

## Modern Atomic Theory

### Electromagnetic Radiation and the Idea of Quantum

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Think of a rainbow. The light that comes out of the sun is spread apart by many, many droplets of water acting like teeny prisms, spreading out all the different colors of light. We can do the same thing in the laboratory using a prism. Well, if we take sunlight and pass it through a prism, we find something absolutely astonishing. All the colors are there, but there are few exceptions. In fact, in the visible range there are four discrete lines that are not there, four frequencies that are simply missing in sunlight. What's going on?

Well, what's more astonishing still is that those four frequencies that are missing happen to be exactly the same as the four frequencies of light that we saw in hydrogen emissions spectrum, at least in the visible range—exactly the same. So something very strange is going on, and in fact, what it suggests, and in fact turns out to be true, is that hydrogen is part of the sun, and that hydrogen is acting on the light somehow, but in complimentary ways. In the case of sunlight there are frequencies that are missing. In the case of a hydrogen emissions spectrum, those are the only frequencies that we see.

Now this is, in fact, something that was discovered by Fraunhofer back in 1825, almost 100 years prior to the birth of quantum mechanics and so forth, so this is a very puzzling thing. No one had an explanation for it. But now the idea of quantized energy, suddenly we have a new tool to help describe old events, old phenomena.

Now, imagine the following. Remember, an emission spectrum has to do with an electron traveling from one energy to a lower energy, and in that process a photon, a packet of energy, is emitted. Absorption is the reverse of that process. A packet of light is absorbed by an electron as it travels from one energy to a higher energy, and what this is suggesting is that the lower and higher energy levels, if you will, are the same for this process and this process. In other words, think of a well. Remember, we talked about energy wells before, the idea that an electron, when it's attracted to a nucleus, is in a potential well. This all comes about because we talk about energy equal to zero at the point where we have a plus and a minus charge infinitely separated. But as we bring them together the energy decreases for the system. Energy is released because it's an attraction. So the energy of the electron we say is negative relative to energy of zero being infinite separation.

Well, these lines come about by an electron traveling from one energy to a different energy level. Maybe that energy is all the way out here; maybe it's in between here someplace, but wherever it is that corresponds to an absorption of a photon, and then if the electron drops back down to where it started, that would correspond to an emission at the same frequency of light.

Now, given that energy is quantized and we have that as a possibility, imagine that the electrons in an atom also have quantized energy. This is something suggested by Bohr, and we'll talk about this a little more in a moment. But for a moment, just think about what that means. If the electrons in an atom had quantized energy, only specific allowed energy that they could have, our picture might be modified to look like this. Instead of a well we might think of a staircase where the electron perhaps started out at the lowest energy level. We put in a packet of energy, a photon of light, and moved it not any arbitrarily place but up to another defined allowed energy level. That would require a very discrete, a very specific amount of energy. If the electron returned to the original energy level, that would give off a photon of the same frequency that we had to put in to move it up to this level. We could then go from this level to the next highest level, but notice that we could not go in between. If this is a staircase, we could not put in any arbitrary amount of energy. If we put in just this much energy, for instance, the electron only makes it to here and it comes right back down again.

So the idea is that by having only specific allowed energies of the electron in an atom, the consequence of that would be that the energy absorbed or emitted of a photon would have to be only certain allowed values. So you see, that was a very appealing idea there. By going to an idea of quantized energies we could explain the Fraunhofer lines and the hydrogen emission spectrum.

Now why would energies be quantized for an atom? After all, our picture of what an atom looks like is this, just the idea that we have orbit, that electrons travel in orbit around the nucleus. This is the Rutherford planetary model, and this, again, was in vogue in 1912, the idea that electrons are just traveling in these orbits, much like planets travel around the sun, and there were no restrictions on where those electrons could be. But the idea that the electrons could only have specifically allowed energy levels meant that the electrons couldn't be in any orbital. There would be specific restrictions on the kinetic energy of the electron as well as the distance that the electron could be in orbit around the nucleus.

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So what Bohr postulated was that angular momentum was quantized. Now, that's not important to us, but the consequence is that if angular momentum is quantized, then the actual distance that the electron could be away from the nucleus was quantized. It only could be at certain allowed levels, and most importantly that the energy of the electron in those different orbits was quantized.

So we get a set of energy allowed that the electron can have, and that would look, let's say, like this. On this axis this is just energy. And so this is the lowest allowed energy state for the electron. The next allowed energy state would be all the way up here. And again, remember, zero energy is all the way at the top. The third highest energy level is up here. Again, this is not distance away from the nucleus. This is now just the energy that the electron can have. Zero being here; everything below zero would be negative.

Now, it is true that as go—by the Bohr model, as we go to higher energy states it also means that the electron gets further from the nucleus, and indeed, that's defined by this expression. Now, what does this tell us? This tells us the energy of the electron in the different allowed states. We have a lot of physical constants here that we don't need to pay attention to. But what it says is with these volumes, which are known—mass of an electron, charge of an electron, charge of the nucleus and so forth—we can figure out what the energy of the electron is. And notice this variable here,  $N$ , that's an integer. So  $N$  can only be 1, 2, 3 and so on. This refers to the different allowed energy levels that the electron can have.

So, for instance, if we're considering what happens when an electron drops from the  $N=3$  state to the  $N=2$  state, we would simply solve for the value of energy for each one of those different states,  $N=3$  versus  $N=2$ , solve this equation, and that difference in energy should correspond to the energy of the photon emitted. Now, it would be a real pain to have to carry around values for all these physical constants. They're condensed into one value, just packaged in this letter  $R$  here. This corresponds to the Rydberg constant, and it has a value of  $2.18 \times 10^{-18}$  joules and so this describes in a nice, compact form, the energy of each one of these levels.

So what if we wanted to calculate then what the wavelength is over the photon emitted when an electron drops from this level to this level. So here's my problem. I want to know what the wavelength is of a photon given off when an electron in hydrogen drops from the  $N=3$  level to the  $N=2$  level, and I want to know what wavelength that corresponds to. So what I'm going to do is calculate the difference in energy from one energy state to the other, which is the final energy minus the initial energy. It's the energy of the electron in its final state—that's the  $N=2$  state, and the initial state—that's the  $N=3$  state. I'll simply plug in numbers into that equation, knowing what the Rydberg constant is, and there it is, and I end up with the change of energy corresponds to  $-3 \times 10^{-19}$  joule. It's negative because the system is giving off energy. We're going from a higher energy state to a lower energy state, and so we have the energy of a photon emitted.  $Z$  is one because it's a hydrogen atom.

Now, that energy we know is related to frequency, just rearranging. That frequency is solved by knowing what Planck's constant is, and then finally we need to convert that frequency into wavelengths, so just simply using what we know about wavelength and frequency equals the speed of light, we end up with a value of 656 nanometers. That corresponds to red light. Well, that exactly corresponds to this transition, the transition going from the  $N=3$  level to the  $N=2$  level. That's the red line, in fact, that we see in the hydrogen emission spectrum. That is the color that is missing—one of the four colors that's missing, in the Fraunhofer lines. That would correspond to an absorption of energy when an electron goes from  $N=2$  up to  $N=3$ . It's all making sense now.

What about the other lines? Well, those turn out to correspond to an electron dropping from  $N=4$  to  $N=2$ , 5 down to 2, and 6 down to 2. Well, what about 7 and 8 and 9? Those turn out to be in the ultraviolet. Notice those are larger energy differences than the visible region here. So we only see four lines, but there are many more.

Well, wait a minute. At the  $N=2$  level why don't the electrons go all the way down to the lowest energy level? Well, they do. In fact, most of them do. But the problem is there's such an energy difference that the energy of the photon emitted is in the ultraviolet, and just simply can't see that. But they're there. The energies of those photons are also present in hydrogen emission spectrums, but a lot of them are absorbed, as it turns out, by the glass and other things, and we certainly can't see them. But if you use special equipment they're all there, and they all correspond perfectly to these energy levels set out by Bohr's equation that we looked at.

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So everything is starting to fit in place. What about the  $N=3$  level? Sure enough, there's another series of lines, the Paschen series, all corresponding to electrons dropping to the  $N=3$  level. So everything is falling into place.

Now, this is a marvelous achievement in that by basically using first principles of physics, of mechanics, essentially, plus the addition that angular momentum is quantized, we've perfectly explained the hydrogen emissions spectrum, and the Fraunhofer lines—tremendous achievement. But it turns out it's wrong. It fits, but when you go from hydrogen to helium or lithium, something that involves more than one electron, everything falls apart. We no longer can explain it by the planetary model. This was the last gasp of the notion of a planetary model. It worked for hydrogen, but nothing else. The fatal mistake is to assume that the electron is a particle with a fixed distance from the nucleus in a particular orbit. We have to abandon that whole idea and think about a particle as having particle properties and an electron as having both particle properties and wave properties, just like we think of light as having wave properties and particle properties.