Electronic Structure of Atoms

The electronic structure of a one-electron atom is described by an orbital (ψ) characterized by three quantum numbers (n, ℓ, m_ℓ). The orbital gives location probability information, as well as information regarding other observable quantities for the electron, such as electron energy.

The electronic structure of a multi-electron atom can be described by a **total electronic wavefunction (ψ_{total})**. This total wavefunction is "built-up" from one-electron orbitals. Each electron in the atom is described by a one-electron orbital (ψ), the product of all these one-elctron orbitals gives the electronic structure, or electron configuration, of the atom.

Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the main group elements.

Groundstate (lowest energy) electron configurations of atoms

In ground state electron configurations, the electrons fill orbitals in a way to minimize the total energy of the atom. The following rules must be followed when writing the groundstate (lowest energy) electron configuration:

1) Pauli Exclusion Principle

The Pauli exclusion principle states that no two electrons can have the same four quantum numbers. The first three (n, l, and ml) may be the same, but the fourth quantum number must be different. A single orbital can hold a maximum of two electrons, which must have opposing spins; otherwise they would have the same four quantum numbers, which is forbidden. One electron is spin up ($m_s = +\frac{1}{2}$) and the other would spin down ($m_s = -\frac{1}{2}$).

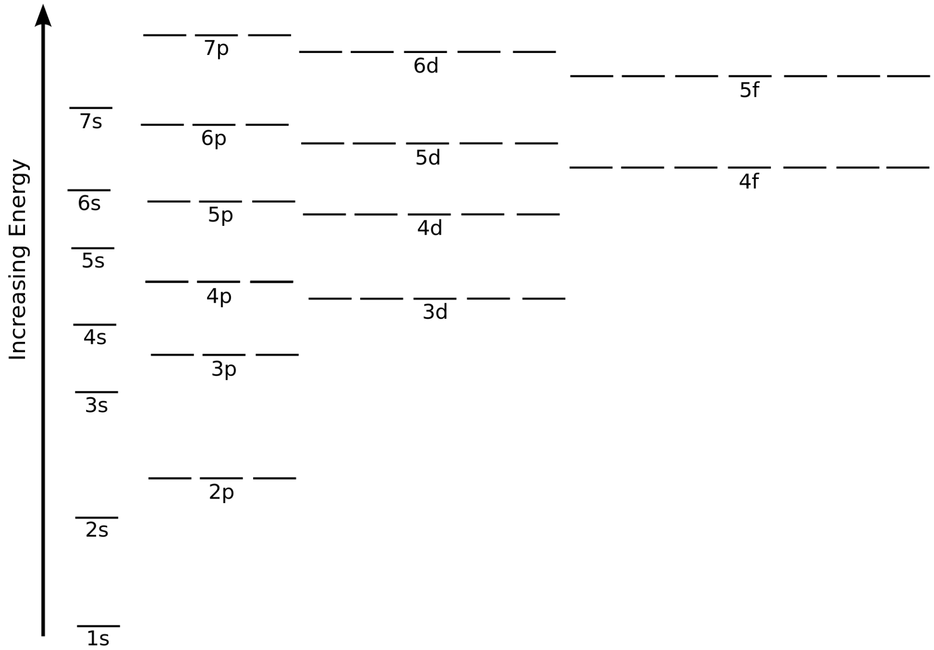
2) Hund's Rule

When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this process, think about how electrons are exhibiting the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals they first try to get as far as possible from each other before having to pair up.

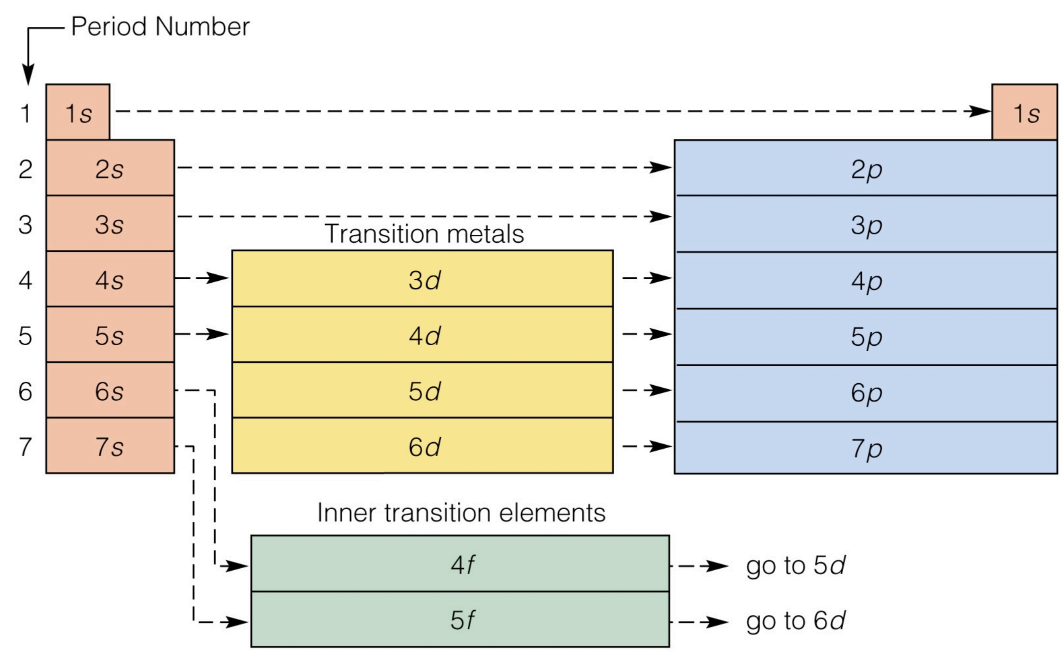
3) The Aufbau Principle

Aufbau comes from the German word "aufbauen" meaning "to build." When writing electron configurations, electrons fill the lowest available energy levels before filling higher. In this way, the electrons of an atom, molecule, or ion allow the most stable electron configuration possible. (So, for all ground state electron configurations, any one empty orbital must be higher in energy than an occupied orbital.)

For a typical multi-electron atom, the following is a general orbital energy diagram:



Use the periodic table to follow this **standard filling order**:



Although the Aufbau rule accurately predicts the electron configuration of most elements, there are notable exceptions among the transition metals and heavier elements. *Please memorize the following two exceptions to the standard filling order:*

Chromium:	[Ar] $3d^5 4s^1$
Copper:	[Ar] $3d^{10} 4s^1$

<u>Groundstate (lowest energy) electron configurations of ions</u>

Commonly, the electron configuration is used to describe the orbitals of a neutral atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion.

Main group element ions

Electrons are removed from (or added to) the highest energy orbitals according to following the standard atomic energy order.

Transition metals

Electrons are removed from the highest energy *ns* orbital first, followed by the *(n-1)d* orbitals, as necessary.

<u>Excited state (higher energy) electron configurations of atoms/ions</u>

Any electron configuration or orbital diagram that does not follow the three groundstate rules (excluding the known 0exceptions, such as Cr and Cu) will represent an excited state.

<u>Paramagnetic/Diamagnetic electon configurations of atoms/ions</u>

Paramagnetic configuration

An electron configuration containing one, or more, unpaired electrons. Atoms with these configurations will be attracted to an external magnetic field.

Diamagnetic configuration

An electron configuration where all electrons are paired! Atoms with these configurations will NOT be attracted to an external magnetic field.

Example problem:
The ionization energy of sulfur is 999.6 kJ/mol. The emission spectrum of sulfur includes the following transitions:

Wavelength (nm)	**Initial Configuration**	**Final Configuration**
180.7	[Ne]$3s^2 3p^3 4s^1$	[Ne]$3s^2 3p^4$
168.8	[Ne]$3s^2 3p^3 3d^1$	[Ne]$3s^2 3p^4$

A) Use the above information to construct an energy diagram for sulfur which shows the energy levels of the 3p, 4s and 3d orbitals along with the energy for the ionized state. Clearly show the energy value for each of the four requested levels in kJ/mol.

B) What is the energy change, in kJ/mol, for the following electron transition?

Initial Configuration	**Final Configuration**
[Ne]$3s^2 3p^3 3d^1$	[Ne]$3s^2 3p^3 4s^1$