QUANTUM NUMBERS, ATOMIC ORBITALS, AND ELECTRON CONFIGURATIONS

Quantum Numbers and Atomic Orbitals

By solving the Schrödinger equation ($H\psi = E\psi$), we obtain a set of mathematical equations, called **wave functions** (ψ), which describe the probability of finding electrons at certain energy levels within an atom.

A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light).

Each electron in an atom is described by four different **quantum numbers**. The first three (n, l, m_l) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital.

1. **<u>Principal Quantum Number</u> (n): $n = 1, 2, 3, \ldots, 8$.**
   Specifies the **energy** of an electron and the **size** of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot). All orbitals that have the same value of n are said to be in the same **shell** (**level**). For a hydrogen atom with n=1, the electron is in its *ground state*; if the electron is in the n=2 orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2.

2. **<u>Angular Momentum (Secondary, Azimunthal) Quantum Number</u> (l): $l = 0, \ldots, n-1$.**
   Specifies the **shape** of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called **subshells** (**sublevels**). Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3	4	5	. . .
Letter	*s*	*p*	*d*	*f*	*g*	*h*	. . .

   The subshell with n=2 and l=1 is the 2*p* subshell; if n=3 and l=0, it is the 3*s* subshell, and so on. The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l (s < p < d < f).

3. **<u>Magnetic Quantum Number</u> (m_l): $m_l = -l, \ldots, 0, \ldots, +l$.**
   Specifies the **orientation in space** of an orbital of a given energy (n) and shape (l). This number divides the subshell into individual **orbitals** which hold the electrons; there are $2l+1$ orbitals in each subshell. Thus the *s* subshell has only one orbital, the *p* subshell has three orbitals, and so on.

4. Spin Quantum Number (m_s): $m_s = +½$ or $-½$.

Specifies the **orientation of the spin axis** of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

The **Pauli exclusion principle** (Wolfgang Pauli, Nobel Prize 1945) states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**.

Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be **paired**. These substances are not attracted to magnets and are said to be **diamagnetic**. Atoms with more electrons that spin in one direction than another contain **unpaired** electrons. These substances *are* weakly attracted to magnets and are said to be **paramagnetic**.

Table of Allowed Quantum Numbers

n	*l*	m_l	Number of orbitals	Orbital Name	Number of electrons
1	0	0	1	1*s*	2
2	0	0	1	2*s*	2
	1	-1, 0, +1	3	2*p*	6
3	____	____________	____	____	____
	____	____________	____	____	____
	____	____________	____	____	____
4	____	____________	____	____	____
	____	____________	____	____	____
	____	____________	____	____	____
	____	____________	____	____	____
5	____	____________	____	____	____
	____	____________	____	____	____
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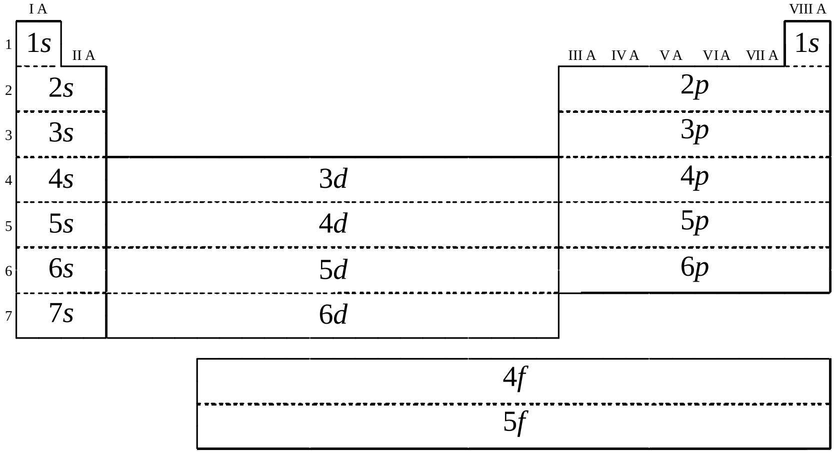
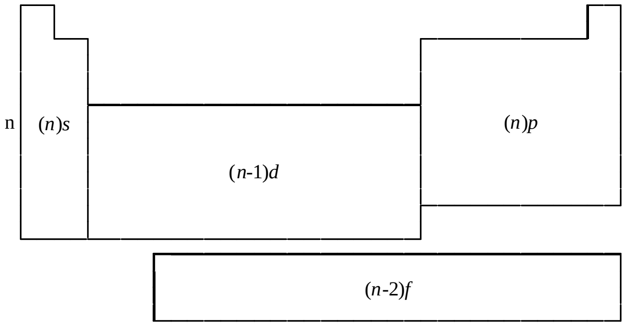
Writing Electron Configurations

The distribution of electrons among the orbitals of an atom is called the **electron configuration**. The electrons are filled in according to a scheme known as the **Aufbau principle** ("building-up"), which corresponds (for the most part) to increasing energy of the subshells:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

It is not necessary to memorize this listing, because the order in which the electrons are filled in can be read from the periodic table in the following fashion:





In electron configurations, write in the orbitals that are occupied by electrons, followed by a superscript to indicate how many electrons are in the set of orbitals (e.g., H $1s^1$)

Another way to indicate the placement of electrons is an **orbital diagram**, in which each orbital is represented by a square (or circle), and the electrons as arrows pointing up or down (indicating the electron spin). When electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible (**Hund's rule**).

In a **ground state** configuration, all of the electrons are in as low an energy level as it is possible for them to be. When an electron absorbs energy, it occupies a higher energy orbital, and is said to be in an **excited state**.

Properties of Monatomic Ions

The electrons in the *outermost shell* (the ones with the highest value of *n*) are the most energetic, and are the ones which are exposed to other atoms. This shell is known as the **valence shell**. The inner, *core* electrons (*inner shell*) do not usually play a role in chemical bonding.

Elements with similar properties generally have similar outer shell configurations. For instance, we already know that the alkali metals (Group I) always form ions with a +1 charge; the "extra" s^1 electron is the one that's lost:

IA	Li	$1s^22s^1$	Li^+	$1s^2$
IA	Na	$1s^22s^22p^63s^1$	Na^+	$1s^22s^22p^6$
IA	K	$1s^22s^22p^63s^23p^64s^1$	K^+	$1s^22s^22p^63s^23p^6$

The next shell down is now the outermost shell, which is now full — meaning there is very little tendency to gain or lose more electrons. The ion's electron configuration is the same as the nearest noble gas — the ion is said to be **isoelectronic** with the nearest noble gas. Atoms "prefer" to have a filled outermost shell because this is more electronically stable.

- The Group IIA and IIIA metals also tend to lose all of their valence electrons to form cations.

IIA	Be	$1s^22s^2$	Be^{2+}	$1s^2$
IIA	Mg	$1s^22s^22p^63s^2$	Mg^{2+}	$1s^22s^22p^6$
IIIA	Al	$1s^22s^22p^63s^23p^1$	Al^{3+}	$1s^22s^22p^6$

- The Group IV and V metals can lose either the electrons from the *p* subshell, or from both the *s* and *p* subshells, thus attaining a **pseudo-noble gas configuration**.

IVA	Sn	$[Kr]\ 4d^{10}5s^25p^2$	Sn^{2+}	$[Kr]\ 4d^{10}5s^2$
			Sn^{4+}	$[Kr]\ 4d^{10}$
IVA	Pb	$[Xe]\ 4f^{14}5d^{10}6s^26p^2$	Pb^{2+}	$[Xe]\ 4f^{14}5d^{10}6s^2$
			Pb^{4+}	$[Xe]\ 4f^{14}5d^{10}$
VA	Bi	$[Xe]\ 4f^{14}5d^{10}6s^26p^3$	Bi^{3+}	$[Xe]\ 4f^{14}5d^{10}6s^2$
			Bi^{5+}	$[Xe]\ 4f^{14}5d^{10}$

- The Group IV - VII non-metals gain electrons until their valence shells are full (8 electrons).

IVA	C	$1s^22s^22p^2$	C^{4-}	$1s^22s^22p^6$
VA	N	$1s^22s^22p^3$	N^{3-}	$1s^22s^22p^6$
VIA	O	$1s^22s^22p^4$	O^{2-}	$1s^22s^22p^6$
VIIA	F	$1s^22s^22p^5$	F^-	$1s^22s^22p^6$

- The Group VIII noble gases already possess a full outer shell, so they have no tendency to form ions.

VIIIA	Ne	$1s^22s^22p^6$
VIIIA	Ar	$1s^22s^22p^63s^23p^6$

- Transition metals (B-group) usually form +2 charges from losing the valence *s* electrons, but can also lose electrons from the highest *d* level to form other charges.

B-group	Fe	$1s^22s^22p^63s^23p^63d^64s^2$	Fe^{2+}	$1s^22s^22p^63s^23p^63d^6$
			Fe^{3+}	$1s^22s^22p^63s^23p^63d^5$

Lecture 6

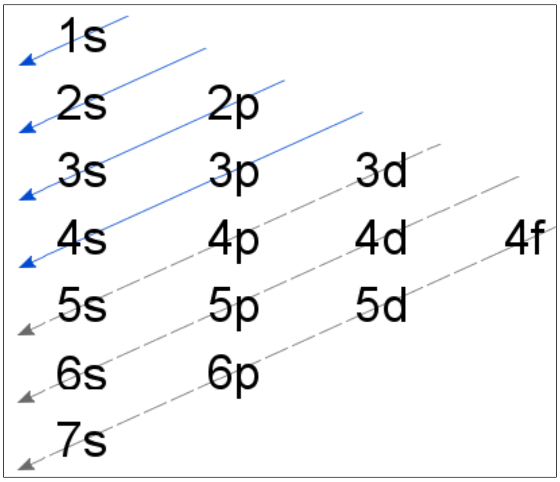
Rules related to electron filling in orbitals and shape of the orbitals

- **Aufbau Principle**: lower energy orbitals fill before higher energy orbitals.
- **Hund's Rule**: one electron goes into each until all of them are half full before pairing up.
- **Pauli Exclusion Principle**: no two electrons can be identified by the same set of quantum numbers (i.e.must have different spins).

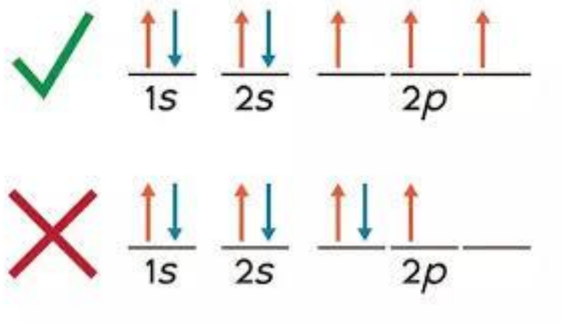
Explanation:

Let's start by explaining what each means, and then we'll talk about how they're related:

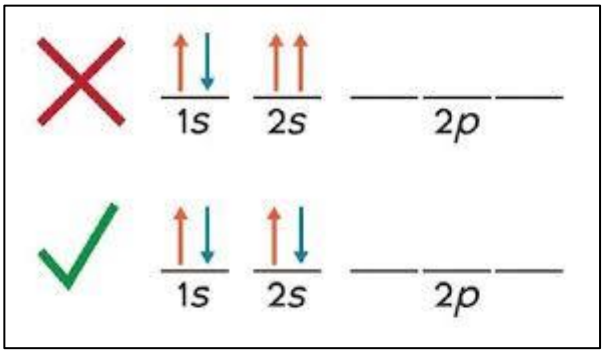
The Aufbau Principle states that lower energy orbitals fill before higher energy orbitals. For example, the orbitals in the n=1 energy level will fill up before the orbitals in the n=2 energy level.



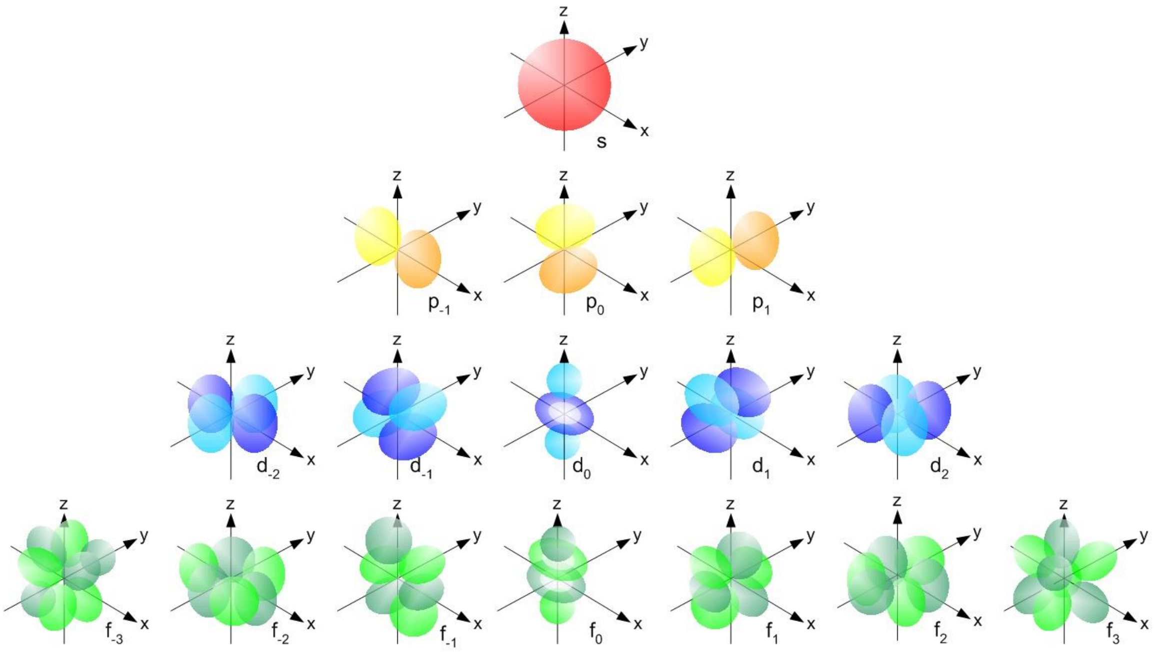
Hund's Rule states that if 2 or more degenerate (i.e. same energy) orbitals are available, *one electron goes into each until all of them are half full before pairing up* .

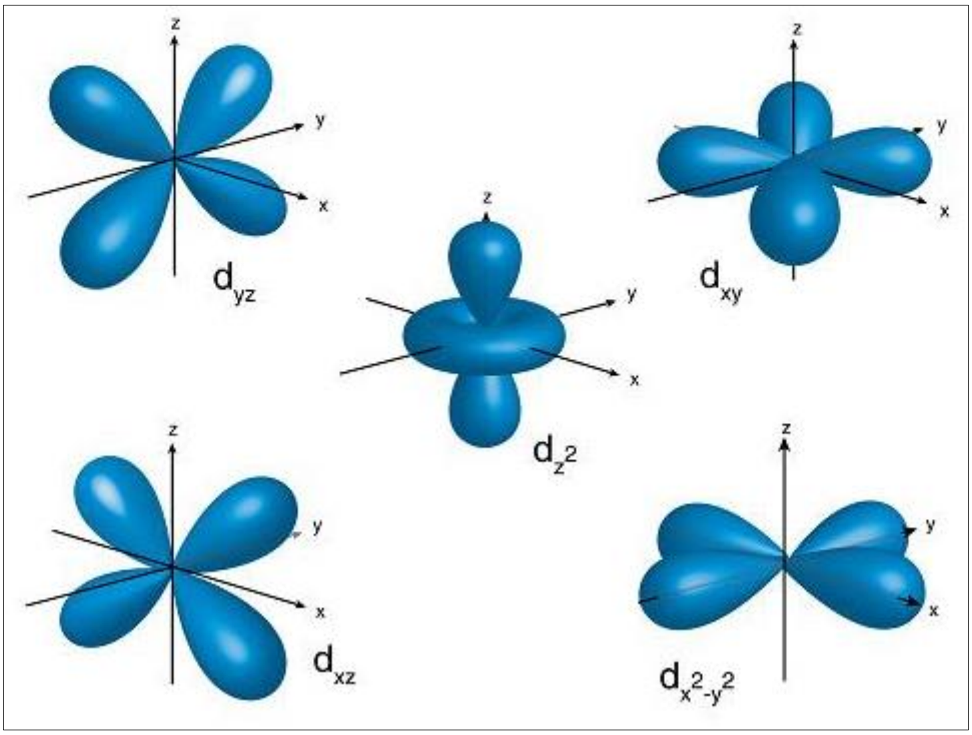


The Pauli Exclusion Principle states that *no two electrons can be identified by the same set of quantum numbers*. This is actually why we have the spin quantum number, m_s, to ensure that two electrons within the same orbital have unique sets of quantum numbers. You may also hear this in the form that the *two electrons in an orbital must have opposite spins*, which essentially means the same thing.

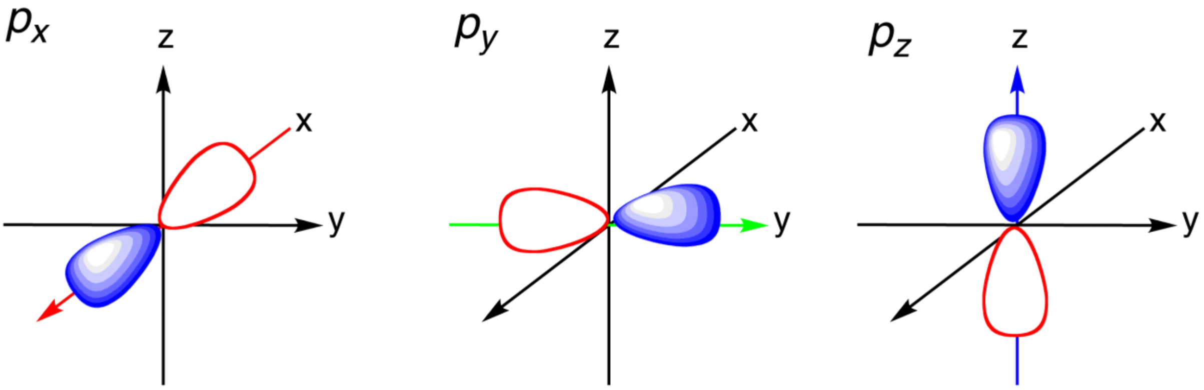


Size and Shape of the orbitals:





d-oirbitals



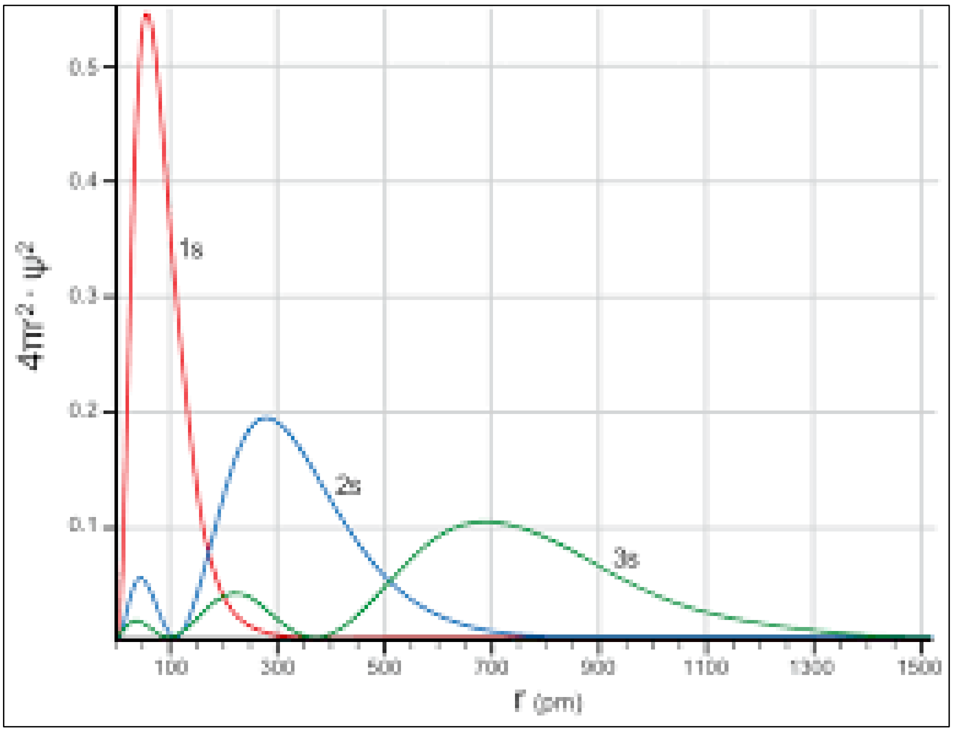
The three p orbitals are aligned along perpendicular axes

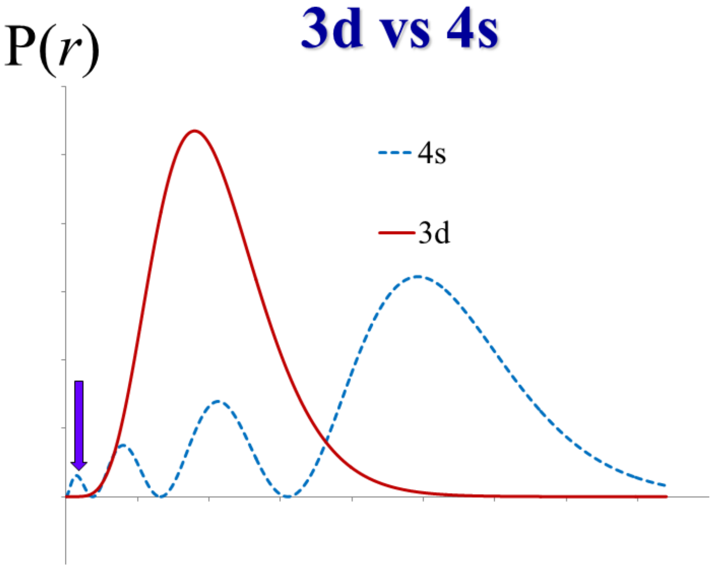
Radial Distribution Functions

When the wave function, ψ, is squared the result is a number that is directly proportional to the probability of finding and electron at specific coordinate in 3D space. The radial portions of the wave function really only tells us if there is high or low probability at various distances from the nucleus (possible radii for the electrons). Multiplying this probability by the area available at that distance will give us the *Radial Distribution Function* for the given electron. The concentric spherical shells have areas equal to the surface area of a sphere which is $4\pi r^2$.

Although the calculus/math can be very complex, we can still view these plots and easily interpret the fact that there are distinct regions outside the nucleus where there is the best chance of finding an electron with a given set of quantum numbers. Below is a plot showing the first three *s*-orbitals for the hydrogen atom (1s, 2s, and 3s). The maxima for each plot shows the distance (rr) from the nucleus for this region. Remember that in spherical coordinates, this maps to a spherical region in space. All s-orbitals are spherically symmetric.

What you need to notice: Note that the greatest probability for the 3 curves progresses to distances further away from the nucleus (nucleus is at zero). So you conclude that a 3s-orbital is slightly larger than a 2s-orbital which is slightly larger than a 1s-orbital. And, even though we don't show more orbitals, you can conclude that the trend will continue for the 4s-orbital all the way through to the 7s-orbital.




3d vs 4s