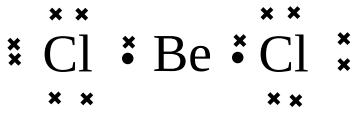
SHAPES OF MOLECULES AND IONS

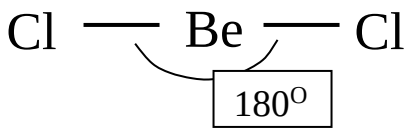
The shape of a molecule depends upon its electronic structure. It is the outer shell or valence shell electrons which are responsible for forming bonds and it is the arrangement of these electrons which determine molecular shape.
The electrons are all negatively charged and so will repel each other.
Each electron region takes up a position to minimise repulsion.
By considering the valence shell electron regions and their positions according to repulsive effects we can explain the shape of molecules.
This is called the **electron pair repulsion theory**.

Beryllium chloride, $BeCl_2$

Dot and cross diagram.

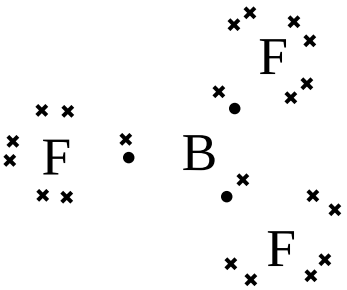


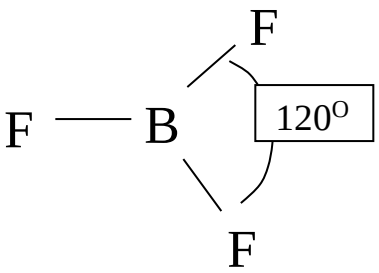
Beryllium chloride has two bonding pairs in the valence shell. These position themselves as far apart as possible – at 180º. The molecule is **linear**.



Boron trifluoride, BF_3

Dot and cross diagram.



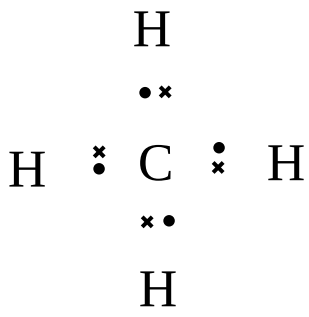


There are three bonding pairs (electron area in a bond); these will spread the maximum distance apart - that is at an angle of 120º.

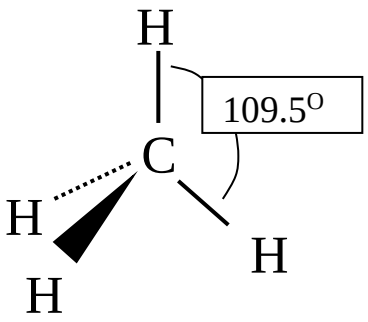
This molecule is flat, that is it lies in a plane; such a molecule is said to be planar. With three bonds at an angle of 120º BF_3 is said to be **trigonal planar**.

Methane, CH_4

Dot and cross diagram.

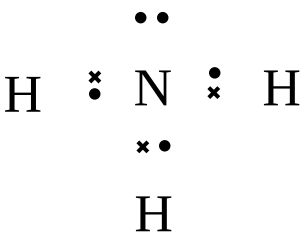


Methane has four bonding electron pairs in the valence shell. These position themselves as far apart as possible to form a **tetrahedral shape** with a bond angle of 109.5°.

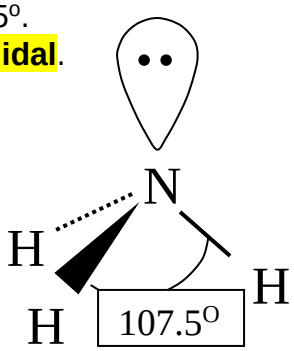


Ammonia, NH_3

Dot and cross diagram.



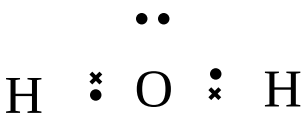
Ammonia has three bonding electron pairs and a lone pair of electrons in the valence shell. These position themselves as far apart as possible, but the lone pair has a greater repulsion than the bonding pairs pushing the bonding pairs closer together and reducing the bond angle to 107.5°.
The molecule is **pyramidal**.



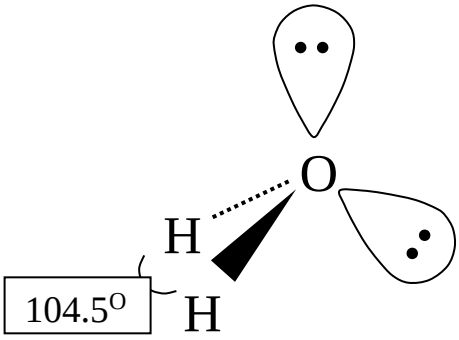
Molecule

Water, H_2O

Dot and cross diagram.

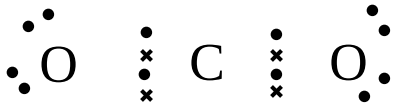


Water has two bonding electron pairs and two lone pairs of electrons in the valence shell. The two lone pairs have a greater repulsion than the bonding pairs, pushing the bonding pairs closer together and reducing the bond angle to 104.5°.
The molecule is **bent**.



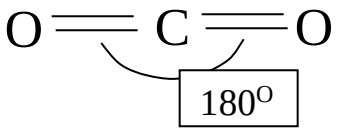
Carbon dioxide, CO_2

Dot and cross diagram.

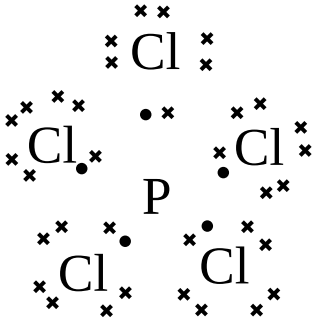


Carbon dioxide has two electron regions in the valence shell. These position themselves as far apart as possible. The molecule is **linear**.

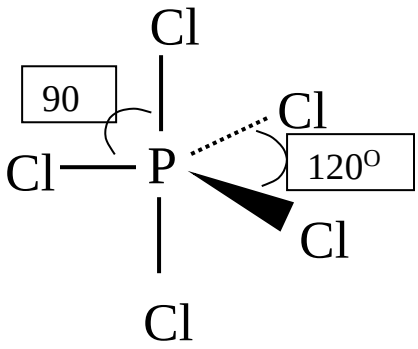
Molecule



Phosphorus pentachloride, PCl_5



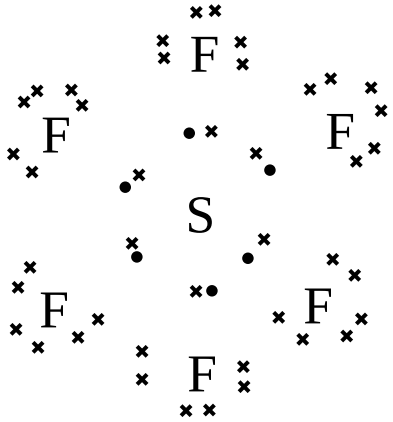
Phosphorus pentachloride has five bonding electron pairs in the valence shell.
The molecule is **trigonal bipyramidal**.



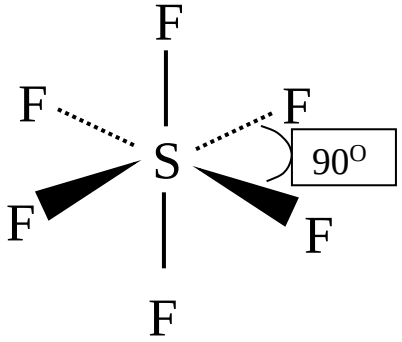
Two of the bonds are at 180º. The other three are in a plane at 120º.

Sulphur hexafluoride, SF_6

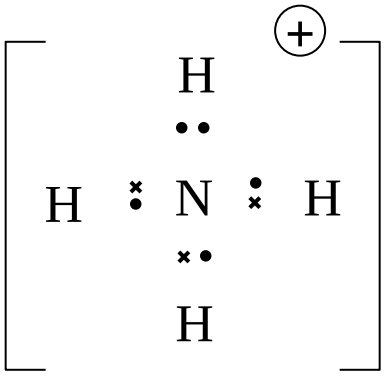
Dot and cross diagram.



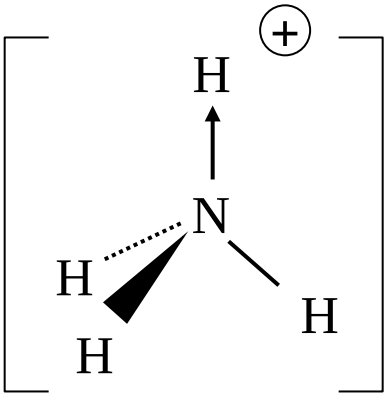
Sulphur hexafluoride has six bonding electron pairs in the valence shell.
The molecule is **octahedral** with bond angles of 90º



Ammonium ion, NH_4^+



The ammonium ion has four bonding pairs of electrons in the valence shell (one of theses being a dative bond). The molecule is **tetrahedral** with bond angles of 109.5°.



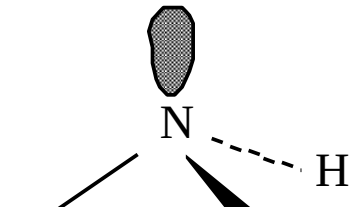
Bond angles in CH_4, NH_3, H_2O

It is important to note that although there are four pairs of electrons arranged approximately tetrahedrally around the N in NH_3 and the O in H_2O, the lone pairs cannot be "seen" experimentally, so the shapes of these molecules are described by the actual positions of the atoms: ammonia is *pyramidal* and water is *bent*.

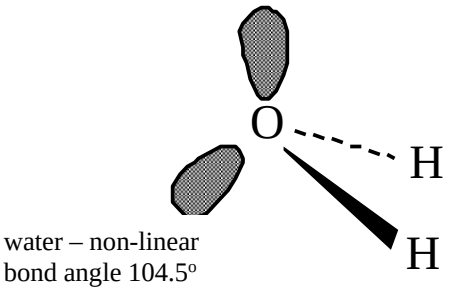
We can explain the differences in the bond angles in CH_4, NH_3 and H_2O by noting that repulsions get less along the series:

lone pair/lone pair > lone pair/bonding pair > bonding pair/bonding pair

This occurs because a lone pair is closer to the nucleus of the atom, and so takes up more room than a bonding pair. When this principle is applied to CH_4, NH_3 and H_2O, CH_4 is a regular tetrahedron (angles of 109.5°); NH_3 has one lone pair, which squashes the H atoms down (angles reduced to 107°); and H_2O has two lone pairs, which repel the H atoms even more (angle now 104.5°):



ammonia – pyramidal
bond angle 107°



water – non-linear
bond angle 104.5°

ammonia – pyramidal

bond angle 107°

water: non-linear

bond angle 104.5°

More complicated molecules

The shapes of more complicated molecules and ions can also be "explained" by electron pair repulsion theory, or EPR.
In applying this principle, we must include both bonding and non-bonding (or "lone") pairs, and we must count a double or triple bond as if it were one pair (or one region of electron density).
The table shows the shapes expected for different numbers of electron pairs.

Number of electron pairs	Shape	Bond angles	Examples
Two	linear	180º	$Ag(NH_3)_2^+$, CO_2
Three	Trigonal planar	120º	$CH_2=CH_2$, BF_3
Four	tetrahedral	109.5º	CH_4, NH_3*, H_2O
Six	octahedral	90º	SF_6, $Fe(CN)_6^{3-}$

We can use advanced EPR theory to predict the shape of any molecule or ion.

1) Decide on the central atom **Record its number of outer electrons**

2) Count the number of bonding atoms **Add 1 e- for each atom**

3) If the species is – charged **Add 1 e- for each charge**

4) If the species is + charged **Subtract 1 e- for each charge**

5) Find the total number of electron pairs.

6) Determine the shape of the species;

Pairs	Shape
2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

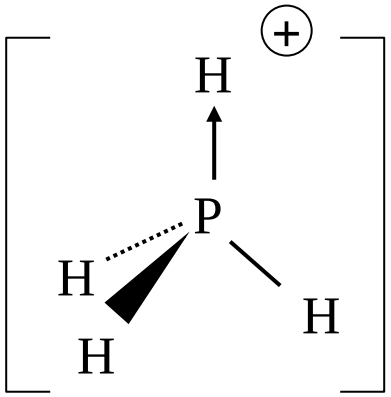
7) Show any lone pairs.
The number of Lone pairs = Total number of pairs – bonding pairs

Example

		Electrons
PH_4^+	Central atom = P	5
	Bonding atoms = 4 x H	4 (Forms 4 bonding pairs)
	Positively charged	-1

Total = 8 **4 pairs = Tetrahedral**

The number of Lone pairs = Total number of pairs – bonding pairs = 4-4 = 0

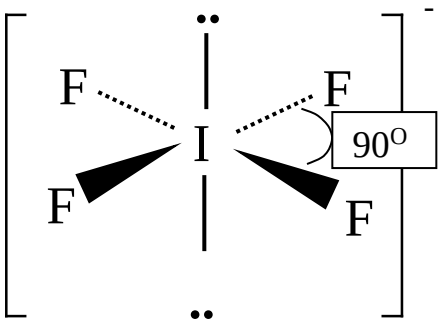


Example

		Electrons
IF_4^-	Central atom = I	7
	Bonding atoms = 5 x F	4 (Forms 4 bonding pairs)
	Negatively charged	+1

Total = 12 **6 pairs = Octahderal**

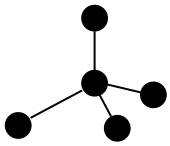
The number of Lone pairs = Total number of pairs – bonding pairs = 6-4 = 2



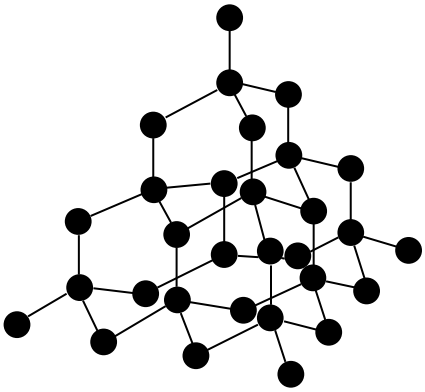
Structures of Carbon Allotropes

Diamond

Diamond is composed of carbon atoms. Each carbon atom is connected to four other carbon atoms



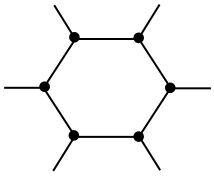
Each of these atoms is also connected to three other carbon atoms. In this way a giant structure is built up from these tetrahedral units.



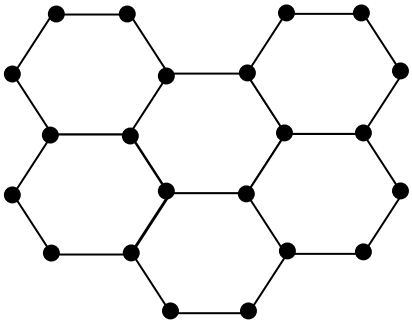
This structure, held together by strong covalent bonds, is very difficult to break apart. So diamond has very high melting and boiling points. It is the hardest natural substance. Since all the electrons are taken up in bonding diamond is a non-conductor.
Diamonds are attractive which means they are used as jewellery. Its hardness makes it useful for cutting instruments such as drill tips.

Graphite

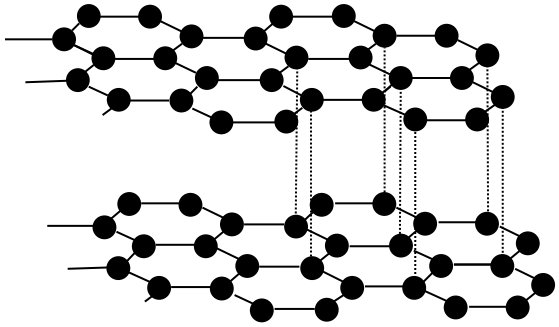
In graphite each carbon atom has three bonds, so three of the four electrons are taken up in forming these bonds. The remaining electron is allowed to move from atom to atom - it is delocalised.
Since three bonds form, the bond angle around each carbon is 120^{o} and a hexagonal arrangement is set up.



These hexagons join together in a plane forming a sheet of hexagonally arranged carbon atoms.



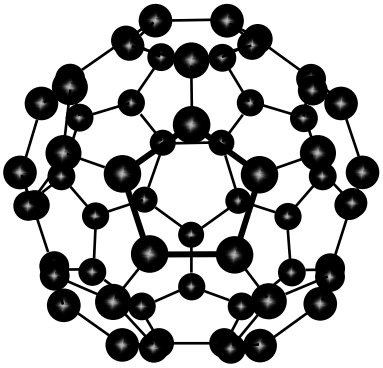
Graphite is made up of these layers held together by London forces (Van der Waals' forces). Sometimes it is referred to as a layer structure.

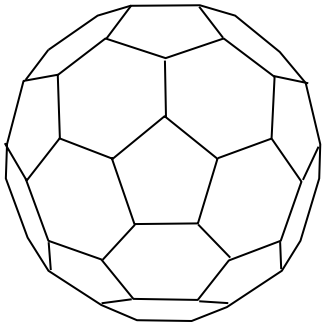


The carbon atoms in graphite are held together by covalent bonds forming a giant structure, so the melting and boiling points are high. Since each atom has a free electron, graphite is able to conduct electricity. The layers held together by weak intermolecular forces can slide over each other, making a soft slippery substance. Graphite can be used for electrodes as it is a conductor, and unlike metals it does not react during electrolysis. It can be used as a lubricant because of its slippery nature.

Fullerenes

Diamond and graphite were thought to be the only allotropes of carbon until late in the twentieth century. In 1985 a new form of carbon was discovered that consisted of spherical molecules containing 60 carbon atoms.





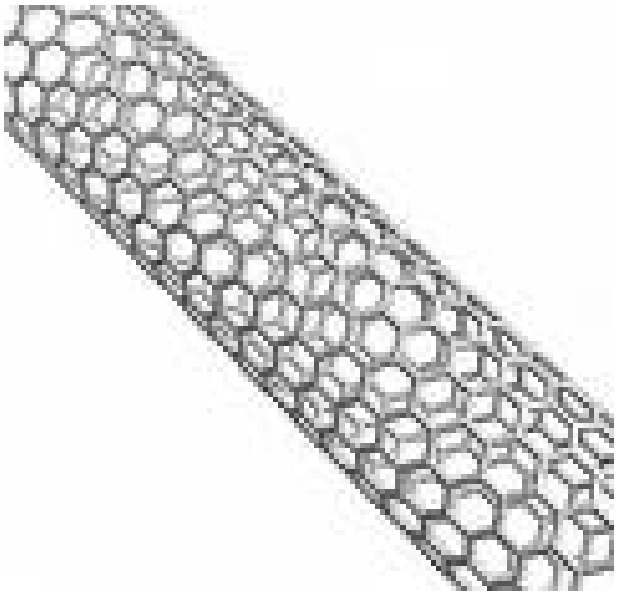
These molecules resembled the construction of a building by an architect called Buckminster Fuller. As a result, the molecule was named buckminsterfullerene. The molecule also resembles a football, so it is often called a “bucky-ball”.

Similar molecules have since been made that contain 70 or more carbon atoms. This family of molecules are called fullerenes.

Nanotubes

Another form of carbon developed as a result of the discovery of fullerenes is the nanotube.

The individual layers in graphite are called graphemes. A nanotube can be regarded as a grapheme which has rolled up to form a cylinder. The name comes from the diameter of the cylinder. A single-walled carbon nanotube is a one-atom thick sheet of graphite rolled up into a seamless cylinder with diameter 1-2 nm.



Such cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science.

They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat.