Lecture 2B • 09/28/11

How many of you read the sections of the syllabus for Tuesday and today? For the rest of you, why not?

We're going to do an overview of just those things we need to know for o-chem. Standing waves. I'm going to do a demonstration with a telephone cord. That will let me model a simple system of standing waves. The reason we're doing that is because electrons act as standing waves. We're going to make that connection between standing waves and quantization of energy: the fact that electrons can only had very specific energy values. That's going to lead us into the shapes of atomic orbitals, which 99% of the time we're only going to be worried about s & p orbitals, so we need to understand where those shapes come from. We're going to review the electron filling rules cause we'll use that all three quarters, especially once we get to spectroscopy. Related to that we need to know what an electron configuration is, because there's a connection between electron configuration, valence electrons, and the behavior of atoms. This is going to be a reminder, for example, of why oxygen would have a –2 charge. Carbon and hydrogen, we do exploit both of them in their isotopes for spectroscopy and kinetics.

I want to show you a little bit of phone cord behavior. If you watch the way that I move this at some steady but slow pace, there isn't anything that interesting that happens with this cord. It kinda wobbles around in a random way, until I get up to some minimum speed, and then you can see with very little effort I am able to keep the cord going at a very consistent pace. Slow down again and it very rapidly just decays back into random motion. Speed up again, there's that nice stead pace. If I speed up just a little bit more, you see that it also starts getting into random motion, until I slow down again and all of a sudden that first wave pops right back into action. That means that at some specific energy that I'm putting into it, this system is able to persist. A little bit on the low side, it disappears; a little bit on the high side it disappears. But if I keep increasing in energy, then you'll see that a new wave pops into existence. If I do this correctly, there's one place in the middle here where the wave appears not to be moving. What is that position where no movement is occurring called? A node. Again, as I slow back down, this wave will disappear, it'll be totally random, until I slow down enough that I get back to that specific energy level. So there's one energy level here, then if I speed up a little bit there's another energy level. If you hit just the right energy amount, for a moment there I had a wave that had two nodes in the middle of it. So, the lowest wave, n = 1, that had zero nodes; the second wave had one node; the third wave had two nodes. The more energy we put in, the more nodes that are generated and it's specific amounts of energy that correspond to these specific waves that have whole numbers of nodes.

That's the whole point of a standing wave: that there are only specific standing waves that can exist based on the boundary conditions established by whatever physical system we've got. This is a case where we had, principally, two fixed endpoints. This is not a perfect system, so I did have to wiggle it. But we can imagine that we had two fixed endpoint like a string on a musical instrument, for example. There is a principal wave that could exist that stretched all the way from one end to the other. Then, mathematically, you can think of that as a sine function, you call it sine theta. The only next wave that would match both of those endpoints would be sin 2theta, and then sine 3 theta. So we get something that looks like this. Here's that first principal wave stretching all the way across; that's n = 1, and we have zero nodes. The next higher wave, chopped exactly halfway through; that's n = 2, where we had one node. Then we have the last one I successfully generated, where it crossed the axis twice; that was n = 3, and that's two nodes.

In general, we can define a standing wave as some kind of non-propagating wave. A propagating wave would be something like light or sound that moves through a medium. This is fixed, in a sense. However, if you take two propagating waves that are synced exactly right and have them move in opposite directions, that ends up mathematically being the same as a standing wave. A standing wave is a non-propagating wave with one or more boundary conditions. I could say endpoints, but when we get to electrons that would be kind of a incorrect term to use.

A node is a place on a wave that has a value of zero.

Quantization refers to the fact that energy only occurs in these very specific packets. There are two experiments you might have learned about in the past that demonstrate the quantization of energy in electronic system. The first is the photoelectric effect: the fact that if you have a metal sheet that is responsive to light, there is some minimum frequency that you must cross over before that metal will respond. For example, you can shine red light .... By the way, is red light shorter or longer in wavelength than blue light? It is longer. Does that mean the frequency of red light is higher or lower than blue light? It's lower. Longer wavelength means lower frequency, which means lower energy per photon. A photon, that's a piece of piece, which is a wave, which is a particle, which is a wave, and a particle, and both, and neither, which is quantum summed up in a nutshell. In the photoelectric effect, each one of these photos has to have a minimum packet of energy in order to excite electrons, in order for the metal to respond.

We see a similar response in atomic spectra. If you looked through a hydrogen tube through a prism to find the different color bands that show up, there's technically and infinite number, but a countably infinite number, of these different wavelengths that come out. These very specific wavelengths are caused by specific transitions between different energy levels. You don't just have any old random energy level for an electron; they're very specific or quantized values. That's the connection to showing you standing waves. Standing waves, that's another type of system in which energy an only have specific values.

In a standing wave, there are only certain waves that can exist based on the boundary conditions. Think of what we saw. There was this long wave I could generate, but a low in energy, a little high in energy, nothing useful happened. If I went up enough in energy, then I got that second wave that had a node in it. Again, a little bit below or a little bit above, and that wave could not exist. Because you can have only these certain waves, these waves will only have very particular energy levels associated with them. In short, energy is quantized.

This system, you could say, is a one dimensional system that's then being made to wave. This is similar to a simple quantum experiment known as a particle in a box. If you trap an electron in a one-dimensional line.... We can cut to the end of the story and say that electrons have wave behavior. In this particle-in-a-box system, waves generated by an electron will look exactly like these same waves that we saw in this phone cord system. It being a relatively simple mathematical system to model, if you took physical chemistry or advanced physics, that's problem that's very commonly done. How does this lead to atomic orbitals? We'll take this one step at a time. Imagine that we took this linear system and turned it into two dimensions, wrap it around into a ring. You might have seen diagrams like this, where a wave propagates around a ring. The wave starts somewhere on the curve, crosses, and eventually comes back and overlaps with itself again. This is similar to what happens in .... Have any of you ever seen a wine glass or some other thin kind of glass container, where you take your finger and run around the edges of it? That glass will only generate one specific musical note that depends on how big is the glass, what kind of glass you have, how much water is in it – in other words, all that physical aspect of that glass sets up the boundary conditions that allow only the specific note to be able to exist. That note exists because as it's wiggling around, it exactly reinforces itself. That's the same kind of thing I'm trying to demonstrate here. Because this wave overlaps with itself, it will just keep on persisting. But if you had instead a wave that didn't overlap itself properly, as it's going around and around and around and when it comes back, it doesn't overlap. Which means it's going to end up interfering with itself.

Interference needs qualification, because it's not necessarily a bad thing. There is such a thing as constructive interference, where waves reinforce themselves, or deconstructive interference, which is waves will cancel each other out. This second example, where the wave does not match itself, that would end up generating deconstructive interference, so that wave would dissipate. Although I'm showing you circular systems, this idea of standing waves shows up all over the place. For those of you who've got really fancy car audio systems, you know you've got that one sample CD that you have that one note that, when you hit it, the entire neighborhood around you will rattle because your car hits the right resonant frequency. So, we started with the linear system. The generates only specific waves with specific shapes. Then we hit these fancier two-dimensional systems. Because the wave exactly overlaps itself, it is compatible with the boundary conditions of this system and will reinforce itself. Because the wave does not overlap itself, then it will deconstructively interfere with itself and disappear. it will eventually dissipate, disappear due to deconstructive interference.

So, first, the phone cord experiment, to show only specific waves exist. Second, we pull it around into a loop and show there's other, more-complicated systems where the same situation occurs – only specific waves can exist.

{In order to have deconstructive inteference, don't the two waves have to be exactly opposite of each other?} To have perfect deconstructive interference, yes. But, even if it's not completely opposite, it's still going to attenuate that wave, and as it goes around again, it may further attenuate itself, and so, on average, eventually the wave will just dissipate. Two different waves, to exactly cancel themselves out, they have to have exactly the same amplitude, the same frequency, but opposite phase; where one's going up, the other's going down at exactly the same time.

Atomic orbitals

Take this two-dimensional system, pull it into a sphere, and the same story occurs: where there are only very specific waves that can exist. In this case, for an atom, the boundary condition is the fact that you've got a nucleus right in the center of the atom. Since the nucleus is positively-charged and the atom is negatively charged, that interaction is what sets up all the shapes of the different atomic orbitals. Electrons are describe by these things called wavefunctions, which are just equations of a wave, but we give it this special name. Electrons are described by wavefunctions, which are mathematical representations of the wave behavior of an electron. The common symbol for a wavefunction is the capital Greek leter psi. These waves have the nucleus as the boundary condition for these waves, so they are standing waves. That means that the unique shapes of the atomic orbitals are all caused by the presence of exactly and only one nucleus. All of the atomic orbitals, if you look at them, they all have symmetry that revolves around that nucleus.

Because these are standing waves, only a certain number of these waves can exist. There are, technically, an infinite number.... We know that there's a 1s orbital, a 2s orbital, where an orbital is just the space described by a wavefunction, but there's not such thing as a 1.5s orbital. That's because energy only occurs in fixed quantities. Because wavefunctions act like standing waves, only certain wavefunctions can exist.

You could have two [systems] that have exactly the same frequency, but they would have to be identical system. The two glasses would have to have exactly the same physical conditions, if you started a wave off in one glass, in real life, the sound wave will induce a resonance in the other glass. If, for example, you have a piano around, and you have some other instrument that's playing near it, you'll hear little echoes of that instrument in the piano as the correct strings are caused to resonate by something else near by it. You can have the same wave, but you have to have the same or similar physical systems. It can happen with an electron. To move electrons between energy levels, all electrons are equal in a sense, you have to have the right packets of energy.

What do these atomic orbitals look like? An orbital is a region in space described by a wavefunction. But these wavefunctions have nasty equations associated with them. Unless we are particle physicists, there's no need for us to know that equation. Instead, we can represent those equations by a set of what are known as quantum numbers. It's from those quantum numbers that we get the names of those orbitals, like 1s, 2s, 2p. We only really need two quantum numbers in this class.

So, a wavefunction is generally written in what are known as spherical coordinates. Normal Cartesian space has three dimension: x, y, z. But we can represent that space also with coordinates r, theta, phi. This equation would more appropriately be written by something known as a Hamiltonian operator. More simply put, playing around with the equation a bit, you can actually split this up into two different functions. One of these functions depends only on r, how far away you are from the atom. An electric force depends on two charges, the size of those charges, and then just how far away apart they are from each other. Start with the atom that's got a positively-charged nucleus; you've got an electron that's negatively charged. And so that distance sets up a certain energy level. So one of these functions is dependent just on that distance. The other function is related to where around the sphere is that electron. One of these we call the radial function, dealing with just how far away from the nucleus an electron is, and the other is called the spherical. There's a connection between the radial and spherical.

Let's now define these quantum numbers.

The quantum numbers represent the different possible wave functions in an atom. Three of the quantum numbers describe an orbital. The fourth one, spin, just says whether the electron is spinning up or down. Quantum numbers are used to represent the possible wavefunctions in an atom. Three of the numbers are used to describe a specific orbital.

What are these two quantum numbers that you need to know? One of them is called the principal quantum number, n, which represents the total number of packets of energy in an electron. If you're think of this demonstration that I did, below a certain energy level, nothing useful was happening. Once you reached a certain magic energy level then something could exist. For an electron to exist around the nucleus, it can't fall below a certain energy level, because there's nothing below it that exists, which is why an electron can't fall into the nucleus. So n = 1 is the lowest energy. Put additional packets of energy in it and that's how we get n = 2, n =3, so on and so forth. This n value is the number in the orbital name. If you say 2s, that's an n = 2 orbital. n is the principal quantum number that represents the total number of packets of energy in an electron. n has to be greater than or equal to one; you don't have that packet of energy, you don't have an electron. What's the other one? Here's why I explained this difference between the radial and the spherical functions. What that means is, let's say you start out with an electron with just one packet of energy. When you put that second packet of energy in, there's a choice of where that energy can go. That energy could be used to get the electron further from the nucleus, so then that energy then shows up in the radial function. Or, that energy might be used to send, effectively, the electron spinning more rapidly around the nucleus.

If you have an object with a certain mass that's zooming along all by itself in space, the classic "an object in motion stays in motion", what quantity, what physical property do we say that object has as it's zooming along. Inertia, and inertia is related to what? Force, but what if a force isn't acting on it? It's just going to keep moving all on its own until a force changes that. But what is it that it changes? Momentum. If we take an object that has momentum but momentum because it's turning around, what do we call that? Angular momentum. This second quantum number is call orbital angular momentum, which might have been just a term you memorized, but what that means is how much is that orbital rotating around that nucleus. That's one way to visualize what's going on. So orbital angular momentum can be interpreted as how much energy is directed around the nucleus.

Because one packet of energy is always used just to keep the electron from the nucleus, the maximum of l is n − 1, that's where that rule comes from. What's the practical upshot of all of this? Let's look at the l values first. Think of that phone cord demonstration first. When you had the lowest possible level, there were zero nodes. When you had the next-highest level, you had one node; the next-highest level, two nodes. Imagine you were travelling around in a sphere. If you've travelling around in a sphere and you have no nodes, then that means you're going to have an object that looks just like a sphere. But let's say instead as you go around the sphere, you've got one node. Due to symmetry, that node is going to cut through the sphere.

If we did that, what do we generate? We end up generating a kind of dumbbell shape. Go up one more energy level, throw one more packet of energy around the nucleus, and you're going to have a second node which one of ways of doing it is having the two nodes perpendicular to each other, which will generate this kind of shape. We recognize these as s, p, and d orbitals. This has all been a complicated story to explain why do these orbitals have these specific shapes. It's related to the number of nodes, which is related to the specific energy packets you can throw into an atom.

This connection between n and l. l only has a certain maximum value. This is why, for example, there's no such thing as a 1p orbital. Because in the 1 energy level, there's just not enough energy to generate that node to made a p-orbital. You've gotta have at least two energy packets [total]. That's why the p-orbital only shows up at the second level. That's why a d-orbital only shows up starting at the third level, you have to have enough energy packets.

Let me show you a bit what the alternate possibility is. We know there's such thing as a 1s orbital, a 2s orbital, a 3s orbital, a 4s orbital. All of those orbitals would be ones in which you're not throwing those energy around the nucleus. But then where's the energy going? In that radial function, moving the electron further away from the nucleus. That means in the radial function, you're going to start having nodes. If you look at a 1s orbital and you look at the wave function, it's just going to be a declining function. But if you look at the function for a 2s orbital, it crosses the axis just once. It has one more node. If you look at a 3s orbital, it will cross the axis twice.

What is the meaning of the y-axis? That's a complicated question, because there's no direct physical meaning to that psi value. The Born interpretation of quantum mechanics says that the square of that is the probability of finding an electron somewhere in space. But it is one interpretation, the main one. But therefore, these is no easily-expressible physical meaning for psi. What's the big deal about there being these nodes? This is just the value of the function as you go one direction along the radius. Whip that around in a sphere now, and what's that going to get us? Well, a 1s orbital look just like what you expect it to, a sphere. A 2s orbital is not a sphere; it is a sphere within a sphere. Between those spheres is a node. This is what's always confusing: spherical nodes are lines; linear nodes are spheres. If you from the radius and you have a node one point on the radius, pull that around in a circle you're going to make a circle. If you have a node that just shows up at a point, it turns into a sphere once you wrap it all the way around. A 3s is therefore a sphere inside a sphere inside a sphere. On a practical level, all we're going to use are the simplified s and p orbital picture. So the 2p orbital looks just like the one here. A 3s orbital looks like a dumbbell inside a dumbbell; we just don't worry about that.

Electron configuration. Related to electron configuration is the octet rule. What is the octet rule? Atoms somehow behave unusually stably. Think about something like fluorine. Fluorine violently reacts in order to get electrons. Once it gets that electron and becomes F–, it kinda just sits around. The nobel gasses, because they have this octet configuration, normally don't react. Turns out we can force them to react, but they don't like to react. There's something magic about having the number eight, which there is a reason for that. Does anyone remember what a shell is? A shell is a particular value of n, the principal energy value. A shell is an energy level which is a specific value of n. What is a subshell, then? It's a specific value of l, it's all of the same kind of orbital within a shell. So if I say 2p, there's really three different 2p orbitals. If you're talking about all of those combined, that is the 2p subshell. So the subshell is a specific value of l inside a shell.

The octet rules states that atoms are unusually stable when the s and p subshells are filled, for the outermost shell, which is where we get our value electrons. Why is it that the octet rule works; what's going on? If you're treating electrons like waves .... If you think about music and think about instruments playing, if they play in just the right way then, to us, it sounds pleasing. These notes reinforce themselves; they're waves. Wel, electrons, being waves, can end up interacting with themselves, to cause some kind of reinforcement. When you fill subshells, you get that synergy ocurring. You get an unusually low-energy configuration by having exactly that number of waves. Valence electrons are the electrons of the outermost shell, which are the most energetic electrons.

What I wanted to wrap up with was showing you the electron configurations for fluorine, chlorine, and bromine. If you don't remember how to do electron configurations, how can you cheat? How can you use the periodic table to come back to them?

Fluorine has a configuration of $1s2s^22p^5$; chlorine, $1s^22s^22p^63s^23p^5$; bromine, $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$. What are the valence electrons of fluorine. They're all of the electrons in the outermost shell, not the outermost subshell, so it's all of the ones in the 2 level for fluorine. So the valence electrons for chlorine, then, would be everything in the 3 level. The valence electrons for bromine, then, would be everything in the 4 level. These elements are elements in the same group and act similar because they have the same number of valence electrons.

There is a way to use the periodic table to cheat and figure out electron configurations – for the most part. There are elements like copper and chromium that can have exceptions, but we're hardly going to be dealing with any of those types of elements in this class. We're almost always going to be confined to carbon, hydrogen, nitrogen, oxygen, phosphorus, sulfur; just a handful of elements. If I was to write out the periodic table in this kind of form, and ignoring those trans-uranic elements, those elements that include things like uranium – you see that I've divided this up into three blocks. Two columns on the periodic table that would be on the left, what's the name we assign to that block? The s-block.

For the six columns on the righthand side of the periodic table? p-block. And in the middle, where the transition metals are? That's the d block. Why do we call these the s, the p, and the d blocks? The last electron that you put in for that particular element is going to be the type of orbital that's listed on these blocks. So hydrogen, that's in the s block; the first electron that you put in goes into a 1s orbital. You can squeeze two electrons into a single orbital, so for helium the next electron that goes in alo goes in a 1s orbital. There's only an s orbital on the 1 level, so the very next electron that goes in would have to go into a 2s orbital, that would be for lithium. Then beryllium would also be in the s block, so that would be the next electron – a 2s. Boron is over here in the p-block, and that matches with the fact that the next electron, the fifth electron that you would put in is a p-electron. As you go along the periodic, for the most part, that structure of the periodic table matches electron configuration. When we're not dealing with elements like copper that have exceptions, you just keep following along, that's how you get this 1s2s2p3s3p order. To clarify, it's not electron configuration that establishes where an element goes on the periodic table. It's atomic number, the number of protons, which for neutral elements, the number of protons is the number of electrons. But it is atomic number that is used to determine position on the periodic table.

There are these electron filling rules, which work not just for atomic orbitals, but they work for molecular orbitals as well. What is one of the filling rules. Hund's rule – if you have multi equal-energy orbitals, or what are called degenerate orbitals, one electron will fill each orbital first before you pair electrons up. The Pauli exclusion principle is the one that says an orbital can have a maximum of two electrons, technically only if they have opposite spins. The Aufbau principle, which means "building up" – the electrons will fill from lowest energy up through the highest energy.

Isotopes. What are isotopes? Same number of protons, different number of neutrons. So the same element, but different flavors of that element. The isotopes I'd like to mention are the three forms of hydrogen. This would be their partial atomic symbols, where I show their mass number and atomic number. Even more frequently, we use just simple one-letter abbreviations. Technically, the hydrogen that i just a proton is called protium. The hydrogen that is the second form that has a mass number of two, deuterium. The third form, tritium. 99% of hydrogen is "normal" protium, but we'll used deuterium when we get to magneti resonance spectroscopy. We'll also encounter deuterium when we tall about kinetics.

There is an isotope of carbon, 13C, that we use in spectroscopy.

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standing waves; quantization; atomic orbitals (nodes & shapes); electron configurations; valence electrons; isotopes

standing wave – a non-propagating wave with one or more fixed endpoints
node – place on a wave that is immobile (value of the function is 0)
quantization of energy - in a standing wave system, there are only certain waves with certain energy levels that can exist
because the wave exactly overlaps itself, it matchs the conditions of the system
because the wave does not overlap itself, it will eventually dissipate due to deconstructive interference
Electrons are described by wavefunctions, which are mathematical representations of the wave behavior of an electron. Wavefunctions are standing waves with the nucleus as a boundary condition. The unique shapes of the wavefunctions are caused by the nucleus.
Because wavefunctions act like standing waves, only certain waves can exist.
Quantum numbers represent the different possible wavefunctions in an atom. Three of the quantum numbers are used to describe an orbital, which is a region in space that an electron is likely to be found.
n = principal quantum number – represents the main energy level – represents the total available packets of energy in an electron
l = orbital angular momentum – maximum is n - 1
filling rules: Aufbau – lower energy orbitals fill first; Pauli exclusion – two electrons can fit in one orbital; Hund's rule – if there are multiple equal-energy orbitals, each gets an electron before pairing occurs.
octet rule – when the s &p subshells of the outermost shell are filled an atom is unusually stable.
shell – energy level
subshell – specific value of l inside a shell
valence electrons – the most-energetic electrons in the outermost shell that participate in bonding

F: 1s22s22p5
Cl: 1s22s22p63s23p5
Br: 1s22s22p63s23p64s23d104p5

These elements all act similarly because they have the same number of valence electrons.

isotopes – same element, different # of neutrons
protium, deuterium, tritium