Chapter 20

THE ATOM

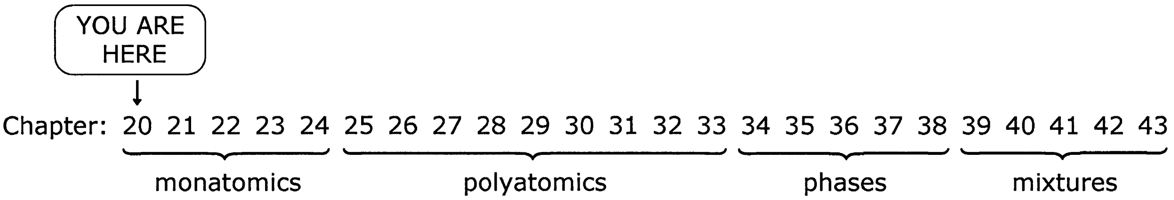
Stop and pause. We are changing directions. We are changing directions in a big way.

20.1 Welcome

You have kept pace for nineteen chapters, covering various portions of the Grand Puzzle. We've touched on all sorts of things so far. We started with atoms and elements, we went to molecules and compounds, we covered reactions and stoichiometry, we dove into the aqueous world, we expanded upon gases, and then we did some work on energy. Much of that jumped around a bit but I explained that purpose in the beginning of Chapter 1.

> “ I am going to introduce sections and work with them. I may partially build the section and then move to another. This may seem scattered but, with time, I will bring these sections together. In the earlier chapters, I will refer to fuller explanations in the later chapters. If you want to, you can look ahead for more. In the later chapters, I will tie back to the earlier chapters. If you're rusty, go back to those pages and refresh. Sometimes, you will need to go back and read a portion. This approach is not idle repetition. These are the links which will hopefully thread the various sections together. You must understand this process. Nature does not work in isolated bits and pieces. Nature is inherently interconnected. All pieces are part of the Grand Puzzle. ”

With this Chapter we launch a major undertaking, since we now start tying things together. We return to the beginning, to the atom, but now in far greater detail. We will develop this picture for all things monatomic. This much will take us through Chapter 24. Then we will bond these pieces to form molecules and all things polyatomic. That will take us through Chapter 33. Monatomic and polyatomic units make up the microscopic world. Beginning in Chapter 34, we jump to the bigger part, the macroscopic world, and we look at how molecules interact with each other to give bulk properties including the very phases of matter. The next jump after that is how different compounds interact with each other in mixtures. This massive sequence is a study of matter as you know it. Keep in mind where we are at, what we are doing and where we are going.



For now, we are going back to the world of the atom. And our primary emphasis is the electron. Why? Chapter 2:

> “ For the most part, CHEMISTRY INVOLVES ELECTRONS. Not protons. Not neutrons. (Unless you're nuking things.) ELECTRONS DO CHEMISTRY! This will be a recurring theme throughout the entire course. This makes electrons a primary focus in our coverage. We need to know three key pieces of information regarding electrons.
>
> We need to know how many there are.
> We need to know their locations within the atom.
> We need to know their energies.
>
> Beginning in this Chapter, we will see how many electrons there are. Locations and energies are more complicated; we begin those details in Chapter 20. ”

As promised, here we are. By now, we can determine how many electrons there are in a chemical unit, but we still need to know locations and energies. This material is often referred to as "atomic structure", but this does not touch at all upon the structure of the nucleus. It's really the structure of the electrons in the atom. You might also see the term "electronic structure", which is a better term. Now, I must warn you. We will be treading on strange turf. Outside chemistry or physics, most people do not encounter this. It is difficult to comprehend because it is so contrary to our normal expectations and experiences. There are many strange things to be found among the family of atoms. They're creepy and they're kooky. Mysterious and spooky. And what's worse, they're real.

Welcome to the quantum realm.

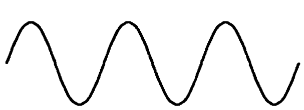
20.2 Basics and background

Before we embark into the quantum realm, you must be reasonably prepared. You can be prepared, but you can never be certain.

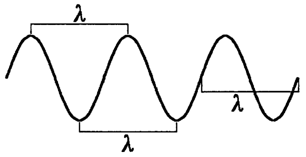
Much of our modern understanding of the atom was developed in the early 1900's. For hundreds of years prior to that, classical laws of motion prevailed. Those laws arose from and dealt with the macroscopic world, the world we are used to seeing. Those laws covered the trajectory of a ball and other normal objects. (Those laws also covered gas phase molecules, as described in Chapter 17.) When it came time to apply these laws of physics to the behavior of the electron in the atom, they were a flop. The old laws failed miserably to describe the behavior of the electron within an atom. Do electrons violate the laws of physics? No, they merely violated the laws of physics as known at that time. Nature had other laws, laws that apply to the quantum realm, and it took a while to realize this. Within the grip of the atom, those are the laws which the electron obeys. Now don't get this picture wrong. These two sets of laws are not totally separated. There is overlap. It is simply easier for us to think about the classical laws for normal objects and the quantum laws for electrons in atoms.

Part of developing the picture of the quantum realm requires light and other forms of electromagnetic radiation, so I will provide some basics here. There is much to be seen. I mean that literally. Your vision depends on it.

Electromagnetic (EM) radiation encompasses the visible (vis) light which you see and light which you don't see, such as ultraviolet (UV), infrared (IR), radiofrequencies (rf), microwaves, etc. It is common to describe EM radiation as waves, so we need to summarize some terminology about waves to the extent that we need to deal with it now. If you've studied waves in classes before, then you'll be familiar with these basics. (Sine and cosine functions, sin x and cos x, are common examples of waves.)



- Wavelength: the wavelength is the distance between two equivalent points in a wave. The two points can be maxima, minima, or whatever, as long as they are equivalent. Wavelength is designated by lower case, Greek lambda, λ. The units are normal length units such as m, cm, nm, etc. Be sure you know your numerical prefix symbols. We will be doing some of the odd ones such as nano, pico, giga, etc. Go back and review these (Chapter 1) if necessary.



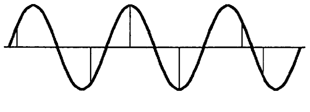
- Frequency: the frequency is the number of wave cycles per second. It gets the symbol of lower case, Greek nu, ν. The "number of wave cycles" is just a number and it does not carry a unit, but "per second" is written "per s" or just s^{-1}. This also goes by the unit hertz, Hz; thus, Hz = s^{-1}. Like many units, Hz's can also take a prefix: for example, there are kHz (10^3 Hz) and MHz (10^6 Hz).

- Velocity: the velocity is the speed and direction of the wavefront, or simply how fast the wave is moving through space. Arithmetically, it is equal to wavelength times frequency, $\lambda \times \nu$. The velocity for EM radiation is what we commonly call the speed of light. The speed of all forms of EM radiation is the same and constant through a vacuum, regardless of whether it's vis, UV, IR or whatever. (Light is slower going through air, water, glass, plastic, etc., but we won't worry about that here.) This speed gets the symbol c (not to be confused with specific heat capacity which also uses c) and the value is defined to be exactly 2.99792458×10^8 m/s. Nine digits is too tedious for us to work with, so I will cut this to 3.00×10^8 m/s for our purposes here. Since no longer exact, then we deal with this as having three sigfigs.

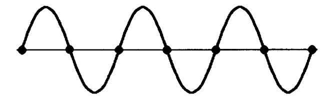
$$c = \lambda\nu = 3.00 \times 10^8 \text{ m/s}$$

That's three hundred million meters per second, or 186,000 miles per second. That's fast. Real fast. THIS RELATIONSHIP IS TRUE FOR ALL EM RADIATION. Same speed for everybody, but different combinations of λ and ν. Since c is fixed, then λ and ν are reciprocally related: as one goes up, the other must go down so that c stays the same.

- Amplitude: the amplitude is the height of the wave at some point. For a simple wave such as a sine or cosine wave, it's the height above (positive amplitude) or below (negative amplitude) its axis. An amplitude can be measured at any point along the wave.



- Node: a node is a point of the wave with zero amplitude. Although it has zero amplitude, a node is still a part of the wave and the wave still exists at that node.



OK, that covers the wave terms which we need. Let's get more into EM radiation and EM waves.

Let me bring in the word, "spectrum". (The plural is "spectra", not spectrums. Latin again.) A spectrum is a range of EM radiation. You can talk about the entire EM spectrum which covers everything, or you can talk about one range in particular. For example, the visible spectrum of EM radiation is the part displayed by a rainbow; it's the range of colors as detected by human eyeballs.

The entire range of EM radiation is immense, spanning a million-billion-fold in terms of λ and ν, although they all move at the same c. Nature designed human eyeballs to sense EM radiation within a tiny stretch of wavelengths from about 390 to 720 nm. All of color is there, in that tiny stretch which we call the visible (vis) region. Different wavelengths in that stretch correspond to different colors or different shades of color. Put all the wavelengths together and you perceive white light but, as Roy G Biv would tell you, spread out the wavelengths and you get the rainbow.

Since colors are spread by wavelength, they are also spread by frequency. For example, consider EM radiation with a wavelength of 390. nm: calculate the frequency of this radiation. In order to do this, we take the equation from above, re-arrange, and then plug-and-chug.

$$c = \lambda\nu = 3.00 \times 10^{8} \text{ m/s}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{ m/s}}{390. \times 10^{-9} \text{ m}} = 7.69 \times 10^{14} \text{ s}^{-1} \quad \text{OR} \quad 7.69 \times 10^{14} \text{ Hz}$$

Look at how I did the denominator: I just inserted 10^{-9} m for nanometer, nm; that's an easy way of handling these units. Notice also how Hz can substitute for s^{-1}. The final result tells us that EM radiation of 390. nm wavelength has a frequency of 7.69×10^{14} Hz. By the way, if you were hit in the eyes with this radiation, then you would perceive this as the color violet.

Let's go to the other end of vis, to 720. nm. Do the same calculation. You get 4.17×10^{14} Hz for the frequency. If you were blasted in the eyes by EM waves of λ = 720. nm, which has $\nu = 4.17 \times 10^{14}$ Hz, then you would perceive red. Notice that red has a longer wavelength but a smaller frequency than violet. This is a simple illustration of the inverse relationship between λ and ν. In between 390 and 720 nm lies the rest of color.

	red	. . . orange . . . yellow . . . green . . . blue . . .	violet	
λ	720	. . . .	390	nm
ν	4.17	. . . .	7.69	$\times 10^{14}$ Hz

The colors are not evenly spaced by λ or ν, but the progression is in the above sequence.

Like I said, the visible spectrum is a tiny fraction of the whole picture. At wavelengths longer than 720 nm, we enter the infrared (IR) region of EM radiation. IR waves extend from 720 nm out to about 1 mm. I say "about" because the borders are not rigorously nor uniformly defined. IR is a huge range just by itself, which is perhaps easier to see if I rephrase it as 720 nm to 1,000,000 nm. Humans cannot "see" this with their eyes, but our skin can detect some of it as the warmth of a fire nearby. Some critters can see or sense better than humans in this range. Although we can't see IR with our eyes, we use devices that operate in this region, such as night-vision devices, heat sensors, etc.

Just past the IR range is the microwave range, whose wavelengths extend from 1 mm out to 0.1 - 1 m or so. Microwave ovens operate here, with a frequency of ~2.45 GHz. When you cook your food, you're actually blasting it with EM radiation of 2.45 GHz frequency. This corresponds to a wavelength of

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8} \text{ m/s}}{2.45 \times 10^{9} \text{ s}^{-1}} = 0.122 \text{ m} \quad \text{OR} \quad 12.2 \text{ cm}$$

At longer wavelengths than microwave, we enter the radiofrequency (rf) range. The rf range gets into all sorts of stuff such as broadcast TV, FM, AM, CB, remote control devices, etc. That's what those symbols, MHz and kHz, mean on a radio tuner. Go look next time. Let's say you listen to an FM station at 95.0: that's 95.0 MHz, and that means the station broadcasts using EM waves with a frequency of 95.0×10^{6} Hz. A lot of electronic communications occur in the rf region although some devices such as cell phones transmit in the microwave range.

Notice as we've been going along through the different EM regions that the wavelengths increased while the frequencies decreased. Keep this inverse relationship in mind. It's important.

For what we want to do right now, these EM regions with long wavelengths and low frequencies are not of primary concern. We must go back and return to visible, which is where EM radiation can take on important chemical consequence. Furthermore, we need to continue our survey beyond visible in the other direction toward shorter wavelengths and higher frequencies. This is where more and more things can happen.

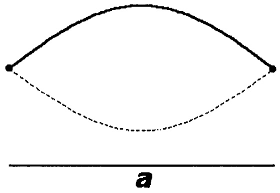
Starting from the shortest visible wavelength of 390 nm, let's trek to even shorter wavelength, into the ultraviolet (UV). The UV range extends from 390 nm down to about 10 nm. UV light is also invisible to the human eyeball. This is unfortunate, since UV is more harmful than vis and we are therefore not aware of it when we are in danger. By the way, this is the reason for the warnings during solar eclipses: do not stare directly into the sun or you can be permanently blinded. The reason is that you can be unknowingly taking in far more UV than your retina can safely handle. You also suntan with UV, and you should be aware of the hazards of suntanning under any conditions. "Black lights" also use UV; they are called "black light" since the UV light cannot be seen, although many of these do show some violet from the visible.

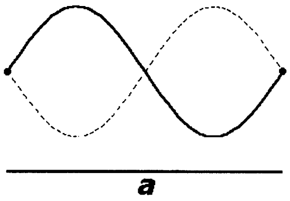
Continuing to shorter wavelengths and higher frequencies, we reach X-rays whose range reaches to about 0.01 nm or 10 pm. X-rays are even stronger and more deadly than UV, although they do find important medical use. Even this is not the end, since gamma rays, γ, overlap and extend beyond X-rays, and γ is the strongest, most powerful, and deadliest of all EM radiation. Fortunately, γ rays are not typically encountered on Earth's surface, although low levels are produced in some thunderstorms. Gamma rays are common in nuclear processes (which we'll see starting in Chapter 66), and there are some nuclear medicine procedures which use γ. There are many sources of γ rays in space including the sun, but the atmosphere pretty much protects Earth's surface-dwellers from the those extra-terrestrial sources.

This completes our survey of EM radiation. From deadly gamma to the wimpy radio range, all have the same c and all differ only in their specific λ and ν combination. We have traversed a range of $\sim 10^{15}$ or so in wavelength and frequency. This is a massive, massive range covering a massive, massive range of energies, as we shall see. Before that, however, we must introduce another type of wave and a bit of terminology to go with it.

20.3 Stand and wave.

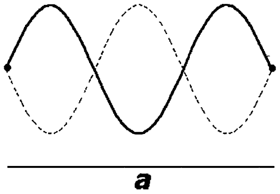
Light waves are traveling waves. This means that the wave moves from one place to another. You are familiar with other traveling waves also, such as the ripples in a pond. On the other hand, you are also familiar with some kinds of waves which do not travel. These are called standing waves or stationary waves. These go through wave motions but the motions are confined to a fixed region. Common examples include a stretched rubber band or various stringed instruments such as a guitar or violin. The band or string is held taut between two end points. When plucked, it undergoes wave motion, but all motion is confined to that region in space as defined by the ends. The string's vibrations are within a fixed, stationary region relative to the end points. Since stationary, these waves don't have velocity but they still have wavelength, frequency, amplitude and nodes.





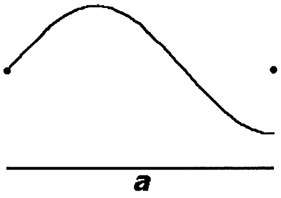
Let's look at a few examples of standing waves. We can imagine these to be plucked strings whose ends are fixed at some distance "a". If you grab the string in the middle and let it go, you get a wave as shown at right, vibrating from one extreme position (solid line) to the other extreme (dashed line). This wave is the easiest to do and it's the simplest wave which is possible. At left, I show another possible wave. It can vibrate within the region shown. This wave is composed of one full waveform. (One full waveform corresponds to equal regions of both positive and negative amplitudes.) In this case, one full wavelength exists between the fixed points, and we can write $\lambda = a$. For our first wave, above right, we only had a half-waveform; thus, one half-wavelength exists between the fixed points, and $(1/2)\lambda = a$ or $\lambda = 2a$.

Check out the nodes: the one at above right has two nodes while the one at above left has three nodes. Since the end points are fixed and cannot move, then these are always two of the nodes.



Let's go one step more complicated and add another half-waveform to the picture, at left. Now we have three half-waveforms which span the distance a, so $(3/2)\lambda = a$ or $\lambda = 2/3\ a$. This wave has four nodes.

We could continue this, adding half-waveforms as we go, but hopefully you're starting to get the picture. I am doing these examples to illustrate a very important point about stationary waves as they compare to traveling waves. Although traveling waves (such as EM) can be any wavelength whatsoever, this is not true for stationary string waves. There are restrictions due to the fixed end points. Although we can construct string waves from <u>half</u>-waveforms, we can't do just any fraction of a waveform; if we tried, then there would be a violation of the boundary condition imposed by the end points. I show this at right: it's an attempt to use a three-quarter waveform, but it fails. Yes, it is indeed a three-quarter waveform, but it fails because one end does not connect to the fixed end point. This string wave cannot exist.



Let me summarize these observations.

A stationary, string wave can be constructed using some multiple of half-waves; no other variation is possible. We can derive a mathematical expression for this. First, notice how the first three examples above can be written.

<u>one</u> half-wave	<u>two</u> half-waves	<u>three</u> half-waves
$\underline{1} \times \frac{1}{2}\lambda = a$	$\underline{2} \times \frac{1}{2}\lambda = a$	$\underline{3} \times \frac{1}{2}\lambda = a$

We can generalize this as follows. We'll let n be any whole-number, positive integer. Since only some multiple of half-waves is allowed for our string, we can write this limitation as

$$n \times \frac{1}{2}\lambda = a$$

which re-arranges to

$$\lambda = \frac{2a}{n}$$

Now, remember: a is a fixed distance; it is a constant for a given set of end points. On the other hand, n is a restricted variable. It can vary but it is restricted, in this case, to positive whole numbers. Nothing else is allowed. With these restrictions in mind, this equation defines every wavelength which is possible for our string wave.

So what does string have to do with an electron? Our discussion here of a string wave introduces two essential concepts to prepare you for your venture into the quantum realm. It introduces the notion of the stationary (standing) wave, which we shall come back to later. It also introduces you to the notion that mathematical equations and their variables can have restrictions on the value which they can be. This restriction to specific values, which are not continuous, is called "quantization". The verb is "quantize", which means to restrict to such types of values. For our vibrating string, we say that "the wavelength is quantized". Given the equation for λ above, we can further say that "the wavelength is quantized by n", since n contains the restriction for a whole number.

Quantization is extremely important in the quantum realm, but don't be confused by it. The notion is actually known to you, even if the term is not. Just think: how many things can be described mathematically, but not just using any number? How about people? How many people can be in a room?

1? Yes. 2? Yes. 23? Yes. 39.06483? No.

Any mathematical equation for the number of people in a room would have to be restricted to whole numbers. Here's another example: cash. How much cash can you carry?

\$1.43? Yes. \$13.56? Yes. \$22.01? Yes. \$15.06372196? No.

Carryable cash is quantized: we can describe it by the mathematical relationship $n \times \$0.01$, where n is any whole number. Thus, we can even describe some normal, everyday things in terms of quantization.

On the scale of the atom, many things are quantized. This, however, is only a small part of the strangeness of the quantum realm. There is another part to introduce at this time.

20.4 Duality

I mentioned in the beginning of this Chapter how the classical laws of physics failed to describe the electron in the atom, although those laws successfully describe the motion of a ball. The classical mathematics of waves had also been developing over centuries, but waves were not originally linked to the electron. This link was ultimately required before the electron could be understood. You see, by the rules of the quantum realm, everything has both particle properties and wave properties. In the normal, macroscopic world in which we live, however, the wave properties are completely overshadowed by the particle properties. Since the wave properties are overshadowed, classical physics prevails and those old laws work just fine. On the other hand, for particles of subatomic dimension such as electrons, the laws of classical physics are not adequate because both the particle and the wave properties are important. Sound weird? It should. It is. This is another important part of the quantum realm and it is called "wave-particle duality". Every object has both wave and particle properties. Everything, including you, has wave properties, but the wave properties are not significant except for things with extremely minuscule momentum. Since momentum equals mass times velocity, then an object's mass and/or its velocity must be minuscule in order to exhibit significant wave character. (We'll look at the mathematical relationship for this in the next Chapter.) You're not minuscule and a ball is not minuscule, but an electron is. Thus, you'll never measure the wave properties of you or of a ball, but you can measure the wave properties of electrons since their masses are minuscule. Before we go to the electron, let's return to light.

In our discussion above of EM radiation, I talked of light as waves but light is also subject to duality: light has both wave and particle properties. One particle of light is called a photon. The photon moves through space at the speed of light. It has momentum as it goes. It carries an energy as it goes; that energy is proportional to the frequency of the associated wave. It is common to refer to this specific amount of energy as an energy packet; this energy packet is often called a "quantum" (plural, quanta). That amount of J's is the energy of that photon. That amount of J's is the energy of that wave.

The connection of energy to the frequency of the wave is extremely important. The mathematical relationship is a simple proportionality: $E = h\nu$. The proportionality constant, h, is called Planck's constant. (Planck is pronounced "*plonk*".) The value of Planck's constant is defined to be exactly $6.62607015 \times 10^{-34}$ J•s. Once again, we don't need nine digits, so we cut this to 6.626×10^{-34} J•s for our purposes here and we treat this as four sigfigs. Note that the value of h is incredibly small, but this is because we are dealing with one particle at a time here. We are not doing moles of things right now, so our numbers are going to be extremely tiny.

Now, remember that $\nu = c/\lambda$, so we can also write

$$E = h\nu = h\frac{c}{\lambda}$$

This equation provides a grand result: the energy of a single wave is proportional to its frequency and inversely proportional to its wavelength. This relates to the earlier notions which I had presented about "stronger" or more harmful radiation such as UV, X-rays or gamma rays, while rf waves were relatively harmless. Higher frequency is higher energy. Longer wavelength is lower energy. Lower frequency is lower energy. Shorter wavelength is higher energy. Get these connections down. You must keep these in mind. They're very important.

Let's do a simple illustration and calculation. We'll compare the energy of one FM radio photon which has a frequency of 100. MHz (common broadcast station range) to the energy of one UV photon which has a wavelength of 280. nm. In order to find the energy for each, just plug into Planck.

‣ FM photon, 100. MHz

$$E = h\nu$$

$$E = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})(100. \times 10^{6}\ \text{s}^{-1}) = 6.63 \times 10^{-26}\ \text{J}$$

This is the energy of only one photon of 100. MHz frequency.

‣ UV photon, 280. nm

$$E = h\frac{c}{\lambda}$$

$$E = (6.626 \times 10^{-34}\ \mathrm{J \bullet s})\,\frac{3.00 \times 10^{8}\ \mathrm{m/s}}{280. \times 10^{-9}\ \mathrm{m}} = 7.10 \times 10^{-19}\ \mathrm{J}$$

This is the energy of one photon of 280. nm wavelength. Again, note that we are dealing with only one photon in each case, so both energies appear very small. The important point from these results is that the energy of the UV photon is over ten million times the energy of the FM photon. This is a huge difference.

Let's go ahead and put this into a more familiar perspective: we'll bring this up to mole scale, and then we can get a better idea of how much energy these represent. To get to mole scale, simply take a mole of each kind of photons, which means multiply by Avogadro.

▸ One mole of FM photons, 100. MHz

$$E(\mathrm{mol}) = (6.022 \times 10^{23})(6.626 \times 10^{-34}\ \mathrm{J \bullet s})(100. \times 10^{6}\ \mathrm{s^{-1}}) = 0.0399\ \mathrm{J}$$

▸ One mole of UV photons, 280. nm

$$E(\mathrm{mol}) = (6.022 \times 10^{23})(6.626 \times 10^{-34}\ \mathrm{J \bullet s})\,\frac{3.00 \times 10^{8}\ \mathrm{m/s}}{280. \times 10^{-9}\ \mathrm{m}} = 428{,}000\ \mathrm{J} = 428\ \mathrm{kJ}$$

Look at the numbers: 0.0399 J versus 428 kJ. There is major significance to this result. Recall from Chapters 18 and 19 that the energies of chemical reactions are on the scale of hundreds of kJ's per mole and more. Notice that the mole of FM photons is a total wuss in this regard. But UV? These carry millions of times greater punch and their energies are now on the scale to do chemical reactions. This leads to a very important observation: photons of higher frequency carry sufficient energy to cause chemical reactions to occur. The EM regions which involve these high-energy photons are the vis, UV, X-ray and gamma ranges, although some IR can also get involved.

This aspect will get us into the fundamental manner by which light and matter interact. There is one more key point to know: under typical circumstances, one individual atom (or molecule or other chemical unit) interacts with one photon at a time. This is very important to understand. A photon can deliver J's to a molecule and pay the price for a reaction or a process to occur. If it costs "*x*" joules, then that one photon must carry "*x*" joules and not just any number. Since a specific energy is required, then only photons of a certain frequency (and wavelength) can do the job. You can't send in two or more photons whose energies add up to "*x*". It's got to be one photon at a time and that photon must have the right energy. (Exceptions to this can occur with high intensity light sources (e.g., lasers) or very high energy light sources (especially γ) but those are not typical circumstances within our coverage here.)

Believe it or not, there are many things in your life which involve light and which are explainable with just this much. These include your vision, photosynthesis, radiation-induced cancer, and other things, as we shall see later. In the meantime, notice what we've done. We have assigned particle properties to EM waves. This is part of the wave-particle duality of light.

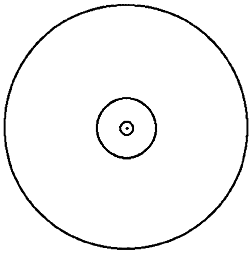
With the critically important notions of quantization and of duality, you are ready to enter the quantum realm. It is time to start on the electron within the atom.

20.5 Orbits

Electrons. We seek their location and their energies since these things are of fundamental importance in chemistry. Everything we've done so far in this Chapter is leading up to this.

There's something you should understand about this energy business. When we say the "energy of the electron", that includes several things. It includes the energy of the attraction between the negative charge of the electron and the positive charge of the nucleus. It includes terms related to the motion of the electron within the atom. It also includes repulsions to other electrons if any are also present in the atom. In this Chapter and the next, we keep things simple and deal primarily with only one electron at a time. We'll do more and more electrons starting in Chapter 22.

Much of the historical development of this picture happened in the early 1900's, which is recent in terms of the history of science. In the early days of the field, a main hang-up was trying to apply the old laws of physics to the electron but this failed miserably as was mentioned earlier. They couldn't even understand the simplest case to study, which is a single hydrogen atom. The H atom is the simplest because it has only one electron surrounding its single proton in the nucleus. (By now, of course, you may realize that the element hydrogen exists as diatomic H_2, but there are ways of breaking that covalent bond to give separate H atoms. This is what they had to do first in order to study H atoms by themselves.) I won't go into much of the background history but I will pick up the developments beginning with Bohr. Bohr took a radically different approach to the behavior of the electron within the atom. This would prove to be a huge step forward, although his theory had shortcomings as we shall see.

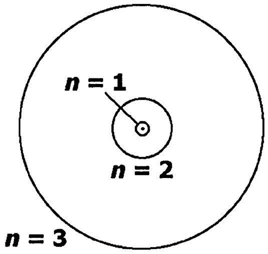


At the time Bohr came into the picture, it was thought that an electron moved around the nucleus, pretty much anywhere. They knew there were problems with this interpretation but it's all they had at the time. Bohr introduced the notion that an electron orbits around the nucleus but not just anywhere. Instead, only certain orbits were possible and these orbits formed a series of rings around the nucleus. Three such rings are shown at left around the nucleus (which is the tiny dot in the center). An electron must be in one of the possible orbits and it could not be in between. Notice what this is saying: the location of an electron is quantized by orbit; only certain orbits are possible and the electron cannot be in between orbits or anywhere else in the atom. Bohr also said that, for any specific orbit, there is a specific energy associated with that orbit. Since orbits are quantized and since the energy depends on the orbit, then energy is also quantized.

The incorporation of quantization was a really big deal. With classical laws of physics, it was a simple assumption that the electron could go anywhere around the nucleus and have any energy. That was wrong. Within the grip of the atom, the electron is in quantized locations with quantized energies. Bohr developed an equation for calculating the energies of the electron in the different orbits.

$$E = -\frac{Rhc}{n^2}$$

In this equation, the *h* is still Planck's constant and *c* is still the speed of light. A new constant is introduced, *R*, called the Rydberg constant, and it is equal to $1.097 \times 10^7\ \mathrm{m^{-1}}$. (Sorry, I know it's another *R* just like gas constant *R*, but there's absolutely no connection between the two.) The real magic lies in *n*, which is now a restricted variable: it can be any integer 1 or higher. No zero, no negatives, and no fractions are allowed. Just 1, 2, 3, 4, etc. This value, *n*, is the orbit number, and this provides the quantization of *E*. The smallest orbit is $n = 1$. This is the closest circle around the nucleus. Keep in mind that the electron is negative and the nucleus is positive, so the closest orbit provides the strongest attraction between the two. Thus, the $n = 1$ orbit is the favorite. By the way, my emphasis here is on the calculation of the energies of the electron in the various orbits. Bohr also provided a means to calculate the size of each orbit, but that is not our concern for now (for reasons to be evident later). Our focus for now is energies and, for that, we use the above equation. But, first notice that the numerator on the right of the equation is the product of three constants, which gives a new constant.



$$Rhc = (1.097 \times 10^{7}\ \mathrm{m^{-1}})(6.626 \times 10^{-34}\ \mathrm{J \bullet s})(3.00 \times 10^{8}\ \mathrm{m/s}) = 2.18 \times 10^{-18}\ \mathrm{J}$$

So the equation can be written

$$E = -\frac{Rhc}{n^2} = -2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{n^2}\right)$$

Some students ask what the minus sign is for. Remember that this is the energy of the interaction between a negative electron and a positive nucleus. When you multiply a negative charge times a positive charge, you get a negative energy for the interaction. A negative energy is attractive; the more negative, the stronger is the attraction. Negative is good for energy.

Now, let's do some things with the energies of these different orbits. Calculate *E* for the first three orbits, $n = 1$, 2 and 3.

‣ $n = 1$ orbit

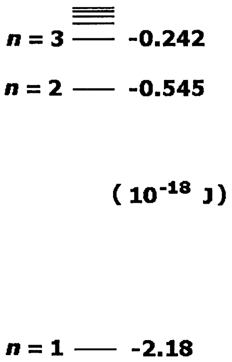
$$E = -2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18}\ \mathrm{J}$$

‣ $n = 2$ orbit

$$E = -2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{2^2}\right) = -5.45 \times 10^{-19}\ \mathrm{J} \quad \text{OR} \quad -0.545 \times 10^{-18}\ \mathrm{J}$$

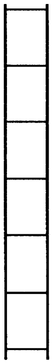
- $n = 3$ orbit

$$E = -2.18 \times 10^{-18}\ \text{J} \left(\frac{1}{3^2}\right) = -2.42 \times 10^{-19}\ \text{J} \quad \text{OR} \quad -0.242 \times 10^{-18}\ \text{J}$$

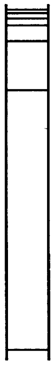


The exponents here can confuse the issue, so I converted the second and third energies to 10^{-18} for direct comparison to the first. We can plot these energies vertically as shown at right. The energies for n = 1, 2 and 3 are labeled; I've included lines for 4 - 7 also, just to see the trend. (You can calculate their energies.) This plot is called an energy diagram. It shows different energy levels for the electron in different orbits. Notice that the energy for n = 1 is the most negative (lowest); each orbit's energy after that is less negative (higher). Notice that the spaces between consecutive levels get smaller and smaller as n gets bigger and bigger; the biggest gap is between n = 1 and n = 2. As you go higher in the diagram, the gaps between levels get so tiny that the levels never make it much higher than what is shown; arithmetically, the levels approach E = 0. (If you're into limits: as n goes to infinity, E goes to zero because n^2 is the denominator. If you're not into limits, pretend you didn't read that.) There is also an important physical meaning behind all of this: as n gets larger and larger, the orbit gets further and further away from the nucleus. That's why the attraction gets weaker and weaker and that's why E gets smaller and smaller (less negative) towards zero. The zero point for energy is the totally separated electron and nucleus; as an electron comes into the atom and takes up some position in some orbit, then it has some E which is negative (attractive).

Keep in mind that attraction is good and that such attraction is given by a negative energy. In normal conversation in the normal world, we tend to think of positive energy as being favorable, but that's not the case here: the strongest attraction is the most favorable; it has the most negative energy and therefore is the lowest position in the diagram. Down is good.



Another way to look at these diagrams is to compare them to a typical, normal, everyday ladder, as shown at left. We can even define a ladder by a nerdy description: a ladder is a device used to achieve a quantized vertical position. It's quantized by the rung locations; you can't be in between (unless you're doing something weird). Nature (here, due to gravity) wants you at the lowest rung position. To go up the ladder will cost you J's; to fall down will release those J's. Now, compare all of this to the energy diagram above, but redrawn as a ladder at right. In an energy diagram, each energy level represents a rung. The rungs are not evenly spaced, but that doesn't matter. Nature (here, due to attractive forces) wants the atom to be at the lowest energy position and this corresponds to n = 1. The electron can move out to a bigger orbit, which means higher n and higher E, but that will cost some J's because you are pulling it away from the nucleus. If the electron finds itself in a higher n orbit, then it can fall back toward the n = 1 orbit and energy is released.



This bit about moving up and down on the energy scale is very important.

20.6 Relax, don't get too excited.

The movements between orbits and energy levels are called "transitions". We distinguish two kinds of transitions by their direction as follows. An "excitation" is a transition to a bigger n orbit (higher E level). Since you're going up the energy ladder, this will cost J's. Using terms from Chapters 18 and 19, the atom is the system. The system starts the process at some low energy level and ends at some higher energy level. The difference is ΔE and it will be a positive value. Those J's must come from somewhere, namely the surroundings. Now, go the other direction with the other kind of transition. A "relaxation" is a transition to a smaller n orbit and down to a lower E level. The system (atom) starts at some higher energy level and ends at some lower energy level. The difference between the two energy levels is ΔE, and now it's a negative value. Those J's left the atom and went to the surroundings.

Read that paragraph again. You need to understand those concepts and the terms involved.

The "ground state" is the condition of lowest energy for the system. We also say the atom or the electron is "at rest". Remember that lowest energy is the most favored. For a hydrogen atom, it means that the electron is in the n = 1 orbit. An "excited state" is any other condition, such as when the electron is in the orbit with n = 2, 3, 86, 438, etc.

Let's do some illustrations and calculations for transitions. I'll show you how this terminology works, too. We start with our hydrogen atom with its electron in the $n = 1$ orbit. This is the ground state. The energy of the system in this state is -2.18×10^{-18} J. The electron "undergoes a transition" to the $n = 2$ level. This is now an excited state. We can also say that the electron "gets excited" from $n = 1$ to $n = 2$. The energy of the system in this excited state is -0.545×10^{-18} J. We can depict this using a small portion of the prior energy diagram as follows. I'll use a black dot, •, for the electron energy in the diagram.

	initial state		final state	
$n = 2$	——	electron	—•—	$E = -0.545 \times 10^{-18}$ J
	↑	undergoes transition		
$n = 1$	—•—	(gets excited)	——	$E = -2.18 \times 10^{-18}$ J

Keep in mind that this is a representation of energies only. It is not a physical representation of location. I'm not showing orbits and I'm not showing their sizes. Right now, it's energy that matters.

For this transition, we can calculate the energy ("transition energy") by just subtracting the two E's. This becomes ΔE and this Δ is again final-minus-initial energies.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$\Delta E = (-0.545 \times 10^{-18}\ \text{J}) - (-2.18 \times 10^{-18}\ \text{J}) = 1.64 \times 10^{-18}\ \text{J}$$

Note that the answer is positive. Just like in Chapters 18 and 19, the sign of ΔE will also mean direction. Here, the system gains 1.64×10^{-18} J. That energy came from somewhere. Something had to pay in order for this excitation to occur. Of course, 10^{-18} J does not sound like much, but remember that this is for one atom. Let's put it back into our mole perspective: multiply 1.64×10^{-18} J by Avogadro. That comes out to 988 kJ, and that is what must be paid just to excite one mole of hydrogen atoms from $n = 1$ to $n = 2$. That's extremely expensive in energy! Again, when working on the scale of a single atom, we lose sight of how expensive these things can be. These things aren't cheap.

Let's go back to exciting only one atom from $n = 1$ to $n = 2$: the cost is 1.64×10^{-18} J. How would you like to pay for that? Cash? Check? Photon?

Yes, that's right: photon. We can send in a photon to pay this price but remember that the atom can only interact with one photon at a time. That one photon must have just the right energy: it must possess 1.64×10^{-18} J. No more, no less. What kind of photon is this? What wavelength? Time for Planck again.

$$E = h\frac{c}{\lambda}$$

The energy of the photon is the payment for the transition: 1.64×10^{-18} J; for this energy, find λ.

$$\lambda = h\frac{c}{E}$$

Plug-and-chug.

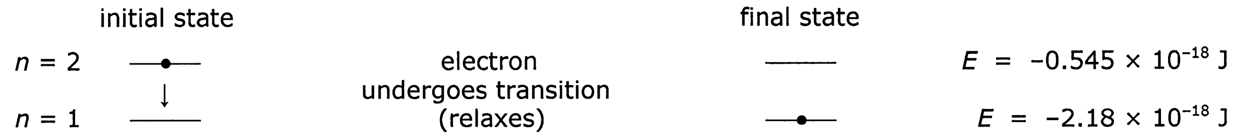
$$\lambda = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})\,\frac{3.00 \times 10^{8}\ \text{m/s}}{1.64 \times 10^{-18}\ \text{J}} = 1.21 \times 10^{-7}\ \text{m}$$

1.21×10^{-7} m corresponds to 121 nm, which is deep, deep UV range. This is a very high energy photon. After all, this is a very expensive transition.

So what does all this mean?

We can shine UV radiation onto hydrogen atoms in their ground state. A photon of 121 nm can be absorbed by one atom, exciting the electron into the $n = 2$ state. That photon is gone. That one wave of light is no more. Light is energy. If you consume the energy, then you consume the light. This is what is meant by "absorbing light" or "absorbing a photon". You're actually consuming its energy, using it to pay for an excitation. The photon is gone and its J's are now in the system.

Let's do a relaxation. We'll just reverse what we did so that we can keep the numbers the same. Start with the hydrogen atom with its electron in the $n = 2$ orbit. The energy of the system in this state is -0.545×10^{-18} J. The electron "undergoes a relaxation" to the $n = 1$ level, the ground state. We can also say that the electron "relaxes" from $n = 2$ to $n = 1$. The energy of the system is now -2.18×10^{-18} J. Here's the picture this time.



You can do the full math like we did above, but all we did is reverse the process. When you reverse a process, the energy takes opposite sign, remember? The previous excitation example had $\Delta E = 1.64 \times 10^{-18}$ J, so the present relaxation has $\Delta E = -1.64 \times 10^{-18}$ J. The H atom gives off 1.64×10^{-18} J and the system ends with less energy than it started with. That energy can leave the atom as light energy. If so, then only one photon is involved and it must have that amount of energy, 1.64×10^{18} J. That means that it, too, would have a wavelength of 121 nm. By the way, when a photon comes out of an atom, it's called "emission". We say the atom emits a photon.

What we have done here is only one example of many possible transitions. From ground state, the H atom can be excited by a photon to some excited state. From an excited state, the H atom can be excited further to even higher energy by another photon or it can relax and emit a photon. Remember: one photon for each transition. When relaxing, it doesn't have to relax all the way to $n = 1$. It can do it in steps. Let's say you excite the atom to $n = 4$ from ground state. Then it relaxes to $n = 2$, giving off some energy. Then it relaxes to $n = 1$. There's a shorthand notation for transitions, and we can write this sequence as $n = 1 \rightarrow n = 4$ as the excitation, followed by $n = 4 \rightarrow n = 2$ and then $n = 2 \rightarrow n = 1$ as the two relaxation steps. Needless to say, many different transitions are possible between the different energy levels. We can derive a general equation for the energy of any transition as follows.

Initial state: electron in n_{initial} orbit

$$E_{\text{initial}} = -2.18 \times 10^{-18}\ \text{J} \left(\frac{1}{n^2_{\text{initial}}} \right)$$

Final state: electron in n_{final} orbit

$$E_{\text{final}} = -2.18 \times 10^{-18}\ \text{J} \left(\frac{1}{n^2_{\text{final}}} \right)$$

Transition energy

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18}\ \text{J} \left(\frac{1}{n^2_{\text{final}}} - \frac{1}{n^2_{\text{initial}}} \right)$$

Photon energy

$$E_{\text{photon}} = |\Delta E|$$

Notice that I wrote the photon energy as the absolute value of the transition energy, ΔE. Why absolute value? Photon energies can only be positive, but ΔE can be positive or negative. But remember: sign is direction. Positive ΔE means photon into system, negative ΔE means photon out of system. Let's summarize several things to this point.

Excitation	Relaxation
E (of atom) increases	E (of atom) decreases
ΔE is positive	ΔE is negative
photon is absorbed	photon is emitted

Let me show an example of these equations, using one of the transitions which I mentioned above: calculate the energy of the transition and the wavelength of the photon which is involved for the transition $n = 4 \rightarrow n = 2$.

In order to do this, you set $n_{\text{initial}} = 4$ and $n_{\text{final}} = 2$. These plug into the equation for transition energy, ΔE, from above.

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18}\ \text{J} \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

A common error here is messing up the part in parentheses, so be careful. Here, the parentheses part is 0.1875. (By the way, all n's are exact integers, so the part in parentheses is exact for sigfig purposes; don't round off the part in parentheses.) In the end, you should get $\Delta E = -4.09 \times 10^{-19}$ J for your transition energy. It's negative, as to be expected for a relaxation. Thus, a photon shoots out of the atom with an energy of 4.09×10^{-19} J, and the wavelength can be calculated from that.

$$\lambda = h\frac{c}{E_{\text{photon}}}$$

Plug it in, punch it out, round it off.

$$\lambda = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})\,\frac{3.00 \times 10^{8}\ \text{m/s}}{4.09 \times 10^{-19}\ \text{J}} = 4.86 \times 10^{-7}\ \text{m}$$

That wavelength of 4.86×10^{-7} m is the same as 486 nm, which puts us smack in the visible region. So, if you had some huge number of H atoms, all in the $n = 4$ excited state, and they all relaxed to $n = 2$, you would see blue-green light. That's not a realistic occurrence, however, so don't hold your breath.

Here, you do one.

……

Example. Calculate the energy for the excitation $n = 1 \rightarrow n = 3$ and calculate the wavelength of the photon which would be required to pay for this transition.

……

What do you need for this problem? You need your transition energy equation from above, filling in the correct n's. Don't forget to square them.

$$\Delta E = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{\quad} - \frac{1}{\quad}\right) = \underline{\hspace{6cm}}$$

I won't tell you the answer, but here's one clue: the parentheses part gives you negative eights. If you do it right, you'll know what I mean. If not, ask someone. Now, after you get ΔE, find the wavelength of the photon which packs that amount of energy.

$$\lambda = h\frac{c}{E_{\text{photon}}} = 6.626 \times 10^{-34}\ \text{J}\bullet\text{s}\ \frac{3.00 \times 10^{8}\ \text{m/s}}{\hspace{5cm}} = \underline{\hspace{6cm}}$$

Would this photon be vis? UV? X-ray? Other?

Although it may take some practice, hopefully you will see that these calculations are fairly straightforward from the given equations.

20.7 Obit for orbits

We have now covered numerous aspects of Bohr's explanation of the electron in the atom. Bohr's explanation was a major advance at the time and many things fell better into place. The notion of quantization of electron energies was a major step forward. It explained all sorts of experimental evidence at the time, including "line spectra". A line spectrum is an experimental measurement of transition wavelengths for an element. Each line represents one $\Delta E_{\text{transition}}$ and it is an experimental confirmation of what transitions are actually possible. If there was no quantization, E's could be anything; if E's could be anything, then ΔE's could be anything, and you would get a blur instead of specific lines. Bohr's equations gave excellent agreement to the experimental line spectrum for H, thereby giving credibility to the notion of quantization.

Unfortunately, Bohr's explanation had limitations. It only worked when only one electron was involved, such as in the hydrogen atom. It also worked for some cations, too, if they had one electron. For example, they could generate some He^{+} ions which they could also study. Since He^{+} has two protons in the nucleus instead of one, then the electron is more strongly attracted and all the energies are greater (more negative). This requires modifying the equation for the energy of the different n levels; the general equation for a single electron around any nucleus is the following.

$$E = -2.18 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$$

Z is atomic number, like always. For hydrogen, $Z = 1$, and you get the equations which we used earlier. For He^{+}, $Z = 2$; this makes the energies four-fold compared to H. So, yes, they could do other things with only one electron, but that's still very limiting.

But the Bohr picture had bigger problems, too. Despite all that it did to get things going, despite its ability to explain transitions, despite its interpretation of experimental results such as line spectra, despite everything it was able to do, it had a major drawback: THERE ARE NO SUCH THINGS AS ORBITS IN THE ATOM.

Problems

1. True or false.
   a. A photon of red light has more energy than a photon of violet light.
   b. Electromagnetic waves are stationary waves.
   c. The energy of the atom increases during a relaxation.
   d. All excitations require an input of energy.
   e. The electron in the He^+ cation is at lower energy than the electron in the H atom.
2. True or false.
   a. In a vacuum, a UV photon travels faster than a visible photon.
   b. A standing wave cannot have nodes.
   c. The energy of photons increases with increasing frequency of the radiation.
   d. A transition in the hydrogen atom from $n = 1$ to $n = 3$ is a relaxation.
   e. An atom in a ground state cannot undergo relaxation.
3. What is the energy (in J) for one photon of 8.23×10^{17} Hz frequency?
4. What is the energy (in <u>kJ</u>) for one <u>mole</u> of UV photons with a wavelength of 204 nm?
5. What is the energy (in <u>kJ</u>) for one <u>mole</u> of IR photons with a wavelength of 994 nm?
6. What is the energy (in J) of the electron in the $n = 3$ level for the H atom?
7. The solar wind contains many unusual and very high energy ions flying through space. One such ion is O^{7+}. What is the energy (in J) of the electron in the $n = 2$ level of O^{7+}?
8. For an electronic excitation involving a photon of wavelength 682 nm, what is the difference (in J) between the two energy levels?
9. What is the transition energy (ΔE, in J) when a hydrogen atom undergoes the excitation $n = 2 \rightarrow n = 7$? What is the wavelength (in nm) of the photon absorbed in such a process?
10. What is the transition energy (ΔE, in J) when a hydrogen atom undergoes the relaxation $n = 5 \rightarrow n = 3$? What is the wavelength (in nm) of the photon emitted in such a process?