Review: Atomic Structure

A nucleus consists of nucleons: Protons and Neutrons; p^+, n^0

The mass number of a species is: $A = p^+ + n^0$

Number of neutrons = atomic mass - atomic number

Atomic number N^0 represents:
- Number of protons in the nucleus
- Number electrons in the neutral atom
- Position of the element in the Periodic Table

Isotopes:
- Species with the same Atomic Number, but different Mass Number.
- Species with the same number of protons, but different number of neutrons.

Relative Atomic Mass:
- The ratio of the average mass per atom of a naturally occurring form of an element to one twelfth the mass of an atom of the isotope C-12 (Carbon 12) exactly.

Example table of atomic mass calculation:

Isotope	Relative Atomic Mass	Relative abundance
^{35}Cl	35	75%
^{37}Cl	37	25%

Relative Atomic Mass = $\dfrac{75(35) + 25(37)}{100} = 35.5$

Note: *Mass spectrometry* – used to determine the masses of elements and their isotopes. (Recall: [VIADD], also the amount of deflection depends inversely on the mass and directly on the charge of the ion, hence by varying the strength of the magnetic field it is possible to separate the ions of different mass.)

The hydrogen spectrum

In the visible part of the hydrogen spectrum four separate, (distinct or discrete), lines can be seen. Each of these lines represents electrons falling back to the *second energy level* from one of the levels above.

Lines are seen in the spectrum because the energy of the electrons is 'quantised'. This means that only certain energy levels are allowed in the atom and the electrons can only move between these separate (or discrete) energy levels. So each line in the emission spectrum is the result of electrons moving from a higher quantised energy level to a lower energy level. The difference in energy between the two level is related to the frequency of the radiation by Planck's constant: $\Delta H = hf$

The lines in the spectrum become progressively closer together to each other, i.e. they converge, as the frequency or energy of the lines increases. This is because the energy levels in an atom also get closer together; thus the relative energy given out when an electron falls back from say n = 4 to n = 1 is less than when it falls from n = 3 to n = 1. When the electron falls back into the first energy level, then the lines are seen in the ultraviolet region; whilst those falling back to the third energy level are seen in the infrared.

Orbitals
- A region of space in which there is a high probability of finding an electron
- Orbitals differ from each other in shape and in their special orientation

Different orientations of the s and p Orbitals
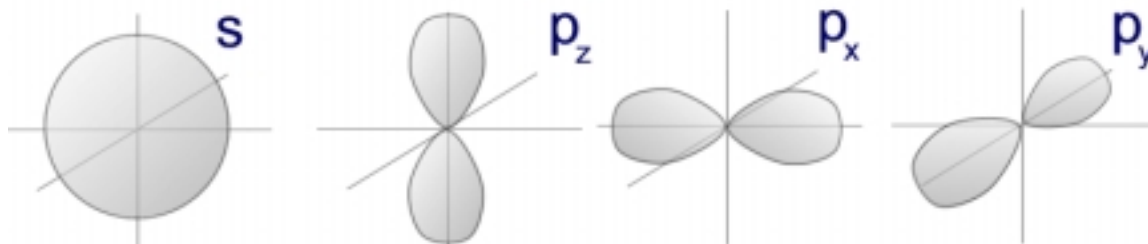
d -Orbitals are shaped either like a 4-blade propeller or like an hourglass with a belt around it.

There are n^2 orbitals possible in an energy level, since only two electrons may occupy an orbital hence the maximum number of electrons in an energy level is $2n^2$.

Energy levels and orbitals:

n	Number of Orbitals (n^2)	Number of each type of orbital		
		s	p	d
1	1	1		
2	4	1	3	
3	9	1	3	5

Electronic Energy Levels
Electrons arrange themselves in the energy levels as described in the diagram.

Electron configuration Rules:
- Electrons fill up orbitals starting with those of lowest energy.
  - Building up process referred to as "Aufbau Principle"
- Maximum of 2 electrons per orbital, Pauli's Exclusion Principle.
- Hund's rule: all degenerate orbitals fill with one electron before pairing up with others.

E.g.: $_{17}Cl - 1s^2 2s^2 2p^6 3s^2 3p^5$
E.g.: $_{25}Mn - [Ar] 3d^5 4s^1$
Note: for transition metals the 4s is filled before the 3d, however when writing the electron configuration, it is written as 3d followed by 4s. Example: Sc: $[Ar] 3d^1 4s^2$

Calculation involving electron transitions:

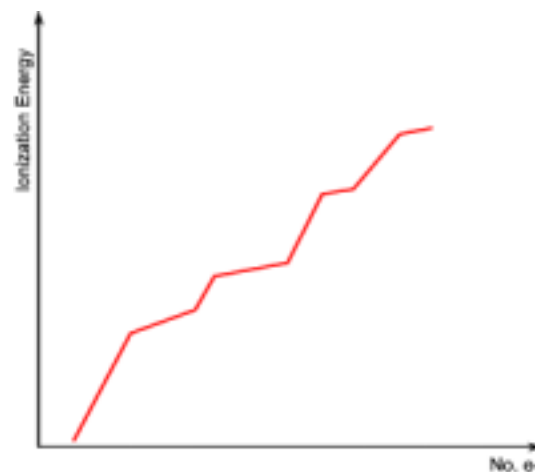$$\lambda = \frac{hc}{\Delta E} \qquad \Delta E = -R_H \left(\frac{1}{n^2_{inner}} - \frac{1}{n^2_{outer}} \right)$$

Evidence for Electronic Structure of Atoms
Ionization Energy: $X(g) + IE \rightarrow X^{+1} + e^-$ $\Delta E = IE$
Use of Successive Ionization Energies to explain the existence of sub-levels:
Graph supports theory about orbitals, as there are breaks in the graph. E.g: $_{23}Na: 1s^2 2s^2 2p^6 3s^1$ note the break in the 7 and 8 electron: due to 2s and 2p; also $2p^6$ is seen as two: $2p^3 2p^3$

Periodic trends in the Periodic Table

1.Atomic Radius decreases across a period:
- o Effective nuclear charge increases
- o Since # of protons increases, electrostatic attraction of the nucleus for electrons increases

Atomic radius increases going down a group: number of energy levels increases

Size of cations and anions:

Cations are smaller than the parent atom. Anions are larger than the parent atom.

2. 1st IE generally increases across a period. 1st IE generally decreases going down a group. The value of the first ionization energy depends upon: (1) the effective nuclear charge, (2) the distance between the electron and the nucleus, and (3) the 'shielding' produced by lower energy levels.

- Note the following exceptions:

$_4Be \rightarrow$ B $_7N \rightarrow {}_8O$

$_4$Be: $1s^2 2s^2$

$_5$B: $1s^2 2s^2 2p^1$
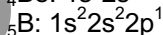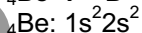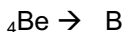
*Sharp Decrease
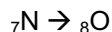
3. Electronegativity increases across a period.
- o This is the relative measure of the attraction an atom has for electrons in a covalent bond between it and another atom. Use of the Pauling scale to predict the polarity of a bond:

o	Li	Be	B	C	N	O	F	Ne
	1.0	1.5	2	2.5	3	3.5	4	

Note: noble gases are assigned a value of zero.

4. Electron Affinity: this is another useful measure of electron attraction by atoms is called the electron affinity; this is the energy change when a mole of electrons is added to a mole of atoms in the gas phase: $X(g) + e^- \rightarrow X^{+1} + EA$ $\Delta E =$ electron affinity

The electron affinity is a measure of the attraction an atom has for other electrons apart from its own.

Values of electron affinities do not show a clear trend, also note second electron affinity values are generally endothermic.

5. Periodic trends in the oxides and the chlorides of the elements

Bonding

I. Metallic

Close packed lattices of ions surrounded by a "sea of delocalized electrons"

Metallic Bond: Electrostatic force of attraction that two neighboring nuclei have for the delocalized electrons between them.

Lattice Energy: This is the energy needed to break up one mole of atoms in the lattice into separate atoms. $M(s) \rightarrow M(g)$

Going down a group: Lattice Energy decreases as the size of the metallic ions increases (melting point decreases, reactivity increases) because reaction involves losing electrons.

Going across the period left to right, from group 1 to 2 to 3 the lattice energy increases as the charge on the ion increases.
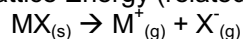
So high lattice energies result from small highly charged ions.

Common Properties of Metals: Conductivity, Ductility

II. Ionic

An ionic bond is the electrostatic force of attraction between two oppositely charged ions formed as a result of electron transfer → forming a 3D-lattice structure.

Ionic Lattice Energy (related: **Born Haber Cycle**)

$$MX_{(s)} \rightarrow M^+_{(g)} + X^-_{(g)}$$

The lattice energy is the energy required to decompose 1 mol of ionic lattice into its separate ions in the gas phase.

Lattice Energy depends on:

Size of ions: LE $\propto$ -1/size: small ions attract more strongly than large ones.

Charge: LE $\propto$ product of charges: highly charged ions attract more strongly than ones with less charge.

Properties of Ionic Compounds:

Solid

Melting Point / Boiling Point, generally high, why?

Condition / State:

Solid: none, why?

Molten, and in aqueous solution, why?

Solubility in polar solvent: hydration of ions: LE versus HE (exothermic or endothermic upon dissolving)

Brittleness: When a force is applied to the lattice structure, the layers in the lattice structure slide past each other until ions of the same charge are next to each other – so they repel each other, and thus the lattice breaks.

III. Covalent bonding

The Covalent Bond:

A covalent bond is the electrostatic force of attraction between two nuclei for a localized pair of electrons shared between them
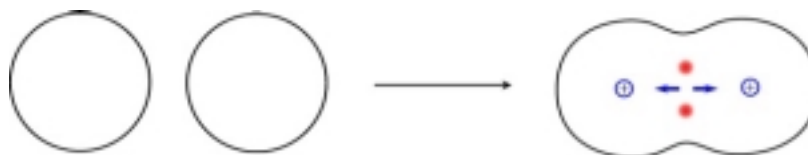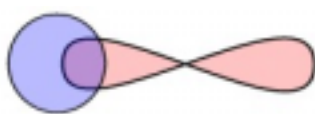

Two kinds of Covalent bond:

Covalent bonds form when the orbitals of two neighbouring atoms overlap so that both nuclei attract the pairs of electrons between them. This can happen in two different ways making two different kinds of bond:
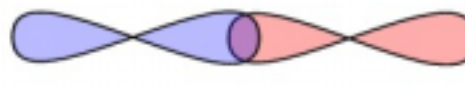
σ : when the orbitals from two atoms overlap along the line drawn through the two nuclei.
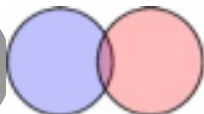
| s-s | s-p | p-p |
| H-H | H-Cl | Cl - Cl |

Greater the overlap, stronger the bond

π : Occasionally, after a sigma bond has formed between two atoms , the p-orbitals of the two atoms also overlap above and below the line drawn through the two nuclei and another bond forms, i.e. perpendicular to the bond nuclear axis → results in two regions of electron density. This is called a pi bond:
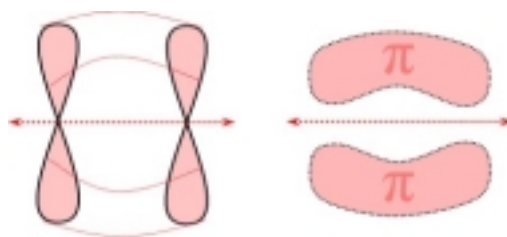
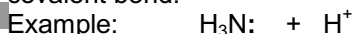Overlap above and below the nuclear axis

Π-bonds are shorter and weaker than sigma bonds

Co – ordinate (Dative) Bond:
Sometimes both the electrons in a covalent bond come from only one of the atoms. This is called a dative or coordinate covalent bond. Once the bond has formed, it is identical to any other covalent bond.
Example: H_3N**:** + H^+ H_2O**:** + H^+

Shapes of molecules

Lewis structures

Electron pair repulsion and VSEPR: The shape of a molecule can be worked out using the following rules about electron pairs:
(1) the pairs of electrons in a molecule (both bonded and lone pairs) behave as though they repel each other and so move as far apart as possible;
(2) lone pairs, LP, repel more than bonding pairs, BP: LP—LP > LP----BP > BP---BP

Working out shapes of molecules: 2 + 0 =linear, 3+0 = trigonal planar, 4+0 = tetrahedral

Explaining different bond angles: the exact angles between bonds can be found using X-ray diffraction. These angles are evidence for the idea that lone pairs repel more than bonding pairs. Example: CH4, (109) NH3, (107), H2O (104)

Resonance and Delocalisation: evidence seen in bond length, e.g. SO3

Polarity of molecules: once the shape of the molecule has been worked out, we can decide if it is polar or non-polar: non-polar if the bond dipoles cancel each other, however if the bond dipoles add up, the molecule will be polar, (this means that there are two separate regions of charge).

Forces between molecules: IMFA's
1. London dispersion forces, (van der Waals), 2. Dipole –dipole 3. Hydrogen bonds

The structure of solids: macromolecular
Covalent: 3—D: diamond, silicon dioxide, quartz, 2---D: graphite

Relate the structure and bonding in each type of crystal to physical properties observed:

Metallic bonding	ionic bonding	covalent bonding Molecular or macromolecular		atomic
Cu, Al	NaCl	CH4,	diamond, graphite	He, Xe