

Lab 10A • 05/21/12

[lab directions]

The harmonic oscillator

Imagine that we have some kind of surface that is frictionless, in which there's no air resistance, in which there's no nothing; pretend that this is in a perfect vacuum, with maybe some gravity to keep the weight from floating away or something like that. Imagine that we have a weight of some sort, an object, that is tied by a spring to this wall. Let's say that it has some rest position of zero. Imagine that we displace this object, that we move this object one way or another by some amount x . In this case, we're talking about some mass that's just sliding back and forth across a table. We could, to some degree, be talking about a pendulum moving. If you lift the pendulum up, if there weren't air resistance or other factors that we could ignore, it would just keep moving back and forth and back and forth and back and forth and back and forth – with a regular periodic motion. If you pull a spring a little bit, it tries to pull back a little bit. If you pull a spring a little bit more, it pulls back a little bit more. We pull a spring enough and eventually you might deform it; the perfect behavior of this spring only goes so far, depending on how far you displace it. Once you release that spring, it's going to go oscillating back and forth and back and forth and back and forth.

Let's try putting some math behind it. For the perfect spring system, we have this equation: $F = -kx$. What does this mean? F is force, [which] means how hard is the spring pulling back. The spring is going to pull the opposite direction of the displacement. The k is a proportionality constant called the spring constant. Depending on exactly the type of material, the length of the spring, and all that, that's going to determine how much tug there is to that spring.

Force can be expressed by mass times its acceleration. Acceleration is the change in velocity over time, how much does the speed change. Of course, speed itself is the change in position over time. If you wanted to think of it that way, acceleration's like a double delta, cause it's the change in the change. If you have something cruising along at a constant speed, there's no acceleration, it's not changing its speed. Force is related to how is that force changing the speed of an object. If we say that force is equal to mass times acceleration, which is equal to $-kx$, acceleration is the second derivative, with respect to time, of position. This in calculus form is what I just said with the deltas a minute ago; that means that the change in the change in position is what I'm representing there, but it's related to the position of the object itself. This brings up an interesting problem in mathematics: what kinds of functions are the negative second derivatives of themselves? It turns out that there's [at least] two classes of functions: one are the complex exponentials which, with the proper series expansion, can also then be shown to be related to sine and cosine functions. Here are two functions that would actually fit this equation. Second derivative of $e^{i\omega x}$ would be $i^2\omega^2 e^{i\omega x}$, which would be $-\omega^2 e^{i\omega x}$, that falls into that function. Second derivative of sine is $-\text{sine}$, so again it would satisfy this function. The point of showing you this little flourish in math is to show that, mathematically, we can model this movement of a spring back and forth like a sine wave. The importance of the above set of equations is to demonstrate that the motion of an idealized spring can be modeled by a sine wave. ω is related to angular frequency, how rapidly, if we're talking about a spinning object, is that thing spinning, that's what ω 's related to.

Depending on how far we displace the spring, we're going to end up with different amounts of displacement, different speeds, different speed of oscillation. In theory, we could displace the object a little bit, or a little bit more, a little bit more, a little bit more, and get all these different frequencies possible. In quantum mechanics, you can only have very specific energy values. But, instead of having a mass attached to a wall like this, imagine you had two atoms attached to each other. This same model can be used to model, ideally, the behavior of two atoms vibrating. In that case, you can't choose any energy that you'd want to; it has to be specific energy level. That's the idea of quantization, quantum mechanics, that you can't put a packet of energy in, but you can't break it down to some small step in energy, anything smaller than that. In atomic systems, energy is quantized, so only certain frequencies of vibration are allowed; these would be the vibrational energy states. If we were to graph this somehow, then we would end up with something that looks like this. Ideally, this energy curve, if I plotted the effective displacement positions and energies of a spring, it looks something like this: they form a parabola, so it's related to x squared, and the energy levels would start getting closer and closer and closer to each other – kinda like the energy levels in atomic orbitals. Of course, these are two different things that we're talking about: these are vibrational levels, having nothing to do with electrons, just having nuclei moving relative to each other. Atomic energy levels, that's what electrons are doing, which is a separate story. As the molecule is vibrating, it can speed up and slow down that vibration, but only by stepping between these specific energy levels. Notice that there's a minimum energy level that you can't drop below, which is similar to the fact that electrons also have a minimum energy level that they can't get below. This is demonstrating what these different vibrational levels look like.

What this difference between ideal and actual? As you stretch a spring to its breaking point, that ability to fight that deformation starts to ... as the spring is stressed too much, it can't respond the way it did, so the symmetry of that vibration breaks down. In real life, stretch two atoms far enough? You break the bond, so at some point they simply just don't vibrate, they just break.

That's partly what's in the shape of this curve. All I'm showing here is that there are vibrational energy levels, and they can only have specific values. This is if you only had two atoms that are simply vibrating relative to each other. If we had just three atoms, then we have to worry about modes of vibration. If you have three atoms, those two [end atoms] can have a scissor type of vibration, where they open and close just like a scissor would, so the two bonds move relative to each other. Maybe they vibrate along the bonds, you have symmetric stretching. Maybe they still vibrate along the bonds, but as one zigs, the other zags, so you end up with asymmetric stretching. What ends up happening, for one set of atoms, you can have many different modes of vibration. We can take an IR of a sample and get all these different absorbance, which corresponds to the variety of vibrational modes. If we did have just HCl if we had the ability to take an IR of a diatomic gas molecule like that, they can capture and show you all of these different vibrational energy levels. Rotational energy levels. Imagine that we had that same molecule HCl; imagine we talked about it rotating upon its axis. Just like vibrational energy levels are quantized, so are rotational energy levels. This molecule cannot just have any speed of rotation it wants to; it can only have limited values of how fast its rotating. Specifically, the value that's limited is angular momentum. Rotational energy levels are also quantized.

Lets say the electrons have some configuration. Within that main energy level, there are all these different vibrational energy levels, and we also have these different rotational energy levels. Now let's focus on the electronic side of things. Electronic states. Ground state and excited state. You add energy. You can excite an electron up to an excited state. The ground state has a wavefunction associated with that orbital, where the electron comes from. The excited state has a wavefunction that's associated with that orbital as well. The transition from one orbital to another ends up being a big problem in what I call classical quantum mechanics – which is kinda a weird term. Quantum mechanics didn't get invented overnight, meaning that what we say [about the wavefunction] that all came over many years of development. Things like the Pauli exclusion principle came after the idea of a wavefunction. They had to put all the pieces together. One of the problems with it is this: imagine, back in Bohr's day, when he was coming up with the model of the atom, and if that was the model of which they were trying to get quantum mechanics from. You can have an electron in some orbital spinning around, and then there's this moment in time where, all of a sudden, it's in a different position, whizzing around. Wavefunctions are supposed to solve this Schrödinger equations. There's lots of restrictions to what those wavefunctions could be, including that they must be continuous, that they must have first derivatives, they must have second derivatives; there's some number theory behind it. In order for electrons to transition between energy levels, there must be some kind of overlap between the wavefunction it's coming from and the wavefunction it's going to. If that overlap doesn't exist, then that electron doesn't have a way to move, so there are what are known as selection rules, in this kinda of situation, where electrons are moving between levels. There are what are known as spin-allowed transitions and spin-forbidden transitions. As an electron moves just one level like this, it's not allowed to change its spin. When an electron moves between energy levels, there are normally restrictions on how the spin can or can't change as the electron moves between levels. [selection rules, spin-allowed transition] A spin-allowed transition is one that obeys these spin rules. Here's one of these rules: for moving up and down energy levels, a single electron must maintain its spin.

You see in the ground state, you see we have a set, a pair of electrons. In the first excited state, they're still paired, in a sense; one's pointed the opposite way of the other. This is a situation in which the total angular momentum equals zero. What's angular momentum? To oversimplify, how fast does something spin. It's not actually speed, it's momentum, but think of it [as] how much does something spin. We have one electron that's spin up, one electron that's spin down; $+1/2$, $-1/2$. Put them together, that means the total spin between the two of them is zero.

In atomic structure, we have four quantum numbers: principle, orbital angular momentum quantum number, magnetic quantum number, and the spin. That l value, the orbital angular momentum, what does that mean? That means not the electron and its little spin, but the whole thing, effectively how fast does that going around a nucleus? When, in that situation, $l = 0$, we say that we get an s orbital. If you have an s orbital, how many different kinds of s orbitals do you have in the same energy level? Just one. When $l = 0$, there's only one type of it. When $l = 1$, that's one particle of energy used to move around the nucleus. Because the nucleus is three-dimensional, though, we get three unique cases. For an l orbital, $l = 1$ orbital, that's a p orbital, we end up with three of them. If we have $l = 2$, that's d orbital, how many of them do we end up with? 5. In other words, we could figure out how many of those different orbitals, which means how many unique ways was that spin oriented, that's equal to $2l + 1$. The same thing happens here. What is known as the multiplicity of spin states is related to the total spin by the equation $2S + 1$. If our total angular momentum is zero, which means spin zero overall, there's only one way to have the number zero; we call this a singlet – not the same kind of singlet as in splitting, but similar meaning: there's only one arrangement that occurs that way. [In the previous diagram], ground state would be S_0 , lowest energy singlet state. By default, if you have all pair electrons to begin with, then your ground state is a singlet state. The first excited state we could label S_1 , meaning still a singlet, the electrons did a spin-allowed transition; they're just one energy level higher.

There are what are known as forbidden transitions, which means that the spin changes in a way that's normally not physically possible for the electron. If it's not normally physically possible, why does it happen? The total angular momentum here is now 1. I'll use that same spin multiplicity equation, $2S + 1$, $2*1 + 1 = 3$: it turns out there's three unique ways that the total momentum in this system can be distributed to give that same total. Since there's three ways, that's why we call this a triplet. [one case both spin up, one case both spin down, what's the third case] In quantum mechanics, when you start interacting spins, they create new systems, new sets of energy levels, that are different than either individual spin. [similar to bonds] A bond is this new orbital that doesn't look like either atom, and yet we can use the two atoms to represent the bond.

That's the kind of situation that's going on with spins. To oversimplify, if I've got two spins, when they come together, there are four possibilities of interaction. One of those is the singlet state; the other three have the same total momentum, that's why it's a triplet state.

How do we put all of these pieces together? I'm trying to draw [the diagram] in such a way that, between these two different systems, there's overlap. Let's look at these labels and talk about what this is. S₀, that's the ground state, that's a singlet. Electrons are paired. You pump a photon into them, it takes you up to the next-highest singlet state. What could happen then is: it might fall down in energy a little bit, from one vibrational level, slowing down to the next, slowing down to the next. At some point, it loses the right packet of energy where the electron falls back down to the ground state, maybe to the same vibrational level it started [out at], maybe a slightly different one. This means that the exact frequency of absorbance or release, there might be a little wiggle room too just cause there are these different vibrational levels [black light poster, purple light bulbs, Small World] You shine the blacklight, which is a UV light, light of a shorter frequency, somewhere in the range of 235 – 270 [nm], something like that. It gets absorbed by the molecule. Maybe, it loses some of its energy before it falls down, because it transitions between different vibrational states. When it finally released that photon of energy again, it's a different color than what you observed originally. This process is called fluorescence. Fluorescence is nothing more than spin-allowed release of a photon from one higher-energy singlet to a lower-energy singlet state. Because these are spin-allowed transitions, they're extremely fast; turn the light off, the glow stops. Because the energy of absorbance is not necessarily the same as the one you released, you shine UV light, but you see all these different colors come back.

[theater tape, park in driveways, drive in parkways, cleaning up] You can have a spin-forbidden transition if the vibrational states are similar enough to each other. That's why we [discussed] what vibrational energy levels are. In other words: you pump energy into a molecule: it has an electron level, but it's also got a particular vibrational level. If that vibrational level just happens to match with another vibrational level of one of these forbidden states, then the spin can slip, even though it's not supposed to, even though it's technically impossible to. That's because if you only look at quantum mechanics, yeah, it tells you it can't happen, but quantum mechanics does not happen in a stationary system; it happens in a vibrating molecule. These vibrational effects sometimes allow what is referred to as intersystem crossing. What can happen to glow-in-the-dark items is that you shine light on it, it absorbs a photon in the way that it's supposed to, a spin-allowed transition. Then, you cross over to the triplet state, if it's vibrational levels, between the singlet and triplet, happened to match. For a triplet to get back down to the ground state is one of these forbidden transitions; it's called phosphorescence. Since it's spin-forbidden, it's much more difficult for it to occur; that's why, when you add light energy to one of these glow-in-the-dark objects, it causes all of these electrons to go into an excited state, which, because they then transfer to a triplet state, they can't get back to the ground state right away. You turn the light off, and the electrons are still falling, falling, falling for a long time afterwards, until finally it runs out of energy again. That's phosphorescence.

Fluorescence [and] phosphorescence: two ways that light can be generated by an object by its electrons falling from high energy to lower. There are two ways it can fall: an allowed way – that's fluorescence, which means it stops as soon as the light goes off – and phosphorescence, which is not a physically easy path for the electron to take, which is why it takes much longer for the energy to be released, which is why it lasts a while.

What makes the luminol glow? That's chemiluminescence. [luminol] When this decomposes, it puts exactly the right amount of energy into the exactly right electronic and vibration states that, when this molecule decomposes, it causes light to be released; that's chemiluminescence. [oxygen] The reaction of luminol causes an intermediate with the exactly energy and structure to allow that energy to be released in the form of a photon – what can be called radiative decay. Non-radiative means that it happens through vibration or some other physical way without light being released. This process is therefore chemiluminescence. Luminol, it forms a triplet first, which takes a while, and it goes back to the singlet state and then emits light. That intersystem crossing takes some time, which is why the glow lasts for a little while. [how things like glow sticks work, James][difference between halogen lights and mercury vapor lamp or neon lights] Depending on the different vapors, you have different excitations between energy levels, which gives you the different kinds of light. Those different components, depending on their proportion, you get what are called different white points. If you go buy a lightbulb, you look at the back, it'll say it's a 4000 Kelvin bulb, or it's a 2500 K bulb, which is a type of white produced by a flame that's that heat that gives you a certain proportion of blues versus reds, so that if you're putting on make-up versus on-stage, versus in here, you want different kinds of white to see different palettes of colors. I presume that those different components are put in there to achieve those different balance[s] of colors. [sodium yellowish, low white point color][halogen?][efficiency and solar panels] Light hits a solar panel, this tiny proportion of it actually gets converted into electricity; most of it's just wasted. If somehow we could raise the efficiency, that means we could raise a roof full of voltaic panels and reduce it down to that size – or, keep it the same size but get that much power out of it. That's why solar technology's still maturing, because we're figuring out how to increase that efficiency. [DMSO garlic trick myth?]

Harmonic Oscillator

The importance of the above sets of equations is to show that the motion of an idealized spring is to show that the motion of an idealizing spring can be modeled by a periodic function (sine wave). This same model can be applied to the idealized case of two bond atoms vibrating.

* In atomic systems, energy is quantized, so only certain frequencies of vibration are allowed → vibrational energy states.

Rotational energy levels – Rotation[a] energy levels are also quantized

Electronic states – When an electron moves between energy levels, there are normally restrictions on how the spin can or can't change as the electron moves between levels → selection rules

total angular momentum = 0 → singlet

total angular momentum = 1 → triplet – $2(1) + 1 = 3$

spin forbidden – spin changes in a way that is normally not physically possible.

ISC – inter-system crossing

phosphorescence – spin-forbidden photon release

fluorescence – spin-allowed release of a photon

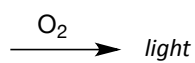
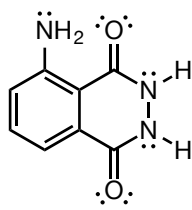
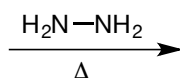
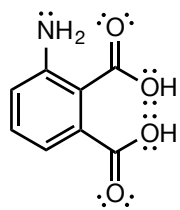
The reaction of luminol causes an intermediate with the exactly correct energy & structure to allow that energy to be released in the form of a photon (radiative decay) → chemilluminescence

spin-allowed transitions – obeys rules of spin

For moving up & down energy levels, a simple electron must retain its spin.

Structures

05/21/12 lab • 1



05/21/12 lab • 2

