

2.2 Electrons, bonding and structure

2.2.1 Electron structure

- Definitions

Term	Definition
Atomic orbitals	A region around the nucleus that can hold up to two electrons with opposite spins.
Sub-shells	A group of orbitals of the same type within a shell.
Electron configuration	A shorthand method for showing how electrons occupy sub-shells in an atom.

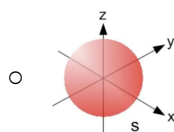
- Number of electrons that can fit in each shell

Shell number n	Number of electrons ($= 2n^2$)
1	2
2	8
3	18
4	32

- Types of orbitals

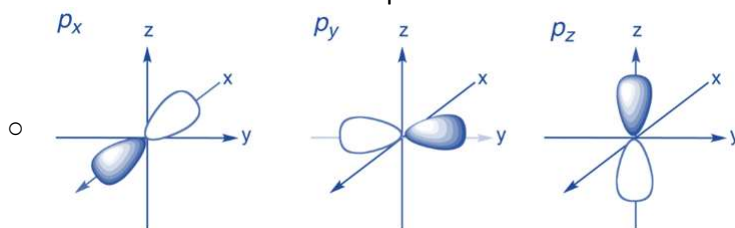
- s-orbitals

- Spherical** shape
 - Each shell from $n = 1$ contains 1 s-orbital
 - Greater shell number n = greater radius of its s-orbital



- p-orbitals

- Dumb-bell** shape
 - Three separate p-orbitals at right angles to one another: p_x , p_y , p_z
 - Each shell from $n = 2$ contains 3 p-orbitals
 - Greater shell number n = its p-orbital is further from the nucleus



- d-orbitals

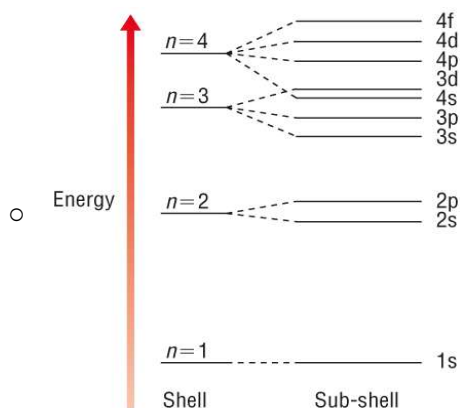
- Each shell from $n = 3$ contains 5 d-orbitals

- f-orbitals

- Each shell from $n = 4$ contains 7 f-orbitals

- Filling of sub shells and orbitals

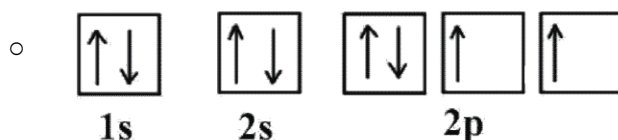
- Sub shells fill in the order of increasing energy ($1s \rightarrow 2s \rightarrow 2p \dots$)



* 4s is filled before 3d

- Inside each sub-shell
 - The orbitals all have the same energy within a sub-shell
 - One electron occupies each orbital before pairing starts to prevent any repulsion between paired electrons
 - Opposite spins within each orbital (one \uparrow and one \downarrow) as both electrons are negatively charged and repel one another so this minimises repulsion
 - The paired electrons are easier to remove than the unpaired ones

Oxygen



- More than one orbital within a sub-shell = the orbitals are degenerate (all the same)
- Writing electron configuration of atoms
 - e.g. Li = $1s^2 2s^1$, F = $1s^2 2s^2 2p^5$
 - Shorthand notation: in terms of the previous noble gas + outer electron sub-shells
 - e.g. Krypton = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ = [Ar] $3d^{10} 4s^2 4p^6$
 - **Always show outer shell electrons**
 - (4s can be written before 3d)
- Exceptions of atom electron configurations
 - Chromium: [Ar] $3d^5 4s^1$
 - Copper: [Ar] $3d^{10} 4s^1$
 - Chromium and copper do not follow the expected pattern
 - Half-filled / fully filled d sub-shell gives **additional stability**
- Electron configuration of ions
 - The highest energy subshell gain or lose electrons
 - d-block elements
 - 4s is at a lower energy level than 3d sub-shell so it is filled first
 - Once filled the energy level of 3d falls below 4s so 4s empties before 3d

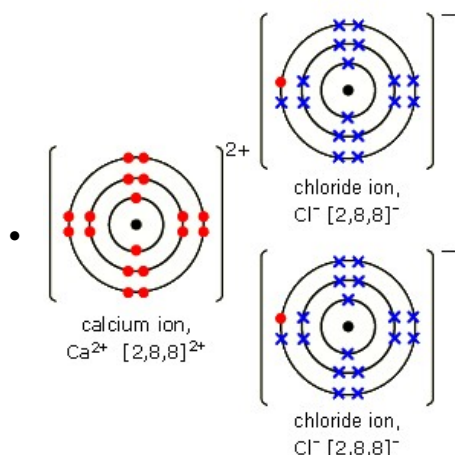
2.2.2 Bonding and structure

- Definitions

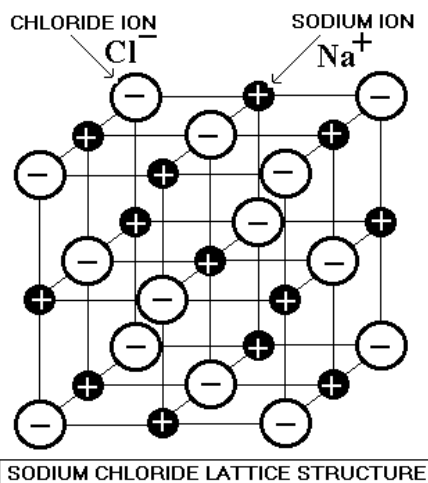
Term	Definition
Polarity	There is an uneven distribution of electrons.
Polar molecule	A molecule with an overall dipole, having taken into account any dipole across bonds and the shape of the molecule.
Bond angle	The angle between 2 bonds in an atom.
Electronegativity	A measure of the attraction of a bonded atom for the pair of electrons in a covalent bond.
• Dipole	A separation in electrical charge so that one atom of a polar covalent bond, or one end of a polar molecule, has a small positive charge, δ^+ , and

	the other has a small positive charge, δ^- .
Intermolecular forces	An attractive force between molecules. Can be London forces, permanent dipole-dipole interactions or hydrogen bonding.
Giant ionic lattice	A three dimensional structure of oppositely charged ions, bonded together by strong ionic bonds.
Simple molecular lattice	A three dimensional structure of molecules, bonded together by weak intermolecular forces.

- Ionic bonding
 - The electrostatic attraction between positive and negative ions
 - Occurs between atoms that have a **big difference in electronegativity** (usually metals and non-metals)
- Dot and cross diagram



- Structure of ionic compounds
 - Each ion attracts oppositely charged ions strongly in **all directions**
 - Forms a **giant lattice structure** containing many ions
 - Every positive ion is surrounded by negative ions; every negative ion is surrounded by positive ions
 - Regular arrangement of ions = regular, predictable shapes depending on size of ions
 - NaCl = always cubic
 - MgSO₄, CuSO₄, etc. = not cubic

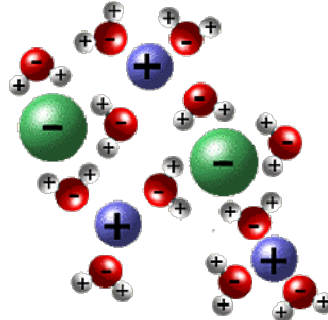
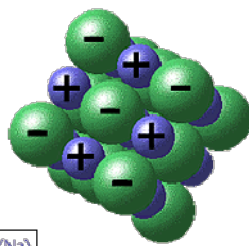


- Properties
 - High melting and boiling points
 - **Strong** electrostatic forces of attraction between oppositely charged ions in the **giant ionic lattice**
 - A high temperature is needed to provide the large amount of energy needed to overcome the strong electrostatic attraction
 - Higher for ions with greater ionic charges due to stronger attraction between ions
 - * Ionic substances with complex ions: can decompose before they reach melting point
 - Dissolve in polar solvents (e.g. water)

- Salvation / hydration
 - Polar solvent molecules attract the ions
 - Anions to positive dipole, cations to negative dipole
 - Energy is released in the process
 - Molecules break down the lattice + surround each ion in solution
- Strong ionic bond must be overcome for the substance to dissolve
 - Energy to do this is supplied by solvating / hydrating the ions / absorbed from the surroundings
- If the compound is made of ions with strong charges the attraction can be too strong to be broken down → less soluble
- Solubility depends on
 - Relative strengths of attractions within the lattice
 - Attraction between ions + water molecules

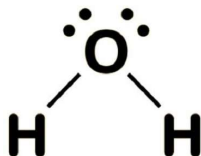
NaCl crystal structure

NaCl in water

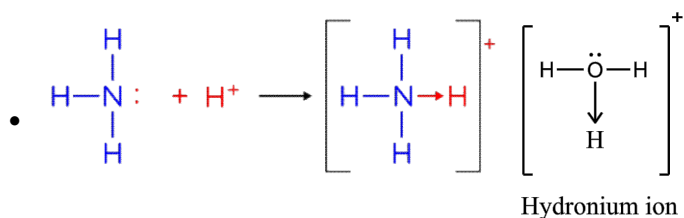


sodium (Na)
chlorine (Cl)

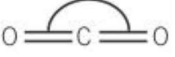
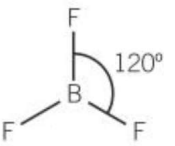
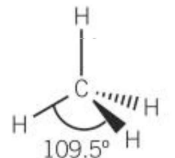
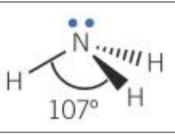
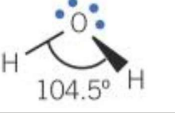
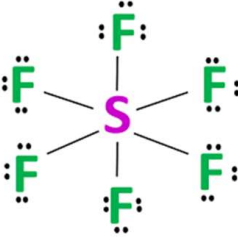
- Does not conduct electricity in solid state
 - Ions held in fixed positions
 - No mobile charge carriers
- Conduct electricity when dissolved or molten
 - The solid ionic lattice breaks down
 - Ions are free to move as mobile charge carriers
- Covalent bonding
 - The **strong** electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms
 - Occur between atoms that have a **small difference in electronegativity**
 - Formed when the atomic orbitals of the two atoms overlap and combine to form a new orbital (still holding 2 electrons max)
- Covalent substance structure
 - Attraction is localised between the shared pair of electrons and the nuclei of the bonded atoms only
 - Results in small molecules consisting two or more atoms (simple molecular lattice if solid)
- Lone pairs / non-bonding pair
 - Paired electrons that are not shared



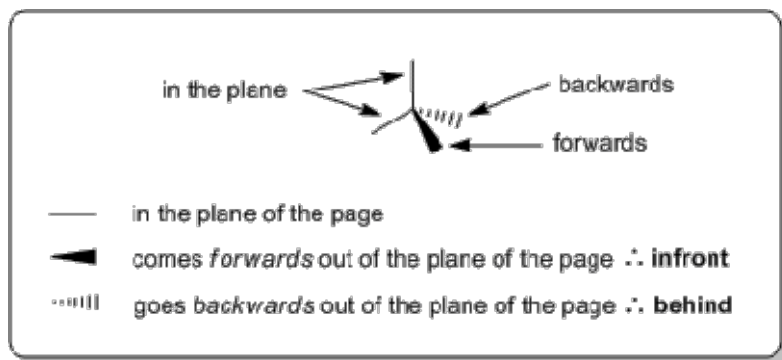
- Multiple covalent bond
 - The electrostatic attraction is between two / three shared pairs of electrons and the nuclei of the bonded atoms
- Dative covalent bonds / coordinate bonds
 - The shared pair of electrons is supplied by one of the bonding atoms only
 - The shared pair is originally a lone pair of electrons on one of the bonded atoms
 - e.g. ammonia molecule donates its lone pair of electrons to a H^+ ion to form NH_4^+ ion



- Exceptions
 - Boron
 - Only 3 outer shell electrons can be paired → only forms 3 pairs
 - e.g. BF_3 only has 6 electrons around the boron atom
 - Phosphorus, sulfur, chlorine (expansion of the octet)
 - Outer electrons are in $n = 3$ shell which can hold up to 18 electrons
 - More electrons are available for bonding (can have more than 8 electrons in outer shell e.g. ClF_7)
- Average bond enthalpy
 - A measurement of covalent bond strength
 - Higher average bond enthalpy = stronger covalent bond
- Molecule shape and bond angles
 - Electron pairs around the central atom repel each other as far apart as possible
 - Lone pairs repel more strongly than bonded pairs
 - They repel bonded pairs slightly closer together → reducing the bond angle
 - 4 pairs / regions: bond angle reduced by approx. 2.5° per lone pair
 - The greater the number of electron pairs the smaller the bond angle
 - (Mention the number of bonded pairs and lone pairs)

Electron pairs / regions	Name	Shape and bond angle
2	Linear	180° 
3	Trigonal planar	
4 (no lone pairs)	Tetrahedral	
4 (1 lone pair)	Pyramidal	
4 (2 lone pairs)	Non-linear	
6	Octahedral	 <p>Remember SF_6 as an example of this</p>

- Bond representations



- Predicting molecular shape of ions
 - Ions with oxygen
 - Add an electron to an oxygen atom for every negative charge
 - Bonds can be single or double bond
 - Cations with hydrogen
 - Add positive charge by H^+ ions
 - Others
 - Add / remove electrons from the central atom to match the charge
 - Pair up surrounding atoms and count bonded pairs and lone pairs
- Electronegativity
 - A measure of the attraction of a bonded atom for the pair of electrons in a covalent bond
 - Measured using Pauling electronegativity values (higher = attract bonded electrons more strongly)

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	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	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

- Important electronegativity values

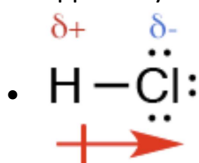
Element	Electronegativity
Fluorine	4.0
Oxygen	3.5
Chlorine	3.0
Nitrogen	3.0
Carbon	2.5
Hydrogen	2.1

- Electronegativity pattern
 - Electronegativity increases across the periodic table and up the periodic table
 - Across the periodic table the nuclear charge increases and the atomic radius decreases → attraction increases
 - Atomic radius increases down the table → attraction decreases
 - **Fluorine is the most electronegative element**
- Predicting type of bond

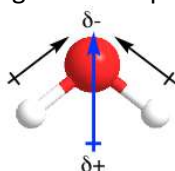
Bond type	Electronegativity difference
Covalent	0

Polar covalent	0 - 1.8
Ionic	> 1.8

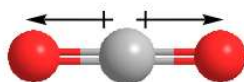
- Pure covalent bond
 - Non-polar bond
 - The bonded electron is shared equally between the bonded atoms
 - Happen when:
 - The bonded atoms are the same
 - The bonded atoms have same / similar electronegativity (e.g. carbon and hydrogen)
- Polar covalent bonds
 - Polar bond
 - The bonded electron pair is shared unequally between the bonded atom
 - When the bonded atoms are different and have different electronegativity values
 - Form permanent dipole: small positive ($\delta+$) / negative charge ($\delta-$) on the two bonded atoms, oppositely charged on each



- Polar / non-polar molecules
 - Polar molecules require polar bonds with dipoles that **do not cancel out** due to their direction
 - If the molecule is symmetrical in 3D **and** the polarities cancel out the molecule is non-polar
 - e.g. overall dipole in H_2O , cancels out in CO_2 and methane



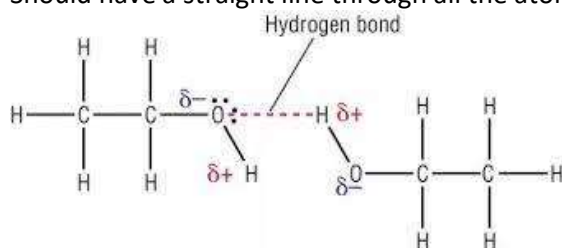
H_2O , bend shape
polar



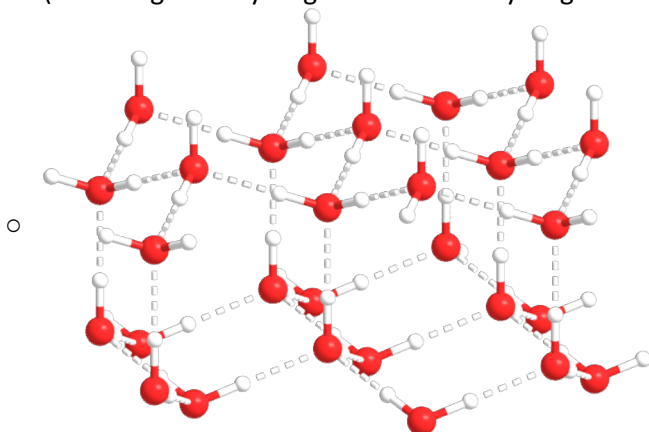
CO_2 , linear shape
non-polar

- Types of intermolecular forces
 - London forces / induced dipole-dipole **interactions** / dispersion forces (van der Waals' forces)
 - Permanent dipole-dipole **interactions** (van der Waals' forces)
 - Hydrogen bonding (a special type of permanent dipole-dipole interactions)
- London forces / induced dipole-dipole interactions
 - Exist between all molecules, only temporary
 - Creation
 - Movement of electrons produces changing dipole in a molecule
 - There is an uneven distribution of electrons which causes an instantaneous dipole
 - At any instant an instantaneous dipole will exist but position shifts constantly
 - Instantaneous dipole induces a dipole on a neighbouring molecule
 - The induced dipole induces dipoles on further molecules, they then attract one another
 - Electrons move and the dipole is gone and the attraction disappears and re-appears elsewhere
 - Very weak - the weakest of all intermolecular forces
 - The **only intermolecular** force that exist between non-polar simple covalent molecules
 - They have very low melting and boiling points (normally gases / volatile liquids under room temperature)
- London forces strength pattern
 - Stronger down the periodic table
 - More electrons in each molecule
 - Larger instantaneous + induced dipoles
 - Greater induced dipole-dipole interactions
 - Stronger attractive forces between molecules
- Permanent dipole-dipole interactions
 - Act between **permanent dipoles** in polar molecules

- Permanent dipole-dipole interactions is much stronger than London forces
 - Polar molecules have both London forces and permanent dipole-dipole interactions
 - Mean melting and boiling point of polar molecules is much greater
- Hydrogen bond
 - Occurs when a highly de-shielded hydrogen in one molecule is attracted to a lone pair on a **N, O or F** atom in another molecule
 - Highly de-shielded hydrogen: a hydrogen atom directly bonded to an **very electronegative** atom (**N, O or F**)
 - A lone pair of electrons on an electronegative atom forms bond with the δ^+ of a hydrogen atom in a different molecule
 - Strongest type of intermolecular attractions
 - Molecules with hydrogen bonds between them have relatively high melting and boiling points
 - More hydrogen bond = greater increase in melting and boiling points
- Hydrogen bond diagram
 - Shown by a dotted line between lone pair + hydrogen atom
 - Should have a straight line through all the atoms involved



- Anomalous properties of H_2O
 - Solid less dense than liquid
 - Each water molecule can form **4 hydrogen bonds** (2 lone pairs + 2 hydrogen atoms in O-H bond)
 - Hydrogen bonds extend outwards and hold water molecules apart in an **open lattice structure**
 - Water molecules form an tetrahedral lattice full of holes
 - Water molecules in ice are further apart than in water
 - (Bond angle for hydrogen involved in hydrogen bond is 180°)



- Relatively high melting and boiling points
 - Has hydrogen bond (much stronger) + PDD + IDD between molecules
 - A large quantity of energy is needed to break hydrogen bonds
 - When ice lattice breaks the arrangement of hydrogen bonds is broken
 - When water boils hydrogen bonds break completely
- Simple molecular substance
 - Made of simple molecules (small units with a definite number of atoms)
 - Simple molecules form a regular structure called a simple molecular lattice in the solid state
 - Shape of the lattice is determined by the packing pattern of the molecules
 - Molecules held together by weak intermolecular forces
 - Atoms within each molecule bonded together by strong covalent bonds (intramolecular forces)

- Properties of non-polar simple molecular substances
 - Low melting and boiling point
 - Only weak London forces between molecules
 - Weak intermolecular forces can be broken by energy present at low temperatures
 - Solubility
 - Non-polar solvent
 - Tend to be soluble
 - Intermolecular forces form between the molecules and the solvent
 - Weaken the intermolecular forces in the simple molecular lattice
 - The intermolecular forces break and the compound dissolves
 - Polar solvent
 - Tend to be insoluble
 - Little interaction between the lattice and the solvent molecules
 - Intermolecular bonding in solvent too strong to be broken
 - Non-conductors of electricity
 - No free electrons or mobile ions in simple molecular substances, cannot complete a circuit
 - No mobile charge carriers
- Properties of polar simple covalent substance
 - Higher melting and boiling point
 - Permanent dipole-dipole interactions are stronger than London forces
 - More energy is required to break them
 - Solubility
 - Hard to predict
 - Usually soluble polar solvents: polar solute/solvent molecules can attract each other
 - If they contain a significant non-polar region they may also be soluble in non-polar solvents
 - Solubility depends on strength of dipole
 - Electrical conductivity
 - Can conduct electricity if they can ionise and form mobile ions