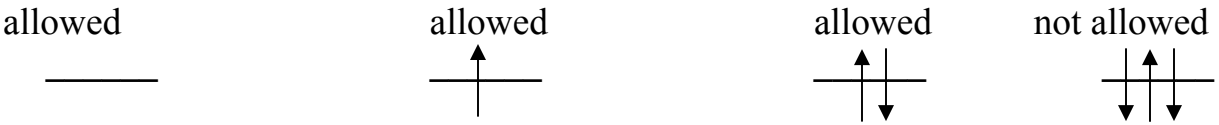
LECTURE 4: HOW TO GENERATE ELECTRONIC CONFIGURATIONS FOR ATOMS AND IONS

We are about to do something incredibly useful—create the electronic configurations for every kind of neutral or charged atom we can find in the periodic table. And we will do it by applying the boundary conditions (quantum rules) for the n, ℓ, m_ℓ, m_S . We will also need to implement three rules for how one "builds up" the electrons in an atom.

Three rules for building up the electron configuration for an atom

Rule 1: Aufbau principle. Always fill electron orbits starting with the orbits that are closest to the nucleus. This is the lowest energy or ground state configuration. What are the lowest energy orbits? Look at the periodic table. You will see that the n= 1 and ℓ = 0 orbit comes first. The n= 2 and ℓ = 0 comes second and the n =2 and ℓ = 1 orbits come third. So according to Aufbau, you fill the 1s first, then the 2s, then the 2p, and so on.

Rule 2: Pauli Exclusion Principle. Never put more than 2 paired electrons in an orbit. This is actually the consequence of the larger idea promoted by Pauli that no two electrons can have the same four quantum numbers. So since the $m_{S\ \text{boundary}}$ conditions only allow up to two electrons of opposite spin, you can't add a third electron to an orbit without it taking on either the +1/2 or -1/2 spin number which violates Pauli.

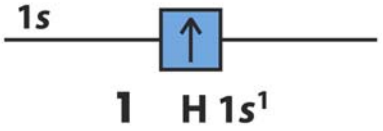


Rule 3: Hunds Rule. The quantum rules produce energy levels that are the same (degenerate) for p and higher orbitals. In building up the electrons in an orbit, you must distribute the electrons between the orbitals as much as possible to minimize electron repulsion effects.

Putting it all together for the smaller atoms

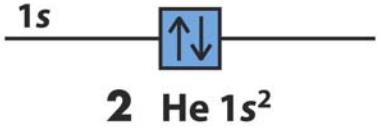
So now we can start building up electronic configurations, starting at the lowest energy n = 1, and $\ell = 0$. We will first place a single electron into the 1s orbit that is created. Note that among the various possible charged and uncharged atoms, the first, and simplest is the hydrogen atom which has a single electron to put in an orbit. Following Aubau, Hund and Pauli we have:

The neutral hydrogen electronic configuration



We can now add a second electron and again follow Aubau, Hund and Pauli to put another opposite spin electron in the 1s orbit. Helium atom is the obvious example of this electronic configuration since it is the neutral atom with two electrons.

The neutral helium electronic configuration



Pauli and Hund Spring to Action.

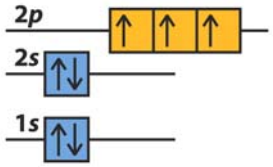
As we add a third electron, we get really excited because we can use on of our rules, the Paul Exclusion Principle that doesn't let us put a third electron into a single orbital. So we have to use the next lowest orbital allowed by the boundary conditions. When n= 1 we don't get to use $\ell = 1$, so we are going to have to move to n = 2 and $\ell = 0$. The 2s orbital which will house our third and fourth electrons.

The neutral lithium electronic configuration

3 Li $1s^2 2s^1$, $[He]2s^1$

An obvious progression through the first several neutral atoms will take us into the 2p orbtitals where for the first time we are dealing with ℓ equal to something other than zero. Recall that when $\ell = 1$ we have a p orbital and there are three degenerate (equal) energy levels for it that we can write as three horizontal dashes on the same line. With these three energy lines, we can now apply Hund's Rule that makes us spread out the electrons across the equal orbits as much as possible.

The neutral nitrogen electronic configuration

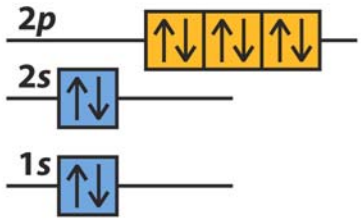


7 N $1s^2 2s^2 2p^3$, $[He]2s^2 2p^3$

The Idea of Filled and Half Filled Shell Stability: a Harbinger of Things to Come

I don't really know what a harbinger means, but it sounded like a good word to use here. Anyway, the nitrogen example above, and the neon electronic configuration I will present next are examples of what are called half-filled (three electrons in a six electron subshell) and filled (eight electrons in the n = 2 shell) electronic configurations. It will turn out that filled and half-filled shells and sub-shells have added stability. As a consequence, all kinds of physical and chemical consequences are realized. You know, for example, that Neon is unreactive. The reason? It has a filled shell configuration. There is much more to come on this concept since it is at the root of just about everything to come in this course.

The neutral neon electronic configuration—a VERY stable atom

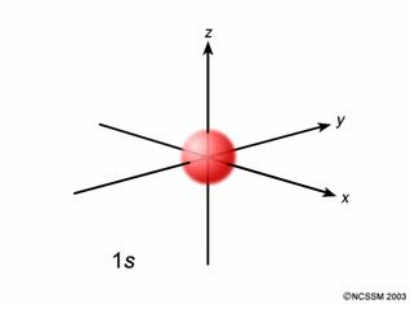


10 Ne $1s^2 2s^2 2p^6$, [He]$2s^2 2p^6$

I don't feel like doing this "building up" routine for 100 atoms. So why don't you. Meanwhile, some other related concepts.

What is that Shorthand Under All the Electronic Configurations

Chemists are lazy, and except for organic chemists, we can't draw very well either. So rather than draw all those three-dimensional pictures of the wave equations squared, or even drawing the orbitals with the up and down arrows, we would rather create some line notation that says the same thing. So very simply, rather than draw you this or that to show you two electrons in a 1s orbital, we would rather simply write $1s^1$



vs 1s **vs** **$1s^1$**

So when you see line notation like 1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p2 it is just lazy chemists at work..

Getting lazier. Actually, since there is so much repetition to our electronic configurations given the Aubau Principle, we can even decide to substitute chunks of filled orbitals as noble gas symbols like [He] or [Ne]. Thus:
1s2 ≡ [He] and 1s2 2s2 2p6 ≡ [Ne] and 1s2 2s2 2p6 3s2 3p6 ≡ [Ar] and so on

So what is the actual sequence of orbitals for this building up? Do I have to memorize them?

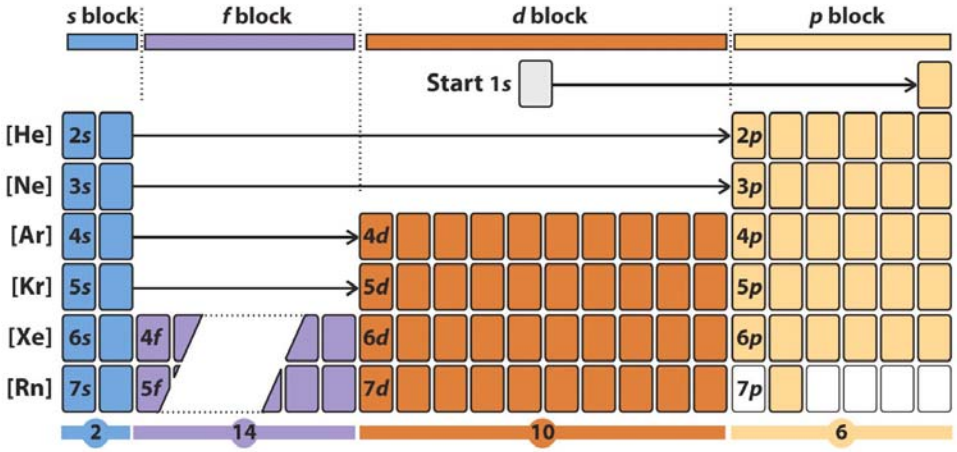
We don't get to violate Aufbau which means that we have to make sure we use the correct increasing energy levels. Is it simply what we get from following the boundary conditions for the quantum numbers?

1s 2s, 2p 3s, 3p, 3d 4s, 4p, 4d, 4f ……

Sadly, no. It is what falls out from the enregy calculations of the wave functions as an increasingly arbitrary sequence:

1s 2s 2p 3s 3p 4s 3d 4p …

Do we have to memorize this order? No. Why? It is found right in the way the periodic table is sequenced:



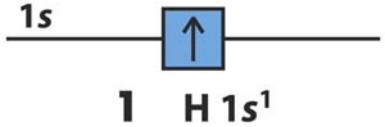
Building up from 1s, the correct sequence follow the table.

4f __ __ __ __ __ __ __
6s __
5p __ __ __
4d __ __ __ __ __
5s __
4p __ __ __
3d __ __ __ __ __
4s __
3p __ __ __
3s __
2p __ __ __
2s __
1s __

What about the electronic configuration of charged atoms? It's just the number of electrons that matter!!

As you will soon come to learn, when drawing electronic configurations, the number of protons in the nucleus is not all that important except to determine how are extended from the nucleus the electrons are. But as far as defining where out electrons are, all that matters is the number of electrons.

What are the electronic configurations for the 1 electron ions He^{+}, C^{+5}, Po^{+83} ? They are the same as:



What are the electronic configuration of Si^{-} or P^{-} or Cl^{+}? Note that all 3 ions have 16 electrons, so all 3 ions have the same electronic configuration as neutral S.

$$S \equiv Si^{-} \equiv P^{-} \equiv Cl^{+} \equiv 16e^{-} \blacktriangleright [Ne]\ 3s^2\ 3p^4$$

What is the electronic configuration of Bi, Tl^{-2} and Po^{+}? In each case there are 83 e^{-}. So find the closest noble gas, [Xe] in this case, and add additional e^{-} till you get to 83 e^{-}.

$$\text{Bi electronic configuration} \equiv [Xe]\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$$

You can now create electronic configurations for charged and neutral atoms. Congratulations.

As we finish the first four lectures, the great thing is in all the grief to understand Wien's Law, particle in a box, Schrödinger, orbital angular momentum, and radial probability densities, there is a real pay off. Being able to generate electronic configurations just by staring at a periodic table sets the table for you to be able to do the most important thing in chemistry:

Create Bonds between Atoms