Lecture 2A • 09/28/11

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

Atomic structure

We're going to cover just enough so we can function with organic molecules. This is the series of topics I want to cover today. First we need to talk about standing waves. If you've had me as an instructor before and seen the rude things I do to phone cords, there'll be yet another demonstration of that. Because standing waves really are what electrons are around atoms. First we'll start with a simpler system like the phone cord then move to atomic orbitals, which are somewhat more complex shaped. We'll then talk about electron configuration. We won't be using electron configuration all that much in class, but it is useful to know what oxygen would be a –2 ion or chloride would be a –1 ion. From that, when we get electron configurations, we'll automatically be able to talk about valence electrons. You need to be able to determine how many valence electrons are around an atom. Then we'll round up today with isotopes.

How many of you read the sections of chapter 1 indicated for Monday's and today's lecture? For all you that didn't raise your hands, why not? That is the point, you don't have a good excuse. This is the easy part of the quarter, where you don't have a whole bunch that you're worrying about yet. I tried to warn you that I know how this class starts and I know how this class ends, and this is exactly the start that I expected. Do not follow the patterns of past o-chem classes and ignore what I have to tell you. When I tell you that I expect that you've read the textbook before you come to class, it's not just talk. It's cause I know what's going to happen in the middle of the quarter if you don't start now. Some of you won't have problems with this material. I'm not trying to scare you and say: "This chapter 1 is going to be impossible." No. But what your study habits today are when you're fresh and the quarter's just started are, unfortunately, probably about as good as they are going to get, unless you're working on your act some. So for all of you that did not raise your hand, seriously consider, do you really need to be in this course? Are you serious about being in this course? Because there's people chomping at the bit to add into here. So when I come Friday and ask that question, I better see everyone's hand go up and it better not be that you're faking it so I won't lecture you again.

I want to show you a little bit of phone cord behavior. If I just sit here and wiggle the phone cord at some slow pace, even if it's consistent, notice how there's not all that much going on with the phone cord. Nothing really happens, in fact, until I reach just a certain minimum amount of energy that I'm putting into it. And once I get to that minimum amount of energy you can see that this bounces almost on its own. I'm not having to put that much more effort into it. It's just that there is friction and such that it would slow down otherwise. Now what would happen if I sped up a little? You can see that the phone cord adopts a random motion. It doesn't have that nice period motion that you get if you slow down a little bit again. There's that magic pattern. Now, if I slow down even further, again the phone cord goes into some sort of random pattern. So there's some sweet spot, some optimal energy for me to put into that phone cord to get some kind of wave going. I'll go up to that wave again. I'll go faster and it disappears. Then I go enough faster, and notice now I have another wave, one in which the two halfves of the wave appear to be moving opposite of each other. If I do things really well you can see there's a spot in the middle where it almost appears as if the wave is not moving. What is that middle part of a wave called? A node, exactly. Again, this is a very specific amount of energy that I'm putting into the system, and if I slowed down a little bit again, it's going to disappear into random motion until I slow down enough that there's that first or what we call principal wave. This principal wave has one harmonic that has one node in it. If I can do it successfully without ripping it off the wall, I can generate another wave above that in energy that would have two nodes in it. In other words, there's only very fixed waves that are able to exist in this system: a principal and certain other higher-order waves.

Let me put a picture representation of what we just saw. If we fix two endpoints, what we're creating is a standing wave. A standing wave is a non-propagating wave with one or more fixed endpoints. There is a fundamental energy level that corresponded to the wave going all the wave from one side to the other and exactly matching those endpoints. Those endpoints, in fact, determine the type of wave that can exist because the wave has to overlap exactly with those endpoints. In Chem 1A terminology we would call it $n = 1$, the lowest energy level. If we then bumped it up we did then see another wave that passed exactly through the middle, so that point is a node where it is a place on a wave that is immobile, or you could say that the value of the function – whatever that wave happens to represent – is permanently 0. If you are mathematically inclined, which the little joke I make sometimes is (especially for ESL students): if you think of the words we're not supposed to use in English in polite company and most of them have four letters, well how many letters does the word math have? For most people, if you say "math", it's just as if you had said something else rude. But for those of you who do like math, imagine that you have a sine function that was describing that first wave. Make it sine 2 theta, and that's what that other wave would look like. For whole-number values of n theta, those are all the waves that are going to be generated that match those same boundary conditions. Put one more on top of here, now we have two nodes. $n = 2$ for the second wave, $n = 3$ for the third wave. What is the relationship between the number of nodes and the number that we assign to the energy level? That the number of nodes is $n - 1$. Do you remember ever in Chem 1A that quantity $n - 1$ showing up? It's the maximum value of l if we're talking about atomic orbitals.

Why am I showing you these standing waves? To show you that, for these standing wave systems, there's only very specific energy values that can exist. This is called quantization of energy: that you can't just put in any value of energy that you might want to into a system like this. It has to be very specific values. Quantization of energy: in a standing wave system, there are only certain waves with certain energy levels that can exist. That quantization has to do with the fact that it is specific amounts of energy. How does this relate to atomic theory? To give you the super-short version of the story, there are two main experiments that you might have discussed in Chem 1A that revolve around it. The main one is the photoelectric effect, which is the fact that if you have a metal sheet that is responsive to light, depending on the type of metal, there is a certain minimum frequency of light that you have to shine on that metal for any kind of response to be generated. To give an easy example, let's say you have red light that you're shining on the metal. Is red light longer or shorter in wavelength than blue light? It is longer. So does that mean it has a lower or higher frequency than blue light? It has a lower frequency, which corresponds to a lower energy per photon. A photon is a "piece" of light, it is a particle of light. Because light is a wave, but it's a particle, but it's a wave, but it's a particle, but it's really both and neither. And that's quantum mechanisms in a nutshell.

The photoelectric effect has to do with the fact that these packets have to be a minimum size; in other words, there's a certain quantized energy levels. The other way that we see this quantization is in atomic spectra: the fact that electrons move between different energy levels. Just like if I sped up and slowed down, I could move between the different energy levels of this phone cord. That's the connection. How do we get to these atomic orbitals, then? This simple phone cord demonstration is identical to a problem known as the particle in a box. That's where you imagine some kind of electron trapped in a one-dimensional system. Electrons act likes, and if you confine them to a system like this, the possible wavefunctions look exactly like this. The lowest level one stretched from one side of the system to the other; the second level has one node that goes into it. The next higher level has another node that goes into it.

What if we turn this into a two-dimensional system? What if we take this line and wrap it around into a ring. The wave starts at some point on the circle and crosses the circle one or more times, but comes back and meets where it starts. This is trying to show that the boundary conditions match. In these kinds of ring systems these are the kinds of waves that can exist because the do overlap with themselves exactly. If they did not exactly overlap, it we had something that looked more like this. You can see that at one point in time the wave was on the outside of the circle; let's call that positive. In another point in time, it would be negative. But if this kept oscillating, that means it's really going to interfere with itself. {constructive and deconstructive interference} Waves add together and subtract from each other. In this case, if you have a wave overlapping with itself and part of the time it's positive and part of the time it's negative, it's just going to disappear. So this wave would not match the boundary conditions for this ring system.

Because the wave exactly overlaps itself, it matchs the conditions of this ring system. Because the wave does not overlap itself, it will eventually dissipate, disappear due to deconstructive interference.

Any of you ever seen the trick where you can a wine glass or some other sore of thin glass and rub your finger along the edge of it and make a particular musical note? The note that that glass produces is entirely dependent on the physical properties of that glass. You can't produce any other note easily because that's a standing wave being generated within the glass. It's a similar situation. If you hit the right frequency, it reinforces itself, which is why you get that ring that will even last after you take your finger off of it. But other notes don't come out because they're generating waves that interfere with themselves, and that's why you only get particular musical tones. For those of you who are musically oriented, if we go back up to the first diagram: if you played a "C", for example, and that corresponds to this first wave, the next octave above would be another "C" that has exactly a wave that's double the frequency, half the wavelength. The next octave above would be a quarter of a wave, the next wave that I haven't shown. There an entire overtone sequence that's generated by all these different waves that match these boundary conditions.

I took that line and wrapped it around in a ring. The whole point of this is: there are still only specific waves that can run around that ring and continue to exist. In the exactly the same way, if we fold this into a sphere, if we fold this into three dimensions, there are still only going to be specific waves that can exist. I'll say it this way. Electrons are described by wavefunctions, which are mathematical descriptions, representations of the wave behavior of an electron. Wavefunctions are standing waves with the nucleus as an endpoint, or more correctly called a boundary condition. The unique shapes of the wavefunctions are caused by the nucleus. Because wavefunctions are standing waves, there are only specific wavefunctions that can exist, like the different waves I showed you with the phone cord. Because wavefunctions act like standing waves, only certain waves can exist.

How do we describe these waves? It turns out that mathematically we can split this problem up into two pieces. One piece is how far away is the wave from the center, from the nucleus, so there's an "r" component. Then, separate from that, we can talk about what happens to the wave as it goes around the nucleus. These are known as the spherical and radial components of the wavefunction. A wavefunction is represented by capital letter psi. There is an equation known as the Schrödinger equation, a big nasty long equation, which describes how the electron moves around.

That equation can be broken into two other functions. These r, theta, and phi, these are the three coordinates in the spherical coordinate system. r is how far away you are from the nucleus, theta is where you are degree-wise around one direction, and phi is the third dimension. In 3D space, you have to have three variables to describe position. R is this radial portion of the wavefunction, then there's the spherical.

Why am I showing you any of this? It's related to quantum numbers. What are quantum numbers? They are called n, l, ml, and ms. But what do they represent? Not what does each of the numbers represent, but the four of them together? So the position of the electron, but it's which wavefunction are you describing the electron with. So these wavefunctions, there are only certain ones that can exist, but there's technically an infinite number of them, but what is known as a countably infinite number, because there's only certain ones that can exist. They all have nasty equations, which at our level we don't care about the nasty equations, we want to be able to name them. To make it easier to talk about, we have these quantum numbers. So the quantum numbers represent wavefunctions, which represent electrons as they travel in what are known as orbitals. An orbital and a wavefunction really are kinda the same thing. 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 is which quantum number? what's it called? the principal quantum number, the fundamental quantum number, which represents the main energy level, and it also represents the total available packets of energy in an electron. So n = 1: think of that largest wave this phone cord was generating, and now try to imagine that's an electron that has a certain energy level to it. In order to get up to the next energy level, you can't just put any random amount of energy it; you have to put a specific quantum – that's why it's called quantum mechanics. You have to put a specific amount to energy into that system to get it up to the next higher level. Just as I showed you a minute ago, if you go below n = 1, nothing exists. So an electron can only exist if it has that lowest energy level. That's why electrons don't fall into the nucleus; that's why electrons don't have anything called an n = 0 level. There's therefore that one packet of energy that's keeping the electron away from the nucleus.

Once you put more energy in, two things can happen. It can go further away from the nucleus – that's that radial function – or it can start travelling "faster" around the nucleus. When an object is in motion at a constant velocity with a certain mass, it has a certain amount of momentum. If I send that momentum around in a circle, it's called angular momentum. If we were talking about orbitals, that's where this term l, orbital angular momentum, comes from, because it represents effectively how much motion is there going around in a circle around the nucleus. l is the orbital angular momentum quantum number. The maximum is n − 1. What does l cause in terms of shapes of orbitals? Think again of this phone cord example, and think what the lowest energy level would look like in a sphere. It's a function that never cross the line, a function whose value is alway greater than zero. When l = 0, you generate a function that has spherical symmetry.

If you kick in one more energy level, when we had the simple phone cord waves, what happened to the shape of the waves? It got a node in it, didn't it. If you have a sphere that gets a node in it, what is that going to look like? For l = 1, you're going to have a node. Since these spherical functions go around, since you have some fixed place on a sphere that's a node, that means that node is going to be a line. In the spherical function, you're going to end up with lines as nodes. So if you draw a line through a sphere, you're going to end up with a shape that's this kind of symmetry. That's what a p-orbital is caused by, sending some of that energy around the nucleus instead of sending it away from the nucleus.

In this linear phone cord example, I went from energy level 1 to 2 and I added one node. When I went from energy level 2 to 3, I added another node. So if I do the same thing with these spherical systems, I'm going to end up something that has two nodes in it, which is why I end up with this kind of shape – a d-orbital. l = 0 corresponds to s, l = 1 corresponds to p, l = 2 corresponds to d. Why is it that in the lowest energy level, there's no such thing as a p-orbital? Not enough energy. That's the reason. It's not just some rule that maximum value is n − 1, there's a reason for that. It's how many packets of energy do you have available to play with. If you went up to the third energy level, one of those energy packets is just keeping the electron away from the nucleus. That means you've got two more you can play with. And so you can either send the electron further out, make a bigger sphere, make a 3s orbital. If you only send one packet of energy out, and you send the rest of it around, you make a spherical node, so you end up with a p-orbital. If you take both packets of energy and you send them around, you make a d-orbital. The reason these shapes look like they do is because they have fixed nodes. There's no such thing as l = 0.5 or l = 1.5, because those would be standing waves that can't exist.

To summarize: the shapes of these orbitals are caused by the fact that electrons are standing waves, by the fact that electrons can only have very specific functions, because of how they move around the nucleus.

What do you mean by further away from the nucleus?

If you look at a 1s orbital, what does the 1 mean? n = 1, the main quantum number. If I look at a 1s, it does have that spherical shape. If I look at a 2s orbital, it's not a sphere, it's a sphere inside of a sphere. A 2s orbital has a sphere, and around that inside sphere is a node, and then there's another sphere, which if I'm doing this properly, I need to color the two spheres two different colors. This color that I'm putting in, what does it represent. The sign of the wavefunction itself.

A function is something that can have positive and negative values. So these colors represent positive and negative – not charges, in this universe, all electrons are negative, antielectrons are positive, we call them positrons. These do not represent charge of the electron, they represent whether psi is plus or psi is minus. One color doesn't correspond to one sign, it just shows that they're opposite. This color matters when we start talking about bonding. There's a node that goes as a sphere around the 2s orbital. Why does it happen that way? Because if I look at the radial function, for a 1s orbital, it look like this, it doesn't cross the x-axis, that's why it's only one sign all the way through. For a 2s orbital, the radial function looks like this, where it does cross the x-axis once. When you start from the center and go out, there's a node along the way. Take that same situation and turn around in a circle, you just drew a circle. Take that into three dimensions and you just made a sphere. So that's why in the radial function if you have a node, it make something that looks like a sphere.

On average, as you start putting more and more and more nodes radially, the average position of the electron gets further and further away. Just like each bit of energy I put in the phone cord, each bit of energy pushes the electron further and further away from the nucleus and causes more nodes. In fact, if we go to a 3s orbital, the wavefunction would look like this, it crosses the x-axis twice. And then, because if you take that around in a sphere, that's going to generate a sphere within a sphere within a sphere. For this class, we will never see these pictures of s-orbitals again, I'm just trying to point out what this distinction between the radial and the spherical functions is.

Notice I didn't mention the ml quantum number. I don't care if you know px, py, pz for the moment. The practical upshot of this whole lecture is right here: what do the s, p, and d orbitals look like, and do you have some vague idea why there's only certain shapes and not any old shape at all. Notice that all of these shapes are symmetric around the nucleus. That's why I said earlier that wavefunctions are standing waves that have the nucleus as a boundary condition.

These orbitals do have certain patterns. The 1 level only has one kind of orbital, an s orbital; the 2 level has s and p; the 3 level has s, p, d; the 4 level s, p, d, f. Once you start putting multiple electrons in an atom, those orbitals don't necessarily come in a nice order. It doesn't happen that you have just the 1's then just the 2's then just the 3's. Unfortunately, they get all intermingled with each other. If I was to ask you for the electron configuration for an element, and you can't remember the order, what's your cheat sheet? The period table. Because if we take the periodic table and we divide it up this way, we ignore the transuranics – uranium and things like that. These are known as blocks. What is the lefthand block called? This is the s block. What is the righthand one called? p. What is the middle one called? d. Why are they called this? Because these orbitals are the last type of orbital filled with electrons in these atoms that are in these blocks. If you have just one electron.... there are these filling rules. What are the filling rules? The Aufbau principle – building from the lowest energy level to the highest. Things call down, not up. Plus and minus charge attract, so unless something blocks it, it wants to get as close to the nucleus as possible. Lower energy orbitals fill first. Pauli exclusion principle – two electrons can fit in one orbital [if they have opposite spin]. Hund's rule – if there are multiple equal-energy orbitals, one electron each fills before the next one fills up, each gets an electron before pairing occurs.

Ignoring copper and chromium and other elements that have exceptions, when you start piling electrons into an atom, they fill up according to these rules, and that's how they end up having their particular behavior; it does not determine their position on the periodic table. What does determine where an atom goes on the periodic table? Nuclear charge, which for a neutral atom is the same as the number of electrons. Electron configuration does not determine its place on the periodic table, because there are exceptions.

For those things that are well-behaved, if you have just one electron, it's going into an s orbital, because there's only an s orbital in the first energy level. Put two electrons in, it's still just going to go into the s orbital. The next one that you put in is still going to be in an s orbital, but in the 2 level. Then for berylliium, it's still an s orbital. The next element, boron, you finally get to the p-block, which it's called that because that electron that you put in is going to go into the p block. So if you look at the periodic table, you can usually find that the electron configuration order is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p. I will stop here, because except for iodine, we're hardly going to deal with elements that have more than this number of electrons.

What is the octet rule? An atom is unusually stable when its outmost s & p subshells are filled. What's a shell? An energy level, which means it's a specific value of n. What is a subshell? It's a specific value of l inside a shell. So the octet rule is when the s & p subshells of the outermost shell are filled, the atom is unusually stable. This outermost shell, that's the valence shell. That leads to the valence electrons. Valence electrons are the most energetic electrons in the outermost shell that participate in bonding.

Let me write out three elements. We've got fluorine, chlorine, and bromine. Fluorine would be $1s^2 2s^2 2p^5$; chlorine would be $1s^2 2s^2 2p^6 3s^2 3p^5$; bromine, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. In fluorine, what are the valence electrons? All seven of these, because it's those in the outermost shell. A shell is an energy level. So energy level 2 is the outermost one so everything in that outermost one is a valence electron. What about for chlorine then? $3s^2 3p^5$. And for bromine? $4s 4p^5$; again, only those electrons in the outermost shell. This is the origin of periodic behavior, because atoms with similar number of valence electrons have similar reactivity. These elements all act similarly because they have the same number of valence electrons.

Unusually stable – If you take fluorine, for example, it's really, really reactive, but once it gets that electron, it doesn't want to react hardly at all. You get F– which is a nice, stable ion. The noble gases, they all have this s2p6 configuration. You can make them react, but it's tough. That's what I mean by unusually stable. They're less reactive that way. They want to have that configuration.

What are isotopes? They're the same element, different number of neutrons. You need to know about the common forms of hydrogen. This is one way to write them; more commonly, we'll do this, use one-letter abbreviations, so we're not bogged down by our mass numbers and atomic numbers. That first form is called protium; that second form, deuterium, deut- referring to two; and then tritium, that tri- prefix shows up in nearly every European language, it means three. So the first form, second form, and third form of hydrogen. 90-something percent of hydrogen is regular old hydrogen.

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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
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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