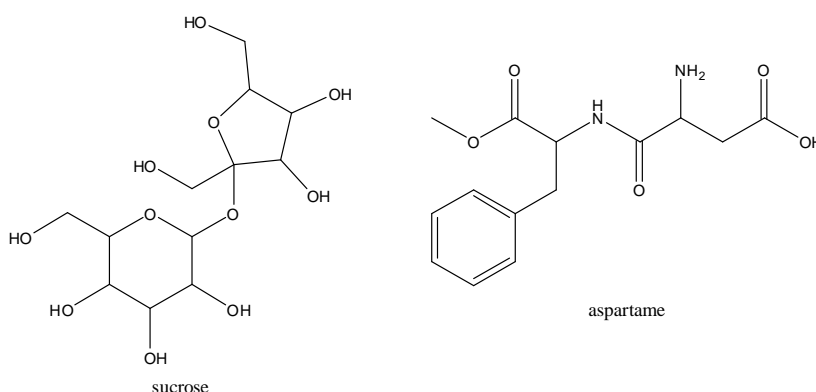


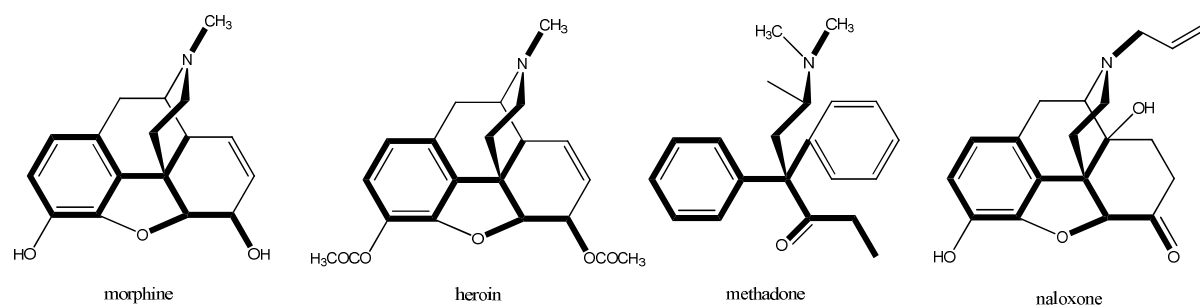
The Shapes of Molecules

The chemical bonding in a compound is very obviously related to its reactivity and properties – Na_2O and H_2O being quite different materials. It is perhaps less obvious that the shape of a molecule may also be crucial to its physical and chemical properties.

The artificial sweetener, aspartame, appears quite different to sucrose (table sugar) yet gives a sweet sensation in the mouth. Note these 'stick' structures will be explained in week 5.



Note the similarity in part of the shape (in bold) of the following four molecules.



Morphine is an alkaloid derived from the opium poppy. It is effective at blocking the perception of pain by the brain while allowing the normal function of the nervous system. It is also able to produce a feeling of euphoria which is why it is sometimes misused. This is particularly the case with heroin which is devastatingly addictive. Heroin users become physically dependant on opioids which means they have to continue to take them to avoid withdrawal symptoms such as chills, sweating, stiffness, cramps, vomiting and anxiety. Methadone is used to treat heroin addiction. It is an agonist i.e. it binds to the opioid receptors and causes an opioid response. It is prescribed as a way of regulating and ultimately reducing heroin addiction. Naloxone is an antagonist (i.e. it binds to the opioid receptors but does not give a response) used to treat heroin overdose. It binds to the opioid receptors in the brain, displacing heroin and reversing the effects of the narcotic (eg respiratory depression). It is given intravenously and its effects are produced almost immediately. However it is rapidly metabolized by the liver and its effect lasts only 2-4 hours, which is considerably shorter than the metabolism rate of most morphine-like drugs. Thus it may have to be given repeatedly. It has no side effects of its own but can precipitate withdrawal symptoms in addicts.

The VSEPR model

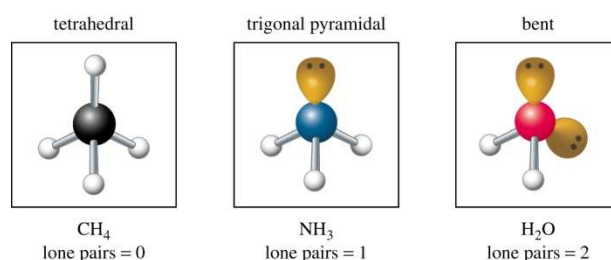
The valence shell electron pair repulsion model assumes that electron pairs repel one another. This produces a set of molecular geometries which depend only on the number of valence shell electron pairs and not on the nature of the atoms present. Once again we are concerned only with valence shell (e.g. bonding) electrons and the inner-shell(s) or core electrons play no part in determining the shape of a molecule.

To determine the molecular geometry:

- Draw the Lewis structure
- Count the number of electron pairs (bond pairs and lone pairs but count multiple bonds as one pair)
- Arrange electron pairs to minimise repulsion
- Position the atoms to minimise the lone pair - lone pair repulsion if > 1 lone pair
- Name the molecular geometry from the atom positions

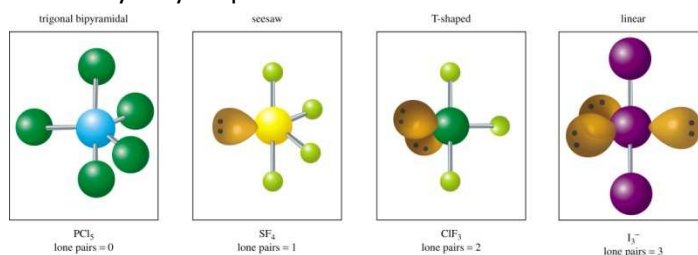
This works well from simple molecules in which there is a central atom to which others are bonded. For more complicated molecules the geometry at each atom may have to be determined in order to get an idea of the overall shape.

For example; four electron pairs are distributed in a tetrahedral shape. If these are all bond pairs the molecular geometry is tetrahedral (e.g. CH₄). If there is one lone pair of electrons and three bond pairs the resulting molecular geometry is trigonal pyramidal (e.g. NH₃). If there are two bond pairs and two lone pairs of electrons the molecular geometry is angular or bent (e.g. H₂O).

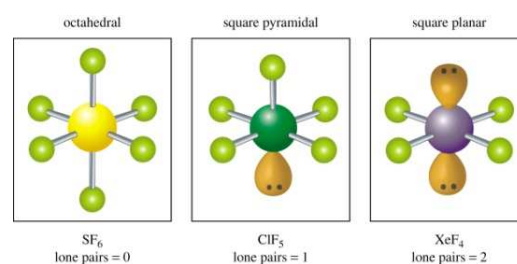


Five electron pairs give a starting point that is a trigonal bipyramidal structure. While the four points of a tetrahedron are equivalent to one another; this is not the case with the five points of a trigonal bipyramid. When there are lone pairs of electrons present they may be positioned in axial or equatorial positions.

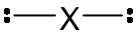
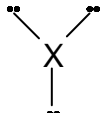
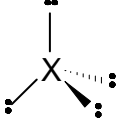
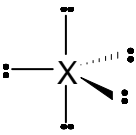
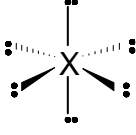
Lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion resulting in the positioning of lone pairs in the equatorial position.



Six electron pairs results in an octahedral structure which possesses a high degree of symmetry. The 'arms' of an octahedron are equivalent so there is only one possible structure for a species with five bond pairs and one lone pair of electrons (e.g. ClF₅). If two lone pairs are present, they are situated at 180° to one another.



In summary:

No of Electron Pairs (Lewis Structure)	Arrangement of Electron Pairs	No of Bond Pairs	No of Lone Pairs	Molecular geometry	Examples
2	 Linear	2	0	Linear	BeCl ₂ , CO ₂ , N ₃ ⁻
3	 Trigonal planar	3	0	Trigonal planar	BCl ₃ , SO ₃ , CO ₃ ²⁻
4	 Tetrahedral	2	1	Angular	SO ₂ , O ₃ , NO ₂ ⁻
		3	1	Trigonal pyramid	H ₃ O ⁺ , NH ₃ , XeO ₃
		4	0	Tetrahedral	CH ₄ , NH ₄ ⁺ , PO ₄ ³⁻
5	 Trigonal bipyramidal	2	2	Angular	H ₂ O, NH ₂ ⁻ , ClO ₂ ⁻
		3	2	T-shaped	ClF ₃ , XeF ₃ ⁺
		4	1	"See-saw"	SF ₄ , PBr ₄ ⁻
		5	0	Trigonal bipyramidal	PCl ₅ , SF ₅ ⁻
6	 Octahedral	2	3	Linear	ICl ₂ ⁻ , XeF ₂
		5	1	Square pyramidal	IF ₅ , SF ₅ ⁻ , SbF ₅ ²⁻
		6	0	Octahedral	SF ₆ , SiF ₆ ²⁻ , AsF ₆ ⁻
		4	2	Square planar	ICl ₄ ⁻ , XeF ₄

Note: the electron pair distribution and the molecular geometry are different if there are lone pairs of electrons present. Having determined the arrangement of electron pairs, take off one "arm" of the structure for every lone pair present.

Multiple bonds are treated as a single area of electrons; ie the carbon of CO₂ contains two areas of electrons, O=C=O, and is treated in the same way as a molecule with two electron pairs.

Question: Determine the molecular geometry of the following species. Start by drawing the Lewis structure, and then apply the VSEPR model.

CH ₄ Geometry =	CH ₃ ⁻ Geometry =	
NH ₄ ⁺ Geometry =	NH ₃ Geometry =	NH ₂ ⁻ Geometry =
	H ₃ O ⁺ Geometry =	H ₂ O Geometry =

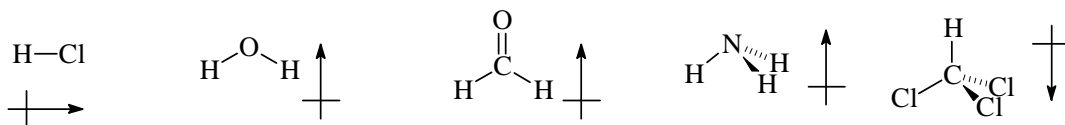
Dipole Moments

Any bond between atoms of different elements will be polar as a result of the electronegativity difference between the atoms. A molecule has a permanent *dipole moment* if it contains polar bonds *and* is not a symmetrical shape.

Examples of

polar

molecules:



Examples of non-

polar molecules:



Question: State whether the following molecules are polar or non-polar. Start by determining the Lewis structure, then the molecular geometry of the molecules.

SO₃

SO₂

CH₄

SF₄

PCl₅

IF₅

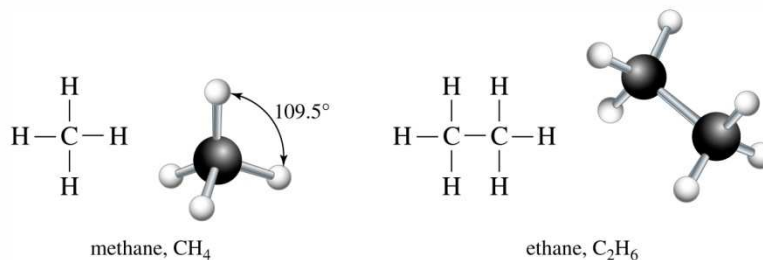
Sigma and pi bonds

All single bonds are referred to as 'sigma' bonds (σ -bonds). The electron density is concentrated along the bond axis.

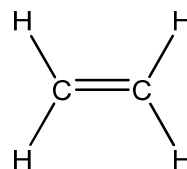
A multiple bond is made up of a combination of sigma and pi bonds (π -bonds). The electron density of a π -bond is concentrated above and below a plane containing the bonded atoms and arises from overlap of two p-orbitals pointing in the same direction.

So, a double bond contains $1\sigma + 1\pi$ bond and a triple bond contains $1\sigma + 2\pi$ bonds.

e.g. CH_4 and C_2H_6 contain all σ -bonds.



Ethylene, C_2H_4 has the Lewis Structure:



The molecular shape is predicted to be trigonal planar around each carbon atom. This is composed of a σ framework and a π -bond.

σ framework		
π -bond		
Overall structure		

Question: Identify the σ framework and the π -bonds in acetylene, C_2H_2 , $\text{H}-\text{C}\equiv\text{C}-\text{H}$.

Hybridisation

To determine the hybridisation of an atom:

- Determine the number and type of atomic orbitals used by the atom; include all the electrons in the valence shell. For example, boron, with three valence electrons, uses one s and two p orbitals; nitrogen, with five valence electrons, uses one s and three p orbitals.
- If there are π bonds present, determined by the Lewis structure, discount one partially filled p orbital for every π bond to the atom of interest. Remember a double bond $\equiv 1\sigma + 1\pi$ bond and a triple bond $\equiv 1\sigma + 2\pi$ bonds.
- "Mix" the remaining orbitals to form hybrid orbitals.

One s + one $p \Rightarrow$ two sp hybrid orbitals

One s + two $p \Rightarrow$ three sp^2 hybrid orbitals

One s + three $p \Rightarrow$ four sp^3 hybrid orbitals

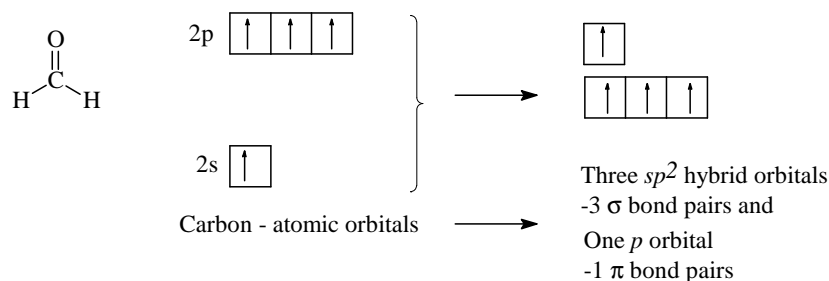
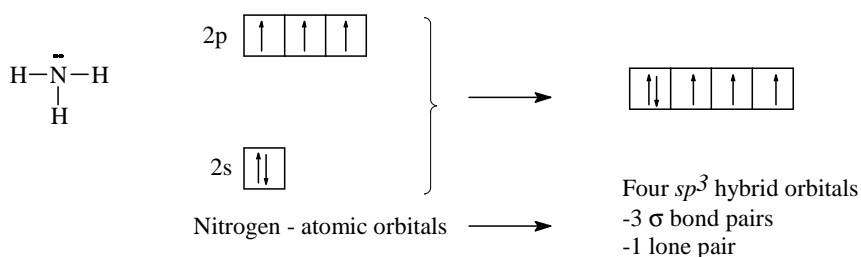
One s + three p + one $d \Rightarrow$ five sp^3d hybrid orbitals

One s + three p + two $d \Rightarrow$ six sp^3d^2 hybrid orbitals

Alternatively...A quick way of determining the hybridisation of an atom is to count the σ bonds *and* lone pairs around that atom and assign one hybrid orbital to each.

2 electron pairs $\Rightarrow sp$ hybrids, 3 electron pairs $\Rightarrow sp^2$ hybrids, 4 electron pairs $\Rightarrow sp^3$ hybrids

Examples:



Question: Determine the hybridisation of carbon in the following molecules or ions. Start by determining the Lewis structure, then count the number of σ -bonds attached to the carbon atom.

