Chapter 15

The Periodic Table of the Elements

In Section 13.4, we saw the example of a square potential well. In that example, there were three bound states. This is the solution for a single electron moving in that potential, so each of these levels represents a possible energy state available to that electron. There are in fact six total states available, because there are two spin states available to an electron as well. Under the approximation that electrons do not interact with each other, we could take exactly these energy levels and put up to six electrons in the potential well. Because electrons are fermions, no two electrons can be in the same state. (If we were putting bosons into the potential well, there would be no limit, as you can put multiple bosons in one state.)

The process of constructing the periodic table of the elements is similar to the process of filling up this square well with electrons. In the previous chapter, we saw that the states available to an electron are indexed by three quantum numbers: n, the principle quantum number, l, the total orbital angular momentum quantum number, and m, the quantum number indexing the z projection of orbital angular momentum. In addition, there is electron spin, allowing two electrons to go into each $|n, l, m\rangle$ state.

On the periodic table, the "atomic number", usually indicated as the largest number in a display and often represented with the letter Z, is the total number of protons in the nucleus of the atom. The charge on the proton is exactly opposite the charge on the electron; whereas electrons have a charge of -1.602×10^{-19} C, protons have a charge of $+1.602 \times 10^{-19}$ C. Thus, for a neutral atom, the number of electrons is equal to the number of protons. Chemistry is all about the dynamics of electrons as atoms interact with each other, form bonds, trade electrons, and so forth. Therefore, from a chemical point of view, it might be more useful to think of Z as the number of electrons in a neutron atom of an element. (What if there is an additional electron added, making the atom negative, or if there is an electron removed, making the atom positive? In that case, we call it an ion, but we still name the ion based

on the number of protons. A Chlorine atom with an extra electron would be called a negative Chlorine ion.)

Elements are constructed by filling in electron states until the number of electrons matches the number of protons in a nucleus. The number of states available at each shell is dictated by how angular momentum functions under quantum mechanics: as we saw in the previous chapter, l must be less than n, and m varies from $-l$ through l. If you put these two things together, it would be fair to say that angular momentum at the quantum level is responsible for the structure of the periodic table of the elements, the chemical properties of the different elements, and thus for chemistry and life as we know it. The number of states available is influenced, for instance, by the fact that angular momentum can only have definite states for projection along one axis at a time. The structure of the periodic table would be very different if x, y, and z angular momentum operators all commuted.

15.1 Interacting Electrons, Energy Levels, & Filled Shells

In fact, electrons *do* interact with each other. In the previous chapter, we made arguments that these interactions should be smaller than the interaction with the nucleus. Because electron probability clouds are spread out, and outer shell clouds only have relatively small overlap with inner shell clouds, often, especially when viewing inner shells, you can approximate them as just lowering the net effective charge of the proton. That is, if you look at a Sodium atom, it has 11 electrons. The first 10 electrons will fill up the $1s$, $2s$, and $2p$ states. That leaves the outermost electron in the $3s$ state. Because there isn't a whole lot of probability for that $3s$ electron to be found where the inner electrons are usually found, you could approximate the situation for that outer electron that it's orbiting a ball of charge with a net charge of $+1$ (in atomic units), neglecting the fact that that charge is made up if $+11$ in the tiny nucleus and -10 in the outer electron cloud. However, even though interactions between electrons are secondary to the interaction between each electron and the nucleus, they are there, and they do ultimately have a lot of influence as to how elements at different places on the periodic table behave.

One of the primary effects of electron interactions is that the s, p, and d orbitals for a given value of n are *not* at exactly the same energy. In a Hydrogen atom— or any ion that only has one electron— they are, to a fairly good approximation. If there is more than one electron, however, the electron-electron interactions modify the energies of these states. In general, levels with higher l will be higher energy states than levels with lower l but the same n. In the absence of something external (such as a magnetic field), levels of different m but at the same n and l will still have

approximately the same energy. Sometimes, you will find levels with a higher n but a lower l to be at a lower energy level than levels with a lower n and higher l. For instance, the $4p$ states tend to be filled before the $3d$ states. This isn't always a hard and fast rule; sometimes you will see the states filled out of the "standard" order. The interactions between electrons make the entire system a many-body system, and many-body systems are often notoriously difficult to solve in Physics.

For the most part, atoms are "happiest" (if you will allow for some anthropomorphization for purposes of discussion) if the number of electrons equals the number of protons. If there is one too many electrons, the ion will generally be happy to give away one of its negative electrons to the first positive charge that goes along. Likewise, if there is one too few electrons, the ion has an extra positive charge, and will tend to snap up any spare electrons in its vicinity.

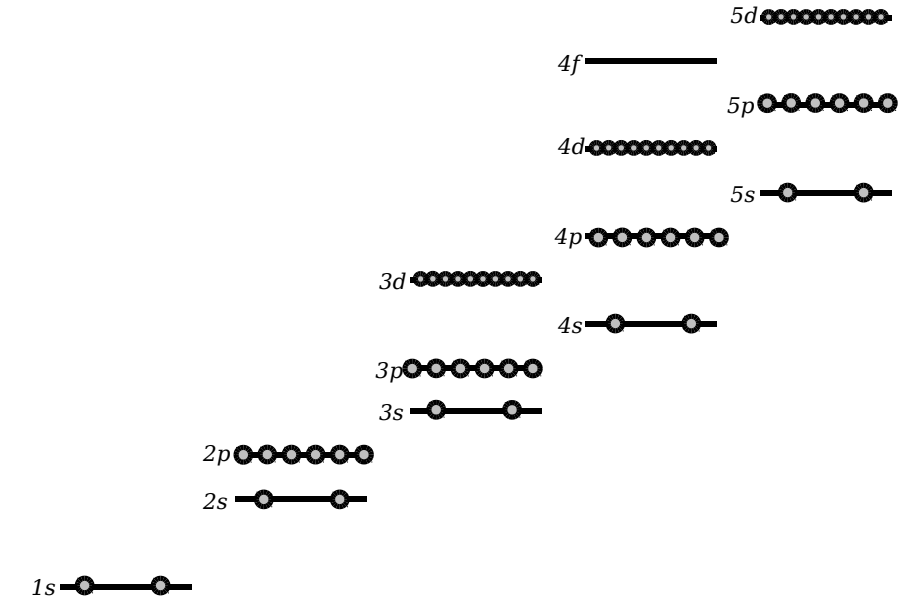
However, this is not the only consideration for atom happiness. Atoms also like to have a filled shell. That is, Helium is more chemically stable than Hydrogen, because whereas Hydrogen only has one of two possible electrons in the $1s$ state, Helium has entirely filled the $n = 1$ shell by placing two electrons in the $1s$ state. Likewise, Neon, with 10 electrons, has filled up both $1s$ states, both $2s$ states, and all six $2p$ states, making it a very chemically stable element. The elements down the right column of the Periodic Table are called "noble gasses". They are so called because they are chemically stable, and don't tend to interact with other atoms or form molecules. (They're noble, and thus above it all, or some such. Doubtless sociologists of science love to tear apart this nomenclature to display cultural bias in scientists.) The reason they are so stable is that each one of these noble gasses is an element that has just completely filled a set of p orbitals. (The one exception is Helium. It has completely filled the $n = 1$ shell, where there are no p orbitals.) Ne has completely filled its set of $2p$ orbitals. Ar has completely filled its set of $3p$ orbitals. Kr has completely filled its set of $4p$ orbitals. And so forth.

You can get a first guess at the chemical properties of an element by comparing how close it is to a noble gas. If an element has just one or two electrons more than a noble gas, the easiest way for it to be more like a noble gas would be for it to lose an extra electron. Elements like these are more apt to form positive ions than negative ions. An example is Sodium. Sodium has atomic number 11. The first 10 electrons fill up the $1s$, $2s$, and $3p$ orbitals; that is, they're like a Neon inner core. Then, just outside that, is a single $3s$ electron. If Sodium loses that electron, then it is electrically positive, but now it has a happy noble-gas-like electron configuration. In contrast, Chlorine has 2 electrons in the $3s$ shell and 5 electrons in the $3p$ shell. All it needs is one more electron to have a full $3p$ shell, giving it the electronic configuration of Krypton. If you put these two elements together, each Cl atom will tend to take away an electron from each Na atom, leaving the Cl a negative ion and the Na a positive ion. Those two ions then will have an electrostatic attraction towards each other as a result of their opposite charges. The result is a crystal, Sodium Chloride,

more commonly known as salt. In this case, the bonds holding the crystal together are "ionic bonds". In most molecular bonds, an electron is shared between elements. In this case, however, the Sodium is so eager to get rid of an electron and the Chlorine is so greedy for another one that effectively the electron transfers all the way across from the Na to the Cl.

15.2 Filling Up Orbitals

You can use the diagram below to figure out where an element will fall on the periodic table. Start with the lowest energy states, and fill in available states with electrons. Keep filling them in until you have as many electrons as you need. If you have just a single spare electron in an s shell, then that is an element like Hydrogen, Lithium, or Sodium; it goes on the left column of the periodic table. As you fill in more and more levels, you move farther and farther to the right on the table. If you completely fill a p orbital, then you're on the very right side of the table, and the element you've constructed is a noble gas.



States available to electrons in atoms. States higher in the diagram are (usually!) states at higher energy, although the exact spacing on the diagram should not be interpreted as meaningful. Although not drawn, there are 14 states available in the $4f$ orbital. Additionally, to fill out the current modern periodic table, we'd need to extend this to include the $5f$, $6s$, $6p$, $7s$, and $7p$ orbitals.

Because the chemical properties of an element are approximately determined by how far away it is from a noble gas, constructing the periodic table in this manner means that every column should have somewhat similar chemical properties. Thus, each column on the periodic table is called a "Group". Each row on the periodic table is called a "Period". The name "Periodic Table" is not arbitrary. When something is periodic, it means that it has regular cycles. The period of the Earth's orbit around the Sun is about 365 days; after that much time, the Earth is back where it started. On the periodic table, it's element numbers that are periodic. After you add just enough electrons to fill up a p orbital, the next electron you add is as if you were starting over on a new shell.

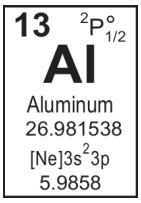
However, there is a difference with the Periodic Table. In a simple orbit such as the Earth going about the Sun, each period is exactly the same length. However, on the Periodic Table of the Elements, periods get longer and longer. As you go to higher and higher values of n, there are more and more states available. At a given n, you can have values of l between 0 and $n-1$. Thus, for $n=1$, there are only two states available, and thus the first period has only two elements: H and He. At $n=2$, there are now eight states available (two s states and six p states), so there are eight elements in the period: Li, Be, B, C, N, O, F, and Ne. You might then expect there to be 18 elements in the third period, as for $n=3$ there are 18 states: two s states, six p states, and ten d states. However, it turns out that the $4s$ states are at a lower energy level than the $3d$ states. Thus, the third period only fills up the $3s$ and $3d$ states, and has eight elements just like the second period. In the fourth period, starting with Potassium, we fill in the $4d$, $3d$, and $4p$ states (*approximately* in that order), and now have eighteen elements. The same thing happens with f orbitals; it isn't until the sixth period, after the $6s$ states are filled, that the $4f$ orbitals start to get filled.

The fact that as you go to higher and higher periods, there are more and more states available before you can completely fill a p orbital, is what gives the periodic table its iconic "stepped" structure. The first step comes after Hydrogen and Helium. The first period only has the $1s$ orbital available, and only has two elements in it. The second and third periods each have 8 elements, filling up the $2s$, $2p$, $3s$, and $3p$ orbitals. The fourth period now has 18 elements in it, because in addition to the $4s$ and $4p$ orbitals, it also has to fill up the $3d$ orbitals.

15.3 Reading a Periodic Table

If you look at a periodic table, there is a variety of information you may find on it. Every periodic table includes the symbol of the element (one or two big bold letters at the center of the element's box), and the atomic number of the element (the number of protons in that element, usually shown as a number in the upper

left). For example, below is the entry for Aluminum from the NIST Periodic Table (Dragoset et al., 2003).



Here, you can see the symbol for the element is Al, and the atomic number is 13.

Usually, below the element symbol, you will find the atomic weight of the element. This is in units of "atomic mass units" or amu; one amu is equal to 1.66×10^{-27} kg. In this example, the atomic weight is given to eight significant figures, and is 26.981538 amu. The atomic weight in amu is *approximately* the number of protons and neutrons— which, together are just called "nucleons"— in the element, but there are a number of complications. First is the complication that for some elements, there are multiple *isotopes*. Different isotopes have the same number of protons but different numbers of neutrons. For example, the atomic weight of Chlorine is 35.45 amu. This is largely because in nature, we find Chlorine in two isotopes: Cl-35 and Cl-37, with 35 and 37 total nucleons respectively. There is a second complication, however. The mass of a nucleus is *not* exactly equal to the sum of the masses of the protons and neutrons that compose it! Each nucleus has what's called a *binding energy*. This binding energy is equivalent to the 13.6eV of energy that holds an electron on to a Hydrogen atom. It is the total energy for all of the nucleons in their bound states, and is negative for a stable nucleus. This binding energy is taken away from the effective mass of the nucleus, using the conversion $E = mc^2$. In fact, exactly the same thing is true for atoms! However, the binding energy compared to the mass of atoms is something like one part in a billion, so as such when dealing with chemical reactions and other electronic transitions, we can approximate mass as being conserved. Nuclear binding energy can get up to a few percent of the total mass. (It is this difference that makes nuclear power so much more efficient, in terms of energy produced per mass of fuel used, than chemical power.)

15.3.1 Electronic Configuration

Often, but not always, the periodic table will include one or two sets of symbols intended to convey information about the ground state of the atom's electron cloud. The one seen more rarely includes information about the spin, orbital, and total angular momentum of the atom. In the NIST entry for Aluminum above, you can see this information in the upper right as $^2\mathrm{P}^{\mathrm{O}}_{1/2}$. The letter in the middle represents

the total orbital angular momentum of all of the electrons the atom put together; S means $l = 0$, P means $l = 1$, D means $l = 2$, and F means $l = 3$. For Hydrogen, the single electron is in the $1s$ orbital, which has no orbital angular momentum, so that letter is S. For Aluminum, the letter is P. This results from the single electron in the $3p$ state. There are two electrons in each of the $1s$, $2s$, and $3s$ states, and none of them have any orbital angular momentum. However, for Aluminum, there are also six electrons in the $2p$ state. But, because that shell is filled, there will be as many electrons with z-angular momentum of $+\hbar$ as there are with $-\hbar$ (two each, in this case), so all of their orbital angular momentum cancels out.

The superscripted number before the letter tells you about the electron spin state. It is equal to $2s + 1$, where s is the *net* electron spin divided by $\hbar$. For Hydrogen, this is ${}^2S_{1/2}$. In Hydrogen, the net electron spin is 1/2, because there is just one electron that has spin $+\hbar/2$, so $2s = 1$. In Helium, that number is 1, because the two electrons have spins in the opposite directions, so $s = 0$. For aluminum, the net electron spin is the result of a single electron in the $2p$ state (as all of the filled states will have as many spin up as spin down electrons, thereby cancelling out each other's angular momentum). Thus, the net electron spin is 1/2 (as always in units of $\hbar$), so the number we see in the example above is $(2)(1/2) + 1 = 2$. Finally, the subscripted number after the letter is J, the quantum number associated with the *total* electronic angular momentum of the atom. J represents a combination of orbital and spin angular momentum for the electrons. For Hydrogen, $J = 1/2$, because the angular momentum is entirely in the spin of the electron; for Aluminum, it's also $J = 1/2$, but the reason is more complicated. Both the spin and orbit of the $3p$ electron contribute, but it would have been possible for them to combine yielding either $J = 1/2$ or $J = 3/2$. For Helium $J = 0$ because there is no net angular momentum: there's no orbital angular momentum for two electrons in the $1s$ state, and the two spins cancel each other out. (As a caution, adding angular momenta in quantum mechanics can become complicated for cases with higher numbers than these examples.[1]) Similar to what we see with orbital angular momentum, the physical amount of angular momentum for an atom with total orbital quantum number J is $\hbar\sqrt{J(J+1)}$.

(The superscripted O— it's a capital O, not a zero— on the notation you see for Aluminum indicates that Aluminum has "odd parity". Parity is another quantum

[1]For example, with Aluminum, it turns out that for the total spin+orbit angular momentum of the $3p$ electron to be in a definite state $J = 1/2$, neither the orbital z component nor the spin z component may individually be in definite states. If we write the state of the $3p$ electron as $|m, s_z\rangle$, for an Aluminum atom to have $J = 1/2$ and $J_z = 1/2$ (i.e. we've specified the orientation as well as the total angular momentum of our Aluminum atom), then the angular momentum state of the outermost electron would be

$$\sqrt{\frac{2}{3}}\,|+1, -1/2\rangle \; - \; \sqrt{\frac{1}{3}}\,|0, +1/2\rangle$$

.

property that you don't need to worry about here.)

You may also see a series of letters and numbers that tell you how many electrons there are in each orbital. For Hydrogen, this is $1s^1$. That is, there is but a single electron in the $1s$ orbital. For Helium, it's $1s^2$: there are two electrons in the $1s$ orbital. For Nitrogen, it's $1s^2 2s^2 2p^3$. The $1s$ and $1s$ orbitals are filled, and the $2p$ orbital is half-filled. For periods after the second, it's often conventional not to list the full state, but to list the noble gas that has the same configuration as the inner core of electrons, and then just the states of the electrons outside of that. In our example of Aluminum above, the configuration is [Ne]$3s^2 3p$. It's got all the electrons that Neon does— $1s^2 2s^2 2p^6$— plus an additional two electrons in the $3s$ state and one in the 3p state.

The number at the very bottom of the box for Aluminum, 5.9858, is the *ionization potential* in eV for Aluminum. Many periodic tables will not include this number. This is the amount of energy it takes to remove one electron from the atom, forming a positive ion.