

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, ml) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital.

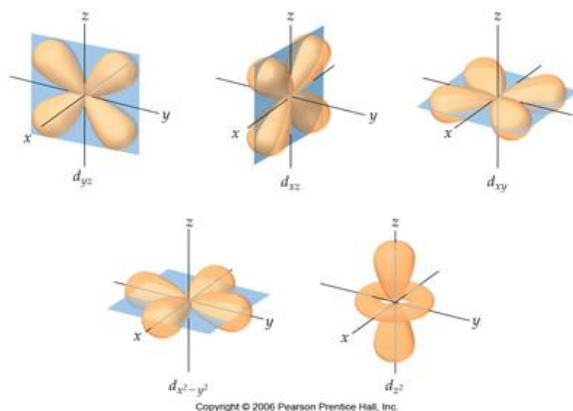
Principal Quantum Number (n): $n = 1, 2, 3, \dots, \infty$

Specifies the **energy** of an electron and the **size** of the orbital (the distance from the nucleus to the peak in a radial probability distribution plot) and also defined by the period the element is in on the periodic table. 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 .

Angular Momentum (Secondary, Azimuthal) Quantum Number (l): $l = 0, \dots, n-1$.

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 :

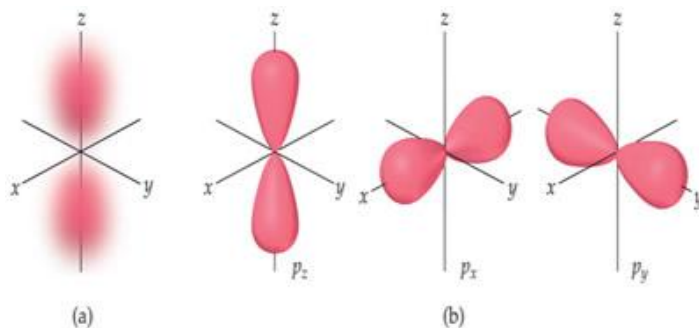
l	0	1	2	3	4	5	...
Letter	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	...



The subshell with $n=2$ and $l=1$ is the $2p$ subshell; if $n=3$ and $l=0$, it is the $3s$ 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 ($s < p < d < f$).

Magnetic Quantum Number (ml): $ml = -l, \dots, 0, \dots, +l$.

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.



Spin Quantum Number (m_s): $m_s = +1/2$ or $-1/2$.

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*. This means 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**. Substances with paired spins/electrons 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**. O₂ is a common example of paramagnetism.

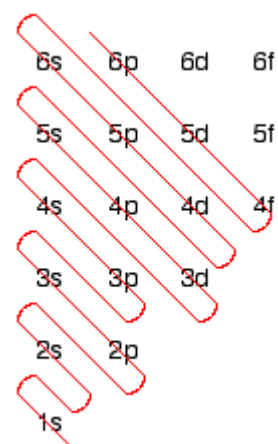
Table of Allowed Quantum Numbers

<i>n</i>	<i>l</i>	<i>ml</i>	Number of orbitals	Orbital Name	Number of electrons
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, +1	3	2p	6
3	0	0	1	3s	2
	1	-1, 0, +1	3	3p	6
	2	-2, -1, 0, +1, +2	5	3d	10
4	0	0	1	4s	2
	1	-1, 0, +1	3	4p	6
	2	-2, -1, 0, +1, +2	5	4d	10
	3	-3, -2, -1, 0, +1, +2, +3	7	4f	14

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

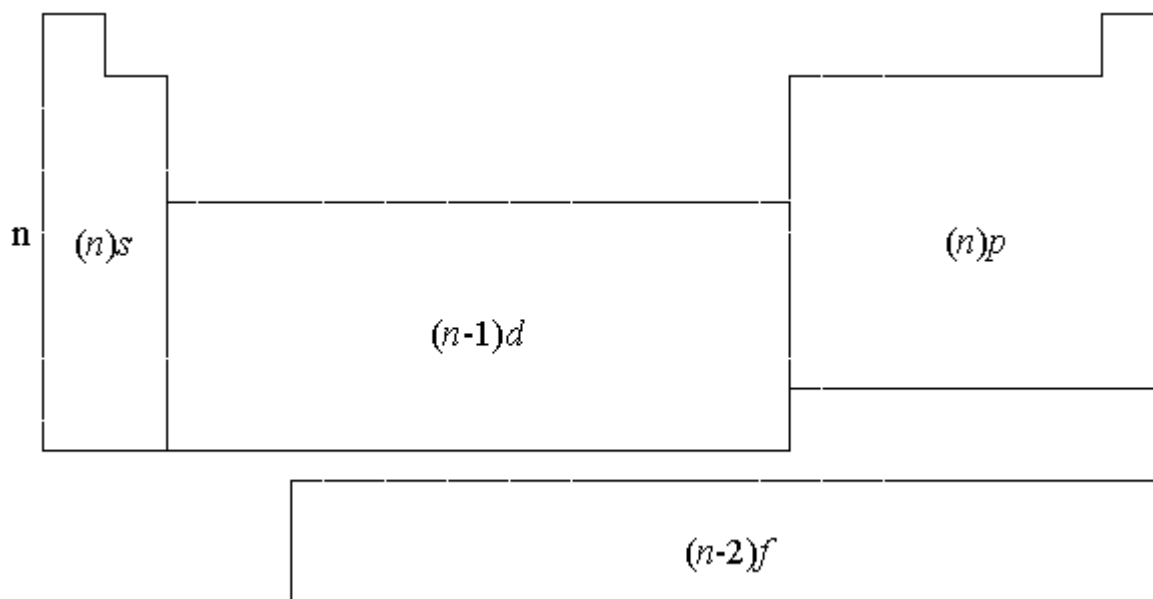


It is not necessary to memorize this listing, because the order in which the electrons are filled in can be read from the periodic table in the following fashion:

	IA								VIII A
1	$1s$	II A							$1s$
2	$2s$							$2p$	
3	$3s$							$3p$	
4	$4s$			$3d$				$4p$	
5	$5s$			$4d$				$5p$	
6	$6s$			$5d$				$6p$	
7	$7s$			$6d$					

$4f$
$5f$

Or, to summarize:



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 1s¹)

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 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 ² 2s ¹	Li ⁺	1s ²
	Na	1s ² 2s ² 2p ⁶ 3s ¹	Na ⁺	1s ² 2s ² 2p ⁶
	K	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴ 4s ¹	K ⁺	1s ² 2s ² 2p ⁶ 3s ² 3p 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 ² 2s ²	Be ²⁺	1s ²
	Mg	1s ² 2s ² 2p ⁶ 3s ²	Mg ²⁺	1s ² 2s ² 2p ⁶
IIIA	Al	1s ² 2s ² 2p ⁶ 3s ² 3p ¹	Al ³⁺	1s ² 2s ² 2p 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 ² 5p ²	Sn ²⁺	[Kr]4d ¹⁰ 5s ²
			Sn ⁴⁺	[Kr]4d ¹⁰
	Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	Pb ²⁺	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²

VA	Bi	[Xe]4f145d106s26p3	Pb4+	[Xe]4f145d10
			Bi3+	[Xe]4f145d106s2
			Bi5+	[Xe]4f145d10

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

IVA	C	1s22s22p2	C4-	1s22s22p6
VA	N	1s22s22p3	N3-	1s22s22p6
VIA	O	1s22s22p4	O2-	1s22s22p6
VIIA	F	1s22s22p5	F-	1s22s22p6

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

VIIIA	Ne	1s22s22p6
	Ar	1s22s22p63s23p6

- 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	1s22s22p63s23p63d64s2	Fe2+	1s22s22p63s23p63d6
			Fe3+	1s22s22p63s23p63d5

References

http://www.angelo.edu/faculty/kboudrea/general/quantum_numbers/Quantum_Numbers.htm

Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change, 2nd ed.* Boston: McGraw-Hill, 2000, p. 277-284, 293-307.