

Chemistry

What is the world made of?
Why does “stuff” do what it does?

Electronic Structure

Start at the bottom: Matter is made of atoms (and ions).

Properties of atoms and ions are determined by their *electronic structure* – the arrangement of the electrons.

To understand how we can know about the electronic structure of atoms, we must first learn about light.

It is through the *interaction of light and matter* that the electronic structure of atoms was elucidated.

Light

Light is an *electromagnetic wave* which carries energy. Different colors of light correspond to different *wavelengths* (and *frequencies*).

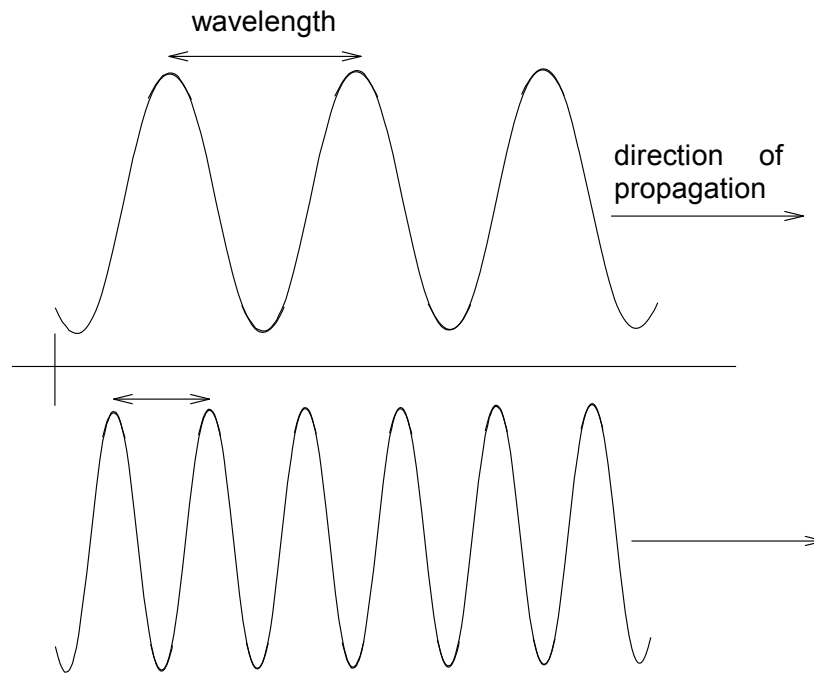
In one period, t , one wavelength passes an *observation point*. The wave travels one wavelength which equals $c \times t$, where c is the *speed of light*. Since frequency, $\nu = 1/t$,

$$c = \lambda \nu$$

Frequency, ν , is the *number of peaks* passing the observation point *per unit time*. The SI unit of frequency is Hz, ($1 \text{ Hz} = 1 \text{ s}^{-1}$).

Wavelength is the *distance between peaks* measured in m.

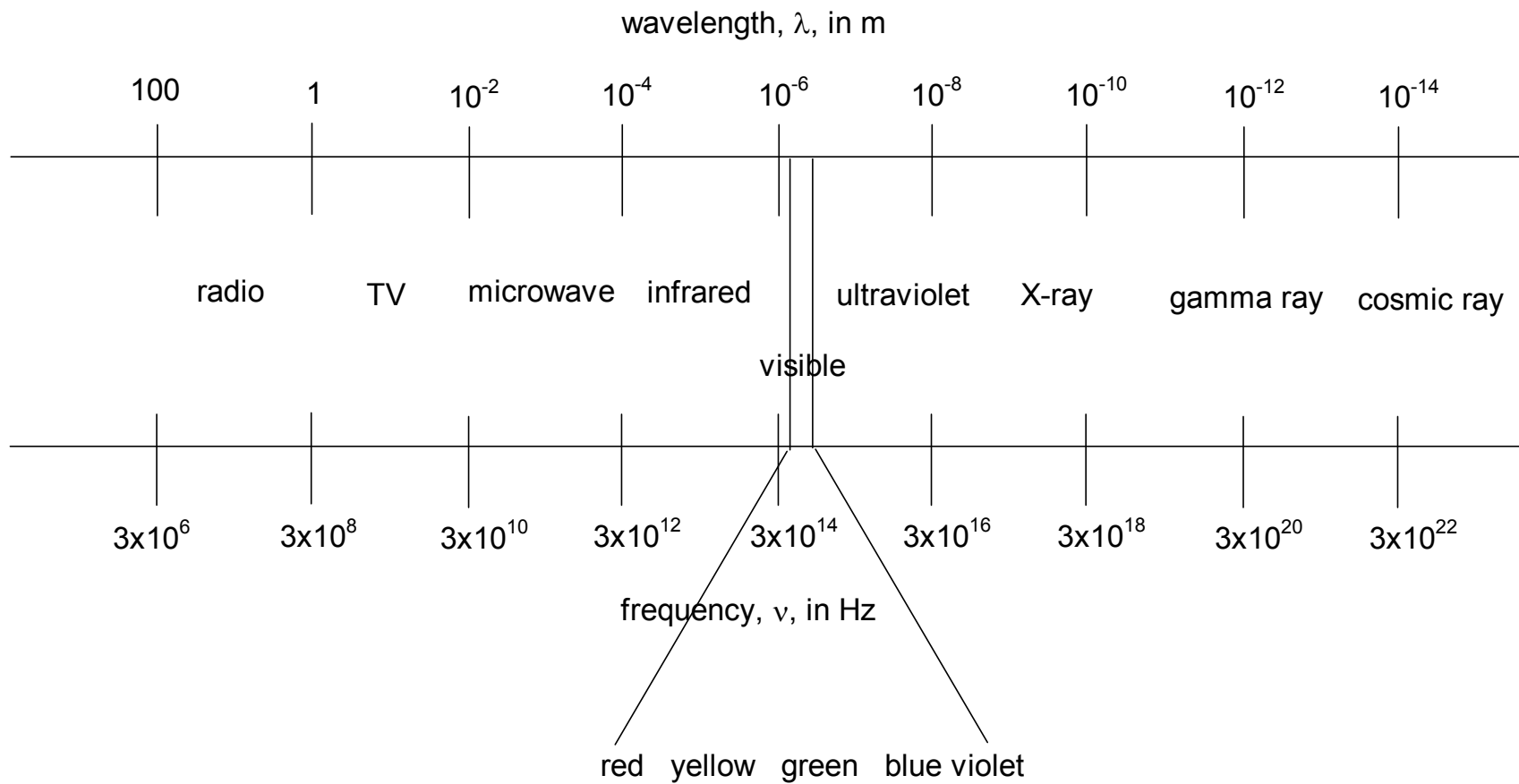
Nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$) are often used in the case of visible light.



The speed of light in a vacuum, $c = 2.9979 \times 10^8 \text{ m s}^{-1}$, is the same for all wavelengths. Consequently, wavelength and frequency have a simple reciprocal relationship.

$$\lambda = \frac{c}{\nu} \quad \text{and} \quad \nu = \frac{c}{\lambda}.$$

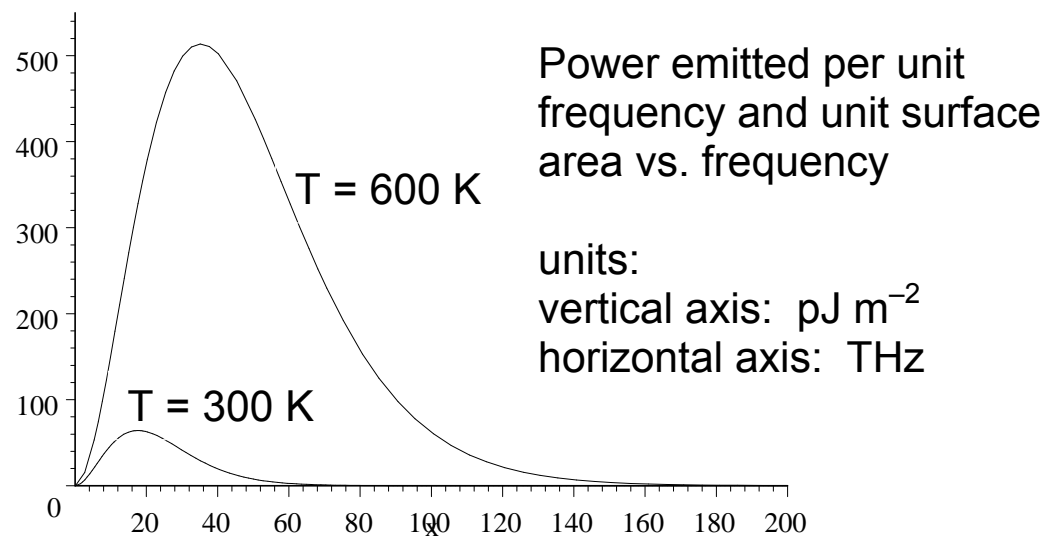
The *electromagnetic spectrum*



Blackbody Radiation

Except at absolute zero temperature, all objects emit electromagnetic radiation due to thermal energy. This is called *blackbody radiation*.

Classical wave theory could not predict the observed spectrum – the *ultraviolet catastrophe*.



Planck explained the observed spectrum – its exact shape – by postulating that light energy is quantized.

The smallest increment of light energy is the energy of a single particle of light, a *photon*.

The energy of one photon of light with frequency, ν , is given by

$$E_{\text{photon}} = h\nu \quad ,$$

where $h = 6.62606957 \times 10^{-34} \text{ J s}$ is called *Planck's constant*.

Other evidence for the particle character of light (and that of matter) comes from Einstein's explanation of the *photoelectric effect*.

Photoelectric Effect

Sufficiently high frequency photons eject electrons from the surface of a metal. The photon energy equals the energy required to eject the electron plus the kinetic energy of the ejected electron.

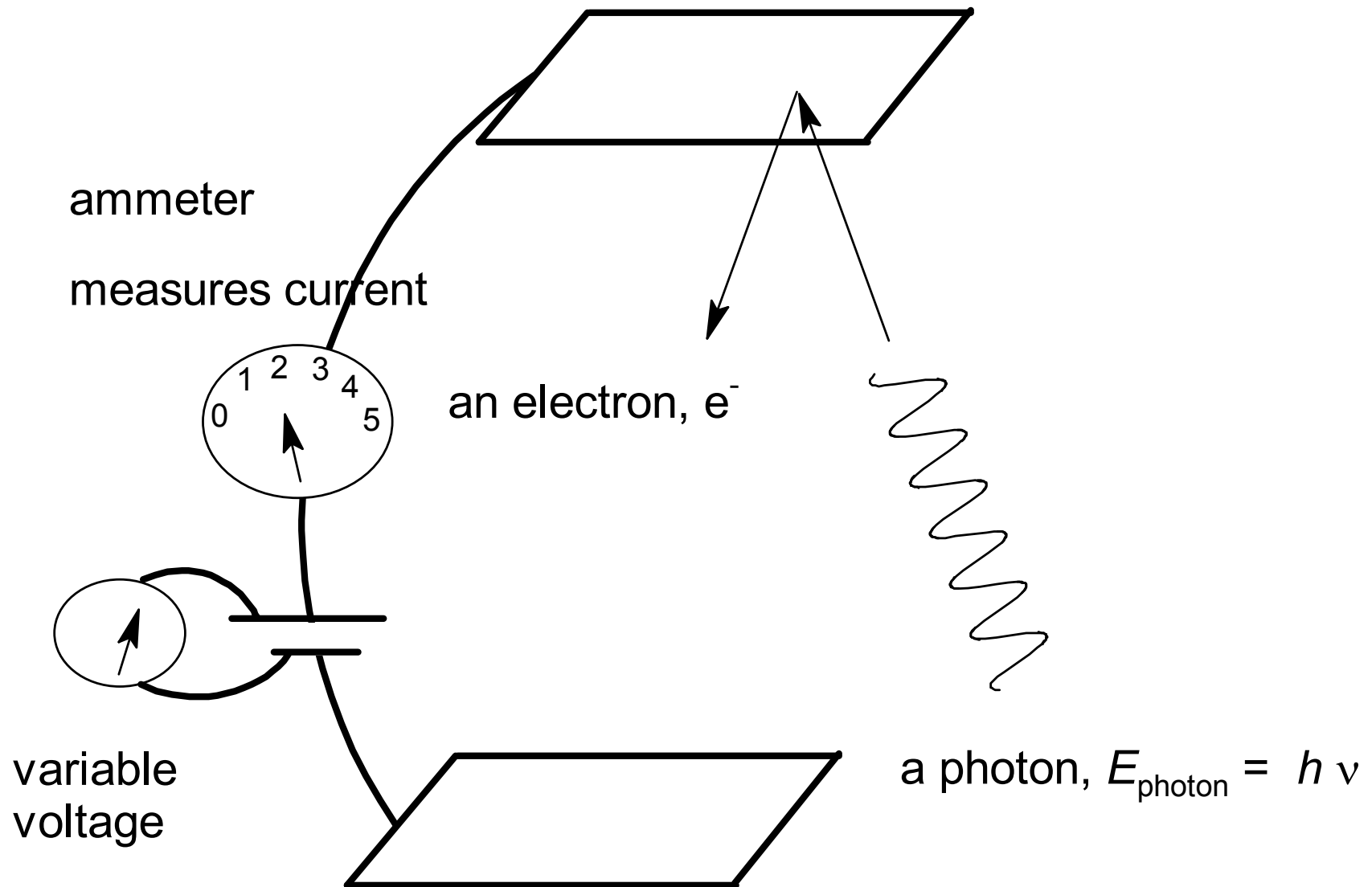
$$E_{\text{photon}} = h\nu = \frac{1}{2}mu^2 + \varphi_{\text{metal}} \quad ,$$

where m and u are the electron mass and velocity, respectively, and φ_{metal} is called the *work function* of the metal.

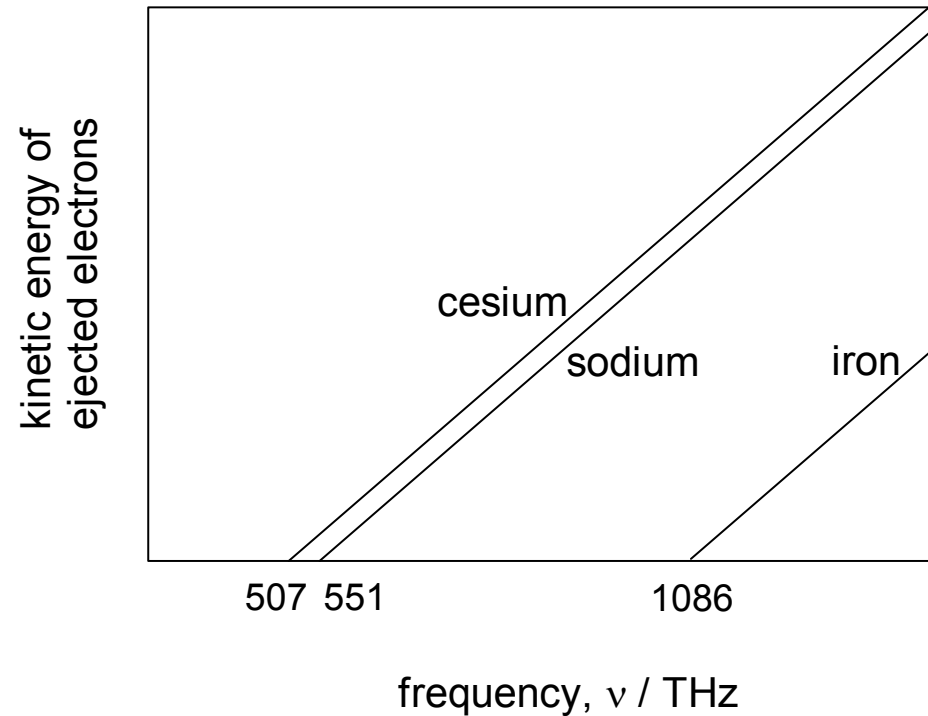
Alkali metals have the *smallest* work functions - it takes less energy to eject an electron from an alkali metal.

According to decreasing work function,

lithium > sodium > potassium > rubidium > cesium.



Observed **photoelectric effect**:



Since electron kinetic energy must be positive, there is a lowest frequency of light that can emit electrons – the threshold frequency, $\nu_{\text{thres}} = \phi_{\text{metal}} / h$.

Example: The work function for calcium is 4.64×10^{-19} J (or 279 kJ mol^{-1} – this is the energy needed to eject 1 mol of electrons).

(a) What is the threshold frequency above which calcium will exhibit the photoelectric effect?

(b) What is the kinetic energy of an electron ejected from calcium by a photon of wavelength, 300. nm?

(a) The threshold photon energy equals the work function,

$$h\nu_{\text{thres}} = \phi_{\text{calcium}} = 4.64 \times 10^{-19} \text{ J}$$

Therefore,

$$\nu_{\text{thres}} = \frac{\phi_{\text{calcium}}}{h} = \frac{4.64 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 700 \text{ THz}$$

(b) The frequency of the incident light is

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} = 999.3 \text{ THz}$$

The kinetic energy of the ejected electron is

$$\begin{aligned} E_{\text{kin}} &= \frac{1}{2} m u^2 = h\nu - \varphi_{\text{calcium}} \\ &= 6.626 \times 10^{-34} \text{ J s} \times 999 \times 10^{12} \text{ s}^{-1} - 4.64 \times 10^{-19} \text{ J} \\ &= 1.98 \times 10^{-19} \text{ J} . \end{aligned}$$

Quantum Mechanics and the Hydrogen Atom

Atoms can also absorb photons of light.

An electron can be ejected from the atom - this is called *ionization*).

For lower energy photons (i.e., lower frequency), an *excited state* of the atom can be produced.

A transition to an excited state results when the photon energy equals the difference in energy between the initial state (typically the ground state – the lowest energy state of the atom) and the excited state.

Quantum mechanics tells us that an atom has a discrete set of energy levels – i.e., only certain energies are allowed.

Quantization of energy arises from wave properties of matter described by quantum mechanics.

The *hydrogen atom* – the simplest atom with only one electron – has the simplest set of energy levels,

$$E_n = -\frac{hcR_H}{n^2}, \quad n = 1, 2, 3, \dots$$

where $R_H = 1.0974 \times 10^7 \text{ m}^{-1}$ is called the Rydberg constant, and n is called the *principal quantum number*.

The difference between two of these energies determines a *transition* energy equal to the energy of the photon emitted or absorbed. The associated transition frequency is the frequency of the photons emitted or absorbed – it is given by dividing the transition energy by h .

$$\Delta E = E_{n'} - E_n = -hcR_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) = h\nu, \quad n' > n.$$

Example:

(a) Determine the frequency of the emission lines resulting when an *excited state* with $n' = 3$ drops to the (i) $n = 2$, or (ii) $n = 1$ level. Are either of these emissions in the visible range?

(b) Of all the absorption frequencies associated with transitions between all levels up to $n = 4$, which transitions have the largest and the smallest frequencies?

(a)

$$\begin{aligned} \nu &= cR_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \\ &= 2.9979 \times 10^8 \text{ m s}^{-1} \times 1.0974 \times 10^7 \text{ m}^{-1} \times \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 457 \text{ THz} \end{aligned}$$

for $n = 2$. For $n = 1$, we have $\nu = 2924 \text{ THz}$. The first of these absorption lines is in the visible range. It corresponds to violet-blue light. In general, all transitions with n equal to 2 produce an absorption or emission line in the visible range. This series of lines is called the Balmer series. If n is 1, then the line is in the UV range. This series of lines is called the Lyman series. Other named series are the Paschen ($n = 3$) and the Brackett ($n = 4$) series, both in the infrared range.

(b) The largest transition frequency corresponds to the $n = 1$ to $n' = 4$ absorption transition - or the reverse, the $n' = 4$ to $n = 1$ emission transition. The lowest frequency corresponds to $n = 3$ to $n' = 4$ absorption or corresponding emission transition.

Orbitals of Hydrogen

Because of the spherical symmetry of the hydrogen atom (and electron spin), there is more than one *state* for each energy level.

The electron in hydrogen has an orbital angular momentum associated as it orbits about the proton nucleus.

Angular momentum has a magnitude, with associated quantum number - *angular momentum quantum number*

$$\ell = 0, 1, 2, \dots, n-1,$$

and an orientation, with associated quantum number - *magnetic quantum number*

$$m_\ell = -\ell, -\ell + 1, \dots, \ell - 1, \ell.$$

Specifying the (n, ℓ, m_ℓ) values determines an *orbital* of the hydrogen atom, which determines the state of the electron with respect to its motion about the nucleus.

For $n = 1$, there is only one ℓ value, $\ell = 0$.

For $\ell = 0$, there is only one m_ℓ value, $m_\ell = 0$. Therefore, the $n = 1$ energy level has only one orbital – the 1s orbital.

For $n = 2$, there are two ℓ values, $\ell = 0$ and 1.

For $\ell = 0$, we have only $(n, \ell, m_\ell) = (2, 0, 0)$ (the 2s orbital).

For $\ell = 1$, we have $(2, 1, -1)$, $(2, 1, 0)$ and $(2, 1, 1)$, the three 2p orbitals.

Orbitals are labeled by their principal and angular momentum quantum numbers, n and ℓ . The ℓ value is denoted by a letter (s for $\ell = 0$, p for $\ell = 1$, d for $\ell = 2$, f for $\ell = 3$, g for $\ell = 4$, ...).

In addition to the orbital quantum numbers already introduced, the electron has a *spin quantum number*,

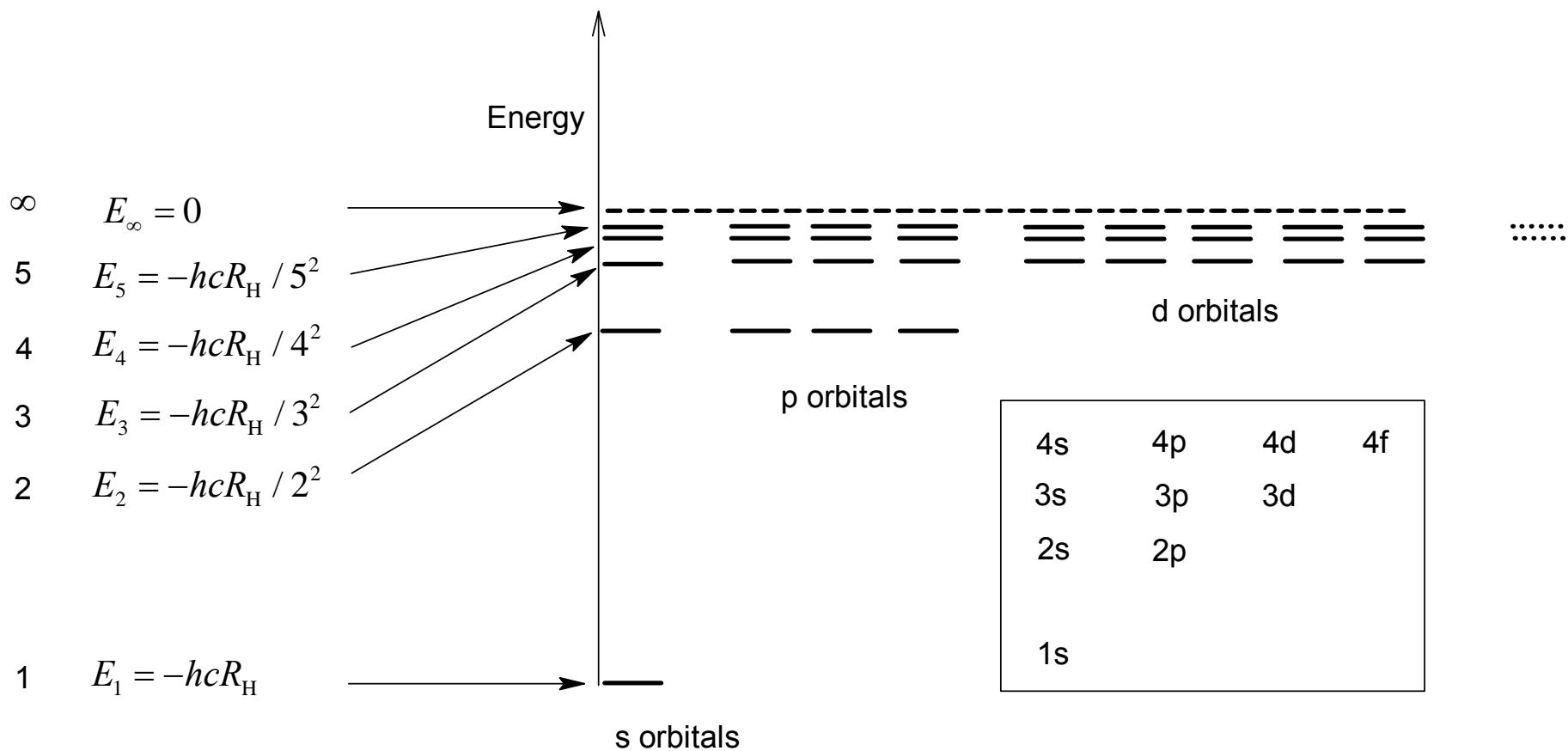
$m_s = \frac{1}{2}$ or $-\frac{1}{2}$, spin angular momentum pointing up or down, respectively.

There are two states associated with the lowest energy level:

$$(n, \ell, m_\ell, m_s) = (1, 0, 0, \frac{1}{2}) \text{ and } (1, 0, 0, -\frac{1}{2})$$

The *ground state* of hydrogen is actually two states differing only in the orientation of electron spin. All other states of hydrogen are *excited states*. If excited states are produced, they lose energy by emitting photons until the ground state is reached. Thus, in the absence of radiation exciting the hydrogen atoms, they will be in their ground state.

In general, there are two states (with opposite spin) for every orbital. Hydrogen orbitals can be arranged according to energy and angular momentum as follows:



For the hydrogen atom, the orbital energy depends *only* on the principal quantum number. The number of orbitals with energy E_n is

$$1 + 3 + 5 + \dots + 2n - 1 = n^2.$$

Numbers of orbitals and states of hydrogen

n	ℓ	<i>Number of Orbitals total</i>		<i>Number of States total</i>	
1	0	1	1	2	2
2	0	1		2	
	1	3	4	6	8
3	0	1		2	
	1	3		6	
	2	5	9	10	18
4	0	1		2	
	1	3		6	
	2	5		10	
	3	7	16	14	32

Example:

(a) Which of the following sets of quantum numbers, (n, ℓ, m_ℓ, m_s) , corresponds to an actual state of a hydrogen atom?

- (i) $(1, 0, 1, \frac{1}{2})$ (ii) $(2, 1, -1, -\frac{1}{2})$ (iii) $(2, 2, 0, -\frac{1}{2})$ (iv) $(3, 1, -1, 0)$
(v) $(3, -2, -2, \frac{1}{2})$

(b) How many orbitals are there with energy up to and including E_4 ? How many electron states are there with energy up to this value?

(a) Only $(2, 1, -1, -\frac{1}{2})$ corresponds to an actual state of hydrogen.

$(1, 0, 1, \frac{1}{2})$ violates $m_\ell \leq \ell$.

$(2, 2, 0, -\frac{1}{2})$ violates $\ell \leq n - 1$

$(3, 1, -1, 0)$ violates $m_s = \pm\frac{1}{2}$

$(3, -2, -2, \frac{1}{2})$ violates $0 \leq \ell$

(b) There are $1 + 4 + 9 + 16 = 30$ orbitals with energy up to and including E_4 . There are $2 \times 30 = 60$ electron states up to this energy.

An orbital of hydrogen corresponds to a *wave function* which (together with the spin) describes the state of the electron in the atom.

A wave function is an oscillatory function of position about the nucleus. They can be positive or negative values – or even complex.

The *square* of the wave function at each position gives the likelihood of finding the electron in that location. Where the magnitude of the wave function is largest is where the electron is likely to be.

The $\ell = 0$ orbitals have *spherical shape*.

The 1s orbital is like a spherical ball.

The 2s orbital has a single oscillation in the radial direction. It consists of a small inner sphere surrounded by a large outer spherical layer. Between these radial *lobes* is a *nodal* sphere where the wave function is zero.

The 3s orbital has two nodal spheres. The ns orbital has $n - 1$ nodal spheres.

The $\ell = 1$ orbitals have a barbell shape with two lobes – positive and negative – pointing in opposite directions along an axis. These lobes are separated by a nodal plane where the wave function is zero.

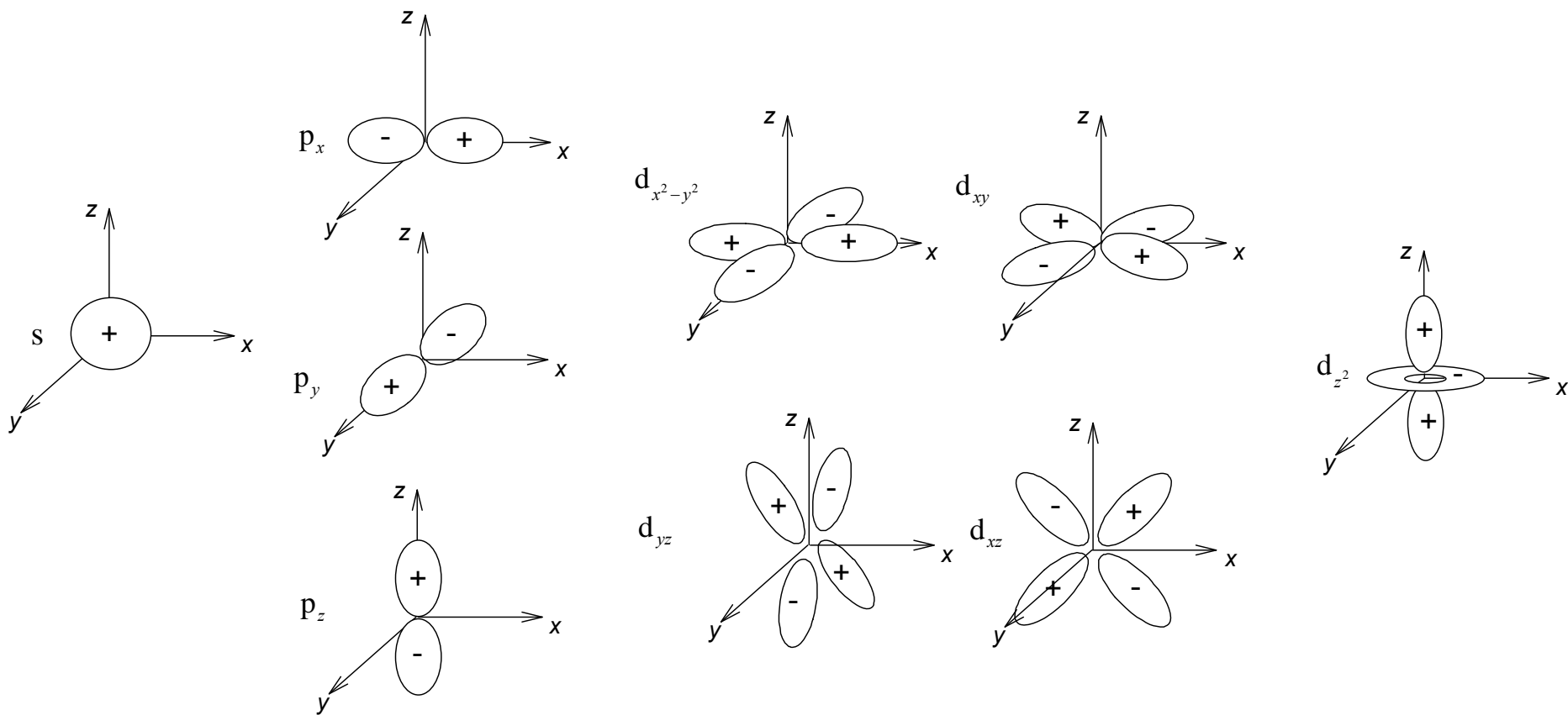
There are three np orbitals.

The $m_\ell = 0$ orbital is called np_z orbital. It is concentrated about the z axis. The xy plane is the corresponding nodal plane.

For $m_\ell = \pm 1$, the orbitals are complex valued. However, since these orbitals have identical properties (except in the presence of a magnetic field), it is admissible to form + and – combinations that are real. These are np_x and np_y – like np_z , except aligned with x and y axes, respectively.

Like s orbitals, p orbitals have nodal spheres. The np orbital has $n - 2$ nodal spheres.

The $\ell = 2$ orbitals have a double barbell or cloverleaf pattern with four lobes – alternately positive and negative. Each d orbital has two nodal planes where the wave function is zero. There are five $(2\ell+1)$ nd orbitals. The $m_\ell = 0$ orbital is called nd_{z^2} . It is concentrated about the z axis, with a doughnut-shaped lobe in the xy plane. The $m_\ell = \pm 1$ orbitals are combined to make nd_{xz} and nd_{yz} orbitals, while the $m_\ell = \pm 2$ orbitals are combined to make nd_{xy} and $nd_{x^2-y^2}$ orbitals.



The Periodic Table

Ions with only one electron – i.e., He^+ , Li^{2+} , ... – have the same orbitals as hydrogen, except that they held more closely to the nucleus by the larger nuclear charge.

The larger nuclear charge also lowers (i.e., further stabilizes), the energy levels of the ion – in comparison with hydrogen.

$$E_n = -\frac{Z^2 hc R_{\text{H}}}{n^2}, \quad n = 1, 2, 3, \dots$$

for nuclear charge, $+Ze$. Thus, the energy levels of He^+ are four times deeper than those of H because the nuclear charge is doubled.

For atoms and ions with more than one electron – i.e., almost all atoms and ions – the states and associated energy levels are calculated on computers.

The difficulty arises because of repulsion between electrons.

If there were no electron repulsion, then each electron in a many electron atom would be in a *hydrogen-like orbital* – an orbital of hydrogen, shrunk into the nucleus, with lower energy because of the $+Ze$ nuclear charge.

Electron repulsion modifies this picture. Though, the *independent electron approximation* is a good starting point. It provides an approximate state which corresponds to each electron assigned to a hydrogen-like orbital (henceforth just called orbital). The energy of the state is given by summing the *occupied* orbital energies, then adding corrections to account for electron repulsion.

The above picture is complete when we account for electron spin and the *Pauli exclusion principle*: two electrons with the same spin cannot occupy the same orbital. This is a fundamental property of *fermions*, and electrons are fermions.

The *electron configuration* is the set of occupied orbitals. The ground state electron configuration is obtained if the orbitals are filled in order of increasing energy.

Ground state electron configurations:

H: $1s^1$

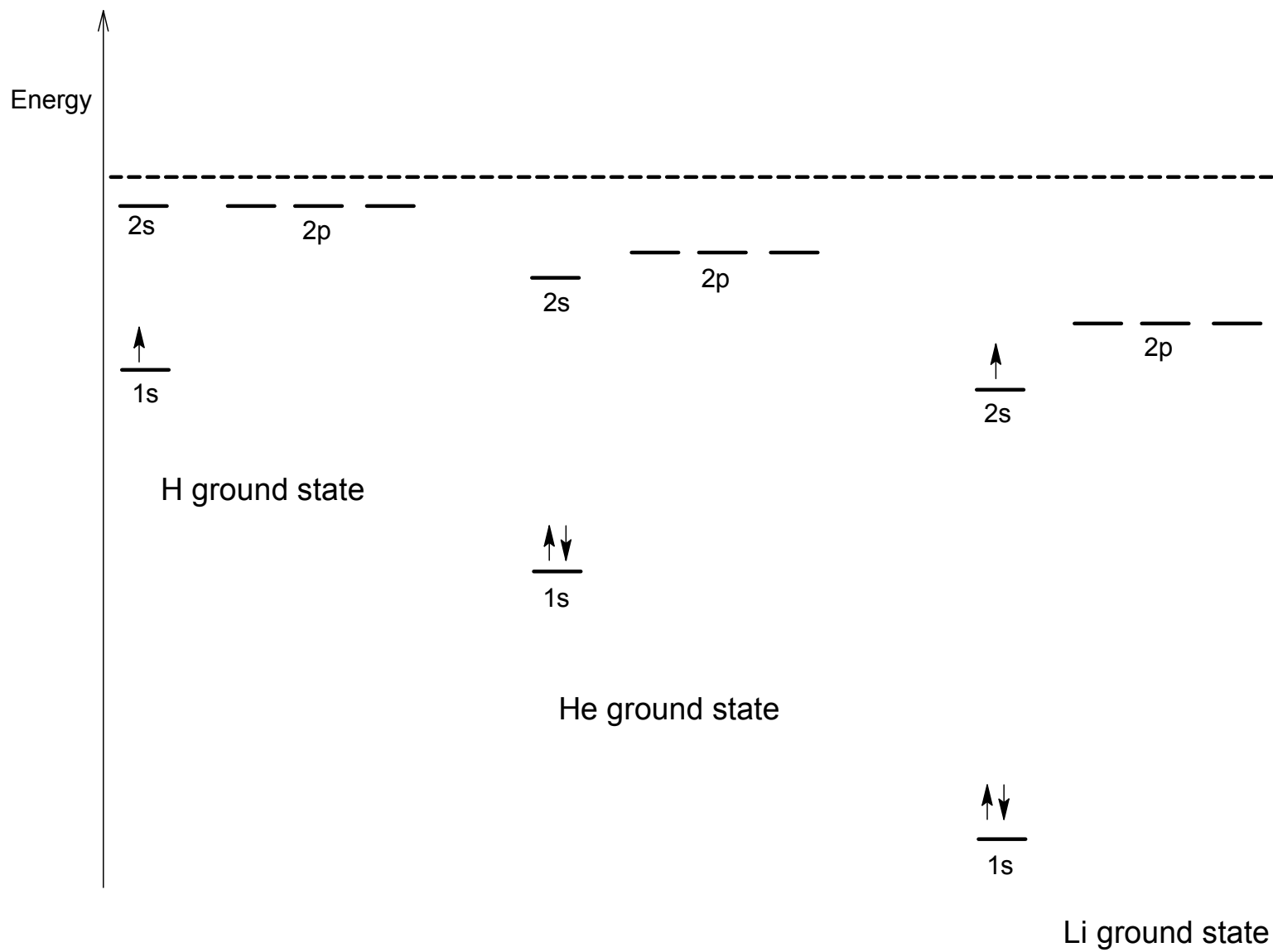
He: $1s^2$

Li: $1s^2 2s^1$

The ground state electron configuration of lithium is not $1s^2 2p^1$ because, in a lithium atom,

2p has higher energy than 2s

- the two 1s electrons screen a 2p electron better than a 2s electron.



The electron configurations of Be, B and C:

Be: $1s^2 2s^2$

B: $1s^2 2s^2 2p^1$

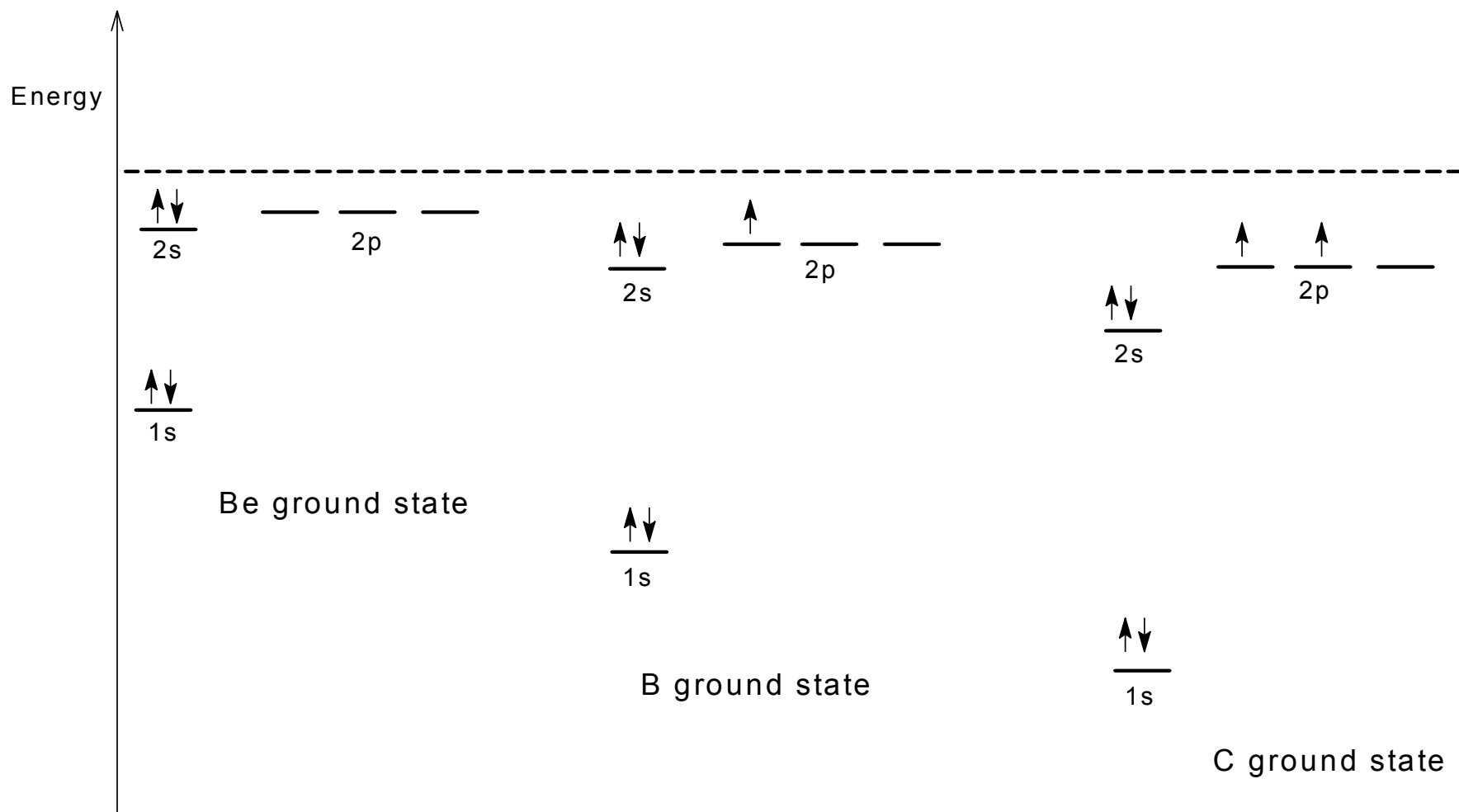
C: $1s^2 2s^2 2p^2$

Repulsion between the two 2p electrons in C is minimized when the electrons have the same-spin – they are in different orbitals.

Electrons in different orbitals are further apart, on average, than electrons in the same orbital.

Electrons with the same spin avoid each other and thereby minimize repulsion.

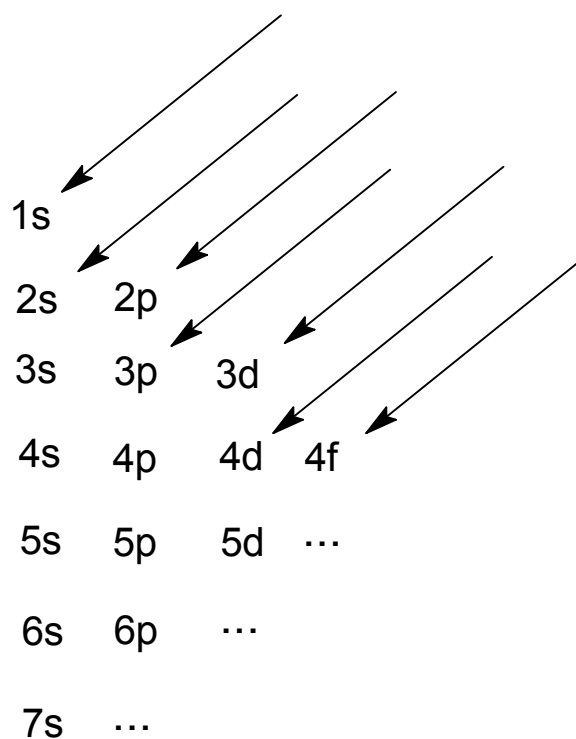
Hund's Rule



The ground state electron configurations of all the atoms is determined in this way - the *Aufbau principle* ("building up").

Orbital Subshell filling order:

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

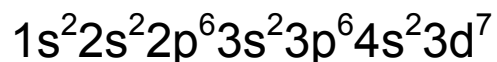


Example:

(a) Determine ground state electron configurations for the following atoms. Use the noble gas shorthand notation (except in case of Ne). The electron configuration of Ar determines the core of fourth row elements. The electron configuration of fourth row elements is then written as [Ar] followed by the valence configuration.

(i) N (ii) Ne (iii) P (iv) Ca (v) V

(b) To which element does the following atomic ground state electron configuration correspond?



(a) N: $1s^2 2s^2 2p^3$
Ne: $1s^2 2s^2 2p^6$
P: $[\text{Ne}] 3s^2 3p^3$
Ca: $[\text{Ar}] 4s^2$
V: $[\text{Ar}] 4s^2 3d^3$

(b) There are 27 electrons in this atom. Therefore, it is cobalt ($Z = 27$).

Chromium and copper are the two exceptions to the orbital filling order of Fig. 3.9, that occur in the first 40 elements. The electron configurations of chromium and copper are as follows (noble gas shorthand notation to the right):

Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
filled 3d subshell

$[Ar] 4s^1 3d^5$ half-

Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

$[Ar] 4s^1 3d^{10}$ filled 3d subshell

Patterns in the electron configuration of the atoms determine the block structure of the periodic table. The periodic table is arranged in blocks according to the subshell of the highest energy electrons. Elements in the same column, *group*, have the same number of *valence electrons* – the number of electrons in the outer shell.

The block structure of the periodic table

s block f block d block p block

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

Periodic Properties

Atomic/Ionic Radius

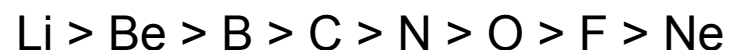
Size of an atom is determined by its shell structure.

Atoms with the same number of valence electrons – i.e., atoms in the same group – increase in size with increasing number of shells – i.e., *atomic radius increases going down a group*.

For example, with respect to atomic radius, $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

Atoms in a row of the periodic table have the same number of shells – and the same number of inner shell electrons. They differ in the number of valence electrons, and in the charge on the nucleus. Since nuclear charge increases across a row, with fixed number of screening electrons, the *effective nuclear charge* felt by the valence electrons increases across the row. Larger effective nuclear charge pulls the valence shell closer to the nucleus, and *atomic radius decreases across a row* – from left to right.

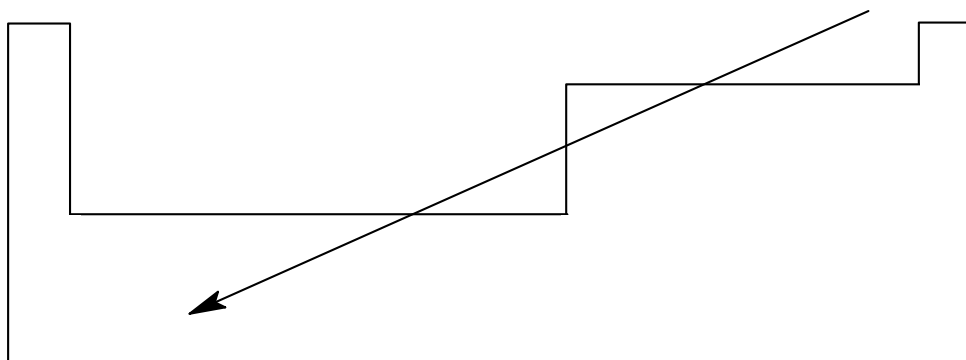
For example, with respect to atomic radius,



The effective nuclear charge is approximated by *core charge*, the charge of the nucleus plus the (negative) charge on the inner shell electrons – core charge equals group number for main group elements.

The trends in atomic radius

Atomic radius increases down and to the left



Rules regarding ionic radius:

The radius of the ions of an element – i.e., nuclear charge is fixed – increases with increasing number of electrons. Thus,



The radius of ions, or atoms, with the same number of electrons - *isoelectronic* species – increases with decreasing nuclear charge. For example,



Example:

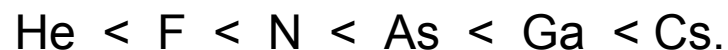
(a) Order the following elements according to increasing atomic radius:

Cs F N He Ga As

(b) Order the following ions/atoms according to increasing radius:



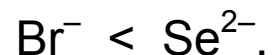
(a) He is the highest and rightmost element. The He atoms are the smallest. The next such element is F, then N, As, Ga and Cs – i.e.,



(b) (i) These are isoelectronic species. The smallest radius occurs for the highest atomic number. Therefore,



(ii) Br^{-} and Se^{2-} are isoelectronic. Therefore,



Br , Kr^{+} and Rb^{2+} are also isoelectronic. Therefore,



Since, $\text{Br} < \text{Br}^{-}$, we have



Atomic Radii of Main Group Elements (in pm)

<div>H</div> <div>32</div>								<div>He</div> <div>37</div>
<div>Li</div> <div>130</div>	<div>Be</div> <div>99</div>	<div>B</div> <div>84</div>	<div>C</div> <div>75</div>	<div>N</div> <div>71</div>	<div>O</div> <div>64</div>	<div>F</div> <div>60</div>	<div>Ne</div> <div>62</div>	
<div>Na</div> <div>160</div>	<div>Mg</div> <div>140</div>	<div>Al</div> <div>124</div>	<div>Si</div> <div>114</div>	<div>P</div> <div>109</div>	<div>S</div> <div>104</div>	<div>Cl</div> <div>100</div>	<div>Ar</div> <div>101</div>	
<div>K</div> <div>200</div>	<div>Ca</div> <div>174</div>	<div>Ga</div> <div>123</div>	<div>Ge</div> <div>120</div>	<div>As</div> <div>120</div>	<div>Se</div> <div>118</div>	<div>Br</div> <div>117</div>	<div>Kr</div> <div>116</div>	
<div>Rb</div> <div>215</div>	<div>Sr</div> <div>190</div>	<div>In</div> <div>142</div>	<div>Sn</div> <div>140</div>	<div>Sb</div> <div>140</div>	<div>Te</div> <div>137</div>	<div>I</div> <div>136</div>	<div>Xe</div> <div>136</div>	
<div>Cs</div> <div>238</div>	<div>Ba</div> <div>206</div>	<div>Tl</div> <div>144</div>	<div>Pb</div> <div>145</div>	<div>Bi</div> <div>150</div>	<div>Po</div> <div>142</div>	<div>At</div> <div>148</div>	<div>Rn</div> <div>146</div>	

Ionic Radii of Main Group Elements (in pm)

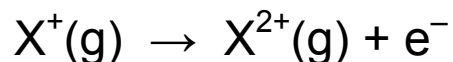
Li⁺ 76	Be²⁺ 45			N³⁻ 171	O²⁻ 140	F⁻ 133
Na⁺ 102	Mg²⁺ 72	Al³⁺ 54		P³⁻ 212	S²⁻ 184	Cl⁻ 181
K⁺ 138	Ca²⁺ 100	Ga³⁺ 62			Se²⁻ 198	Br⁻ 196
Rb⁺ 152	Sr²⁺ 118	In³⁺ 80	Sn⁴⁺ 69	Sb³⁺ 76	Te²⁻ 221	I⁻ 220

Ionization Energy

The *first ionization energy*, I_1 , is the energy needed to eject an electron from an atom in the gas phase – the change in energy for



The second ionization energy, I_2 , of X is the ionization energy of the cation, X^+ – i.e., the energy change for



First ionization energy *generally increases, moving from left to right across the periodic table.*

The highest energy electron (the electron ejected) is in the same shell for these elements – while the effective nuclear charge increases from left to right.

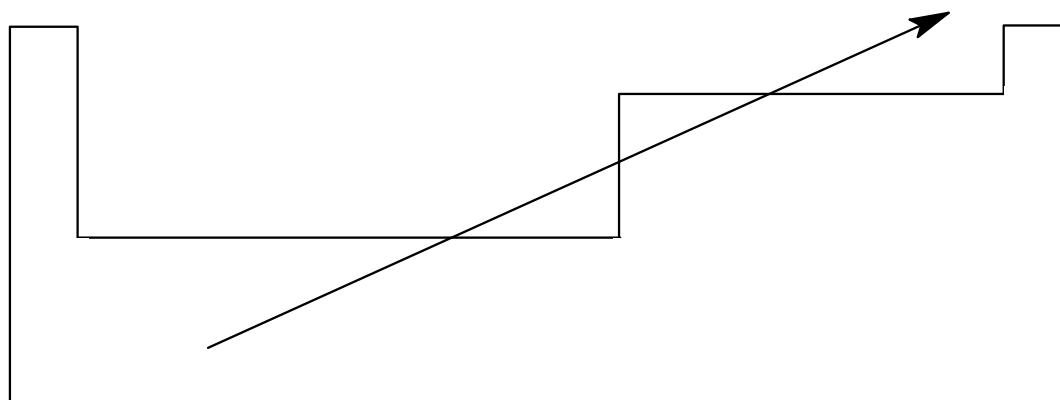
First ionization energy *decreases moving down a group*.

Electrons ejected upon ionization of each successive element come from successive shells – successively more distant from the nucleus, and are less tightly held.

For example, with respect to ionization energy, $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

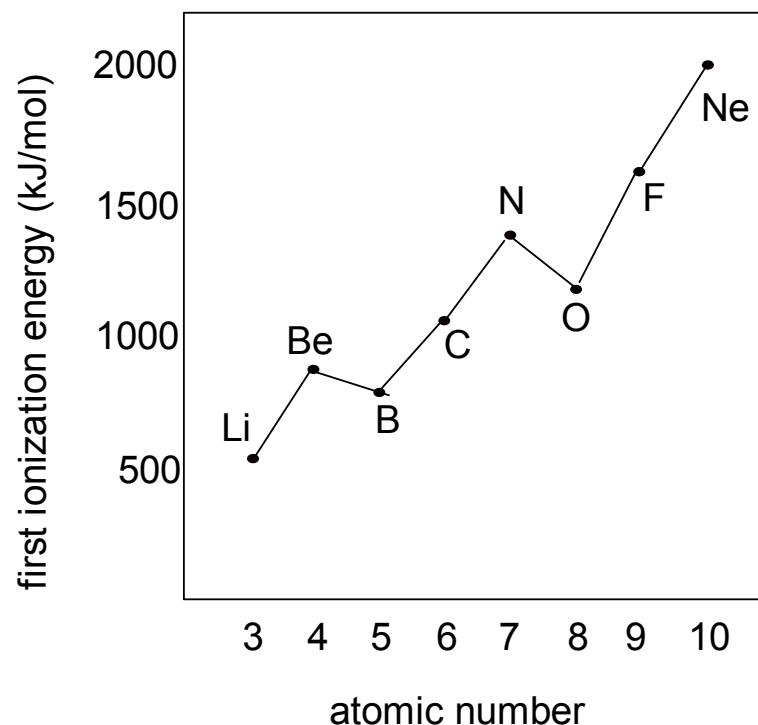
General trends in ionization energy

First ionization energy increases up and to the right



The first trend – ionization energy increases across a row – requires adjustment.

Ionization energy exhibits *filled and half-filled subshell effects*. Consider the second row:



First ionization energy drops from Be to B because the electron ejected from Be is in the 2s subshell whereas the electron ejected from B is in the higher energy 2p subshell – Be has a *filled subshell*.

For N, the electron is ejected from a half-filled 2p subshell, $2p^3$. Each electron in the *half-filled subshell* occupies a different orbital, but with the same spin – this configuration minimizes repulsion.

Ionizing O achieves the stable $2p^3$ configuration starting from $2p^4$. Ionization of O is more favorable than ionization of N, in spite of the increased nuclear charge of O.

The same increasing zigzag pattern is seen for the third row elements, Na, Mg, Al, Si, P, S, Cl and Ar, with local peaks at Mg and P.

First Ionization Energies of Main Group Elements (in kJ mol⁻¹)

H 1312.1							He 2372.3
Li 520.2	Be 899.5	B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.1	Ne 2080.7
Na 495.9	Mg 737.8	Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
K 418.8	Ca 589.8	Ga 578.9	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
Rb 403.0	Sr 549.5	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	I 1008.4	Xe 1170.4
Cs 375.7	Ba 502.9	Tl 589.4	Pb 715.6	Bi 703.0	Po 811.8	At	Rn 1037.1

Example:

(a) Order the following elements according to increasing first ionization energy:

Cs F N He Ga As

(b) Which of the following orderings, according to increasing first ionization energy, is correct?

(i) $\text{Mg} < \text{Si} < \text{P} < \text{Ar}$

(ii) $\text{Li} < \text{N} < \text{O} < \text{F}$

(iii) $\text{Ga} < \text{Ca} < \text{Se} < \text{As}$

(iv) $\text{Mg} < \text{Al} < \text{S} < \text{P}$

(a) Cs has the lowest first ionization energy in the group. Next is Ga, then As, N, F and He. The filled and half-filled subshell effects do not arise in this series of elements. Therefore, according to increasing first ionization energy,



- (b) (i) This is correct – this ordering is in accord with the general trend.
(ii) $\text{N} < \text{O}$ is incorrect. $\text{O} < \text{N}$ because of the half-filled subshell effect.
(iii) This is correct. Here, we see the filled subshell effect, $\text{Ga} < \text{Ca}$, and the half-filled subshell effect, $\text{Se} < \text{As}$.
(iv) $\text{S} < \text{P}$ is correct – the half-filled subshell effect. However, $\text{Mg} < \text{Al}$ is not correct because of the filled subshell effect.

Successive ionization energies – ionization of A , A^+ , A^{2+} , and so on.

Each successive ionization process takes more energy – there are successively fewer electrons and correspondingly less screening of the nucleus. Thus,

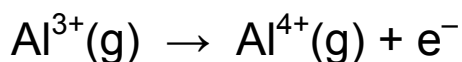
$$I_1 < I_2 < I_3 < \dots \quad \text{the sequence is strictly increasing}$$

When the next electron comes from a *lower energy shell* than the previous electron, there is a *big jump in ionization energy*. For example, the first five ionization energies of Al:

Ionization Energy
(I_n) in kJ mol^{-1}

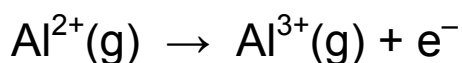
1	578
2	1817
3	2745
4	11577
5	14842

Big jump between I_3 , I_4 .



electron comes from 2nd shell

requires much more energy than



electron comes from 3rd shell

Electrons in the second shell are much more tightly held – they experience a much larger core charge.

Example:

An atom exhibits the following pattern of successive ionization energies:

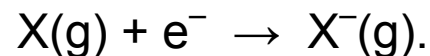
$$I_1 < I_2 \ll I_3 < I_4 < I_5 < I_6$$

Which element would this most likely be, among Ne, Li, B or Be?

The element is in group 2. Therefore, it is Be.

Electron Affinity

Electron affinity, A_1 , is the energy change when an gas phase atom gains an electron.



Whenever the anion is *stable* (usually so), electron affinity is *negative*.

There are some positive electron affinities – e.g., He, Ne, Be and N. These atoms form singly charged anions in the gas phase, but the anions are not stable – they lose the electron and return to the neutral atom state.

Since the electron affinity is otherwise negative, it is customary to compare electron affinities in terms of absolute value.

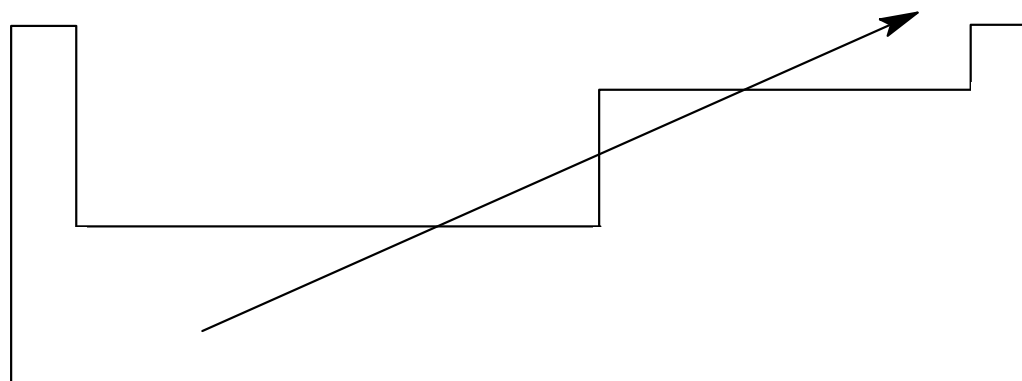
For example, we say the magnitude of the electron affinity of fluorine ($A_1 = -328 \text{ kJ mol}^{-1}$) is greater than that of oxygen ($A_1 = -141 \text{ kJ mol}^{-1}$).

A larger magnitude of electron affinity corresponds to a more favorable singly charged anion.

Magnitude of electron affinity generally *increases up and to the right*, just like ionization energy.

However, there are many exceptions – primarily because of very strong *filled* and *half-filled subshell* effects. For example, group 2 and 15 elements have much lower magnitude of electron affinity than the general trend suggests.

Magnitude of electron affinity generally increases up and to the right



Example:

Order the following elements according to increasing magnitude of electron affinity:

Rb F O Sn Ge As

Electron Affinities of Main Group Elements (in kJ mol⁻¹)

H −72.8							He +	
Li −59.6	Be +							Ne +
Na −52.9	Mg +	B −27.0	C −121.8	N +	O −141.0	F −328.2	Ar +	
K −48.4	Ca −2.4	Al −41.8	Si −134.1	P −72.0	S −200.4	Cl −348.6	Kr +	
Rb −46.9	Sr −4.6	Ga −41.5	Ge −118.9	As −77.6	Se −195.0	Br −321.9	Xe +	
Cs −45.5	Ba −14.0	Tl −36.4	Pb −35.1	Bi −90.9	Po −183.3	At −270.2	Rn +	

Chemical Properties

So far, we have considered non-interacting atoms – separated atoms in the gas phase.

In nature, atoms are constantly interacting, chemically and otherwise.

Chemical properties depend on the number of valence electrons and the effective nuclear charge.

The oxides of third, fourth, ... row elements exhibit a chemical trend.

Metal oxides are basic or amphoteric:

Basic oxides produce basic solutions when dissolved in water
Group 1 and 2 oxides – except beryllium oxide

Amphoteric oxides are insoluble in pure water. They dissolve in aqueous acid *or* base solutions
For example, beryllium, aluminum, zinc and iron oxides

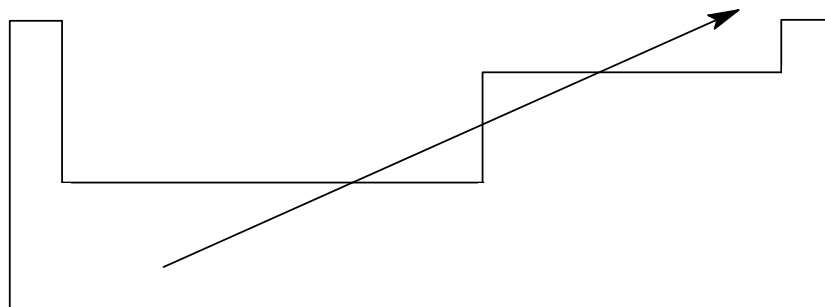
Metals – bottom left of the periodic table – do not hold their electrons as tightly as oxygen.

Group 1 and 2 oxides (except BeO), are *ionic*. They dissolve in water forming $\text{O}^{2-}(\text{aq})$ – a *strong base* – and subsequently, $\text{OH}^{-}(\text{aq})$ – also a strong base.

In other metal oxides, the metal oxygen bond has *covalent* character – electrons are shared. However, they are *unequally* shared – closer to oxygen than the metal.

Electronegativity measures the pull of an atom on the electrons in covalent bonds.

Electronegativity generally increases up and to the right



Difference in electronegativity between bonded atoms indicates polarization of the bond.

Electrons shift toward the more electronegative atom

Large difference – e.g., main group metal and nonmetal – indicates an *ionic bond*.

Small difference – e.g., two different nonmetals – indicates a *polar covalent bond*.

Zero difference – e.g., N₂, O₂, F₂, Cl₂, ... – indicates a *nonpolar covalent bond*.

Basic metal oxides dissolve in water (or acidic aqueous solution) releasing a *metal cation* and the *oxide anion*, O²⁻.

Acidic (nonmetal) oxides react with water to form *oxoacids* which have at least one hydroxyl (-OH) attached to the nonmetal.

The pull of all the oxygen atoms on the nonmetal deplete it of charge, making it pull back harder.

The pull of the nonmetal stabilizes the oxoanion (-O^-) formed when the oxoacid donates an H^+ (i.e., it acts as a *Brønsted-Lowry* acid)

oxoacid



carbonic acid



nitric acid



phosphoric acid

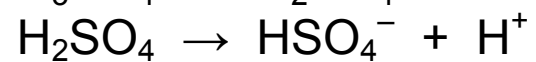
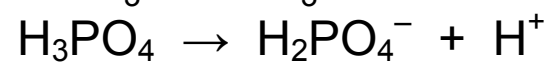


sulfuric acid



perchloric acid

Brønsted-Lowry acids donate H^+



oxoanion

hydrogen carbonate

nitrate

dihydrogen phosphate

hydrogen sulfate

perchlorate

Electronegativities of the Main Group and Elements and Transition Metals

H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66
Cs 0.79	Ba 0.89	La 1.10	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	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2