Electronic Structure and Periodic Properties

C020

Electron Orbitals

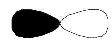
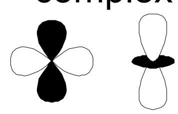
- The properties of elements result from the **electronic structure** of the atom
- Each electron in an tom is in an **orbital** of fixed energy; that is the orbitals are said to be **quantized**
- Each electron is described by **3 quantum numbers**

i) Principle quantum number n:

n = 1,2,3, …. This quantum number determines the energy of the orbital

ii) **Angular momentum quantum number, ℓ:**

ℓ = 0, 1, 2, …., n-1 This quantum number determines the shape of various orbitals having the energy of quantum number n

ℓ	orbital name	shape
0	s	spherical
1	p	dumbbell 
2	d	complex 
3	f	complex

iii) Magnetic quantum number m_ℓ:

$m_\ell = -\ell, \ldots, 0, \ldots +\ell$ in integer steps.

This quantum number determines the number of orbitals of shape ℓ and energy n = $(2\ell + 1)$

∴ For a given n

orbital name	# of orbitals
s	1
p	3
d	5
f	7

iv) **Electron spin quantum number, m_s:**

Electrons act as though they have an intrinsic **spin** which gives them a magnetic moment

Thus, unpaired electrons are acted on by magnetic fields and are said to be **paramagnetic**
substances that are unaffected by magnetic fields are said to be **diamagnetic**

The two possible spin values for an electron are a consequence of the electron spin quantum number m_s where $m_s = \pm \frac{1}{2}$

These spins are often labeled "up" (↑) and "down" (↓) (although this is actually incorrect; electron spin doesn't depend on coordinates!)

A maximum of 2 electrons can occupy each electron orbital, and then, only when their spins are **paired:**

$\boxed{\uparrow\downarrow}$

This is a consequence of the **Pauli Exclusion Principle**:

only 2 electrons maximum can be in any given atomic orbital;

two electrons in the same orbital can not have the same quantum numbers

The maximum number of electrons for any principle quantum number n, is given by $2n^2$.

For example: if $n = 2$, $2n^2 = 2(2)^2 = 8$: 2 in the one s-orbital + 6 in the three p-orbitals

Shape of the orbitals

In quantum mechanics the "shape" of an orbital is defined as 90% probability maps of where spatially one could expect to find the electron in question.

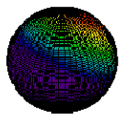
It says nothing about the actually motion (trajectory) of the electron.

We don't indicate 100% probability maps because if the electron exists it must be in the universe somewhere and that's too big to draw!

Luckily, electrons tend to stick "close" to the nucleus!

i) s-orbital

If $\ell = 0$, $m_\ell = 0$ which means there can only be 1 s-orbital for any given principle quantum number n.

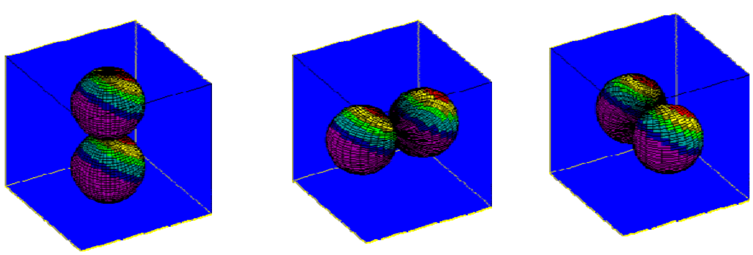


Notation: if, for example the s-orbital for n = 2 has just one electron we denote this by writing: $2s^1$. If it has two electrons (with opposite spins) then $2s^2$.

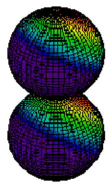
ii) p-orbitals

For a given n, if $\ell = 1$, $m_\ell = +1, 0, -1$.

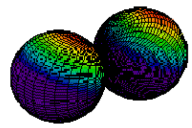
Note the rules indicate that there are no p-orbitals for n = 1 since $\ell_{max} = n-1$.



$\ell = 1$, $m_\ell = 0$ $\ell = 1$, $m_\ell = 1$ $\ell = 1$, $m_\ell = -1$



$\ell = 1$, $m_\ell = 0$

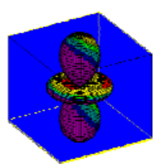


$\ell = 1$, $m_\ell = +1$ or -1

iv) d-orbitals

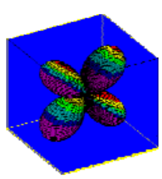
For a given n, if $\ell = 2$, $m_\ell = +2, +1, 0, -1, -2$.

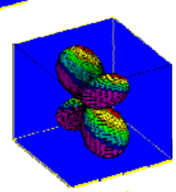
Note the rules indicate that there are no d-orbitals for n = 1 and 2 since $\ell_{max} = n-1$.



$\ell = 2$, $m_\ell = 0$

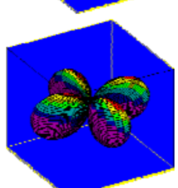
$\ell = 2$, $m_\ell = 1$

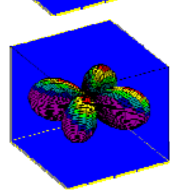




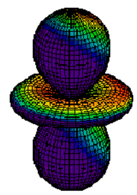
$\ell = 2$, $m_\ell = -1$

$\ell = 2$, $m_\ell = 2$

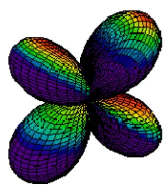




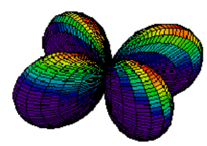
$\ell = 2$, $m_\ell = -2$



$\ell = 2, m_\ell = 0$



$\ell = 2, m_\ell = 1$ or -1

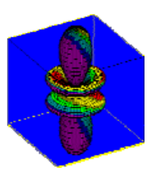


$\ell = 2, m_\ell = 2$ or -2

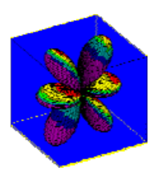
v) f-orbitals

For a given n, if $\ell = 3$, $m_\ell = +3, +2, +1, 0, -1, -2, -3$.

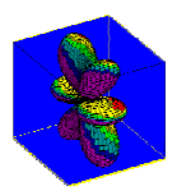
Note the rules indicate that there are no f-orbitals for n = 1, 2, and 3 since $\ell_{max} = n-1$.



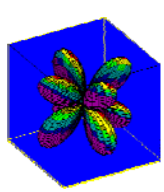
$\ell = 3, m_\ell = 0$



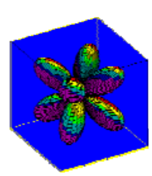
$\ell = 3, m_\ell = 1$



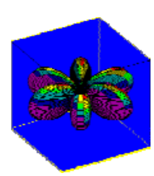
$\ell = 3, m_\ell = -1$



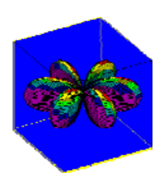
$\ell = 3, m_\ell = 2$



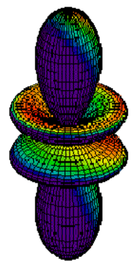
$\ell = 3, m_\ell = -2$



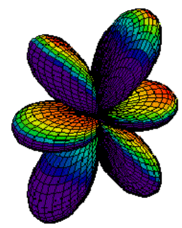
$\ell = 3, m_\ell = 3$



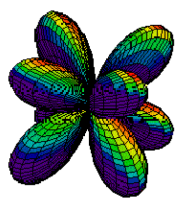
$\ell = 3, m_\ell = -3$



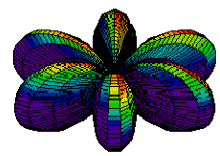
$\ell = 3$, $m_\ell = 0$



$\ell = 3$, $m_\ell = 1$ or -1



$\ell = 3$, $m_\ell = 2$ or -2



$\ell = 3$, $m_\ell = 3$ or -3

Electronic Configuration of the Elements

As the number of electrons increases with the number of protons of a **neutral atom**, they occupy orbitals of increasing energy:

The possibilities are:

Energy ↓

n	ℓ	m_ℓ	m_s	name	max # e^-	$2n^2$
1	0	0	±½	1s	2	2
2	0	0	±½	2s	2	
	1	-1,0,+1	±½	2p	6	8
3	0	0	±½	3s	2	
	1	-1,0,+1	±½	3p	6	18
	2	-2,-1,0,+1,+2	±½	3d	10	
4	0	0	±½	4s	2	
	1	-1,0,+1	±½	4p	6	32
	2	-2,-1,0,+1,+2	±½	4d	10	
	3	-3,-2,-1,0,+1,+2,+3	±½	4f	14	
…	…	…	…	…	…	

For orbital energies:
n = 4 > n = 3 > n= 2 > n = 1
and for ℓ:
f > d > p > s

In general for orbital energies:

1) Orbital energies increase with increasing (n+ℓ)

2) For (n+ℓ) of equal value, that of lower n is more stable

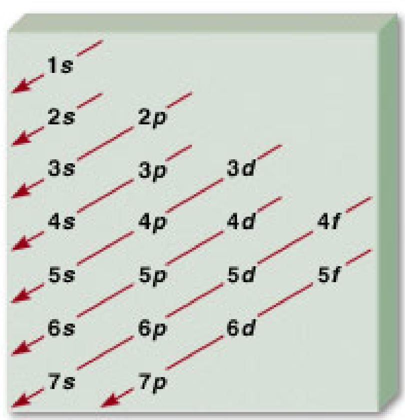
For example:

4s n = 4ℓ = 0 n+ℓ = 4
3d n = 3ℓ = 2 n+ℓ = 5

$\therefore$ Order of energy is 3d > 4s ≡ "(n+ℓ)" rule

A simple guide to the order in which electrons fill orbitals is:

Order in Which Atomic Subshells are Filled



Since each orbital can hold a maximum of $2e^-$, it is possible to construct the electronic configuration of elements as follows:

Example: for $^{13}Al = 1s^2 2s^2 2p^6 3s^2 3p^1 \equiv 13\ e^-$

Here $1s^2$ means 2 electrons in the 1s orbital; $2p^6$ means 6 electrons in the 2p orbitals, etc.

This notation is termed **spectroscopic notation**

A shorter form of the notation gives the symbol for the rare gas whose configuration is identical to that of the closed shells of an element

$\therefore$ for ^{13}Al above: $1s^2 2s^2 2p^6 \equiv$ configuration for ^{10}Ne

$\therefore$ notation becomes $^{13}Al = [Ne]3s^2 3p^1$

Note: electrons in the orbital of highest n are called **valence electrons**; the rest are **core electrons**

If you wish to illustrate orbitals occupied by electrons more clearly you can use an **orbital box** diagram:

Example: $^{13}Al \equiv$

1s	2s	2p			3s	3p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		

Question: Use spectroscopic notation to describe the electron configuration for ^{50}Sn.
What are the quantum numbers of the highest energy electron?

$^{50}Sn = [1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6] 5s^2 4d^{10} 5p^2$

$= [Kr]5s^2 4d^{10} 5p^2$

Main question is how to distribute the 2 highest energy e^- in the 3 5p-orbitals.

Filling of orbitals to give ground state configurations follows **Hund's Rule.**

Hund's rule states that electrons occupy orbitals of equal energy in such a way that the number of unpaired electrons is at a maximum, thus minimizing inter-electronic repulsion

For ^{50}Sn this means $5p^2 \equiv$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

but not: $\boxed{\uparrow\downarrow}\boxed{}\boxed{}$ or $\boxed{\uparrow}\boxed{}\boxed{\downarrow}$

$\therefore$ quantum numbers of the highest energy electron are n = 5, ℓ = 1, m_ℓ = -1, 0, or +1, m_s = +½ or -½

Note : 3d/4s and 4d/5s orbitals are very close in energy.
Therefore, sometimes the scheme does not work for transition metals.

Consider the electronic configuration of ^{24}Cr

Might expect electronic configuration = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
=$[Ar]4s^2 3d^4$

Not the case.
Instead it is energetically favorable to have both the 3d and 4s orbitals half filled to minimize electron repulsions.
≡ Hund's Rule

Similarly complete 3d orbitals are favorable eg ^{29}Cu.
The energy of 3d falls below that of 4s because of the increased nuclear charge.
Electronic configuration of ^{29}Cu = $[Ar]4s^1 3d^{10}$

Cu and Cr belong to the first series of the transition metals.
Second series metals behave similarly.

Atomic Ions

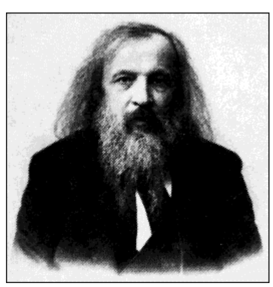
When an atom loses electrons to for a cation, the electrons are always lost from the valence shale of **highest n**

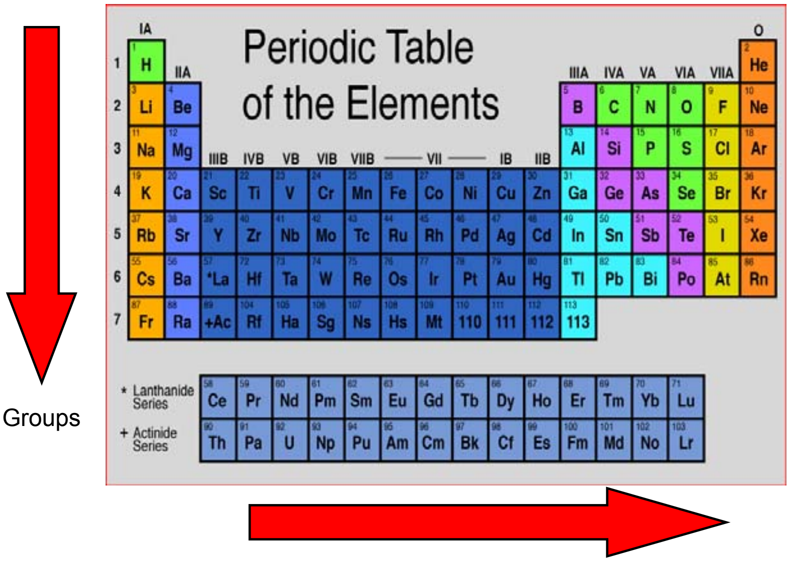
Thus, for transition metals, the electrons remaining over the noble gas core are always found in the 3d orbitals

The Periodic Table

When the elements are grouped together on the basis of their physical and chemical properties, they fall into groups illustrated by the **periodic table**

First devised by D. Mendeleev long before the advent of quantum theory





Groups

Periods

20th century chemistry has shown that these groups have **similar electronic configurations**

This demonstrating that the behavior of the elements is a consequence of the **number and configuration of their electrons only**:

The atomic nucleus is unimportant chemically

The electrons that are the most important in determining the properties of an element are those in the **highest energy**, **incompletely filled orbitals**:

≡ the **valence electrons**

Main group elements are those with s or p subshells being filled, with other subshells being full or empty

Those with d orbitals being filled are termed **transition metal** elements. Each d subshell holds 10 electrons

Elements in the f-block are those with f-orbitals being filled.
These orbitals hold 14 electrons.
The elements with the 4f orbitals being filled are called the **lanthanides**
Those with the 5-f orbitals being filled are called the **actinides**

Since elements in any one group have the same number of valence electrons, it is no surprise that they have similar chemical properties

Group 1A Alkali metals valence config. = $\mathbf{ns^1}$
Li, Na, K, Rb, Cs, Fr

Group 2A Alkaline Earths valence config. = $\mathbf{ns^2}$
Be, Mg, Ca, Sr, Ba, Ra

Group 3A (13) valence config. = $\mathbf{ns^2np^1}$
B, Al, Ga, In, Tl

Group 4A (14) valence config. = $\mathbf{ns^2np^2}$
C, Si, Ge, Sn, Pb

Group 5A (15) valence config. = $\mathbf{ns^2np^3}$
N, P, As, Sb, Bi

Group 6A (16) Chalcogens valence config. = $\mathbf{ns^2np^4}$
O, S, Se, Te, Po

Group 7A (17) Halogens valence config. = $\mathbf{ns^2np^5}$
F, C, Br, I, At

Group 8A (18) Noble gases valence config. = $\mathbf{ns^2np^6}$
He($1s^2$), Ne, Ar, Kr, Xe, Rn

Noble gases are extremely stable and not very reactive due to their full valence shell.

Other elements can lose or gain electron to attain the same electronic configuration as these noble gases.

For example:
K tends to give away one electron and Cl to accept one electron to attain the Ar configuration

Periodic Trends in Atomic Properties

1. Atomic Size

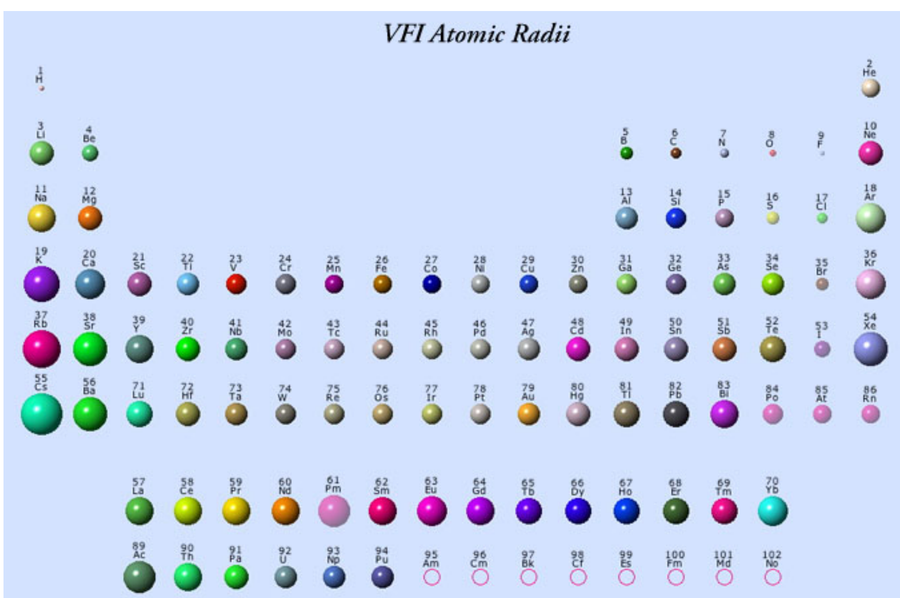
The atomic radius reflects the distance from the nucleus to the highest occupied electronic orbital.
Therefore we expect the following:

i) Atomic radii increase from top to bottom within a group.
For example: r(Li) < r(Na) < r(K) < r(Rb) < r(Cs)

ii) Atomic radii increase from left to right across a period
For example: r(Li) > r(Be > r(B) > r(C) > r(N) >r(O) > r(F)

This is because the electrons in the same n-orbital (here n = 2) are more strongly attracted to the greater number of protons in the nuclei of the heavier elements

Cations are smaller than the neutral parent atom. For example r(Li^+) < r(Li)
Anions are larger than the neutral parent atom. For example r(Cl^-) > r(Cl)



<u>**Ionization Energies**</u>

Ionization energy, IE, is the energy required to remove one electron from an atom or ion;
an **endothermic** process

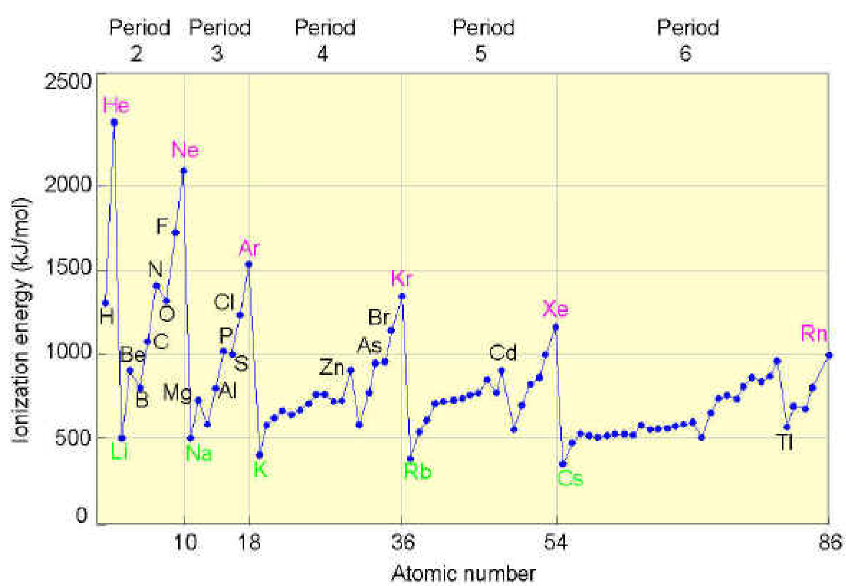
that is, $A \rightarrow A^+ + 1\ e^-$ $\Delta H = +ve$

The energy, in kJ mol^{-1}, required to remove 1 electron from the neutral atom (1st ionization limit) depends on the orbital in which the electron resides

Two general trends:

1.) IEs **decrease down a group**
(an electron removed from an orbital more distant from the nucleus is less tightly bound)

2.) IEs **increase from left to right** across a period
(electrons being removed from orbitals of equal n are subject to increasing nuclear attraction)



There are some exceptions to generality 2).

They occur whenever the removal of $1e^-$ leads to a filled or half-filled orbital.

The extra stability of filled or half-filled orbitals leads to a lower IE for those elements which are one electron away from such a state

Example: IE of B < Be
B ≡ $1s^22s^22p^1$ Be ≡ $1s^22s^2$
$2p^1$ electron more easily lost than 1 electron from the filled 2s orbital

Example: IE O < N
O ≡ $1s^22s^22p^4$ N ≡ $1s^22s^22p^3$

By losing $1e^-$ O attains half-filled 2p-orbitals

Electron Affinities

Electron affinity, EA, is the energy change that results from the **capture of an electron** by a neutral atom

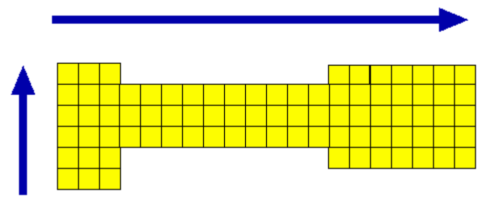
that is, $A + e^- \rightarrow A^-$ EA (=ΔH which can +ve or -ve)

Again there are two general trends:

1.) EAs decrease down a group
(because e^-s are being captured in orbitals more distant from the nucleus)

2.) EAs increase across a period
(because e^-s are being captured in orbitals exposed to a greater nuclear charge)

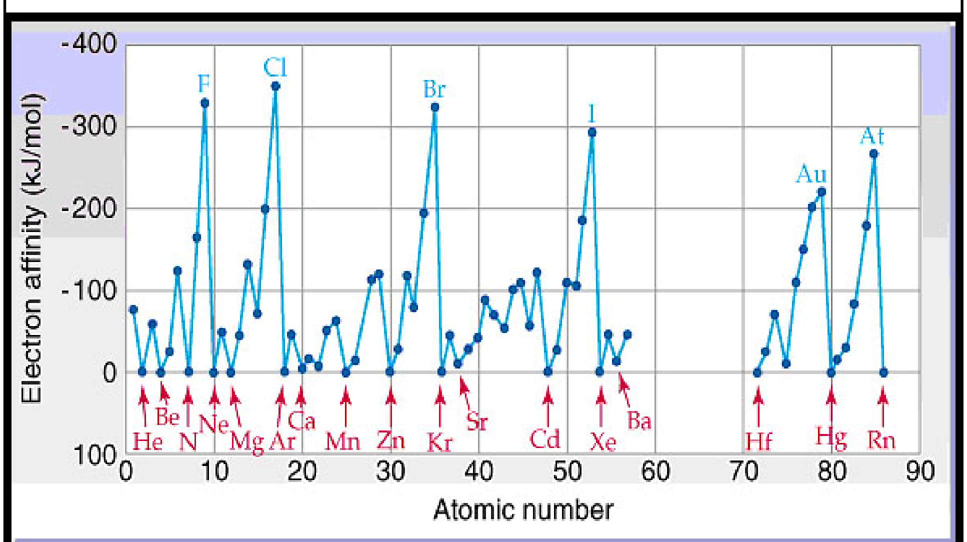
Electron Affinity Increases With Arrows



EAs are especially large (large and –ve) when capture of an e^- leads to filled or half-filled orbitals.

Example: $C + e^- \rightarrow C^-$

$C \equiv 1s^2 2s^2 2p^2$ $C^- \equiv 1s^2 2s^2 2p^3$



Electronegativity

Electronegativity is the tendency of an atom in a covalently bonded molecule to attract the bonding electron pair to itself

It follows the same trend as electron affinity;

that is, it increases going up a group and across a period.

Values are relative and not absolute

The greatest electronegativity values are found with small non-metals.

F is the most electronegative element.

Electronegativity is important in bonding because a bond between two atoms of different electronegativity is polarized, with the e^- pair closer to the more electronegative atom

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn 2.4
Fr 0.7	Ra 0.7	Ac 1.1	Unq	Unp	Unh	Uns	Uno	Une									

Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2
Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr