JF Chemistry CH1101

The Electronic Theory of Chemistry

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Module Aims: To provide an introduction to the fundamental concepts of theoretical and practical chemistry, including concepts of periodicity, bonding and structure, functional group chemistry, thermodynamics and kinetics

Syllabus

- Periodic Classification
    - What are the trends?
    - How can we understand them?

⇒ Atomic or Electronic Structure

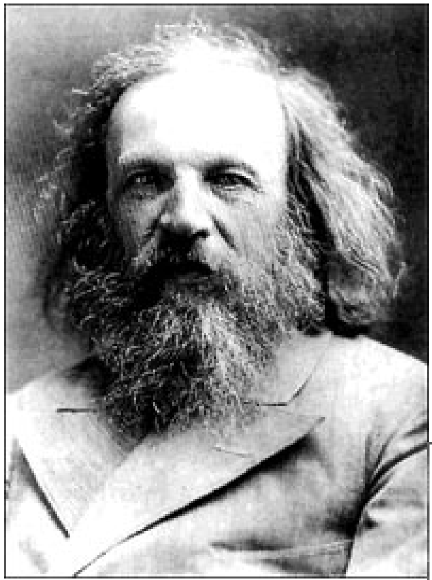
- Structure and Bonding
    - What are the shapes of molecules?
    - Why are they that shape?
    - How can we understand the bonding?

⇒ Hybridisation

Suggested Reading

'Chemistry and Chemical Reactivity' by *Kotz,* Treichel & Weaver	540 P6*6
Basic Inorganic Chemistry by F.A. Cotton, G. Wilkinson & P.L. Gauss	S-LEN 546 L6*2
Chemistry, an Integrated Approach by C.E. Housecroft & E.C. Constable	PL-296-500*
Periodicity and the s- and p-block elements by N.C. Norman	PL-300-173*

* Ussher Stacks



The Periodic Table

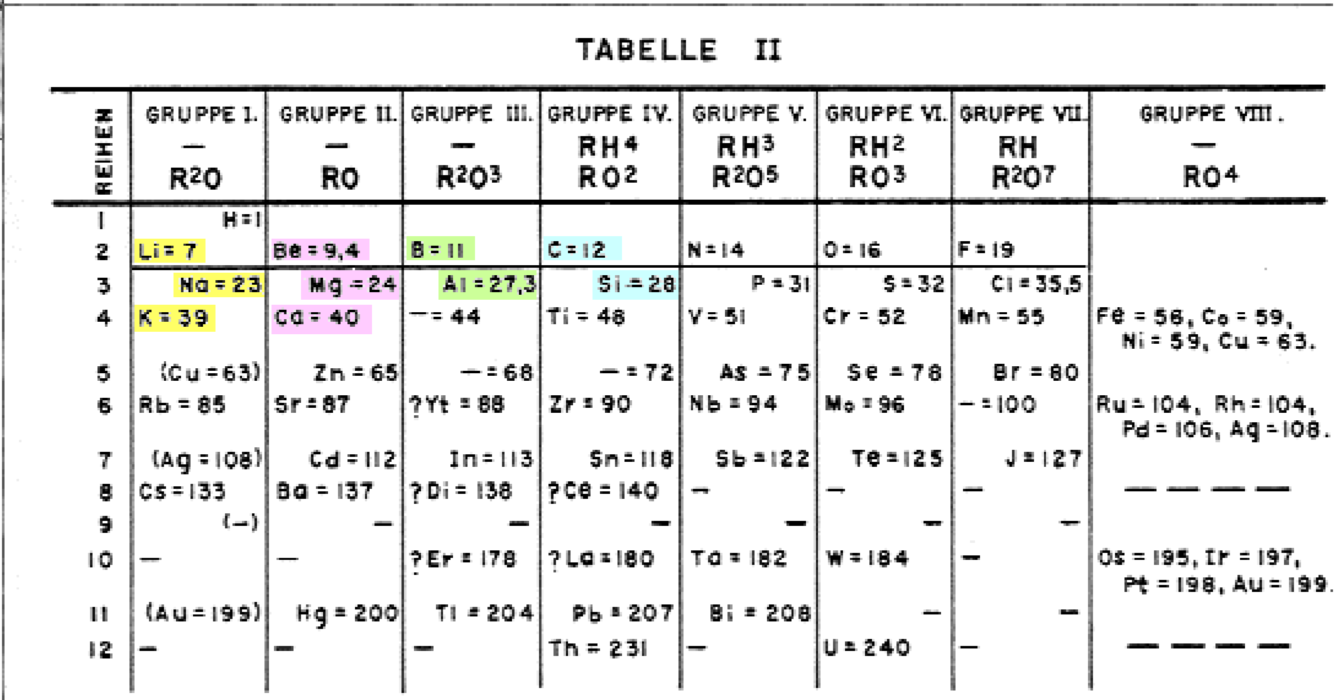


TABELLE II

REIHEN	GRUPPE I. — R^2O	GRUPPE II. — RO	GRUPPE III. — R^2O^3	GRUPPE IV. RH^4 RO^2	GRUPPE V. RH^3 R^2O^5	GRUPPE VI. RH^2 RO^3	GRUPPE VII. RH R^2O^7	GRUPPE VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Figure 2.5 Dmitri Mendeleev's 1872 periodic table. The spaces marked with blank lines represent elements that Mendeleev deduced existed but were unknown at the time, so he left places for them in the table. The symbols at the top of the columns (e.g., R^2O and RH^4) are molecular formulas written in the style of the 19th century.

The Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.409	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 #	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Uub** (285)	113 **Uut** (284)	114 **Uuq** (289)	115 **Uup** (288)	116 **Uuh** (291)		118 **Uuo** (294)

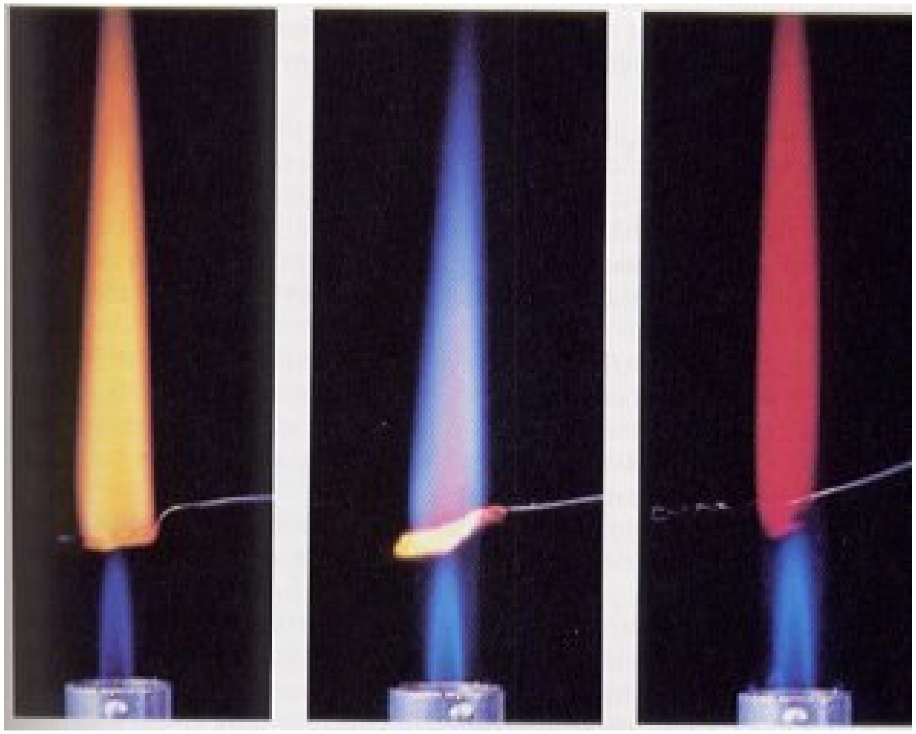
* Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
# Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

A Forensics Example

NaCl or $BaCl_2$?

http://www.rense.com/general32/barium.htm

Flame Tests



Na^+ K^+ Li^+

Ba^{2+}

Emission Spectrum of Hydrogen

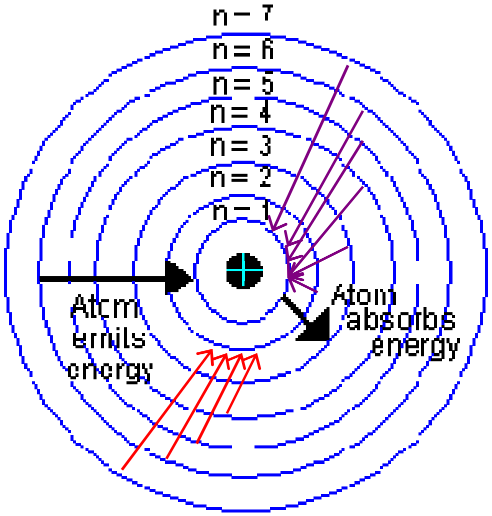
The Bohr Model

- The electron in a hydrogen atom travels around the nucleus in a circular orbit.

- The energy of the electron in an orbit is proportional to its distance from the nucleus. The further the electron is from the nucleus, the more energy it has.

- Only a limited number of orbits with certain energies are allowed. In other words, the orbits are quantized.

- The only orbits that are allowed are those for which the *angular momentum* of the electron is an integral multiple of Planck's constant divided by 2π.

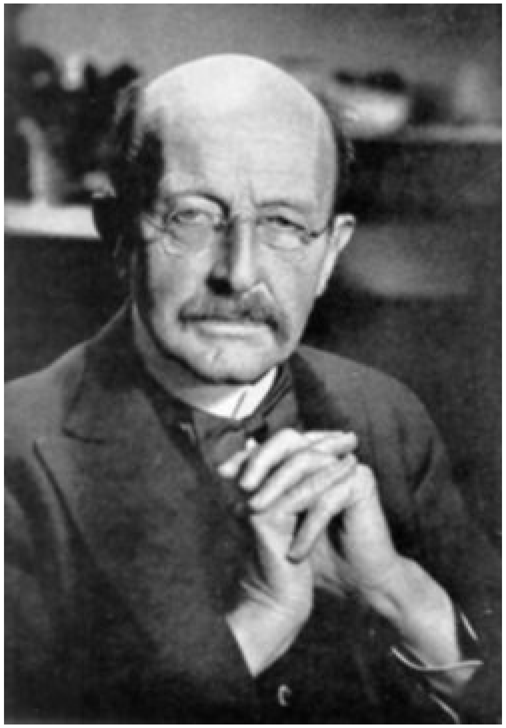


Any object moving along a straight line has a *momentum* equal to the product of its mass (*m*) times the velocity (*v*) with which it moves. An object moving in a circular orbit has an *angular momentum* equal to its mass (*m*) times the velocity (*v*) times the radius of the orbit (*r*). Bohr assumed that the angular momentum of the electron can take on only certain values, equal to an integer times Planck's constant divided by 2π.

$$mvr = n\left[\frac{h}{2\pi}\right]$$

$$n = 1,2,3\ldots$$

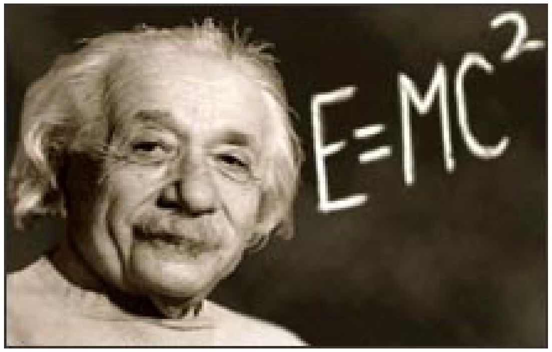
$$\Delta E = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$



Electromagnetic Radiation has associated with it only discrete energies (quantized)

ie. light is an electromagnetic wave

$E = h\nu$



Electromagnetic Radiation can exhibit particle like behaviour

Schrödinger wave equation

$H\Psi = E\Psi$

Wave-Particle Duality proposed by De Broglie

$\lambda = h/m\nu$

Heisenberg Uncertainty Principle – it's impossible to know the position and the momentum of an electron at the same time. Think about the *probability* of finding an electron in a volume of space - Ψ^2

Quantum Numbers

Each orbital in an atom has three quantum numbers *n*, *l* and *m_l*

Arise from quantized energy

PRINCIPLE QUANTUM NUMBER – n

may have any positive integer n = 1, 2, 3, 4…∞

describes the energy of the orbital

ORBITAL QUANTUM NUMBER – l

may have 0, 1, 2, 3 …n-1

describes the shape of an orbital and usually given a letter designation

l = 0 s orbital
l = 1 p orbital
l = 2 d orbital
l = 3 f orbital

Quantum Numbers (cont)

$n = 1$ $l = 0$ 1s $n = 2$, $l = 0$ or 1 $n = 3$, $l =$ 0,   1,   2

2s   2p   3s   3p   3d

Note: 1p or 1d are *not* allowed according to these rules

MAGNETIC QUANTUM NUMBER – m_l

may have any positive integer –l, -l+1,…. 0…,l-1, l

describes the orientation of the orbital

e.g. for $l = 1$ $m_l = -1, 0, 1$ or three types of p orbital

Quantum Numbers (cont)

An electron has an additional quantum number the SPIN QUANTUM NUMBER m_s

can be +1/2 or -1/2

EXAMPLE: Derive a set of quantum numbers for an atomic orbital with n = 3

Firstly what is l?

l = 0 to (n-1) so 0, 1 or 2 (corresponding to an s, p and d orbital)

Now determine all values of m_l

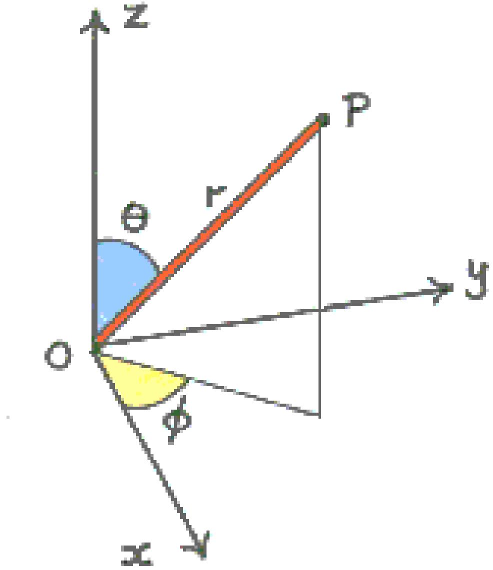
m_l = -l, -l+1…l…l-1

L = 0, m_l = 0

L = 1, m_l = -1, 0, +1

L = 2, m_l = -2, -1, 0, +1, +2

Radial & angular components of the wave-function



$$\Psi_{\text{CARTESIAN}} = \Psi_{\text{Radial}}(r)\ \Psi_{\text{ANGULAR}}(\theta,\phi)$$

The radial part depends only on the distance between the electron and the nucleus

The angular part depends on the direction or orientation

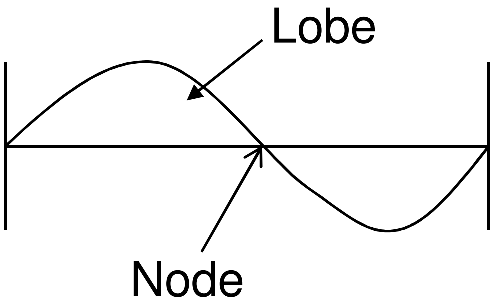
Remember: Ψ^2 is the probability of finding an electron in a volume of space, so this can be described in terms of $R(r)^2$ and $A(\theta,\phi)^2$

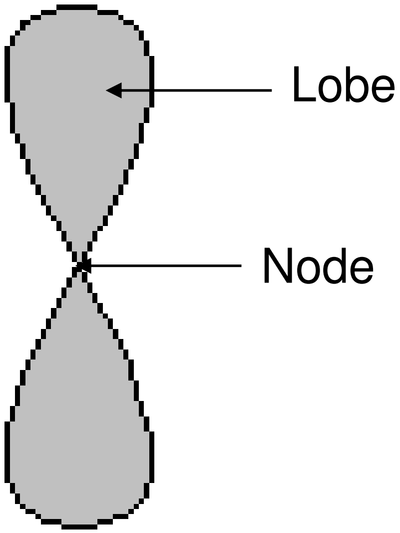
The angular part of the wavefunction

This tells us how the wavefunction varies as a function of an angle from the origin – the shape of the orbital

At certain points the wave function, Ψ, equals zero. At such points there is a zero probability of interacting with the electron. A collection of points where y = 0 create a nodal surface, which can have several different geometries. The wave function can be either positive or negative. On one side of a nodal surface the wave function is positive; on the opposite side the wave function is negative. The sign of the wave function is important when one attempts to superimpose wave functions.

Simply the number of *angular* nodes = l





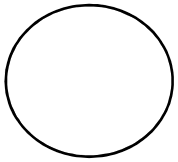
The angular part of the wavefunction (cont)

The case for l = 0

No angular nodes

No angular dependence of the wavefunction

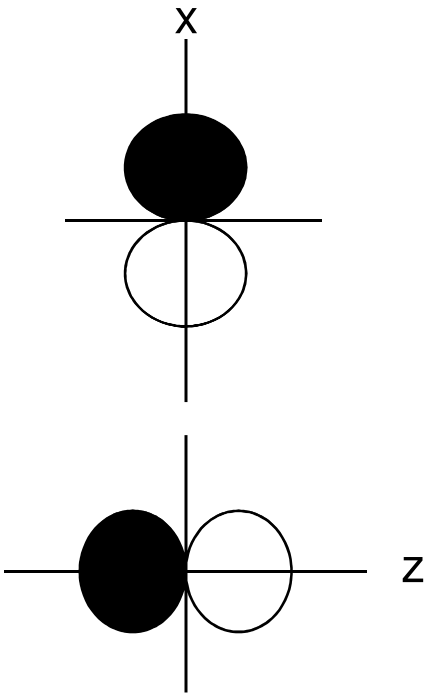
Spherical



The case for l = 1

1 angular node

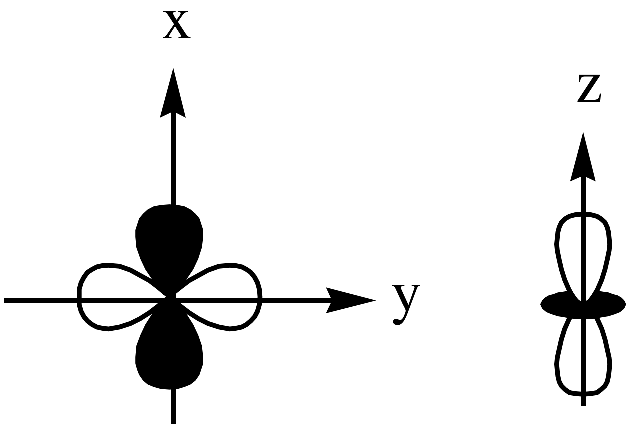
m_l = 3 so three orientations



The case for l = 2

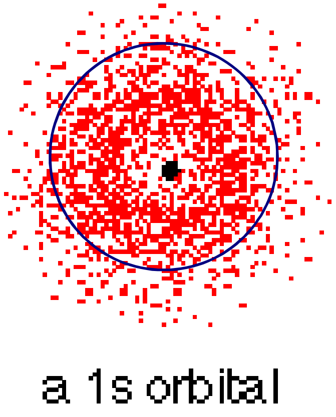
2 angular node

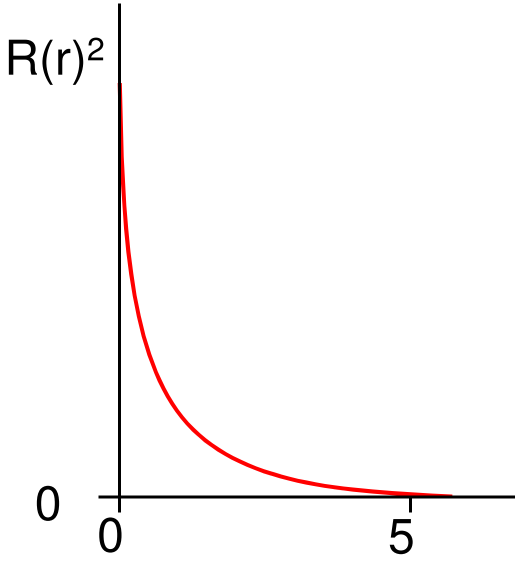
m_l = 5 so three orientations



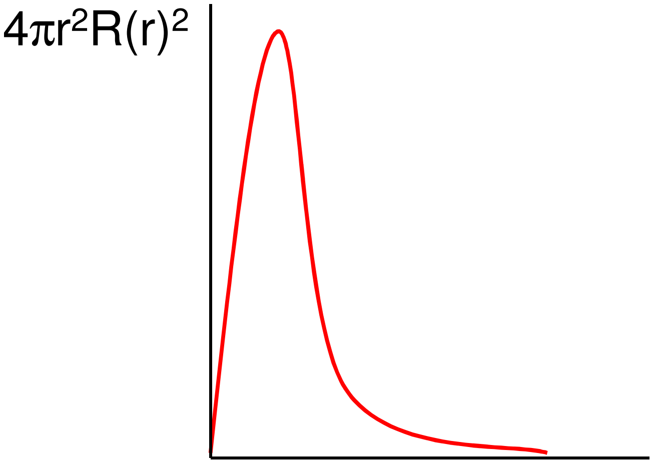
The radial part of the wavefunction

The Bohr Orbital





Distance from the nucleus

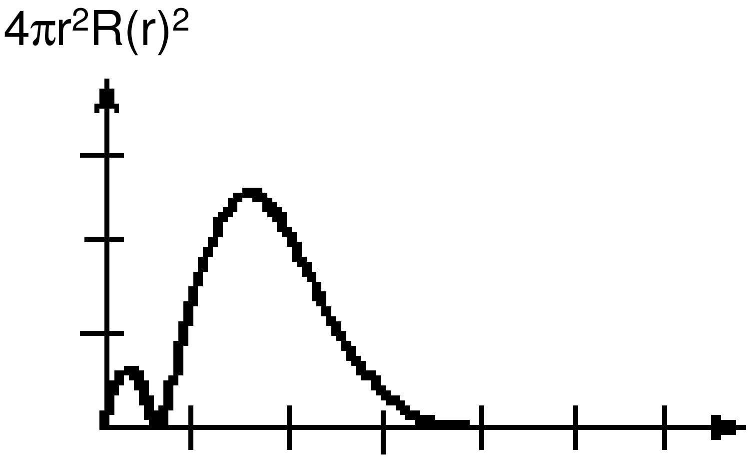


Distance from the nucleus

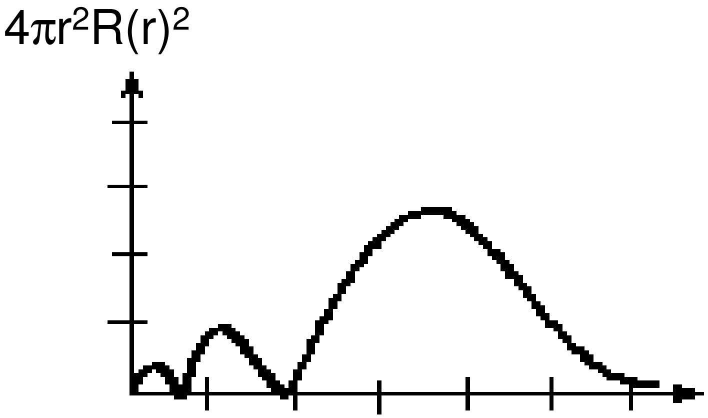
The radial part of the wavefunction tells us how the wavefunction varies with distance, r, from the nucleus – *the size of the orbital*

We want the probability of finding the electron on a 3-dimentional surface (for a 1s orbital a sphere). The function $4\pi r^2R(r)^2$ is called the radial probability factor

The radial part of the wavefunction (cont)

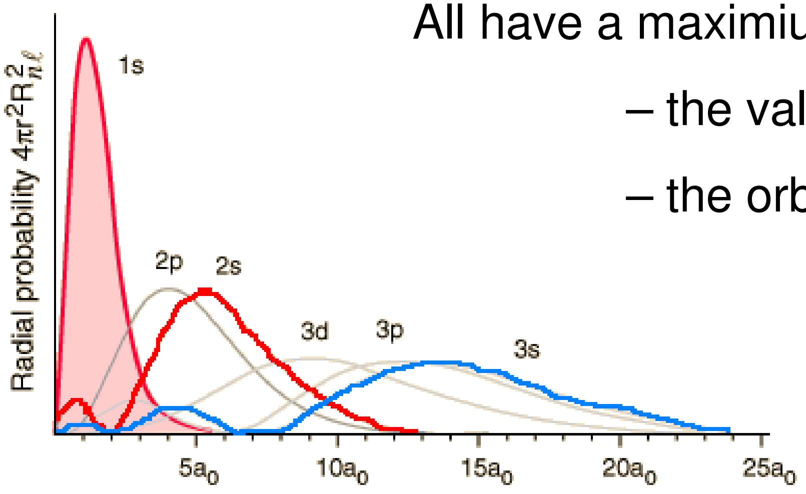


A 2s orbital



A 3s orbital

Note : the appearance of *radial* nodes (number of nodes = n-l-1)



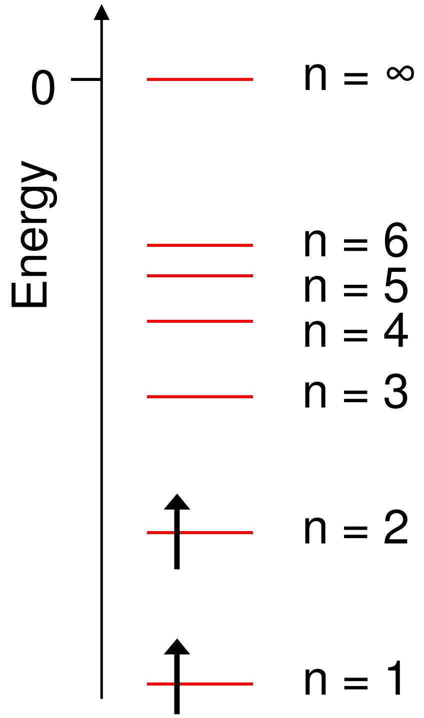
All have a maximum value of r

- the value of n determines the size of the orbital
- the orbital gets larger as n increases

Energies of Orbitals

For a hydrogen atom the energies are ordered purely by the principle quantum number. So the 1s orbital is the lowest in energy.

For n = 2 all orbitals (2s and 2p) are the same in energy and said to be *degenerate*



n = ∞ is the ionisation energy i.e. the energy required to remove an electron

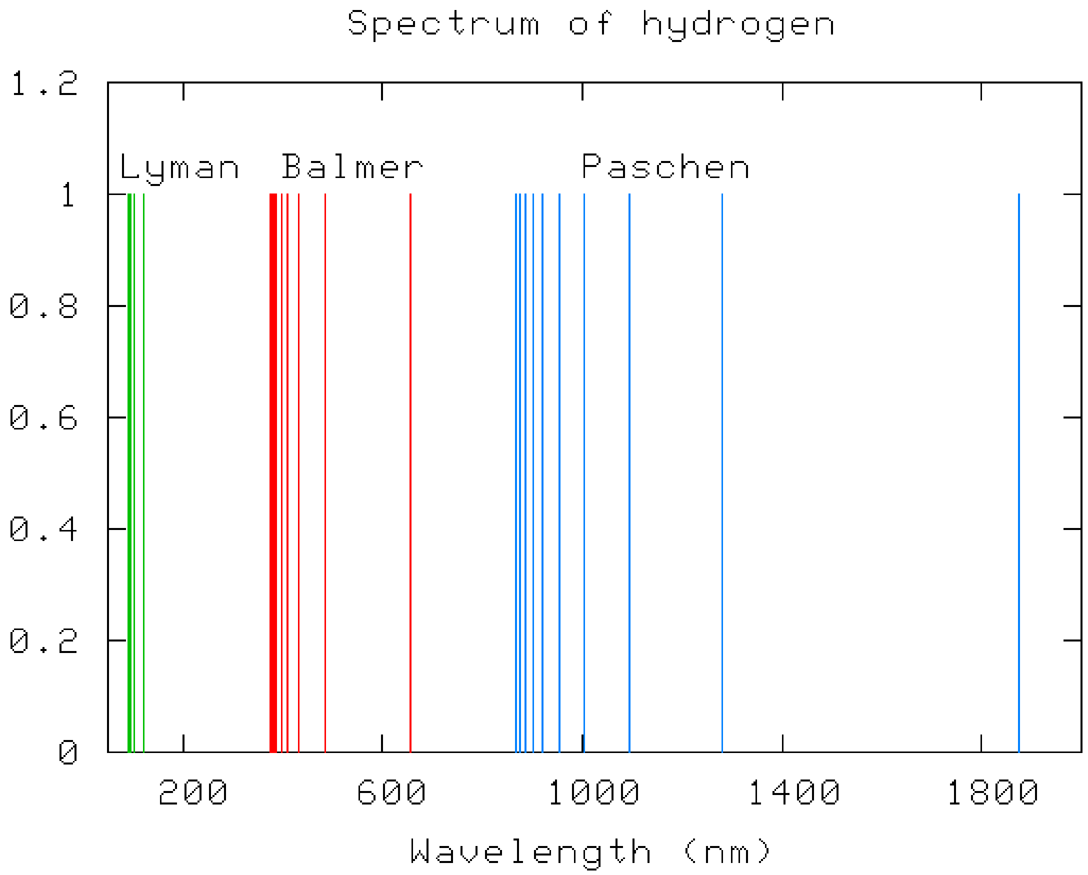
The scale shows a more negative energy as we go to lower quantum numbers – more stable

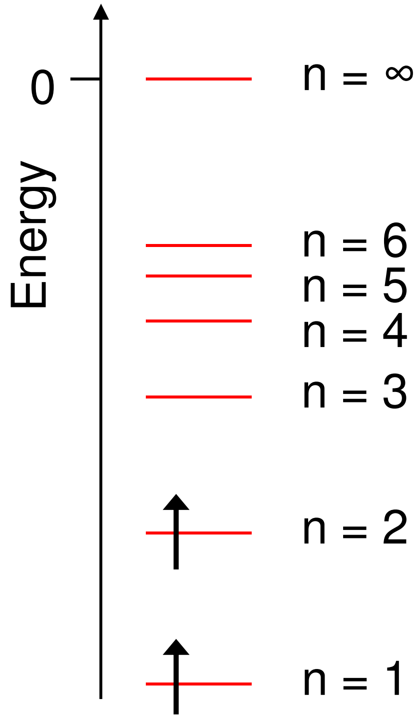
For hydrogen the electron is accommodated in the lowest energy orbital. This is known as its *ground state*.

The ground state electronic structure of hydrogen is $1s^1$

An electron can be raised in energy (promoted) to an orbital of higher energy. *This is an excited state*.

Energies of Orbitals (cont)





Polyelectronic atoms

Cannot solve the Schrodinger wave equation for more than one electron, but:

- The same quantum numbers are found as for hydrogen
- The same angular functions are found
- The radial functions are also similar BUT they are contracted to smaller radii, the energies are lower and THE ENERGY DEPENDS ON THE QUANTUM NUMBERS *n* AND *l*

We need to know how orbitals are filled with more than one electron.

There are three rules we need to know

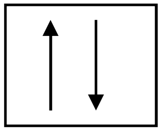
1. The Pauli Exclusion Principle
2. The Aufbau Principle
3. Hund's First Rule

The Pauli Exclusion Principle

The spin quantum number m_s can equal +1/2 or -1/2

The Pauli Exclusion principle states that *no two electrons in the same atom can have the same set of four quantum numbers*. As each orbital is described by three quantum numbers if follows that only two electrons can be associated with one orbital

These two electrons are said to be *spin paired* or have opposite spin



The Aufbau Principle

Electrons go into the lowest energy orbital available

So we add two electrons (with their spin paired) to the lowest energy orbital

H $1s^1$

He $1s^2$

Li $1s^2 2s^1$

Be $1s^2 2s^2$

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

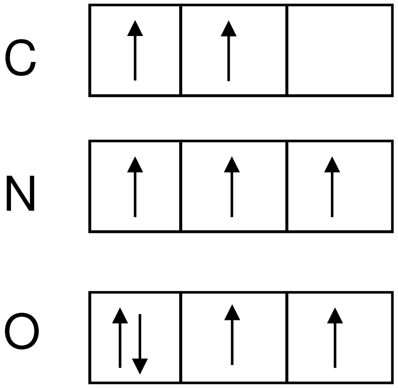
Hund's First Rule

For a set of degenerate orbitals (ie. Orbitals of the same energy) electrons will be placed with their spins *aligned* (or *parallel*)

C $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$

N $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

O $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$



Two reasons for this:

Reduces coulombic repulsion

For quantum mechanical reasons spin parallel is more stable

Energies of Electrons

The energies of electrons in a many electron atom depend on the quantum numbers n AND l

1st IE of H = 1313 kJ mol^{-1} (1 electron)

He^+ = 5250 kJ mol^{-1} (1 electron)

He = 2372 kJ mol^{-1} (2 electrons)

Li = 520 kJ mol^{-1} (3 electrons)

Ionisation energy is proportional to the square of the nuclear charge (Z)

Why is the IE of He much lower than He^+? The 1s electron seem to shield the 1s electron from the full attraction of the nucleus. Similarly for Li - The 1s electrons seem to shield the 2s electron from the full attraction of the nucleus.

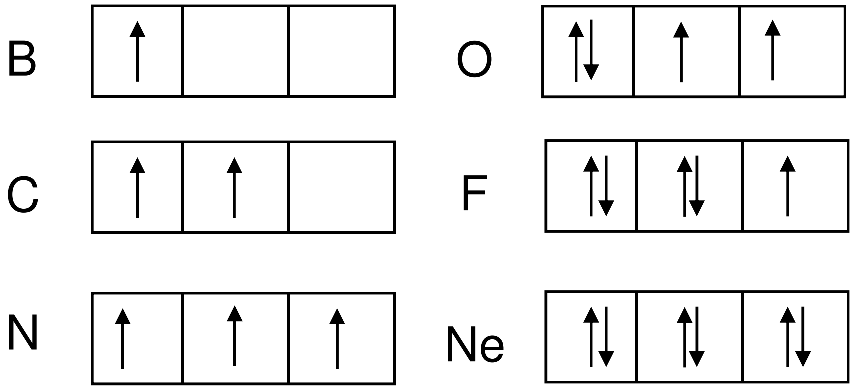
- Effective nuclear charge

Effective Nuclear Charge

The charge felt by an electron is not the actual charge of the nucleus

Look at the elements of row 2 B-Ne

Adding successive electrons to the 2p orbitals – Remember Hunds Rules!



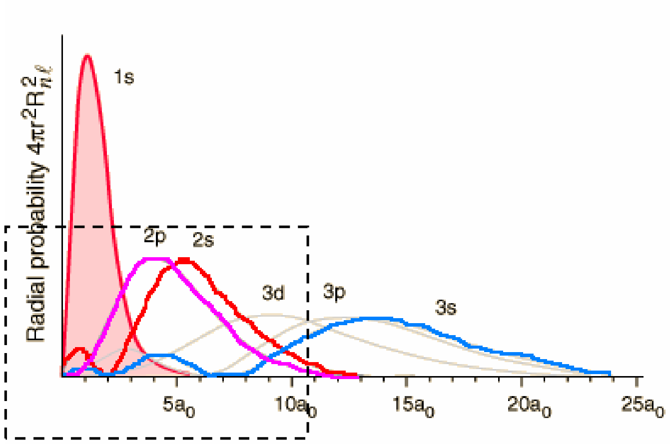
Different geometries of the p orbital affect the effective nuclear charge

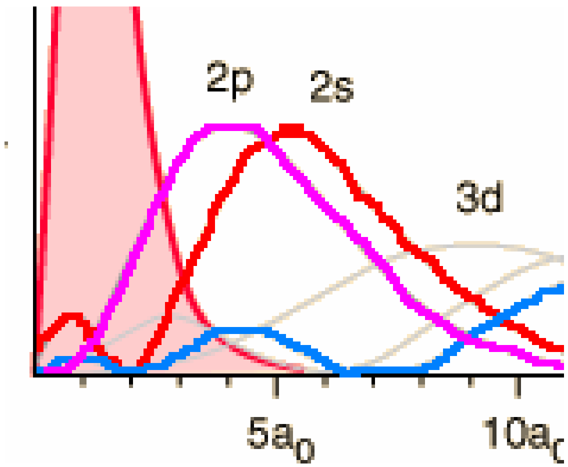
Can now see where Hunds rule arises – Electrons spread out into a degenerate set of orbitals in order to achieve a maximum effective nuclear charge.

Penetration and Shielding

Why is Li $1s^2\ 2s^1$ and not $1s^2\ 2p^1$?

Look at the RDF and we see a small, but significant, part of the 2s lies closer to the nucleus than the maximum in the 1s lobe





This lowers the energy of 2s relative to 2p

⇒the 2s orbital penetrates the core better than the 2p

Penetration and Shielding (cont)

A useful graph is a plot of the energies of the orbitals upto n = 4 with increasing atomic number

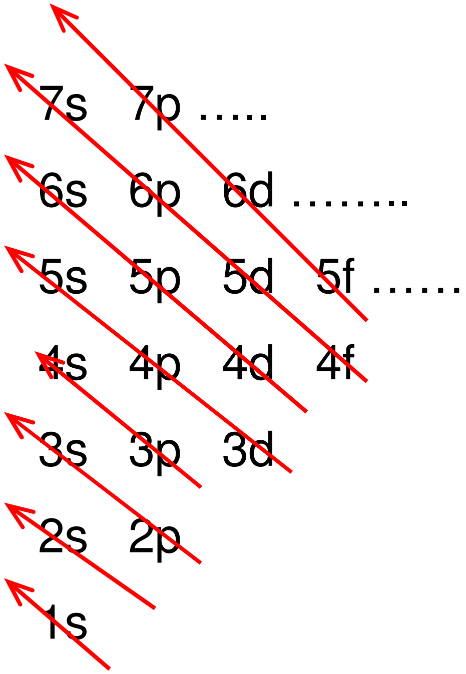
Some final points: once the 3p orbitals are filled the next electrons go into the 4s not the 3d as would be expected.

Once the 3d orbitals are filled they drop in energy as they are poorly shielded by the 4p orbitals

NOTE: this discussion is for neutral atoms, for ions the ordering can change

As a final point, we must be careful when using these diagrams as it is still a matter of debate as to why or even if the the 3d orbitals ever rise above the 4s orbitals. However, for our intentions we can use this assumption

Filling of electrons



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

An aid to remember the order

Electronic structure of ions

What is the electronic structure for Potassium?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

What is the electronic structure for Scandium?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$

What is the electronic structure for Scandium^{2+}?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

Why? Effective nuclear charge

Electronic structure of periods

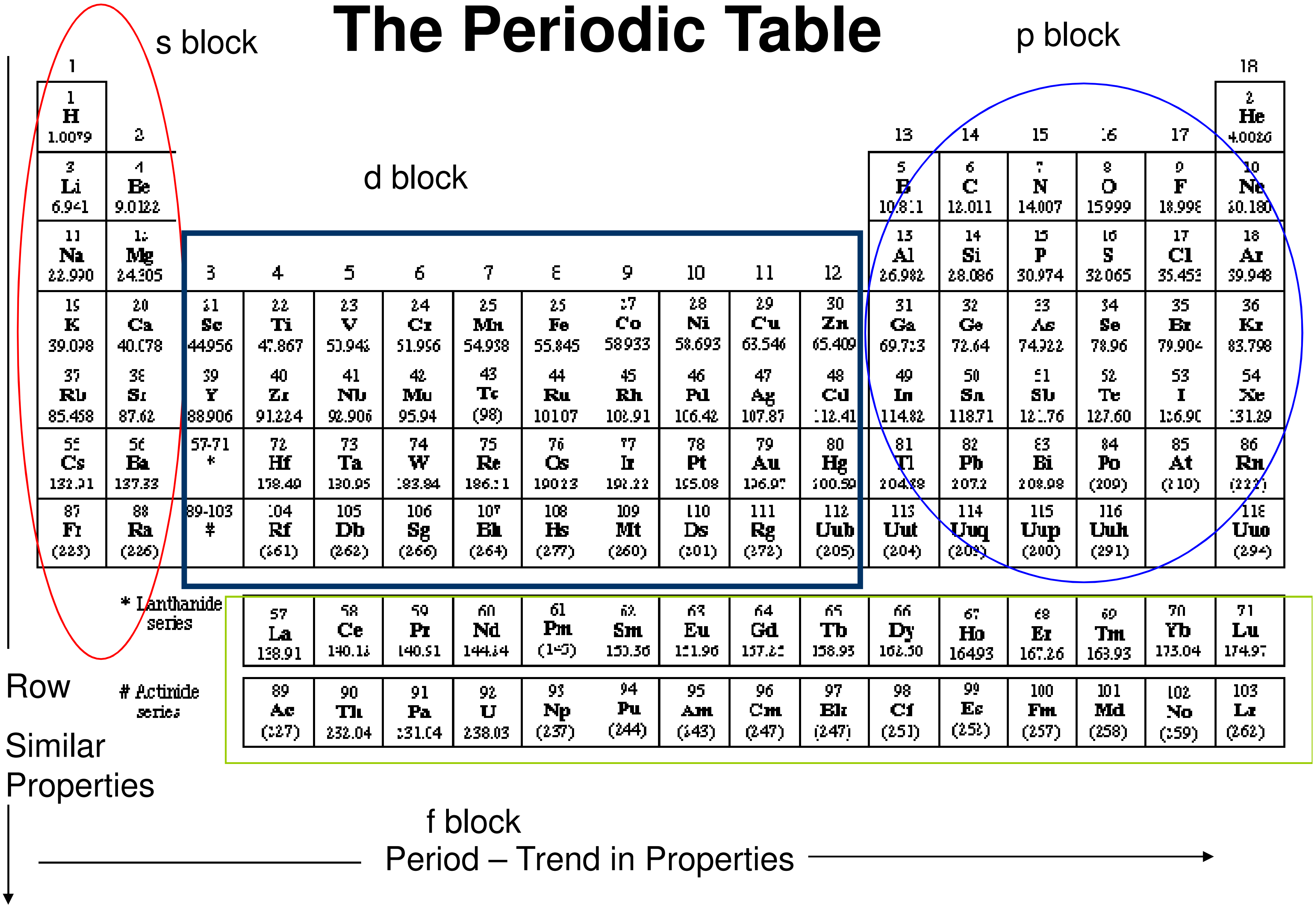
What are the electronic structures of: Li, N, Ne, Mg, Al, Ar, Cr, Cu, Zn and Ga?

Valence orbitals – those electrons that participate in chemistry – the highest energy electrons

Core orbitals – those that do not participate in the chemistry – held tightly to the nucleus

The octet rule can now be understood!

The Periodic Table



s block

p block

d block

1																	18
1 H 1.0079	2											13	14	15	16	17	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (260)	110 Ds (201)	111 Rg (272)	112 Uub (205)	113 Uut (204)	114 Uuq (209)	115 Uup (200)	116 Uuh (291)		118 Uuo (294)
		* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
		# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Row

Similar Properties

f block

Period – Trend in Properties

Summary of Electronic Structure Section

Important points:

From Bohr model to Quantum Mechanics an increasingly sophisticated description of electronic structure

Quantum numbers describe the size, shape and energies of the orbitals

The aufbau principle, Hund's rule and Pauli exclusion principle allows us to fill the orbitals in a many electron atom

Effective nuclear charge, penetration and shielding are also very important

We have enough information to understand how to build up a periodic table AND discuss trends

Trends in the periodic table

How can we use the principles we've described to account for observed trends in:

1. Ionisation Energies
2. Electron Affinity
3. Atomic Radii
4. Electronegativity
5. Reactivity

For example, how can we explain the reactivity of Group 1 metals with water?

Li

Na
(145g)

K

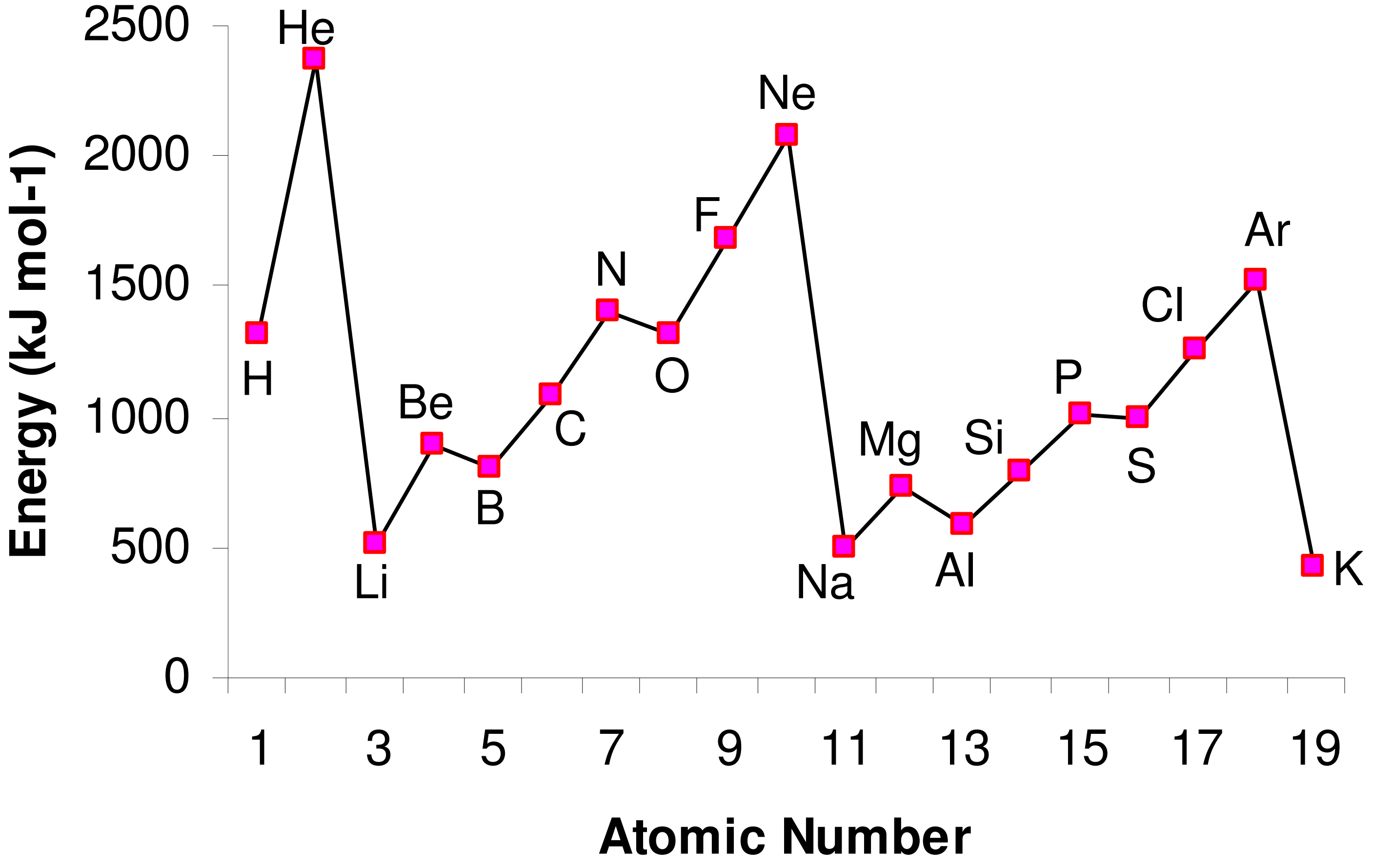
Rb and Cs

http://theodoregray.com/PeriodicTable/AlkaliBangs/index.html

1. Ionisation Energy

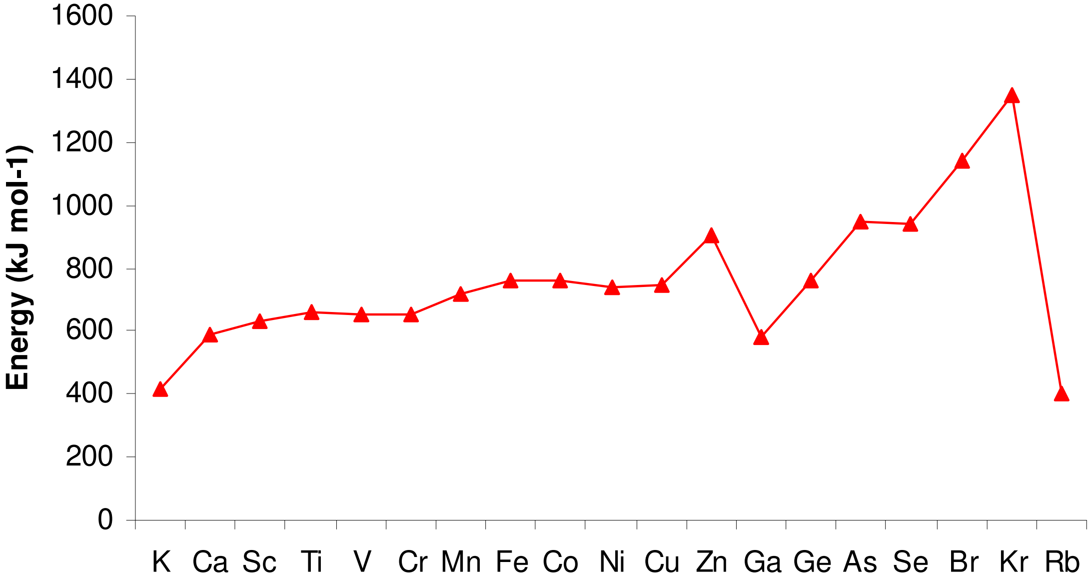
The energy required to completely remove an electron from an atom in the gas phase:

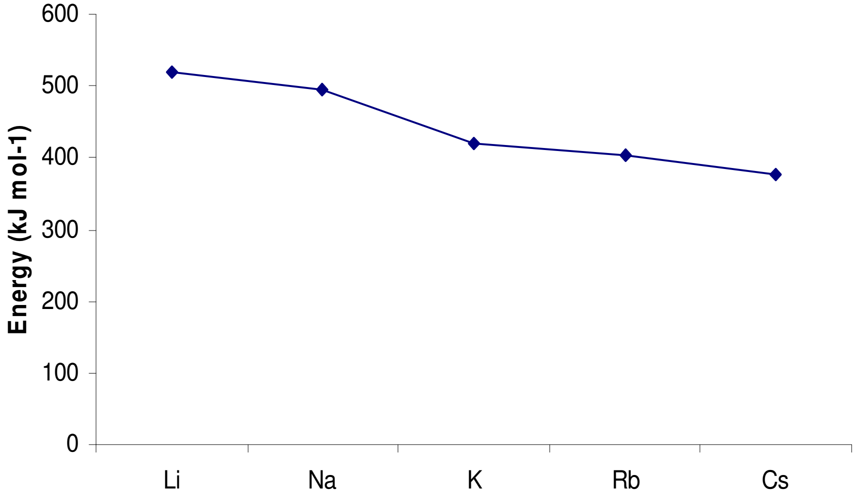
$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-}$$

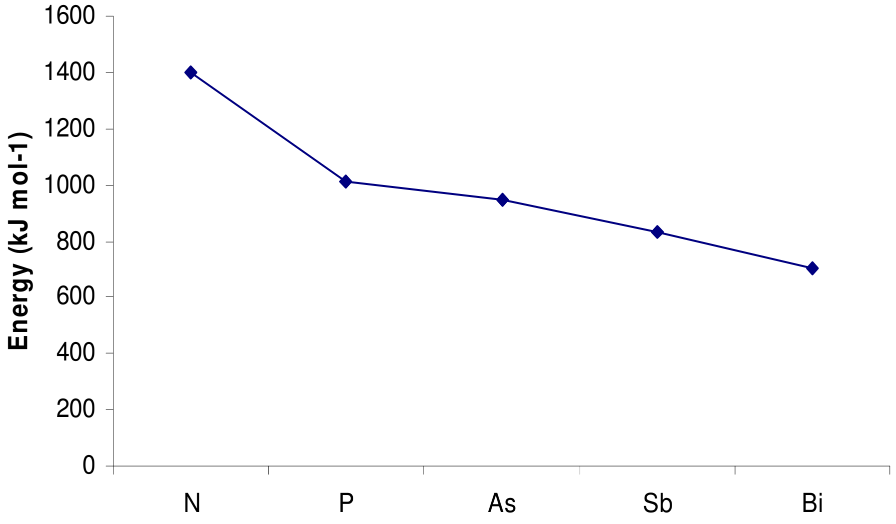


First ionisation enthalpies (kJ mol^{-1}) for the elements Hydrogen to Potassium

1. Ionisation Energy (cont.)

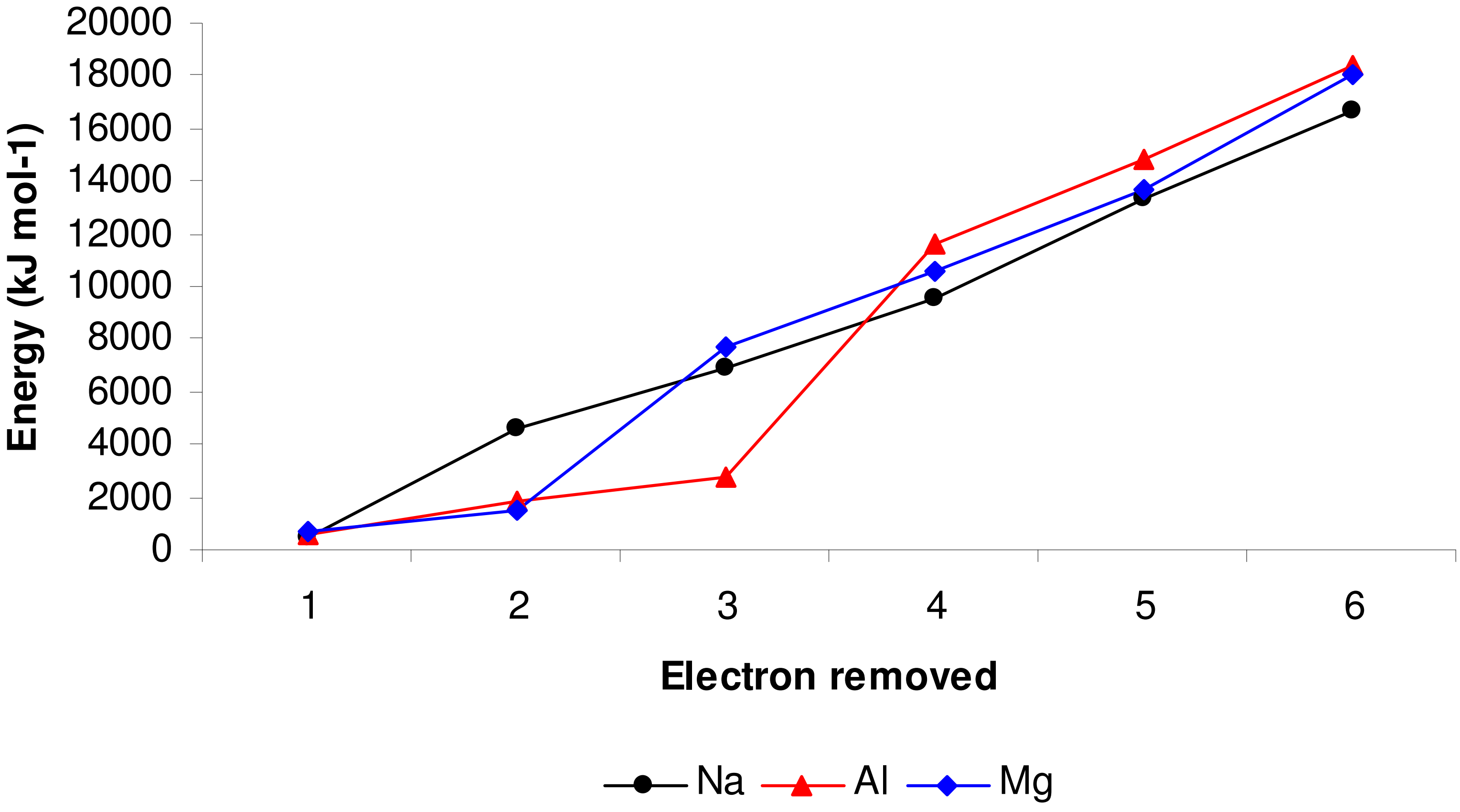






1. Ionisation Energy (cont.)

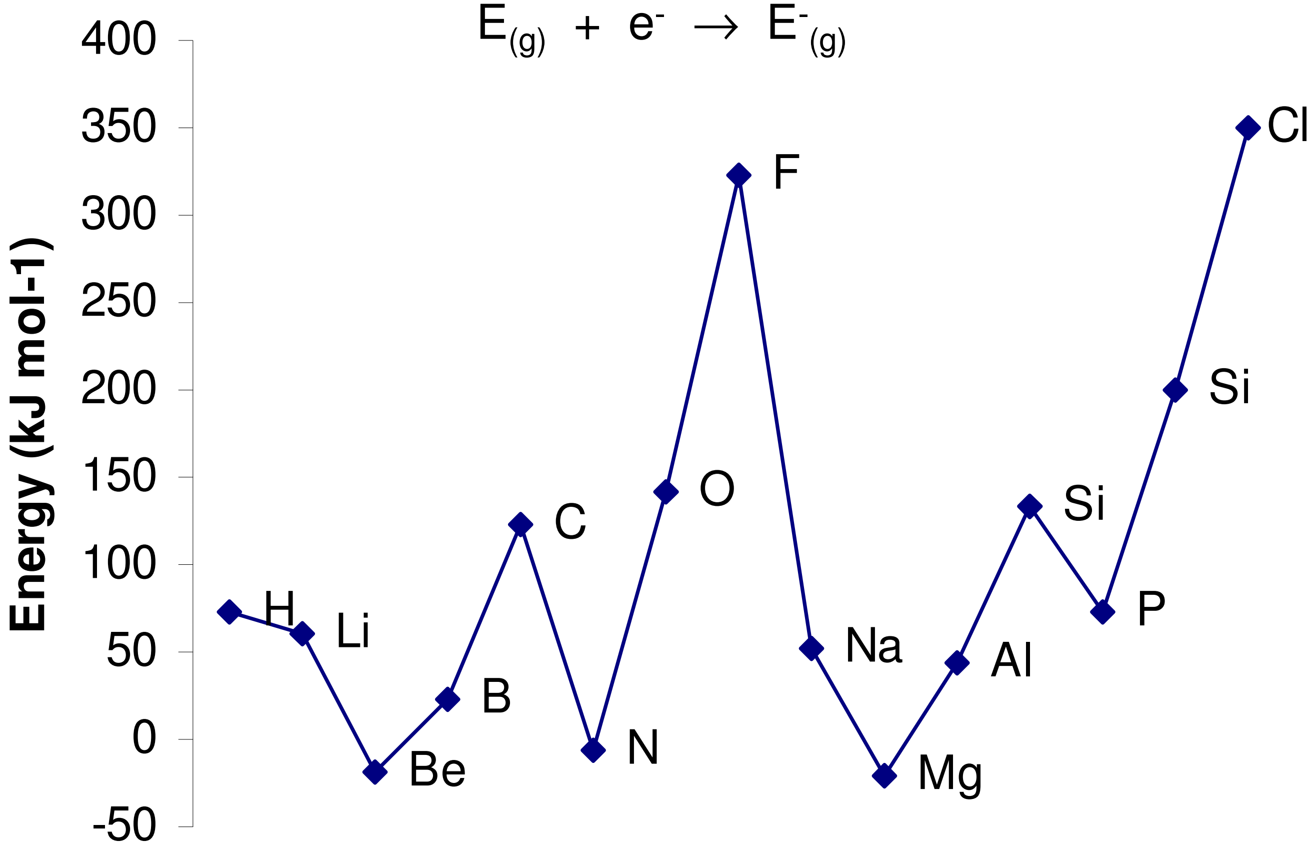
Successive ionisation energies



2. Electron Affinities

The energy change when an electron is added to an atom (or ion). By convention, when energy is given out the EA is positive.

$$E_{(g)} + e^- \rightarrow E^-_{(g)}$$

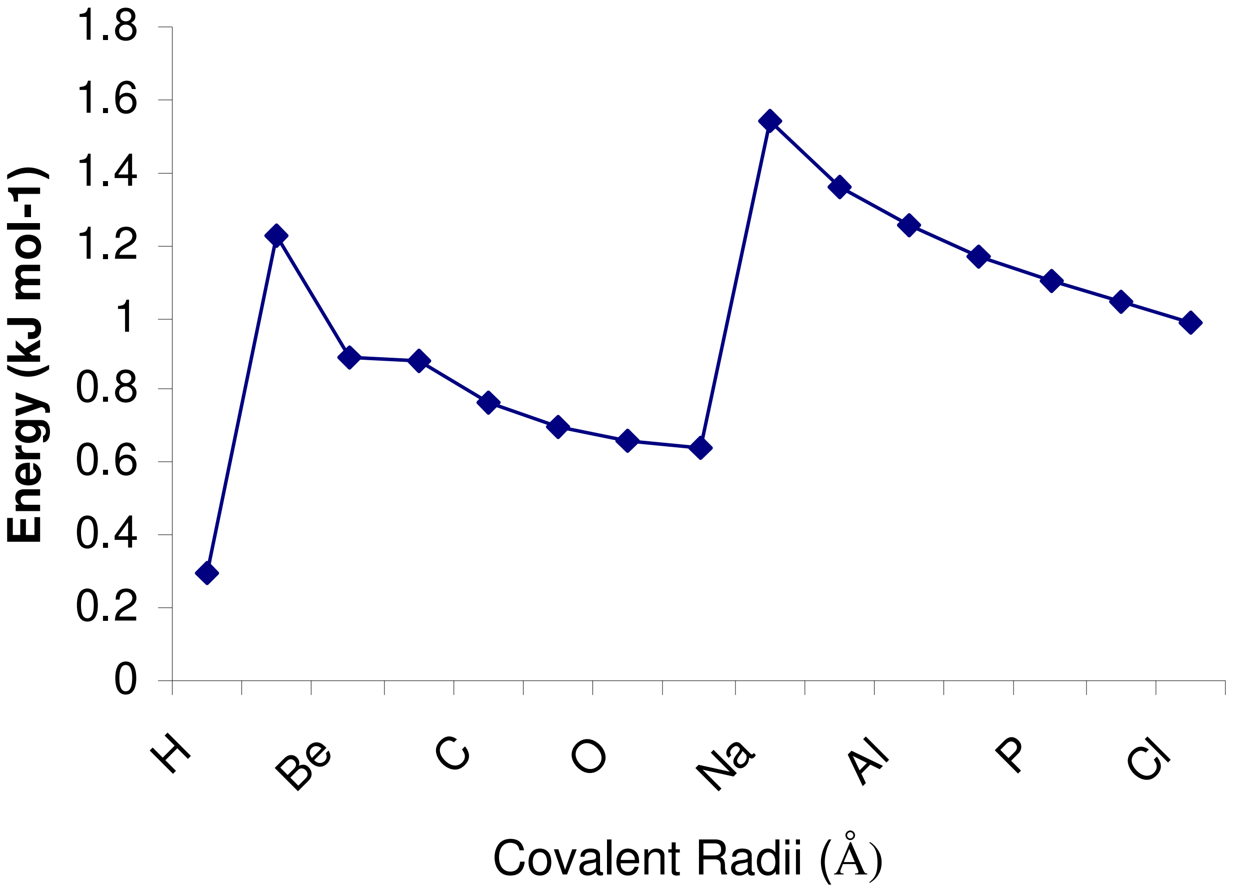


Electron affinities (kJ mol^{-1})for the first two periods (excluding noble gases

EA <0 kJ mol^{-1})

3. Covalent and Ionic Radii

Covalent Radius is defined as half the length of a symmetrical homonuclear element-element bond



4. Electronegativity

Jöns Berzelius (1820s)

Electronegativity is defined as the power of an atom in a molecule to attract electrons to itself

Very powerful principle for understanding the nature of the elements and the types of compounds they form with each other

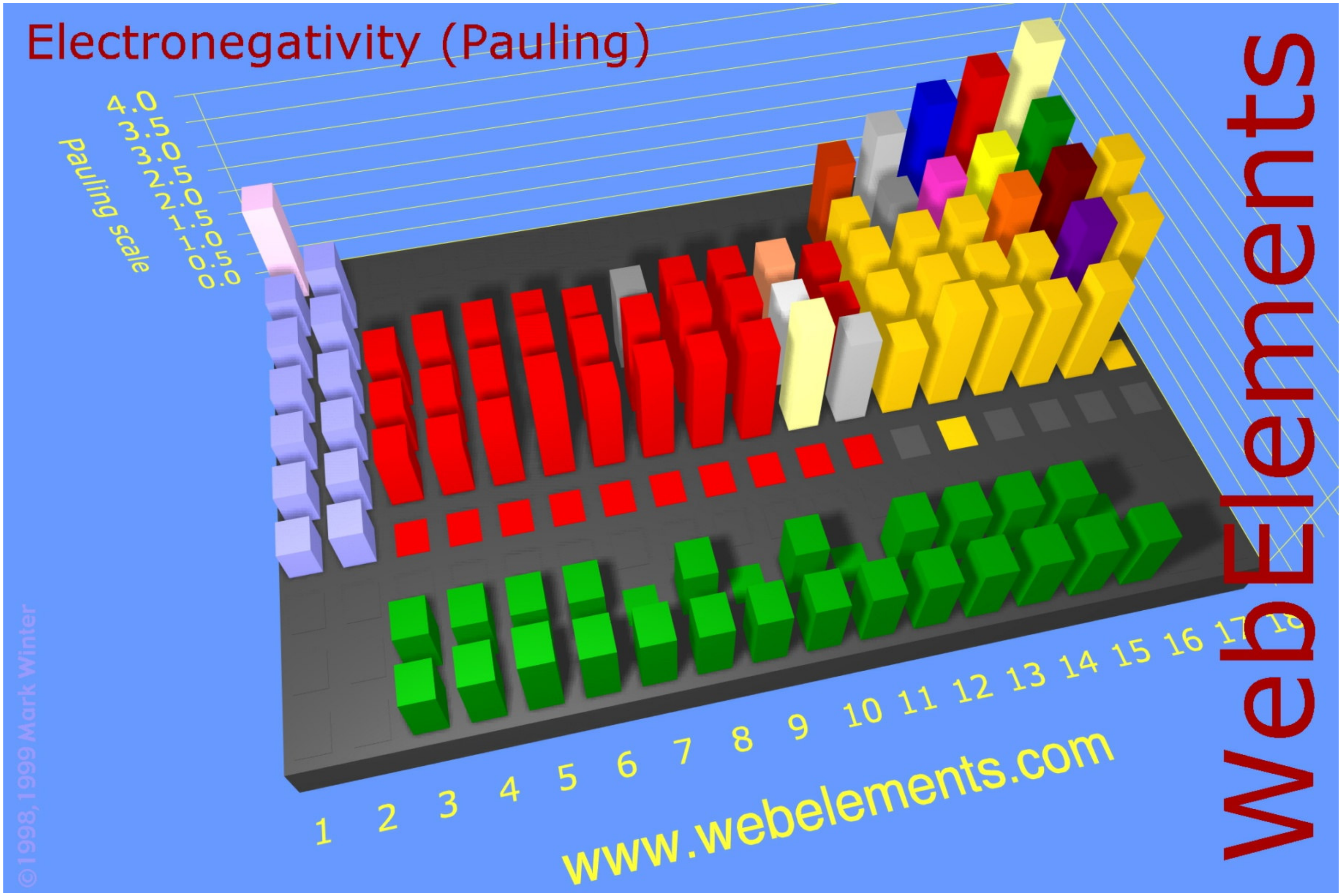
Pauling Electronegativity (χ^P)

Empirical relationship - Pauling assigned the most electronegative element, F, to 4.

He noticed that the bond energy E(AB) in a molecule AB is always greater than the mean of the bond energies E(AA) + E(BB) in the homonuclear species AA and BB. His argument was that in an "ideal" covalent bond E(AB) should equal this mean, and that the "excess" bond energy is caused by electrostatic attraction between the partially charged atoms in the heternuclear species AB.

4. Electronegativity (cont.)

The 3rd dimension of the periodic table?



4. Electronegativity (cont.)

Periodic Trends: As you go across a period the electronegativity increases.
As you go down a group, electronegativity decreases.

Explaining the Trends in Electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus (or Z_{eff})
- the distance from the nucleus (or quantum number n)
- the amount of shielding by inner electrons.

4. Electronegativity (cont.)

We can use the difference in electronegativity to understand simple bonding concepts – covalent and ionic bonding