Chapter 21   **LIGHT, MATTER AND WAVES**

If there are no orbits, what good is Bohr's explanation? Why did I even bother covering it?

Well, no, it's not even close to perfect. But it's still good and it's still a classic. It was a big, albeit limited, step forward.

There's a bit of irony here. It is true that Bohr's idea of orbits is wrong, but the energies are right. So, all of our calculations are right; the notion of quantization of energies is right; and, the explanation of transitions is right. I wanted to introduce all of that without overloading everything at once, and the Bohr atom is a nice way of doing it. On the other hand, the explanation of location was completely wrong. So what was missing here? Duality. Bohr had the quantization, but duality was missing. The Bohr explanation described the electron as a particle in an orbit but, within the grip of the atom, the electron has wave behavior. That was an incredibly strange concept back then, and it's still a very strange concept today. I told you this was going to be strange stuff.

21.1 Here and now

Theories of electrons in atoms are well advanced today. Atoms and ions with more than one electron can be reasonably explained and calculated. Polyatomics can also be reasonably done. I say reasonably, because this isn't necessarily easy and it isn't necessarily exact. Although theories are well advanced, things still aren't perfect, and we don't know everything we want to know. Sometimes only approximations can be obtained. And, quite frankly, many parts of this are not easy to understand. The quantum realm is still a bizarre place.

The quantization of energies remains an extremely important part of the picture. It doesn't matter if it's a single atom, a diatomic molecule or a molecule of fifty atoms. Let me summarize four general features of this. These are not new; you will recognize these from Bohr's hydrogen atom. I am now applying them to everything.

- 1. Electrons are in atoms and in molecules in specific energy levels, not just any energy level.
- 2. The lowest energy level is the most favored. This is the ground state ("at rest").
- 3. An electron can be excited to a higher energy level, giving an excited state. This costs energy. This energy can be provided by an EM photon.
- 4. Once in an excited level, an electron can relax to a lower level, giving off energy. This energy can be emitted as a photon (or it can be given off as heat).

Many things in your world can be explained by these four features. A lot of your world involves energy transitions and EM radiation. Again, this is the way light and matter interact. I'll give you a basic outline of some of these for illustration purpose. I'm going to keep things simple. In reality, especially in polyatomic units, the energy levels can get very complicated and trying to account for all electrons can also get very complicated. There are even different layers of energy levels superimposed on other energy levels. Nevertheless, they all have a specific energy and that is the important part. For now, we're doing it simple. I will work with only two or three energy levels and focus on only one electron at a time.

21.2 Light and matter

Let's start with a simple example of electronic transitions: neon signs. I mean the true neon signs, which are primarily the red-orange ones. Many of the other colors are fakes. Some of the fakes involve a different gas, some of the fakes use colored glass, and some of the fakes are actually fluorescent lights in thin tubes. In a real neon sign, the red-orange glow comes from the middle of the tube because that's where the neon gas is. When the sign is off, the tubing is clear and colorless. If a different gas is used, a similar situation applies but you get a different color when the sign is on. The colored glass ones have a different gas and they have clear but colored tubing. The fluorescent ones have a different gas but they also have a coating on the inside surface of the tube and it is this coating that glows when the sign is on. Different coatings give different colors. When the sign is off, the coating can be seen inside the tube.

So, how do real neon signs work? While the sign is turned off, the neon atoms just fly around inside the tube and mind their own business, doing their gas phase thing with all their electrons at rest in the ground state. Turn on enough electricity, however, and things get very exciting. The juice in a neon sign can be in the range of 15,000 volts (although small neon lamps work with more normal voltages). Under these high energy conditions, an electron can get completely kicked out of its atom to give free-flying electrons and Ne^+ cations. The Ne^+ cations and free electrons are attracted to, and hightail it towards, oppositely charged electrodes at the ends of the tube, giving rise to an electric current. Along the way,

energetic collisions between the free-flying electrons and neutral Ne atoms occur, and these impacts can cause excitation of an electron within the Ne atom. Subsequently, the excited electron relaxes (at right), thereby emitting a photon in the process.   Different transitions are possible between different levels, thus giving photons of different energies and therefore of different wavelengths.   A dominant transition for Ne involves photons in the red-orange region of visible light. When those relaxations are occurring, you see those photons as the red-orange glow of the lamp.
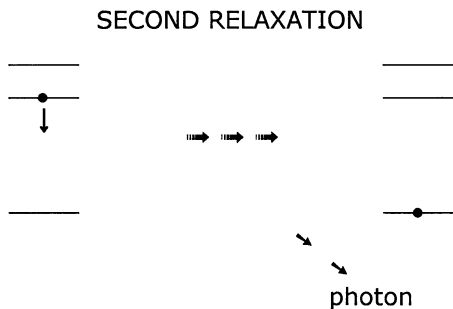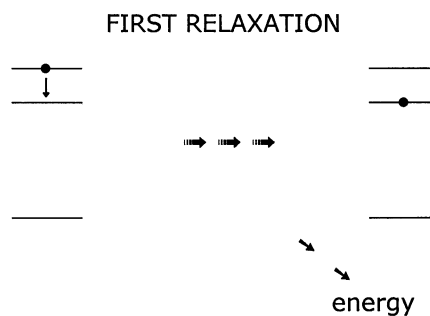
RELAXATION

photon
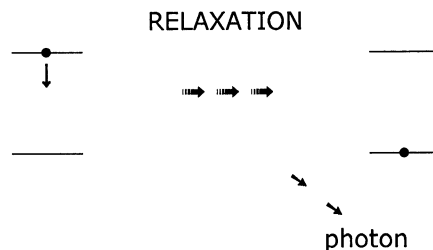
And that's how true neon signs operate.

I mentioned fluorescent lights. As given by their name, these work by "fluorescence". Many things are fluorescent, at least to some extent, and common uses are made of fluorescent paints, markers, posters, etc. These contain a fluorescent compound which appears to glow by itself but, in fact, the glow is a result of black light (UV). You can use an actual "black light" on the object, but the effect can frequently be observed with just normal UV levels in sunlight. Remember: you don't see UV and this is why you're not always aware that it is causing the effect. Let's focus on three energy levels within the fluorescent compound, with an electron in the lowest of the three at ground state.

EXCITATION

UV
photon
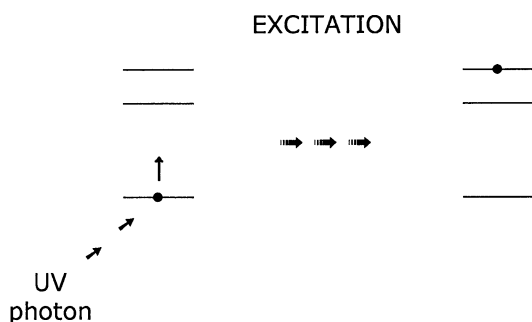
To start the process, we send in a UV photon to cause an excitation directly to the third level, bypassing the middle. Don't forget that UV is higher energy than vis, so a UV photon can cause a higher jump than a vis photon can. This gives us an excited state.

FIRST RELAXATION

energy

Next, the electron relaxes to the middle level.   This relaxation gives off a small amount of energy, possibly as a photon in the IR (which you can't see). This is not the important part.

SECOND RELAXATION

photon

The important part is the next step, which is the bigger relaxation back to the ground state, emitting another photon.   This photon will have less energy than the original excitation photon (UV), since the ΔE is smaller. In a typical application, this photon will be within the visible region.

This photon is what you actually see. The object appears to glow because it's being hit by invisible UV and then it emits visible.   Different fluorescent compounds will have different energy levels and different values of ΔE for their relaxation. This gives you different colors, such as fluorescent green, fluorescent orange, etc. This also gives you the colors in many fake neon signs which I mentioned earlier.

This process is also how normal fluorescent room lights work. For these, different fluorescent compounds are coated on the inside glass surface of the lamp tube. From this combination, you get several colors all at once. These various colors add to give white light, and this is what you see. Where does the UV come from to start the fluorescence inside the tube? Usually from mercury atoms. Elemental mercury is a liquid but it does have a very small amount of vapor. At the conditions inside a fluorescent bulb, enough mercury atoms in the gas phase are getting electrically zapped, somewhat as in a neon sign, but now these relax by emitting UV photons. Mercury is excellent for this, but then this creates an environmental hazard when the fluorescent light is discarded.

Another process which involves electron transitions is phosphorescence. Phosphorescent objects glow after first shining an external source light on them. They work by a process which has some similarity to fluorescence, but a key difference for phosphorescence is that the final relaxation gets delayed. Normally, relaxations occur very fast after the initial excitation, in minute fractions of a second. In phosphorescent compounds, however, the final relaxations can be very slow. When you shine a light on a phosphorescent object, you excite atoms or molecules of the compound; these slowly relax, slowly giving off visible photons. This continues, even after turning off the source light, and the phosphorescent object glows. As time goes on, there are fewer electrons in excited states and fewer relaxations are occurring; this causes the light to dim. Eventually the object goes dark, after everything's back to ground state.

Another common source of light which employs electron transitions are LED bulbs. Light-emitting diodes are electronic components which, upon application of a modest voltage, allow electrons in higher energy levels in one part of the diode to flow into lower energy levels in another part of the diode. In essence, this is somewhat similar to a relaxation, but now it's between atoms or between large groups of atoms. This emits photons of a specific wavelength corresponding to a specific color. Different color diodes are combined in one bulb to produce white light.

I've mentioned colors as we've gone along here, but that's been related to the color of light. Let's talk about reflected color: what makes an object colored? We are taught about colors and color wheels and color opposites (complementary colors) and such. We learn that things absorb parts of visible light and reflect other parts. That provides color. For example, if an object appears blue-green (cyan) in color, then it's because it absorbs red. Well, why does it absorb red? That's electron transitions.

When something absorbs one color, it is absorbing photons corresponding to that color. It absorbs photons because it has energy levels spaced apart by some ΔE which is equal to the energy of those photons. Recall that red is the least energetic of all visible light and that violet has the most energy. To illustrate, we'll take red light of 720. nm, violet of 390. nm and a middle color of 550. nm, which corresponds to yellow-green. You can calculate the energies of the photons involved, using $E = hc/\lambda$.

- One photon of 720. nm light has 2.76×10^{-19} J.
- One photon of 550. nm light has 3.61×10^{-19} J.
- One photon of 390. nm light has 5.10×10^{-19} J.

Let's say that we have three compounds with different electron energy levels. Compound A has two levels separated by 2.76×10^{-19} J; compound B has two levels separated by 3.61×10^{-19} J; and, compound C has two levels separated by 5.10×10^{-19} J.
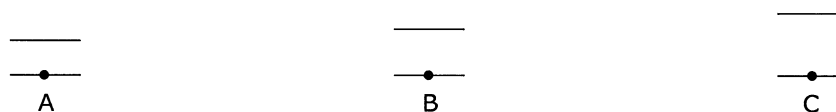
Now shine <u>white</u> light on each of them. Compound A can absorb 720. nm (red) light to do excitations; these photons are now gone and all other colors are reflected. The reflected mix of colors is what we actually see and our brain interprets this mix as blue-green, so we see the object as blue-green in color. Compound B can absorb 550. nm (yellow-green) light, but reflects all others. These reflected colors combine to give the color blue-violet. Compound C can absorb 390. nm (violet) light, but reflects everything else. These reflected colors add to give green, so we perceive the object to be green in color. (By the way, relaxations do occur in these cases, but they occur by a mechanism which is different from emission of a photon in the visible region.)

As described here, colors of objects are due to specific absorption of some photons and reflection of others, corresponding to whatever ΔE that object might possess. But I will point out that there are other ways used in Nature to produce colors. The blue color of the sky is due to light scattering, not

absorption. The blue color of a blue jay (and other blue birds) is caused by nanostructures within the feathers. There is a pigment in the backside of the feather, but it is brown and not blue. This pigment does absorb the colors of sunlight, but the nanostructures selectively scatter the blue light back outward before it ever reaches the pigment. This gives you the blues. (The black color also found on a blue jay is a normal pigment coloration.)

OK, back to transitions. In addition to color itself, we can also consider the lightness and darkness of color. The intensity of a color is due to the probability of the transitions involved. The basic notion is very simple: some transitions are very likely to occur while others are not. Deep colors result when the absorption is very strong, which means the transitions are very likely to occur. A dye is a good example here, such as food colors or the dyes used for coloring clothes. The pure compounds have extremely high probabilities for absorbing particular wavelengths, so they do this readily and the reflected colors are then very intense. On the other hand, pale colors result when transitions are much less likely to happen. An example is elemental sulfur, which is pale yellow: the absorptions in the vis range are of low probability and the color is therefore weak.

While I'm talking about color, I should point out that color is a human perception. It is the brain's response to photons of certain wavelengths which strike the eye. Photons have no color by themselves; they're just a particle with some amount of J's. A "red photon" is not red; a "red photon" causes the perception of red when you see it.

And what is vision? Vision is also exciting: it's exciting electrons. That's photochemistry.

Photochemistry is chemistry with photons. Photochemistry involves the absorption or emission of photons while a molecule (or atom or ion) undergoes some reaction or process. For a typical chemical reaction, energies corresponding to visible or higher frequency photons would be involved. The photon can be absorbed by a system and its energy can pay to get a reaction to go. Or, a photon can be emitted by a system to the surroundings during a reaction. IMPORTANT: Sending in a photon is not like sending in thermal energy; different things can happen. That's because absorbing a photon can get you to an excited electronic state. Thermal energy usually doesn't do this at normal conditions. Excited states can be very different from ground states, and even different reactions can then happen while in excited states. Here's a key point: many reactions which are not possible in the ground state can occur readily in an excited state.

Read the underlined part again. It has important consequences. It's how you see. It's how you are able to live on Earth. But it can also connect to cancer.

Let's go into your eye. Back to the retina, into the rods and the cones. There lie the light-absorbing molecules responsible for primary vision, large protein molecules called "rhodopsin". Part of this protein is called "retinal", and this is the light-sensitive part. The retinal unit begins at rest, in the ground state, waiting for a photon. When light enters the eye, the retinal can absorb a photon and undergo an excitation. In the excited state, retinal undergoes a reaction to produce a different isomer. This reaction cannot happen by itself in the ground state, but it is easy in the excited state. The isomer causes a change in the surrounding protein; this change causes a signal to be sent to the brain which you perceive as sight. That's vision. Everything you ever see in your lifetime begins with a photon which excites an electron in a molecule somewhere in the back of your eyeball.

And how is photochemistry related to how you are able to live? This ties to the most important photochemical process to all life on Earth: photosynthesis. Remember: your Calories essentially came from the Sun, courtesy of plants. Photosynthesis is very complicated and not completely understood, but it still begins with electron excitation within chlorophyll or other light-absorbing molecules in plants. The energies of the photons are used to make sugar molecules and O_2 from CO_2 and H_2O. We can write this for fructose (fruit sugar, $C_6H_{12}O_6$) as follows.

$$6\,CO_2 \;+\; 6\,H_2O \;\rightarrow\; C_6H_{12}O_6 \;+\; 6\,O_2$$
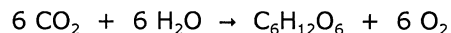
This is the reverse of combustion. As described in Chapter 19, animals combust sugars using O_2 to form CO_2 and H_2O in an exothermic process to derive energy for living. In the endothermic reverse, plants use photon energies to convert CO_2 and H_2O back to sugars and O_2, thus completing one of Nature's most important cycles for life. The plant can use the sugars to make other components (e.g., wood) or to prepare vegetation and fruits which are then consumed by animals. Photosynthesis also puts O_2 into Earth's atmosphere; all the O_2 which you breathe comes from photosynthesis. Without plants, you would lack many Calories for fuel and nutrients for growth, and you would have no oxygen to breathe. Plants make your life possible, using photon energies and electron excitation.

And now a dark side of light: Photochemistry is the basis for a lot of radiation-induced cancer, such as the type involving UV radiation. For example, a lot of skin cancers are caused by UV from the sun or other tanning sources. How does all this happen? A high energy photon strikes a biological molecule somewhere, sending that molecule into an excited state. In the excited state, the biological molecule does a reaction which is not possible in the ground state and which should not have happened. OK, so far, things aren't too awful bad. The fact is that such events are actually quite common; many of these accidents are harmless but some are not. Fortunately, Nature designed surface-dwelling critters, including you, with elegant repair mechanisms to take care of wayward reactions such as these caused by solar radiation (or other causes). Those repair mechanisms, however, aren't entirely perfect. A range of outcomes is possible if not properly repaired. For example, such an accident could lead to the death of just the affected cell, with no ill effect to other cells and tissues. Unfortunately, there is always a small probability that an accident or series of accidents will lead to cell malfunction and proliferation beyond its original design. These are the ones that can lead to cancer.

The photochemical examples which I have given have all involved the absorption of a photon to pay the price to get something to happen. Photochemistry can also involve emission. An obvious example is again provided by Nature: fireflies (lightning bugs). Chemical reactions which give off light are called "chemiluminescent". When a biological organism is doing the reaction, chemiluminescence is also called "bioluminescence". What's going on here? Actually, it's fairly straightforward: during some chemical reactions, a product molecule is formed but it is formed in an excited state. Then, the product molecule relaxes to ground state by emitting a photon or by giving off energy some other way. If a product molecule is formed in an excited state and if it relaxes by emitting a photon of light, then that is chemiluminescence. In a firefly, certain cells execute a chemical reaction and the firefly gets its rear end into an excited state. This is followed by relaxation of the product molecules back to ground state, emitting visible photons. That's the glow. By the way, bioluminescence occurs in many other organisms also, many within the oceans and even deeper than sunlight can reach. Such organisms typically use bioluminescence for feeding, defense, and attracting mates.

A popular commercial application of chemiluminescence is readily available: lightsticks. Lightsticks serve a variety of uses, including as a functional light source or simply as a novelty item. In a lightstick, two solutions are mixed and this leads to several reactions, some of which involve redox. In one redox step, a neutral molecule is oxidized, losing one electron to form a cation. In a later redox step, that cation is reduced by one electron, but this happens to produce an excited state of the original molecule. The molecule then relaxes to ground state, emitting a photon in the process. Large numbers of such relaxations simultaneously give the light which you see. By choosing different compounds, you get different colors.

All of these things are electron transitions. They are a very important part of light and matter. They are a very important part of your world.

Now, let's return to the final step to understanding the electron in the atom: the electron wave.

21.3 Electron duality

The duality of the electron was realized a decade or so after Bohr first introduced quantization. When I mentioned duality in the last Chapter, I said extremely minuscule momentum was the key to having significant wave properties. Momentum (mass, m, times velocity, v) relates to the wavelength of a moving particle by the following equation.

$$\lambda = \frac{h}{mv}$$

Keep in mind that h is on the order of 10^{-34}, so if you really want to start having a measurable wavelength, then that denominator has to be extremely small. A normal object such as you or a ball does not have a measurable wavelength because mv is way too big. On the contrary, for an electron in an atom, mv is extremely small and the electron does have significant wave behavior. In order to understand the electron in the atom, we must include that wave behavior.

This is going to be troublesome to understand for many students. The primary problem is that you have years and years of experience dealing with normal objects and their motions, and your brain will try to fit the electron into this pattern of experience. It won't go. It takes a while to get used to this new way of looking at things. Within the grip of the atom, the electron behaves in a way which is very different from "typical" behavior. Some of the properties of the electron can be explained as a particle. Some of the properties can be explained as a wave. Some of the properties can be explained as both.

And some properties still don't seem to make sense either way. To make things even weirder, what exactly is meant by a "particle" on the subatomic scale? On the normal world scale, a particle of sand or of flour or of dust has a physical size and a physical mass. On the other hand, an electron has mass but it may not have a physical size. A particle which has no size? That's life in the quantum realm. It often takes a different way of looking at things.

The area dealing with these aspects is called "wave mechanics" or "quantum mechanics". This area involves a lot of math, and some of the math relates to particle motion and some relates to wave motion. There are all sorts of functions, operators, integrals, etc. A lot of it looks like Greek alphabet soup. I want to warn you about something: the waves here are really complicated. These things are not simple sine or cosine waves. In fact, they're three dimensional waves and some have bizarre shapes. A common starting place for much of this is called the Schrödinger equation, since Schrödinger played a major role in the wave math early on. Some of this math is downright ugly, but we're not going to do any of the math here. We're going to go to the end results and take it from there. I'm going to be tying things together as we go.

The mathematical function which leads to an explanation of electron behavior is called a wavefunction and it is designated by capital Greek psi, Ψ. Wavefunctions are standing waves. As such, there is some parallel to our example of string waves in the last Chapter. Back then, only certain functions for wavelength were possible. The same is true here: only certain wavefunctions are possible (although they're more complex than the examples last Chapter). In other words, electron wavefunctions are quantized.

Recall Planck's equation: each wave of light corresponds to some specific energy. Now, each electron wave, Ψ, corresponds to a specific energy, E. Since Ψ is quantized, then E is also quantized. Notice that this provides the quantization of energy as suggested by Bohr, although he used a particle approach.

Location. Location. Location. We are finally able to do the location of an electron in an atom. Location is given by the square of the wavefunction, Ψ^2. This is where things can get tricky, and again it's due to duality. What do you mean when you think "location"? In the normal world, we think of an object's location as that specific point in space where the object happens to be at that time. In this way, location is defined as a point. Sorry, that won't work here. You can't determine a point in space at some time for an electron in the atom. It doesn't work that way. There are two interpretations for the location of an electron in an atom: one is based on thinking in the particle sense and the other is based on thinking in the wave sense.

In the particle sense, we still think of the electron as a particle somewhere in the atom but we can only assess its probability of being in a particular region in space. We can never know its exact position at any point in time. Sound strange? It is. In the particle approach to electron location, we talk about some three-dimensional region (Ψ^2) with some probability of containing the electron. We cannot be any more certain than a probability. That's the best we can do.

In the wave sense for electron location, the electron is taken to be a wave with different amplitudes and which corresponds to a three-dimensional shape. We interpret Ψ^2 now as the "strength" of the wave within some region in space.

Which interpretation, particle or wave, is right? Well, neither interpretation is complete by itself but both contribute to how we understand what is going on. It's duality, and the concept of duality takes a while to get used to. Some things are easier to understand using the particle approach and some are easier with the wave approach. And, like I said above, some things may still not make sense either way. Fortunately, Nature knows what Nature is doing whether we understand it or not.

In both approaches, the square of the wavefunction, Ψ^2, gives an "orbital", and this characterizes the region in space for the location of an electron in an atom. NOTICE! This is not an orbit! It's an orbi<u>tal</u>. There are no orbits. There are only orbitals, and they're three-dimensional. In the context of the particle approach, the orbital is a region in space in which an electron is most likely to be found. In the context of the wave approach, an orbital is the region in space of greatest strength of an electron wave. Regardless, orbitals are the allowed 3D regions in space for electrons within an atom; all electrons must be in an orbital and cannot be anywhere else in an atom.

You can think of an orbital as a three dimensional field, for which we can draw loose parallel to a force field. You've probably encountered force fields. I mean real ones, not those of the cinematics of sci fi. A force field can be strong in some places and weak in others. Magnetism is a common example,
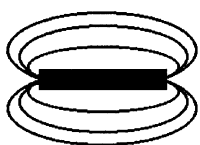
and many students have seen diagrams of magnetic force fields. An example is shown on the left, using a simple bar magnet. It is common to illustrate the magnetic field by the curves that are shown. Although drawn flat, the field surrounds the bar magnet in three dimensions, so it is indeed a three-dimensional field. The curves convey some sense of relative strength of the field. The field gets weaker with distance away from the magnet. Technically, there is no hard cutoff but, beyond some distance, the strength of the field is no longer of practical significance. These same notions describe an electron orbital very well. An orbital field exists in three dimensions. Some regions are stronger than others. The orbital gets weaker and weaker with distance. There is no hard cutoff but, in some areas or beyond some distance, the field is no longer significant.

Since orbitals are quantized, we need to know what's allowed by the quantization restrictions. We also need to know the energies. The mathematical details of the Schrödinger equation lead to this information. We will see how many orbitals of the various kinds and shapes are possible. We will bring in the energies as we go. We are finally approaching our target from Chapter 2: the locations and energies of a electrons in an atom.

21.4 Quantum numbers

From the mathematical toil and trouble of the Schrödinger equation, three separate parameters arise, each of which is quantized of its own. These three parameters are called "quantum numbers". If you do the math, you plug these three numbers into the equations and eventually you get an orbital. We're not doing the math, so you'll have to take my word for it. Each different combination of these three numbers defines one specific orbital but there are restrictions on their values, as we shall see.

The first quantum number is called the "principal" quantum number and it is designated n. Its own quantization requires it to be an integer equal to one or higher. No negatives, no zero. n can be 1 or 2 or 3 or 4 or etc. Each value of n corresponds to an orbital group which we call a shell or level. The word "shell" really means a group. It doesn't mean a shell in the physical sense such as a peanut shell or a seashell; it just means a group: orbitals are grouped according to shell. One aspect of n does have a physical significance: a larger value of n will contain larger orbitals. This will be important, since the size of an orbital has tremendous consequences. The reason is simple: larger orbitals will extend further from the nucleus. Don't forget that everything we are doing is based on the attraction between the electron and the nucleus. This means that the best orbitals are those which are most concentrated near the nucleus, and the all-time favorite corresponds to $n = 1$. The $n = 1$ shell is the smallest and the most favored in energy. Another consequence of the shell is that the energy of the electron is determined only by n and not by the specific orbital within that shell. (That statement only applies for one electron by itself. This will change when we have more than one electron in the atom, as in the next Chapter.)

Now here's another twist: I said earlier that Bohr's explanation had the right energies although location was wrong. This new n, the principal quantum number, corresponds exactly to Bohr's n for purposes of energy calculations. Same n! This is true despite the fact that Bohr based his approach on particle properties.

The second quantum number is called the "angular momentum" quantum number (for reasons that we won't go into) and it is designated l. Every n-shell (group) will have one or more values of l, and each of these is a "subshell" (subgroup). The quantization for l requires that its value can be zero or a positive integer, but that its maximum value is $n - 1$. Notice that the quantization for l is dependent on the group (shell) that it is in. This second quantum number does carry some physical meaning: the value of l determines the type and shape of the orbitals of the subgroup. We do shapes later in this Chapter.

I mentioned above that a shell can be called a level. Likewise, a subshell can be called a sublevel.

Each value of l is assigned a lower-case, letter designation. The $l = 0$ subshell is called an "s" subshell. The $l = 1$ subshell is called a "p" subshell. For $l = 2$, it's "d". For $l = 3$, it's "f". Thus, the sequence starts *spdf* and this was for historical reasons, but after a while they finally went alphabetical: after *f*, the letters continue with *g* for $l = 4$, *h* for $l = 5$, etc. Memorize these labels; we use these letter designations a lot, especially *s*, *p*, *d* and *f*.

$$0 = s \qquad 1 = p \qquad 2 = d \qquad 3 = f \qquad 4 = g \qquad 5 = h \qquad \text{etc.}$$

Let's look at several of the combinations which are possible for n and l. I'll also introduce a very common and very handy notation for subshell types: it's shell number followed by subshell letter.

▸ *n* = 1 shell (This is the lowest value of *n* possible.)

  The values of *l* can run from zero up to *n* − 1; but *n* − 1 equals zero in this case, which means that *l* = 0 (*s* type) is the only possibility. Thus, the quantization restriction leaves us only one possible subshell in the *n* = 1 shell. The notation for this subshell is 1*s*.

▸ *n* = 2 shell

  The values of *l* can run from zero up to *n* − 1, which now equals 1; thus, you get 0 and 1 as two possible values of *l*. These are the *s* type and the *p* type. The quantization restrictions leave us with two possible subshells in the *n* = 2 shell; the notation for these subshells is 2*s* and 2*p*.

▸ *n* = 5 shell (I just skipped 3 and 4.)

  The values of *l* can run from zero up to *n* − 1 = 4; you get five possible values of *l*, namely 0 (*s* type) or 1 (*p* type) or 2 (*d* type) or 3 (*f* type) or 4 (*g* type). The notation for these is 5*s*, 5*p*, 5*d*, 5*f* and 5*g*.

This can be confusing at first, but hopefully you'll catch on to this as you go. Here's a point to note: in the *n* = 1 shell there's <u>one</u> subshell, in the *n* = 2 shell there're <u>two</u> subshells, and in the *n* = 5 shell there're <u>five</u> subshells. This leads to the following generality: the number of subshells within any shell equals the shell number, *n*.

Stop a moment. Go over those combinations again and maybe a few more examples. This stuff can get tedious. I don't expect you to understand <u>why</u> these numbers are the way they are; that's part of Nature's quantization and a lot of it is embedded in the math. You need to be able to work with the results as presented. I know the relationships are weird, but that's life in the quantum realm. If you go further in chemistry or physics, you may get into the math and see more of the details. For now, just try to understand the shell and subshell relationships before going on to the next section.

21.5 Orbitals

Here's the way this picture is developing: individual orbitals are classified according to type (shape); these make up a subshell (*l*) category. One or more subshells can be grouped within a shell (*n*). *n* is "principal": it determines energy and it sets the limits for *l*. Now, we'll see that *l* sets the limits for the third quantum number.

The third quantum number is called the magnetic quantum number (for reasons that we won't go into) and it's designated m_l. The quantization restrictions for m_l are a bit looser: it's still an integer but now it can be negative, zero and positive. It can be as positive as +*l* and as negative as −*l*; this means that the values for m_l run from −*l*...0...+*l* within a given subshell (*l*). This quantum number also carries physical significance: when plugged into the equations, this determines the orientation of an orbital (its direction, where it points in space). Each value of m_l tells us a possible orientation for an orbital. There's an important consequence here: the number of values which are possible is the number of orbitals which are possible.

Let's do some examples of combinations of *l* and m_l and show how this works.

▸ *l* = 0, type *s* subshell

  The values of m_l can run from −*l* to +*l*, which is not real far in this case, since *l* = 0. So, you only get one option here: m_l = 0. Only one orientation is possible, so only one orbital is possible for every *s* subshell.

▸ *l* = 1, type *p* subshell

  The values of m_l can run from −*l* to +*l*. In this case, there are three options: −1, 0 and 1. Each of these provides a separate orientation for an orbital. Thus, the quantization restrictions allow for three orbitals in a *p* subshell.

▸ *l* = 3, type *f* subshell (I skipped *d*.)

  The values of m_l can run from −*l* to +*l*. In this case, there are seven options: −3, −2, −1, 0, 1, 2 and 3. Each of these provides a separate orientation for an orbital. Now, quantization allows for seven orbitals in every *f* subshell.

Notice that, in the *l* = 0 (*s*) subshell, there's one orbital; in the *l* = 1 (*p*) subshell, there're three orbitals; and, in the *l* = 3 (*f*) subshell, there're seven orbitals. This leads to a simple relationship, although it is not an obvious one: in any *l* subshell, there are (2*l* + 1) different orientations, corresponding to (2*l* + 1) individual orbitals. Remember this; it's important.

  • Every *s* subshell (*l* = 0) has <u>one</u> orbital: 2*l* + 1 = <u>1</u>.

- Every *p* subshell (*l* = 1) has <u>three</u> orbitals: 2*l* + 1 = <u>3</u>.
- Every *d* subshell (*l* = 2) has <u>five</u> orbitals: 2*l* + 1 = <u>5</u>.
- Every *f* subshell (*l* = 3) has <u>seven</u> orbitals: 2*l* + 1 = <u>7</u>.

Etc. for the others. Another way to remember this is that the number of orbitals is 1-3-5-7-9... in every subshell of type *s-p-d-f-g*...

For our purposes, the really important conclusion for m_l is not the actual values themselves (–2 or 2 or –1 or 3 or 0 or whatever) but <u>how many</u> values are possible, since this tells us how many orbitals are allowed. Because of this, I will not continue dealing with the –*l* to +*l* business. The absolutely most important part is the 1-3-5-7-9... relationship for <u>how many</u> orbitals. Your instructor may pursue the specific values for –*l* to +*l*, so heed if there's need.

We are now ready to construct an overall summary of the number of different types of orbitals which are available in the atom. I'll show you how all of this falls into place.

GRAND SUMMARY

n	*l*	notation	how many orbitals?
1	0	1*s*	one
2	0	2*s*	one
2	1	2*p*	three
3	0	3*s*	one
3	1	3*p*	three
3	2	3*d*	five
4	0	4*s*	one
4	1	4*p*	three
4	2	4*d*	five
4	3	4*f*	seven
5	0	5*s*	one
5	1	5*p*	three
5	2	5*d*	five
5	3	5*f*	seven
5	4	5*g*	nine

Etc. There are no limits on how high *n* can go. Here, you do *n* = 6.

n	*l*	notation	how many orbitals?
6	—	——	————
6	—	——	————
6	—	——	————
6	—	——	————
6	—	——	————
6	—	——	————

All of these results derive from the mathematics and the quantization limitations. These things are not necessarily obvious, nor are they easy to understand. Of course, neither is gravity and you learned to live with that, didn't you? This Grand Summary is the basis of electronic structure. There's a lot here and we'll be doing a lot with it in future Chapters. You've got to get the patterns down.

✓ In *n* = 1, there's one subshell. In *n* = 2, there're two subshells. In *n* = 3, there are three subshells. Etc.

✓ Within a shell, the subshell sequence is always *spdf* etc., depending on how many are allowed. Every shell has an *s*. The *p* type starts with *n* = 2. *d* starts with *n* = 3. Etc.

✓ All *s* orbitals come as one (per subshell). All *p*'s come in threes (per subshell). All *d*'s come in fives (per subshell). All *f*'s come in sevens (per subshell). All *g*'s come in nines (per subshell). Do you catch the pattern? 1-3-5-7-9... How many orbitals for *h* subshells?

Here's one final piece to add to the pattern: the total number of orbitals in any shell is n^2. There's one (1^2) orbital in $n = 1$. There're four (2^2) total orbitals in $n = 2$. There're nine (3^2) total orbitals in $n = 3$. 16 in $n = 4$. 25 in $n = 5$. Check it out for $n = 6$. The total is $6^2 = 36$. Is this the total for the numbers you wrote above in the fill-ins? These numerical relationships are a bit weird, but Nature can work in strange patterns.

All of this tells us what kinds of orbital fields <u>are available</u> to an electron in the atom. Each specific combination of quantum numbers gives us one <u>possible</u> orbital field. An orbital is not a physical object by itself; it does not have a physical existence by itself; it is simply an allowed region in 3D space for an electron. In theory, an infinite number of orbitals is possible in an atom. (We'll see which ones are actually used starting in the next Chapter.) Besides giving a possible location for an electron in an atom, the electron in a specific orbital has a specific energy. n gives energy and orbital size. l gives shape. m_l gives the direction in which it's pointing. We finally have what we wanted: energies and locations of electrons in atoms. Except I haven't told you about the shapes yet. Let's finish off this task.
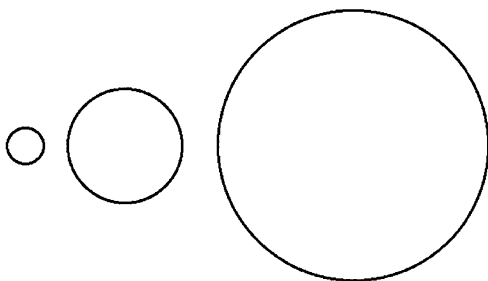
21.6 Shapes of orbitals

Again, Ψ^2 determines the orbital field. These fields can have strange shapes. The fields get weaker with distance, and there are no hard boundaries. Many of the orbital fields have nodes of zero strength, but even the nodes can have funny shapes, such as a plane or even a cone.

When we draw a "picture" of an orbital, it is meant to convey the 3D region of most significant strength. Let me return to the bar magnet for a moment. We can illustrate its region of most significance as shown in the diagram at right. The curves convey general information about the 3D shape of the field. The curves are not hard boundaries. The field extends beyond the curves but it gets weaker and weaker. These simple notions will apply to our orbital drawings. An orbital drawing conveys general information about the 3D shape of the field and where this is most significant. Again, the orbital is not a hard object.
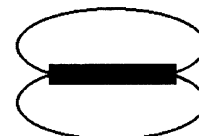
The simplest of all orbitals is the 1s orbital. It is shaped like a simple sphere. It is strongest close to the nucleus and it gets weaker and weaker, symmetrically in all three dimensions, as you go out. The orbital is commonly represented by the simple drawing at left; the drawing looks like a circle in two dimensions but the orbital is really a 3D, spherical shape, as depicted at right to show some depth. All s orbitals (1s, 2s, 3s, etc.) are of this same, general, spherical shape. The most important difference between them is what I said earlier: as n gets larger, the orbitals get larger. Thus, 2s is bigger than 1s. 3s is bigger than 2s. Etc. (There's also a technical difference regarding nodes inside the orbitals but we don't need that here.) As the field extends further and further from the nucleus, the attraction gets weaker and weaker. An electron prefers 3s more than 4s. An electron prefers 2s more than 3s. Mostly, however, an electron wants to be in 1s. The 1s orbital is the most favored orbital in every atom. It is the one which is the <u>most concentrated, closest to the nucleus</u>.

Next: 2p or not 2p, that is the question. The p orbitals get a bit odd. (I told you these waves were going to be strange 3D shapes. Actually, strangeness increases with increasing l.) At left is a standard drawing for a typical p orbital but, again, the orbitals are 3D; they are roundish, as depicted at right. There are two parts to each p orbital. Each part is called a "lobe". The center of the whole orbital lies at the nucleus of the atom; this center point is a node, so the wave has zero strength at the nucleus. Actually, it's not just the center point which constitutes a node. There is an entire plane with zero amplitude, and that is called a nodal plane. There is a nodal plane for every p orbital; for the picture as shown, the nodal plane slices vertically between the two lobes. Within any p subshell, the three orbitals all have the same shape and they have the same center point (at the nucleus), but they are 90° from each other and they point along the x, y and z axes. If you want to discuss one specific orbital of the three, you can do this using subscript notation: for example, the notation $2p_x$ indicates the 2p orbital which points along the x axis.
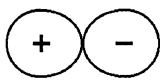
Let me make a brief point about orbital signs right now. Just like normal everyday waves, a wavefunction, Ψ, typically has positive, negative or zero amplitude. An illustration of a p orbital with its Ψ amplitude signs is shown at left. (Here's a minor technical point: the +/– amplitude signs are for Ψ, but the shape is for Ψ^2. Ψ^2 is always positive except for zero at the nodes.) As drawn, the left lobe is positive amplitude, the right lobe is negative amplitude, and the crossover occurs at the node (zero). Note: don't confuse amplitude sign with charge. The electron is always 1– charge, but its wave has positive, negative or zero amplitude. By the way, the s orbitals above also have amplitude signs but all are positive in their outer reaches; as such, the sign distinction is not as important. I won't work with amplitude signs until Chapter 30 and again in Chapter 32, so this is just a brief introductory note. Flag this paragraph for later: put "orbital sign" in the margin.

OK, here's something to note. Since each of the three p orbitals has its center at the nucleus, and since each is a 3D object, then they have some overlap with each other. Although they overlap, each orbital stays itself, separate from the others. Furthermore, they are also overlapping with 1s and 2s, whose centers are also at the nucleus. All of these orbitals retain their own identity even though they might occupy 3D space with other orbitals. Although the orbitals stay separate and retain their own identity, it <u>is</u> true that electrons in one orbital will sense the electrons in other orbitals. This has very important consequences, as we shall see in the next Chapter.

So much for 2p. Orbitals in 3p, 4p, etc. have similar shapes and orientations but, as you can guess by now, the primary difference is size. As n increases, you get bigger orbitals, extending further from the nucleus, with weaker attraction overall to the nucleus.
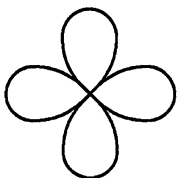
The next subshell type is d. There are five orbitals in every d subshell. I'll just show one of these on the left; again, it's three dimensional and each lobe is roundish. Four of the d's are shaped like this; the fifth looks different but it's still derived from this. I won't describe these further although your instructor may provide more detail.

After d orbitals there are f orbitals with up to eight lobes. Then come g orbitals with up to twelve lobes. These things get really complicated.

Finally, we have what we wanted since Chapter 2. We have locations! We have energies! Well, not quite. So far, the energies are only for atoms or ions with one electron. Energies get more complicated when there are two or more electrons involved. We'll see that in the very next Chapter.

Problems

1. True or false.

   a. Vision involves the absorption of a photon, which causes an electron excitation.

   b. Ψ^2 gives information on spatial location of electrons.

   c. For a given n-shell, there are n number of subshells.

   d. The number of m_l values determines the number of orbitals in a subshell.

   e. In every atom, the 1s orbital is the orbital which is the most concentrated, nearest the nucleus.

   f. In every p subshell, there are three orbitals at 90°.

2. True or false.

   a. Molecules can react differently in excited states when compared to the ground state.

   b. Phosphorescence involves delayed relaxations.

   c. The electrons in an atom are in quantized energy states.

   d. The principal quantum number is the shell number.

   e. Every f subshell has nine orbitals.

    f. A 3*p* orbital is larger than a 4*p* orbital.

3. What is the fundamental reason that different things can have different colors?

4. a. Which quantum number gives the shape of an orbital?

    b. Which quantum number gives the orientation of an orbital?

5. a. How many subshells are in the *n* = 4 shell?

    b. How many orbitals are in the *n* = 3 shell?

    c. How many orbitals are in a subshell with *l* = 2?

6. a. How many orbitals are in the *n* = 5 shell?

    b. How many subshells are in the *n* = 6 shell?

    c. What type of subshell occurs in every shell?

7. Of the following designations, which are NOT possible subshells?

    2d   *3d*   *4f*   *4g*   *5g*