The RADMASTE Centre

University of the Witwatersrand, Johannesburg

Short Course
(Physical Sciences)

FET Chemistry for Educators

COURSE WORKBOOK

PART 1:

MATTER AND MATERIALS

Periodic Table of the Elements

1																	18
1 **H** hydrogen 1.01	2		KEY atomic number **symbol** name standard atomic weight									13	14	15	16	17	2 **He** helium 4.00
3 **Li** lithium 6.94	4 **Be** beryllium 9.01											5 **B** boron 10.81	6 **C** carbon 12.01	7 **N** nitrogen 14.01	8 **O** oxygen 16.00	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium 24.31	3	4	5	6	7	8	9	10	11	12	13 **Al** aluminium 26.98	14 **Si** silicon 28.09	15 **P** phosphorus 30.97	16 **S** sulfur 32.07	17 **Cl** chlorine 35.45	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.41	31 **Ga** gallium 69.72	32 **Ge** germanium 72.64	33 **As** arsenic 74.92	34 **Se** selenium 78.96	35 **Br** bromine 79.90	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.94	43 **Tc** technetium 97.91	44 **Ru** ruthenium 101.07	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.89	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.32	57-71 lanthanoids	72 **Hf** hafnium 178.49	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38	82 **Pb** lead 207.2(1)	83 **Bi** bismuth 208.98	84 **Po** polonium 208.98	85 **At** astatine 209.99	86 **Rn** radon 222.02
87 **Fr** francium [223.02]	88 **Ra** radium [226.03]	89-103 actinoids	104 **Rf** rutherfordium [261.11]	105 **Db** dubnium [262.11]	106 **Sg** seaborgium [266.12]	107 **Bh** bohrium [264.12]	108 **Hs** hassium [277]	109 **Mt** meitnerium [268.14]	110 **Ds** darmstadtium [271]	111 **Uuu** unununium [272]							

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium [144.91]	62 **Sm** samarium 150.36	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.04	71 **Lu** lutetium 174.97
89 **Ac** actinium [227.03]	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium [237.05]	94 **Pu** plutonium [244.06]	95 **Am** americium [243.06]	96 **Cm** curium [247.07]	97 **Bk** berkelium [247.07]	98 **Cf** californium [251.08]	99 **Es** einsteinium [252.08]	100 **Fm** fermium [257.10]	101 **Md** mendelevium [258.10]	102 **No** nobelium [259.10]	103 **Lr** lawrencium [262.11]

Based on the IUPAC Periodic Table of November 2003

INTRODUCTION

Welcome to the short course '**FET Chemistry for Educators'**, developed by the Centre for Research and Development in Mathematics, Science and Technology Education (RADMASTE Centre), University of the Witwatersrand.

In this short course, content from the three knowledge areas for Physical Sciences in the NCS will be covered, namely Matter and Materials, Chemical Change and Chemical Systems. Thus the Workbook will be divided into three parts:

Part 1: Matter and Materials
Part 2: Chemical Change
Part 3: Chemical Systems

We hope you enjoy using this Course Workbook, and find it useful in developing your understanding of some Physical Sciences concepts. If you need any assistance during your self – study you are welcome to telephone or fax us or contact us via e-mail:

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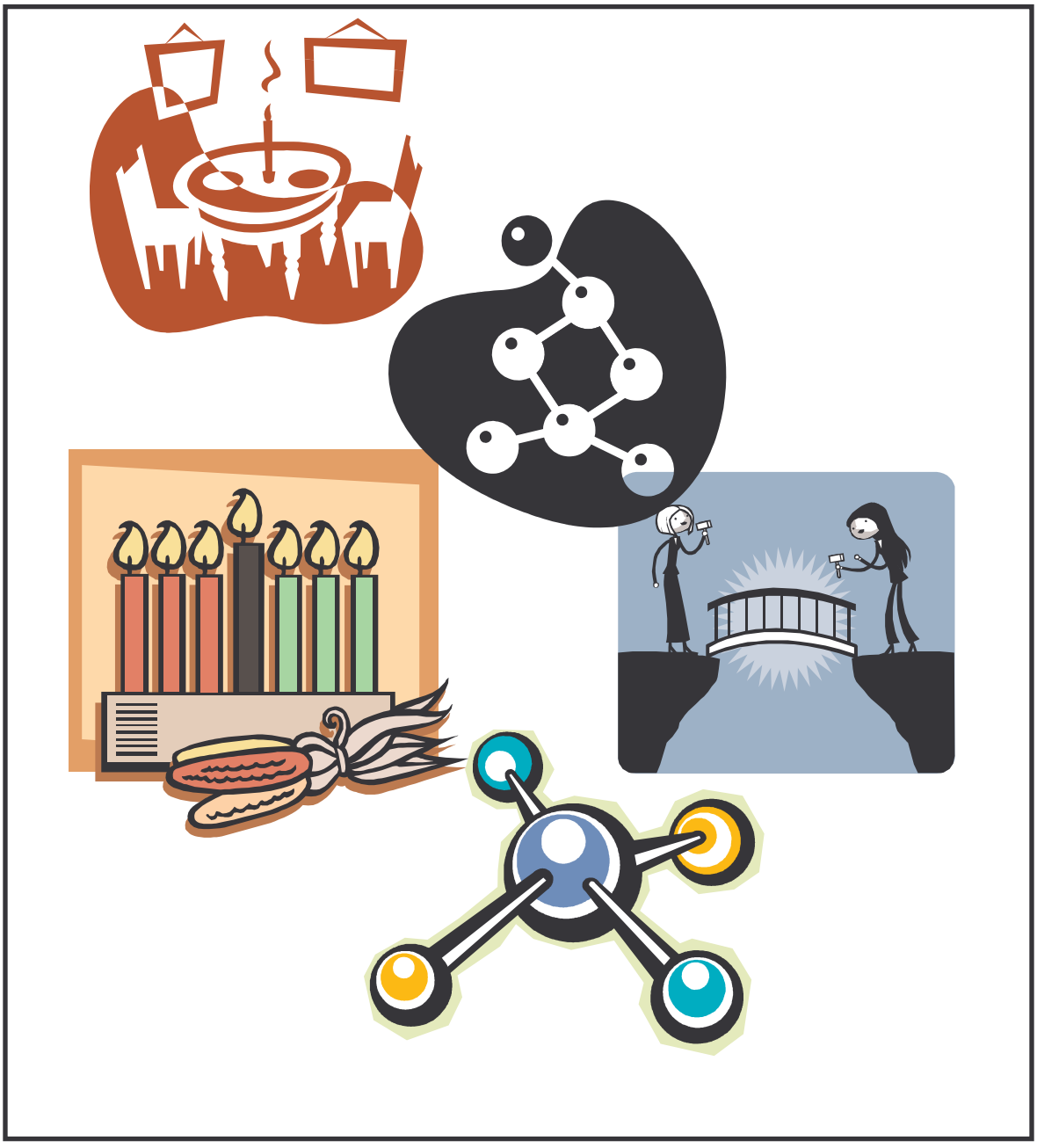
CONTENTS

CHAPTER 1

MACRO AND MICRO PROPERTIES



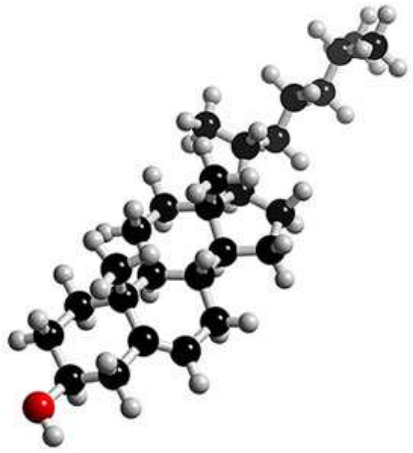
LEARNING OUTCOMES:

After completing this chapter you should be able to:

- **Define what are materials**
- **Explain what are particles of matter**
- **Distinguish between different types of particles**
- **Use symbols and formulae to represent particles of matter**
- **Relate some properties of materials with some properties of particles of matter**

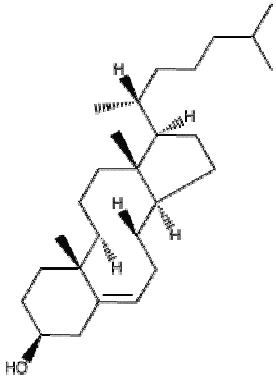
1.1. Introduction

Today, much of technology and medicine has "gone molecular". By this we mean that new developments in these fields are driven today by knowledge of molecular behaviour. The day is not long off that doctors will be able to provide treatment on the basis of their knowledge of our molecular make-up. In fact, this is already happening on quite an extensive scale. The presence of certain molecules in your blood signals the need for certain treatment.



CHOLESTEROL ($C_{27}H_{46}O$)

We all have quite a lot of cholesterol in our blood, and it is an essential chemical for the efficient running of the human body. Only a small amount of this cholesterol comes directly from the food we eat: most of it is made by our own body. Nevertheless, it is not a good thing to have too much. Unfortunately, some individuals have very high cholesterol levels, and the cause is hereditary; about 25 people in 10,000 carry this trait. This is a worrying condition which requires constant monitoring and medical attention to correct it. For such people the battle against cholesterol is never-ending because they are prone to heart disease. If you find your blood cholesterol level is too high you can generally reduce it by following the advice of a trained dietitian, which generally means eating less fat and more fibre, and especially soluble fibre.



Cholesterol is not a life-threatening toxin, but a medium-sized molecule that is really a building block for important parts of the body. In particular it is an essential component of cell membranes. Cholesterol also stabilizes a cell against temperature changes. It is a major part of the membranes of the nervous system, the brain, the spinal cord and the peripheral nerves. In particular it is incorporated into the myelin sheath that insulates the nerves from the surrounding tissue. Cholesterol is also the forerunner of important hormones such as the female sex hormone, oestradiol, and the male sex hormone, testosterone, and of vitamin D, which we need in order to utilize calcium and form bone. Nearly all body tissues are capable of making cholesterol, but the liver and intestines make the most. We require cholesterol to produce the bile we need to digest the fats in our food, and the name itself comes from the Greek words for 'bile solids'.

Essential though cholesterol is, there can be too much of it, and too much causes a build-up of deposits in the arteries, constricts them, and may even block them, with dire consequences. The causes which are now seen as contributing to higher-than-normal cholesterol levels are: hereditary factors, which are the most important; then high blood pressure; followed by stress, smoking, obesity and dietary cholesterol.

But the "molecular power" we now have was gained over the past two hundred years, and its roots lies even further back. It is a spectacular example of what can be achieved by scientific enquiry. The example in this case is enquiry about the relation between the properties of **materials** and the properties of the particles of **matter** that they are made of.

1.2. What are Materials?

We are surrounded by a great variety of objects: a desk, a pool, a loaf, electrical devices. These objects have a composition – **that is a statement of what they are made.** For example, the desk may be made of wood. What the objects are made of has the general description "material". Wood is a material, for example.

Q1.1 Which of the following are objects and which are materials?

Lake, chair, water, steel, bridge, mealie meal, starch, PVC, cellulose, leaf.

1.3. What are Particles of Matter?

Particle, literally translated means a small part of something. But in the present context, it has a more specific meaning. It refers mostly to atoms and molecules. These are in some senses a small part of the materials they make up. We say "in some senses" because it is easy to misunderstand, as the two following cases show.

Anaxagoras and gold

Anaxagoras was a philosopher who lived in Greece before the time of Christ (450 BC approximately). The idea that materials are made from atoms was already around in those times. Anaxagoras explained what he thought about atoms by saying:…"for as gold is made up from gold dust, so all the world is an aggregation of minute bodies, the parts of which are like the whole."

Q1.2. What do you think atoms of gold would look like if they were large enough to see, according to Anaxagoras? Do you agree with him? Explain your view.

Sulfur in a Grade 8 textbook

When the concept of atoms is introduced, perhaps around grade 7 or 8, teachers and textbook authors try to assist learners to get an understanding of the concept in various ways. Here is a quotation from a South African grade 8 textbook:

"If we break a piece of sulfur in half, we get smaller pieces of sulfur. Suppose it were possible to break the smaller piece further each time. Eventually a stage would be reached where the particle is so small it is impossible to break it into smaller pieces of sulfur. This is the smallest particle of sulfur which can exist. Such a particle is called an atom of sulfur."

Q1.3. What do you think an atom of sulfur would look like if it were large enough to see, according to this author? Do you agree with him? Explain your view.

So the notion of particle needs careful thought. In particular we must avoid saying things like: this material is black so the atoms it is made of must be black!

1.4. Types of Particles

As we said, there are two important types of particles to consider: atoms and molecules. In this section we are going to expand on these a little further.

1.4.1. Atoms

These are the simplest particles referred to in the Particle Model of Matter. They are neutral, spherical (approx) particles with a very small diameter (about 100 pm) and a very small mass (about 10 yg). They have an internal structure, comprising a tiny nucleus with a positive charge surrounded by negatively-charged electrons. Atoms of a specific element all have the same nuclear charge. The nuclear charge (measured in terms of the number of units of elementary charge) is the atomic number.

In some elements the particles are single atoms; these are the six elements called the Noble Gases which appear in group 18 of the Periodic Table. In all the other elements (as well as all compounds) the particles are molecules.

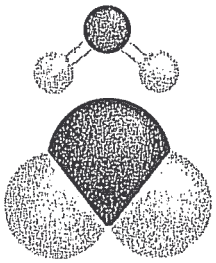
Q1.4. Make a drawing of an atom which has atomic number 2.

1.4.2. Molecules

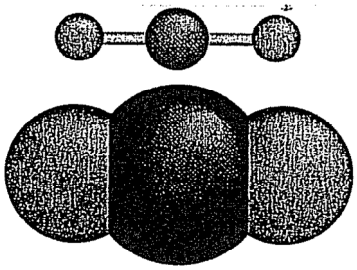
These are particles composed of two or more atoms, bonded together. There is a huge variety of molecules. If the atoms in the molecules are all the same, then they are molecules of elements. If the atoms in the molecules are not all the same, then they are molecules of compounds.

It is very useful to recognise different general categories of molecules.

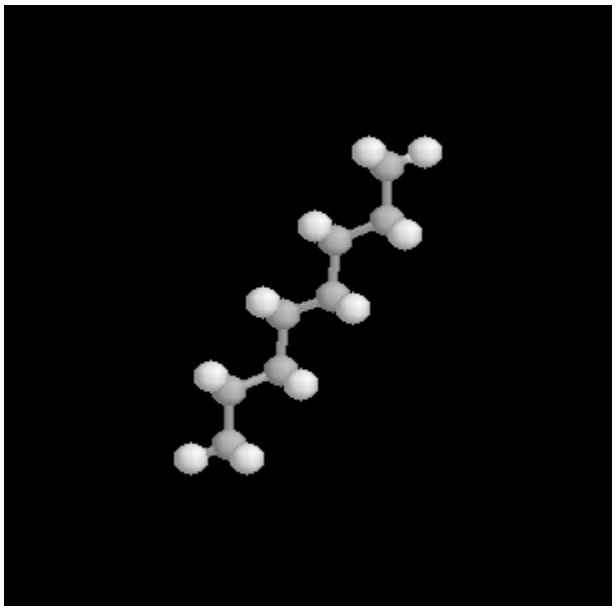
Simple molecules: these comprise a relatively small number of atoms – say, less than 100. Examples of these are molecules of water (H_2O), carbon dioxide (CO_2), octane (C_8H_{18}). Diagrams show these below.

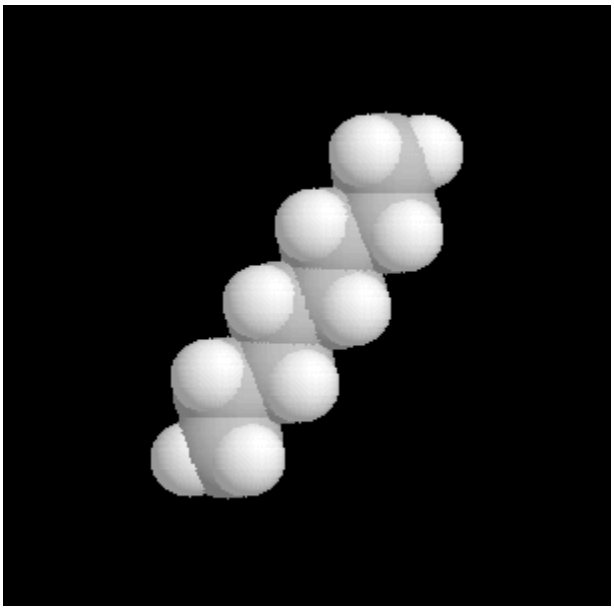


Water (H_2O)



Carbon Dioxide (CO_2)



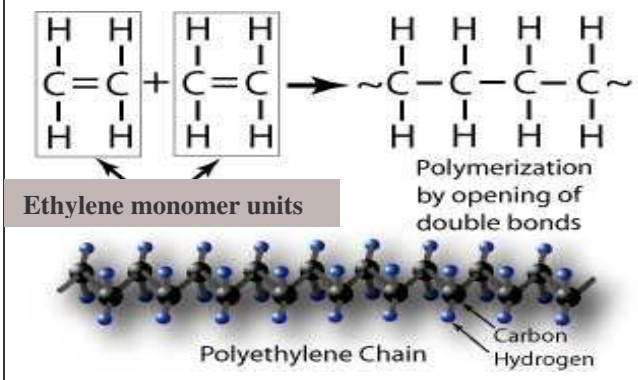


Octane (C_8H_{18})

Fig 1.1: A ball-and-stick and space-filling model of water (H_2O), carbon dioxide (CO_2) and octane (C_8H_{18}) molecules

Q1.5. Name another example of a simple molecule and draw diagrams (space-filling and ball-and-stick) to represent it. You can use the RADMASTE Molecular Stencil to help you.

Macromolecules: these comprise a relatively large number of atoms – say, more than 1 000. Examples of these are molecules of polyethylene ($-(CH_2CH_2)_n-$) and cellulose ($-(C_6H_{10}O_5)_n-$).



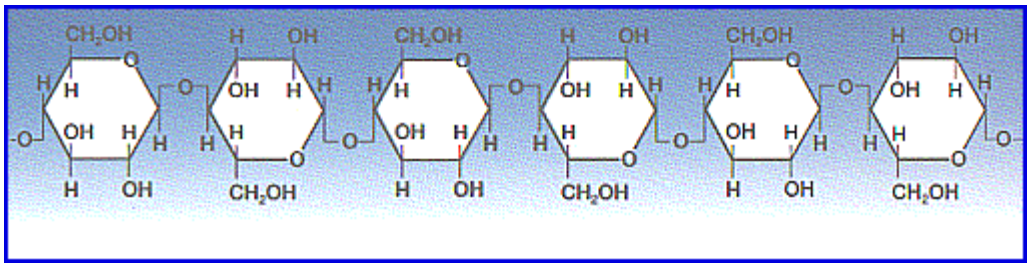
Polyethylene

Polyethylene is formed when numerous ethylene molecules accumulate in a long chain resulting in either a high-density or low-density polymer. High-density polyethylene (HD-PE) is used in the manufacture of bottles, crates, containers, toys, and pipes. The low-density types (LD-PE and LLD-PE) are most widely used as films for packaging and thicker sheets for plastic bags. Flame retardants are added to polyethylene in applications like wire and cable.

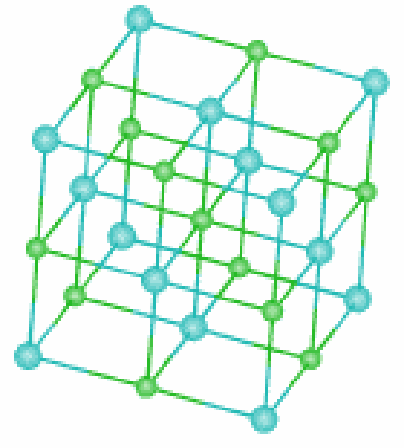
The length of the polymer chain is very important. As the number of carbon atoms in the chain is increased to beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over 1,000, the solid material polyethylene, with its characteristics of strength, flexibility and toughness, is obtained. The change in state occurs because as the length of the molecules increases, the total binding forces between molecules (the intermolecular forces) also increases.

Cellulose

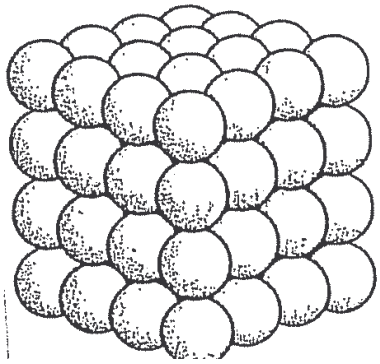
Cellulose is a form of carbohydrate in which some 1500 glucose rings chain together. It is the chief constituent of cell walls in living organisms. It is probably the single most abundant organic molecule in the biosphere. It is the major structural material of which plants are made. Wood is largely cellulose while cotton and paper are almost pure cellulose



Giant molecules: these comprise a very large number of atoms all bonded together into a three-dimensional network. The molecules can have so many atoms that they are visible to the naked eye. Examples of these are molecules of copper (Cu) and sodium chloride (NaCl), diagrams of which are shown below.



Sodium Chloride (s)



Copper (s)

Fig. 1.2: Molecules of sodium chloride (NaCl) and copper (Cu)

Q1.6. Name another example of a giant molecule and draw diagrams (space-filling and ball-and-stick) to represent it.

1.4.3. Ions

Ions are charged atoms and molecules. They may be either positively or negatively charged. Examples of these ions are chloride (Cl^-), and ammonium (NH_4^+).

Q1.7. Name two more examples of ions and give their formulae.

1.5. Symbols and Formulae to Represent Particles of Matter

Pure substances, whether elements or compounds, are represented by formulae. These may or may not be the same formulae as we use to represent the particles they comprise. Chapter 7 provides further discussion of the names and formulae of substances and their particles. The following sections provide a basic introduction regarding particles.

1.5.1. Atoms

Atoms are represented by the symbol of the appropriate element. For example, a chlorine atom is represented by Cl, because this is the symbol of the element chlorine. If a specific nuclide is to be identified, then the mass number of the nuclide is placed in the upper left corner of the symbol, eg ^{35}Cl. If an atomic ion is to be represented then the charge also is shown in the upper right corner of the symbol, eg Na^+ for the sodium ion.

1.5.2. Molecules

Simple molecules have formulae that represent their atomic composition, as for example the water molecule and the octane molecule: H_2O and C_8H_{18} respectively. These formulae do not show how the atoms are bonded together. It may be tempting to think in the case of H_2O that the two H atoms are bonded together, especially if you already know there is a hydrogen molecule, H_2, where of course they are bonded together. But that thinking is wrong! The formula H_2O is merely saying the water molecule is made from 2 hydrogen atoms and 1 oxygen atom.

Q 1.8. How many atoms of what element are present in the molecules of formula:

i)NH_3 ii) Al_2Cl_6 iii) $C_{12}H_{22}O_{11}$

Macromolecules usually have formulae based upon the "constitutional unit" from which they are constructed. The reason for this is that many such molecules are made by polymerisation of one or more monomers. For example, polyethylene, $-(CH_2CH_2)_n-$, is obtained by polymerisation of ethylene, C_2H_4. The constitutional unit in this case is CH_2CH_2. "n" is normally a large number, say greater than 1 000. In most samples of macromolecules there are many different molecules with different values of n.

Q 1.9. (i) If "n" is 10 000, how many atoms of each type are present in a polyethylene molecule?

(ii) What is the constitutional unit in the following macromolecules

(a) $-(CH_2CHCl)_n-$

(b) $-(NH(CH_2)_6NHCO(CH_2)_4CO)_n-$?

Giant molecules are usually represented by empirical formulae. These formulae only show the ratio in which the different atoms occur in the molecules. The number of atoms per molecule tends to infinite, and the atoms in one molecule form a three-dimensional network of atoms and bonds which is virtually endless in extent. For example a grain of salt could be just one giant molecule, which is large enough to be visible.

This giant molecule is represented by the formula NaCl, which can be easily misinterpreted to mean that there are simple molecules of this composition in the grains of salt. Such diatomic molecules do in fact exist in the gas state, but this is a reality only at temperatures around 1 000^0C. It would be helpful for beginners if solid sodium chloride, composed of giant molecules, were represented in the same sort of way as macromolecules, that is by a formula such as – $(NaCl)_n$-. However, probably for historical reasons, this is not done: an empirical formula is used.

Q 1.10. The following substances have giant molecule structures: iron, calcium carbonate, silicon dioxide. Write formulae to represent them.

1.6. Relating Properties of Materials with Properties of Particles of Matter

We have emphasised that we need to be very cautious about trying to relate material properties with particle properties. Nevertheless there are relationships, and science and technology today depend increasingly on knowing them. To get some idea of how it goes we consider below a few relationships which can be understood rather simply.

1.6.1. Physical state of materials

As a student at this level you must already be familiar with how the physical state of substances is explained by the particle model of matter:

Q 1.11. Use the RADMASTE Molecular Stencil to represent the particles of one substance in the gas, liquid and solid state. Assume the same particles exist in all three states.

This should not have been too difficult for you. Please note the specific assumption that the particles should be the same in all three states. This is not always the case. In particular it is common to find the particles in the solid are quite different from those in the other states.

Q 1.12. Use the RADMASTE Molecular Stencil to help you draw a representation of a giant molecule. Then draw a representation of the gas that might be formed when the solid is heated to a sufficiently high temperature.

1.6.2. Strength of materials

There is more than one way of measuring the strength of materials. However, whether the test involves trying to cut or to break a solid material, there is a basic similarity in the outcome. Soft materials have particles that are held together by weak forces. This is usually found when a solid comprises relatively small molecules. Strong materials have particles that are held together by strong forces. Normally this arises when the solid is composed of giant molecules in which all the atoms are held together by strong chemical bonds.

1.6.3. Elasticity of materials

Many materials show some elasticity; that is they deform to some extent when a force is applied but when the force is removed they return to their original shape. But there is a category of materials that are elastic to a remarkable extent; even with a large deformation (extension or compression) this category of material returns to the original shape when the force is removed. It is the kind of behaviour we can observe with a coiled spring. It is also how rubbers behave. In the case of rubbers, the molecules of which they are made are coiled up when the rubber is undeformed. When stretched, the molecules partially uncoil, although we cannot see this of course. When the force is removed the rubber returns to its original shape (length), which implies the molecules are re-coiling and hence shortening their average length.

1.6.4. Viscosity of materials

Viscosity is a property of fluids. Most often we use it in reference to liquids, but it can be used also in reference to gases. Viscosity is the resistance of the fluid to the motion of an object through it. Hence high viscosity means a high resistance to the object's motion, which will be slow. High viscosity is interpreted to mean there are rather strong forces between the particles: they resist being pushed apart by the object moving through it. Since we are dealing with a fluid, the particles must be simple molecules or macromolecules, between which there are relatively strong intermolecular forces.

Q 1.13. Petrol is a familiar liquid and so is syrup. From your experience, which one of these two liquids has the higher viscosity? In which one are the intermolecular forces stronger?

1.6.5. Electrical Conductivity of Materials

Materials conduct electricity if they have mobile charges; mobile means able to move. In a gas there are no mobile charges: the particles are either neutral single atoms or neutral molecules. In liquids, mobile charges may occur in certain cases. Some pure liquids, like molten salts, have positive and negative ions, which are able to move because the substance is liquid. In more normal liquids there are either no ions (eg benzene) or exceedingly low concentrations of ions (eg water). Some liquid mixtures (especially for example aqueous solutions of salts, acids and bases) also contain ions which are mobile.

In solids, there are no mobile atoms or molecules, because they are too tightly packed together. Nevertheless, they may conduct electricity if the electrons in them are mobile. Mobile electrons are found in some types of giant molecules. Depending on the case, the solid may behave as a conductor (as with metals such as copper) or as a semiconductor (as with semimetals such as silicon). Not all giant molecules have mobile electrons; some nonmetals (such as diamond and sodium chloride) do not conduct electricity (they are insulators). Solids comprising simple molecules (such as sugar and sulfur) are also insulators; electrons are not able to "jump" from one molecule to another in the solid.

CHAPTER 2

ALL ABOUT ATOMS

LEARNING OUTCOMES:

After completing this chapter you should be able to:

- Define what is an atom of an element
- Explain what an atom consists of
- Describe how atomic weights are measured and make calculations
- Define atomic radii
- Differentiate between inter- and intra- molecular forces
- Explain what is bond length
- Describe the electronic structure of an atom
- Explain energy levels and ionisation energies of an atom
- Describe the wave- particle duality of electrons in an atom
- Explain atomic orbitals
- Write electron configurations of different atoms

2.1. Introduction

In the previous chapter we showed that the particle model of matter can account for many physical properties of materials. In demonstrating this, we referred principally to two types of particles – atoms and molecules. What was not explained is the nature of the forces at work and how they relate to the identity of the atoms and molecules making up a material. We also did not explain why sometimes we find simple molecules and sometimes giant molecules. In this chapter we begin the process of explaining these things. We start with the atoms, and in later chapters move on to the molecules. We shall do so without much reference to historic discoveries.

2.2. Elements and Atoms

An element (elementary substance) is a substance whose atoms all have the same atomic number. As we have stated before, the atomic number is the positive charge of the nucleus of the atom. This charge is measured in units of elementary charge: the elementary charge has the value 1,9 x 10^{-19}C or 0,19 aC. So when we label or refer to a nucleus of charge +2, it is actually a charge of +0,38 aC. The positive charge and mass of a nucleus is accounted for by assuming that it is formed from two elementary particles: protons and neutrons. The protons have one unit of positive elementary charge. The neutrons are neutral.

Q 2.1. What atom has the largest number of protons in its nucleus? How many protons does an iron atom have in its nucleus? (Hint: look at the Periodic Table.)

In general, as we have implied, nuclei include neutrons as well as protons. Normally the number of neutrons is the same as, or greater than the number of protons in a nucleus. The sum of the number of protons and number of neutrons is called the mass number of the atom. Actually an atom with a specified number of protons and neutrons is called a **nuclide.** It is of course still an atom, but it is an atom with a specified number of protons and neutrons. Symbolically a nuclide is represented as ${}^{A}_{Z}X$, where X is the element symbol, Z is the atomic number, and A is the mass number. Nuclides with the same Z (atomic number) but different A (mass number) are said to be isotopes of one another.

Q 2.2. (i) Name the elements with atoms that have Z = 6, 16, 26, 36.

(ii) Which of the following unidentified nuclides are isotopes of one another? ${}^{40}_{20}X$, ${}^{40}_{21}Y$, ${}^{42}_{20}Z$ **(note X, Y and Z represent the symbols of unspecified elements).**

Electrons are also part of the internal structure of atoms. They move around the nucleus, effectively occupying a very much greater volume than the nucleus. They have a single negative elementary charge, the magnitude of this being identical to that of the proton. Since atoms are neutral, we can understand easily why the number of electrons in an atom is also given by its atomic number.

Q 2.3. How many electrons should be found in atoms of boron, silicon, arsenic, uranium? Explain how you decided.

2.3. Atomic Weights

John Dalton worked out a way to find the relative weights of atoms of different elements. He could not measure their actual masses, although this can be done today with a mass spectrometer. He knew nothing about isotopes: on the contrary he specifically proposed (200 years ago!) that all the atoms of a particular element have the same weight.

Dalton found that the H atom has relatively the smallest weight, and he then defined its atomic weight as 1. All other atoms had larger atomic weights. For example carbon had an atomic weight of 12, meaning that carbon atoms have a weight twelve times greater than hydrogen atoms. Since they are relative values, these atomic weights have no units. The Periodic Table today shows "standard atomic weights" which, like Dalton's original figures, have no units. Today hydrogen atoms are no longer the reference atoms for technical reasons, although of course they are still the lightest atoms. For this reason the standard atomic weight of hydrogen is not exactly 1,000.

Today standard atomic weights are measured with high accuracy. They are measured by mass spectrometry which gives (i) the exact mass of each isotope of an element, and (ii) the percentage abundance of each isotope. The way in which this data is used to obtain an atomic weight is shown in the following example:

Nuclide	Relative Abundance	Nuclidic mass/amu
^{10}B	0,1977	10,01294
^{11}B	0,8023	11,00931

Conventionally, nuclidic masses are reported in atomic mass units (amu). These are units based upon the definition that the ^{12}C nuclide has a mass of exactly 12 amu. All that we need to know is that using these unit we shall come out with a standard atomic weight! To calculate this we say that the standard atomic weight is a weighted average of contributions from the two isotopes. Hence.

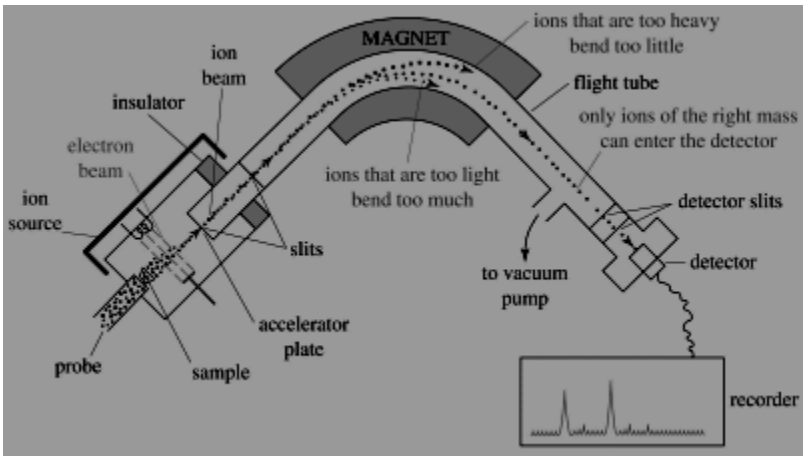
Standard atomic weight of B = (0,1977 x 10,01294) + (0,8023 x 11,00931)

= 1,9796 + 8,8328

= 10,8124

Basic diagram of a mass spectrometer

- **Mass spectrometry** is an analytical technique used to measure the mass-to-charge ratio of ions. It is most generally used to find the composition of a physical sample by generating a mass spectrum representing the masses of sample components. In our context we would work with a pure element.



A **mass spectrometer** is a device that measures the mass-to-charge ratio of ions. This is achieved by ionizing the sample and separating ions of differing masses and recording their relative abundance by measuring intensities of ion flux. A typical mass spectrometer comprises three parts: an ion source, a mass analyzer, and a detector system. In practice ions with a single positive charge are mostly formed,
so effectively the mass spectrometer records the relative abundance of ions of different mass.

Q2.4. Mass spectral study of a sample of lead gave the following data about lead isotopes:

Nuclide	Relative Abundance	Nuclidic mass/amu
^{204}Pb	0.014	203,97302
^{206}Pb	0,241	205,97444
^{207}Pb	0,221	206,97587
^{208}Pb	0,524	207,97663

Calculate the standard atomic weight of lead.

The mass spectrometer is very accurate in providing exact masses and relative abundances. One of the limits to the accuracy of the calculated result for a standard atomic weight is the very small natural variation in relative abundance of the isotopes. Samples of elements drawn from different parts of the World, may have very similar isotopic abundances – but not exactly the same.

2.4. Atomic Radii

Atomic radius has to be measured indirectly for most atoms. The most common type of observation is from X-ray diffraction patterns of crystals. These can be interpreted to show the positions of atoms in a crystal. Specifically they can reveal the positions of nuclei.

A simple case is solid crystals of a noble gas such as argon, Ar(s). This is a simple case because the atoms do not bond to each other. They pack to form crystals like a regular pile of marbles. If the distance between the nuclei of neighbouring atoms is measured, then this must be twice the atomic radius of an Ar atom.

Also simple, and instructive, is a case like crystals of iodine, I_2(s). Here we find diatomic molecules, I_2, packed in a regular, space-efficient manner (Fig. 2.1). We find here that the internuclear distance within the molecules is much smaller than the internuclear distance between I atoms in neighbouring molecules. It is the latter distance (the larger one) that we need to measure in order to deduce the atomic radius of an I atom. The shorter distance within the molecule is the I-I bond length. It is much shorter because the bonding means a strong attractive force pulling the two atoms together. This force is intramolecular, meaning within the molecule.

Q 2.5. Write down other words where "intra" appears and show that they always mean "within".

There is also an attractive force between the molecules, called an intermolecular force, which causes the molecules to pack together as closely as possible, ie in a space-efficient manner. The intermolecular force is much weaker than the intramolecular force, and it is normally assumed that it does not result in significant deformation of the size and shape of a free atom.

Q 2.6. Write down other words where "inter" appears and show that they always mean "between".

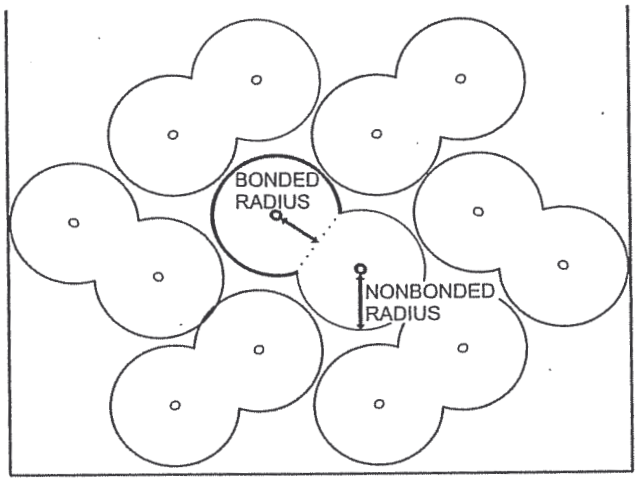


Fig. 2.1: Measurement of the nonbonded and the bonded atomic radius of an iodine atom

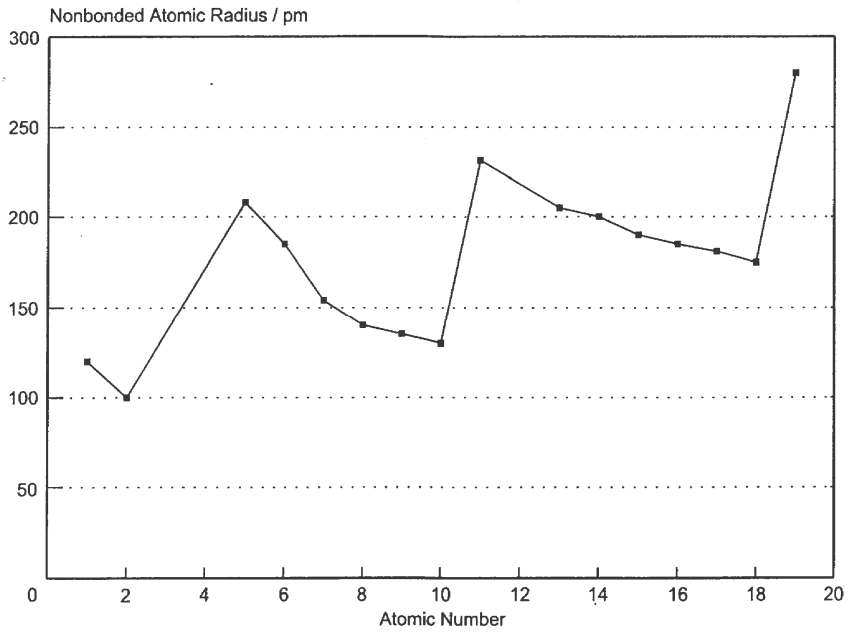


Fig. 2.2: Graph of the variation of the radius of nonbonded atoms with their atomic number

The previous examples also warn us that there will be many cases where we cannot measure an atomic radius in this way. For example, in giant molecules, like those of iron, all atoms are bonded to several neighbouring atoms. Measuring an internuclear distance here leads to a bond length measurement, not an atomic radius. However the bond length measurement can be used to deduce a "bonded atomic radius", by halving the distance between the neighbouring nuclei.

This is an important understanding because there is much potential for misunderstanding in textbooks. Often there are lists of "atomic radii" (or else they appear in a Periodic Table), which are a mixture of bonded radii and non-bonded radii. The mixed data can give a very wrong impression about trends, for example. Noble gas atoms may seem to have the largest radii in their period, when in fact they have the smallest radii!

Q2.7. If your learners had a Periodic Table showing atomic radii and you saw that the atomic radius of neon was larger than that of lithium, how would you explain the error to them?

2.5. Electronic Structure

The behaviour of atoms is strongly related to their electronic structure and their nuclear charge. In this section we take a look at the electronic structure.

2.5.1. Evidence for Energy Levels: Atomic Spectra

Rutherford's famous experiments showed convincingly the existence of a nucleus in atoms. However, these experiments provided no information on the electron arrangement. The earliest evidence on these electronic arrangements was provided by observation of atomic spectra.

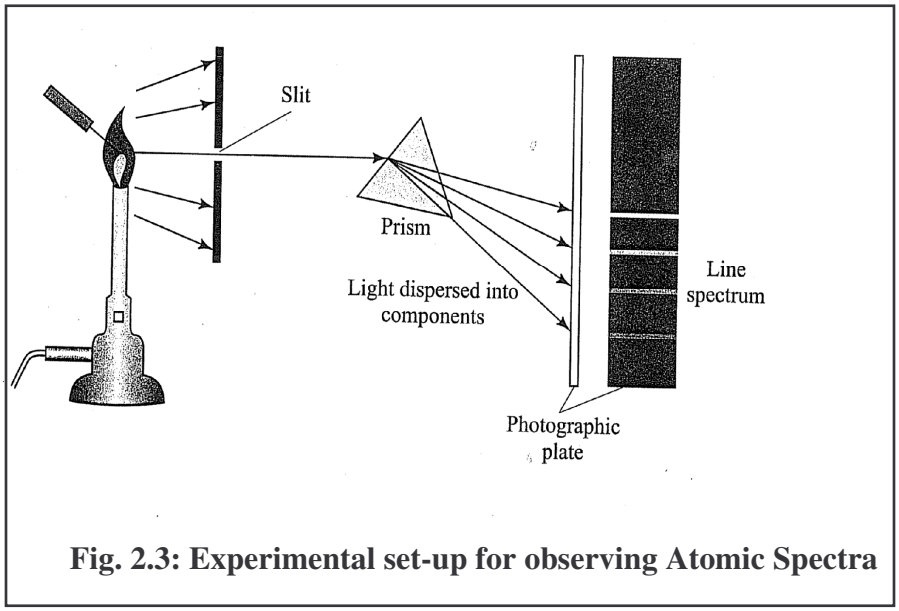


Fig. 2.3: Experimental set-up for observing Atomic Spectra

In the experiment shown, atoms are energised in a burner flame (or in a discharge tube). As they are carried to cooler regions, they lose energy by emitting radiation. Some of this we can see with our eyes, because the flame becomes coloured.

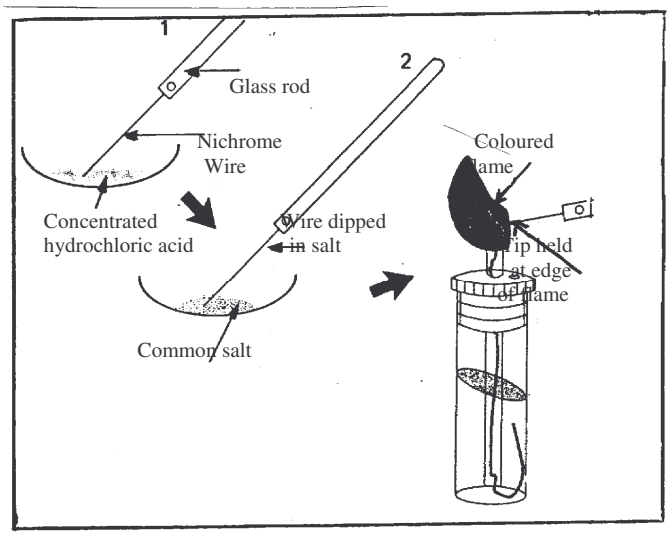
THE FLAME COLOURS OF METAL ATOMS (Requires a Microchemistry kit)

When an electron in an excited state (higher energy) returns to its ground state (lower energy), an atomic spectrum is produced. A specific quantity of energy is associated with each electron, and when an electron returns to a lower energy level, a specific quantity of energy is released. The energy is released as electromagnetic radiation. Certain wavelengths will be visible to the naked eye; other wavelengths can only be detected with instruments. In the activity below, we will investigate the colours emitted by certain metal atoms. Different colours indicate different wavelengths of visible radiation.

REQUIREMENTS:

Apparatus: 1 x comboplate®; 1x microburner; nichrome wire, approximately 10cm in length; 1 x combustion tube; 1 x sample vial; prestik.

Chemicals: NaCl(s); KCl(s); $CuSO_4.5H_2O$(s); $CaCl_2$(s); LiCl(s); $BaCl_2$(s); HCl (conc)



PROCEDURE

1. Pass the nichrome wire through the combustion tube so that at least 2 cm protrudes from the end. Fix the wire in position by placing a small amount of prestik at the other end of the combustion tube.
2. Dip the wire in concentrated hydrochloric acid.
3. Dip the wet nichrome wire in solid sodium chloride. Hold it in the colourless part of the flame of the microburner.
4. Note the colour of emitted light.
5. Clean the wire in concentrated hydrochloric acid.
6. Repeat the procedure with the other salts.
7. Report your results in a suitable table.
8. What can you conclude about the electronic energy level of different atoms?
9. Suggest any practical applications where the colours emitted by certain metal atoms might be seen.

When the emitted light is analysed with a prism or a grating (Fig. 2.3) it is found to comprise very specific wavelengths only. Each element has a unique spectrum and the wavelength of each line within a spectrum has a specific energy. Two examples are shown in Fig. 2.4.

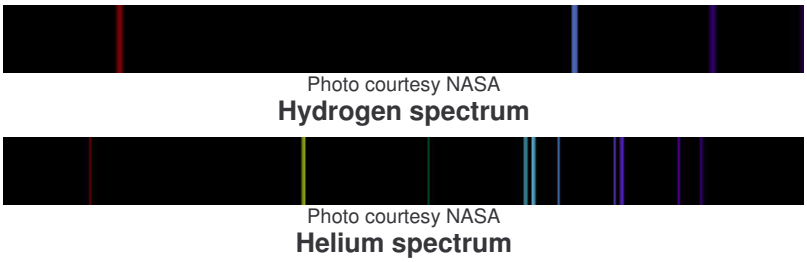


Fig. 2.4: Spectra of a Hydrogen and Helium atom

(NB: This is a black and white picture. The real observation would show coloured (not white) lines on the dark background)

The lines in the picture are images of the slit through which some of the emitted light passed towards the prism. The emitted light is not itself line-shaped! The light is emitted from the flame in all directions.

The observation that very specific wavelengths of light are emitted, suggests that energy changes of the atoms are also very specific. The wavelength of light is related to the energy of the light photons by $E = hc/\lambda$, where E is the energy, h is the Planck constant, c is the speed of light, and λ is the wavelength. So we are saying that an energy change, ΔE, is taking place in the atoms which is evidenced by the specific wavelength we observe:

$\Delta E(\text{atom}) = E(\text{photon}) = hc/\lambda$

If we suppose that the energy change of the atom is due to a change of electronic energy in that atom, then it is implied that the electrons in the atom have specific energies.

Niels Bohr developed a planetary model of the atom on this basis. The model still has value, although it has been superseded by other models. Bohr hypothesised that electrons in atoms move in orbits around the nucleus, in the same sort of way that planets move around the Sun in our solar system. He further supposed that whilst an electron moved in one orbit, its energy does not change. It is only when it changes orbit that there is an energy change. Orbits are of greater energy the further away they are from the nucleus. Hence excitation of an electron (eg by absorption of radiation of a specific energy) causes it to move to a higher energy orbit further

from the nucleus. Conversely, emission of radiation of a specific energy accompanies a change of an electron from a higher energy orbit to a lower energy one, closer to the nucleus.

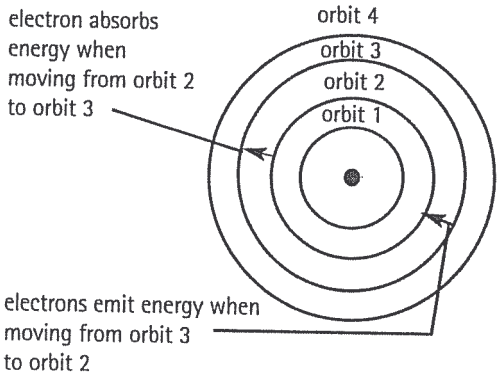


Fig. 2.5: Planetary model of an atom

Q 2.8. One of the wavelengths of light emitted by excited hydrogen atoms is 486 nm. It is blue-green in colour. What is the change in energy of the atom that accompanies this emission? Give your answer in aJ. (It has been worked out that this energy change corresponds to a change of an electron from orbit 4 to orbit 2.)

2.5.2. Evidence for Energy Levels: Ionisation Energies

Although atomic spectra demonstrate the existence of energy levels for electrons in atoms, they are too complicated to demonstrate other important aspects of these. For this purpose, ionisation energies give a much more simple picture.

Ionisation of atoms in the gas state may take place in a very strong electric field or when exposed to radiation of sufficiently high energy.

$A \rightarrow A^+ + e^-$

Ionisation in general refers to a process of ion formation, which in this case occurs by loss of an electron from a neutral atom, A. The energy required for this process is called the ionisation energy of A. To be more specific, it may be described as the first ionisation energy, because further electron loss can be observed, as follows:

$A^+ \rightarrow A^{2+} + e^-$

$A^{2+} \rightarrow A^{3+} + e^-$

Etc

These further stages of electron loss are then described as the second, third, etc ionisation energy. Each of the further stages requires greater energy so that the energy sequence is $1^{st}<2^{nd}<3^{rd}$, etc. Note that the second ionisation energy is NOT referring to:

$A \rightarrow A^{2+} + 2e^-$

Q 2.9. Write a symbolic equation representing the 4^{th} ionisation of A.

As mentioned before, ionisation energy values of atoms reveal several interesting aspects of electronic energy levels. We follow up on some of these.

The ionisation energy of hydrogen (atoms) is 2,18 aJ, whilst that of helium is 3,94 aJ. We can explain this difference by reference to the nuclear charges. Ionisation involves pulling a negative electron away from the atom against the electrostatic attraction of the positive nucleus. The electron is moved away, effectively to infinity, that is to a point where it does not experience any electrostatic force. The nuclear charge of the He atom is double that of the H atom. Hence the energy required to remove an electron from the He atom might be expected to be double that required for the H atom. However, it is a little less than double, a result we can explain by noting the presence of the additional electron in the He atom. The two electrons repel each other and so tend to stay on opposite sides of the common nucleus. However the repulsion is there and results in an ionisation energy that is less than double that of the H atom.

We can fit these observations to the Bohr model, saying that in H and in He the electrons occupy the first (lowest energy) orbit. In He this orbit has a lower energy and smaller radius, because of the greater electrostatic force of the 2+ nucleus. (The He atom is indeed smaller than the H atom (Fig 2.6).)

Q 2.10. Predict the approximate ionisation energy (first) of the lithium atom, and explain your prediction.

Your predicted value of the ionisation energy of Li is likely to be wrong! But it does not matter, because it highlights the basic idea: electrons in atoms are found in distinct energy levels. The ionisation energy of Li is **smaller** than those of both H and He, despite the **greater** nuclear charge (3+). The most reasonable explanation of this is that the additional electron of the Li atom is in a higher energy orbit than the two electrons of the He atom (and the one electron of the H atom).

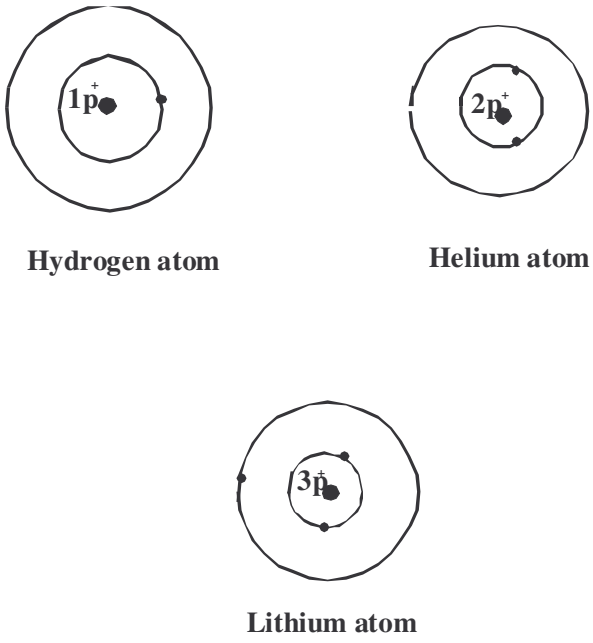


Fig. 2.6: Bohr model of a Hydrogen, Helium and Lithium atom

In this model, the electron in the second orbit experiences an effective nuclear charge of 1+ (+3-2 = +1). Also, it is further from the nucleus than in the H atom. Hence its energy is higher than the one electron in H. Note also that the first orbit in the Li atom is shown as even smaller in radius (and lower in energy) than in He, because of the greater nuclear charge.

Q 2.11. Predict the approximate ionisation energy (first) of the beryllium atom, and explain your prediction.

Your predicted value in this case is likely to be correct! Compared to a lithium atom, there is an increased effective nuclear charge (+4-2 = +2) and this will be offset partially by the repulsion of the additional electron in the same orbit.

As atoms of larger atomic number (and hence greater nuclear charge) are considered we find the ionisation energy increases. At atomic number 10 (Ne) it reaches 2,08 aJ. But then, once again, we are surprised: sodium atoms, atomic number 11, have an ionisation energy of only 0,5 aJ. We are forced again to propose that a third orbit is now being "occupied". The first orbit was "full" with 2 electrons; the second orbit is now full with 8 electrons.

Continuing such an exploration of ionisation energies it is possible to show that further orbits are filled with 18 (3^{rd}), 32 (4^{th}) and 50 (5^{th}) electrons. It is evident that the capacity of an orbit (n) increases as we go to higher energy (more distant) orbits. The discovery of these "magic numbers" aroused much interest historically, and it still intrigues people. Particularly interesting is that the numbers fit a formula, $2n^2$, where n is the orbit number (starting from n=1 as the lowest energy one).

Additional confirmation of electronic energy levels can be found by studying successive ionisation energies of a particular atom. For example for the carbon atom we find the data shown in the table that follows.

	1st	**2nd**	**3rd**	**4th**	**5th**	**6th**
IE/aJ	1,81	3,90	7,64	10,3	62,8	78,5
i(charge left on ion)	+1	+2	+3	+4	+5	+6
IE/i (aJ)	1,81	1,95	2,55	2,58	12,6	13,1

We can most easily interpret this data if we take into account the increasing charge as we progress through the ionisation energies. If we divide the IE by the charge**, i,** remaining on the ion as the electron is removed, we compensate for this effect. We then see more distinctly the evidence for two orbits. The electrons that require less energy to remove (four in the C atom) are called **valence electrons.** The electrons requiring substantially more energy to remove (two in the C atom) are called **core electrons**.

Q 2.12. Consider the following successive IEs (aJ) of a nitrogen atom. Deduce the orbit occupancy of the electrons, showing how you came to this conclusion. How many valence electrons does this atom have?

	1st	2nd	3rd	4th	5th	6th	7th
IE/aJ	2,33	4,74	7,53	12,4	15,7	88,4	106,8

2.5.3. Wave-Particle Duality

When we examine the ionisation energy data more closely, we find evidence that the Bohr model (orbits) is missing some details. For example, if we take the first ionisation energies of atoms of lithium through to neon, it is true that there is a general trend. This trend is one that is often learned as one of the great general trends in the Periodic Table.

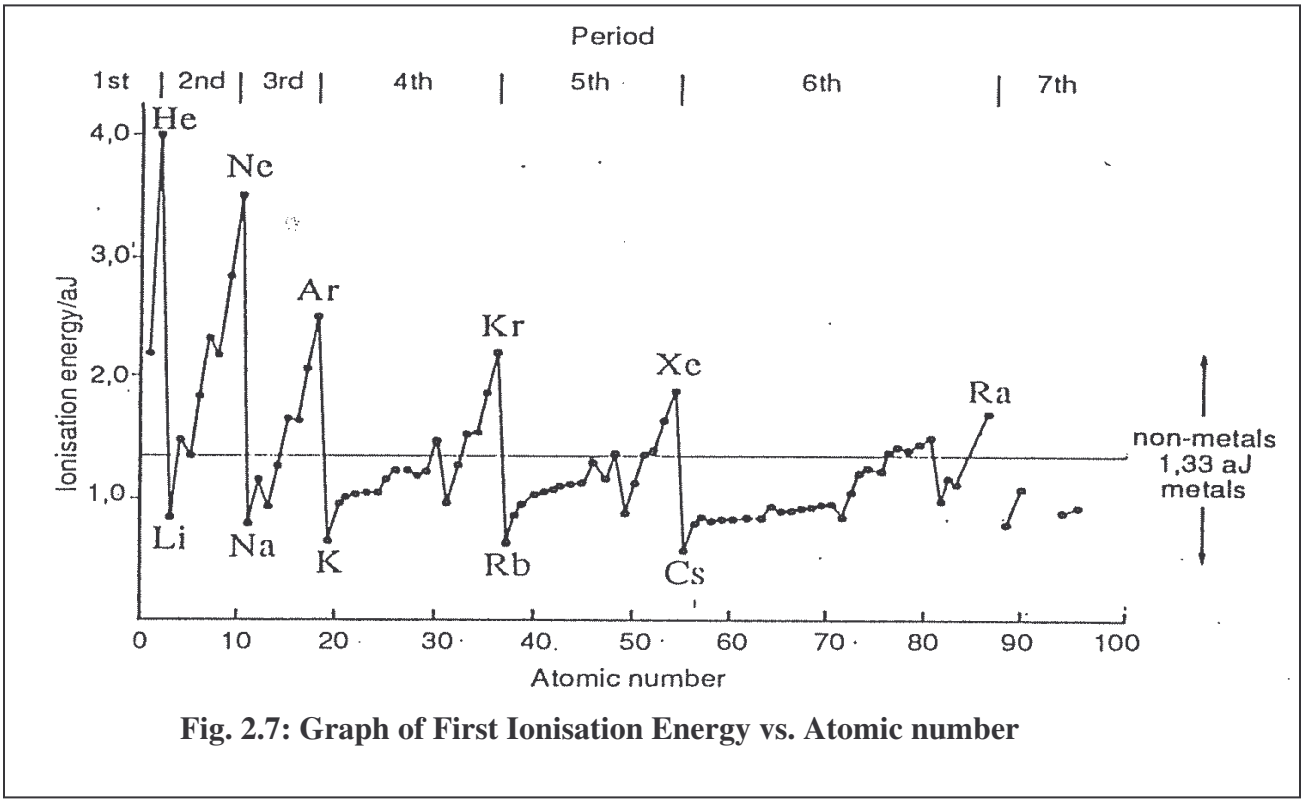


Fig. 2.7: Graph of First Ionisation Energy vs. Atomic number

The 1st ionisation energies increase with increasing atomic number in a period. But look more closely (Fig. 2.7.) and we find this general trend is not completely regular. Some detail is being overlooked.

Apart from this we have to note that even though the Bohr planetary model of the atom is quite successful, we do not have an **explanation** for the existence of orbits of specific energy. Nor do we have an **explanation** for the formula $2n^2$ which governs the capacity of an orbit for electrons. The Bohr model points us in a direction but does not explain.

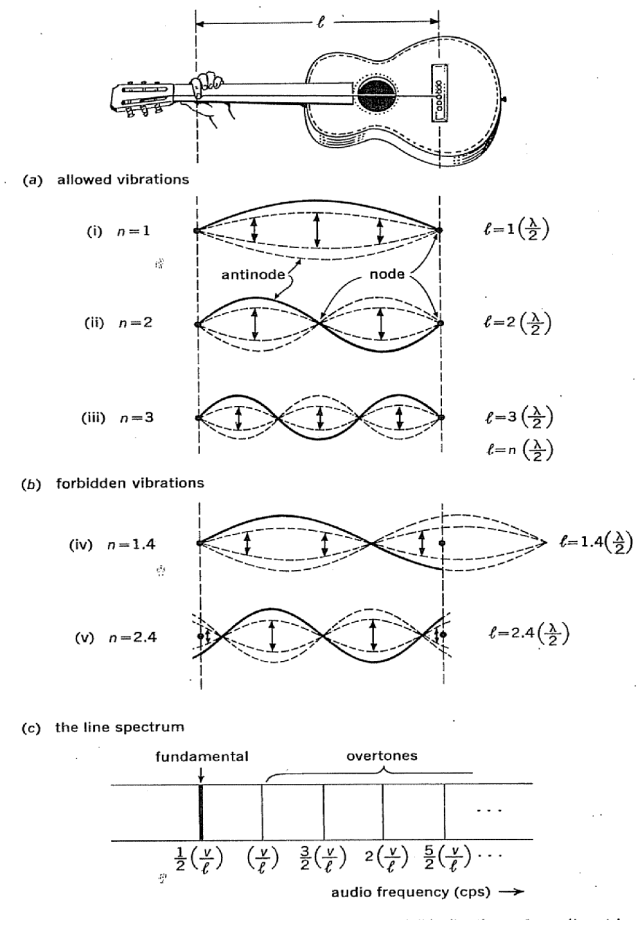


Fig. 2.8: The allowed (a) and the unallowed (b) vibrations of a guitar string and its sound spectrum (c)

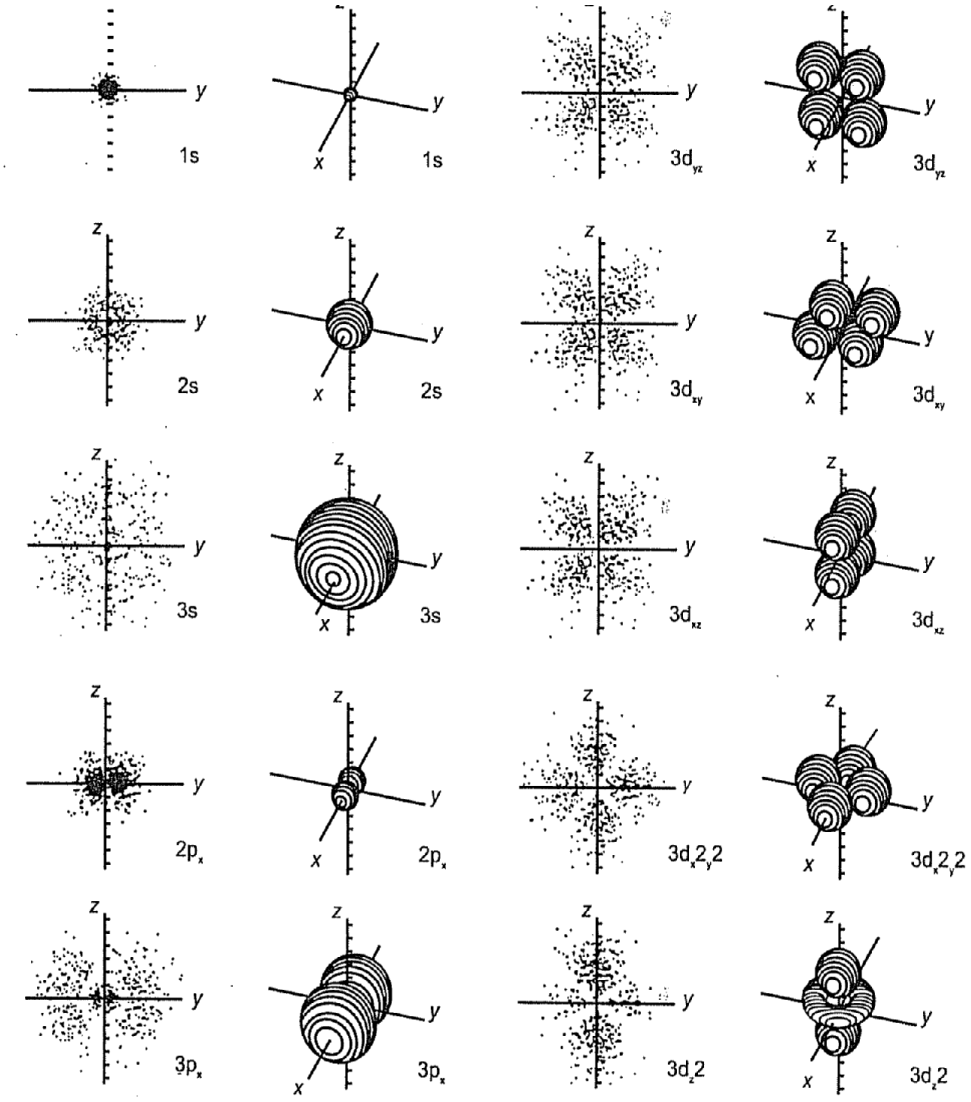
We can only overcome this problem by accepting that in the very small scale world of atoms, the electrons may seem to us to behave sometimes as particles and sometimes as waves. They exhibit **"wave-particle duality",** a phenomenon we also encounter when dealing with some aspects of electromagnetic radiation. In the case of electrons in atoms, we get useful insights from recalling the phenomenon of stationary waves. There we find the idea that there is a specific number of half-wavelengths of a vibration (eg a guitar string, Fig. 2.8.) associated with a stationary state. There is a distinct change in this number to achieve a different stationary state. This is exactly parallel to what we observe with the behaviour of electrons in atoms. From a wave perspective, stimulating electronic energy changes in an atom is like plucking a guitar string! Of course the atom is a 3-D entity whereas the guitar string is a 1-D entity. So the results are more complex in the atom, but recognisably related in appearance to the guitar

Schrodinger developed a wave equation for electrons in atoms and this is the basis of pictures we see of atomic orbitals. Atomic orbitals are the stationary wave patterns of electrons in atoms. The patterns (orbitals) are symbolically labelled as 1s, 2s, 2p, 3s, 3p, 3d, etc.

The term orbital was invented to link with the Bohr idea of orbit. However an orbital is not an orbit; it is a wave pattern. The numbers in the descriptions 1s, 2s, etc, -called the principal quantum number, n – correspond in some senses to the old Bohr

orbit numbers. Like the Bohr usage, as the principal quantum number increases, so does the energy of the orbital. A 2s atomic orbital has a higher energy than a 1s, for example. The principal quantum number is also the number of nodes in the wave pattern, where one node is always at the surface of the orbital. This relates to a characteristic of stationary waves in general: the more nodes, the higher the energy. The letter designation – s, p, d, etc – relates to the shape of the 3-D stationary wave pattern. An s orbital is spherically symmetrical and has only spherical nodes. A p orbital has 1 planar node through the nucleus. A d orbital has 2 planar nodes through the nucleus.

Fig. 2.9: Dot density and boundary surface diagrams of a few AOs



Representing Atomic Orbitals

Textbooks contain a variety of pictures which are intended to give learners a correct understanding. Often these pictures are linked with definitions of atomic orbitals in terms of "regions of space" in which electrons are likely to be found. This is not wrong but it is vague. We now see that what we are actually trying to do is to represent 3-D stationary wave patterns for an electron in an atom. We do this in two ways: the boundary surface diagram and the dot density diagram. The first is a wave description and the second a particle description.

Boundary surface diagram

These are the 3-D equivalent of the one-dimensional stationary wave patterns for the guitar string. In the guitar string wave patterns we see a solid-line wave profile with indications (by dotted lines) of how the profile might appear at different instants of time. The boundary surface diagrams have contour lines on the surface of each shape, to try to convey the fact that these are in 3-D. If you tried to draw these on a blackboard, you might draw the profile and then put some shading (rather than contour lines) to try to get that 3-D spatial effect.
The other thing to say about these diagrams is that, unlike the guitar string which has definitely fixed ends, the orbital does not have a finite end. It sort of fades away very gradually with increasing distance from the nucleus. This means the boundary surface is not a solid skin or wall of a container! The surface is far away from the nucleus, so the stationary wave profile is not sharply defined like that for the guitar string. Nevertheless we need to draw something that shows shape, and the boundary surface diagram does that.
It should perhaps also be emphasized that an electron does not travel over the surface: it is not an orbit of fancy shape!

Dot-density diagram

Given the dual wave-particle character of the electrons in an atom, it is important to give both aspects of this character in a self-consistent way. The dot-density diagram contributes to that goal, presenting the particle nature of the electron in a wave context! The origin of the dot density patterns is an imaginary set of repeated observations of one electron "in" the specified orbital. We cannot observe the electron really, but we can imagine that, say, every millisecond you took a photo with a special camera that allowed you to record exactly where an electron was in relation to the nucleus of an atom. After taking a hundred pictures, you printed out the result.
Examining the print in the case of the 1s AO you would see a symmetrical pattern of dots which are closest together near to the nucleus. They occur further away from the nucleus also, but the density of dots gets less the further away we go. The electron is not fixed in space, and does feel the attractive force of the nucleus. Hence the pattern of dots is reasonable. We can summarise the outcome by saying the electron is most likely to be found (if we make another observation) where the dot density is greatest, but there is some probability it would be found further away.
The dot-density diagrams show a distribution of dots that we can relate to the boundary surface diagrams. The advantage is that they show (i) the varied probability inside the boundary surface (eg the existence of internal nodes) and (ii) the indefinite nature of the boundary surface. As we said before, there is no surface really, the AO just gradually fades away.

Q 2.13. Draw up a table showing, for each type of atomic orbital, the number of spherical nodes, the number of planar nodes, and the total number of nodes. Your table should include the 1s, 2s, 2p, 3s, 3p and 3d orbitals.

Schrodinger's wave equation generated the stationary wave patterns we have shown above. It explains the existence of electronic energy levels in atoms by attributing wave behaviour to electrons. This wave behaviour can also be demonstrated by observing electron diffraction; diffraction of electromagnetic radiation is usually explained by applying the wave theory of light. The wave equation also explains the n^2 part of the formula $2n^2$(the formula giving the number of electrons per orbit in the Bohr model), because this is the number of stationary wave patterns obtained when the principal quantum number is n. For example when n = 2, there are 4 atomic orbitals: one **s** and three **p**.

Once we have accepted the wave-particle duality as a characteristic of electrons then we find that much can be explained about their behaviour in atoms. One thing however it does not alone explain – the 2 in front of the n^2. The meaning of this number 2 is that two is the maximum number of electrons per orbital. The explanation of this is found in another property of electrons, called spin.

The property of spin has two possible values for electrons (+ and – *s*). The final conclusion therefore is that for electrons to occupy the same orbital they must have opposite spin. In this way we can account for the 2 in $2n^2$.

With all this information, it is possible to give a precise symbolic description of the electron arrangement in an atom. Such a description is called the electron configuration of the atom. For example, for the carbon atom (atomic no. 6) we have $1s^2 2s^2 2p^2$, in its lowest energy state (ground state).

Q2.14. Write electron configurations for the following atoms, assuming they are in their lowest energy state (ground state): Li, Ne, P, Mg.

2.5.4. Back to Particles

As a conclusion to the qualitative account of stationary waves above, we return to particle energy levels. Evidently there is some detail to add to the energy level diagrams we drew before.

An example of a more-detailed energy level diagram for atoms is shown below and the three electrons of the Li atom put in place.

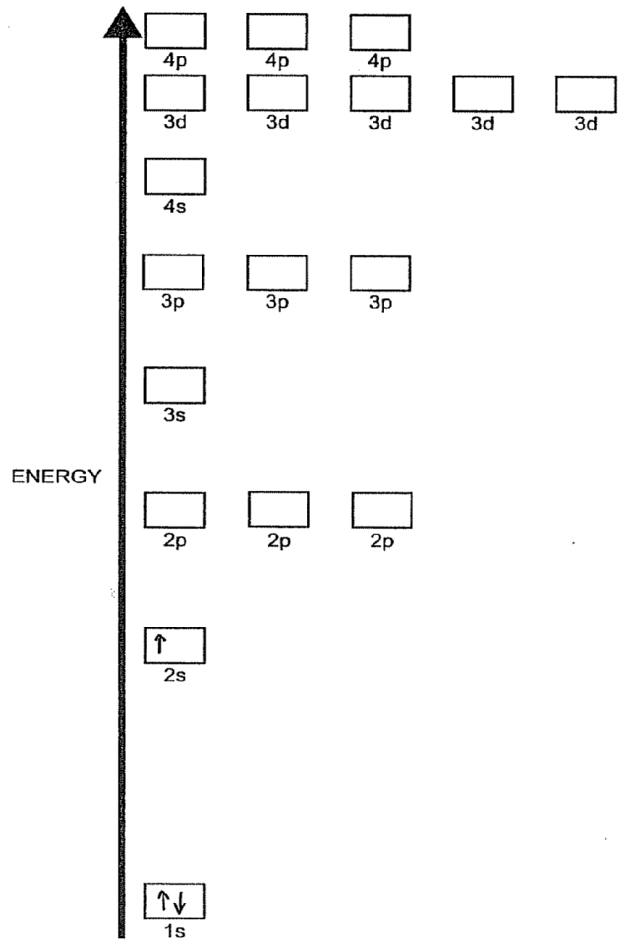


Fig. 2.10:The energy relationship between the various AOs

Note how electron spin is symbolised by a vertical arrow: the two possible spin values are symbolised by the upward and downward-pointing arrows. Notice also that the successive energy levels get more closely spaced at higher levels.

Q2.15. Explain why, in Fig. 2.10., all three electrons have not been put in the 1s AO level.

Q2.16. Draw an energy level diagram for (i) an oxygen atom, and (ii) a sulfur atom. What do you notice when you compare the two diagrams?

Q.2.17. Using the NCS, identify which topics in Grade 10, 11 and 12 can be addressed from this chapter.

CHAPTER 3

SIMPLE MOLECULES

LEARNING OUTCOMES:

After completing this chapter you should be able to:

- Explain what a chemical bond is
- Explain how the wave-particle duality of electrons in atoms is relevant to understanding chemical bonding
- Differentiate between valency and valence electrons of an atom
- Explain what is bond polarity
- Define bond length between atoms
- Define what is bond strength
- Relate the bond strength with bond length in a molecule
- Explain what bond vibration frequencies are
- Explain how molecules adopt certain geometries
- State some of the common misconceptions on chemical bonding
- Explain the origin of intermolecular forces
- Describe hydrogen bonding and recognize molecular structures where it may occur

3.1. Introduction

Of all particles, molecules are the ones that affect us most directly. They are much more varied than atoms: there are more than 10 million different ones identified. These molecules are made from about 100 different atoms (neglecting isotopes) bonded together in very specific ways. We will study this menagerie of molecules in parts, starting in this chapter with simple ones. Subsequent parts will look at macromolecules and giant molecules.

3.2. What do we mean by chemical bonding?

As soon as it was known that atoms have negative and positive particles inside them, it was speculated that chemical bonding involves interaction between these charged particles. When the internal structure of atoms was shown to comprise a positive nucleus with negative electrons around it, then theories of chemical bonding could be developed. It is now possible to say that a chemical bond is a strong electrostatic force between atoms.

3.3. Bonding means sharing: the case of the hydrogen molecule

The Lewis theory of chemical bonding is the one that has stood the test of time since its first full and formal description in 1916. The basic idea is simple: a bond is formed between two atoms by sharing of a pair of electrons. The positive nuclei of both atoms attract the shared pair of electrons and thereby are themselves drawn together. The forces are electrostatic and involve both attraction of opposite charges and repulsion of like charges. When there is nett attraction, a bond forms.

The case of two H atoms forming an H_2 molecule is instructive for us to study by doing a model calculation. We shall do the model calculation using the known charges of the proton and electron and we shall assume the hydrogen nuclei (the protons) are located at the distance apart found in the hydrogen molecule. We then calculate the electrostatic potential energy of this arrangement of four particles and compare it with the two separate atoms.

We shall do the model calculation just to show how a decrease in potential energy can happen, as a result of sharing when $2H \rightarrow H_2$.

We start with one H atom and say the radius of this is 120 pm. If the electron is at this distance from the nucleus then the PE (electrostatic) is,

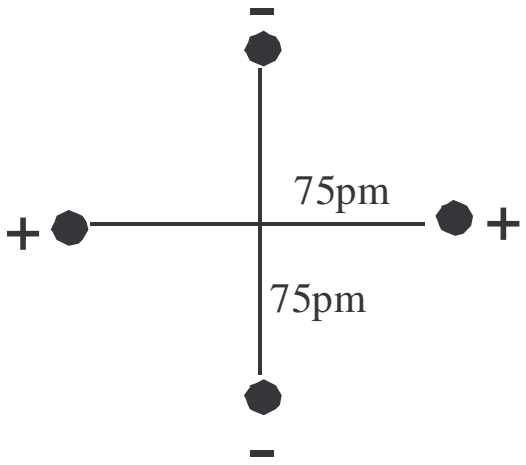
$$PE_H = \frac{-q^2}{120x10^{-12}}$$

Where ***q*** is the elementary charge (this has the same magnitude for the electron and the proton (nucleus), but one is +ve and the other is –ve).

Since we start with the two separate H atoms, our PE is then:

$$PE_{2H} = \frac{-2q^2}{120x10^{-12}} = \frac{-q^2}{60x10^{-12}} = -0.017 \times 10^{12}\ q^2$$

For the H_2 molecule, we place the nuclei (protons) at the known internuclear distance in this molecule: 75pm. Then we place the two electrons at the same distance apart from each other (75 pm) and symmetrically in between the two nuclei as follows:



If we do this we find that the distance between each electron and each nucleus is 53 pm. Then

$$PE_{H2} = \frac{+q^2}{75x10^{-12}} + \frac{+q^2}{75x10^{-12}} - \frac{4xq^2}{53x10^{-12}}$$

($p^+ + p^+$ repulsion) ($e^- + e^-$ repulsion) ($e^- + p^+$ attraction)

$$= \frac{-3{,}66q^2}{75x10^{-12}} = -0{,}049 \times 10^{12}\ q^2$$

Therefore the PE has decreased from -0,017 x 10^{12} q^2 to -0,049 x 10^{12} q^2 that is by **0,032 x 10^{12} q^2.**

It must be emphasized that this is a very simplistic model calculation. The point it highlights is however accurate and important: an overall decrease in PE occurs because,

1) There is a decrease in PE due to 2 electrons, both moving closer to 2 nuclei

2) There is an increase in PE due to 2 nuclei moving closer to each other

3) There is an increase in PE due to 2 electrons moving closer to each other, and

4) The contribution made by (1) is larger than the sum of (2) and (3).

The outcome will only be achieved if the 2 electrons are located in the region between the 2 nuclei, so they both attract both nuclei (and vice versa). This result therefore provides some credibility to the Lewis theory.

Although this model calculation is "successful", we should be careful not to misinterpret it. For example the pair of electrons is not really fixed in space between the two nuclei as the model calculation assumed. This does not matter for our purposes as we only aimed to get some measure of credibility. Let us therefore proceed on this basis.

Lewis developed a symbolic way of representing the formation of the bond as follows:

H:H

The symbol of the element is used to represent the atom, excluding the valence electrons. The valence electrons are explicitly represented by dots (or other symbols if necessary). The shared electrons are shown in between the element symbols. One pair of electrons is regarded as one bond.

3.4. Sharing must obey certain rules: the case of the helium molecule

The diatomic helium molecule, He_2 , does not exist. Considering the explanation of the formation of the hydrogen molecule just given above, this is a big surprise. Helium atoms have two electrons in the 1s AO. We might conclude that two electron pairs could be shared between two atoms and hence that two bonds could form. In fact no bonds form under any condition.

We can provide a simple explanation of this result by supposing that when two atoms form a molecule, AOs become MOs (molecular orbitals). In this case two 1s AOs would overlap and become one MO. If this MO, like an AO, can accommodate only two electrons (with opposite spins), then we can see that this will not work for the case of two helium atoms (4 electrons). It will work for the case of two hydrogen atoms (2 electrons).

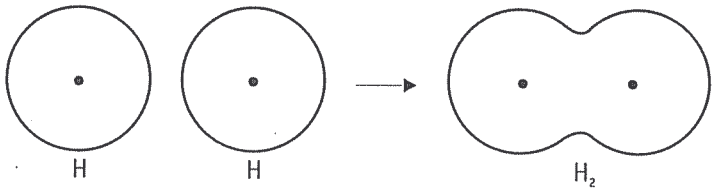


Fig. 3.1: AOs of H atoms and MO of H_2 molecule

3.5. Wave-particle duality revisited

We can get a slightly more sophisticated view of the above situation by remembering that an AO is a stationary wave pattern for an electron in an atom. When two such wave patterns interact, we say (in wave theory language) the waves interfere. This interference may be constructive or destructive. Constructive interference results in an increased wave amplitude in the resultant wave. Destructive interference results in a decreased (or zero) amplitude in the resultant wave.

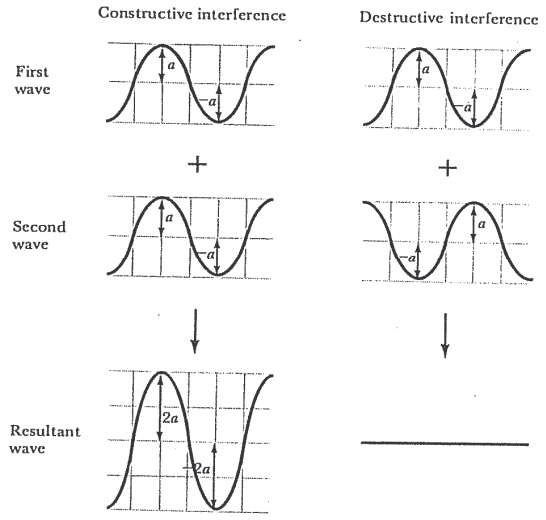


Fig. 3.2: Constructive and Destructive interference of waves

Thus 2 stationary waves may form 2 new stationary waves when they interfere. This applies also when 2 AOs interfere: they form two MOs. One of the MOs, formed by constructive interference, has increased amplitude, and lower energy. It is called a bonding MO. The other MO, formed by destructive interference, has decreased amplitude, and higher energy. It is called an antibonding MO.

Note that it is not just no-bonding; it is antibonding because the energy is higher than the original AOs.

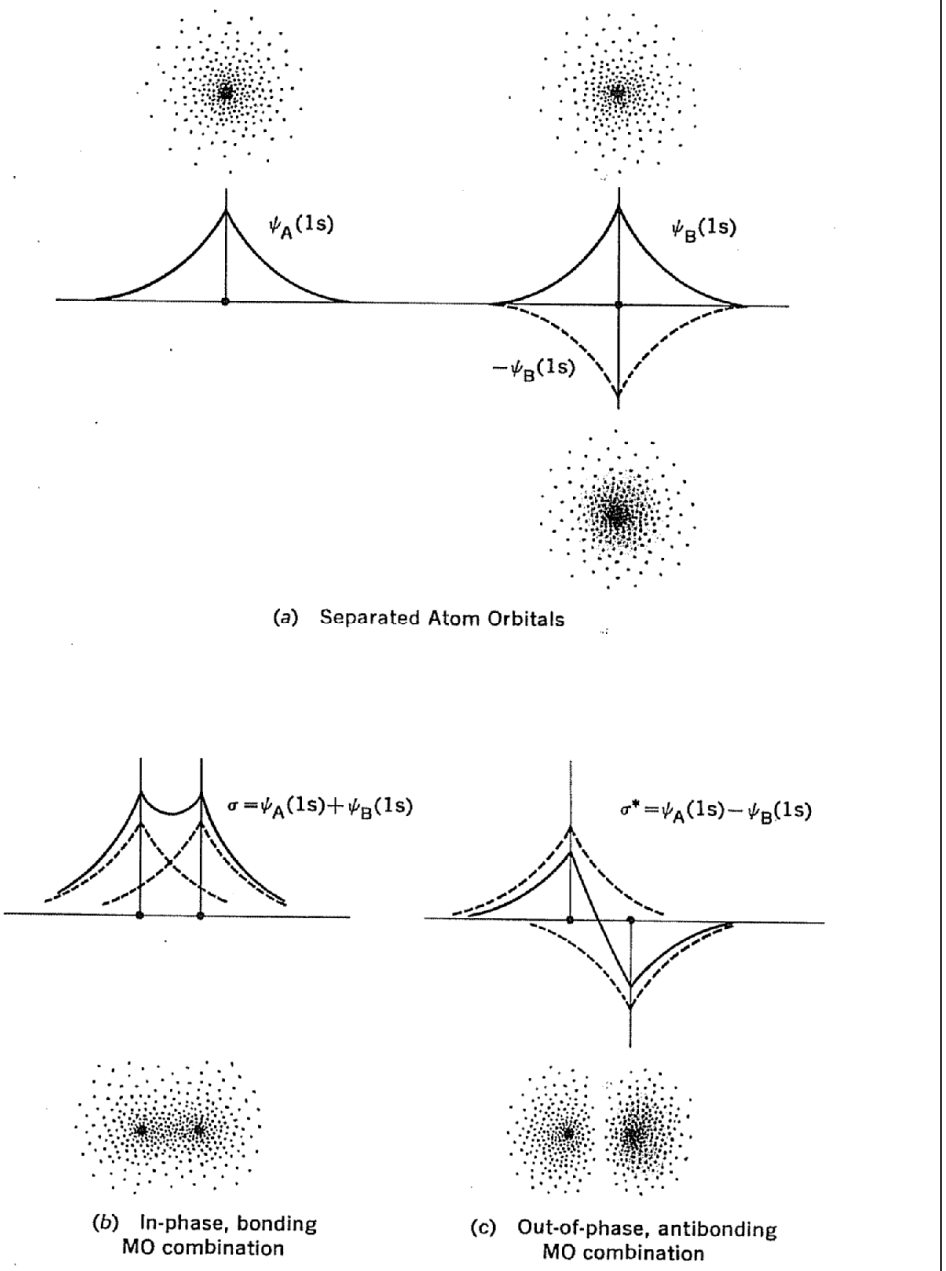


Fig. 3.3: Approximate molecular orbitals in H_2

The descriptions bonding and antibonding can be related to the particles involved – in this case the electrons. When there is increased amplitude of the wave, it implies the electrons are more likely to

occur in that region of space. We can relate this to the Lewis idea of sharing electrons between two atoms: they are concentrated between the two nuclei. Once again let us remember, we are not meaning that they are fixed in space there. We are only saying there is a greater likelihood of them being found there (see dot-density pattern in Fig. 3.3). In this region, as we saw by calculation, the attractions between electrons and nuclei are optimized. An energy lower than that of the separate atoms is achieved.

By contrast, when there is a decreased amplitude there is a decreased probability of the electrons being between the nuclei (at the node (zero amplitude) there is zero probability). Attractive forces are then less, and the repulsive forces between the 2 nuclei dominate. An energy higher than that of the separate atoms results.

These ideas and outcomes are sometimes presented diagrammatically in an energy correlation diagram. We show below the case of two H atoms and a hydrogen molecule.

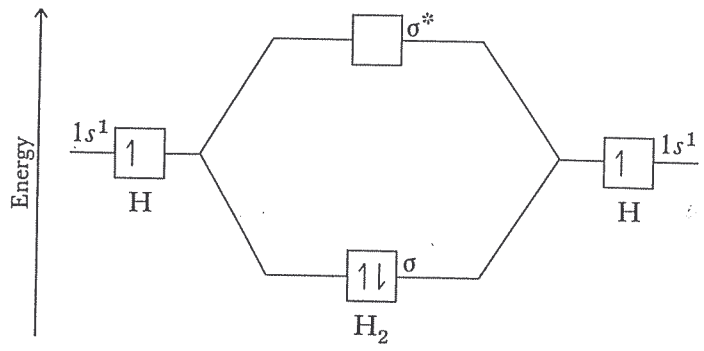


Fig. 3.4: Energy correlation diagram of the H_2 molecule

The energy lowering on molecule formation is evident in the lower energy of the 2 electrons in the BMO, as compared to their original energy in the AOs.

Q 3.1. Use an energy correlation diagram similar to that of H_2 to represent the interaction between two He atoms. Use the diagram to explain why a He_2 molecule does not exist.

3.6. Valency and the Rule of Two

Valency is an old concept that describes the combining capacity of atoms. For many years the phenomenon could not be explained. The concept can now be expressed as the number of bonds that an atom forms. From the cases of hydrogen and helium we can see how it can be explained. If an atom has one singly-occupied AO, this can overlap with a singly-occupied AO of another atom and form a bonding MO with a pair of electrons. The result is one bond and a valency of one. If there are more singly-occupied AOs, then more bonds can form and the valency is greater. For example, consider the nitrogen atom.

Q 3.2. Write the electron configuration of a nitrogen atom. Which electrons are core electrons and which are valence electrons? Write a Lewis diagram for the nitrogen atom: this means you write the symbol of the atom (N) and place around it dots representing the valence electrons (one dot equals one electron!)

Your answer should reveal that there are 5 valence electrons which are distributed over four AOs. Hence 3 valence electrons singly-occupy AOs, whilst one pair of valence electrons occupies another AO. The pair will behave like the pair in the He atom; the three single electrons will behave like the single electron in the H atom. Therefore the valency of the N atom will be 3. Two valence electrons will not be involved in these bonds.

From the foregoing analysis we can explain the trivalency of N atoms and hence account for the well-known ammonia molecule, NH_3. We can also account for the existence of a triple bond between the two N atoms in the nitrogen molecule, N_2.

Q 3.3. Draw Lewis diagrams to represent an ammonia molecule and a nitrogen molecule. Use the RADMASTE Molecular Modeling Kit to make a model of each molecule.

The pairs of valence electrons not involved in bonding which are shown in the Lewis diagrams, are called lone pairs of electrons, or non-bonded pairs of electrons.

Q 3.4. Account for the fact that the oxygen atom has a valency of two.

The example of the oxygen atom warns us that having more valence electrons does not necessarily mean a capacity to form more bonds, ie a greater valency. We have to say valence electrons when we refer to that and not say valency, as a kind of shorthand: they are not the same thing. Valency of an atom is determined by how many singly-occupied AOs it can offer.

This last statement, although true, also needs to be studied carefully, as the example of the carbon atom illustrates.

Q 3.5. Write the electron configuration of a carbon atom. Predict and explain the valency of a carbon atom.

You will probably know very well that the carbon atom is always tetravalent. Yet when we look at the electron configuration for this atom, we might expect a valency of two. However the doubly-occupied 2s AO differs little in energy from a 2p AO and the atom behaves as if it had 4 singly-occupied AOs. This behaviour is common amongst different atoms. Hence we conclude that the valency of an atom is limited by (a) the number of valence electrons, and/or by (b) the number of valence AOs.

It is for this reason also that some atoms exhibit variable valency. Consider for example sulfur atoms, whose valency is commonly found to be either 2, 4 or 6. If we count only the minimum number of singly-occupied AOs, then we shall agree that the valency should be two (as we found for the oxygen atom previously).

Q 3.6. Write the electron configuration of a sulfur atom. Show why this leads to a prediction of divalency for this atom. Draw a Lewis diagram of a molecule of hydrogen sulfide, H_2S. Identify any lone pairs of electrons in the diagram.

If one of the doubly-occupied valence AOs is made singly-occupied, and the extra electron transferred to an unoccupied 3d AO, then we have four singly-occupied AOs for the S atom, and a valency of 4.

Q 3.7. Write the names and formulae of two sulfur compounds in which S atoms show a valency of four. Draw Lewis diagrams for these molecules.

Q 3.8. If both the doubly-occupied AOs of a sulfur atom are made singly-occupied and the extra electrons transferred to other vacant valence AOs, how many singly-occupied valence AOs will the sulfur atom have? What is the maximum valency of a S atom? Give two examples of molecules in which the sulfur atom exhibits this valency and draw Lewis diagrams to represent them.

3.7. Equal and Unequal Sharing: Bond Polarity

The central idea of chemical bonding between two atoms is that it originates in the sharing of a pair of electrons. Sharing does not however necessarily mean equal sharing. When the two atoms that bond are identical (as in H_2 for example) then the sharing must be equal. When there are two different atoms bonding, the sharing must be unequal. We have seen earlier that one of the ways in which atoms of different elements differ is in their first ionization energies. These measure the energy required to remove one electron from an atom. The greater the ionization energy, the greater the energy required. This implies a greater attraction of that nucleus for the electron. This would suggest that, in a competition with an atom of lower ionization energy, it would also attract shared electrons more strongly. This is found to be so. Atoms of higher ionization energy attract shared electrons more strongly than atoms of lower ionization energy.

Although we can use ionization energy data to guide us in this regard, another quantity is more commonly used. This is called the electronegativity. This is an atomic property which has no units. It is a relative number calculated in a complicated way that may involve bond energies, ionization energies and electron affinities. It is a relative measure of the attraction of one atom for shared electrons in a bond. Table 3.1 lists the electronegativities of selected atoms.

Table 3.1: Table of electronegativities for selected atoms

Name and symbol	Electronegativity
Hydrogen H	2,1
Lithium Li	1,0
Beryllium Be	1,5
Boron B	2,0
Carbon C	2,5
Nitrogen N	3,0
Oxygen O	3,5
Fluorine F	4,0
Sodium Na	0,9
Magnesium Mg	1,2
Aluminium Al	1,5
Silicon Si	1,8
Phosphorus P	2,1
Sulphur S	2,5
Chlorine Cl	3,0
Potassium K	0,8
Calcium Ca	1,0
Titanium Ti	1,5
Chromium Cr	1,6
Manganese Mn	1,5
Iron Fe	1,8
Copper Cu	1,9
Zinc Zn	1,6
Gallium Ga	1,6
Germanium Ge	1,8
Arsenic As	2,0
Selenium Se	2,4
Bromine Br	2,8
Tin Sn	1,8
Iodine I	2,5
Mercury Hg	1,9

Q 3.9. Use the tabulated data (Table 3.1) together with a Periodic Table, to make general statements about trends in electronegativity in relation to the location of elements in the Periodic Table.

When electrons are shared unequally, the bond is polar. This arises because the shared electrons are concentrated nearer to the more electronegative atom. In turn, this means that at that end of the molecule the sum of the negative charges of the electrons exceeds the positive nuclear charge of that atom. Overall there is a partial negative charge in this region of the molecule. Simultaneously, of course, there is a deficiency of electrons at the opposite end of the molecule, ie, a partial positive charge.

In Lewis diagrams it has been suggested that this phenomenon can be represented by placing the dots of the shared electron pair nearer to the symbol of the more electronegative atom, as for example:

versus

H:H

This is not always clear, and it is probably better to employ more explicit indicators of polarity such as:

The symbols δ^+ and δ^- imply nett partial charges in the designated region of the molecule. They do not mean that the molecule has a nett charge: only that the charge distribution is unsymmetrical in a particular bond.

Q 3.10. Draw Lewis diagrams for the following molecules and show any bond polarity by using the δ +/- symbolism:

HBr , NaH, NH_3, CH_4,

Bond polarity is an important molecular property. It influences

(i) the reactivity of a molecule,

(ii) the ability of the molecule to absorb electromagnetic radiation,

(iii) the forces exerted by the molecule on neighbouring molecules (intermolecular forces).

We shall refer again to some of these in later sections.

3.8. Bond Length and Strength

We have learned that bonds between atoms are more than just a line or a couple of dots between element symbols on a piece of paper. They have characteristics that vary from molecule to molecule. Polarity is one such property, which we have just discussed. Another very important one is bond strength, which is related to bond length and also to frequency of vibration of the bond.

3.8.1. Bond strength

The concept of bond energy is often met in discussions of energy changes in chemical reactions. Bond strength is usually measured by the energy required to break the bond. The concept is simple in diatomic molecules. For example, the energy required to break the H-H bond in a hydrogen molecule is 0,717 aJ. This is the energy change in the reaction:

$$H_2 = 2H$$

Of course, it is numerically the same as the energy released when the molecule forms from the atoms:

$$2\,H = H_2$$

Forming a bond is an exothermic reaction (ΔH negative), but the magnitude is the same as that of the bond breaking.

The term "bond energy" unfortunately tends to reinforce a misconception that it is somehow a quantity of energy "stored in the bond". Sometimes the description "high energy bond" is used together with the general idea of energy storage (as for example in biology and the role of ATP). Fuels are said to store energy, which is released on combustion – again suggesting that there is energy in the bonds. Nothing could be further from the truth: bonds form with a decrease in energy of the atoms involved. Bonds represent low energy, not high energy, situations.

Nevertheless, chemical bonds are not all the same. Some bonds are stronger than others and the stronger they are, the lower the energy of the molecule they appear in.

When we compare bond strengths, we can look out for trends. The data in Table 3.2, open the way to such possibilities.

Table 3.2: Table of bond energies (in aJ) and bond lengths (pm) for selected bonds

Bond	Bond energy/aJ	Bond length/pm
H-H	0,717	75
H-F	0,938	92
H-Cl	0,716	127
H-Br	0,604	141
H-I	0,493	161
F-F	0,236	142
Cl-Cl	0,397	199
Br-Br	0,316	229
I-I	0,247	266
O-O	0,229	148
O=O	0,820	121
N-N	0,264	159
N=N	0,694	125
N≡N	1,562	110
C-C	0,578	154
C=C	1,028	134
C≡C	1,348	120
O-H	0,769	96
N-H	0,646	101
C-H	0,686	109
C-O	0,556	143
C=O	1,174	123
C-N	0,487	147
C=N	1,023	138
C≡N	1,460	116
O-Cl	0,340	149
N-Cl	0,334	197

Table 3.2 should really be studied in relation to a table of atomic radii (see Chapter 2), because one of the observable trends is that the smaller the atoms the stronger the bond.

Q 3.11. Study the table of bond energies (Table 3.2) and quote examples of the trend relating them with atomic radii.

The underlying reason for this trend can be found easily. Small atoms have large ionization energies: the nuclei attract electrons close to them strongly. This carries over to the shared electrons of bonds. The attractive forces are stronger at short range. We see the same effect in electronegativity trends: small atoms tend to have a high electronegativity.

It is easier still to see in the data evidence that single bonds are weaker than multiple bonds (double or triple bonds). This trend has to be. However, it should be noted that a double bond may or may not be twice as strong as the corresponding single bond.

Q3.12. Quote evidence to support the above claim, that multiple bonds may or may not be twice or three times as strong as single bonds. Quote examples where they are relatively less strong and examples where they are relatively more strong.

In polyatomic molecules we find bond energies of specific types of bonds are fairly constant, but not necessarily exactly so. Hence tables of bond energies sometimes state "average bond energies". There are a few exceptional cases where discrepancies are unusually large, and sometimes these are noted in tables of bond energies. An example of this is the C=O bond energy in CO_2 as compared to the C=O bond energy in other molecules. It is significantly stronger in the CO_2 molecule.

3.8.2. Bond length

The length of a chemical bond is defined as the distance between the nuclei of the bonded atoms. This is sometimes described as the internuclear distance. This is related to bond strength, such that short bonds are strong bonds and long bonds are weak bonds.

We have already noted that atomic size (radius) is an important factor in determining bond strength. So it is not surprising that this comes to the fore again in the bond length. Small atoms are naturally expected to result in short bonds, and so on. These can be seen from the examples in the table below.

Table 3.3: Table of atomic radii and bond lengths in pm

Bond	Bond length/pm	Atomic radii/pm
H-H	75	120 + 120
F-F	142	140 + 140
Cl-Cl	199	180 + 180
O-O	148	145 + 145
H-O	96	120 + 145
H-F	92	120 + 140
H-Cl	127	120 + 180

Table 3.3 shows that when two atoms bond there is indeed a strong force pulling them together. The bond length is substantially less than the sum of the radii of the unbonded atoms.

Q 3.13. Given that the radius of an iodine atom is 220 pm, predict what the I-I bond length in an I_2 molecule is. Give reasons for your prediction.

3.8.3. Bond vibration frequencies

The bonds between atoms are not rigid. So when we refer to a bond length, we refer to an equilibrium internuclear distance. In the molecule, the two atoms joined by a bond, continuously move relative to each other. This is often modeled by reference to two balls joined by a spring (Fig. 3.5). The two balls are visualized as moving in and out as the spring compresses and extends.

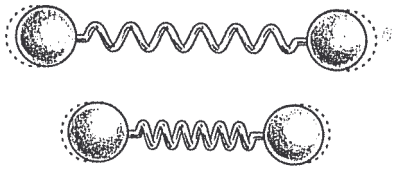


Fig. 3.5: Two balls joined by spring

The stiffness of the spring relates to the frequency of vibration in a spring. The stiffer the spring, the greater the force needed to extend it, which therefore is related to the vibration frequency. Similarly with chemical bonds, the vibration frequency is related to the bond strength. Strong bonds have high vibration frequencies. A few examples appear in the table below.

Table 3.4: Table of Selected Bond Vibration Frequencies

Bond	Vibration frequency/MHz (average)
C-H	8 700
O-H	10 800
C-C	3 000
C=C	4 950
C ≡ C	6 600
C=O	5 040
C ≡ N	6 750

The vibration frequencies listed in Table 3.4 are comparable to the frequency of infrared (IR) radiation. The consequence of this is that molecules may be able to absorb (and emit) IR radiation. The frequency must be correct for this to happen as we found before with atomic spectra and electronic energy changes. However, in addition we find that only if the bond is polar, is the

vibration able to interact with IR radiation. A vibration in a non-polar bond cannot absorb IR radiation. Thus the oxygen and nitrogen molecules in the atmosphere do not absorb IR radiation coming in from the Sun or being emitted from the Earth. By contrast carbon dioxide molecules, water molecules, and a number of pollutant molecules in the atmosphere, do. The result today is the phenomenon of global warming and climate change, because the concentrations of these so-called greenhouse gases in the atmosphere are increasing, due to increasing human activity.

The IR absorption spectra of molecules may be used to identify them; they are said to be the fingerprints of the molecules.

3.9. Bond Angles: the 3-D Shapes of Molecules

In previous sections we have described the bonding in some simple molecules – mostly ones with just a small number of atoms. We have drawn Lewis diagrams on paper and made models of some molecules. How did you decide upon the shape of the models? Did you make them all 2-dimensional like the Lewis diagrams on paper? Or did you give them some 3-dimensionality?

Molecules are fundamentally 3-D particles, and with polyatomic molecules their 3-D shape is an important property. Scientists have found out the shape of many simple molecules and developed ways of predicting these. An important predictive tool is the Valence Shell Electron Pair Repulsion Theory (VSEPR Theory), which can be used as a natural extension to Lewis diagrams.

As we have seen, most molecules have both shared and lone pairs of electrons, and these are both shown in Lewis diagrams. The VSEPR Theory proposes that the pairs of valence electrons around a particular atom in a molecule repel one another. They locate themselves around the atom such that this repulsion is minimized. This minimizes the potential energy. The crucial thing to take into account is that they do this in three dimensions – not just two.

To understand and to visualize this, the molecular models are very useful. So although we shall draw diagrams in this coursebook as well as we can to help you visualize the 3-D molecular shapes, you will probably need and enjoy the making of your own models.

As you probably know, the water molecule is angular (V-shaped), not linear. This is not what intuition would suggest to most people. Since there are two O-H bonds one's natural expectation is that a symmetrical arrangement of these will be found, ie linear. The V shape is proposed to be the result of valence shell electron pair repulsion around the central O atom. There are 4 pairs of electrons around the O atom, and two of these are bonded and two are not. The maximum distance between these 4 pairs is achieved if they are arranged tetrahedrally. Fig. 3.6 attempts to show this, and at the same time shows the bond angle, H-O-H.

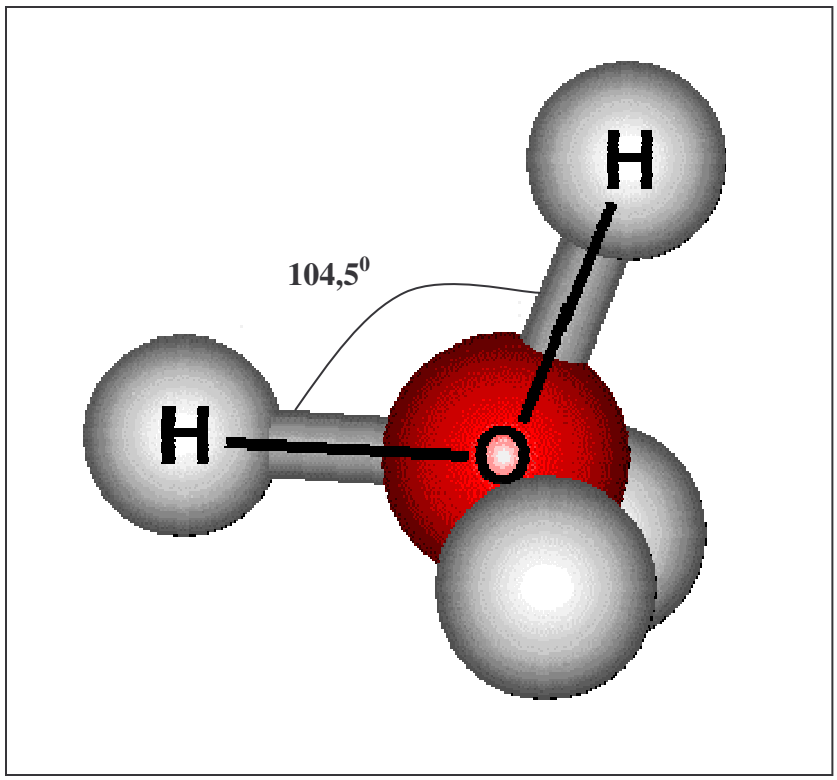


Fig. 3.6: the angular arrangement of a water molecule

Q 3.14. Make a model of a water molecule in accordance with the picture (Fig. 3.6). Have you maximized the distances between the valence shell electron pairs? What is the angle between the bonded pairs?

The descriptive name "tetrahedral" originates from the name of a solid, regular, geometrical figure called a tetrahedron. The appearance of this is shown in Fig. 3.7, and it also shows the tetrahedral arrangement of electron pairs around a central atom inside the tetrahedron.

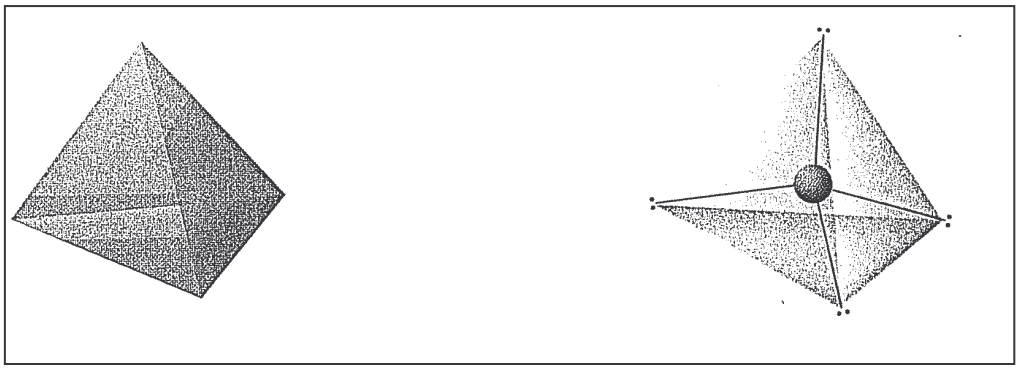


Fig. 3.7: A tetrahedron shape and its relationship with the tetrahedral arrangement of pairs of electrons around an atom

Q 3.15. A similar 3-D spatial arrangement is found in the ammonia (NH_3) and methane (CH_4) molecules. Make models of each of these molecules, using the same VSEPR principles. Each of them has 4 electron pairs around a central atom, with some bonded and some non-bonded, depending on the molecule. Make drawings to show what you have made.

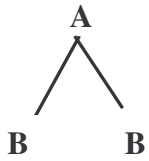
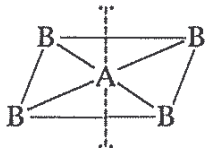
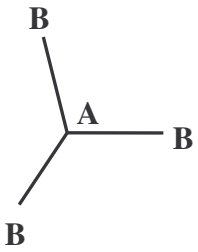
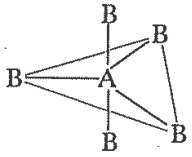
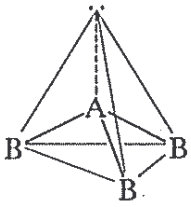
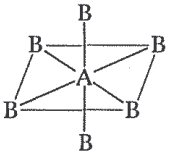
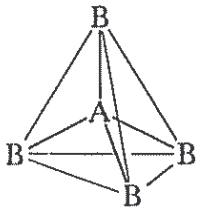
The bond angles in these molecules are 107^o and $109,5^o$, respectively. Amongst these three molecules (water, ammonia, methane) then, the bond angles are similar, but not identical. We often refer to them as if they were the same, because the difference is not usually important. We can account for the small difference by suggesting that a non-bonded pair (lone pair) of electrons occupies more space than a bonded pair of electrons. This is reasonable since the bonded pair will be drawn into the region between two nuclei. When all the electron pairs are bonded then the arrangement is completely symmetrical – the bond angles are all $109,5^o$. When there is one lone pair and three bonded pairs, the lone pair squeezes the other three a little bit closer together, giving the 107^o observed in the ammonia molecule.

Q 3.16. Account for the fact that in the water molecule the bond angle is $104,5^o$.

When discussing molecular shape and VSEPR Theory it is important to make a distinction between the 3-D shape of the molecule and the 3-D spatial arrangement of the electron pairs. In all three of the previous examples, the spatial arrangement of the electron pairs would be described as tetrahedral (even though the angles between them may not be exactly $109,5^o$). However, the molecular shape is described as tetrahedral only in the case of the methane molecule. In this molecule, there are only bonded electron pairs, and so each of these pairs is located between the central C atom and an H atom. The spatial arrangement of the electron pairs coincides completely with that of the atoms. But the shape of the water molecule is not tetrahedral: it is angular (V-shaped) because that describes the atomic arrangement. Similarly the ammonia molecule is not tetrahedral: its shape is called trigonal pyramidal.

Table 3.5 shows the molecular shapes called angular, trigonal planar, trigonal pyramidal, tetrahedral, square planar, trigonal bipyramidal, and octahedral.

Table 3.5: Various molecular shapes

Name	Shape	Name	Shape
Angular		**Square planar**	
Trigonal planar		**Trigonal bipyramidal**	
Trigonal pyramidal		**Octahedral**	
Tetrahedral			

Q 3.17. Draw Lewis diagrams for each of the following molecules and use VSEPR Theory to predict and name their shape. Make models of each one to represent your Lewis diagram and prediction . CO_2, BF_3, SF_6, PCl_5 .

Is the 3-D shape of molecules just a matter of idle curiosity? Not at all! As we shall see more extensively later, the shapes of molecules have some remarkable consequences. The angular shape of the water molecule, for example, contributes to the well-known unique properties of liquid and solid water. The fact that the solid water (ice) has a lower density than the liquid water is almost unique ("all" solids are more dense than the corresponding liquid). Another important example is the

special, remarkable properties of many biologically-important molecules, which depend critically on their 3-D shape.

3.10. Revisiting the Rule of Two

Right from the start of this chapter we have been talking about forming pairs of electrons and all the consequences of this. We saw that the origin of this rule of two is that an orbital can accommodate only two electrons. The rule first came to our attention in Chapter 2 when discussing electrons in atoms; but we have seen in this Chapter (3) that it applies equally to electrons in molecules. We now revisit this rule, not to change it but to make the obvious point that there is more than one way we can get two! After all whilst it is true that 1 + 1 = 2, it is also true that 2 + 0 = 2!

What this means for chemical bonding is that we can form a bond between two atoms when one atom has a pair of valence electrons and the other has none. The implication of this is that some molecules after they have been formed, are still ready for more bonding! If they have a lone pair then they are looking for an atom or molecule with a vacant valence orbital. If they have a vacant valence orbital then they are looking for an atom or molecule with a lone pair of electrons.

Q 3.18. The description in this last paragraph above is written in language suggesting molecules have motives. Of course they do not! Re-state the situation described in suitable scientific language. (Hint: Refer to energy)

If you look back at Lewis diagrams you have already drawn, you will find examples of molecules with a lone pair of electrons or with a vacant orbital. The lone pairs are explicitly shown in Lewis diagrams, so they are easy to spot. The vacant orbitals are not explicitly shown and you have to deduce where they are. You have to think about the number of valence orbitals an atom in a molecule has.

Q 3.19. Draw Lewis diagrams for the following molecules and in each case identify where there are any lone pairs and vacant orbitals.

H_2O , BF_3 , NaCl , CH_4

These example cases of molecules are typical, and they illustrate the point that the majority of molecules have either a lone pair or a vacant orbital, or both. The exception in the above examples is

the molecule of methane. The methane molecule is the simplest hydrocarbon molecule, but there are thousands of different ones known. These molecules are almost unique in having neither lone pairs nor vacant orbitals, and this is part of the reason for their multiplicity.

We can illustrate the consequences of these lone pairs and vacant orbitals on molecules by reference to the bonding between two of the molecules mentioned in Q 3.19: H_2O and BF_3.

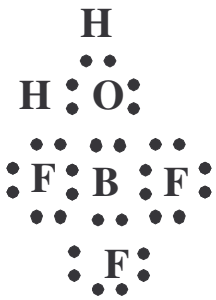


Fig. 3.8: Bonding of H_2O and BF_3

When a bond forms in this way the one atom behaves as a donor and the other as an acceptor of electrons. The bond is therefore polar, with the donor atom being the positive end and the acceptor atom the negative end of the bond. The electrons nevertheless remain a shared pair and there is no reduction-oxidation involved. As with previous examples of polar bonds it may sometimes be desirable to show this polarity with δ +/- signs, but there is no rule that requires it. A bond formed in this way is sometimes referred to as a donor-acceptor bond or a co-ordinate bond. In all essential respects it is no different from the bonds we previously described. Lewis proposed that the molecule which donates the share in a pair of electrons should be called a base, whilst the molecule which accepts the share in a pair of electrons should be called an acid. The combination of the two would then be an acid-base reaction. This proposal has been adopted but scientists distinguish this definition from other definitions of acids and bases, by calling these Lewis acids and Lewis bases.

Q 3.20. Water is a special solvent in many respects. One of these is the formation of ions in aqueous solution when some substances dissolve in it. Draw a Lewis diagram to show a hydrated sodium ion which one finds in aqueous solutions of sodium salts. There are normally

four water molecules bonded to a single sodium ion. Explain how this exemplifies the interaction of a Lewis acid with a Lewis base. Make a model of the molecule $Na(H_2O)_4^+$.

The existence of lone pairs and/or vacant orbitals in the majority of molecules means that the donor-acceptor bonding that we have described must be quite widespread. Indeed it is and it is of great importance for understanding the mechanism of chemical reactions. When different reactant molecules are mixed, there is often an initial interaction between them of the donor-acceptor type. This may then be followed by other bonding changes that result in new product molecules. Catalysts may also act through this kind of bonding between the catalyst molecule and a reactant molecule.

3.11. Bonding in Polyatomic Molecules

We have described the bonding in several examples of molecules, ending up in the last section with some quite large ones. Our approach has assumed that we can describe the bonds between atoms in a molecule as separate things, unaffected by other bonds in the same molecule. This view of chemical bonding is very successful and is the view taken by most scientists, most of the time. Because it works! This approach to describing chemical bonds is called a localized bonding one. Bonds are viewed as localized between pairs of atoms, largely unaffected by other bonds. We shall leave it at that for this Chapter, but we give notice that it does not always work. This is a pity for those who would like to have a simple explanation for everything, but it offers exciting possibilities once we know why it fails in certain circumstances. Because we then find that we can understand the colour and the function of chlorophyll and graphite, the electrical conductivity shown by some solids, and much more. And when we understand it, we can exploit it for our benefit. No pain, no gain!

3.12. Some Popular Misconceptions About Chemical Bonding

The topic of chemical bonding has been in secondary school syllabi for many years and this has given rise to attempts to simplify an apparently difficult topic. Some of these are quite wrong and should not be continued. We give attention to two of these here.

3.12.1. The "octet rule"

It has been suggested that Lewis proposed an octet rule to explain why atoms bond. He did not in fact do so, although some later authors did. The "rule" has limited applicability (more or less covering the elements of the Li-Ne period only) and deflects one from any genuine understanding.

The rule is often put forward in the form that atoms strive to achieve an octet of electrons in the outermost shell. This eight electrons is proposed as a "magic number" associated with "special stability". There is no basic truth in it at all, even if some atoms behave in apparent conformity with the rule. The fact is that there are electrostatic attractive forces between atoms (due to the charged sub-atomic particles) and this is the origin of bonding – not achieving an octet. As we have seen there are rules however, which limit how many bonds an atom can form. The number of bonds is limited by the number of valence electrons it has and by the capacity it has to accommodate more electrons. For elements of the Li-Ne period, this leads to an apparent octet rule conformity. Even then, a molecule like BF_3, formed by a B atom (which is in the Li-Ne period) clearly does not obey the octet rule.

Q 3.21. Name three example molecules (other than BF_3) where you think the octet rule is not obeyed. Draw their Lewis structures to illustrate your case.

As we have said, there is a rule of two: this rule concerns the number of electrons per orbital. This rule applies to both atoms and molecules.

3.12.2. Ionic and Covalent Bonds

Early attempts to explain chemical bonding suggested that electrons might be transferred between atoms. The atoms would then be charged and attract each other, ie bond. Thus bonding of two atoms was actually bonding between two ions. This proposal could not really explain why two identical atoms would bond, because, for example, why would one hydrogen atom give an electron to another hydrogen atom? Eventually it was accepted that there must be another way of bonding, called covalent bonding, where electrons are shared. The sharing of electrons as the mechanism of bonding is what we have presented in this Chapter. Lewis proposed this and at the same time said sharing could be unequal. This would then account for polar bonds which before had been seen as ionic bonds. Lewis argued that there is only one type of bonding and there is no separate and different ionic bonding. However it seems to have been difficult for some authors to abandon the old ionic idea. The description "ionic" may be used if all you wish to say is that the sharing of electrons is very unequal in a particular case. Such very unequal sharing would create a molecule with an electron distribution somewhat like that of two ions stuck together. But if you use the term ionic bonding to mean there is something different from other chemical bonding then you are

misconceiving the position. To introduce the topic of chemical bonding with “there are two types of chemical bonds ionic and covalent… ” is to perpetuate a view that should have been abandoned 80 years ago!

3.13. Intermolecular forces

Chemical bonding refers to intramolecular forces. These forces within the molecule are strong and hold the molecule together. In chemical changes (reactions) it is these intramolecular forces that have to be reckoned with. But whatever is the situation inside the molecule, there is always an outside also: a molecular surface which other molecules “see” and “feel”. It is like the human body: inside is a big collection of pieces held together strongly, that give us our characteristics. But we have an outside also; a surface that our neighbours see and feel.

Molecules of course are not living and do not have a skin. Neighbouring molecules experience them through the forces, called intermolecular forces. Like intramolecular forces, these are also electrical, but they are weaker. The nuclei of one molecule attract the electrons of a neighbouring molecule, and vice versa. There are repulsions as well: nuclei repel nuclei and electrons repel electrons. But, provided we do not force them together or squeeze them hard, the nett force is attractive.

It is common practice to define different categories of intermolecular force. For example there is dipole-dipole, dipole-induced dipole, induced dipole-induced dipole. But this tends to confuse rather than help, unless you have particular quantitative interest in intermolecular forces. All of the ones we have mentioned are just variations of the general intermolecular force description we gave before. There is one distinctive and different intermolecular force and that is the hydrogen bond, to which we shall return shortly.

3.13.1. Molecular size and shape

We can add some remarks about factors affecting the magnitude of intermolecular forces. Firstly the total number of nuclei and electrons has an effect: the more nuclei (and the greater their charge) and electrons in the molecule, the larger the total intermolecular forces. There is an important difference here from chemical bonding, which is largely a force localized between two atoms. Intermolecular forces are summed over the entire molecule; they are not localized but all over the molecule. The more atoms per molecule, the greater the intermolecular forces.

Q 3.22. Octane, C_8H_{18}, is a liquid that boils at about 80^0C, whereas butane, C_4H_{10}, is a gas (the liquid boils at 0^0C) at normal pressure (1 atm). Explain the difference in physical state and the difference in boiling temperatures of the two liquids.

The data quoted in the above question are often misinterpreted as evidence that it is the mass difference that counts. Referring to mass suggests that gravitational forces are involved, because the magnitude of these depends on mass. This is incorrect. The forces between molecules are primarily electrostatic, although because the molecules have mass there must be a small gravitational force also.

Whilst the total number of electrons and nuclei is the major factor, the shape of the molecule also has an effect. Once again, organic chemistry provides good examples of this. We have quoted above the boiling temperature of butane; the substance isobutane (2-methylpropane) also has the molecular formula C_4H_{10}, but its molecular structure is different:

Butane : $CH_3CH_2CH_2CH_3$ (bp 0^0C)
Isobutane: $CH_3CH(CH_3)CH_3$ (bp -10^0C)

Why should the two substances have different boiling points when the composition of the molecules is the same? The answer would seem to be that the isobutane molecule has a smaller surface area than the butane molecule. For this reason the intermolecular forces between isobutane molecules are smaller than those between butane molecules.

Q 3.23. Make models of a molecule of butane and a molecule of isobutane. Do you agree that they differ in surface area? Think of a way to compare their surface areas. Explain in your own words how this difference would affect the intermolecular forces.

The butane molecule is an example of a "straight-chain" hydrocarbon molecule. The isobutane molecule is an example of a "branched-chain" hydrocarbon molecule. There are thousands of different known hydrocarbons, and always we find the same trends as we saw with butane and isobutane. The larger the molecule, the higher the boiling point; the more branched the molecular chain, the lower the boiling point. These effects surely exist with other types of molecules also:

however, organic molecules are very convenient examples because there are so many different ones with just small differences between them.

3.13.2. Hydrogen bonding

Hydrogen bonding is the name given to a special category of intermolecular force. It is stronger than the general intermolecular force we have just discussed and some consider it as an interaction who's character is intermediate between intermolecular and intramolecular. The hydrogen atom is unique in that it has only one electron. When this electron is shared in a bond with another atom, the positive nucleus of the hydrogen atom may be exposed to other sources of electrons. The observation is that hydrogen bonding is significant when the H atom is joined to a very electronegative atom (such as F, O, N, Cl). Then it interacts with another atom with a lone pair of electrons (such as F, O, N and Cl again, but also with anions in general).

The water molecule is the uniquely spectacular case, because the two H atoms joined to the central O atom are both candidates for hydrogen bonding. At the same time, the O atom has the lone pairs that provide the other anchor point for the hydrogen bonds.

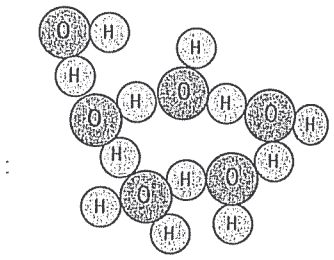


Fig. 3.9: H- bonding between neighboring water molecules

Almost all the strange but familiar properties of water can be related to its extensive hydrogen bonding capabilities (Fig. 3.9).

The water case is spectacular but the hydrogen bonding phenomenon is not limited to this case. Any molecule with an O-H bond in it is a candidate for the interaction.

Q 3.24. Ethanol, C_2H_5OH, is a liquid boiling at 78^0C, whereas propane, C_3H_8, is a gas at all temperatures above -42^0C, at the same pressure. Show that the sum of the positive charges (due to the nuclei) is the same in the two molecules and that the number of electrons is the

same in the two molecules. Explain why, despite these facts, the boiling points of the two liquids differ as they do.

The hydrogen bond is not as strong as a chemical bond (see data in section 3.8). It can be about 0,03 aJ. Nevertheless its effects may be very significant, as we shall see in later sections. Indeed it is no exaggeration to say that our lives depend upon it!