Lab 10B • 05/22/12

Harmonic oscillator

This is a very classic example of a system that has what is known as periodic motion – something where the motion happens at the same rate repetitively. In this example, we have some kind of surface that is frictionless, that has no kind of resistance the object resting on it, so no wind resistance or anything like that. We have a wall that there's a spring attached to, and that spring in turn is attached to this mass that's free to oscillator back and forth and back and forth. I've marked on this diagram the rest position of this mass, where there'd be no energy in the spring, and then we could imagine if this is displaced by some distance x. The interesting thing about this example is what causes that periodic motion, which is example this relation between the position of the spring and the force. Force is how hard the spring is tugging back on this. We can see that there's two variable that will influence that force: one is how hard the spring is pulled, and notice that this is a linear relationship – in other words, how hard you pull on the spring is how hard the spring is pulling back. That's why we have a negative sign, because this is a restorative force. There's also this fudge factor that we put in there in order to make the force and the position proportional to each other; that's called the spring constant, which is going to depend on the size of the spring, what it's made of. The main thing here is that the force is proportional to distance.

Switching over into more mathematical mode, we can remember that force is mass times acceleration. Acceleration is the change in velocity versus time, and velocity itself is the change in position versus time. We can imagine some kind of double delta; the idea is the change in the change of the position is acceleration. The next step [is] to rewrite what acceleration is and rewrite it in terms of position. If we're talking about an object that can move arbitrarily, that's why we have to switch to calculus. Acceleration can be represented as the second derivative of position, with respect to time. It brings up an interesting situation, because we have an equation in which a function has to be linearly proportional to the second derivative of itself. There's not an infinite number of functions that can satisfy this condition. One type of the function that does satisfy it are the set of imaginary exponentials. This equation is related to periodic functions. For something like a spring, we can just say a sine function. If you have e^ix, the double derivative of that would be i^2•e^ix; i^2 is negative, so that gives us the negative equation; same thing with sine and cosine: double derivative of sine is negative sign, double derivative of cosine is negative cosine. These functions satisfy this equation, which is, therefore, how we could describe that spring moving back and forth, like it was on some sort of sine wave. That's the harmonic oscillator: the harmonic part of it is the idea that it's moving back and forth with this regular motion.

Just as we can imagine a spring moving back and forth, or we could somewhat imagine a pendulum swinging back and forth. What if we have two atoms that have a bond that connects them, and if that bon has some kind of stretch to it, what if we could apply the same system to atoms vibrating back and forth. That is the model that we use. The harmonic oscillator reasonably describes the motion of two atoms in a bond. It turns out that not just one type of motion is possible for a system, because, depending on how much energy there is there, depending on how far, in the spring example, you pull that spring, you're going to put more and more energy in that spring, which means that he vibration's going to be larger and larger, in terms of distance. In theory, if we had just the simple spring example, we could have any energy level we wanted to – up to a certain point, because if you stretch a spring too hard, eventually that spring deforms. It only has a certain limit to which that spring can act linearly with respect to force. Same thing in a bond situation: you stretch a bond far enough, it breaks. There's some point where this harmonic oscillator breaks down a bit, there's an asymmetry that gets introduced to it. Principally, then, we could treat the bond the same way, as having all of these different energy states possible, with the caveat that we're dealing atoms, something that's a quantum mechanical system, which means you can't just have any random energy value you want to, you can only have very specific values. [standing waves and quantization of energy] The same thing happens with a bond.

A curve that represents the possible vibrational energy levels of a bond looks something like this. You might notice some similarity to the energy levels of an atom. [parallels between vibrational and electronic energy levels] The two, the vibrational and the electronic, can interact with each other, which is how we get some of these unusual effects. Notice how the energy levels start out more spaced at the lower energies, and then become closer and closer together as you go higher in energy, again paralleling atomic structure. The x here represents distance, so if we have some middle point where it's at rest, the we have a relationship to x squared, so we have a parabolic curve. The main this [is] there's only specific energy levels. Since energy at the atomic level is quantiezed, which means it only comes in discreet packets. There are only specific energy levels, specific vibrational energy levels, available to a bond.

Since we're talking about vibrational energy levels, if we have more that two atoms, then there are many what are known as modes of vibration possible. Imagine we have a three-atom system; there's several modes of motion that are possibly. Imagine, for example, in this three-atom system two side atoms act like wings, where you have scissoring effect; the pair of bonds is opening and closing, relative to each other. We could also have stretching occur in which both atoms are moving in the same direction, from the central atom; we can say that this is a symmetric stretch. We could have another mode of vibration, where one atoms is moving in the opposite direction of the other, relative to the central atom, so it'd be an aymmetric stretch. There's several other mode possible; I'm just showing you a selection so that you have seen this idea that there are modes of vibration.

You've seen the results of this before every time you've looked at an IR spectrum, because in a given set of atoms, energy is quantized; it's quantized into certain moe of vibration. Some of those modes of vibration end up not producing any signat, because the most the motion has to have some kind of ability to interact with light; there are forms of motion that do not cause an interaction with light – which means we can't see them. That's why you get all those different peaks in an IR spectrum, because in the molecules we've had, we've had multiple atoms, so multiple modes of vibration. What we haven't seen is these individual vibrational energy levels, at least not clearly. If we had the equipment to do so, if we had a gas chamber filled with hydrochloric acid, for example, that's only two atoms vibrating, we could see all these different vibrational energy levels – on top of rotational energy levels.

In that example [with] hydrochloric acid. Imagine that you have the central axis of the molecule that the molecule was spinning around. Because it's an atomic system, the angular moment of the system – the amount of motion that you have in a circle – can only adopt very specific values, meaning that the molecule itself, in terms of its rotation, can only have energies of very specific values, meaning that the molecule itself, in terms of its rotation, can only have energies of very specific values – these are the rotational energy levels. The vibrational energy levels, since those can involve more motion, more atoms, they tend to have higher gaps in their space. The rotational energy levels tend to be much narrower, the gaps. If you had a really sensitive IR machine, if you had the ability to do gas phased spectroscopy of HC, there'd be a series of lines that would represent the vibration level, then we'd see this fine structure, little tiny clumps of lines – not like splitting in NMR, not the same physical reason, but maybe the same appearance a bit. Those would be the rotational levels splitting the different vibrational levels.

Electronic levels

Light, when it's absorbed and released, is due to transitioning between different electronic states. In some unspecified system, when the electrons are in the lowest possible energy configuration, that is something known as the ground state. When light interacts with the system, there are multiple excitation possible, depending ont he size of the packet of energy in that photon. If we gave it the smallest possible packet of energy and just bumped one electron up one level – this gets us to the first excited state.

What goes on with the spin of an electron as it transitions from one state to another. In "classical" quantum mechanics, there's a problem that arrises when electrons change their trajectories, change their pathways. [By] "classical" quantum mechanics, what I means is that, when we look back now and say here's this thing called quantum mechanics. It didn't all get invented overnight; it wasn't like everybody woke up the next day and blogged to each other: "is this what quatum mechanics is?" Things like the Pauli exclusion principle were things that were settle much after much of the rest of quantum mechanical formulation had already occurred. It was some way to resolve some of the mathematical and physical observations that they had made. Imagine this: you have am electron that might be in one energy level, in one orbital. That orbital has a certain function associated with it. If you have the same electron in a different energy level, it's in a different orbital with a different mathematical equation. Part of the difficulty with quantum mechanics was: how can something be here and in one instant suddenly be here in a different equation? Those transitions only occur if there is some kind of correspondence between the wavefunction you start with and the wavefunction you end up with. Certain types of transitions, electronically, are just not physically allowed. In most of these transitions, the deal-breaker is: what happens with electron spin?

When an electron goes from one energy level to another, in this kind of situation, it has to maintain its spin during that transition; that's what is known as a spin-allowed transition. If we were to instead flip that spin around to make it where its no longer parallel with the first spin. That, in theory, cannot happen siultaneously with its excitation; that's what is known as a spin-forbidden transition. Why? [?] There are what are known as selection rules that say the spin can do this on this kind of transition but can't do it in this kind. For this situation, when you have an excitation between energy levels, the spin has to be maintained. The normal case, an easy transition is one in which the spin's maintained – that's called a spin-allowed transition. There's then a situation where you could have te spin flipped. If you have that spin flip, it is known as a spin-forbidden transition, since it is technically not possible.

Terminology

When you have two individual spins, they act as individual spins; they have their own states quantum mechanical states. Each spin, on its own, can be spin up or spin down. When you combine two spins together, the spins interact to give you a total angular momentum. In quantum mechanics, once you have two spins that are acting together, they can form spin states that do not necessarily look like the individual spin states. In other words, individually, electrons might be spin up or spin down; when combined together and acting together, they may be at some kind of odd spin angle that is allowed because their total spin adds up to some specific value. When you have two individual spins, they come together; it ends up causing four new spin states. One of those spin states corresponds to having zero total angular moment, total spin. If you notice the top case there, where one electron is opposite the other, one is spin 1/2, the other's spin -1/2, they add up to zero. This has a total spin equal to zero.

Angular momentum is the tendency for an object to spin to want to keep on spinning. [hoola hoops] An electron, even through it has its own individual spin, in its orbital, that whole orbital is acting like it's transiting around the nucleus. Where does this show up? In atomic structure, that orbital angular momentum determines the shape of an atomic orbital. Recall the four quantum numbers: n, l, ml, ms. n's the principal quantum number that tells you the total amount of energy that you've got to play with, but l tells you how's that energy distributed, at least in terms of its rotational motion. When l is zero, we have an s orbital. How many different kinds of s orbitals are there in one energy level? Only one of them. If l = 1, what kind of orbital is that? It's a p orbital. How many different types of p orbitals are there in one energy level? 3. How many d orbitals? 5. How many f orbitals? 7. l, which is [the] orbital angular momentum quantum number, if we take 2l + 1, we get the number of orbitals of the same type. That same 2l + 1 shows up in this case as well, because if you have a total spin of 0, it turns out there's only one state that has that spin of 0, because we have this equation for spin multiplicity, where s is the total spin. s is zero in this case. It's the same situation as l = 0 for atomic orbitals; there's only one way for that energy to somehow be distributed.

What do we have in this other case? The total spin here is equal to 1. It turns out there are three ways to distribute that one packet of energy, that are not necessarily the electrons individually being pointed up and down. I can see in this diagram that I've got two electrons that are both pointed up; that totals to one. You have another case where both electrons are pointed down; that can, when you take the absolute sign, add up to 1. But then how do you get the third case? With this diagram, you can't get it; it's not just as simple as the electrons being up or down when they're adding together, but there are three cases possible. That's why, up top here, this kind of electronic state is called a singlet. Down bottom here, this is called a triplet. Often, we'll use capital letter S and capital letter T to represent those states. The starting point in both of these examples is the lowest energy level possible, so you can say S0, ground state. Then we have the first excited singlet state, and the first excited triplet state. Here would be a ground state singlet state, and then the first excited singlet state. By the transition rules, you're allowed to have an electron excited from one state to another. Notice, though, that unlike an electron simply going from one energy level to another, we're stacking on top of that now the idea that there are different vibrational modes in each one of those electronic states possible, which means the exact energy of absorption between two different electronic states can change a little bit, which is why you don't necessarily have an absorption in these kinds of situations at only one exact frequency, because we do have different vibrational levels possible.

Once you excite up to excited states, some of that energy might be dissipated as heat, going from one higher vibrational level down to a lower vibrational level. When light is released again, it might be a lower-energy photon. [vibronic] Lower energy corresponds to lower frequency of the wave, which corresponds to redder light, so more towards red than purple, if this is visible light. [black light poster][Small World][TLC UV lamps] When you get these different colored dyes, you shine the light, it glows. Why? Because an electron is being absorbed and going from one pair of vibrational and electronic states to another, which it then may fall a certain amount just by vibration, release a photon of a different energy, which is why things glow a different color than the light that's shown upon them. That's what's going [with blacklight posters], and this process is fluorescence – the spin-allowed transition of a high-energy electron down to a lower-energy electron by release of a photon. As you shine light on something, electron keeps absorbing the light, keeps going up, but just like if I throw this light up, once I've released it, it's going to fall back down again. There's nothing that holds an electron in a high energy level, except the energy itself. That energy gets released, the electron falls, absorbs it again, falls, absorbs it again. That is what happens with these kinds of dyes. Of course, you turn the light off, no more energy's being put in, the electrons, once they fall, they stay, hence the glow stops, so this is not the process that happens with glow-in-the-dark tape. [theater]

How does that tape glow once the light turns off? There might be a triplet state that might have a vibrational state that matches the singlet state. Going from a singlet to a triplet is supposed to be one of these spin-forbidden transitions, but that's if no atoms were moving. That's if you just had the electrons the the nuclei to deal with. But we don't, we have motion of them relative to each other, the nuclei that is. It turns out that we end up with a situation where the vibrational energy level of a singlet is the same as the vibrational energy level of a triplet, you can have that spin flip occur, even though it's not supposed to. That leads to what is known as intersystem crossing. It is a spin-forbidden transition enabled due to vibrational states. If it slips into this triplet, it's a difficult process for the energy to be released and return back down to the singlet state. Difficult means: takes time. This is called phosphorescence. You shine light on an object; the energy is absorbed the electrons that going into a high-energy state. Once in that high-energy state, it can, under the right conditions, do this spin-flip that normally is not allowed to occur. Once it's in that state, it wants to lose energy, it has to do some kind of process that's difficult for it to do, so that takes time, which means, you shine on this glow-in-the-dark tape, it absorbs all of that energy, you turn the light off, and it takes time for all of those electrons to fall down again – and that's phosphorescence. Fluorescence and phosphorescence – the spin-allowed and the spin-forbidden transitions of high energy electrons back down to low energy; they're both related to some kind of glowing phenomenon.

Chemilluminescence is not necessarily in itself fluorescence or phosphorescence – it is this: that a chemical reaction, all by itself, causes an excited state to form that has the right energy and right vibrational pattern to then release light to let that chemical energy go. You don't add light to get the electrons excited; it's a unique coincidence that the right molecular structure allows – the reaction itself provides the energy to the electrons that then relax by releasing light.

Chemilluminescence is a phenomenon caused by a chemical reaction in which the reaction itself causes the formation of an excited state intermediate, that then can relax to the ground state radiatively, which means by releasing light. That's what's going on with luminol. [description of reaction of luminol][glowsticks][DMSO]

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Harmonic Oscillator – The harmonic oscillator reasonably describes the motion of the two atoms in a bond.

Since energy at the atomic level is quantized (only comes in discreet packets), there are only specific vibrational energy levels available to a bond.

Modes of vibration

Rotational energy levels

Rotational motion is also quantized @ the atomic level, so only specific rotational energy levels can exist for a system.

When an electron is excited between energy levels, the spin of the electron must be maintained (a spin-allowed transition)

If a spin flips during transition between energy levels, it is called a spin-forbidden transition, since it is technically not possible.

ISC – intersystem crossing – a spin-forbidden transition enabled due to vibrational states

Chemilluminescence – A phenomenon caused by a chemical reaction in which the reaction itself causes the formation of an excited state intermediate that then can relax to the ground state radiatively (by releasing light).

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Structures – Identical to those from lecture 9A (05/21/12)