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Today I would like to start by discussing a timeline.

And you will see in a moment what this timeline has to do with. It is obviously only a partial timeline. But let's start here in 1916, as we have done this semester, by talking about the Lewis theory of electronic structure.

And his electron pair theory is something we are going to come back to a couple of times during lecture today.

Let's move on to 1954. 1954 was an important year in electronic structure theory, because in that year there was awarded, to Linus Pauling, the Nobel Prize in chemistry.

Let me write down Pauling here.

And if you are interested in knowing something about what Pauling was awarded the Nobel Prize in chemistry for, I will show you over here on the side boards.

What you are going to see here, if you read this citation for Linus Carl Pauling in 1954 for the Nobel Prize in chemistry, his prize was awarded principally for his contributions to our understanding of the nature of the chemical bond. If you think back to the elegant title of the paper by Lewis that we started out our discussion of acid-base theory with, it was a paper entitled "The Atom and the Molecule." And now we have gotten to Pauling, in 1954, who is being awarded a Nobel Prize in chemistry for the nature of the chemical bond. That also is the title of a very famous chemistry book by Linus Pauling entitled "The Nature of the Chemical Bond." That was published by Cornell University Press originally, because it stemmed from his set of lectures at Cornell, the Baker lectures, in the 1950s. As we talk about electronic structure theory, I would like you to keep in mind the way in which these different geniuses were approaching the problem, a problem that we are going to launch in on today and spend the next few lectures on.

We will move up here to 1966.

In 1966 there was awarded a Nobel Prize to Mulliken.

Not to be confused with Milliken.

We are going from 1954 to 1966.

You are going to find, as you explore the Nobel Prize website, that there are a lot of informational links on these

people. You can go and read biographies. You can read some of their writings. In the case of Linus Pauling, you have links to all the pages of all of his research notebooks, spanning more than 60 years of research.

Those are pretty interesting supportive materials.

In the case of Robert S. Mulliken, he is being cited for his contributions to the molecular orbital method, which we will also call the molecular orbital theory.

We have the Lewis theory. We have, in the case of Pauling, I am going to say the nature of the chemical bond, described in terms of valence bond theory.

We will come back to that in a moment.

And then, in the case of Mulliken, we have a Nobel Prize for molecular orbital theory. And I just would like to show you something kind of neat, here.

This has to do with the fact that if I go to the section labeled other resources, I can click on MIT digital thesis library. Then I can choose a page of Mulliken's thesis to display. And that is because Robert S.

Mulliken was Course 5 1917. Let's hear it for Course 5 chemistry. [APPLAUSE] Robert S.

Mulliken was one of you guys, and he graduated in 1917.

His undergraduate chemistry thesis at MIT was entitled "The Effective Structure on the Activity of the Hydroxyl Group in Alcohols." Submitted by Robert S.

Mulliken. There is his signature.

Isn't it cool to have your undergraduate thesis linked in from the Nobel Prize website? Robert S.

Mulliken for molecular orbital theory.

And you can see, even as you read his undergraduate thesis, he was talking about the effect of structure on the activity of the hydroxyl group.

He had the idea that if you knew something about the structure of the molecule, even back then, you could make predictions about the properties of the molecule. And that is what we really want to be able to do in chemistry, because we want to be able to control function as much as possible.

I will take that way for now and we'll come back in a moment because I am going to mention to you that in 1998 there was another Nobel Prize given for advances in our understanding of electronic structure of molecules.

And this one was a shared prize, rather than these three other ones that I mentioned. Well, two others.

Lewis was neglected from that category, unfortunately.

In 1998 Kohn and Pople shared the Nobel Prize for furthering our understanding of how to describe electronic structure of molecules. And this is a theory that we are not going to be talking about too much explicitly here in 5.112 this semester, but if you go on in chemistry, you will be exposed to it more and more.

It is called density functional theory.

It is one of the most expedient ways to use computers to get electronic structure information about molecules.

And so, that method has become extremely important.

And I will just show you a little piece of information from that website, so we go to 1998.

And, under the John Pople section, I am going to go to interview. He has given an interview on different topics relating to his involvement in chemistry.

One short piece of that interview is entitled "Interest in Quantum Mechanics and Development of Computer Techniques." We are going to take a look at that and hopefully, if the audio and video are both working, you will be able to see John Pople talking a little bit about this important area of chemistry.

We just don't have time for fixing audio/video problems in real-time here, unfortunately.

Therefore, what I would like you to do is go to NobelPrize.org, Chemistry Laureates on Pople, and actually watch that five-minute segment of his interview that has to do with his feelings about electronic structure theory and advice to students on that topic.

And I will summarize his comments here -- -- by saying that the goal of studying electronic structure of molecules is to try to get predictive power about molecular systems. And we want predictive power in terms of the 3D structure of molecules.

We know how to represent connectivity in molecules in two dimensions. We have been doing that already quite a bit this semester. But we would like to know, if you know which atoms are bonded to which.

And then how does that translate into the intricate three-dimensional structures that molecules can have?

Also, molecules can have color. That is an important property of a molecular system. In addition to which,

molecules can be magnetic. So, magnetism is one of the important properties of molecular systems.

And, as they aggregate into extended solid materials, the way in which magnetic molecules interact to produce macroscopic magnetic phenomena is very much an area of interest to chemists. People want to design molecular magnets in order to be able to make materials that have desired properties that will be useful to us in building things.

And then, of course, we have molecules that are redox-active. And redox properties are very important. We would like to be able to sit down with our computer and draw out a structure.

We would like to be able to pop it into its optimum 3D geometry and find out what that is. We would like to then know how easy is it to remove an electron from that system or how easy it is to add an electron to that system.

Can we sit down and, right from the start, use theory to predict properties like the energies associated with electron transfer to and from a molecular system? That would be important if we are going to do what I talked about last time in terms of inventing systems to transform light energy into chemical energy in terms of the water splitting reaction I discussed last time. Also, molecules have acid-base chemistry. And this is one of the most pervasive forms of chemical reactivity that we can discuss.

And so, we really have been talking, so far in my lectures, about redox chemistry and acid-base chemistry.

And, as I go on, during the next few lectures, we are going to be also talking about properties like color and magnetism and 3D structure from theoretical considerations.

Acid-base is one type of reactivity, but then also there are all kinds of different modes of reactivity that can be classified in different ways. Just to give you an example, there is a class of reactions in organic chemistry called electrocyclic reactions. We will be talking a little bit about reactions of that sort. And then there is something that Professor Ceyer referred to earlier in the semester as stability and the idea that this can take on both kinetic and thermodynamic forms. And so, we would want, from first principles, to be able to sit down and consider a molecular system composed of whatever elements from whatever part of the periodic table it is composed, and just how these properties follow naturally from the collection of elements that you have put together into a molecule. This is really chemistry and this is what we would like to be able to do.

In this next part, what I would like to do is just spend a little time right here in 1957 because that is when Ronald Gillespie published his VSEPR theory.

Ronald Gillespie is now kind of in the twilight of his career.

He has published on his "Lifetime in Chemistry." And so, you can Google Ronald Gillespie and find information about him and his VSEPR theory that will go well beyond what you will find in that section devoted to it in your textbook.

This VSEPR theory, it is an acronym.

And it stands for Valence-Shell Electron-Pair Repulsion theory.

I tell you, the closer you get to the board the less easily you can see the things on that board.

When we talk about VSEPR theory, Ronald Gillespie formulates it simply in terms of five basic considerations.

The first of these, you can tell very easily from the name, and that is that electron pairs repel each other.

And note here I am underlining the word "pairs." And that is because we know that electrons are all negatively charged particles. And so they should all individually repel each other. And they do, in fact. But, based on the ideas of Lewis, you will see that Gillespie is formulating this theory, taking the notion of the electron pair as the fundamental unit to consider. And he is saying that electron pairs are somehow organized in space in a manner that they repel each other, and they try to occupy different regions of space from one another.

And this is going to be useful in terms of predicting the 3D structure of molecules, and this is what this theory is devoted to. And, two molecules can have single bonds, or they can have double bonds, or they can have triple bonds between pairs of atoms.

Maybe we will see this semester also that molecules can have quadruple bonds between pairs of atoms if the orbitals are available for that. But in the VSEPR theory, in this context multiple bonds are treated like single bonds.

You might suspect that that type of approximation is a little crude and that it might lead to certain guesses that might turn out not to be quite right, but actually it is a useful enough approximation for the prediction of the three-dimensional structures of a lot of different molecules that we are actually going to adopt for the purposes of our treatment of VSEPR theory. Number three: if you have multiple central atoms, -- - they are treated independently.

And you will see what I mean by that in a moment.

You should see, from that statement, that in the context of VSEPR theory, we are going to be trying to identify central atoms and peripheral atoms that are attached all to the central atom.

And there may be one or more central atoms in a molecule that themselves are interconnected. And, four, we have two kinds of electron pairs that we consider in VSEPR theory.

We have lone pairs, and we have bond pairs.

And lone pairs occupy more space -- -- than bond pairs do.

And we will discuss the reason for that in a moment.

Finally, I want to give you rule number five for 3D structure prediction using VSEPR.

That is that lone pairs are not included in the description of the structure. And you will see what I mean by that in a moment. The idea is that the names that we give to different molecular structures have to do with the 3D arrangement in space of the nuclei only and not the electrons.

The lone pairs are not included in the structure description.

This is reserved for the nuclei.

Now, let's do a couple of examples.

And, in introducing these examples, I will also be giving you some more of the shorthand that is associated with VSEPR treatment of molecular structure.

Let's talk about this one here.

I have drawn here a very simple Lewis dot structure for a hydrogen sulfide molecule, H₂S.

And for a molecule like this, we really only have two possibilities for the structure because you have three nuclei.

And so, either they can all be arranged -- we are going to assume that nuclei are not going to fuse together and be one on top of another because those positively charged nuclei do indeed repel each other very successfully -- and so, therefore, we could either have a linear or a bent structure.

And we can approach that question using the VSEPR theory very nicely. We start out by recognizing that we have two lone pairs.

That would be this one and this one in the Lewis dot structure that are not interacting with both hydrogen and sulfur nuclei.

And we will call those E. And then we have two bond pairs.

And we will refer to those each as X.

And then we have a single central atom.

We have a central sulfur atom. And the central atom is usually given the label A. And so, that means that we have a system here of the type AX two E two.

And if you look at the general class of molecules of the type AX two E two, it turns out that we can draw their structures this way.

What I am trying to indicate in this structure is that one of these lone pairs is coming up and out of the board this way and the other one is going back behind the board the other way.

These are our two bond pairs that I am representing as lines.

Bond pairs occupy less space than lone pairs do, and that is because you have two electrons interacting with two positively charged nuclei. Whereas, in the case of a lone pair, you have a single pair of electrons interacting only with a singly positively charged nuclei.

Two nuclei cause a greater localization in space of bond pairs, as compared with lone pairs.

And the angle here that this vector associated with the lone pair direction makes to the hydrogen is something approximately tetrahedral. Actually, probably larger than tetrahedral in this case because the H-S-H angle is smaller than tetrahedral in H two S. But this is an angle certainly greater than 90 degrees. And that is one of our angles of the type E-A-X that describes the interaction of a lone pair with a bond pair. What we want to do is maximize those E-A-E and E-A-X angles because, as I was saying earlier, a lone pair of electrons requires a greater amount of space than does a bond pair of electrons.

The magnitude of the repulsions, if we get back to the word repulsion in the name of this theory, the greatest repulsions are found between lone pairs.

And so, next we have repulsions between lone pairs and bond pairs. And then, finally, the weakest repulsions in the system will be between bond pairs. And so, the best three-dimensional structure given by this theory is that which minimizes these different repulsions in the system.

If we considered the linear structure, then what we would have to do is put all the electrons in the same plane of the molecule. And these angles here would have to be 90. And, overall, this would be a higher energy structure because of the necessity of putting in an E lone pair at 90 degrees to a couple of bond pairs and so on around the molecule.

Three dimensionally in space, this quasi-tetrahedral geometry gets the four pairs of electrons of the molecule the

farthest apart in space and minimizes electron pair repulsion.

And that leads, therefore, to a description of the structure as bent. The structure is called bent rather than tetrahedral because we include only the nuclei in the way that we refer to the structure of the molecule.

And we do not include those electron pairs.

Let me give you a feel for how this looks.

And in this picture that I am going to show you, which will recall to mind some that I showed you in my first couple of lectures, you will see that what I have here is an electron density isosurface for the H_2S molecule. And you can see here one of the S-H bonds. Here is another S-H bond.

Over here is that region in space where the electron density isosurface is associated with lone pairs.

And you can see that certainly the electron density is a lot more tightly contracted in the region between the sulfurs and the hydrogens than it is elsewhere, where it bulges out.

And you can see that effect of getting the eight valence electrons in this molecule as far apart from each other in space as you can. And then, furthermore, the coloring in this diagram represents the propensity of electrons at that point in space to come together as pairs.

In effect, that coloring is the three-dimensional manifestation of the Pauli principle mapped onto an electron density isosurface for the H_2S molecule.

This type of picture is very nicely associated with the VSEPR representation of molecular structure.

And I am going to go through another example.

I am numbering this off so as not to distract you with that picture.

This next example is SF_4 .

Let me draw out a Lewis dot structure of this.

As you are looking at this Lewis dot structure, one of the things you should do is to see if the number of electrons that I am including in my drawing is, in fact, the correct number of valence electrons for this system. And that is easy to do.

You know that fluorine is in Group 19 of the Periodic Table.

You know that sulfur is in Group 6 of the Periodic Table.

And so you can quickly figure out how many valence electrons there should be. And, hopefully, I have indicated all of them on my drawing, and no more than all of them. What you might not like about a drawing like this is that while each fluorine has been represented as an octet, as being associated with eight electrons, four pairs of electrons, the central sulfur atom seems to be, in this drawing, associated with ten electrons, -- -- doesn't it? That seems to be a violation of the octet rule. And I will defer that observation for now, but it is an interesting feature of this. And, when you do yourself write down Lewis structures as a prelude to subjecting them to the valence bond theory of Pauling or to the valence shell electron pair repulsion theory of Gillespie or the molecular orbital theory of Mulliken or the density functional theory of Kohn and Pople, you should be sticking with the basics here and making sure you are working with the right number of valence electrons -- -- because your whole initial description of the molecular system is going to revolve around the correct distribution in space of this number of valence electrons that these atoms that you are including in the molecule bring into play. And then you are going to see if you can predict properties based on that.

That is what we do first. And, in terms of bond pairs, based on that structure, we have four.

And, in terms of lone pairs, we have one.

Therefore, the type of system that we are working with here is AX four E. This is one of the possible types, when you have five units, surrounding a central atom.

And the most typical type of geometry that arises when we have five units surrounding a central atom is as follows.

The atom A at the center is intended to be here.

And then I am going to draw five balls.

You can think of them as representing either lone pairs or fluorine atoms. And I am going to color two of them to distinguish them from the others.

And this structure is called TBP.

And that standards for trigonal bipyramidal.

And the reason I have colored this type different from that type is that in a trigonal bipyramidal structure, there are two possible environments, either for a lone pair of electrons or for a bond pair of electrons. You can have axial, and the axial position is easily distinguished from the equatorial position -- -- by virtue of the fact that an atom or a

lone pair in the axial position makes 90 degree angles, three of them to its neighbors. Whereas, an atom in the equatorial position makes two 90 degree angles with respect to its neighbors. It is three versus two that will help you distinguish axial from equatorial.

And understanding that about this molecular geometry, you can see that for the SF four molecule there are two possibilities. Note that when I am drawing a wedge here that means that the atom connected to the central atom is coming out of the plane at us.

And the dashed bond means that it is going back behind the plane so that viewed from the top, this thing would look simply like a Mercedes Benz symbol, just to understand that about the wedges and dash nomenclature on these systems.

And so, the two possibilities that we have for our system is, we can either put our lone pair E up here and our four bond pairs X down here. Or, we can have the lone pair equatorial and our bond pairs, two of them axial and two of them equatorial. As in the case of H two S, we had two structures to distinguish between linear and bent. Over here, we have a structure with an equatorial lone pair or with an axial lone pair for SF four. And when you look at the top one and realize that you have only two of these very bad lone pair-bond pair contacts at 90 degrees, whereas, on the bottom one we have three of these bad lone pair-bond pair contacts at 90 degrees, you might be inclined to pick, in fact, this top one.

And that would be right because it minimizes the number of the worst kind of repulsions. In this case, lone pair bond pair at 90 degrees.

And when we give this structure a name, we are not going to call it trigonal bipyramidal because we do not include the lone pair.

We only include the positions of the nuclei in the naming of the molecular structure. This one is called a seesaw.

Some of you may be aware that there is a piece of playground equipment known as a seesaw. You probably don't get a chance to play on them anymore very much.

Neither do I. This is more fun, anyway. And what I am showing you now on these side screens is a picture of the electron density isosurface for the SF four molecule.

And hopefully, you can see that it looks like a seesaw. These two fluorines down here would be the legs of the seesaw. And then you would sit either here or here and then lean forward and put your hands on the lone pair and then rock up and down somehow.

I don't know. Anyway.

In this system, you should be able to see that the lone pair on the sulfur, which is here, is definitely in this equatorial position, so the electro-density isosurface has a nice dark-blue color where we find that lone pair on the sulfur.

And then the four fluorines are organized, according to the predictions of VSEPR theory, with these 90 degree angles to the fluorines that are oriented in the axial.

The two fluorines are axial. And then here is our two equatorial fluorines here spinning around in the belt of this system. We could also say that you would be sitting on the axial positions if you were going to ride on this particular seesaw. Now, I would like to proceed in time briefly back from '57 to Because we need to discuss some of the issues of the valence bond theory that Pauling brought into the quantum mechanical treatment of molecules.

What I am representing here are a couple of hydrogen atoms 1s orbitals at a distance. We have (H)A 1s and we have the 1s of hydrogen labeled B.

And we are going to say that at some infinite separation between the two, they would not really know much about the spin of the electron on the partner hydrogen.

But as we bring them close together, the spin is going to become very important. And that is by virtue of the Pauli principle. And you should remember that one of the ways of formulating the Pauli principle is that no two electrons in a quantum mechanical system can have the same set of four quantum numbers.

As these two hydrogens get close together, the stable situation for the electrons coming from the two have opposite spin, so I am drawing with spin-up and one with spin-down. And then you are going to notice that here in the center of our H₂ molecule, now, is a region of overlap and of constructive interference of those 1s-orbital wave functions from the two sides.

In this representation of the ground state of the molecule, the Pauli principle is satisfied.

And we can put this pair of electrons into an orbital.

And when that orbital is represented that way, it is cylindrically symmetric.

And we call that a sigma bond.

In chemistry we talk often about the properties of sigma bonds. We talk about also the properties of things called

pi bonds.

And we can even have delta bonds.

Just as I was talking about bond multiplicity a moment ago with reference to VSEPR, let me give you here an x,y-plane. I am drawing in perspective an x,y-plane. And in this x,y-plane we are going to have, actually, six atomic nuclei.

And our z direction is perpendicular to this plane drawn in perspective. And I am drawing in here the positions of four hydrogen and two carbon nuclei.

And when I draw them in like that, you are going to see that all the valence orbitals of this system, except for two, lie in that x,y-plane. And the two that lie out of that x,y-plane, I will show you here, are p orbitals that go above and below the plane.

And I am shading in the negative phase lobe of these p_z orbitals. This is p_z from carbon A and this is a p_z from carbon B. And you can see that these are oriented in a side-on fashion, so that the overlap area that can occur is a side-to-side overlap of two neighboring P orbitals, like this. And the distinguishing feature here, as compared to my description of the sigma bond over there, is that it is not cylindrically symmetric.

This bond has a nodal surface, which is the x,y-plane, where the phase changes as you pass from above that plane to below that plane. We have a nodal surface, a node containing the internuclear axis.

The type of bond that I have drawn there is distinct from a sigma bond. It is a pi bond.

That bond over there, the sigma bond, has no nodal surfaces passing through the internuclear axis.

If I draw the internuclear axis here, you can see that it has the same phase no matter where you are with respect to that axis. Plus, plus, plus everywhere.

And here, if these lobes of these two p_z orbitals are considered to be positive in the positive z direction, then as we go this way, we pass through the x,y-plane and get down into negative z. We now have negative phase, as indicated by the purple shading down here.

The fact that that happens only once with respect to this internuclear axis is what tells us that it is a pi bond.

If there were two such nodal surfaces, then we would have a delta bond, and so on. And next time, we are going to start talking about the progression from these ideas onto hybridization. And then from there onto molecular orbital theory.