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Over on the side board here, I want to show you a few representation of the ethylene molecule that we were talking about at the end of last hour. When you see representations of molecules that appear throughout your textbook, as well as in this class, I want you to see if you can recognize just what property of the molecule it is that is being represented. In this case here, we have arbitrarily sized spheres that represent the two carbon atoms and the four peripheral hydrogen atoms.

And then, what I have plotted around it is a see-through representation of the electron density at a particular isosurface value of 0.1 electrons per unit volume.

So, that is a representation. And we are going to be seeing a number of different kinds of representations, and you will need to be able to distinguish between them.

And, in particular, we were talking last time about different kinds of bonds. We talked about sigma bonds that were cylindrically symmetric about the internuclear axis of the two atoms that are bonded together.

And we also talked about pi bonds.

And I brought up the pi bond in connection with the ethylene molecule that we were just looking at a different representation of. And so now, let me show you what a pi bond can look like. Here is a representation of the ethylene molecule. Again, I have arbitrarily sized spheres that show us just where the nuclear positions are in three-dimensional space. So, we are talking about the equilibrium geometry of the ethylene molecule.

And what you see here is that if the molecule is lying in the x,y-plane, then each of these carbons has a 2p_z orbital that has a positive lobe and a negative lobe, respectively, above and below the plane of the molecule. And so, normally, when we talk about atomic orbitals, we can reference their phase as either positive or negative.

And we often, in representations like this one, associate the positive phase with one color, here blue, and the negative phase with a different color, here yellow. I can choose whatever colors I want for those, but this is also a type of isosurface. And it represents the in-phase side-to-side overlap of the positive above the plane lobes of the carbon 2p_z orbitals and the negative lobes below the plane of the carbon 2p_z orbitals experiencing side-to-side overlap. And so you see the two electrons that could be paired up, spin paired, one spin up, one spin down in this pi bond, are smeared out both above and below the plane. But there is no contribution at all to the electron density in the plane from an orbital like this.

When we looked at electron density isosurfaces, as we have done a few times in this class, what we are looking at there is an isosurface corresponding to all of the electrons in the molecule. And here, what we are looking at is an orbital that can house just two electrons, one spin up and one spin down, so we are focusing our attention on a function that involves just two electrons bonding in a pi bond that has, as a nodal surface, the plane of the molecule. The plane that contains all six of these nuclei, the two carbons and the four hydrogens. We talked about nodal planes last time. And the issue of nodal planes, nodal surfaces, is going to be very important in today's lecture. Let's go over here and start talking about hybridization.

On this board last time, I gave you kind of a timeline, where we talked about contributions to different aspects of electronic structure theory for molecules by different people, some of who were recognized with Nobel Prizes, others who were not.

And one of those people, namely Linus Pauling, who won two Nobel Prizes, not both in chemistry, came up with this idea of hybridization to solve one of the problems associated with atomic orbital nodes.

And let me work on this and illustrate this to you by taking a pretty simple molecule that has only four atoms.

And this molecule is one that, in fact, we have seen before.

It is an example of a Lewis acid, so any discussion of electronic structure of this BH three molecule better come out with a description of why it is a Lewis acid.

But let me now point something out.

That is, if I make the direction that coincides with this top B-H bond, the x-axis.

And in the plane of the board, the y-axis perpendicular to it, as shown. And then, of course, the z-axis coming perpendicularly out of the plane of the board. Linus Pauling recognized a problem. And let me give these hydrogens descriptors. I will make this one A, this one labeled B, and this one labeled C.

And the problem is that we have a p_z orbital with one positive lobe coming out of the plane of the board, up here.

This would be where the blue lobe is.

And the yellow lobe would be back behind the plane of the board, analogous to the pi bond that we just looked at up on the screen. And what you will see is I can draw it this way. I am rotating this planar BH three molecule.

That allows me to draw the p_z orbital in a way that you can visualize. And the observation that I want you to take away from this drawing is it has to do with the relationship in space of the three hydrogen nuclei as an important

property of the 2pz orbital.

What we can say is that these three hydrogens, A, B, and C reside in the nodal plane of the 2pz.

They lie in the 2pz nodal plane.

That is, the 2pz on the boron. And the wave functions that these hydrogens bring into the problem of the electronic structure of the BH three molecule are spherically symmetric. They are simply 1s orbitals.

And so, if you draw one of them here, remember that a 1s orbital is spherically symmetric. You can see that any positive reinforcement that would occur by overlap here is equal and opposite to the negative reinforcement that will occur down here. And this is something that is true whenever a hydrogen s orbital lies in a nodal plane.

There is no net overlap-- --between the boron's 2pz and the hydrogen 1s orbitals.

When we try to describe the bonding in this molecule, we cannot have any bonds that involve 2pz and any of the three hydrogen 1s orbitals because there is no net overlap between them -- -- because those spherically symmetric orbitals lie in the nodal plane of 2pz.

And that means, further, that we need to form three in-plane bonds.

And that is the xy plane in plane bonds.

And these three bonds must be equivalent.

And what is interesting about the fact that they must be equivalent is that what are the three orbitals that the boron has that are in the x,y-plane, the three valence orbitals?

There is the 2s, the 2px, and the 2py.

Three orbitals that are not identical to one another, yet we need to make three identical bonds because all the studies that we do on the BH three molecule tells us that each of these bonds are the same length, the molecule has the perfect symmetry of a Mercedes Benz symbol, it's trigonal planar. It has this three-fold rotational symmetry to it. And so somehow, using a 2s, a 2px, and a 2py, we need to make three equivalent bonds. This is an energy level diagram. And so, Pauling came up with the idea of promotion. And promotion will correspond to the following. I can draw 2px, 2py, 2pz, and 2s. And I can populate with electrons. The boron atom has three.

Now I have put in three electrons into this energy level diagram for the boron atom.

And now, this concept of promotion kicks in -- -- and reorganizes us electronically, as follows.

According to our discussion, we need three equivalent orbitals down here with the three electrons in to pair up with the three electrons that come into the problem from the three hydrogen atoms. At the end, we will show how those electrons from the hydrogen atoms come in and pair up with these three electrons on a promoted boron atom.

Up here, we have the boron $2p_z$ orbital.

That stays by itself. And down here, we are going to have a set of sp^2 hybrids.

The idea is now somehow we are going to get three orbitals down here by mixing one part s and two parts p .

And, if we do this correctly mathematically, these will have the right orientation in space to be hybrids that have proper directionality for good overlap with our hydrogen $1s$ orbitals. These are going to be three equivalent hybrids.

How do we do that? Well, we are going to get our equations for hybridization.

And we are going to develop these using some of the results from quantum mechanics, which is what Pauling did.

And essentially, what we are going to do is seek equations that have one part s and two parts p , each of them, but which point in the correct directions in space for making three separate two electron bonds between the boron and the three hydrogens.

And so, I will just call them sp^2 of A, because we are going to need one that points toward that A hydrogen, which is along the positive x -axis, we are going to need one that points toward the B hydrogen, and we are going to need one that points toward the C hydrogen. And the idea here is that we are going to have some amount of the boron $2s$, p_x and p_y -- -- because p_z is not contributing to these three hybrids.

And each one of these is going to have some quantity of the three orbitals that we have available.

And what you need to keep in mind here in setting up equations like this is that p_x has a definite spatial orientation with respect to the coordinate system that we have chosen. And so does p_y .

And the way that we will make this come out using our blue chalk is to note that we have a coefficient C_1 , C_2 and C_3 . Our job is going to be to find the values of these coefficients, C_4 , C_5 , C_6 , C_7 , C_8 , and C_9 .

We can use the rules of quantum mechanics, and I am going to summarize a few of these rules for you before this lecture ends, to find the values of these constants.

Let's go over here and begin.

Let's make note of the dictates of symmetry.

I will reference symmetry a couple of times today in class in working on this problem of finding those coefficients, one through nine. The neat thing is that the 2s orbital centered on that boron, which is going to be participating in these hybrids that are going to point toward hydrogens A, B, and C, that 2s orbital is spherically symmetric. Its wave function is the same as you go radially out from the boron center in any direction into space. What that symmetry consideration dictates is that there will be the same amount of boron 2s in the hybrids for A, as for B, as for C.

And what that means is that C_1 is equal to C_4 is equal to C_7 .

And we are going to need a value for this.

And we can get a value for that by taking into consideration something called unit orbital contribution.

What that says is that we have to use the boron's 2s orbital completely and identically once in that set of three equations.

In other words, we are going to distribute it evenly among those three hybrids.

And we have to distribute all of it evenly among those three hybrids. And here we are going to be interested in the square of the coefficients.

And that is because when we talk about atomic orbitals, we know that the probability of finding an electron in that orbital is related to the square of the wave function.

And so, normally when we plot orbitals, like I just did with the pi bond of ethylene a few minutes ago, we are making an isosurface that corresponds to some percent probability of finding the electron at that point in space.

So, we are interested in probability distributions.

And these are related to the square of the wave function.

Here, for unit orbital, we are going to say that C_1 squared equals C_4 squared. Sorry, plus C_4 squared plus C_7 squared is equal to one. And, therefore, C_1 is equal to C_4 is equal to C_7 is equal to one over root three.

Now, we have found C_1 , C_4 , and C_7 .

And, if we are going to complete sp two of A, get this first hybrid of the three, I am going to go across this way. I

just went down one, four, and seven and pointed out that by the symmetry of the s orbital is due to the fact that the s orbital contributes once, unit orbital contribution, we could get C_1 , C_4 , and C_7 equal to one over root three.

Now I am interested in C_2 and C_3 , so let's draw a little picture.

This, remember, is our 1s orbital on HA.

And what we are trying to do is to construct a hybrid focusing on that top equation that will be directed at HA.

And we are keeping our axes the same as before, so that x points up and y goes to the left, as I am drawing it here. And z would be coming out at us. What I am going to draw now is a picture of the boron's 2py orbital.

And, as I usually do, I am taking the convention that the negative phase lobe of the boron's 2py orbital-- Negative is shaded. That is my convention.

That 2py orbital lies in the xy plane and points along y.

Its positive lobe, in fact, points along positive y. Its negative lobe points along negative y. And what can we say about the relationship of the HA 1s orbital to the 2py orbital of that central boron atom?

Let me phrase it this way. The 2py orbital of our central boron atom has a nodal plane. What is that nodal plane?

xz is a nodal plane of the 2py orbital, right here.

Just like this. And so, what you see is that this HA is not only in the nodal plane of 2pz, it is also in the nodal plane of 2py.

And that means any positive interference by bonding between HA's 1s and the positive lobe of 2py would be exactly canceled by the equal and opposite negative interference between a hydrogen's 1s orbital and the negative phase lobe on 2py.

And that means that we know the value of C_3 .

We can say, therefore, that C_3 is equal to zero.

That is really cool because now we are going to be able to bring in one more consideration and complete the formula for sp two of A.

We are going to be able to use the normalization condition, -- -- which tells us that C_1 squared plus C_2 squared plus C_3 squared is equal to one.

Once we formed this new hybrid by mixing together s and p wave functions, we are going to find that this normalization condition must be satisfied for the hybrid orbital just as it is satisfied for these atomic orbitals.

That is so that the probability of finding an electron somewhere in space associated with this hybrid wave function is one, if there is an electron in this orbital.

That is where this comes from. And we know that C_3^2 is zero. C_1^2 is one over root three. So, we know that sp^2 squared of A is equal to one over root three.

And then we can say that, by virtue of this and the fact that C_3 is zero, C_2 could be equal to either plus or minus the square root of two over three.

And we have to figure out which one of these to use.

Remember that C_2 is the coefficient on p_x .

Let's reference our diagram on our coordinate system.

We have our x-axis and our y-axis.

And we are looking for the sign of the coefficient on the boron $2p_x$ orbital. That is our C_2 coefficient.

And I am shading negative here. And, in order to overlap constructively and form a bond to the 1s orbital of H, we want positive as our coefficient.

Because that is going to make the same phase lobes interact in a sigma fashion. We know that sp^2 squared of A is equal to one over root three times the boron's 2s orbital plus the square root of two over three $2p_x$ orbital.

And now that we have the coefficients on that hybrid orbital, we can draw a picture of what that is.

That is equal to taking the boron 1s orbital here and adding to it the $2p_x$ orbital that looks like this.

This is the conceptual breakthrough that Pauling made.

You could mix atomic orbital wave functions located on a central atom in order to generate these hybrids that have the proper directionality for good overlap with the peripheral atoms that bond to the central atom.

And when I do this, what you can see is that we are going to get constructive interference with the positive lobe and destructive interference with the negative lobe when we add this boron 2s orbital to the boron $2p_x$ orbital. And that should give us something that looks like this, with an enlarged lobe pointing along positive x and a diminished

negative node pointing along negative x. That is our hybrid.

We have developed some coefficients here.

We just got it pictorially, and here we show you the picture of the hybrid. And then, we need to continue.

We need to use the remainder of our 2px orbital.

The one thing we cannot do in constructing a set of hybrid orbitals from a set of atomic orbitals is forgetting to use part of our orbital. We need to use all of the orbital that we are given to construct these hybrids with.

And what that means is we have now a relationship between C5 and C8, because we now know C2 is plus root two over three.

Let's use this unit orbital idea and reference 2px -- -- and say that C2 squared plus C5 squared plus C8 squared, these are all the coefficients that deal with the px contributions to these three hybrids, is equal to one. And we know C2 squared is equal to two-thirds.

And now let's draw a picture to help us figure out something else about C5 and C8.

Here I am simply representing, with the same coordinate system that I am using throughout, the boron atomic orbital that is the 2px orbital. And, if I consider, down here, the s orbitals on HA and HB, I can say something about the way in which 2px interacts with HA as compared with the way in which it interacts with HB.

Notice that these HA and HB atomic positions are mirror images of each other with respect to this 2px orbital in the middle. That tells us that C5 must be equal to C8. We are using symmetry as a mathematical argument here to say that C5 is equal to C8. Therefore, we can figure out exactly what C5 and C8 are because we already know that C2 squared is two-thirds.

We know that C5 squared plus C8 squared has got to be equal to one-third. And that means that C5 is equal to C6, sorry, C8, which is equal to one over the square root of six.

Because we put this in here, we will get a sixth plus a sixth, two-sixths, which is one-third, plus the two-thirds, which will be one.

And so, we know it is one over root six.

However, it could be a positive or a negative.

And we need to figure out just which it is.

Is it positive or is it negative here?

And I will come back to that issue just in a moment, when we draw these functions. But notice that these are the coefficients on $2p_x$ and the positive lobe points up toward HA. We are going to need it to be flipped around and be pointing down if we are going to form bonds to HA and HB. So, that will dictate the sign here as negative one over root six.

We do not have, yet, the complete equations for sp^2 of B and sp^2 of C because we need C_6 and C_9 . Let's see how we can get those.

C_6 and C_9 relate to the p_y orbital that is oriented like this with reference to our coordinate system, with the negative phase shaded as follows.

And specifically, C_6 relates to the interaction with this HB down here. And C_9 relates to the interaction with the $1s$ orbital on HC down here, on the lower right. And because this p_y orbital changes phase as we pass through the origin, and we want the positive phase to match up both with HB and with HC in the contributions to the hybrid wave functions, we are going to know, and by the symmetry of this problem, that these are negative mirror images of each other. So, we know that C_6 is equal to negative C_9 . And if we put that together with unit orbital contribution, we can see, because we know that we have our sp^2 of B and sp^2 of C, both of them have one over root three of the $2s$ contributing.

And then we are looking for six and nine.

We found out over there that both of them have negative one over root six as the coefficient on p_x .

And then, we know that since this is the one that points to B, we do not need to flip the phase on p_y to get a bond forming between p_y and HB. This is going to be a positive, and then this one is going to be a negative, for the reasons I just mentioned, that we are going to need to flip that p_y contribution to sp^2 of C, as compared to sp^2 of B, in order to get this positive lobe over here interacting with HC in that function.

I am going to draw these functions in just a moment.

But now, when we note that normalization requires that the sum of the squares of the coefficients be equal to one, and we know that C_3 was zero, so that there is no contribution at all of p_y to sp^2 of A, and all of it must be here and here, that means that our coefficient is one over root two of p_y .

Using these restrictions from quantum mechanics, we actually have coefficients on the spx and p_y orbitals that show how they go together. And the way in which these add up is similar to what we have seen over here.

It is a little more complicated because both p_x and p_y contribute. Let me show you what they look like. This mathematical manipulation of these functions produces linear combinations that all three look the same as the symmetry of this problem would dictate. It is a three-fold symmetry type of problem. And this is our sp^2 orbital pointing toward B with this mathematical form.

We have to flip around p_x so that the positive lobe of p_x contributes down here. We do not have to flip p_y .

And we have differing amounts of p_x and p_y in this hybrid wave function. But the math of the atomic orbitals guarantees that this form would be physically indistinguishable from this one over here.

They would look exactly identical if I plotted a probability density isosurface. These two-dimensional pictures that we draw on the board are like slices through three-dimensional probability density isosurfaces.

That is what these representations are.

And then, we note that the p_y orbital is flipped around when we form sp^2 of C.

And that leads to this appearance.

I would like to show you what one of these might look like if you calculated it from the math that we have developed, here.

I have actually got more work to do here in the next five minutes, so let's keep our concentration.

Look at this orbital. This thing is a beautiful hybrid orbital. And I have calculated this with reference to a particular arbitrary molecule.

This was calculated with reference to the water molecule.

The positions of the nuclei in the water molecule are indicated by these arbitrarily sized spheres.

That is a typical ball and stick representation of a molecule in 3D. You can see that the oxygen of the water molecule is colored red, in there.

That is arbitrary. And then we have the hydrogens in white. And then I have a big positive lobe in blue here and then a smaller yellow lobe that is our negative lobe on this orbital, here, which is an added mixture of an s orbital with a p orbital.

I am not telling you the actual coefficients that went into this particular hybrid, but you can see how if I were to take a two-dimensional slice along the long axis of this hybrid orbital, it might look something like what we have drawn

over there. Namely, with one nice large directed lobe, that can have good overlap with a hydrogen 1s orbital in order to give rise to a good two electron bond between hydrogen and boron.

And let me illustrate how that impacts on how we draw our energy-level diagram for the BH three molecule.

What we have now is a situation in which, as you go up in energy, you find three orbitals that are all at the same energy.

These lines indicate places where we can put electrons.

And, in fact, they look like this.

They represent positive interference up along x.

Positive interference between a sp two hybrid that points down at atom B, right here, overlapping nicely with the hydrogen 1s wave function that is sitting out there, surrounding that nucleus. And then over here is our hybrid orbital sp squared of C that points down here and interacts with the hydrogen 1s orbital on atom C.

And so, the idea is now this system, BH three, has a total of six valance electrons.

Valance shell electron pair repulsion theory could be used by you to predict the geometry that we started with for this problem. But now, we can populate these bonding orbitals with electron pairs, as shown here.

And then, this problem has one more aspect to it, namely that up here somewhere higher in energy there is a 2pz orbital on the boron that is empty.

And this empty orbital -- -- is our feature that gives this molecule Lewis acid character. We know that this is an electron deficient system. It does not satisfy the octet rule. And, specifically, where it is missing electrons are in that boron 2pz orbital.

That allows you to predict something about the stereochemistry of reactions, for example.

It says that if some nucleophile or Lewis base, a source of a pair of electrons is going to come in and approach that planar BH three molecule, it will do so either along positive z or along negative z because that is where the big lobes are of that empty pz orbital point.

And, this valance bond theory -- -- satisfies this problem, that Pauling noticed, of how do we make three identical bonds in a plane that contains three dissimilar atomic orbital wave functions, an s orbital px and a py? Well, he found that mathematically you can mix them together in ways that gives you three identical hybrids that have the needed directionality for the forming of these three two electron bonds.

There is an alternative solution to this problem, and we will call that molecular orbital theory.

Don't forget about Robert S. Mulliken, MIT undergraduate thesis 1917. And MO theory is a different perspective on electronic structure theory for molecules.

And we will launch into that on Wednesday.