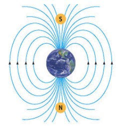
Atomic Electron Configurations and Periodicity

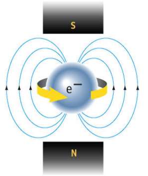
Electron Spin

The 4th quantum number is known as the “spin quantum number” and is designated by m_s. It can have the value of either + ½ or – ½

It roughly translates to refer to the spin orientation of an electron in an atom.

The spinning electron has an associated magnetic field similar to the Earth’s magnetic field.





A complete description of an electron in an atom must have four quantum numbers: n, ℓ, m_ℓ, m_s

Pauli Exclusion Principle

No two electrons in an atom can have the same set of four quantum numbers (n, ℓ, m_ℓ, and m_s).

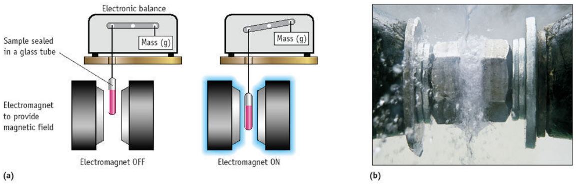
⇓ which leads to

No atomic orbital can contain more than two electrons.

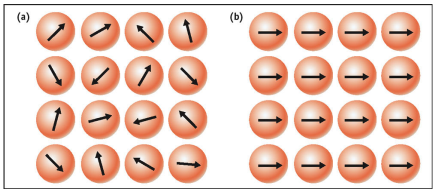
Depending on the arrangement of the electrons in an atom, the atom may be *paramagnetic* or *diamagnetic*.

Paramagnetic atoms tend to be attracted to an external magnetic field. As we will see, these atoms have one or more “unpaired” electrons in the atom.

Diamagnetic atoms are slightly repelled by an external magnetic field.



There is a third type known as ferromagnetic (iron, nickel, cobalt, neodymium, and certain alloys). These substances have permanently aligned electron spins in “domains” of the substance.



Circles represent domains. In a) (paramagnetic), the domains are not aligned until an external magnetic field is present. In b) ferromagnetic, the domains are aligned even in the absence of an external magnetic field.

There are three ways of representing the electrons in an atom.

1. Spectroscopic notation (spdf notation) given by:

$1s^22s^22p^2$, etc.

The leading numbers are the n numbers, the letters are the ℓ numbers and the superscripted number gives the total number of electrons within that suborbital.

2. Condensed spectroscopic notation given by:

$[Ne]3s^23p^4$

Only the higher energy electrons are explicitly given. The core electrons are represented by the noble gas symbol in brackets.

3. Orbital box diagrams. Given by:

Where the arrows denote m_s

Two other important rules to keep in mind besides the Pauli exclusion principle:

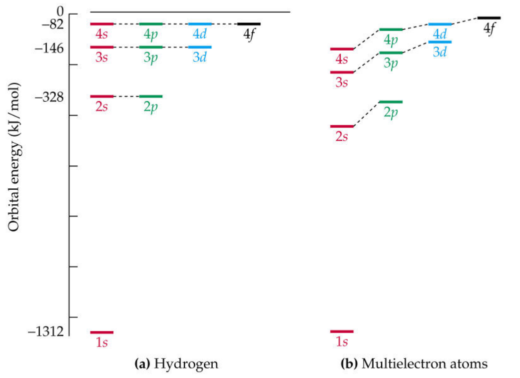
The Aufbau ("building up") principle: Electrons should be filled in using the lowest energy state possible.

Hund's Rule: When filling in electrons in a sublevel (such as the p sublevel), one electron should be placed in each orbital with parallel spin orientations before pairing them up.

Table 8.1 Number of Electrons Accommodated in Electron Shells and Subshells with $n = 1$ to 6

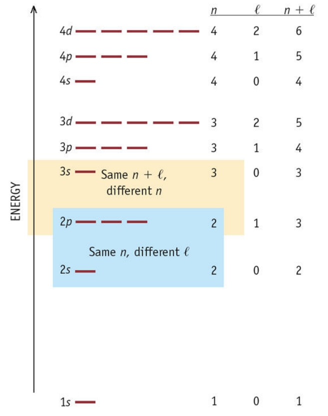
Electron Shell (n)	Subshells Available	Orbitals Available ($2\ell + 1$)	Number of Electrons Possible in Subshell [$2(2\ell + 1)$]	Maximum Electrons Possible for nth Shell ($2n^2$)
1	*s*	1	2	2
2	*s*	1	2	8
	p	3	6	
3	*s*	1	2	18
	p	3	6	
	d	5	10	
4	*s*	1	2	32
	p	3	6	
	d	5	10	
	f	7	14	
5	*s*	1	2	50
	p	3	6	
	d	5	10	
	f	7	14	
	*g**	9	18	
6	*s*	1	2	72
	p	3	6	
	d	5	10	
	f	7	14	
	*g**	9	18	
	*h**	11	22	

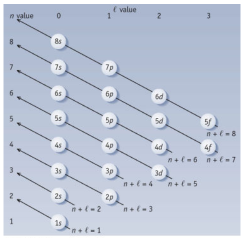
Hydrogen atom energy vs. multielectron atom energy



(a) Hydrogen

(b) Multielectron atoms



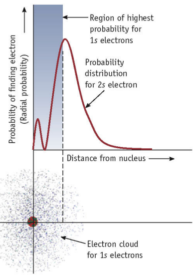


When filling orbitals of the same n+ℓ value, the lower n value is filled first

Effective Nuclear Charge Z*:

How much positive charge from the nucleus does an electron actually see?

Depends on the distance from the nucleus and shielding from other electrons.



Z* for *s* and *p* Subshells

Z* is greater for *s* electrons than for *p* electrons in the same shell. This difference becomes larger as *n* becomes larger. For example, compare the Group 4A elements.

Atom	Z* (*ns*)	Z* (*np*)	Value of *n*
C	3.22	3.14	2
Si	4.90	4.29	3
Ge	8.04	6.78	4

Table 8.2 Effective Nuclear Charges, Z*, for $n = 2$ Elements

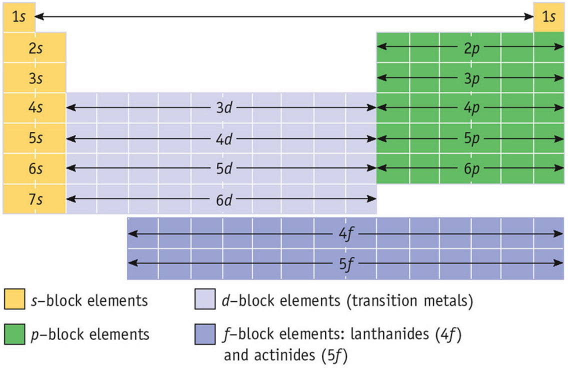
Atom	Z* (2*s*)	Z* (2*p*)
Li	1.28	
B	2.58	2.42
C	3.22	3.14
N	3.85	3.83
O	4.49	4.45
F	5.13	5.10

Example:

Give the proper spectroscopic, condensed spectroscopic and orbital box notations for the following elements:

Oxygen, Gallium and Calcium

Predict whether each is expected to be paramagnetic or diamagnetic.



Exceptions to the Aufbau principle

Note Cr and Cu

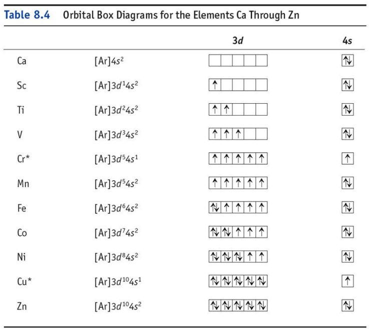


Table 8.4 Orbital Box Diagrams for the Elements Ca Through Zn

		3d	4s
Ca	[Ar]$4s^2$	☐☐☐☐☐	[↑↓]
Sc	[Ar]$3d^1 4s^2$	[↑]☐☐☐☐	[↑↓]
Ti	[Ar]$3d^2 4s^2$	[↑][↑]☐☐☐	[↑↓]
V	[Ar]$3d^3 4s^2$	[↑][↑][↑]☐☐	[↑↓]
Cr*	[Ar]$3d^5 4s^1$	[↑][↑][↑][↑][↑]	[↑]
Mn	[Ar]$3d^5 4s^2$	[↑][↑][↑][↑][↑]	[↑↓]
Fe	[Ar]$3d^6 4s^2$	[↑↓][↑][↑][↑][↑]	[↑↓]
Co	[Ar]$3d^7 4s^2$	[↑↓][↑↓][↑][↑][↑]	[↑↓]
Ni	[Ar]$3d^8 4s^2$	[↑↓][↑↓][↑↓][↑][↑]	[↑↓]
Cu*	[Ar]$3d^{10} 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑]
Zn	[Ar]$3d^{10} 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]

Electron Configurations of Ions

When cations are formed, electrons are removed from the highest n number first.

Ex. The ground state electron configuration for zinc is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$.
When it becomes a 2+ ion, the electrons are removed from the 4s sublevel to become
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$.

All common transition metal cations have electron configurations of the general type
[noble gas core]$(n-1)d^x$.
In the process of ionization, the ns electrons are lost first.

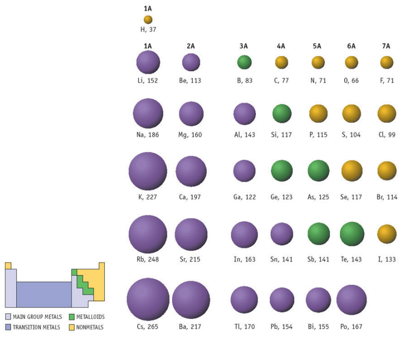
The paramagnetic properties of transition metal ions can provide clues as to which sublevel the electrons are removed from.

Example:

Depict the electron configurations for V^{2+}, V^{3+}, and Co^{3+}. Use orbital box diagrams and noble gas notation. Are any of the ions paramagnetic? If so, give the number of unpaired electrons.

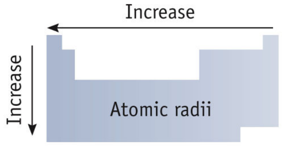
Atomic Properties and Period Trends

Atomic Radii



The trend for the sizes of the atoms on the periodic table is influenced by two factors:

a. As you work your way across a row (period) on the periodic table you are filling up electrons within the same principal energy level, which means that the electrons are all being added to approximately the same distance away from the nucleus. As this is occurring, each successive element is also adding more positively charged protons to the nucleus, thus increasing the force on each electron. The combined effect causes the electrons to be pulled closer to the nucleus as you move across the row and the radius gets smaller.



b. As you work your way down a column (group or family), the principal energy level is increasing for each successive element. This means that the average distance from the nucleus is also increasing. This is similar to the different layers of an onion. Also, there are more core electrons (electrons between the valence electrons and the nucleus) causing the repulsion on the outer electrons to be greater and the pull from the nucleus to be weaker. These combined effects cause the radius to increase as you move down the group.

In summary, although there are some exceptions, the general rule for atomic radii is that:

The atomic radii of the elements decrease as you go right and up on the periodic table.

Generally speaking, a jump up or down on the periodic table has a larger effect on the atomic radii that a jump to the left or right.

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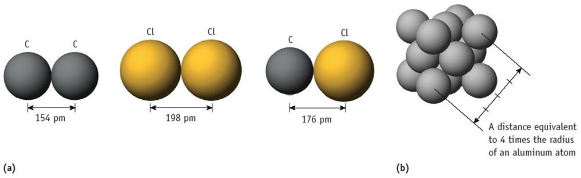
a) Using ½ the internuclear distance between atoms in a diatomic molecule allows approximate atomic radii to be determined.

b) Knowing the arrangement of atoms in a metallic crystal allows determination of the radii of metals.



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Ionization Energy: The energy required to remove an electron from an atom in the gas phase.

$$\text{Atom in ground state}_{(g)} \rightarrow \text{Atom}^{+}_{(g)} + e^{-}$$

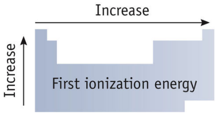
$$\Delta E = \text{ionization energy, IE}$$

All ionization energies are endothermic.

It is more difficult (i.e. higher ionization energy) to remove electrons from stable and semi-stable electron configured atoms.

Such As:

Filled Sublevel, half-filled sublevel or noble gas configuration. Also IE increases for each successive electron removed from an atom (build up of surplus positive charge.)



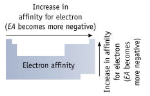
Electron Affinity (EA): The energy involved in the process of an atom (in its gas phase) gaining an electron. Values range from 0 (for atoms that do not form stable anions in their gas phase) to large negative numbers (indicating a high "affinity" or attraction for electrons). The larger the negative number, the more exothermic the process is.

$$A_{(g)} + e^{-} \rightarrow A^{-}_{(g)} \quad \Delta E = \text{Electron affinity.}$$

Units: J/atom or more commonly kJ/mol.

Based on the definitions of EA and IE, elements with high ionization energies generally have high electron affinities.

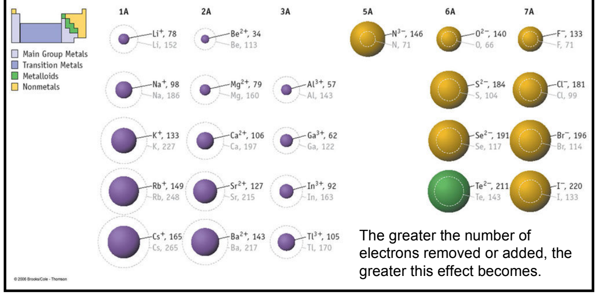
The general trend is that *electron affinity increases to the right and up on the periodic table* (i.e. the values become more negative.), however it should be noted that there are *many* exceptions to this trend.



Radius of Ions:

Anions will always have radii that are larger than their neutral atom (increased repulsive electron forces).

Cations will always have radii that are smaller than their neutral atom (increased effective nuclear charge).



The greater the number of electrons removed or added, the greater this effect becomes.

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