Atomic Structure

Part 3 & 4

Dr Bob Baker

School of Chemistry

TCD

Emission Spectrum of Hydrogen

The Periodic Table

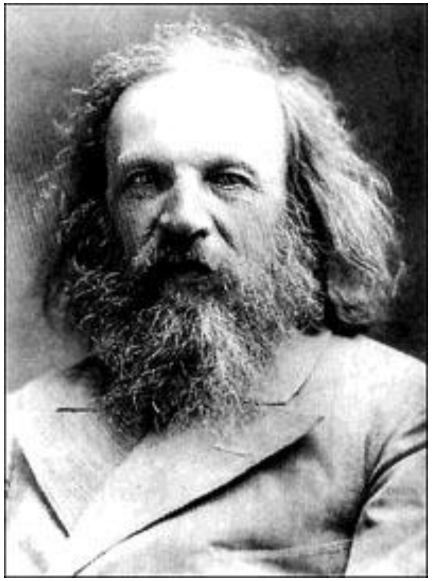


TABELLE II

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 **Cp**	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)

Naturally Occurring Man-Made

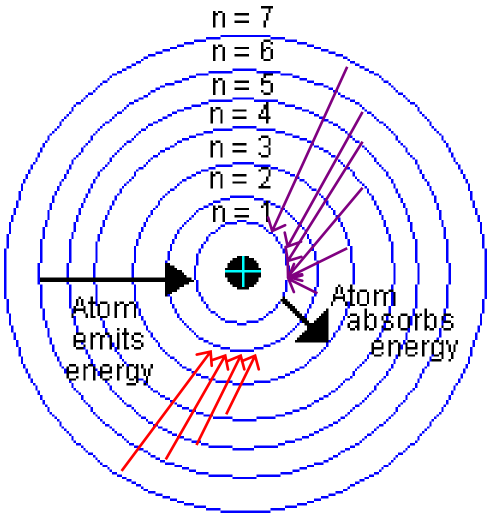
The Bohr Model

- 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.

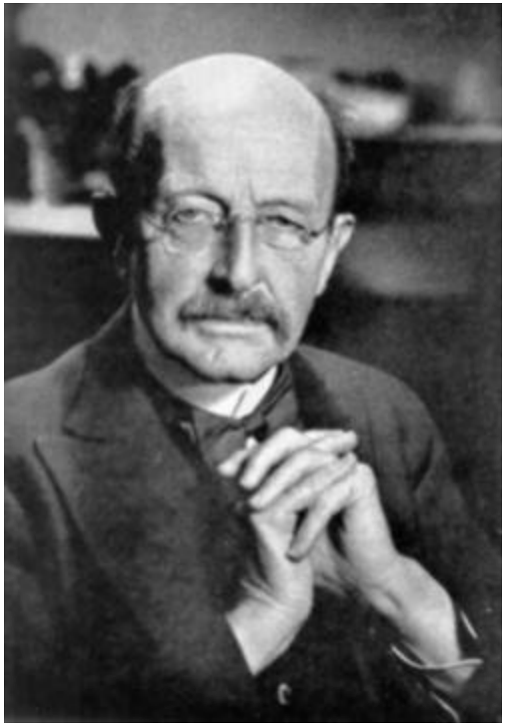


Any object moving along a straight line has a *momentum* equal to the product of its mass (*m*) times the velocity (*v*) with which it moves. An object moving in a circular orbit has an *angular momentum* equal to its mass (*m*) times the velocity (*v*) times the radius of the orbit (*r*). Bohr assumed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

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

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

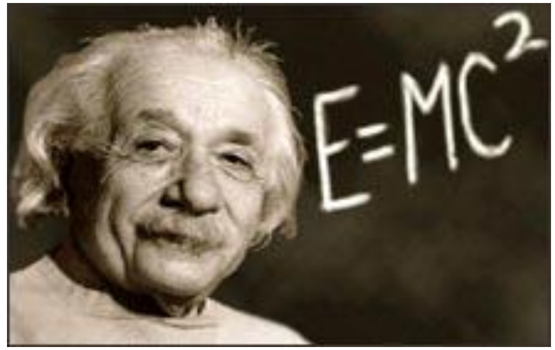
$$\Delta E = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$



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

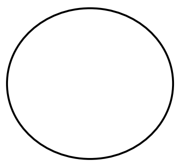
$H\Psi = E\Psi$

Wave-Particle Duality proposed by De Broglie

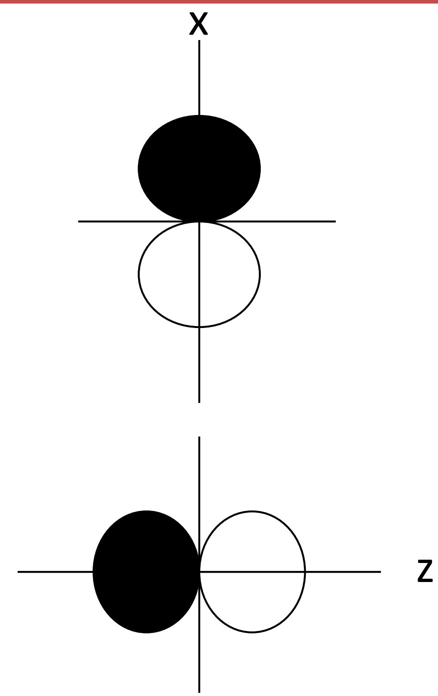
$\lambda = h/m\nu$

Complex physics and mathematics! BUT chemists want to know what it says about molecules not maths

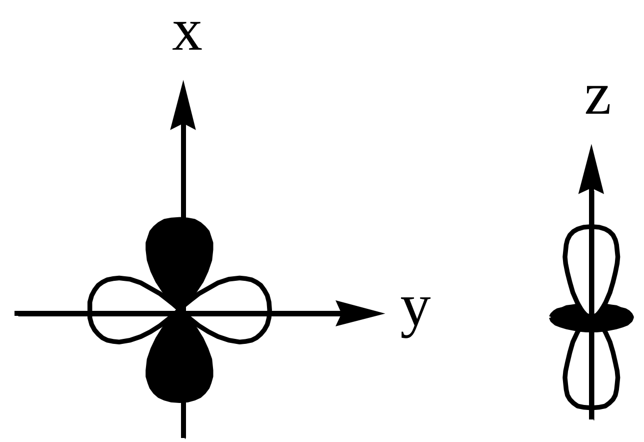
Shapes of orbitals



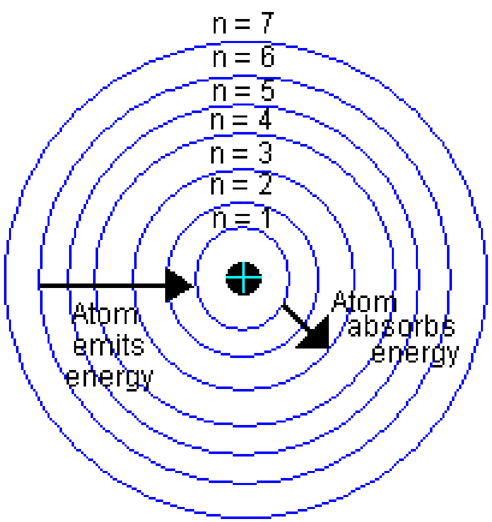
s orbital



p orbital



d orbital



Why do they take this shape?

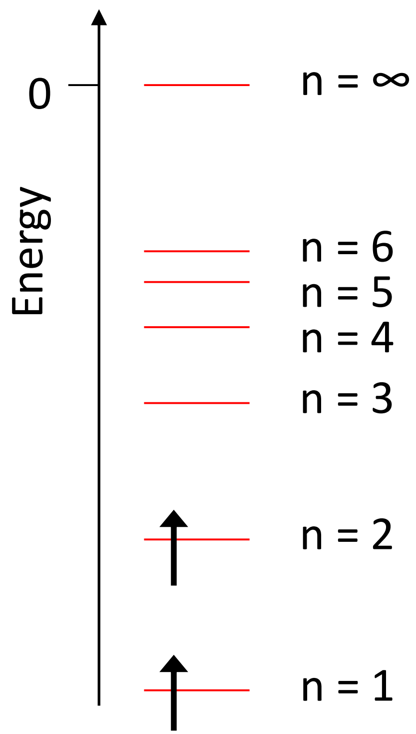
Quantum Mechanics!

Energies of orbitals

For a hydrogen atom the energies are ordered purely by quantum numbers.

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

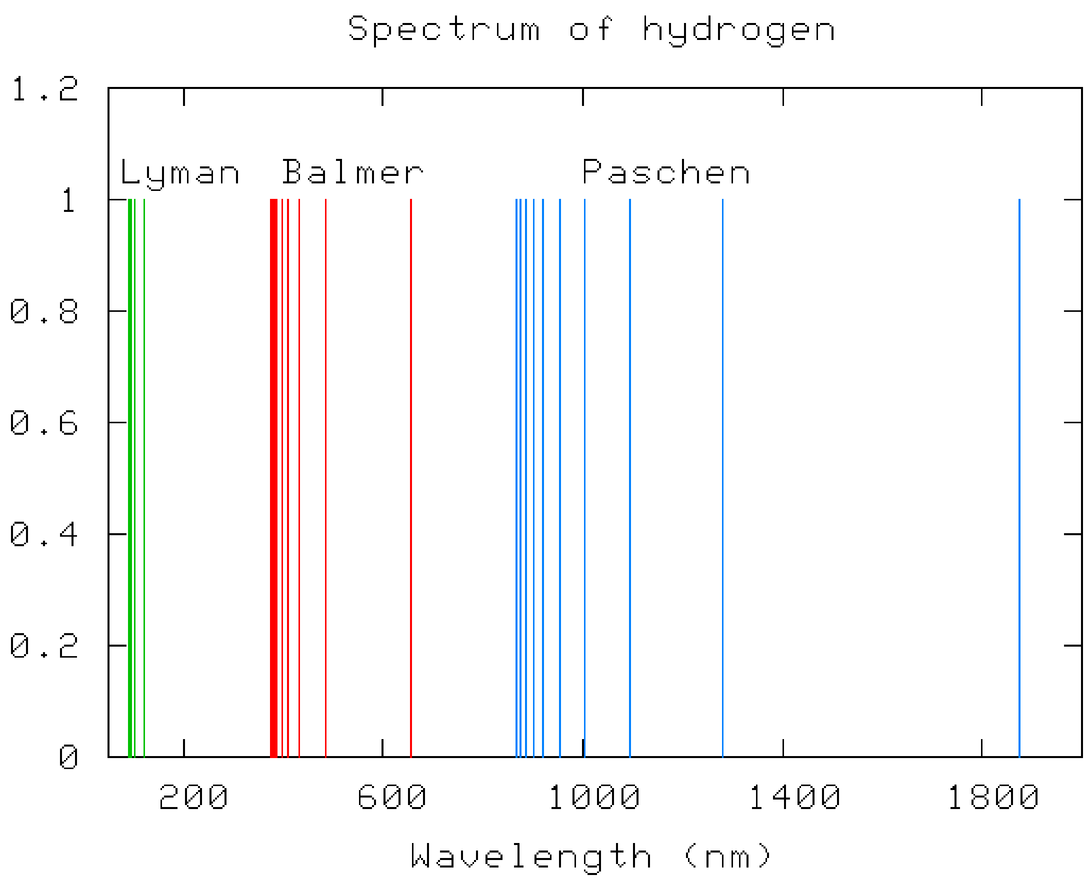
The scale shows a more negative energy as we go to lower quantum numbers – more stable

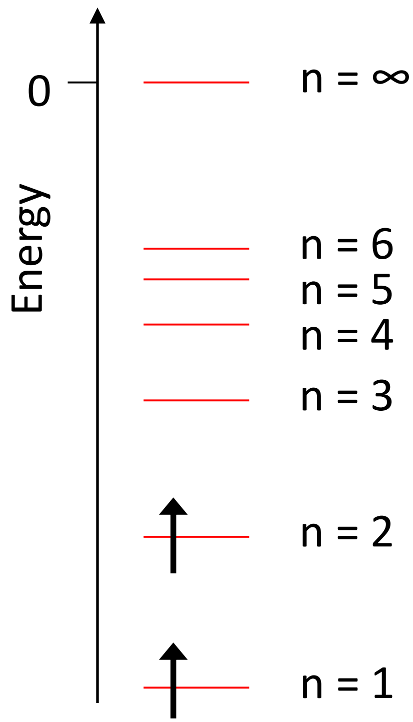
For hydrogen the electron is accommodated in the lowest energy orbital. This is known as its *ground state*.

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*.

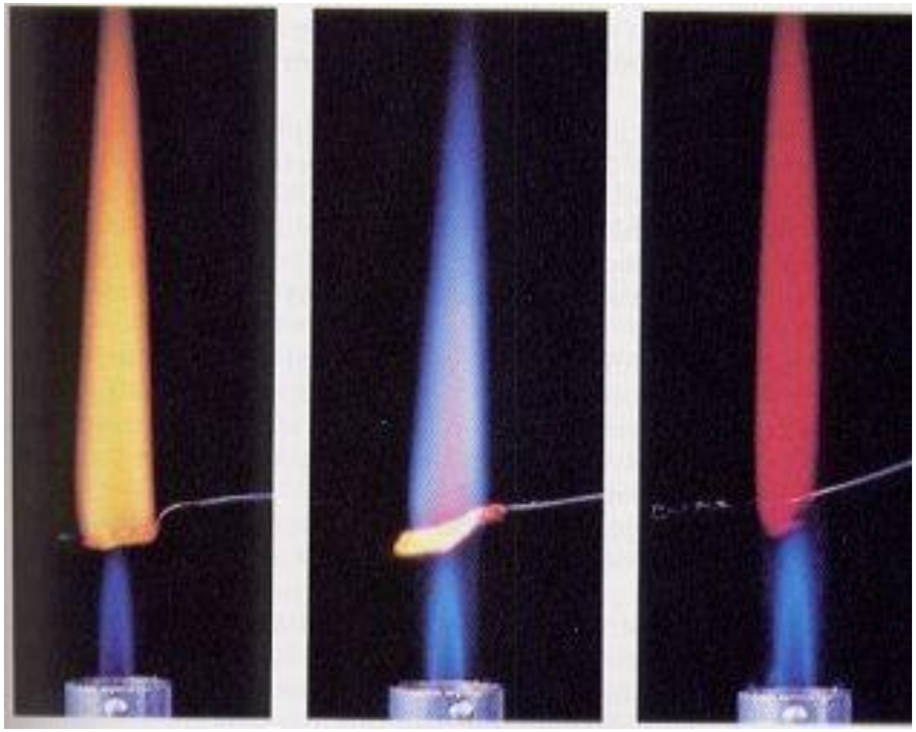
Energies of orbitals





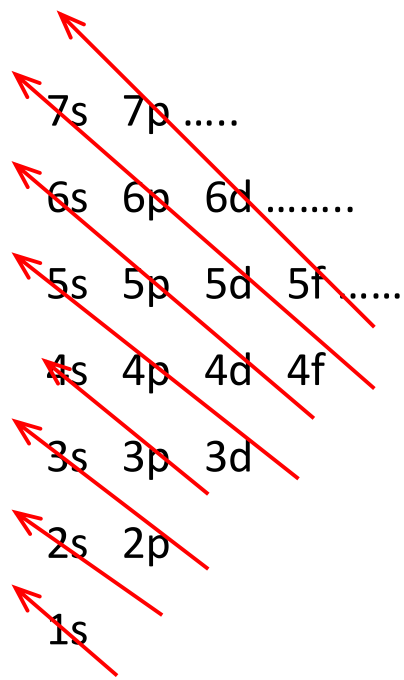
Emission Spectrum of Hydrogen

Flame tests of other elements



Na^+ K^+ Li^+ Ba^{2+}

Filling of electrons



An aid to remember the order

Electronic structure of periods

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!

Electronic Configurations

The Octet Rule:

Atoms try to obtain the noble gas configuration by loss or gain of electrons.

How does that work?

Lithium has 3 electrons: $1s^2 2s^1$

If it loses an electron to form Li^+: $1s^2$

$\Rightarrow Li^+ \equiv He$

Electronic Configurations

The Octet Rule:

Atoms try to obtain the noble gas configuration by loss or gain of electrons.

Fluorine has 7 electrons: $1s^2 2s^2 2p^5$

If it gains an electron to form F^-: $1s^2 2s^2 2p^6$

$\Rightarrow F^- \equiv Ne$

Electronic Configurations

The Octet Rule:

Atoms try to obtain the noble gas configuration by loss or gain of electrons.

Carbon has 6 electrons: $1s^2 2s^2 2p^2$

Does it gain 4 electron or lose 4 electrons?

Answer is neither – it shares its electrons

Electronic Configurations

The Octet Rule:

Atoms try to obtain the noble gas configuration by loss or gain of electrons.

Carbon has 6 electrons: $1s^2 2s^2 2p^2$

Carbon in CH_4 shares 4 electrons with hydrogen so as to obtain its octet

The Periodic Table

s block

p block

d block

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Row

Similar Properties

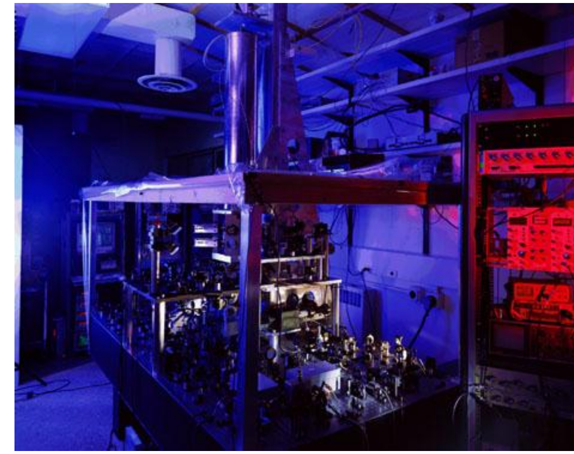
f block

Period – Trend in Properties

Group Trends -The Alkali Metals

$LiCO_3$ pills for mood disorders

Potassium is found in foods



Cs (and Rb) used in clocks

Li

Na (145g)

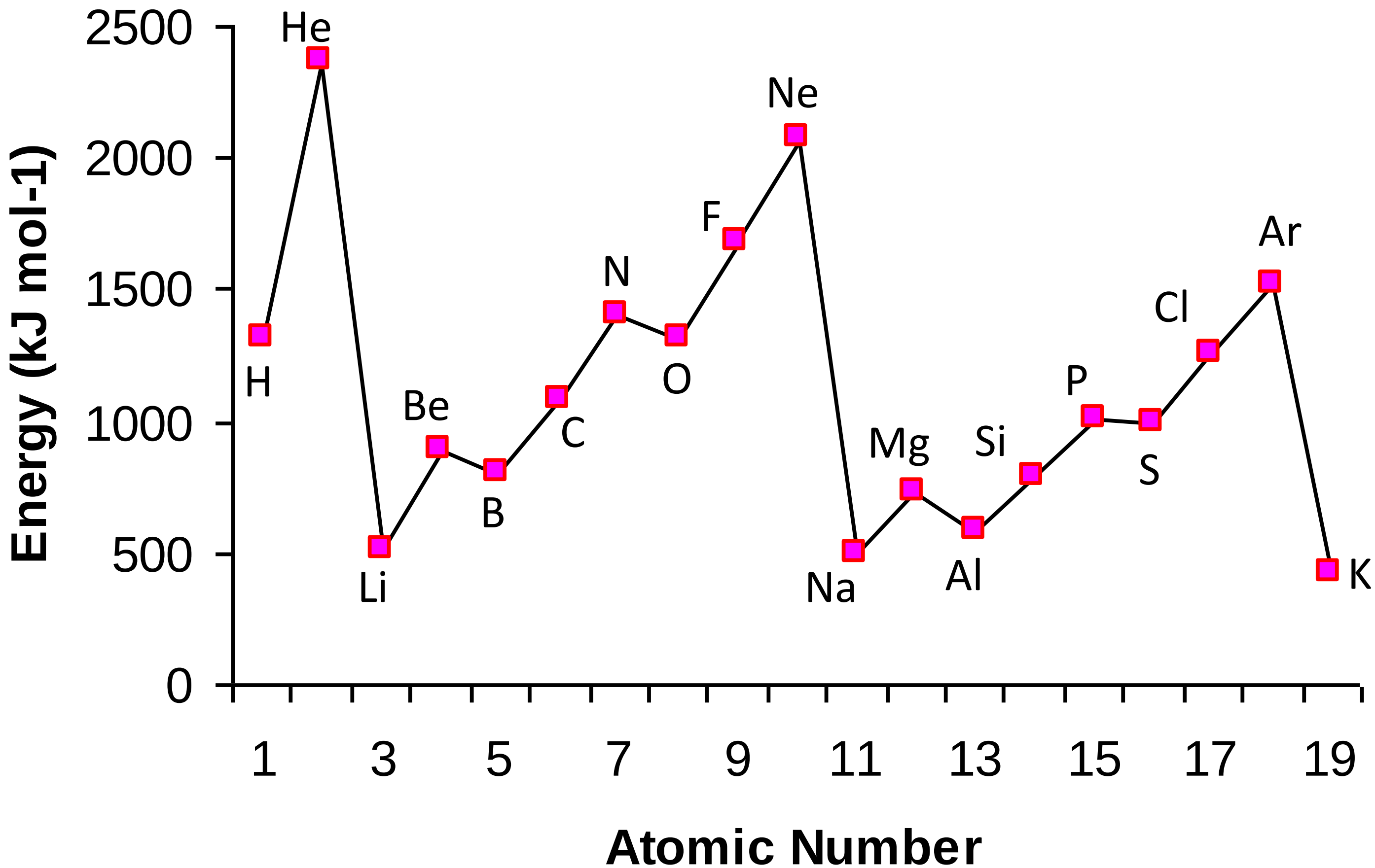
K

Rb and Cs

Ionisation Energy

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

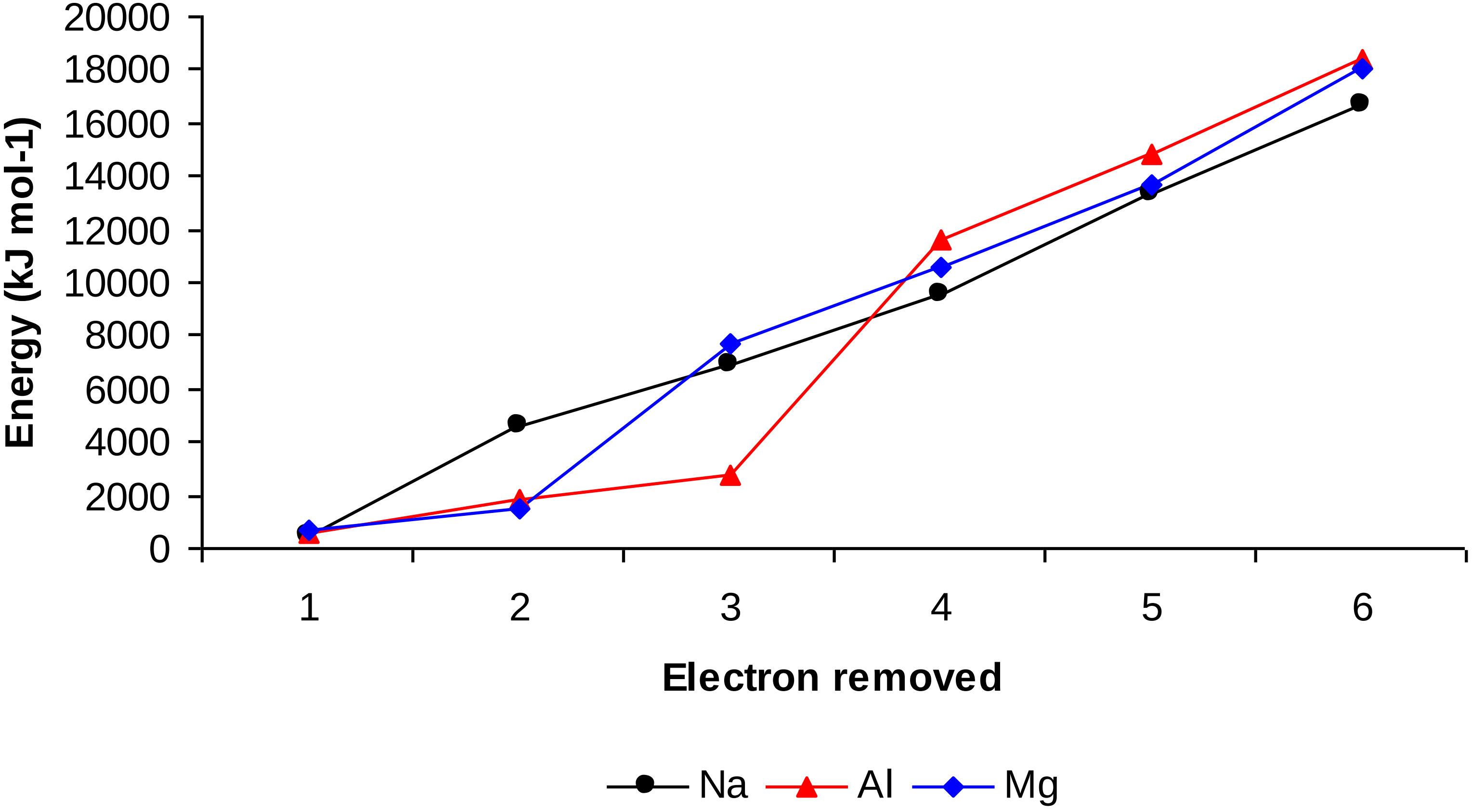
$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-}$$



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

Ionisation Energy

Can we use ionisation energies to rationalise Na^{+}, Mg^{2+}, Al^{3+}?



Successive ionisation energies

Electronegativity

Jöns Berzelius (1820s)

Pauling Electronegativity (χ^P)

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

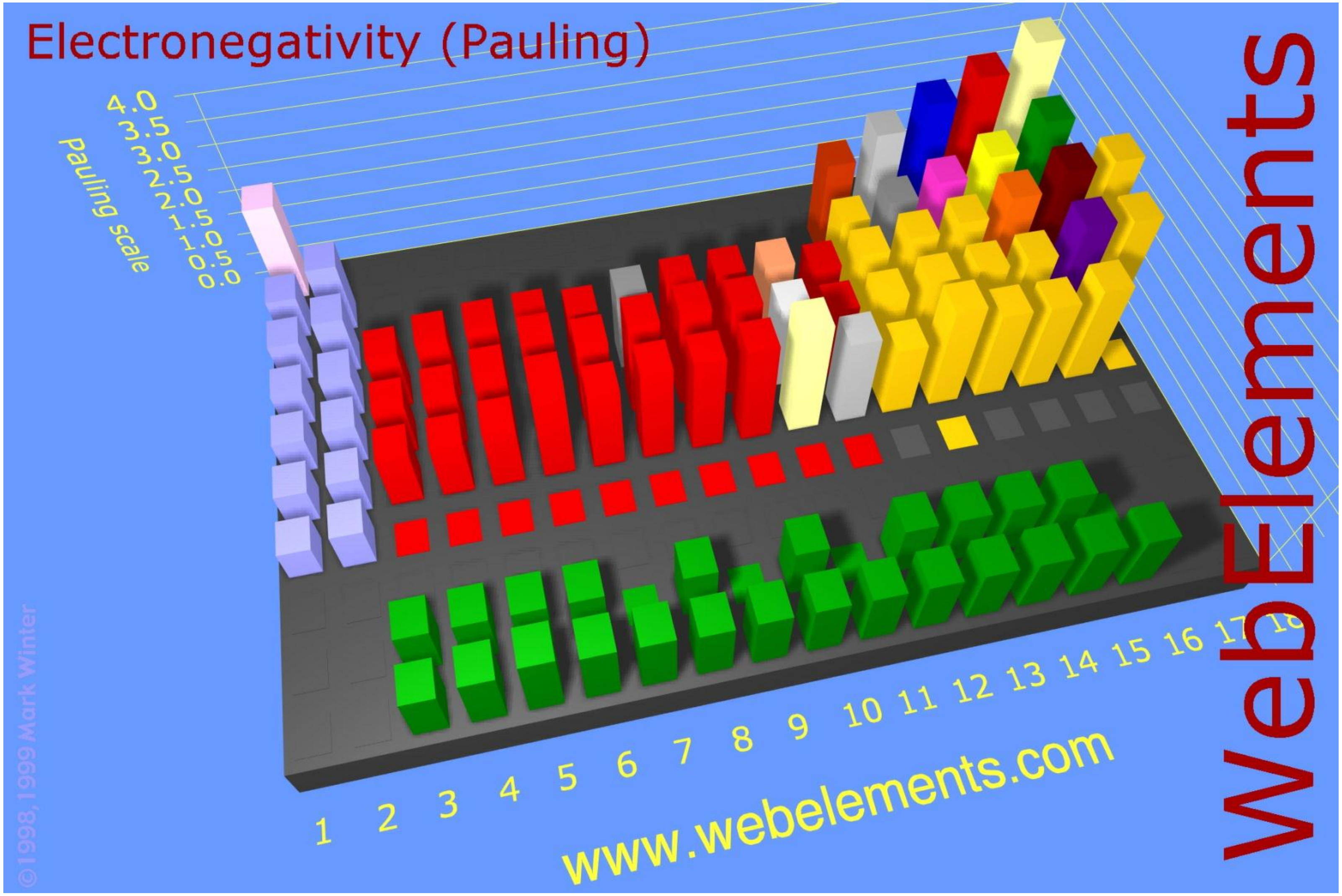
Very powerful principle for understanding the nature of the elements and the types of compounds they form with each other

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.

Electronegativity

The 3rd dimension of the periodic table?



Electronegativity

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
- the distance from the nucleus
- the number (and type) of inner electrons.

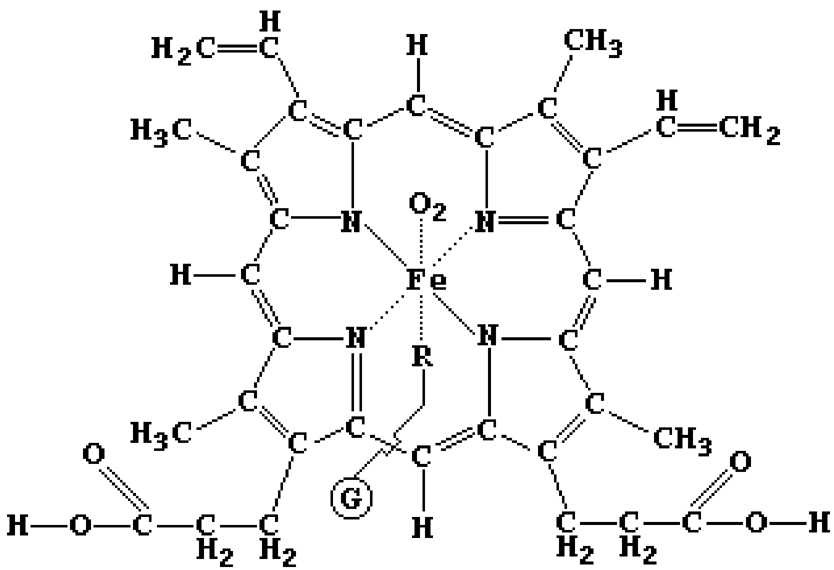
Naming Oxoacids

Oxoanion		Oxoacid	
Formula	Name	Formula	Name
ClO^-	hypochlorite	$HClO(aq)$	hypochlorous acid
ClO_2^-	chlorite	$HClO_2(aq)$	chlorous acid
ClO_3^-	chlorate	$HClO_3(aq)$	chloric acid
ClO_4^-	perchlorate	$HClO_4(aq)$	perchloric acid
NO_2^-	nitrite	$HNO_2(aq)$	nitrous acid
NO_3^-	nitrate	$HNO_3(aq)$	nitric acid
SO_3^{2-}	sulfite	$H_2SO_3(aq)$	sulfurous acid
SO_4^{2-}	sulfate	$H_2SO_4(aq)$	sulfuric acid
HSO_3^-	hydrogen sulfite	$H_2SO_3(aq)$	sulfurous acid
HSO_4^-	hydrogen sulfate	$H_2SO_4(aq)$	sulfuric acid

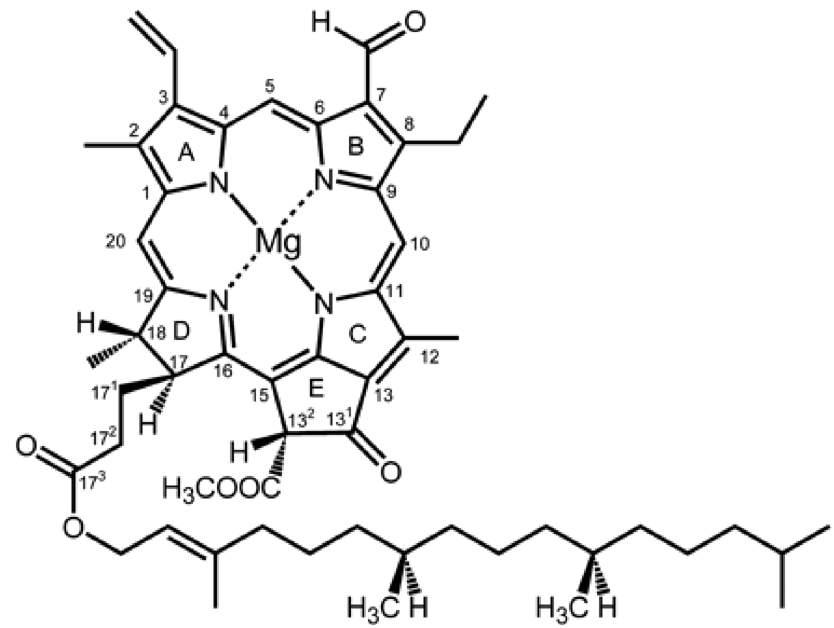
if oxoanion ends in "ite" acid ends in "ous"

if oxoanion ends in "ate" acid ends in "ic"

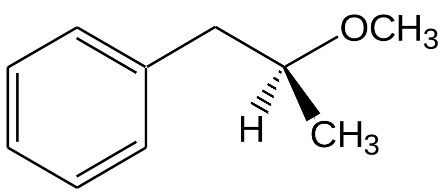
Bonding



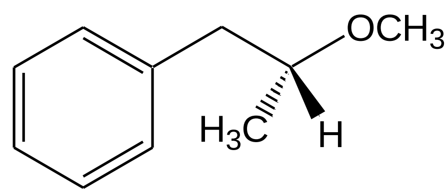
Haemoglobin



Chlorophyll



d-methamphetamine



l-methamphetamine

Bonding

How can we use the ideas previously discussed to understand bonding?

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

e.g. F $1s^2 2s^2 2p^5$

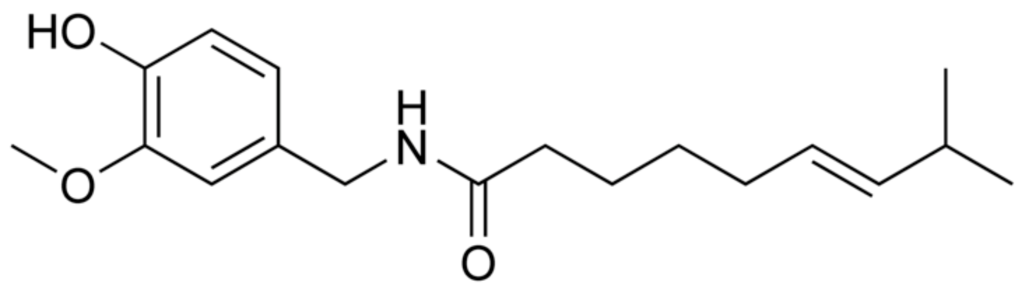
CORE VALENCE

Bonding

2 major types of bond

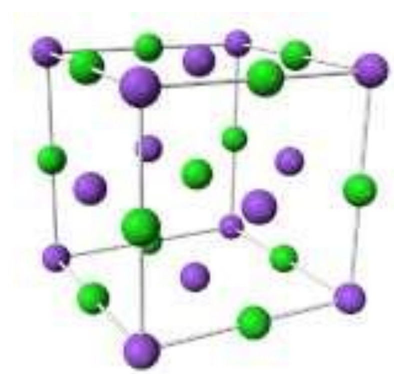
1. COVALENT

2. IONIC



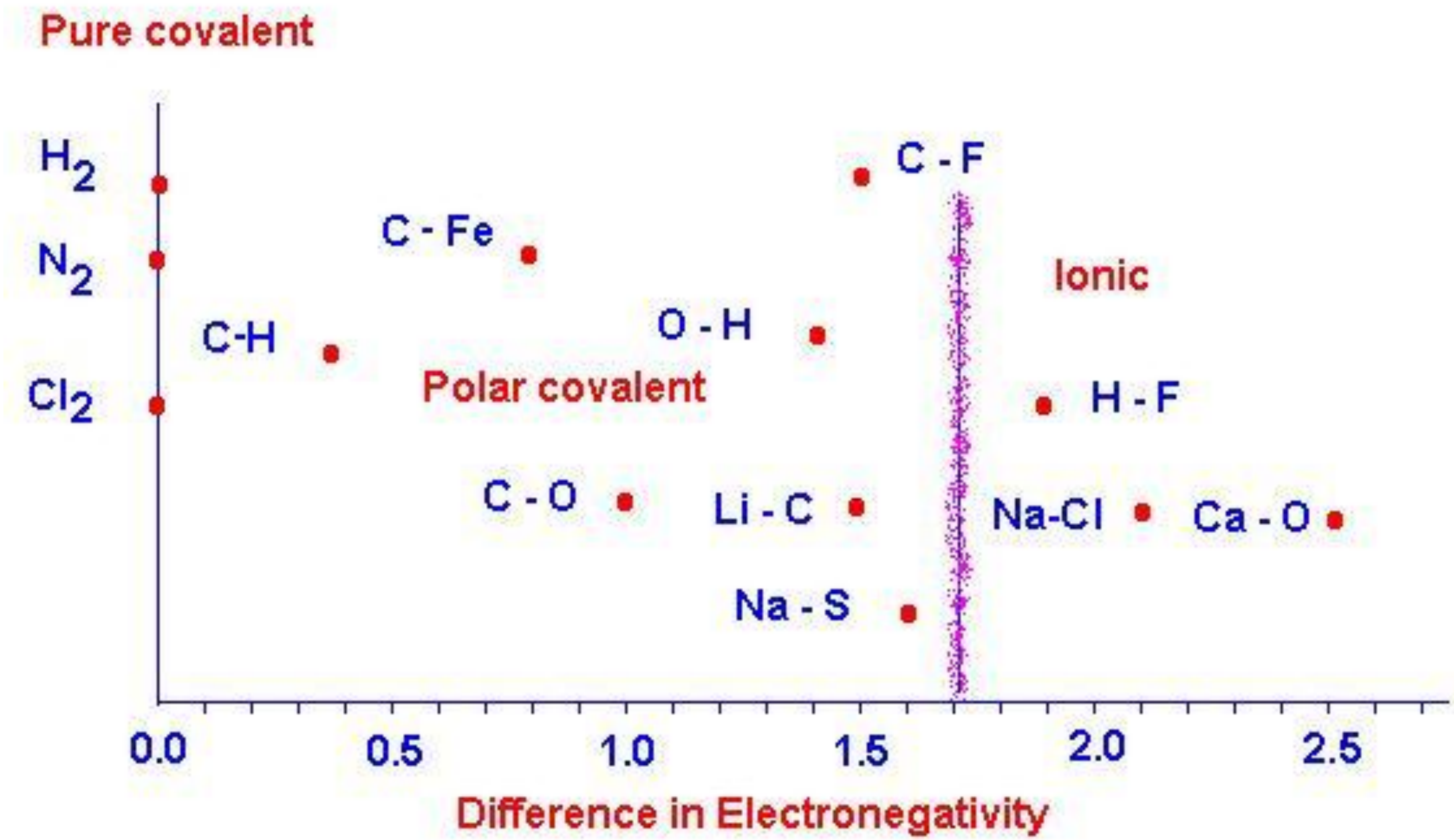
Covalent is a sharing of electrons to form a bond

Ionic is loss/gain of electrons



Electronegativity

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



Lewis Structures

What is a bond?

-Sharing of electrons

-Covalent bond, bonding electrons localised, or fixed, between two atoms

Electrons that are not shared are localised as lone pairs

Lewis theory states that all atoms are trying to achieve a noble gas configuration ⇒ OCTET rule

Some rules for Lewis dot diagrams:

Only use valence electrons

Under most circumstances symmetrical geometry is correct!

Oxygen is commonly and Hydrogen always peripheral

Arrange electrons so that all non-H atoms obtain an octet (exceptions for elements in the 3rd and 4th row)

Lewis Structures – Complex Structures

1 – Determine the total number of valence electrons

Neutral complexes sum the valence electrons

Cationic complexes *subtract* the charge

Anionic complexes *add* the charge

2 – Draw the skeletal structure with single bonds. (H is NEVER a central atom)

3 – Place pairs of electrons around the outermost atom

4 – Place any surplus electrons on the central atom

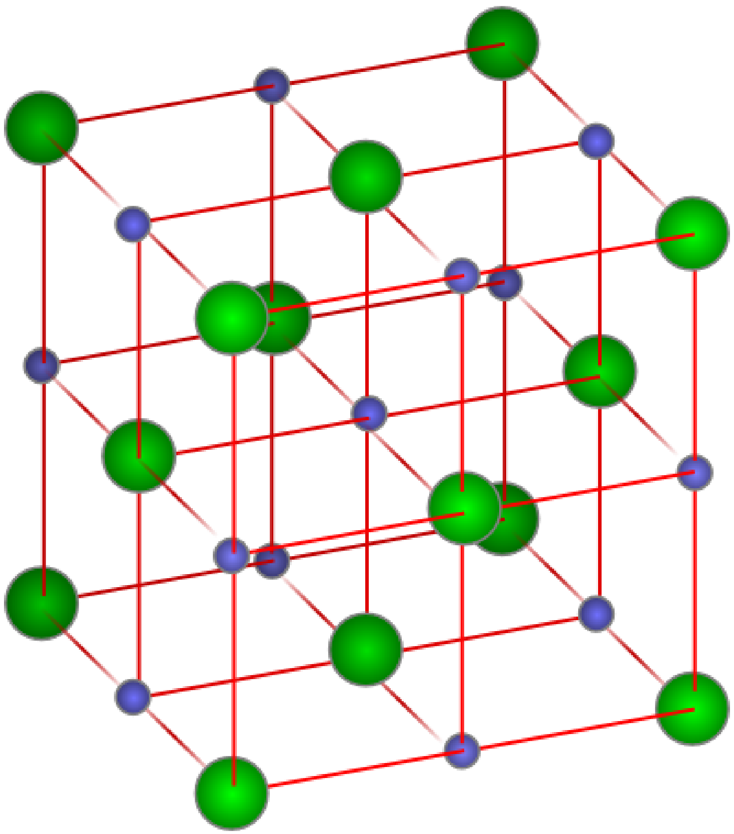
5 – If the central atom does NOT have 8 electrons form a double bond

Ionic Compounds

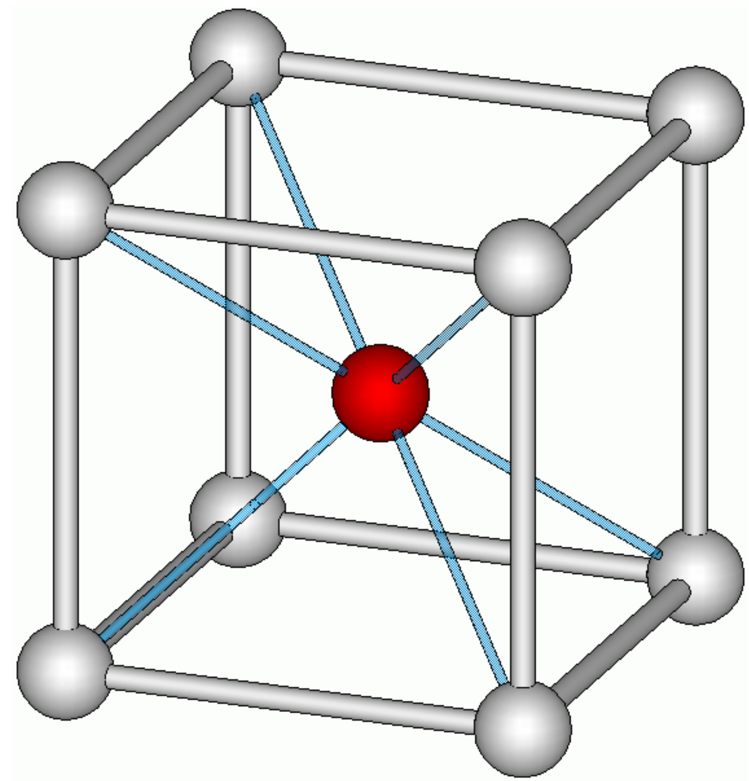
What are the structures of ionic solids e.g. NaCl?

- Can be thought of as effectively packed arrays of ions

- Efficient means maximising the contacts with oppositely charged ions



The structure of Sodium Chloride shows a coordination number of 6.



The structure of Cesium Chloride shows a coordination number of 8.