

Chapter 22

MANY-ELECTRON ATOMS

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To this point, we've identified the many types of orbitals which are available for electrons in atoms. Given this list of orbitals which are available, which orbitals are actually used by the electrons in a given atom?

In the case of an atom or monatomic ion with only one electron, we have already seen that $1s$ is best (lowest energy), so the one electron will be in the $1s$ orbital when in the ground state. This was based on the relative energies of the various orbitals and those energies were based on the principal quantum number, n . This much even goes back to Bohr's energies, just as we showed in Chapter 20. Although Bohr had $n = 1$ as best, he didn't do the s part. It wouldn't have mattered anyway: since energy is determined only by n , all subshells of the same shell have the same energy. Thus, $2s$ has the same energy as $2p$, and both of these are higher energy than $1s$. $3s$, $3p$ and $3d$ all have the same energy and all of these are higher energy than $2s$ and $2p$. Et cetera. Et cetera. Et cetera.

As we go along here, remember that higher energy is less favorable and vice versa. Keep in mind the ladder notion. Nature wants you on the bottom rung, lowest energy. A higher energy rung is less favorable.

With atoms and with ions which have two or more electrons, the energy will depend on factors other than just n . By the way, anything with two or more electrons is called many-electron. These many-electron cases are where we are heading now. This will get more complicated, so keep the eyeballs open. There will be a pattern to this. First, there are new points to introduce.

22.1 Spin

The Schrödinger equation led to three quantum numbers and each possible combination of these three quantum numbers identifies a specific orbital in an atom. Now we bring in an additional quantum number which applies to a specific electron. This relates to a fundamental property of every electron and it is totally independent of orbitals; in fact, the electron has this property even when it's not in an atom. This property is called "spin"; its quantum number is called the "spin" or "spin magnetic" quantum number and it is designated m_s . Electron "spin" is a magnetic property. Each and every electron has magnetism, in addition to charge. The quantization of electron magnetism gives only two possible values: $+1/2$ or $-1/2$. The reason for the one-half part is not important to us right now; the really important part is that there are only two possibilities for this quantum number and that they are opposites (positive or negative). Do not confuse the "spin magnetic" quantum number, m_s , with the "magnetic" quantum number, m_l . The reason m_l is called magnetic is not related to why m_s is called magnetic. Besides, m_l applies to an orbital and m_s applies to an electron.

I must tell you that the term "spin" is an unfortunate misnomer. This is another historical thing: early on, the property was dubbed "spin" and that term simply stuck. When we typically think of "spin", we typically liken it to an object (such as a top or a globe) spinning on its axis. That's not the case here: the property of spin for an electron has nothing to do with the physical act of spinning on its axis. The reality is that electrons don't physically spin. Although the term "spin" is still used, you need to remember that it is a magnetic property of an electron, and not a globe property of an electron.

While we're at it, don't confuse spin with charge. Many quantum particles have this spin property, and that is totally separate from charge. For example, neutrons have spin even though they have no charge at all. SPIN IS MAGNETIC. The $+$ or $-$ value for m_s for the electron corresponds to a magnetic property, much like north and south correspond to the opposite poles of a permanent magnet. In fact, the two different electron spins interact differently with the north and south poles of a magnetic field. There are several important consequences of electron spin, as we shall see. Here's one you're familiar with: permanent magnets, such as the normal, everyday bar magnet or horseshoe magnet. What makes these magnetic? The magnetism arises from the electron spins in the atoms of the magnet.

This notion of opposite spin values is extremely important. If you have two electrons and one has m_s of $+1/2$ and the other has m_s of $-1/2$, then their magnetisms cancel each other. In fact, this is why most things are not magnetic and are not attracted to a magnetic field. Half of their electrons have spin of $+1/2$ and half have spin of $-1/2$. The spins cancel, and there's no magnetism.

OK, now we have four quantum numbers. We have three quantum numbers for an orbital and one quantum number for each electron. We can now specify each and every electron in an atom by the orbital it is in (n, l, m_l) and by its spin (m_s).

The next point which I need to introduce is spin exclusion. Two electrons of the same spin exclude each other from close proximity; in other words, they avoid each other. You might wonder, "So what?", since electrons are negative charges and negative charges avoid each other anyway. That is correct, but that is charge (electrostatic) repulsion and that is different from spin exclusion. Charge repulsion exists between all electrons because all electrons have a negative charge. Spin exclusion (avoidance) exists between electrons of the same spin but not between electrons of different spin. These are totally separate effects. When operating, spin exclusion is much more important than charge repulsion for keeping electrons away from each other.

Spin exclusion is a bit strange and it does not have an easy explanation. It is a law of the quantum realm so we must deal with it even if we don't understand it. We need it right now because it leads to a very important principle, called the exclusion principle: Nature excludes two electrons with the same spin from being in the same orbital. This has two really big consequences. First, if there are two electrons in the same orbital, then they must have opposite spins. Second, an orbital can hold up to two electrons but no more; any more than two would require two electrons of the same spin and that is not allowed. Let me restate these points for emphasis.

NATURE DICTATES THAT A SINGLE ORBITAL CAN HOLD AT MOST TWO ELECTRONS AND, IF TWO ARE PRESENT, THEN THEY MUST HAVE OPPOSITE SPINS.

When two electrons have opposite spin, we say that they are "paired". This term is very important. We can say that the electrons are paired or we can say that the spins are paired or we can say that the electrons are "spin-paired". Some compounds have all of their electrons paired, and some compounds don't. In the latter cases, at least one electron is "not paired" or "unpaired". Here's the thing to remember about this "pair" business: pairing refers to two opposites. It's just like a pair of shoes or a pair of gloves. Two opposites.

We are now ready to tackle the problem of the many-electron atom.

22.2 Splitting subshells

Well, the easy part is over. Now things get a bit complicated.

The easy part was the one-electron atom or ion, such as H or He^+ . The energy of the orbitals was directly calculated from n , and all subshells within one shell had the same E . All of this arises from the attraction of the negative electron for the positive nucleus. I'll start referring to this as electron-nuclear attraction. When only one electron is present, that's all we need to worry about.

This is not true in the many-electron case. As soon as you bring a second electron into the picture, you get into new complications. There are now charge repulsions between the different electrons; collectively, these are called electron-electron repulsion. There is also spin exclusion between electrons of the same spin. These factors now influence the total energy picture in a way which cannot be easily envisioned. Let's illustrate this effect with the simplest case. Start with one electron in $1s$ (for example, as in H). Now, put a second electron into the same orbital (for example, to get H^-). The two electrons must be spin-paired in order to satisfy the exclusion principle. That much is OK in this case. Charge repulsion, however, cannot be so readily dismissed. The two electrons are separately attracted to the nucleus but they also are repulsive to each other. Electron-electron repulsion always detracts from total energy. Pay particular attention here: I said total energy. Total energy includes all electron-nuclear attractions plus all electron-electron repulsions.

So if electrons repel each other, isn't the second electron better off in the $2s$ orbital instead of cramming into the $1s$? This would eliminate some of the repulsion from being in the same orbital.

No, not necessarily.

This simple question underscores one of the most important matters for dealing with the problem of many-electron atoms. You see, we are again dealing with the question of balance. I've been telling you off and on since Chapter 1 about the importance of balance in so many different aspects of chemistry. We are now dealing with another case where balance is absolutely, critically important. All many-electron cases are the result of the balance between electron-nuclear attractions and electron-electron repulsions. This is not entirely straightforward, and there are numerous variations which can arise due to the subtleties involved. Nevertheless, a majority pattern does emerge, and we shall adopt this as our general result. Let's first consider the two sides to the story separately.

We already covered the part fairly well about electron-nuclear attraction in the last two Chapters. The strength of this attraction is dominated by the size of the orbitals and the charge of the nucleus.

Larger orbitals from higher n shells will have less attraction and are less favorable. More protons in the nucleus give greater attraction due to higher positive charge.

The part about electron-electron repulsion is more tedious to explain. There are several aspects here to consider. Let's say you're an electron in some orbital in some many-electron atom. The question is: how repulsive are you to other electrons in the atom? Well, you're repulsive to another electron in your orbital, if there is one. You're repulsive (to a different extent) to any electrons in other orbitals of your same subshell. You're repulsive (to another different extent) to any electrons in other subshells of your shell. You're repulsive (to another different extent) to electrons in other shells. You have to consider all of those electrons in all of those different orbitals, all in proximity but still separate and still sensing one another. It gets complicated.

Let's try a different picture. You have an atom with one electron in $1s$. Now add a second electron, which is where we left off above. The second electron will also end up in $1s$ despite the fact that it detracts to be in the same orbital with another electron. The reason it does this, instead of going to $2s$ (or to any other orbital), is a trade-off: it still comes out ahead overall by pairing in $1s$ because $2s$ is larger around the nucleus and therefore less favorable. The trade-off is the balance.

Now add a third electron. Where will it end up? Exclusion limits all orbitals to two electrons, so $1s$ is booked up. Sorry, no vacancy. Let's go to the next larger group, $n = 2$. Will the third electron go into $2s$ or $2p$? In a one-electron atom, $2s$ and $2p$ have the same energy, so they would be equally favorable. Now, however, we have other electrons in the atom and now we have more problems. It's still TOTAL ENERGY which must be considered. The determining factor here is electron-electron repulsion between the two electrons in $1s$ and the third electron we are dealing with. This repulsion differs depending on whether that third electron is in $2s$ or in $2p$, since these orbitals differ by their shapes with their different regions of different concentration of the orbital field. Due to differing repulsions, SUBSHELLS WITHIN A SHELL ARE NO LONGER EQUAL in terms of the total energy picture. The answer here is that the third electron goes to $2s$. By the way, a fourth electron will also go to $2s$. It's still better to pair up in $2s$ than go to $2p$ because the total energy is better. On the other hand, a fifth electron has no choice. $2s$ is booked up, and $2p$ is the next available.

Let me summarize this so far.

For a many-electron atom, the general trend remains that energy is less favorable with higher n shell. Now, in addition, we have a new consideration: within a given shell, the subshells are no longer equal towards the total energy outcome. This gives an energy spread, and the different subshells will differ in total energy for electrons. This relationship goes by the l values as follows.

$l = 0$	$l = 1$	$l = 2$	$l = 3$	etc.....
s	p	d	f	
most preferred	➡	➡	➡	less preferred

Keep in mind that this is for subshells WITHIN THE SAME SHELL. Don't go applying this to $2p$ versus $3s$. That won't work. This relationship only works in the same shell.

The inequality of the subshell energies is part of what makes the many-electron cases more complicated. This becomes even worse when the subshell energies spread out so far that they overlap the subshell energies of another shell. Although this is complicated, we do need to cover this; we need to see what orbitals are actually in use for a given atom. The general notion for putting all this together is that the electrons will be in the orbitals which give the best (lowest) total energy for the atom as a whole.

We've already considered the orbitals for the first five electrons that would be present in an atom: two go into $1s$, two go into $2s$ and the fifth goes into one of the $2p$ orbitals. Which $2p$? It doesn't matter: $2p_x$ or $2p_y$ or $2p_z$. At this stage of the game, for an isolated atom all by itself, all three are equal in energy, all three are equally favorable, and all three are equally available, so it doesn't matter which and we don't need to specify which.

But I'm getting ahead; let me back-up a moment and introduce a few more items.

As we add more electrons to the picture, these additional electrons do not benefit from the full nuclear charge because they are repelled to some extent by the electrons already present. This gives us two new terms. We say the additional electrons are "screened" or "shielded" from the full nuclear charge by the other electrons. The nouns for the process are "screening" or "shielding". Since an electron may

not benefit from the full nuclear charge due to other electrons present, we can say that the electron senses a reduced nuclear charge; this is called the "effective nuclear charge". Effective nuclear charge (symbolized Z_{eff}) is always less than true nuclear charge, Z , for any many-electron atom or ion. How much less? It depends, and there are ways of determining this but we won't go into that. We'll stick with the general idea. For the general idea, there are two effects of significance to note as more and more electrons are added to the picture.

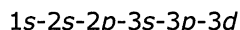
- Screening effects are substantial between the added electrons and the electrons already residing in smaller n -shells. These cases weaken the nuclear attraction (decrease Z_{eff}) the most for additional electrons.
- Screening effects are not as strong between the additional electrons and other electrons already in the same n -shell, but they can still be significant.

These aspects will be important in setting up the total energy picture.

The sequence $1s$ then $2s$ then $2p$ is based on total energy and it represents the sequence by which electrons will be found in the orbitals in an atom or monatomic ion. We now extend this sequence further in order to accommodate any realistic number of electrons. In this Chapter, we develop the sequence for single, neutral atoms; in the next Chapter, we deal with monatomic ions. As I had mentioned before, variations are possible for different circumstances due to the subtleties involved but there is a general pattern which emerges for the majority of cases. I shall be calling this pattern a "general fill sequence", or simply "fill sequence", since it refers to the sequence by which the electrons will fill the orbitals in a single, neutral atom in its ground state. Keep in mind that all of this is the overall result of the total energy balance of electron-nuclear attractions and electron-electron repulsions.

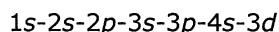
Let's just work with fill sequence for now, without worrying about how many electrons are involved. We'll come back to number of electrons in the next Section.

So far, we have the fill sequence $1s-2s-2p$. After $2p$ fills up, the $n = 2$ shell is done and we then turn to $n = 3$. In $n = 3$, there are three subshells, $3s$, $3p$ and $3d$, in that order of preference. This brings our fill sequence to

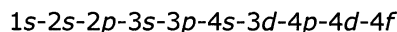


and that ends $n = 3$.

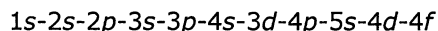
We turn to $n = 4$, which has $4s$, $4p$, $4d$ and $4f$. We now encounter our first complication: $4s$ will fill before $3d$. In other words, once all of the subshell stretch, $1s-2s-2p-3s-3p$, is full, then the next electrons go into $4s$ instead of $3d$. Thus, the fill sequence has an overlap between different shells.



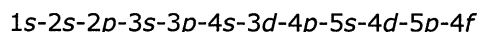
The rest of $n = 4$ adds on, after $3d$.



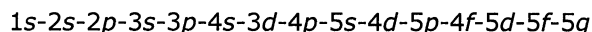
Next: with $n = 5$, we have the subshell spread $5s$, $5p$, $5d$, $5f$ and $5g$. We have another overlap problem: just as $4s$ fills ahead of $3d$, so also does $5s$ fill before $4d$. So, we squeeze $5s$ in ahead of $4d$ in our fill sequence.



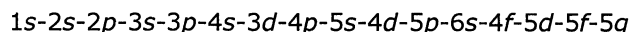
We also have another overlap problem, but now of a different sort involving $5p$. After filling up the sequence through ... $4d$, the next electrons go into $5p$, ahead of $4f$.



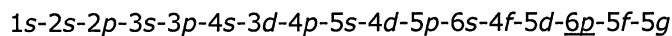
The other 5's add on to the end so far.



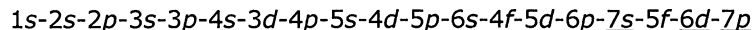
Now we introduce $n = 6$. $6s$ fills ahead of $5d$, just like the above cases. But $6s$ even comes in ahead of $4f$.



It turns out that $6s$ and $4f$ and $5d$ are close in the sequence. All three constitute an overlap region which will have frequent exceptions. Again, we're sticking with the majority of cases right now. After $6s$, we turn to $6p$, which gets inserted before $5f$.



I could continue this story on and on, but we are approaching the end of all known atoms. At this point, I shall go to the final result.

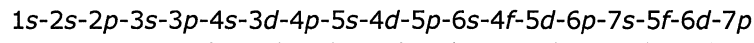


This adds $7s$, $6d$ and $7p$, and it also adds another overlap region, now involving $7s$, $5f$ and $6d$. Although $7s$ is in this overlap region, it does not give rise to any exceptions for neutral atoms; $7s$ will always follow $6p$. $5f$ and $6d$, however, will occasionally swap places. Note in the above sequence that $5g$ got bumped out completely. Now, don't get me wrong: there is still a $5g$, but no known elements have enough electrons for one to be in $5g$ in an atom in the ground state. You can do an excited state with an electron in $5g$, but we're doing ground states here. This fill sequence business is for ground states.

(Down the road, as more elements are made, it is expected that $8s$ will fill after $7p$ above. Then, $5g$ does come into play, but there arises an extremely complicated overlap region involving $5g$, $6f$, $7d$, $8s$ and $8p$. Don't worry: we're not touching any of that here.)

Alright, let's recap.

This crazy-looking string of subshells is the general fill sequence for the ground states of most many-electron, neutral atoms. The sequence ultimately results from the balance of opposing forces related to electron-nuclear attraction and electron-electron repulsion. Exceptions do occur, but these are limited to the overlap regions involving some of the s , d and f subshells. The places where exceptions can happen are underscored below.



Let me add a technical point at this time. This is a general fill sequence which shows which subshell will get the next electron after some number of electrons are already present. For example, if all subshells through $3p$ are full, then this sequence tells you that the next electron goes into $4s$. Or, if all subshells through $5d$ are full, then this sequence tells you the next electron goes into $6p$. What can happen along the way, however, is that the energies of previously filled subshells can shift, especially those in the overlap regions, and the energies of some earlier subshells may not be in the sequence as above. For example, if all subshells through $5d$ are full, then the next electron does indeed go into $6p$ but, by the time $5d$ is full, $4s$ and $3d$ have swapped places in terms of relative energies. Fortunately for us, this technicality does not impact where we are going with this; as you will see in upcoming Chapters, chemistry is primarily about electrons in later-filled subshells, not about electrons in early-filled subshells. So, for now, the simple distinction is that this sequence is not a universal sequence for subshell energies; instead, it's a general sequence for how electrons will fill into the various subshells. And that's the important part for us. This sequence answers the critical question as to which orbitals are actually in use for any particular atom.

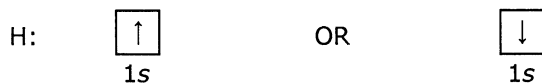
You can memorize this sequence, and some instructors may require that. This sequence, however, has been staring at you since Chapter 2. I'll show you this later.

22.3 Configurations

Given the general fill sequence, we can begin listing the orbitals which are used for the electrons in any neutral atom. As mentioned earlier, we are covering neutral atoms here; we extend this, with modifications, to monatomic ions in the next Chapter.

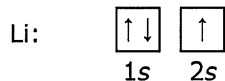
This listing of electrons by their orbitals is called an "electron configuration" or just a "configuration". We use a written format to show configurations. This written format lists each subshell followed by the number of electrons as a superscript. This is done for all electrons in a given atom, written in the order of the fill sequence. For example, we can write the configuration for H as $1s^1$, meaning it has one electron in the $1s$ subshell. The configuration for He, which has two electrons, is written $1s^2$. These are pronounced "one-ess-one" for H and "one-ess-two" for He. Notice that the superscripts are pronounced as a number, not as an exponent. (We don't say "one-ess-squared" for He.) The next element is Li, and one of its atoms would have the configuration $1s^22s^1$, pronounced "one-ess-two, two-ess-one".

There is another way to present configurations, using a box or a circle or just a line for each orbital and a vertical arrow for an electron. This method is better at illustrating essential features of magnetism. Although the arrow is always vertical, it can point up or down to indicate $m_s = +1/2$ or $-1/2$. The simplest case is H. Here's the configuration for H, using boxes.



Both diagrams are correct, since the spin can be either way for one electron by itself in a subshell. Some people use half-arrows instead of full arrows, such as \uparrow . That's fine, too.

Let's do the box notation for Li. Its configuration in written format is $1s^2 2s^1$.



The two electrons in the $1s$ box are shown in opposite directions, meaning that they have opposite spins as required by the exclusion principle. We can easily see by the box notation that a lithium atom has two paired electrons and one unpaired electron. By the way, please note that we are doing monatomic atoms only here. This is not the normal elemental form for Li (which is a metal network), but single atoms can be generated and can be studied.

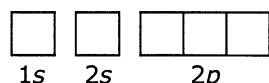
Be sure to show your superscripts for all subshells in your written configurations. Again, those are not exponents and this is not a math problem. Also, you typically do show ones, so the configuration for lithium is written as $1s^2 2s^1$. (Whether you need to show ones or not is up to your instructor.)

OK, at this time, we've completed our preliminaries and we have our essentials in place. We are now ready to delve into the diverse details of electron configurations in general. In order to do configurations, you need three things: the general fill sequence from above, the total number of electrons in the atom (which equals Z for a neutral atom), and the number of electrons allowed per subshell. The number of electrons which are allowed in a subshell is just twice the number of orbitals. That's because each orbital in the subshell can hold two electrons max. So,

- ▶ all s subshells have one orbital and can hold at most two electrons;
- ▶ all p subshells have three orbitals and can hold at most six electrons;
- ▶ all d subshells have five orbitals and can hold at most ten electrons; and,
- ▶ all f subshells have seven orbitals and can hold at most fourteen electrons.

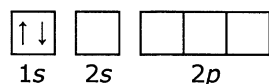
We had previously gotten up to five electrons. That corresponds to one atom of what element? Look on the Periodic Table. What neutral atom has five electrons? Boron, B. Let's look at the configuration of monatomic boron. We alluded to it earlier when we said two electrons would be in $1s$, two would be in $2s$ and one would be in $2p$. We can write that as $1s^2 2s^2 2p^1$. Here's another point to note in general about the written notation: all superscripts will add up to the total electron count. Although this is an easy case (the superscripts are $2 + 2 + 1 = 5$), you can use this to check more complicated cases.

Now let's turn to box format. We need $1s$, $2s$ and $2p$; set up those boxes.

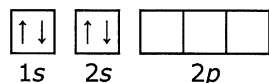


First, here's another new point to note. When you draw boxes, leave a gap between different subshells, but, within a subshell, stick the boxes together. For this reason, I drew a $1s$ box, then a gap, a $2s$ box, then a gap, and finally a set of three boxes for $2p$. Each box means one orbital.

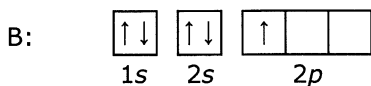
Start adding electrons. Enter your first two electrons, paired; this fills $1s$.



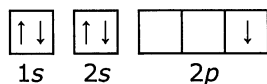
Enter the next two electrons into $2s$.



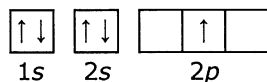
Finally, the last electron goes into $2p$. At this stage, all $2p$ orbitals are empty and equal, so the electron doesn't care which orbital (box) it goes into. It also doesn't matter which spin it has. **THE FIRST ELECTRON INTO A SUBSHELL CAN GO INTO ANY ORBITAL WITH ANY SPIN.**



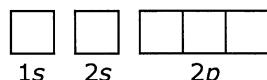
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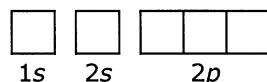
Etc. There are three other options. Here, you do another one:



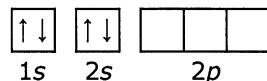
In all cases, we see that a boron atom has four paired electrons and one unpaired electron.

This example illustrates that there are numerous options for only one electron by itself in a subshell. The number of options decreases, however, when there are more electrons in the same subshell. We'll see this as we go.

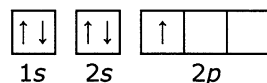
Next: carbon, with six electrons. First, we do the written notation. The first two electrons go to $1s$. The next two fill up the $2s$. This leaves two more electrons, and these are easily accommodated within $2p$. That gives $1s^2 2s^2 2p^2$. Now, go to boxes. We need the same subshells as above.



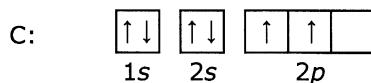
We'll put in the first four electrons, paired in their boxes.



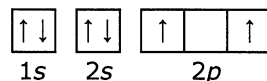
Now we'll go stepwise. Number five electron can go into any of the $2p$ orbitals, with either spin. I'll just take the first one.



We have only one electron left: where will it go? It will go into one of the empties yet available in $2p$. It won't pair with the one electron already in $2p$. Why should it? Pairing in the same orbital always detracts significantly from total energy due to charge repulsion; there are empty orbitals available in the same subshell for which the charge repulsion is less. So, the sixth and final electron will go into either of the empty $2p$ orbitals; it doesn't matter which one.



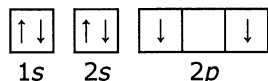
OR



Notice that a carbon atom has four paired electrons and two unpaired electrons.

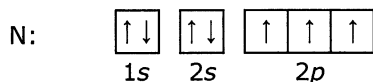
This example introduces the next rule for electron fill. This new rule has two parts. The first part says that electrons will spread out into empty orbitals within a subshell before pairing. That's the easy part and I hope you can understand this just based on charge repulsion. There's a second part to this rule, but this one is not obvious and it ties into exclusion. Notice that I gave the sixth electron the same spin as the fifth. This is required for a ground state configuration. All unpaired electrons within a subshell

must have the same spin. It does not matter which spin value they take, as long as they take the same one. For C, both electrons in $2p$ can be shown downward; this is also correct.

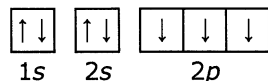


Here's the bottom line when electrons start to fill a subshell: electrons go into empty orbitals first and all with the same spin; then, they pair up. This didn't matter for s subshells since these only have one orbital, but it does matter for all other subshell types.

Let's carry this a bit further. Let's do seven electrons, which would be the case for a nitrogen atom. The written notation is $1s^2 2s^2 2p^3$. The box notation is the following.

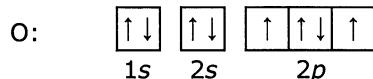


You only have one other option:

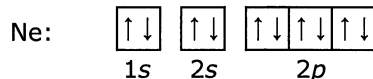


Nitrogen has four paired electrons and three unpaired electrons.

An eighth electron would be needed for an atom of oxygen. The written notation is $1s^2 2s^2 2p^4$. For the box notation, we simply add one more to the nitrogen case above. That eighth electron now has no choice but to pair with an electron already in $2p$. Which $2p$ orbital gets number eight? It doesn't matter. There are three equal options, one of which is the following.



If we add a ninth electron (corresponding to F) and then a tenth (corresponding to Ne), we would exactly fill up the $2p$ subshell, giving $1s^2 2s^2 2p^6$.

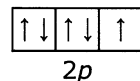


Now, all electrons are paired.

Here are two important points to note from the examples so far.

- Whenever subshells are completely filled, all electrons in them will be paired.
- Whenever a subshell is only partly filled, one or more electrons will be unpaired.

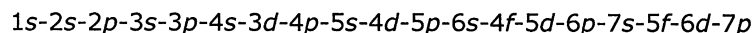
These statements are always true. As I mentioned earlier, paired and unpaired electrons are more easily seen in box notation than in written notation. For example, can you tell how many electrons are unpaired in the configuration $1s^2 2s^2 2p^5$? The number of unpaired electrons has important consequences, but it's not so straightforward to see from the written configuration alone without boxes. It will help if you apply these two points. For this configuration, $1s$ and $2s$ are filled so their electrons are all paired up; don't bother to look for unpaired electrons there. $2p$ is only partly filled, so that guarantees that one or more electrons are unpaired. Once you've reached that conclusion, it's easier if you visualize the box notation for that portion. How would five electrons in a $2p$ subshell look? Picture it.



This clearly shows that there is one unpaired electron.

Again, unpaired electrons allow for magnetic properties, so this is important stuff. I will come back to magnetic properties in Chapter 24. For now, however, I want to focus primarily on configurations.

All atom configurations are done the same way as the examples above. First, you need to know how many electrons you are dealing with. Then, you enter these into the general fill sequence.



As you go through the sequence, you must take into account the number of electrons which are allowed per subshell. Configurations can get lengthy, depending on how many electrons are involved. Let's go to chlorine: what's the electron configuration for an atom of Cl? Well, how many electrons do we have? Look at the Periodic Table. There are 17 electrons in a neutral Cl atom. Start putting these into the fill sequence beginning with 1s. (As you write a configuration, if you want to keep track of where you are, add your superscripts as you go.)

$1s^2$ ---That's two electrons of the seventeen. Fifteen remain.

The next subshell is 2s, which can hold two more electrons.

$1s^2 2s^2$ ---That's a total of four electrons of the seventeen. Thirteen remain.

Next is 2p, which can hold six more electrons.

$1s^2 2s^2 2p^6$ ---That's a total of ten electrons of the seventeen. Seven remain.

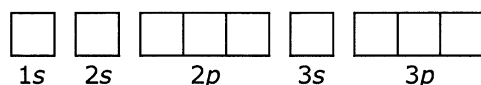
Next is 3s, which can hold two more electrons.

$1s^2 2s^2 2p^6 3s^2$ ---That's twelve of the seventeen. Five remain.

Next is 3p, which can hold six max, but only five are left.

$1s^2 2s^2 2p^6 3s^2 3p^5$ ---That's it.

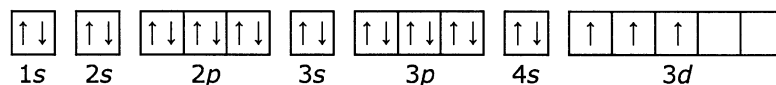
Here, you fill in the boxes.



Let me show you an example with a *d* portion. We'll do the configuration for vanadium, V. How many electrons are involved? Check the Periodic Table: 23. Write the configuration, plugging 23 electrons into the fill sequence. This is what you get.

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Set up the boxes. There are a lot of them this time. Here's one possible answer.



From this diagram, we see that a vanadium atom has three unpaired electrons.

Through our many examples here, we've been doing the written format and the box notation. The box notation gets very tedious, as you can see by vanadium which only has 23 electrons. The written format is much more compact and it gets even more compact than what I've shown you. We will do this more compact form in the next Chapter but there are other matters which we must first tend to.

22.4 The general fill sequence in table format

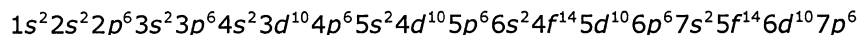
Several pages ago, I told you that the general fill sequence for electrons has been staring at you since Chapter 2. The reason for this is that the Periodic Table is the general fill sequence: it's arranged according to the order of subshells in the fill sequence, with some exceptions. This arrangement accounts for the somewhat strange shape of the Table and it also accounts for the information contained within the order of the Table. There's a lot of information to be gleaned from this, as we shall see. For now, you should learn how to "read" an electron configuration directly from the Periodic Table. And in order to explain how to read the Table, I will first explain how to build the Periodic Table.

Before you go on, you must do two things here. First, be ready to flip to the inside front cover to view the Periodic Table in full. The versions of the Periodic Table which I show here and into the next Chapter will not show all the details and they will only contain specific points for emphasis. Second, go back to Chapter 2 and read the section with the red star. It's not long, so it'll just take a moment. There are terms in there that we will again be using at this time. Frankly, it would be very useful to re-read both Sections 2.4 and 2.5 at the present time.

Let's start building the Periodic Table. We begin with the full fill sequence.

$1s-2s-2p-3s-3p-4s-3d-4p-5s-4d-5p-6s-4f-5d-6p-7s-5f-6d-7p$

Now, max out all the subshells with electrons.



If you add up all the superscripts, you get 118; this is the electron configuration for 118 electrons in an atom of oganesson, Og. Now, take this sequence and break it into a new row at every *s* subshell. This gives you seven rows.

Row 1	$1s^2$
2	$2s^2 2p^6$
3	$3s^2 3p^6$
4	$4s^2 3d^{10} 4p^6$
5	$5s^2 4d^{10} 5p^6$
6	$6s^2 4f^{14} 5d^{10} 6p^6$
7	$7s^2 5f^{14} 6d^{10} 7p^6$

Separate the subshells and align them by columns. The *s* subshells are already in a column. Align the *p* subshells, but align them in a column at the far right since they are the last in their rows.

Row 1	$1s^2$	
2	$2s^2$	$2p^6$
3	$3s^2$	$3p^6$
4	$4s^2 3d^{10}$	$4p^6$
5	$5s^2 4d^{10}$	$5p^6$
6	$6s^2 4f^{14} 5d^{10}$	$6p^6$
7	$7s^2 5f^{14} 6d^{10}$	$7p^6$

Separate the *d* subshells into a column by themselves, just before the *p*'s. This will leave the *f* subshells also in their own column.

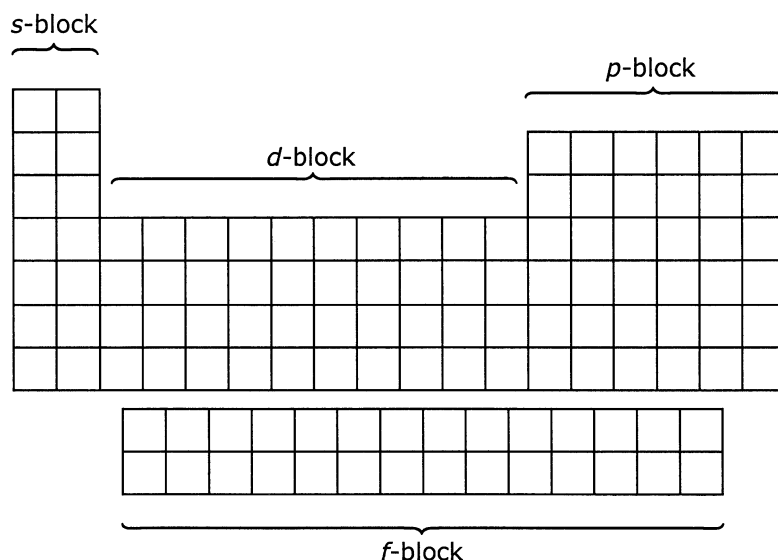
Row 1	$1s^2$		
2	$2s^2$		$2p^6$
3	$3s^2$		$3p^6$
4	$4s^2$	$3d^{10}$	$4p^6$
5	$5s^2$	$4d^{10}$	$5p^6$
6	$6s^2$	$4f^{14}$	$5d^{10}$
7	$7s^2$	$5f^{14}$	$6d^{10}$

There you have it. This is the Periodic Table, although not quite in its most common form. This is actually the "long form" of the Periodic Table, as described in Chapter 2. (I hope you re-read the red star section.) In the common form of the Periodic Table, the *f*'s are placed below the main body.

Row 1	$1s^2$		
2	$2s^2$		$2p^6$
3	$3s^2$		$3p^6$
4	$4s^2$	$3d^{10}$	$4p^6$
5	$5s^2$	$4d^{10}$	$5p^6$
6	$6s^2$	$5d^{10}$	$6p^6$
7	$7s^2$	$6d^{10}$	$7p^6$
		$4f^{14}$	
		$5f^{14}$	

This is now the general outline of the common form of the Periodic Table. It's all done by vertical arrangement of subshells. Each vertical portion is called a block, so we have four blocks: the *s*-block, the *p*-block, the *d*-block and the *f*-block.

Now, let's expand this and proceed to the final picture. We insert one square for each electron which can be in each subshell. That means that each *s* subshell gets two squares, each *p* subshell gets six squares, each *d* gets ten and each *f* gets fourteen.



Things are shaping up. Each square corresponds to a specific electron configuration, corresponding to a specific neutral atom of an element. The very first square is H. The second is He. Li follows that. Etc. Remember that we have been dealing with the electron fill sequence for 118 electrons, so we have 118 squares and our last square belongs to Og. Let's now bring back some of the terminology from Chapter 2. Each row is a Period, numbered 1 - 7. Each individual column is a Group numbered 1 - 18.

	1	2											13	14	15	16	17	18
1	H	He																
2																		
3			3	4	5	6	7	8	9	10	11	12						
4																		
5																		
6		56	71															
7		88	103														118	
			57														70	
			89														102	

Compare this to the general design of the full Periodic Table (on the inside front cover). Only two minor differences remain. The square for He is moved to Group 18, the noble gases. This is because helium is closest to the Group 18 elements in its properties, especially related to its inert nature; in fact, helium is the most inert of all elements. The second point to note concerns two elements in particular: lanthanum (La, $Z = 57$) and actinium (Ac, $Z = 89$). According to the general fill sequence, their configurations should end in $\dots 6s^2 4f^1$ and $\dots 7s^2 5f^1$ and they would start the two f rows at the bottom, as illustrated above. These two, however, are exceptions to the general fill sequence: instead of the expected configuration, they end in $\dots 6s^2 5d^1$ and $\dots 7s^2 6d^1$. Because of their true sequence, they are placed in the d -block. Although there are other exceptions to the general fill sequence, those others remain in the position according to where they would be if they followed the general fill sequence.

Taking these last points into consideration, we modify the Table above to give the final form atop the next page.

	1	2												13	14	15	16	17	18
1	H																		He
2																			
3			3	4	5	6	7	8	9	10	11	12							
4																			
5																			
6		56	57	72															
7		88	89	104															118

58																			71
90																			103

Notice that when we moved 57 and 89 up into the d portion, we bumped down 71 and 103. That's the way it goes.

In Chapter 2, we introduced additional terms such as Main Group elements, transition elements and inner transition elements. These can also be cited by their subshell block designations. The s -block and the p -block elements make up the Main Groups. The transition elements are from the d -block and the inner transition elements are from the f -block.

This concludes our construction of the Periodic Table. It's all based on configurations. By seeing how the Table is built from configurations, I hope that you will be able to read configurations from the Table. That's where we go next.

Problems

- True or false.
 - Exclusion limits every orbital to a maximum of two electrons.
 - The maximum number of electrons in the $n = 4$ shell is 18.
 - In a neutral Li atom, an electron in the $2s$ orbital will have the same energy as an electron in a $2p$ orbital.
 - For a neutral atom, $4s$ usually fills before $3d$.
 - Lead is in the p -block.
- True or false.
 - Spin exclusion only occurs between two electrons with opposite spin.
 - There are no shielding effects in a neutral hydrogen atom.
 - Electron-electron repulsion is responsible for the spread of subshell energies within a shell.
 - The s -block and the p -block make up the Main Groups.
 - Magnesium is in the d -block.
- Write the full electron configuration for each of the following.
 - Be
 - Si
- Draw a box diagram for the configuration of each of the following. How many unpaired electrons are there in each?
 - Be
 - Si