3 Chemical bonding

This topic introduces the different ways by which chemical bonding occurs and the effect this can have on physical properties.

3.2 shapes of simple molecules ☐

SHAPES OF MOLECULES

3 Chemical bonding

This topic introduces the different ways by which chemical bonding occurs and the effect this can have on physical properties.

	Learning outcomes Candidates should be able to:
3.2 Covalent bonding and co-ordinate (dative covalent) bonding including shapes of simple molecules	a) describe, including the use of 'dot-and-cross' diagrams: (i) covalent bonding, in molecules such as hydrogen, oxygen, chlorine, hydrogen chloride, carbon dioxide, methane, ethene (ii) co-ordinate (dative covalent) bonding, such as in the formation of the ammonium ion and in the Al_2Cl_6 molecule b) describe covalent bonding in terms of orbital overlap, giving σ and π bonds, including the concept of hybridisation to form sp, sp^2 and sp^3 orbitals (see also Section 14.3) c) explain the shapes of, and bond angles in, molecules by using the qualitative model of electron-pair repulsion (including lone pairs), using as simple examples: BF_3 (trigonal), CO_2 (linear), CH_4 (tetrahedral), NH_3 (pyramidal), H_2O (non-linear), SF_6 (octahedral), PF_5 (trigonal bipyramidal) d) predict the shapes of, and bond angles in, molecules and ions analogous to those specified in 3.2(b) (see also Section 14.3)

SHAPES OF MOLECULES

The shape of a molecule plays a large part in determining its properties and reactivity.

The specific orientation of electron pairs in covalent molecules imparts a characteristic shape to the molecules.

The shape of a molecule made of only two atoms, such as H_2 or CO, is easy to determine. Only a linear shape is possible when there are two atoms. Determining the shapes of molecules made of more than two atoms is more complicated.

Using **Valence Shell Electron Pair Repulsion (VSEPR)** theory one can predict the shape of a molecule by examining the Lewis structure of the molecule.

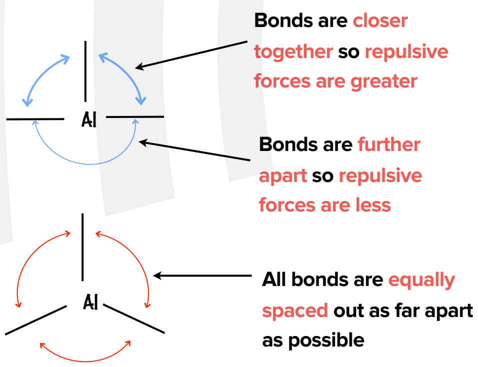
VSEPR THEORY

The electron pairs around the central atom of the molecule arrange themselves to minimise electronic repulsion and so that they can be as far away as possible from each other.

This fact is used to predict molecular shape.

Molecules contain covalent bonds.

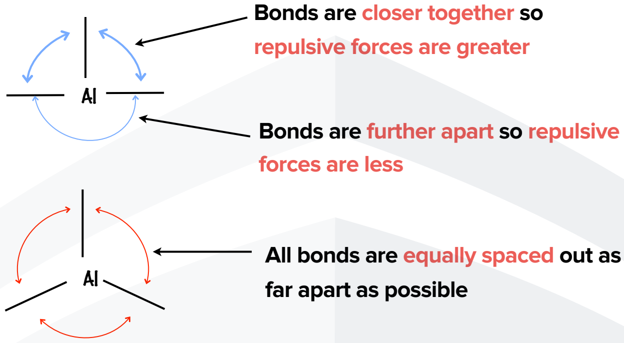
As covalent bonds consist of a pair of electrons, each bond will repel other bonds.



VSEPR THEORY

Bonds will therefore push each other as far apart as possible to reduce the repulsive forces.

Because the repulsions are equal, the bonds will also be equally spaced.

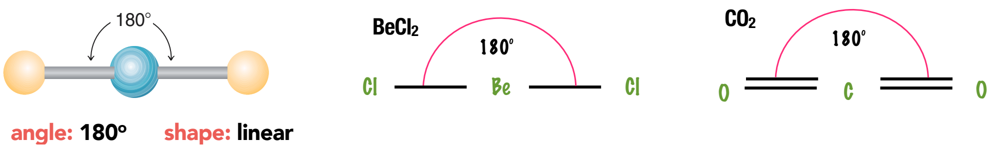


LINEAR

Beryllium chloride has two shared electron pairs around the beryllium atom.

These electron pairs have minimum repulsion if they are located as far apart as possible while still bonding the chlorine to the central atom.

This condition is met if the electron pairs are located on opposite sides of the molecule, resulting in a linear structure, 180º apart:

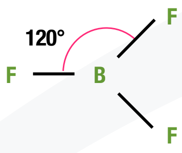


TRIGONAL PLANAR

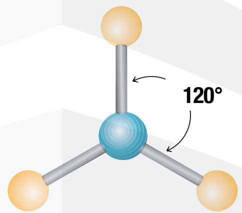
Now think about what happens when the central atom is surrounded by three shared pairs. Look at BF_3.

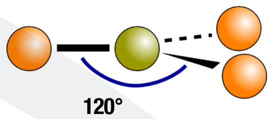
Boron trifluoride has three shared electron pairs around the central atom.

Placing the electron pairs in a plane, forming a triangle, minimizes the electron pair repulsion in this molecule.



angle: 120º shape: trigonal planar





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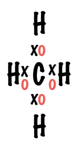
TETRAHEDRAL

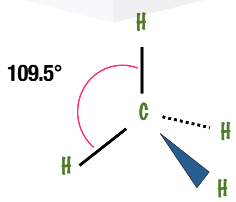
Methane has four shared pairs of electrons.

Here, minimum electron repulsion is achieved by arranging the electrons at the corners of a tetrahedron.

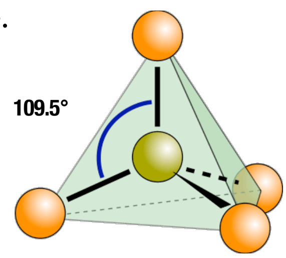
Each H—C—H bond angle is 109.5º.

Methane has a three – dimensional tetrahedral structure.





angle: 109.5º shape: tetrahedral



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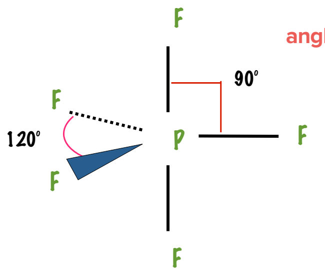
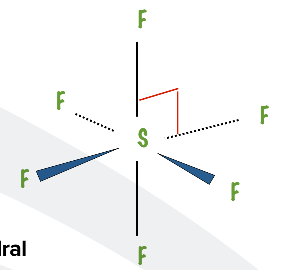
5 AND 6 BONDS



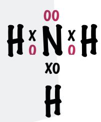
angle: 90° and 120° shape: trigonal bipyramidal



angle: 90° shape: octahedral

IRREGULAR SHAPES

NH_3 also has four electron pairs about the central atom. In contrast to CH_4, in which all four pairs are bonding, ammonia has three pairs of bonding electrons and one nonbonding lone pair of electrons.

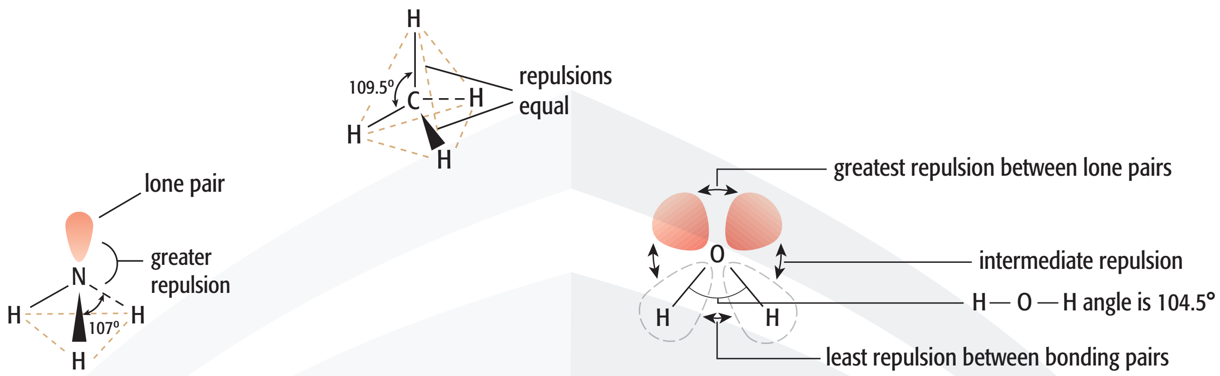


The lone pair in ammonia is closer to the central atom, N, than the bonding pairs and has greater repulsion.

Thus the arrangement of electron pairs in ammonia is distorted.

IRREGULAR SHAPES

The **H** atoms in NH_3 are pushed closer together than in CH_4. The bond angle is 107° because lone pair–bond pair repulsions are greater than bond pair–bond pair repulsions.

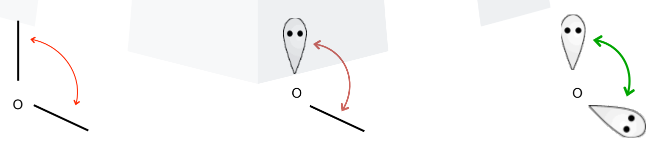


IRREGULAR SHAPES

If a molecule, or ion, has lone pairs on the central atom, the shapes are slightly distorted away from the regular shapes.

This is because of the extra repulsion caused by the lone pairs.

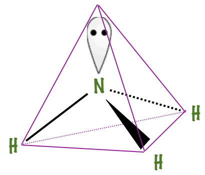
BOND PAIR – BOND PAIR < LONE PAIR – BOND PAIR < LONE PAIR – LONE PAIR

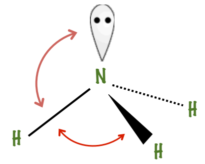


As a result of the extra repulsion, bond angles tend to be slightly less as the bonds are squeezed together.

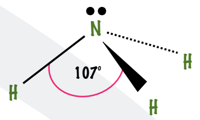
AMMONIA

- Nitrogen has five electrons in its outer shell
- 3 covalent bonds are formed and a pair of non-bonded electrons is left
- As the total number of electron pairs is 4, the shape is BASED on four bond tetrahedral shape
- Not all the repulsions are the same.
  Repulsions: LONE PAIR - BOND PAIR > BOND PAIR - BOND PAIR
- The N-H bonds are pushed closer together
- Lone pairs are not included in the shape





angle: 107° shape: trigonal pyramidal



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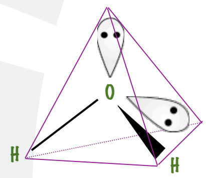
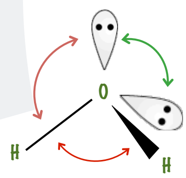
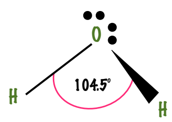
WATER

- Oxygen has six electrons in its outer shell
- 2 covalent bonds are formed and 2 pairs of non—bonded electrons are left
- As the total number of electron pairs is 4, the shape is BASED on the four bond tetrahedral shape.
- Not all the repulsions are the same.
  Repulsions: LONE PAIR — LONE PAIR > LONE PAIR — BOND PAIR > BOND PAIR — BOND PAIR
- The O—H bonds are pushed even closer together
- Lone pairs are not included in the shape





angle: 104.5° shape: angular / bent



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SUMMARY OF SHAPES

bonds	lone pairs	shape	angle	example
2	0	linear	180°	$BeCl_2$ CO_2
3	0	trigonal planar	120°	BF_3 $AlCl_3$
2	1	bent / angular	117°	SO_2
4	0	tetrahedral	109.5°	$SiCl_4$ CH_4
3	1	trigonal pyramidal	107°	NH_3 PCl_3
2	2	bent / angular	104.5°	H_2O
5	0	trigonal bipyramidal	90° & 120°	PCl_5
6	0	octahedral	90°	SF_6

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CALCULATING SHAPES

The shape of a molecule or a complex ion is calculated by:

1. Calculating the number of electrons in the outer shell of the central species
2. Pairing up electrons, making sure the outer shell maximum is not exceeded
3. Calculating the number of bond pairs and lone pairs
4. Using VSEPR to calculate shape and bond angle(s)

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CALCULATING SHAPES

For IONS:

The number of electrons in the outer shell depends on the charge on the ion

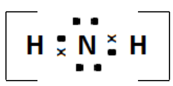
- if the ion is positive you remove as many electrons as there are positive charges
- if the ion is negative you add as many electrons as there are negative charges

e.g. for PF_6^- add one electron to the outer shell of P

for PCl_4^+ remove one electron from the outer shell of P

EXAMPLES

NH_3	BOND PAIRS	3	PYRAMIDAL
	LONE PAIRS	1	H–N–H 107°
NH_4^+	BOND PAIRS	4	TETRAHEDRAL
	LONE PAIRS	0	H–N–H 109.5°
NH_2^-	BOND PAIRS	2	ANGULAR
	LONE PAIRS	2	H–N–H 104.5°

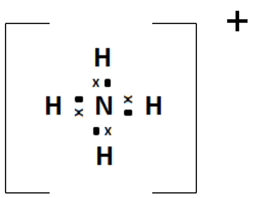


A compound with an overall charge may not be ionic, it can also be covalent.

e.g: NH_4^+

Number of valence electrons = 5

But due to "+" it loses 1e– $\therefore$ = 4



SKILL CHECK 1

Determine the number, and type, of electron pairs around the central atom(s) in each of the following. Predict the shape and bond angles of each. (Hint: it may help to draw 'dot-and-cross' diagrams)

(a) phosphine, PH_3

(b) sulfur dichloride, SCl_2

(c) dichloromethane, CH_2Cl_2

(d) cobalt(II) chloride, $COCl_2$

(e) xenon tetrafluoride, XeF_4

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MORE

BF_3	3 bp 0 lp	120°	trigonal planar	boron pairs up all 3 electrons in its outer shell
$SiCl_4$	4 bp 0 lp	109.5°	tetrahedral	silicon pairs up all 4 electrons in its outer shell
PCl_4^+	4 bp 0 lp	109.5°	tetrahedral	as ion is +, remove an electron in the outer shell then pair up
PCl_6^-	6 bp 0 lp	90°	octahedral	as the ion is −, add one electron to the 5 in the outer shell then pair up
$SiCl_6^{2-}$	6 bp 0 lp	90°	octahedral	as the ion is 2−, add two electrons to the outer shell then pair up

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SKILL CHECK 2

Draw the shapes for the following molecules. The underlined atom is the central atom

a. $\underline{N}F_3$ b. $CH_3\underline{O}H$ c. $\underline{Be}F_2$ d. $\underline{C}Cl_2F_2$ e. $H\underline{O}Cl$

SKILL CHECK 3

Draw the shapes of the following molecules

a. CF_4 b. Cl_2O c. PF_3 d. NCl_3 e. $SiCl_4$ f. SO_3

SKILL CHECK 4

Deduce the shapes of the following ions:

a. NH_4^+ b. CH_3^+ c. CH_3^- d. CO_3^{2-} e. SO_4^{2-} f. AlH_4^- g. AlF_6^{3-}

SKILL CHECK 5

Lycra® is a polyurethane fibre used in the fashion industry. It is a polymer made from two monomers, one of which has the following formula.

$$O{=}C{=}N{-}(CH_2)_n{-}N{=}C{=}O$$

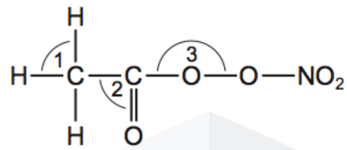
What is the O-C-N bond angle in this molecule?

A 90° **B** 109° **C** 120° **D** 180°

SKILL CHECK 6

Organic nitrates in photochemical smog can cause breathing difficulties.

The diagram shows an example of an organic nitrate molecule.



What is the correct order of the bond angles shown in ascending order (smallest first)?

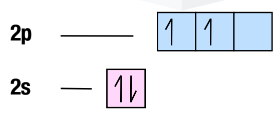
A 1 → 2 → 3 **B** 2 → 1 → 3 **C** 3 → 1 → 2 **D** 3 → 2 → 1

HYBRIDISATION

Hybridisation is the mixing of atomic orbitals to produce a new set of orbitals (the same number as originally) that have characteristics of the original orbitals and are better arranged spatially for covalent bonding.

To form a covalent bond, an orbital containing one electron is required. These orbitals overlap to form a covalent bond.

Carbon has six electrons and and the outer shell electronic configuration $2s^2\,2p^2$:

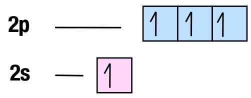


As it has only two unpaired electrons, carbon should form two covalent bonds.

HYBRIDISATION

However, it is well known that carbon virtually always forms four covalent bonds.

One of the electrons in the 2s orbital must then be promoted to the 2p sub-shell to give four unpaired electrons. This requires energy.

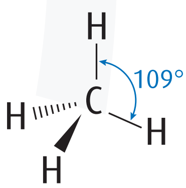


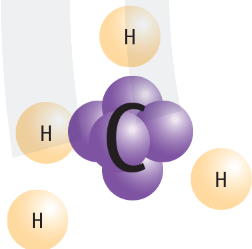
However, bond formation releases energy and the formation of four bonds instead of two more than pays back the energy needed to promote an electron to a higher sub-shell.

Carbon now has four unpaired electrons and can form four covalent bonds, but the atomic orbitals do not point in the correct direction for bonding.

HYBRIDISATION

CH_4 is tetrahedral with bond angles of 109.5° but the p orbitals are at 90° to each other.

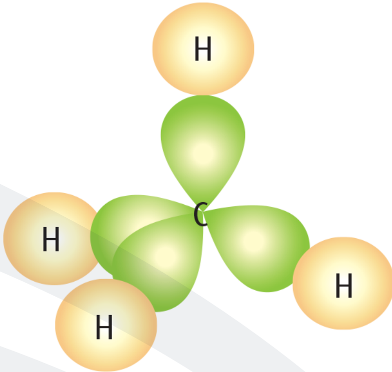




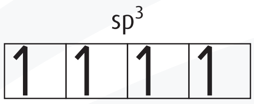
SP³ HYBRIDISATION

When carbon forms methane, the four atomic orbitals on carbon, one s and three p, then mix to give four sp^3 hybrid orbitals, which point to the vertices of a tetrahedron.

This is the process of hybridisation.



The four sp^3 hybrid orbitals all have the same energy



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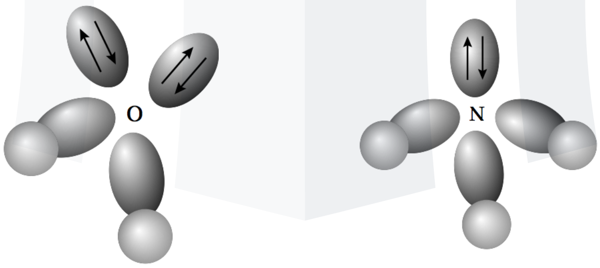
SP³ HYBRIDISATION

Should only three atoms bond to the sp^3 hybridised atom, then the molecular geometry is trigonal pyramidal. Ammonia is an example of this.



In water the oxygen is sp^3 hybridised but because only two atoms have bonded to the oxygen, the molecular geometry is bent.

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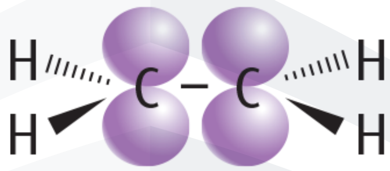
SP² HYBRIDISATION

In an sp^2 hybridisation one 2s and two 2p orbitals combine to form a new hybrid shape.

In this hybridised state the carbon will make two single bonds and one double bond.

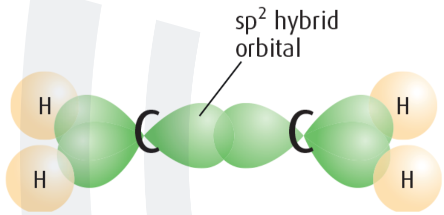
Of the three p orbitals on each C atom, one of them is not in the same plane as the H atoms or the other C atom.

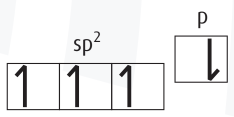
This p orbital is not involved in hybridisation.



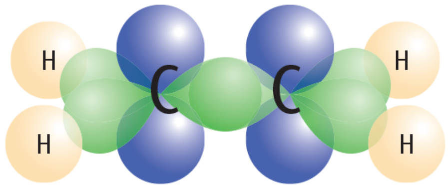
SP² HYBRIDISATION

Mixing the two p orbitals and one s orbital all in the same plane produces three sp^2 orbitals pointing towards the corners of an equilateral triangle:





This leaves one p orbital, containing one electron, perpendicular to the single bond () framework on each C atom:



HYBRIDISATION

	sp^3 hybridisation	sp^2 hybridisation	sp hybridisation
Number of Atoms Bonded to the Central Atom	4	3	2
Angle between Atoms Bonded to Central Atom	109.5°	120°	180°
Molecular Geometry	Tetrahedral with four atoms bonded. Trigonal pyramidal with three atoms bonded. Bent with two atoms bonded.	Trigonal planar with three atoms bonded.	Linear with two atoms bonded.
Types of Bonds Found	Four single bonds.	One double bond and two single bonds.	One single and one triple bond. (Or) Two double bonds.