand at position one and we need to know what the relative response will be of d_{z^2} to a ligand along position one versus the other five positions.

We can say something about that by symmetry already. And so we are going to find out that the value that you get for evaluating d_{z^2} at position one is the same as you would get for evaluating it at position six. And that is because the big lobes of d_{z^2} are along plus and minus z . That is where ligands one and six are. And then, because the torus is also cylindrically symmetric, two, three, four and five have the same value when you evaluate d_{z^2} at those positions.

But that value is smaller than along z , as illustrated by this graph over here. But we just want to know how much smaller.

And so this is position one. We get a value of five-quarters. And down here, position two, a value of five-sixteenths. I am leaving off a factor

of π . Please don't be concerned by that. But these are the relative values that you get when you evaluate this function at ligand positions one and two, which is all we need to do because of the symmetry of this. Because that value for position one is also true for position six.

So we have positions one and six. And then this is also three, four and five. By doing two quick evaluations at two different theta positions, position one, of course, theta is equal to zero up here. And we evaluate that squared function for theta equals zero.

And we get five-fourths π , but I am leaving off the π . And down here, at position two, we evaluate this for theta equals π over two. Because two, three, four and five are all in the xy plane at 90 degrees to z. So the value of theta anywhere for those four ligands would be π over two. You evaluate this function for π over two and you will get five-sixteenths π .

And I have just left off the π . That is useful. Let's take this one up to the top.

Here we have done one of the d-orbitals. This is d_{z^2} for all six ligand positions.

Now let's do $d_{x^2 - y^2}$ for all six ligand positions.

First of all, $d_{x^2 - y^2}$ has a pretty interesting relationship with ligands one and six. What is that relationship?

Zero. Because $x^2 - y^2$ has two nodal surfaces that intersect along the z-axis. And so those ligands, four and six, lie on a nodal surface.

And so we know that that is going to be equal to zero. If, however, we go ahead and evaluate the square of $d_{x^2 - y^2}$, let me just write it up. And I have to switch it since they are wrong in the book. $\frac{15}{16\pi} \sin^2 \theta \cos^2 \phi$.

We have that. Now, just as we do, we are converting an orbital angular property into a probability density by squaring it. This is what we normally do. When you see pictures of orbitals, they are representing the square of the wavefunction in space. We need to evaluate this as a function of theta and phi in order to find out what --

The first two, one and six, we did by inspection, but what about positions two, three, four and five? In the case of those four, you can

see that where they lie in the xy plane with respect to the $x^2 - y^2$ orbital is all identical to each other by symmetry. Because $x^2 - y^2$ has lobes that extend along x and y and $-x$ and $-y$. And that is where all these ligands lie, at positions two, three, four and five.

We know that θ is equal to what? It is going to be $\pi/2$. And ϕ , of course, can be zero, $\pi/2$, π , and $3\pi/2$ for any of those positions. And what we will find is that this evaluates --

For any of those let's just use $\phi = 0$. This evaluates as $15/16\pi$. And I am dropping the π . Now we have d_{z^2} and $d_{x^2 - y^2}$ evaluated for all six ligand positions. And then let's make a table of this.

d_{z^2} , $d_{x^2 - y^2}$. Let's do xz , yz and xy . And here are our ligand positions. And in the table here we are going to put what these relative evaluated squared wavefunctions are. And the biggest one of all is this one here that we got at position one for d_{z^2} , which is five-fourths.

I am going to divide everybody through by five-fourths so that I can make our biggest value equal to one for simplicity here. And then, when we do that, you are going to see that two gives a value of a quarter. That is position two down in the torus. Three down in the torus is one-quarter relative to that one. Four is one-quarter. Five is one-quarter. And six down in $-z$ is one. So we have evaluated the d_{z^2} orbital squared at the ligand positions one through six.

And these are the relative values that we got for the probability of finding an electron at that point in space given a constant value of R . And $d_{x^2 - y^2}$, we got for positions one and six zero, we just said that. And then, on the same scale here, we get three-quarter, three-quarter, three-quarter and three-quarter.

And then for xz , yz and xy , we have gone through these two steps to do d_{z^2} and $d_{x^2 - y^2}$ explicitly. Now we have to look at where ligands one through six are relative to the nodes of xz or yz and xy .

And what we will find is that, in each case, these ligands lie on nodal surfaces of xz , yz and xy . This is zero, zero, zero, zero, zero, zero, zero and so on. OK?

All the ligands, one through six, lie on nodal planes of xz , yz and xy . Only four the ligands interact with x^2 minus x^2 , ligands two through five, because those are the ones that lie in the xy plane. And they interact strongly, this relative value of three-quarters, but not as strongly as the two ligands in positions one and six interact with the big lobes of dz^2 .

And then also ligands two through five, which lie in the xy plane, interact with the torus of dz^2 , but to a much smaller extent because the torus does not have as great a radial extent. And these ligands are all at the same radius out from the metal center. And so what this corresponds to is now an energy-level diagram as follows. And this is for an octahedral complex --

-- where we have relative energy units of zero, one, two and three. And what we have to do is say that the amount an electron in dz^2 would be repelled simultaneously by electrons in positions one through six would be the sum of these values.

And so we add that up and get, in fact for dz^2 , up here a three. And, interestingly, for dx^2 minus y^2 , if we take a sum of the four interactions that we found that are non-zero, we also get a three for dx^2 minus y^2 . So then the net of all their interactions is the same for x^2 minus y^2 and z^2 .

And then down here, we found that these three orbitals, xz , yz and xy , where the ligands at positions one through six lie on their nodal surfaces, lie right on their nodal surfaces. And so the number evaluates to zero. And so a wavefunction squared will evaluate to zero any time you are looking at a position that is on one of its nodal surfaces. It evaluates to zero. And so we have dxz , dyz and dxy .

And then a diagram like this, which is a d-orbital splitting diagram --

--is associated with a couple of different parameters. One is down here we have a triply degenerate energy level.

Previously, we had only seen doubly degenerate energy levels. Now we have a triply degenerate one composed of xz , yz and xy . And that level we are going to be calling t_{2g} . And then, up here, we have a doubly degenerate level that will get the label e_g . And then, whatever the value of the splitting of these two energy levels, one triply and one doubly degenerate, we are going to give that the label ΔO for octahedral.

And at the beginning of next hour, I will say more about tables like this. And I will show you how you can actually figure out d-orbital splitting diagrams for other coordination geometries and how they compare for a couple of the most popular coordination geometries.