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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 10

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PROFESSOR: Settle down. Settle down. Settle down. All right, first announcement is the celebration of learning. Reminding you that the celebration of learning is a week from today. Go to your assigned rooms. A through Ha will write in here. This group will go into 26-100. And the last group over to 4-270.

And you will take with you your periodic table, table of constants, aid sheet, something to write with. And we'll give you paper. You'll write on the exam paper itself. And I'll say more about test taking strategies on Monday. Coverage will be right up through Monday. With emphasis obviously on the material that you've had some time to digest. And there will be no weekly quiz next week.

So let's get right into the lesson. Last day we looked at Louis, who gave us the notion of achieving octet stability by electron sharing. And that led to the concept of covalent bonds. And then Pauling helped us understand the energetics of covalent bonding by putting forth the idea in a heteronuclear molecule there's unequal sharing of the electrons. And out of that emerged the concept of polar covalency and the definition of electronegativity.

And on the slide you see how electronegativity varies across the periodic table. Electronegativity being a measure of the pull an atom has for electrons within a covalent bond. And as you would expect, the non metals which are good electronic receptors are also the ones that have the highest electronegativity. And the metals, over here, which are good electron donors are those that have the the lowest value of electronegativity.

And Pauling was quantitative in his formulation and gave us this equation that tells us how to measure the energy of the x-y covalent bond. If x is not equal to y, then axiomatically this is going to be a polar covalent bond. And you take the geometric mean of the homonuclear bond energies. This is x-x bond energy in x two. This is the y-y bond energy in y two. You take the product square root of which.

And then the partial ionic character, this is the contribution to unequal sharing of the electrons. You take the square of the difference in the electronegativities of the two elements. And the 96.3 is a factor that allows you to get the overall quantity in kilojoules per mole. So you need these numbers in kilojoules per mole.

And we further had a formula for the percent ionic character, which you can get by looking at the difference in electronegativity. And then through this formula, you end up with a scale that runs from 0 to 100%.

And just by way of example, we had a look at H-F. We spent a fair bit of time on that. Obviously, it's a heteronuclear molecule. We calculated its bond energy and so on. And then to indicate polar covalency, we use the dipole notation. The dipole shown here. It's just an oval. It's net neutral. But the charge is not uniformly distributed. You see one end is a little more negative. The other end is a little more positive. Sometimes people write lowercase Greek delta, indicating little bit negative here, a little bit positive here, net neutral. There's the arrow indicating the dipole.

And furthermore, we argue that this is a polar bond. And since this is just a molecule with the two atoms, then this is also a polar molecule. Which means it has a net dipole moment. And I made some observations about dipole moments and the ability to store energy capacitively. And how you'd go about finding a really good capacitor. And so that all came out of the desire to find something that has a net dipole moment.

And I want to continue that conversation. And so I want to look at some other elements. And what I want to look at in particular is the compound methane. Let's look at methane from this new found appreciation of polar covalency.

So first thing I want to do is to put it's structure up. We've gone through the Lewis notation and the structure. It forms  $sp^3$  hybrids. And you end up with a structure that looks like this. These are all at a 109 degrees, symmetrically disposed in space. And we know since we have a heteronuclear system here, we're going to have some polar covalency.

You can look up that the electronegativity of carbon is 2.55 electronegativity of hydrogen is less than that from its position in the periodic table. But to be quantitative it's 2.2. So that means if I look at the carbon hydrogen bond, carbon has the higher electronegativity. So it's going to pull the electrons. So that means that the carbon end is going to be a little bit negative. And the hydrogen end is going to be a little bit positive. So that means I've got a dipole moment here. Polar bond.

Everything is the same as above here. Polar bond. But, I want to address the question, is the molecule polar? So the way I interpret the question, is it a polar molecule, I ask is there a net charge displacement? Well, we're off to a good start here. We see that we have charge displacement on the bonds. But, is there a net dipole for the molecule.

So the way I think about that is to say, where is the center of positive charge for the molecule? Where's the center of negative charge? So I know all the hydrogens are a little bit positive. And they're all the same distance from the nucleus. And I can draw a circle that will capture all four hydrogens. Or more appropriately, it's a sphere, right? These three on the bottom don't lie in the plane.

So the corners of the tetrahedron lie on a sphere. So where is the center of positive charge? The center positive charge is right here at the center of the molecule. And where's the center of local negative charge? It's on the carbon because the carbon is the negative end of all the bonds. So the centers of positive and negative charge for the entire molecule are colocated at the center of the molecule. So this means no net dipole moments. No net dipole moment for the molecule.

So this is a non polar molecule. It's a non polar molecule consisting of polar bonds. Non polar molecule. So there's two ways that I can get a non polar molecule. One

way is to have a homonuclear molecule, right? So, homonuclear molecule. Homonuclear molecules axiomatically must be non polar. Because they have equal sharing.

So if I give you anything that's homonuclear trivially, it's non polar. So you can look at things like H<sub>2</sub>, P<sub>4</sub>, S<sub>8</sub>. These things are all non polar. I don't care what their structures are, it doesn't matter.

This one here is definitely polar. And then the last one here that we're looking at, the methane, is non polar because we have spatially symmetric disposition of identical polar bonds. So spatially symmetric, that means there's three dimensional symmetry. Spatially symmetric disposition of identical polar bonds leads to non polar molecule. Because the centers of positive and negative charge are collocated.

So, now it's time to move on. Now I want to look at covalent bonding from an energetic standpoint. I want to go back to energy level diagrams. We've looked at energy level diagrams in the past for atoms, single atoms. But now, what I want to do is build energy level diagrams for molecules.

So, for that we're going to go back to the Schrodinger equation. I want energy level diagrams for molecules. And for that I'm going to call upon the Schrodinger equation. And we're not going to go through the quantum mechanics in mathematical detail. We're going to do quantum mechanics pictorially. We've got a long way.

And in particular, what I want to do with regard to the Schrodinger equation is to recognize that we can move from atomic orbitals to molecular orbitals by exploiting the fact that the Schrodinger equation is a linear equation. Using the linearity property of Schrodinger equation.

All right, what do I mean by linearity? Well, I'm going to do just a little bit of math. Just enough to make you sit up in your math classes and find out that there's some utility there. Here's what I mean. Let me talk about what the linearity principal is.

So if I have some equation,  $f$  of  $x$ ,  $y$ , and  $z$ . It's a three variable equation. And the equation is  $f$  of  $x$ ,  $y$ ,  $z$  is  $k_1$ .  $k_1$  could be a constant, it could be a function, it could be anything. And let's say that it has as its solution, the solution is  $s_1$ .

And then I've got a second variant of this  $x$ ,  $y$ ,  $z$ . And it equals  $k_2$ . So it's the same function but it equals  $k_2$  here. It could be a constant, it could be something else. And it has as its solution,  $s_2$ . If this  $f$  of  $x$ ,  $y$ ,  $z$  is a linear equation, then if I'd give you  $f$  of  $x$ ,  $y$ ,  $z$  equals  $k_1$  plus  $k_2$ , you don't have to go and solve the equation with impunity. You can write that the solution is equal to  $s_1$  plus  $s_2$ . And that doesn't hold if it's a non linear equation.

Just put  $y$  equals  $x$  squared. And if I tell you  $y$  equals one,  $y$  equals two, and then I give you  $y$  equals  $1$  plus  $2$ , it doesn't equal the sum of the solution to that. You can prove it to yourself. So this is the fact that superposition holds. You can superpose solutions and build a library. So superposition holds when you have a linear equation.

And that's all we're going to use in order to make equations for the molecular orbital. So that way I can write that the wave function of a molecular orbital then is a linear

combination of the atomic orbitals. That's all this is doing. This is setting the stage for, if you take quantum mechanics later, you'll go through this in gory detail. But I'm saying that you know enough now to appreciate that we can do what we're about to do so.

That means I'm just going to sum the wave functions of the atomic orbitals. In this case,  $i$  goes from 1 to 2 because there's only two orbitals in a bond. And there will be some pre factor here, a sub  $i$  times  $c_i$ .

And this whole business is called linear combination of atomic orbitals into molecular orbitals. So it's an SLI, it's a six letter initialization. You know like FBI is a TLI, it's a three letter initialization. This is an SLI, in 3L91 we go big. This is an SLI, six letter initialization.

So we're going to do some examples here. And all you need to do in order to run the examples is use two ideas in LCAO-MO. First of all, conservation of states. Conservation of orbital states. And the second one is, we're going to fill the newly created molecular orbitals according to the Aufbau principle. Fill MOs by Aufbau. If we do that, we're in good shape.

So let's take a look. So first think I want to do is just rationalize this one here.  $H + H$  goes to  $H_2$ . I want to demonstrate that there's a rational basis for this. So what I'm going to do is make energy level diagrams. So there's an energy coordinate here. Energy goes up in the vertical direction. And out here is zero. And what I'm going to draw for you is energy level diagrams for two atomic hydrogen gas atoms.

So if this is the zero, we know that somewhere down here is the 1s. And I'm going to be complete in my label. This is the 1s atomic orbital of hydrogen. And over here there's a 1s atomic orbital of atomic hydrogen. And furthermore, I've got an electron sitting in 1s.

Now these are at infinite separation. These are far apart. Far, you know what that means. Far with quotation marks means that they're separate quantum systems. So I'm not violating the poly exclusion principal by having both of these electrons sitting in the ground state. So they both have the same set of quantum numbers. 1, 0, 0, 1/2. Both of them. Same thing. Let's put it over here, 1, 0, 0, 1/2. So they're very, very far apart.

Now if I bring them close enough together to make the molecule  $H_2$ , what happens is I'm going to violate the poly exclusion principal if I have both of these atomic orbitals at the same level. Because I start filling them according to Aufbau principal I'm going to end up with more electrons than two at the same state.

So what happens is this splits. One orbitals ends up at a lower energy and one orbital ends up at a higher energy than the ground state energy in the atom itself. And so now this is called the sigma 1s molecular orbital. And the one above it is called sigma star 1s molecular orbital.

And sigma is at a lower energy. So if electrons populate this orbital, the system's energy will decrease and a bond will form. So this is called a bonding orbital. If electrons populate the upper orbital, they will raise the energy of the system, destabilizing it. And so this orbital denoted with the star is called antibonding. It's an antibonding orbital.

So now I've got the energy level diagram for molecular hydrogen. So now let's go and populate according to the Aufbau principal. I've got two electrons and they go in spin up spin down. And now you can see that this occupancy put the electrons at lower energy than they were by being in the energy state of the atoms.

And so I can argue that by this diagram, I haven't predicted anything, but I can use this diagram to rationalize that for this reaction  $\Delta E$  is negative. And we know how negative it is. It's minus 435 kilojoules per mole. It's hugely negative. Minus 435 kilojoules per mole. All right. So, that's good. In fact I think I've got some pictures.

You can go through the whole quantum mechanics. And just as is the case for a single atoms, you can use the product of the wave function and it's complex conjugate and so on and make plots. Oh by the way, this was just making the point that you can pull out the electronegativity off of the periodic table. It's given here. And the periodic table is pretty good. But obviously somebody got a little bit ahead of himself. They called this the first ionization potential, which is the potential you'd put across the plates in a gas discharge tube.

But the unit is not the electronvolt. If it's a potential, it's a volt. Somebody here that put this together seemed to think the electronvolt is a unit of potential. And I want to make sure that nobody in this class believes that. You got to get a little bit of nail polish or something and cover up the little e there. Or take the nail polish, paint over potential and write first ionization energy. One or the other, but not this.

This was a plot of percent ionic characters. You can see that the strongly covalent compounds down here have very very low electronegativity differences and therefore very low ionic character. And way up here are the ionics. And in between is HF. It's almost at the cusp.

But, can you see that there must be a mistake on this diagram? Because this thing has got a greater electronegativity difference than lithium iodide and yet lithium iodide has a higher percent ionic character. How can this function zigzag like that? Something's wrong.

So when you look at something, you go wait a minute, that doesn't make sense. So I go back and I say, do I trust anything here? Trust, but verify. Read critically. It's a good book. But, it's a big book and there's going to be some mistakes.

All right, so here's some pictorial stuff of what we were just doing over here. So here are the two spherical 1s orbitals and now they come closer and closer together and they overlap. And this is what the shape of the sigma 1s orbital looks like. It's like an oval with the two nuclei inside.

Here's taken from a different text book. The overlap of atomic 1s atomic and now here's the molecular orbital.

Now you can also look at what the shape of the antibonding orbital would be. This is what the shape of the antibonding orbital would be. It would have two lobes with a nodal plane in between. I think this is taken from yet another book. Oh this is our book. There we go. 1s, 1s, as there we go. Hydrogen molecular orbitals.

Now look, suppose we do the same thing for helium. If we do the same thing for helium, helium starts with two electrons in 1s. And now it's going to have four electrons. Two will go in the bonding and two will go in the antibonding. And the two that go in the antibonding raise the energy of the system more than the two that go into bonding decrease the energy of the system. There's a net increase in energy.

And this is the way you could rationalize that helium exists as the atom in the gas phase. You don't see He<sub>2</sub> gas molecules. So using this energy level diagram you can go through and rationalize. I would never ask you to predict. I would say, fact, helium is found as the atomic species in the gas phase. With the use of energy level diagrams, rationalize. And that's what I would expect you to do. Take this and show that the two are of different stability.

One other point to make, the level of 1s. If I wanted to put helium on this board here. Not the scale, but just roughly. Where would helium 1s be relative to the hydrogen 1s. We got three choices. Same level, closer to zero energy, or more negative.

How do you think about the problem? What determines what this energy is? It's the electrostatic force of attraction. Is the electrostatic force of attraction on the 1s electron in helium greater than or less than it is in hydrogen? It's greater. So that means that the energy is going to be more negative.

And so if I were to put over here helium, I'd put down here this would be 1s atomic orbital for helium and then we go through the analysis. And why does that come into play? Well you might want to do a heteronuclear molecule. Suppose you wanted to do the bonding diagram for hydrogen fluoride.

So we'd have hydrogen here and the fluorine and would be here. And all the fluorine orbitals would be much lower and then they'd combine to make the molecular orbitals. And I think there's some opportunities to practice that in the homework.

OK let's do one more. Let's do one more. How about lithium. Let's do lithium. I want to ask, is dilithium stable? Li<sub>2</sub>. And this is all gas phase. Is dilithium stable? So I'll start off with here's the zeroes. The zero of energy for infinite separation. So this'll be a lithium gas atom.

And this is the putative dilithium gas atom. We're going to figure out if it's stable or not. So it's going to have bonding and antibonding orbitals. And then this is the 1s, 2s. And this will be sigma 1s, sigma star 1s, and so on. And then we'll have 2s atomic orbital splitting into sigma and sigma star of 2s.

And now lithium is 1s<sup>2</sup>, 2s<sup>1</sup>. So there's one, two, three. And one, two, three. And so now let's use the Hund rule. So I've got four electrons in the n equals one shell, and they populate in this manner. And then I've got two electrons that go only into the bonding orbital. And according to this it appears that lithium 2 is favored over atomic lithium. And that in fact is the case.

That in fact is the case and so that applies to all of the alkali metals. Because they all have the ns<sup>1</sup> configuration. So when you're driving down the highway and you see those orange yellow low pressure sodium vapor lamps. What you're looking at is emission not from atomic sodium but from Na<sub>2</sub> vapor. And

you've got the energy level diagram to convince yourself of that. So next time you see those, just smile, knowing that you're looking at disodium, not sodium.

OK, well so far we've only looked at single bonds. Now I want to look at multiple bonds. Double and triple bonds. So let's look at nitrogen now.  $N_2$ . Remember that gave us the triple bond? We had nitrogen, one, two, three, four, five. Second nitrogen, one, two, three, four, five. So in order to get octet stability, we had three pairs of electronic sharing. Which then give us a triple bond here.

And so what's that going to look like? what's that going to look like pictorally? And the way to think about that is first of all these are all p orbitals. If we look at, this is  $2s^2, 2p^3$ . So 2s and these are the 2d orbitals. So I've got s is filled first and then I've got the lone electrons in each of the p orbitals. And these things are shaped like figure eights.

And the p orbital, this is the p atomic orbital. It has two lobes. Each of these zones are just called lobes. Same word is earlobe. And this zone in the middle, this one point in the middle, is called a node. And that's a sight of zero electron density. Zero electronic density.

And remember the electron, even if it only has one electron here, the electron can be in either a lobe. It can move from lobe to lobe even though it can never be at the nucleus. And how does it get from one lobe to the other while never crossing the nucleus because it's never supposed to be in the nucleus?

By behaving as a wave. The same way that you can have a jump rope and you can have a fixed point of zero motion, yet you can transmit energy down the rope passed the node.

So, let's draw these things. A word about how you draw, you have to use the right hand rule. Have to use the right hand rule. So when I put the coordinate system up, it's going to have to conform so that the thumb is x and they go y and z. And if you don't use the right hand rule later on if you get into electromagnetics, you start looking at forces and vectors, you're going to end up with things moving in the wrong direction. So we conform to the right hand rule.

And the other thing, and it's kind of nice, it's not mandatory. But chemists generally like to have atoms bond along the z-axis. So that means we start with the z-axis here, if I'm going to put my second nitrogen, have them bond on the z-axis. And so that means if z is in the plane of the board pointing to the right, then pointing up must be y, and then pointing into the board must be x.

So I'll have, here's my  $p_x$  orbital, then the  $p_y$  orbital, and the  $p_z$  orbital. And the three of these are all symmetrically disposed around the nucleus. And next to it at the same kind of floral arrangement. I'll start with  $p_x$ ,  $p_y$ , and  $p_z$ . And now these are going to come close together and overlap. So I want to figure out what those orbitals are going to look like.

So let's start along the z-axis. The z-axis is the easy one. So I've got two of these things lying on their sides like infinity signs. We're going to do quantum mechanics pictorally. Why? Because it's a linear equation. So I can add pictural. So this is  $2p_z$  of one of them. And a  $2p_z$  of the other. And this is the nitrogen atomic orbital.

And I'm going to smear these things and what are they going to look like? The nucleus is here, the nucleus is where I'm indicating the dot. These two combine, very simply, it's going to look like this. So there's one nitrogen. Here's the other nitrogen. And what's this thing? This is electronic density. And so this is our sigma bond.

Looks a little bit different from the case of hydrogen, because hydrogen was the blending of two s orbitals and s orbitals are spherically symmetric. In this case, we've got two lobes. But what's characteristic about this one and hydrogen, hydrogen looked like this, remember? This was hydrogen. This was H<sub>2</sub>. And this was a sigma bond.

The characteristic of a sigma bond is that when you start from one nucleus and you go to the other nucleus, you move through unbroken electron density. So there are no nodes, no holidays, between the nitrogen nucleus on the left and the nitrogen nucleus on the right.

There is a node here, but that's different. I can go from one nitrogen to the other with unbroken electron density. That's what makes this a sigma bond. So that's good.

So this thing here is going to be called stigma 2p molecular orbital. Sigma 2p molecular orbital And I think I've got the slide that shows this. There's some art work. People really get excited about this. OK there's dilithium. Or dipotasium, disodium.

OK so here we are. This is the smearing of two pz atomic orbitals to make the sigma 2p bonding orbital. And there just for grins and chuckles is what the antibonding would look like. But we don't care, because it doesn't form.

Well this is the book. And you know what I'm going to say. I've got my little hobby horse here. I don't know why they change color on the lobes. Because when I look at that, it starts conjuring up to me the image that one electron stays in the blue lobe and one electron stays in the yellow lobe. Besides, I've seen them and they're not different colors. They're the same color.

So now let's look at what happens when we blend off of the z-axis. So let's blend the two py orbitals. See what that goes like. OK so let's do that one. And that one is going to look like this. We're to start with, again figure eights. But now they're their side by side, they're lateral.

So this is 2py atomic orbital. 2py atomic orbital. And then we're going to blend them along the z-axis to give us, and I'm going to do this stylized, OK? So there's the the two nitrogen nuclei. So I put the nuclei up. And I'm going to smear the upper lobes. So these two lobes are going to smear. And I'm going to get really stylized. I feel like it's France and it's the late 1800s. So there it is.

And I'm going to smear the two bottom ones. And it's going to look like this. So what do I have here? Now I have two lobes as before. But if I look at the second nucleus from the first nucleus, not only do I fail to have unbroken electron density, I have zero electron density.

See, this was a nodal point in the atom. With the two atoms together, the plane orthogonal to the board is a nodal plane. There's no electron density in the plane



orthogonal to the board. Nodal plane. So this is definitely not a sigma bond, this is a pi bond. This is a pi bond.

And it's characterized by smearing of atomic orbitals, just as the sigma bond is. But it has a nodal plane that separates the two lobes. I think I've got some cartoon illustrations from other books Here OK this is from one book. This is good. They call the px, I call it py. There it is.

And I'd go further and I'd say that if I were to slice this and look at it from angle, if we were to cut this and look from here, I'd venture that you'd see something that's sort of figure eightish. Oh here's our book, bless them with two colors. But anyway, there's what it looks like. That's the pie.

And then the same thing happens with the x. So this is this is going to be pi 2py. This is pi 2py. And it's a molecular orbital. And there's going to be a pi 2px. And it's going to blend front and back.

So we can make a catalog. So we're going to do quantum mechanics in pictures here. So I know that s plus s must always make a sigma bond. There's no other way. Because I've got electron density all around. Let's do it pictorially. That's easy. And this is sigma. We know this has to be sigma.

What about something like HF where the H is an s and the F is going to have the one last electron missing in the p orbital. S plus p must give sigma always. Because that's this cartoon.

See there's no way that when this smears with this, there's going to be zero electron holidays from the hydrogen nucleus to the fluorine nucleus. So you're going to end up with something that looks like this. It starts around and gives you something that's going to be a little bit asymmetric. So this will also be a sigma. So I'll just put HF here as sort of prototypical of that.

And then if I take p plus p axially, on axis, that also gives us a sigma. Because that's this one, the infinity signs. Two infinity signs give us this.

And then finally, if we get p plus p longitudinally. So that will give us a pi bond and that's the 88. 8 plus 8 gives me, and this is pi. So that's quantum mechanics. The math will follow.

So now what I want to do is go back to this energy level diagram and show how these energy level diagrams can work. So here's the energy level diagram for nitrogen, N<sub>2</sub>. There's two f's, two p, and the scaffolding is in place. There's the energy levels.

Now here's the molecular orbitals and here are the atomic orbitals. And now here they are occupied. So nitrogen has one, two, three, four, five according to the Hund rule. And here is the set up for the N<sub>2</sub> molecules. So the 2s's and the 2s's go bonding antibonding. Now I've got three plus three is six. Two, two, two. Everything's paired. So we get the triple bond, 946 kilojoules per mole. Enormous energy in nitrogen. Enormous energy in nitrogen.

Now, let's keep going. Now let's look at oxygen. This is the scaffolding for oxygen and fluorine. And there's a little change here. A little change, I'm going to draw your

attention to it. And you can't predict this. We would give you this. I would tell you what the energy sequence is of the energy levels.

But look here carefully, you see in the case all nitrogen, the pi's lie below the sigma. In the case of oxygen and fluorine the sigma lies below the pi's. These are tiny, tiny differences. But, they are measurable. That's the little difference. Now let's see what happens.

Actually here's from our text book and it shows the sigma 2p<sub>x</sub> slowly meandering down, down, down, down, down. And somewhere between nitrogen and oxygen it crisscrosses.

All right, so now let's fill oxygen. So oxygen is two, four, five, six. So two plus two is four. There's the two, two, two. And then these last ones go up into the antibonding. But look at the antibonding. We have, according to the Hund rule, not two electrons in the first orbital, but one and one. So we end up with unpaired electrons in the antibonding orbital.

So these offset the three pairs here, and so we end up with a double bond. And its energy is 498 kilojoules per mole. Substantially less than nitrogen. And this energy level diagram rationalizes that.

And then here's for fluorine. If you go to fluorine it's the same scaffolding only there's two more electrons. These are paired and you have a single bond. 160 kilojoules per mole. Now there's a property that we get from the fact that we have these unpaired electrons. We're going back oxygen now. We have unpaired electrons in the antibonding orbitals. We saw unpaired electrons. What did they do in the Stern-Gerlach experiment? Changed the magnetism substantially, right? We ended up with the splitting of the silver beam.

So this will also have an impact. An impact known as paramagnetism. What's paramagnetism? It's shown in this little cartoon. If you have a substance here that's balanced and it is paramagnetic, if you engage the magnetic field, the magnetic field will pull on a substance that's paramagnetic.

And oxygen is paramagnetic. Not only in a gas state, but paramagnetic as liquid. And here's an illustration from your text book. You may have seen this and said, yeah a guy is pouring liquid oxygen, wow. Look carefully now. The boiling point of oxygen at one atmosphere pressure is 90 Kelvin. So room temperature is substantially higher.

This is the equivalent of taking water and putting it in an oven at about 300 degrees Celsius and watching it pour. It would still be liquid, but it would be liquid trying to boil. Why doesn't it all turn to gas? Because there's a time to heat everything.

So this is sitting at 90 Kelvin, he pouring it down, or she's pouring it down, and these are the jaws of a permanent magnet. And it's in a gravity field, it doesn't keep falling, it stops. And it continues to boil away and as fast as you can pour it, it sits between the jaws of the magnet. Because it's paramagnetic.

You can think of this as the liquid equivalent of iron filings. If I told you that were these were iron filings you'd say, yeah the iron filings go and they stick to the magnet, that's what magnets do to iron filings. They do the same thing to liquid

oxygen. And why? Because of this. This explains this. So we can do a lot with these primitive little diagrams.

Let's do one more. I want to do one more of these things. I want to go to hybridized systems. I want to go to a hybridized system. And I want to look at ethylene.  $C_2H_4$  is ethylene. OK, so if I told you give me the Lewis structure of ethylene, you just start going according to the rule. So I'm going to have carbon, carbon, hydrogen, hydrogen.

And carbon has one, two, three, four electrons. The hydrogen has one electron. I'll put the one electron from hydrogen. And then the other carbon over here, I'm going to give it dots. One, two, three, four. And then these hydrogen each have one. And now let's see what I have here.

These hydrogens are all isoelectronic with helium, so they're happy. And the carbon now has two, let's see, what does he got? Yeah, carbon is happy. Two, four, six, OK good. So now carbon is. Happy as well. So what do we have here? This is the equivalent to a carbon carbon double bond.

So what have I learned with the nitrogen example? What I learned with the nitrogen example was, that if I want to make more than one bond, I have to have a combination of a sigma and a pi. You can only make one sigma bond because there's no room. Once you've got zero electron density between the two nuclei you're going to violate the Pauli exclusion principle if you have another orbital cutting through that same domain.

So this means that multiple bonds require a mix of sigma and pi. Multiple bonds require a mix of sigma and pi. If you have a single bond, all you need is the sigma.

So let's go back to how we got the original hybridization. Remember, we started with carbon, with the box notation looking like this. Here's the 2s and the 2p's and we started with just native carbon off the periodic table. And we have this. Just if we go according to the  $2s^2, 2p^2$ .

And then in order to get hybridization to rationalize methane, where we've got four equivalent bonds. In that case, we hybridize the s and all of the p's. We took the s and all three of the p's to make the  $sp^3$  hybrid orbitals. And then we were able to take these electrons and put them in one at a time. And then bring in the four hydrogens and we end up with something that is symmetrically disposed in space. The carbon, hydrogen and so.

So now I give to you ethylene I say, well how do I make ethylene. Well, if I started with this  $sp^3$  thing maybe I could bring another carbon over here. And I'd have three hydrogen sticking out. So there's my sigma bond. So I'm off to the races. This is good.

But now I need to build a second bond. I'm going to throw away a couple of hydrogen. So I'll throw this hydrogen away and this hydrogen away. So I'm going to have now  $C_2H_4$ . I'm almost there. The only problem is, this orbital is sticking out this way, this orbital is sticking out this way. And I don't have the license to bend these orbitals. And build a double bond. Because they're 109 degrees apart and they're inflexible and they won't bend.

So this hybridization technique will not work as such to give me what I need to build ethylene. What do I need? If I'm going to build a sigma and a pi bond, I'm going to need to preserve one of the p orbitals so that it can still be available for lateral smearing

Because how do I make a pi orbital? I make a pi orbital middle with an 88. So I need to preserve a p orbital so that in both of the carbons I still have this pi bonding capability. So what I'm going to do is instead of taking the s and all three of the p's I'm going to take the s and only two of the p's and reserve one of the p's to be sitting there for lateral smearing.

So instead what I'm going to do is this. So this is going to be an unmixed p and this is going to take the s and not three p's but only two p's. And this would be called sp<sup>2</sup>. And now what do I have? I've one, two, three. And how do I put three of these in space? They lie symmetrically in a plane at 120 degrees. And then this thing is normal to the plane of the board. It's sticking out. Actually, I should've maybe drawn it in perspective like this.

And so now I've got the ability to put two of these together. This'll giving me my sigma. And then these two things lying on their side will smear with the lobes to give me the pi. Now that's what gives me the double bond. And here are the cartoons that show this. Oh here, I took this from an old text book, it's text book I had when I was your age. The wrote great books.

And then I flipped this around see. I did all this just for you. So I took this one, I flipped the image around. So there are the sp<sup>2</sup>'s these are the unmixed p's. And you bring them close together and bingo. There's the sigma. That's this one, p plus p axially, that gives me the sigma bond. And then I smear those two and that gives me the pi. And there's ethylene.

You put the hydrogens here, one, two, three, four. Two carbons. Tada. Isn't that cool? Here's from another book. It's looks like a Boston traffic map, doesn't it? Just crazy. This is from our book. So they're showing you there's the sigmas and the pi's. There we go. More pictures.

OK, I'm going to take three minutes at the end here and show you an example of electronegativity at the extreme. So if you take a look at the periodic table and look at a compound like sodium iodide. If I just told you sodium iodide, covalent or ionic? You'd say, ionic. Because you got something from the the most metallic of the metals and something from the most non metallic of the non metals. And you're right. And the delta chi is 1.73. And the covalent character is high. And you end up with something that's very polar and so on.

Now here's a very interesting one, if you compare cesium and gold, you get 1.75. Which is greater than what it was for sodium and iodine. Now no one would argue that sodium and iodine is covalent, you'd argue that's ionic. Well by the same metrics, cesium and gold is as ionic. The plot thickens.

Cesium, if you melt it it's a metal, liquid metal. If you melt gold, it's a liquid metal. But if you mix them in equal number. So you make a alloy of 50 mole percent cesium and 50 mole percent gold and you've got a delta chi 1.75, you've essentially made a cocktail with equal numbers of really good electron donors and really good electron acceptors.

And guess what happens, electron transfer. And the melt is not metallic, it turns clear and colorless just as molten sodium iodide would be. It turns into a molten salt. So cesium gives its electron to gold. And gold becomes the negative gold ion. And what color is every ion? It's got stable octet configurations. It's got to be the same color as neon, argon, and helium. They are clear and colorless.

Big drop in electrical conductivity and a shift from electronic to ionic conduction. Metals have electronic conductivity, ions, what do ionic liquids have? They have like ionic conductivity. Here's some data from the literature. This is the log on the conductivity as a function of concentration.

So here's pure cesium over here, here's pure gold over here. This is 600 degrees C. So the line stops here because gold melts at about 1060. So gold is a solid beyond this alloy concentration. But you can see this is roughly what you'd get.

So electronic conductivity up here at about  $10^4$  siemens per centimeter, this is reciprocal ohms, but siemens per centimeter. And down here, this is very low value ionic conductivity. So this is a liquid metal. And this is a molten solid.

And it all happens just when you get very very close to 50/50. So you end up with something called cesium auride. And it's sorcery. You have one vial of liquid metal. You have a second vial of liquid metal. You pour them together and it turns clear and colorless. And the conductivity drops three orders of magnitude all because of electron transfer due to this electronegativity difference. That's so cool. That is so cool. OK, with that I'll let you go. We'll see you on Friday.

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