Lecture 13B • 02/16/12

There's a problem that's one of the starting points for any discussion of quantum mechanics; it's this problem known as a particle in a box. The particle in a box problem is the following: it's a thought problem of how do we describe electrons, how do we come up with these equations for wavefucntions. This problem deals with a wavefunction that only exists in one dimension. Imagine that you've got a well that the electron is trapped in. Either side of the well, those infinity signs, what that means is infinite potential energy; in other words, to cross over those barriers, the electron would have to have an infinite amount of energy, which is doesn't, so it's trapped in between. Otherwise, in between the two, there's no potential, there's just whatever energy the electron happens to have. It turns out that, in one dimension, the Schrõdinger equation, which is the equation we use to generate the equations for orbitals for wavefunctions, the solutions to the Schrõdinger equation in one dimension like this, one set of solutions are sine functions – but the sine functions have to be such that the value of the function is zero at one wall and also zero at the other. Because, if you had a non-zero value, that means that the zero point would come outside the well here, which would imply that the electron could somehow exist outside of the well, which is not physically possible. The wavefunction has to start and end at these boundary conditions.

If you come up with a sign function that could possibly describe the motion, like if we wanted to just show half a sine wave, then we're going to have some kind of proportionality constant in front of the x coordinate. That proportionality constant, there are multiple values that would work. If I were to double the coefficient, it would be like I shrank in half the function. If this sine function exactly spanned from one side of the well to the other and I shrink it in half, that means that there's another equation that will start and end still at the correct endpoints, but will have one more wiggle in it. As you keep increasing that value of that coefficient, there's a whole set of wavefunctions that satisfy those conditions. The first four look like this, which you might recognize as being exactly the same functions that I got with the phone cord demonstration, cause that's the exact same type of situation – you've got two endpoints that have to be fixed (in the phone cord case, there is no more cord once you've run out of cord, so the ends of the cord and the ends of the system). The only waves that can exist along it are ones where the ends match these endpoints and generate these symmetric waves that can be modeled by sine functions. The reason to show you this particle-in-a-box problem is to show you it's an example of electrons having the same behavior as this phone cord thing that I demonstrated. Why does that matter for our discussion of conjugation? Because if you think of a conjugated system, you could view that as a series of p orbitals that are all in a line, a line being a one-dimensional object. So the molecular orbitals – the bonding, non-bonding, or antibonding orbitals of a pi system, could be modeled by waves just like this, where you have a function that spans across the whole molecule, or it has a node halfway through the molecule. We're going to use these functions to guide us in shading in these molecular orbital diagrams that we're going to draw, these diagrams that show how can we use p orbitals to come up with a shape that looks like the real bonding and antibonding and non-bonding orbitals that present in on these conjugated systems.

Let me add a little bit of detail to these small drawings. These first four functions correspond to what would be the first four energy levels of that one-dimensional electron; same n as n, l, ml, and ms, the four quantum numbers. n is the principal quantum number, which tells you two things: the total energy of the system, effectively; and, n-1 is the total number of nodes in that system. Notice that we have zero nodes, one node, two nodes, three nodes. What happens when we go into a three dimensional system when we get to an atom, the nodes can be distributed in more than one way; they don't just exist along one axis. That's how we end up with all the different shapes of atomic orbitals. Where I want to bring this to is to conjugation. We have seen ethene and the allyl system, but we need to generalize to be able, in theory, to handle a whole series of conjugated systems. From left to right, these involve 2, 3, 4, 5, and 6 p orbitals – which, due to symmetry, generate 2, 3, 4, 5, and 6 molecular orbitals. We're going to figure out how to draw pictures for these different molecular orbitals.

Before we get there, we've got to talk about what constitutes a conjugated system. Look at these two example molecules: this is buta-1,3-diene, and this is buta-1,2-diene. The dot in the middle of that second structure is intentional; no everyone uses it. Here's the issue: there is a carbon where that dot is located. The dot is help to make sure that you realize that it's not someone that was writing a double bond that had some kind of pen issue; or, if you were really sloppy, you might accidentally connect the two double bonds. To make sure you really know there's a carbon there, that dot [is often used]. What is the hybridization of that carbon? sp. If it's sp, it's linear, so you can't draw it bent, because that would be misrepresenting the structure. Does conjugation occur in both of these molecules?

What is the difference between hyperconjugation and conjugation? Hyperconjugation is when you have an interaction that does not involve bonding; notice that I'm careful not to say non-bonding because, we're going to find out that is bonding, just not – meaning the non-bonding orbital is a molecular orbital that happens to have zero energy relative to the atoms, but what I'm trying to say here is there's just not any kind of orbital interaction like that that would be considered bonding, non-bonding, antibonding. It's just a little bit of donation of electron density to a neighboring orbital. It usually happens from a bond into an orbital; that's different from conjugation, in which you have full overlap of all the orbitals involved, and the electrons can freely float throughout that whole system. Let me write those definitions down. Hyperconjugation is the partial donation of electron density to a neighboring orbital through an interaction that does not involve a bond. That's separate from conjugation which is the full delocalization of electron density across multiple orbitals due to bonding overlaps.

Now let's back up to these two example molecules. How can we demonstrate that conjugation should be occurring? How can we know experimentally that conjugation is occurring? What is there unusual about 1,3-butadiene that indicates to us that conjugation's occurring? Because there's a single bond between there, the two double bonds can rotate independently. It's the single bond itself that turns out to be the key. The same discussions we're having now about conjugation – both how do we represent it and how do we know it happens – the same story we're going to talk about with benzene. Benzene has six carbon-carbon bonds that are all exactly equal to each other, but we write it with double bonds and single bonds. But there is no such thing as a double bond and a single bond in benzene; it's just the inadequacy of our writing system that leads us to do that. [explanation why benzene hasn't been in a problem] For most of the reaction that you've learned – hydroboration-oxidation, oxymercuration-demercuration, simple addition of halogens – none of those work with benzene, even though we write it with what looks like could be a double bond. Experimentally, all six bonds are equal in length, and they're somewhere between a single and double bond in length.

Which is generally the shorter bond: a single or double bond, if we're comparing the same two atoms in those two different bonds. A double bond is shorter. If you've got more electrons in between the two nuclei, which is going to help bring the two nuclei together. The single bond of buta-1,3-diene is shorter than a regular single bond, so there's something bringing the two double bonds closer together, causing that single bond to contract. That is due to conjugation. Due to conjugation, the carbon-carbon single bond in buta-1,3-diene is shorter than a standard carbon-carbon single bond. The way we can observer whether there's conjugation or not: draw a SMOG. What is the hybridization of every one of the carbons in this molecule? Sp2, because there's three sigma bonds on every one of those, and only sigma bonds or lone pairs count for hybridization. If we have four atoms that are all sp2 hybridized, then we're going to have four of these three-fold flowers, along with a raft of hydrogens. Then we have our p orbitals, of course. Here, we encounter exactly the same issue as in the allyl system: which of the p orbitals do we overlap now? Yes, which would help explain why that single bond is shorter than it should be, because all four of the p orbitals do overlap. Again, use your imagination to think that's a line of p orbitals, and now we have electrons going into this linear system, which is kinda like the particle in the box: once you fall off the end of the molecule, you're off the end of the molecule, so the electron isn't really going to do that on either end. Those are your boundaries, so the wave function has to span those boundaries.

Let's look at this other system. Let me ask the same questions: do you think that that other system is also going to experience conjugation? The buta-1,2-diene. Why not? That central carbon is sp-hybridized. If you have sp hybridization, that does mean you have two different p orbitals on that carbon. But the two p orbitals are crossed from each other. One carbon on one side forms a double bond facing one way; the other carbon on the other side forms another double bond that's perpendicular to the first one. If they're perpendicular to each other, they have no interaction with each other, so there's no conjugation. This is what is known as a cumulated diene. Let's draw a SMOG for it. We know that one carbon is sp-hybridized; the carbons on either side of it are sp2-hybridized; then we have a methyl group at the end which is sp3-hybridized. [color key] I'm going to draw one set of p orbitals not shaded; that's not meaning wavefunciton, it's just to distinguish the two sets from each other. One set of p orbitals forms its pi bond, then the other set of p orbitals is perpendicular. Since the two pi bonds are perpendicular to each other, there is no conjugation.

First, let me one last time remind us about those standing wave functions that I showed you in the context of the particle-in-a-box problem, which are the same functions that we saw in the phone cord, which underneath are the same things that happen in these p systems. The number of molecular orbitals – which means bonding, non-bonding, or antibonding orbitals – the molecular orbitals in a pi system – you can't really call it a pi bond because it's more than two p orbitals involved – the number of MOs is always equal to the number of p orbitals used to represent that system. If we have the molecule 1,3-butadiene, we have four p orbitals and, it turns out, a total of four electrons. [One important quantity to be able to determine is] how many pi electrons are there. Even if we get to the point where we say that there's no such thing as a pi bond in some of these systems, at least when we write it on paper, that does represent a specific number of electrons, and it's valid to count it that way. Even though we may argue this is not a normal double bond in this molecule, we could still look at that the way it's written and say, oh, four electrons distributed in the pi system. We know it's four electrons cause each bond has two electrons in it, and the sigma bonds are all perpendicular to the pi bonds, so none of those electrons count.

What we're going to end up with, then, are four representations for each of the four molecular orbitals, each of which, in turn, has four p orbitals that comprise them. Let me put on top of here that lowest-energy standing wave, the next highest energy standing wave, next highest, and next highest. How did I know to draw it this way? Experience. How could I figure out how to draw it this way? Notice that is one that spans; this is half of each of these sides, they're equal; this wave's split into third; and this, the wave's split into quarters. This brings up an odd issue, though, because if you look at the p orbitals themselves, they're always set to be in thirds, so you're going to have ... it's going to be interesting to figure out how to shade it. This is what we do: overlap the wave, shade it based on that. What do we get? So that you could still see those waves afterwards, let me make another set that we'll actually color in. We have zero nodes, one node, two nodes, three nodes, which must be symmetric. Every places there's node, you flip sign of the wavefunction, which means you change which way you shade it. So the lowest-energy system – think of that phone cord demonstration: the least amount of effort I had to put in is the one that generated this wave that spans all the way across.

To make something that looks like that, you can use p orbitals that all have the same sign of the wavefunction. In real life, we don't add all four p orbitals equally, cause if you added this, what you'd really end up with is a function that's effectively even all the way across, a line all the way across. In reality, you would take a small version of this p orbital, a large one of that one, a large one of that one, a small one of that one, to match the amplitude of this function that spans it.

We go to the next orbital up: since there's a node, two of the p orbitals that we use to represent the orbital are going to be one shading; the other two are going to be opposite. Let's go back to both the first and the second molecular orbital and use our very fancy notation [smiley faces] to show that in that lowest-energy orbital there's only favorable overlap that occurs, which means there's electrons between all of the nuclei, which maximizes the interaction of plus and minus charge, which is why this is the lowest-energy orbital. In fact, because the favorable interactions, that's all you've got, that means it's going to be lower in energy than if the orbitals had never interacted in the first place. I'm putting a line here with the zero marker on it, which represents non-bonding, which represents a situation in which the atoms combining don't do any better energetically than if they had never combined in the first place. Because this is all favorable interactions, it's below that in energy, so that is a bonding orbital. Everything below zero is bonding; everything above zero is antibonding; everything at zero is non-bonding, which we don't have in this case, so I'm not going to put that label on this time. The second orbital, you have a favorable interaction on each side of the node, but the node itself represents an unfavorable interaction. But overall, the interaction is favorable, so we have another bonding orbital. A way that we've written this in the fact, the favorable interactions outweigh the unfavorable; [that's why it makes it] a bond. The third orbital: the middle two orbitals would be shaded the same way, but opposite from either orbital on either side of it. That means that there are two unfavorable interactions, versus the one favorable one. That's why we make that an antibonding orbital. Finally, the highest energy one is where every other orbital is shaded oppositely, which means all that you have is unfavorable interactions, no electrons between any of the nuclei, which is totally unfavorable; that's why that's the highest-energy orbital.

But, these are just the spaces. None of this stabilize or destabilizes the molecule until you actually put electrons in it. Since we had counted earlier that there are four electrons, we're going to fill up these four orbitals, which work exactly on the same principles as atomic orbitals: Aufbau principle, which says an electron's going to try to attain as low an energy as possible, so we start with the lowest-energy orbital; Hund's rule, which says that if we have multiple degenerate orbitals, which means orbitals all the same energy, you put one electron into each; Pauli exclusion principle, you've filled up each of the orbitals once, you can put a second electron, but only if it has opposite spin. We filled up the lowest orbital, so again back to the Aufbau principle, we have to go to the next-highest energy orbital, which can accomodate two more electrons. We've now put the four electrons in; that's it. Electrons only went into bonding orbitals, so only favorable interactions occur. Two things I want to point out: the picture that we drew with two separate double bonds does not match the picture that we get from the lowest-energy orbital; it would seem to more match the second one. That's why this single bond doesn't act like a normal single bond, because we have more than just a separate interaction; we have one interaction that crosses the whole molecule. The second thing is that there is this kind of quickie calculation that's done called bond order, which is the number of bonding electrons minus the number of antibonding electrons, that whole thing divided by two. In this case, we only have the four bonding electrons; divide that by two, that gives us a total of two bonds. So across the whole system, we effectively have two bonds; that part matches the way that we draw the structure. The same set of principles, we could apply to five, six, any number of orbitals. If you have an even number of p orbitals, you'll have orbitals be bonding, half be antibonding; just like this system that we saw, just like in our standard, individual pi bond – two p orbitals turn into two molecular orbitals, one bonding, one antibonding. When you have an odd number of orbitals, like the allyl system, one orbital will always be non-bonding; of the remaining orbitals, half will be bonding, half will be antibonding.

[Why do valence electrons matter]? They're the most energetic electrons – out of any electrons in the system, they've already got the energy to try to escape out from an atom. We have the equivalent situation here: we've got two different orbitals, one that's got higher energy electrons than the other. Those are going to be the electrons that react. Where do they go, though? The first place they can. If you think about the reduction of an alkyne with sodium, you think about the initiation of a Grignard preparation – in both of those cases, an electron goes into a bond. But it can't go into a bond – a bond's already got two electrons in its orbital, so where it goes into is an antibond, it goes into the lowest-energy place it possibly can. There are what are known as the highest occupied molecular orbital electrons, and there are what are called the lowest unoccupied molecular orbital [electrons]. This is one way that interactions between two pi systems. Highest energy electrons go to the lowest energy orbital available. These kind of interactions are the we describe what are called pericyclic reactions, the Diels-Alder reaction. This also shows up in spectroscopy. If you think about atomic spectra – atomic spectra occur because you excite electrons and they fall back down between different energy levels. Spectroscopy is where you do the reverse: you add energy and you cause electrons – or, in the case of NMR, we add energy to flip the spin of a nucleus. In other words, there's some exact packet of energy that corresponds to a photon that corresponds to a specific frequency of light that could, for example, bump one of these highest-energy electrons up into the next orbital up. In conjugated systems, that generally happens somewhere in the UV spectrum. Or, if you get molecules that are long enough – like carotene, it's an enormous number of double bonds [in a row], it actually brings that energy gap into a range that, due to complimentary colors, causes us to perceive orange, like carrots are orange. [story of carotenosis] That's that gap between the highest energy occupied orbital and the lowest energy unoccupied orbital that you access in spectroscopy.
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Particle in a box

Due to conjugation, the C-C bond in buta-1,3-diene is shorter than "normal".

Since the two pi bonds are perpendicular, there is no conjugation

hyperconjugation – the partial donation of e- density to a neighboring orbital through an interaction that does not involve a bond.
conjugation – the full delocalization of electron density across multiple orbitals due to bonding overlaps
The # of MOs in a pi system is always equal to the # of p orbitals used to represent the system.

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Structures – Identical to those from lecture 12A (02/15/12)