

Chapter 21 LIGHT, MATTER AND WAVES

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

Well, no, it's not perfect. But it's still good and it's still a classic. It was a big 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. How could energies be right if locations were wrong? It's part of 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 is also a wave. That was a strange concept back then, and it's still a strange concept today for many people. I told you this was going to be strange stuff.

21.1 Here and now

Theories of electrons in atoms are much better 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 better, 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 weird, strange 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).

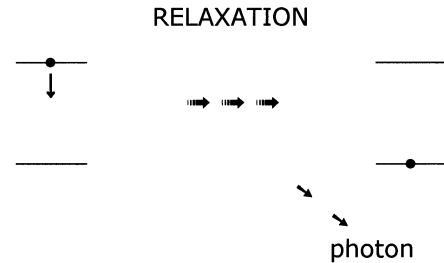
Many things in your world can be explained by these four features. A lot of your world involves energy transitions and EM radiation. Again, this is the way light and matter interact. I'll give you a basic outline of some of these things. I'm going to keep things simple. In reality, especially in polyatomic units, the energy levels can get very complicated and trying to account for all electrons can also get very complicated. There are even 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 very skinny 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's 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.

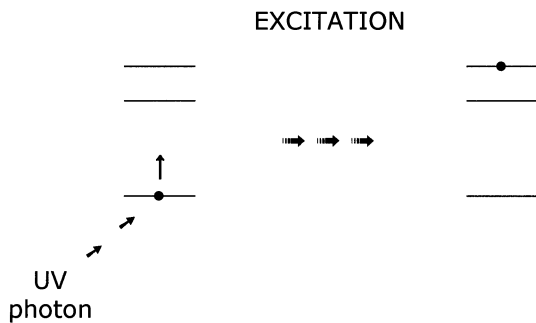
So, how do real neon signs work? While the sign is off, the neon atoms just fly around inside the tube and mind their own business, doing their gas phase thing with all their electrons at rest in the ground state. Turn on the juice, however, and things get very excited. The juice in a neon sign can be several thousand volts, although small neon bulbs work with more normal voltages. Under these conditions, electrons in the neon atoms are getting completely kicked out of the atoms to form Ne^+ ions. The ions and electrons recombine, but this first produces neon atoms with the electron in one of various possible

excited states. Electrons in an excited level then relax and shoot out photons. Different transitions are possible between different levels, thus giving photons of different energies and therefore of different wavelengths. For Ne, there are numerous transitions occurring which correspond to photons in the red-orange region of visible light. When those relaxations are occurring, you see those photons.



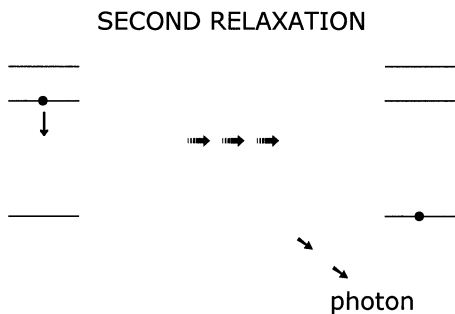
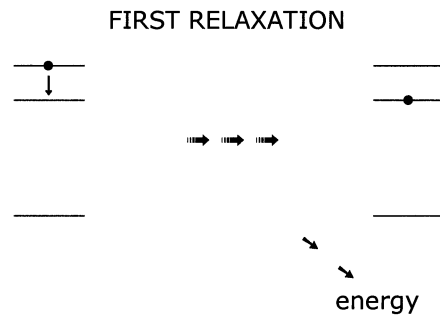
So that's how true neon signs operate. Zillions of neon atoms get electrically zapped; electrons get kicked around, eventually ending up in an excited state of a neon atom. They then relax, shooting out a photon. Many of those photons have wavelengths which correspond to red-orange light.

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 especially with 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.



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.

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



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 a range of colors all at once. These 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 and these emit 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 in the dark after first shining light on them. They work by a process which is similar to fluorescence but which involves an extra step. The key feature to phosphorescence is that the final relaxation gets delayed. Normally, relaxations occur very fast after the initial excitation, in mere fractions of a second. In phosphorescent compounds, however, the final relaxations can be very slow. When you shine the light on the object, you excite zillions of atoms or molecules of the compound. When you turn the light off, these slowly relax, slowly giving off visible photons. As time goes on, there are fewer electrons in the excited states and fewer relaxations are occurring; this causes the light to dim. Eventually the object goes dark, after everybody's back to ground state.

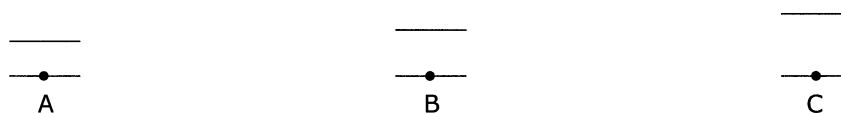
Interestingly, fluorescent lights are also a bit phosphorescent. This is more commonly noticeable these days with the increase in use of compact fluorescent lights. After you turn off the last light in a room or house at night, you may notice that a compact fluorescent light glows although this does fade out over several seconds. That fading glow is the phosphorescent part.

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 of 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 white 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.)

All colors of all objects are due to specific absorptions of photons, corresponding to whatever ΔE that object might possess. That's color. How darkly colored? The answer to that lies in something else: there are probabilities for transitions. I won't go into much explanation on this, but the notion is very simple: some transitions occur very readily while others do not. Differences in absorption probability give color

intensity. Extremely deep colors result when 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 visible light photons, so they do this readily and their colors are 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. It's a human vision thing.

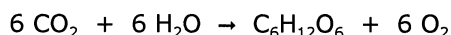
And what is vision? Vision is also exciting: it's exciting electrons. That's photochemistry.

Photochemistry is chemistry with photons. Photochemistry involves electron transitions and the absorption or emission of photons while a molecule (or atom or ion) undergoes some reaction or process. For a typical chemical reaction, we need energies corresponding to visible or higher frequency photons. 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. Sending in a photon is not like sending in thermal J's; different things can happen. In fact, very 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. Weird things can happen in excited states; excited states can be very different from ground 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's how you see, it's how you are able to live on Earth, and it can be how you die.

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 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 O₂ from CO₂ and H₂O. We can write this for fructose (fruit sugar, C₆H₁₂O₆) as follows.



This is the reverse of combustion. As described in Chapter 19, animals combust sugars using O₂ to form CO₂ and H₂O in an exothermic process to derive energy for living. In the endothermic reverse, plants use photon energies to convert CO₂ and H₂O back to sugars and O₂, thus completing one of Nature's most important circles of life. By the way, photosynthesis doesn't just provide sugars; in fact, photosynthesis is what put O₂ into this planet's atmosphere and continues to do so on a daily basis. Without plants, you would have no Calories for fuel 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: how does photochemistry relate to how you might die?

Photochemistry is the basis 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; you still have a good chance. You see, Nature knew accidents like this would happen, especially due to solar radiation. Nature designed surface-dwelling critters, including you, with elegant repair mechanisms to take care of

accidental reactions like this. Unfortunately, those repair mechanisms aren't entirely perfect: if enough "accidents" happen, cancer can result.

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 butt 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 other organisms also, mostly within the oceans and even deeper than sunlight can reach. All such organisms typically use bioluminescence for feeding, defense and attracting mates.

A popular commercial application of chemiluminescence is easily available: lightsticks. Lightsticks can be bought in many stores and serve a variety of uses, including novelty uses. In a lightstick, two solutions are mixed and a reaction occurs. The product is formed in an excited state and it then relaxes, but it relaxes by emitting a UV photon. The UV photon gets absorbed by a fluorescent molecule which is also present in the solution, and a visible photon is subsequently emitted. By choosing different fluorescent molecules, you get different colors. That's how lightsticks work: a combination of chemiluminescence and fluorescence.

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 after Bohr. When I introduced duality 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 significant 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 properly describe 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. That's life in the quantum realm.

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. Some of it uses cartesian (xyz) coordinates and some uses spherical coordinates ($r\theta\phi$). 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. The starting place for much of this is called the Schrödinger equation, since Schrödinger played a major role in the wave math early on. One form of his equation is the following.

$$\frac{h}{4\pi} \nabla^2 \Psi + (E - V) \Psi = 0$$

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 (as seen above). 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.

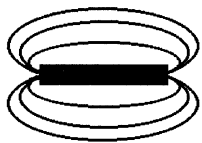
In the particle sense, we still think of the electron as a particle somewhere in the atom but we can only assess its probability of being in a particular region in space. We can never know its exact position at any point in time. Sound strange? It is. In the particle approach to electron location, we talk about some three-dimensional region (Ψ^2) with some probability of containing the electron. We cannot be any more certain than that. 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? It's not a question of which is right. 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 orbital. There are no orbits. There are only orbitals, and they're three-dimensional things. In the context of the particle approach, the orbital is the region in space in which the 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 the electron wave.

You can think of an orbital as a three dimensional field, for which we can draw some 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 force field by the curves that are shown. Although drawn flat, the force 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 an electron 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" can be confusing and it throws off some students, but we're stuck with it. "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 also be called a level. Likewise, a subshell can also 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*.

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

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 *1s*.

► $n = 2$ 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 *2s* and *2p*.

► $n = 5$ 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 $5s$, $5p$, $5d$, $5f$ and $5g$.

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 one subshell, in the $n = 2$ shell there're two subshells, and in the $n = 5$ shell there're five 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 why 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 the way it works out. 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 $-l \dots 0 \dots +l$ 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 $(2l + 1)$ different orientations, corresponding to $(2l + 1)$ individual orbitals. Remember this; it's important.

- Every s subshell ($l = 0$) has one orbital: $2l + 1 = 1$.
- Every p subshell ($l = 1$) has three orbitals: $2l + 1 = 3$.
- Every d subshell ($l = 2$) has five orbitals: $2l + 1 = 5$.
- Every f subshell ($l = 3$) has seven orbitals: $2l + 1 = 7$.

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 ...

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 how many 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 how many 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	1s	one
2	0	2s	one
2	1	2p	three
3	0	3s	one
3	1	3p	three
3	2	3d	five
4	0	4s	one
4	1	4p	three
4	2	4d	five
4	3	4f	seven
5	0	5s	one
5	1	5p	three
5	2	5d	five
5	3	5f	seven
5	4	5g	nine

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

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 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.

Remember: all of this tells us what kinds of orbital fields are available to an electron in the atom. Each specific combination gives us one possible field. An orbital field does not actually exist by itself

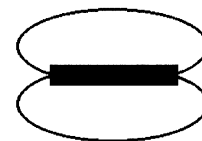
unless an electron is in it. Think about it. Since the orbital originates from the electron's attraction for the nucleus, then this attraction can only exist when an electron is actually present. Orbitals with no electrons do not physically exist at the time, but they still represent where an electron can be if one gets excited or if more electrons are added.

Each orbital represents a possible location for the electron in the atom and each orbital has some 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.

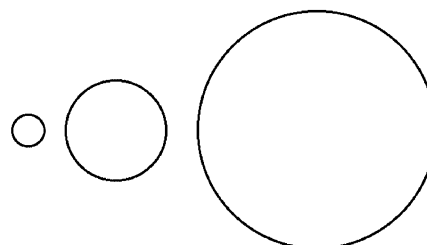
21.6 Shapes of orbitals

Remember that Ψ^2 determines the orbital field region in 3D space. This is where the field is the strongest. These fields 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.

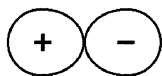
When we draw a "picture" of an orbital, it is meant to convey the 3D region of most significant strength. Let me return to the bar magnet for a moment. We can illustrate its force field as shown in the diagram at right. The curves convey general information about the 3D shape of the field and where the field is most significant in strength. The curves are not hard boundaries. The force 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. 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 strong close to the nucleus and it gets weaker and weaker, symmetrically, in all three dimensions, as you go out. We can represent this pictorially by the simple drawing at left. The drawing looks like a circle in two dimensions but this orbital is really a 3D, spherical shape. 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 most concentrated, closest to the nucleus.



$2p$ 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 .) Here is a drawing for a typical p orbital. These are really 3D fields, although the drawing doesn't show that well. 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.

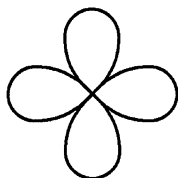


Let me make a brief point about orbital signs right now. Just like normal everyday waves, a wavefunction, Ψ , typically has positive, negative or zero amplitude. An illustration of a p orbital with its Ψ amplitude signs is shown at left. (Here's a minor technical point: the $+/-$ amplitude signs are 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 is 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. 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 real messy after a while.

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 $3p$ orbital is larger than a $4p$ 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?
 $2d$ $3d$ $4f$ $4g$ $5g$