6.1 Water and intermolecular forces

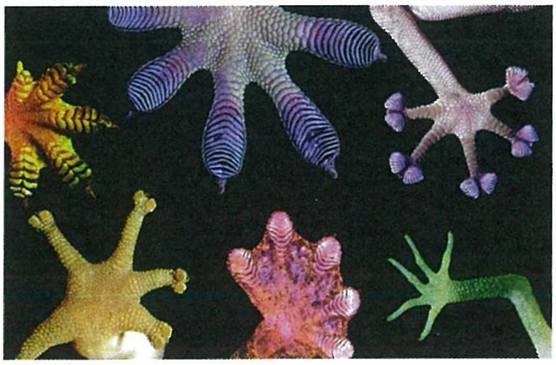
Water has unique physical and chemical properties. For a small molecule, it has a big influence on life on Earth. Water's unique properties arise partly from the strength of the intermolecular forces between the water molecules. These forces are affected by the shape of the water molecules and are important for some practical applications.

WOW

Small but powerful

Intermolecular forces are extremely small. Yet they are used by geckos to perform amazing feats. A gecko can hang from a polished surface, supporting its entire body weight, with only one toe. Aristotle wrote about these feats 2300 years ago. Now scientists think they have determined how they can happen. There are 14 000 tiny 'hairs' called setae on every square millimetre of a gecko's footpad. Each individual seta has a diameter of 5 micrometres, thinner than human hair. These tiny setae have even smaller curved pads that create billions of interactions between the gecko's foot and the surface. This explains why a 5 cm long gecko can support the equivalent weight of a 9-year-old child.

The study of how geckos adhere to a surface has influenced the design and fabrication of bio-inspired dry and reversible adhesive surfaces.



Science Photo Library/Paul D. Stewart

Figure C6.1 ▲
The feet and toes of gecko lizards use powerful intermolecular forces to support their weight

GECKO ADHESIVE FIT FOR SPIDERMAN

Watch this video to learn about making new adhesive materials that don't feel sticky.

Forces between molecules

You need to heat water to over 3000°C to break its covalent bonds and isolate hydrogen and oxygen. When ice melts at 0°C and water vaporises at 100°C, water is merely changing state. These relatively low temperatures are evidence that covalent bonds are not breaking. The bonds between the water molecules, the **intermolecular forces**, are broken. The low melting point shows that the intermolecular forces are much weaker than the covalent bonds within the molecule.

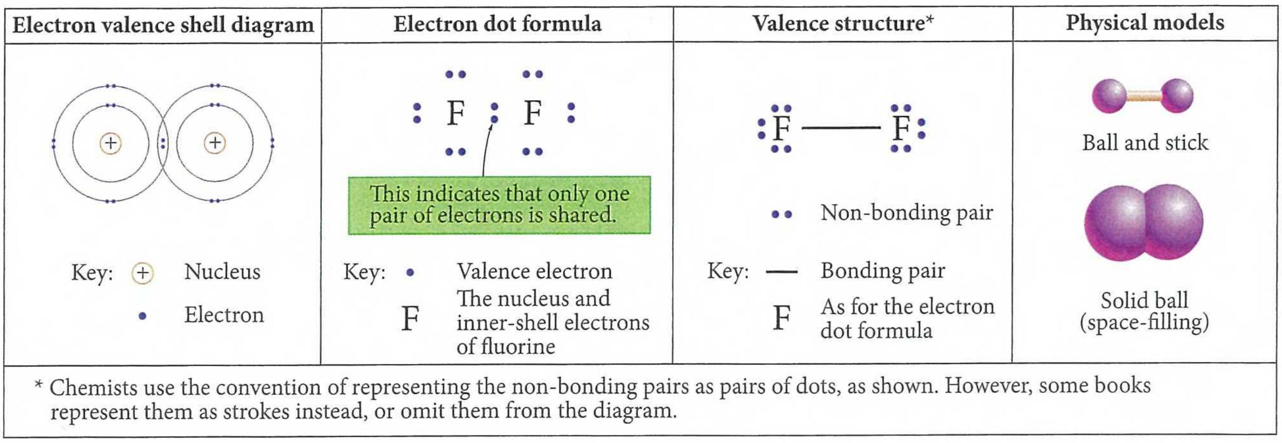
Intermolecular forces between molecules are much weaker than covalent bonds within molecules. The structure and composition of molecules determines which intermolecular forces are present. These forces determine the properties of the material.

6.2 Shapes of molecules

To explain the properties of materials, chemists need to understand their underlying structure. Molecules exist in a three-dimensional space, but we generally represent molecules in two dimensions. The structure and bonding in molecules is described by using either electron dot formulas or **valence structures**.

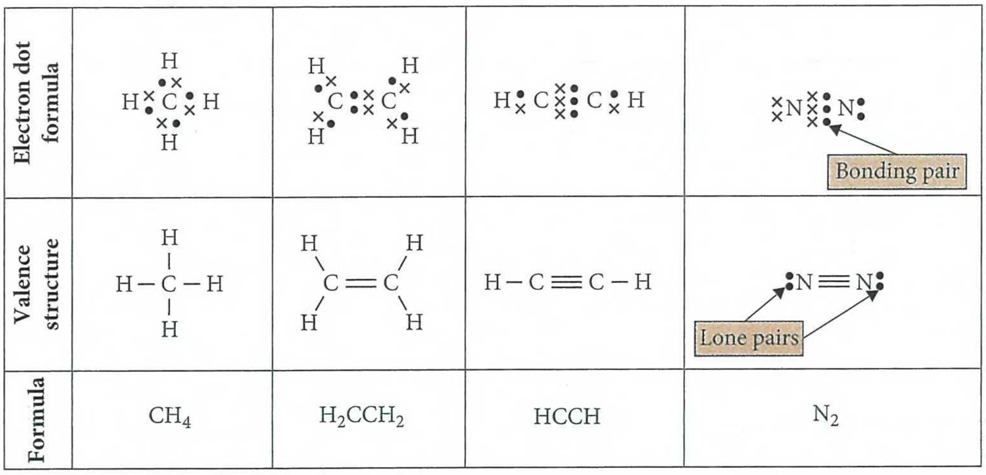
Electron dot formulas

Atoms tend to be more stable when there are eight valence electrons around the central atom. This is known as the octet rule. In electron dot formulas, each of the outer valence electrons is shown as a dot (or '×') around the chemical symbol, as shown in Figure C6.2 on page 259. Eight valence electrons would be shown by four pairs of dots circling the central nucleus. They are not shown as pairs until four positions are occupied. So, for the element nitrogen, there would be one pair and three separate electrons.



▲ Figure C6.2
Representing the shape of molecules

In covalent bonds, the electrons shared between two atoms are called the **bonding pair** of electrons, so the dots are placed between the symbols for the two elements. A single bond is formed when one pair of electrons is shared. A double bond occurs when two pairs of electrons (two sets) are shared between the two atoms. The pairs of valence electrons not involved with bonding are called the **lone pair** or non-bonding pair of electrons. The lone pairs are shown around the element as a pair of dots or crosses.



◀ Figure C6.3
Electron dot formulas and valence structure for the molecules CH_4, H_2CCH_2, HCCH and N_2. Note that dots or 'x's are used to distinguish which electrons are from the different atoms.

Valence structures

Valence structures can be used as an alternative to drawing electron dot formulas. A single bond, shown by a line joining the two atoms, has one pair of electrons. A double bond, shown by two short lines, has two pairs of electrons. A triple bond has three short lines or three pairs of electrons. Lone pairs of electrons are drawn around the element as either two dots, a short line or another line that points away from the element. Valence structures have the advantage of showing the structure of the molecules and are often called the **structural formulas**.

To revise covalent bonding and multiple bonds, refer to Chemistry section 3.5 on page 178.

Electron dot formulas use pairs of dots to represent the bonding between atoms. Valence structures use lines to show the bonding, and non-bonding or lone pairs of electrons are shown as a pair of dots, crosses or a line and can be used to represent the shape of molecules.

ACTIVITY 6.1

REPRESENTING MOLECULES

Aim

To draw electron dot formulas and the valence structures for a range of molecules

What to do

1 Determine the maximum number of covalent bonds an atom of each of the following elements can form: H, C, N, O, F, Ne, P, Cl

2 Draw electron dot formulas for fluorine (F_2), hydrogen fluoride (HF), water (H_2O), carbon tetrachloride (CCl_4), phosphine (PH_3), carbon dioxide (CO_2), hydrochloric acid (HCl), nitrogen dioxide (NO_2) and neon (Ne).

What did you discover?

Can you use the formula to predict the arrangement of atoms around the central atom? Which atoms are more likely to be central to the molecules?

Predicting the shape of molecules

It is important to know the shape of molecules because the shape will determine the intermolecular bonding and properties of the substance. The valence structure of water shows a two-dimensional shape, in which oxygen is central to two hydrogen atoms. The three-dimensional shape could be
the three atoms in a row, a V-shape molecule or two hydrogen atoms at right angles to the central oxygen.

Valence shell electron pair repulsion (VSEPR) theory has been used for over 50 years to determine the shape and hence the function of many molecules. It gives an understanding of how proteins may bond to an enzyme, essential for many medical applications.

Although the 'R' in VSEPR stands for the word 'repulsion', the theory is based upon the **Pauli exclusion principle**, not electron repulsion. Pauli's exclusion principle states that each orbital can only have 0, 1 or 2 electrons. If two electrons are present, then they spin in opposite directions around the nucleus. The discovery of this electron spin is fundamental to the Pauli exclusion principle. Two electrons of the same spin have a zero probability of being found in the same location and will be found in locations as far apart as possible.

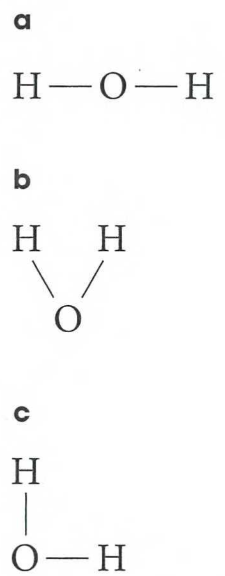


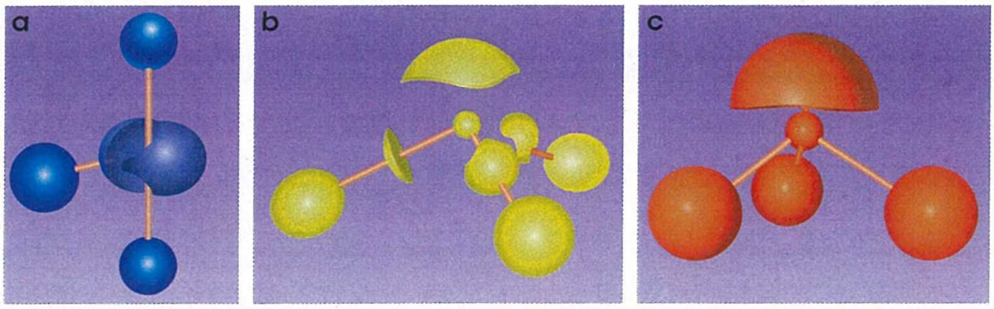
Figure C6.4 ▲ The possible shape of the water molecule: a) two-dimensional shape, b) V-shaped molecule and c) two hydrogens at right angles. Which one is correct?

> VSEPR (valence shell electron pair repulsion) theory is based upon the number of electron pairs surrounding the central atom. The electron pairs arrange themselves *as if* they repel each other.

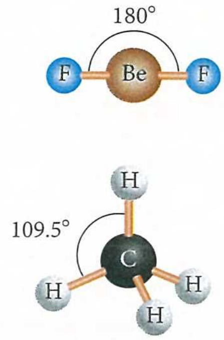
The three-dimensional structure of simple molecules depends upon the number of electron pairs around the central atom. The electron dot formulas are used to indicate electron pairs. These may be bonding and/or lone pairs. The electron pairs will be at a maximum distance from each other. It helps to think of the electron pairs as points on a sphere with the central atom in the middle.

Lone pairs are closer to the single nucleus and so occupy more space. Bonding pairs are shared by two atoms and are attracted by the two nuclei. Hence, they occupy less space and cause less repulsion than lone pairs.

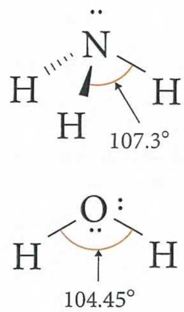
The common shapes of molecules are summarised in Table C6.1 on page 262.



▲ **Figure C6.5**
The electron density surrounding molecules calculated by the VSEPR theory. a) ClF_3; b) NH_3; c) PF_3. Note that lone pairs take up more space than bonding pairs of electrons.



▲ **Figure C6.6**
The molecule BeF_2 is linear and CH_4 is tetrahedral.



▲ **Figure C6.7**
Ammonia is pyramid-shaped and water is bent or V-shaped.

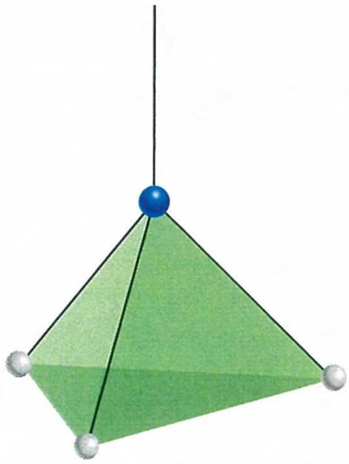
To work out the shape of a molecule:

- draw the electron dot formula
- count the lone pairs and bonding pairs. Remember that lone pairs are electron pairs that are not shared, while bonding pairs form the covalent bonds
- treat the electrons in a covalent bond, whether a single, double or triple bond, as one set of electrons
- use Table C6.1 on page 262 to predict the shape based upon the number of bonding and lone pairs.

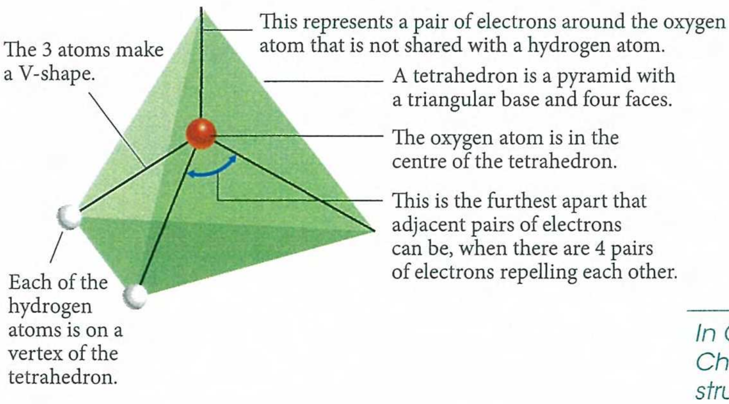
The simplest example to show the application of the VSEPR theory is BeF_2 (Figure C6.6). Here the central Be atom has only two electron pairs, one to each F atom. The three atoms are in a line, which means that the bonding pairs are at 180° from each other. The shape is linear.

The carbon atom in methane (CH_4) has four bonding pairs to the hydrogen atoms. The four hydrogen atoms and their bonding pairs of electrons are furthest apart in a tetrahedral shape (the angle between the bonds is 109.5°).

The nitrogen atom in ammonia (NH_3) has four electron pairs, which includes three bonding and one lone pair. The hydrogen atoms are at three corners of the tetrahedral and the lone pair occupies the final spot. This results in a pyramid shape for ammonia (the angle between the bonds is 107.3°) (see Figures C6.7 and C6.8).



▲ **Figure C6.8**
Explaining the pyramid shape of ammonia

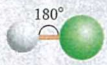
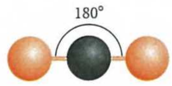
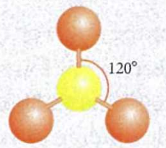
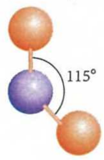
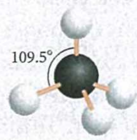
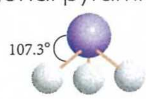
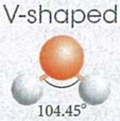
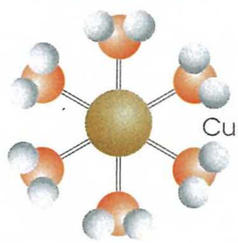


▲ **Figure C6.9**
Explaining the V-shape of water

In Chemistry Chapter 3, the structure of pure carbon in diamond form was described as tetrahedral, with C atoms at each vertex of the tetrahedron. The electronic configuration of a carbon atom is $1s^2\ 2s^2\ 2p^2$.

Oxygen is the central atom in water. Oxygen has two lone pairs and two bonding pairs of electrons. These four pairs are directed to the corners of the tetrahedron. Two of these are taken up by oxygen's lone pairs. This results in a V-shape for water molecules. Water is often called a bent molecule (see Figure C6.9).

Table C6.1 Shapes of molecules

Generic formula (M, X = atoms; E = lone pair of electrons)	Number of electron pairs	Lone pairs on M	Molecular shape
MX	1	0	Linear  HCl
MX_2	2	0	Linear  CO_2
MX_3	3	0	Trigonal planar  SO_3
MX_2E	3	1	V-shaped  NO_2
MX_4	4	0	Tetrahedral  CH_4
MX_3E	4	1	Trigonal pyramidal  NH_3
MX_2E_2	4	2	V-shaped  H_2O
MX_6	6	0	Octahedral  $Cu(H_2O)_6^{3+}$

VSEPR AND THE 3D STRUCTURES

Visit this website to see the VSEPR structures of some common molecular geometries.