Fundamentals of Chemistry, Module II: Organic Chemistry

Semester-1, CCF-2022 (NEP)

Course: CHEM-H-CC-1-1-TH

Course taught by: Kaushik Basu, Department of Chemistry, SPCMC, Kolkata

email: chiralkaushik@gmail.com

Organic chemistry is often called "*the chemistry of life*" because certain types of compounds, and the reactions they undergo, are suitable to sustain life, while others are not. What are the characteristics of such compounds and what advantages do those compounds afford living organisms? Here in we begin to answer these questions.

Organic chemistry is the branch of chemistry involving *organic compounds*. What, then, is an organic compound?

In the late 1700s, scientists defined an organic compound as one that could be obtained from a living organism, whereas inorganic compounds encompassed everything else. It was believed that organic compounds could not be made in the laboratory; instead, only living systems could summon up a mysterious "*vital force*" needed to synthesize them. This belief was called vitalism (Berzelius, 1807). By this definition, many familiar compounds, such as glucose (a sugar), testosterone (a hormone), and deoxyribonucleic acid (DNA), are organic.


Jöns Jacob Berzelius
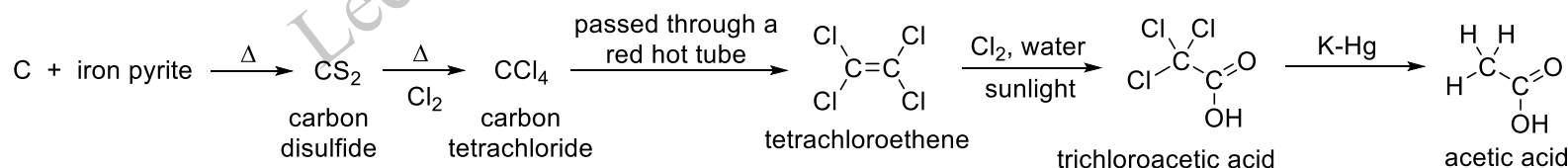(1779-1848)

Glucose

Testosterone
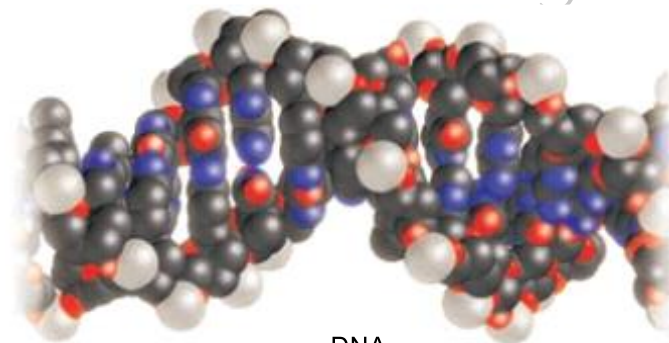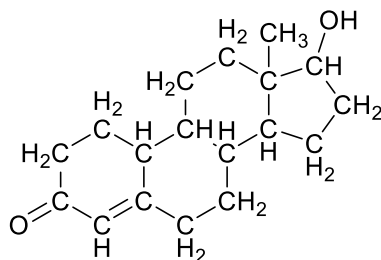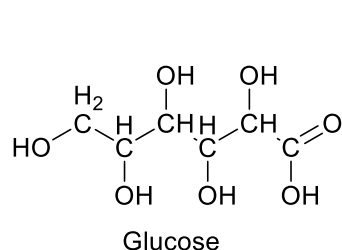
DNA

This definition of organic compounds faced a strong challenge in 1828, when Friedrich Wöhler, a German physician and chemist, and a student of Berzelius, synthesized urea (an organic compound known to be a major component of mammalian urine) by heating a solution of ammonium cyanate (an inorganic compound). The ammonium cyanate was prepared in a number of ways, e.g.

$Ag(OCN) + NH_4Cl \longrightarrow AgCl + NH_4OCN$

silver cyanate   ammonium chloride   silver chloride   ammonium cyanate

$H_4N^{\oplus}{}^{\ominus}O-C\equiv N \xrightarrow{\Delta}$

ammonium cyanate
- an inorganic compound

urea
- an organic compound
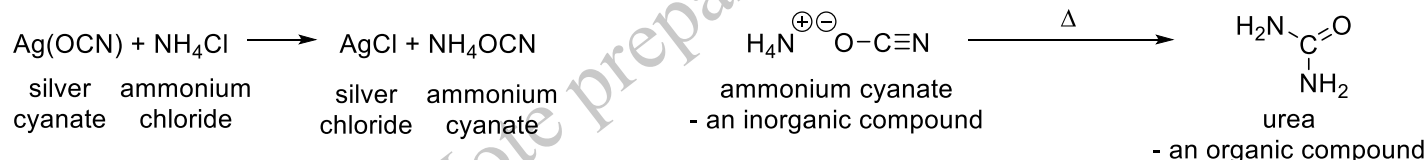
Friedrich Wöhler
(1800-1882)

On the formation of urea from ammonium cyanate, Wöhler himself wrote: "curious fact that presents an example of the artificial production of an organic, in fact a so-called animal substance from inorganic substances."

Vitalism was dealt a fatal blow in 1845, when Hermann Kolbe, another German chemist, synthesized acetic acid (vinegar, a well-known organic compound) by a series of reactions starting form inorganic precursors:

$C + \text{iron pyrite} \xrightarrow{\Delta} CS_2 \xrightarrow[Cl_2]{\Delta} CCl_4 \xrightarrow{\text{passed through a red hot tube}}$ tetrachloroethene $\xrightarrow[\text{sunlight}]{Cl_2, \text{water}}$ trichloroacetic acid $\xrightarrow{K-Hg}$ acetic acid

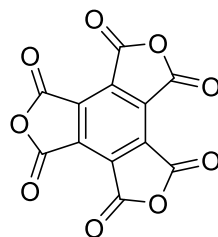carbon disulfide   carbon tetrachloride

A. W. Hermann Kolbe
(1818-1884)

If vitalism couldn't account for the distinction between organic and inorganic compounds, what could? Gradually, chemists arrived at our modern definition:

"An organic compound contains a substantial amount of carbon and hydrogen."

This definition, however, is still imperfect, because it leaves considerable room for interpretation.

For example, many chemists would classify carbon dioxide (CO_2) as inorganic because it does not contain any hydrogen atoms, whereas others would argue that it is organic because it contains carbon and is critical in living systems. In plants, it is a starting material in photosynthesis, and in animals, it is a by-product of respiration. If, in the strict sense of the definition we exclude the oxides of carbon from the realm of organic compounds, what can we say about the following?

mellitic anhydride - $C_{12}O_9$ - no hydrogen!
Apparently isolated first by Wöhler and von Liebig in 1830

J. F. von Liebig
(1803-1873)

Similarly, tetrachloromethane (carbon tetrachloride, CCl_4) contains no hydrogen, but many would traditionally classify it as an organic compound.

Therefore, a single, all encompassing definition of organic compounds is still lacking. The one that we have outlined above certainly have ambiguities and exceptions, but this definition does allow chemists to classify most molecules. So we will work with this one for now. Let us revisit the definition of organic chemistry in light of this information: organic chemistry is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, including hydrogen (most compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, halogens, phosphorus, silicon, and sulfur.

Role and scope of organic chemistry:

Organic chemistry is a highly creative science in which chemists create new molecules and explore the properties of existing compounds. It is by far the most popular field of study for chemists.

Organic compounds form the basis of all earthly life and constitute the majority of known chemicals. The bonding patterns of carbon, with its valence of four - formal single, double, and triple bonds, plus structures with delocalized electrons - make the array of organic compounds *structurally diverse*, and their range of applications enormous. They form the basis of, or are constituents of, many commercial products including pharmaceuticals; petrochemicals and agrichemicals, and products made from them including lubricants, solvents; plastics; fuels and explosives. The study of organic chemistry not only overlaps with organometallic chemistry and biochemistry, but also with medicinal chemistry, polymer chemistry, and materials science. What began as a tentative attempt to understand the chemistry of life, has grown into the confident basis of worldwide activities that feed, clothe, and cure millions of people without their even being aware of the role of organic chemistry in their lives.

Why does the carbon atom play such a central role in the chemistry of life and what is so special about it?

Life needs a diverse set of chemicals with different functions. On Earth, the diverse set of chemicals are amino acids (to make proteins), sugars, and nitrogenous bases (to make nucleic acids), hydroxyl and keto acids (as core metabolic intermediates), lipids (to make membranes), and more. To build a diverse set of chemicals, life needs a set of elements capable of building molecules composed of many atoms that will provide sufficient biological functionality.

Sufficient chemical diversity needed to build a molecular repertoire suitable for life can only be achieved by a *scaffolding element* bonded with heteroatom elements. The scaffold atom is one that can join in chains and clusters to construct the skeleton or shape of a molecule, and the heteroatoms provide chemical activity in a molecule. Scaffolds provide the ability to make large molecules, and hence a large number of different molecules. The scaffold needs to be relatively stable and unreactive, while at the same time bonding to functional atoms (heteroatoms) that provide chemical functionality and distinctiveness to each molecule

On Earth, carbon forms the major scaffold element (hence the term "carbon-based life"). But, why?

First of all, the compounds possible when carbon is their chief structural component are incredibly diverse. The carbon atom can form four covalent bonds to other atoms - especially other carbon atoms - *catenation* - the ability to link up with same element, forming a chain structure.

Consequently, carbon atoms can link together in chains of almost any length and rings of various sizes, allowing for an enormous range in molecular size and shape.

Moreover, the ability to form four bonds means there is potential for *branching* at each carbon in the chain. And each carbon atom is capable of forming not only single bonds, but double and triple bonds as well. These characteristics make possible a tremendous number of compounds, even with a relatively small number of carbon atoms.
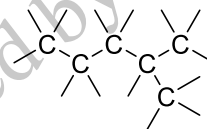
Indeed, to date, tens of millions of organic compounds are known, and the list is growing rapidly as we continue to discover or synthesize new compounds.
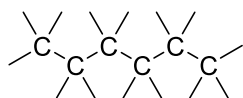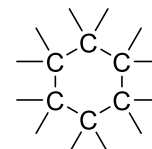

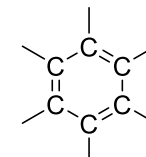a chain of carbon atoms with single bonds only
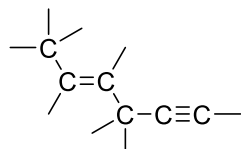
a chain of carbon atoms with single, double and triple bonds

a branched chain of carbon atoms

a cyclic array of of carbon atoms with single bonds

a cyclic array of of doubly bonded carbon atoms

Far less diversity would be possible in compounds based on another element, such as oxygen. Oxygen atoms tend to form two covalent bonds, which would allow for a linear chain only (as shown in the hypothetical example). *No branching* could occur, nor could other groups or atoms be attached to the chain except at the ends.

Furthermore, the O atoms along the chain *could not participate in either double or triple bonds*.
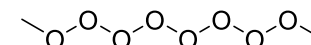
With a chain of oxygen atoms, no double bonds, triple bonds, or branching is possible.

What about N? Compare the number of stable molecules of the type X_nH_m that can be formed with X = N (three – NH_3, N_2H_4, N_2H_2) and with X = Carbon (an essentially infinite number of hydrocarbons).

Because the scaffolding of carbon (and hydrogen) alone provides only the very limited chemical function required for metabolism, heteroatoms are needed to provide chemical reactivity. Heteroatoms can form covalent bonds to carbon (or other scaffolding elements) but are more electropositive or electronegative. This difference in electronegativity provides the reactivity of molecules. Heteroatom reactivity is responsible for the great majority of the metabolic reactions occurring in Earth's organisms. Life on Earth uses several heteroatoms (e.g., O, N, S and P) that form covalent bonds with the carbon scaffold of biomolecules and with each other.

If carbon works so well, then why not silicon, which appears just below carbon in the periodic table? Elements in the same group (column) of the periodic table tend to exhibit similar chemical properties, so silicon, too, can form four covalent bonds, giving it the same potential for diversity as carbon. Also note that Si is *135 times more abundant* than carbon in our planet.

The answer is *stability*.

The carbon atom forms rather strong bonds with a variety of atoms, including other carbon atoms.

For example, it takes 339 kJ/mol (81 kcal/mol) to break an average C-C single bond, and 418 kJ/mol (100 kcal/mol) to break an average C-H bond.

By contrast, it takes only 223 kJ/mol (53 kcal/mol) to break a typical Si-Si bond. Chains of silicons break apart on contact with water and most life on earth is water-based!

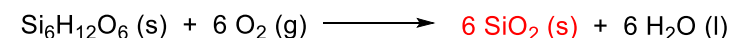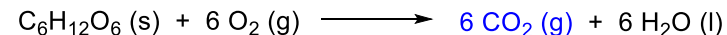OTOH, C-C bonds are unaffected by water.

The strength of typical bonds involving carbon atoms goes a long way toward keeping biomolecules intact - an essential characteristic for molecules whose job is to *store information or provide cellular structure*.

Silicon is more electropositive as compared to C, N, O, and H. The higher electropositivity of Si creates an electron-deficient center in silicon and results, e.g., in a stronger bond polarization as compared to analogous carbon bonds, or in a reversed bond polarization of the C–H and Si–H bonds. As a result of those differences, most bonds that silicon forms with non-metals are more strongly polarized than their carbon counterparts and thus more susceptible to electrophilic and nucleophilic attack.

Even bonds that are considered to be very stable, like Si-C, have higher reactivity as compared to their carbon analogues. For example, silicon tetrachloride (containing Si–Cl bonds) is hydrolyzed almost instantly in water, whereas carbon tetrachloride (containing analogous C–Cl bonds), which is also thermodynamically unstable to hydrolysis, is stable for years in the presence of water. Silanes (SiH_4, Si_2H_6 etc.) are stable as pure chemicals for many years but are very sensitive to water in the presence of trace alkali, unlike alkanes. Ethane (C_2H_6) may be mixed with oxygen at 200 °C without reacting, whereas disilane (Si_2H_6) spontaneously combusts in air at 0 °C.

Even though organic molecules are based on the carbon atom, what would life be like, hypothetically, if silicon atoms were to replace carbon atoms in biomolecules such as glucose ($C_6H_{12}O_6$)?

Glucose is broken down by our bodies through respiration to extract energy, according to the overall reaction shown. One of the byproducts is carbon dioxide, a gas, which is exhaled from the lungs. In a world in which life is based on silicon, glucose would be $Si_6H_{12}O_6$, and its by-product would be silicon dioxide (SiO_2), as shown in the relevant equation.

$$C_6H_{12}O_6 \text{ (s)} + 6\ O_2 \text{ (g)} \longrightarrow 6\ CO_2 \text{ (g)} + 6\ H_2O \text{ (l)}$$

$$Si_6H_{12}O_6 \text{ (s)} + 6\ O_2 \text{ (g)} \longrightarrow 6\ SiO_2 \text{ (s)} + 6\ H_2O \text{ (l)}$$

Silicon dioxide, a refractory solid, is the main component of sand; in its crystalline form, it is known as quartz. This solid mass will definitely pose a disposal problem for a living system!

The strength of a C–O bond (358 kJ/mol) is a little bit greater than of a C–C bond (339 kJ/mol), while the analogous Si–O bond (452 kJ/mol) is much stronger than the Si–Si bond (223 kJ/mol). As the Si–O bond is disproportionately stronger than any other Si-containing bond, the Si–Si catenated structures (e.g., in silanes) are much more reactive than their C–C counterparts (especially in water). Consequently, the most common stable polymers of silicon are built from Si–O chains, and Si chemistry in oxygen-rich environments (e.g., water) ultimately leads to silica (SiO_2).

Its greater bonding flexibility and strength, and its better adaptability to changing dry-wet conditions have made carbon best suited to act as the backbone of the long-chain molecules required for life.
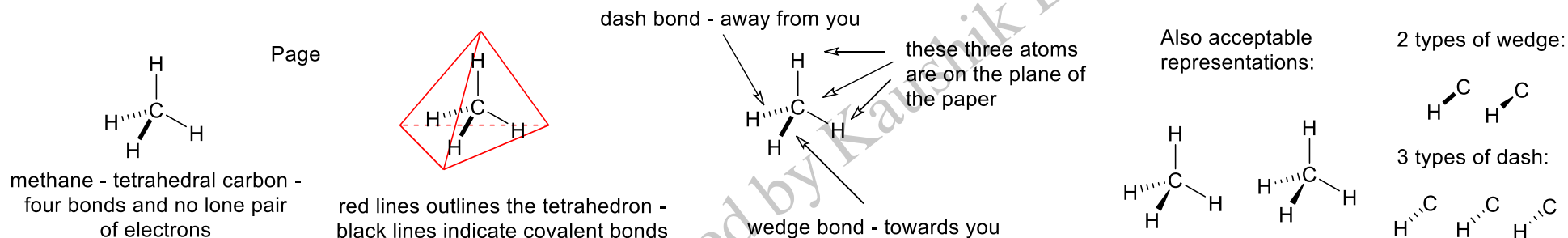
Molecules are not simply a jumble of atoms: they are atoms held together in a defined three-dimensional shape. A compound's properties are determined not only by the atoms it contains, but also by the spatial arrangement of these atoms. Graphite and diamond - the two other allotropes of carbon - are both composed only of carbon atoms and yet their properties, both chemical and physical, are completely different because those carbon atoms are arranged very differently. Graphite has carbon atoms arranged in sheets of hexagons; diamond has them arranged in a tetrahedral array.

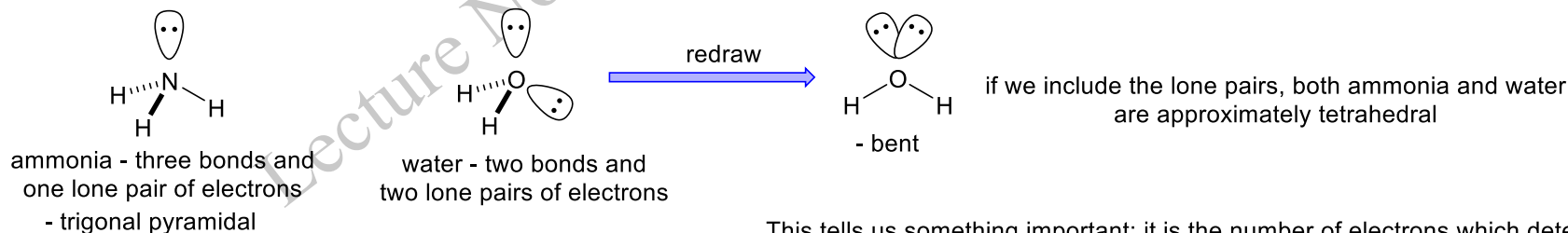Graphite Structure

Diamond Structure
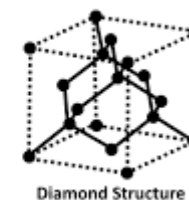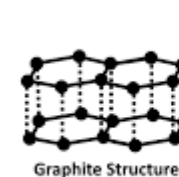
Now we need to tackle the question of why molecules have the shapes they do. What is it about the properties of their constituent atoms which dictates those shapes?

First of all, we need to consider why atoms form molecules at all. Some atoms (helium, for example) do so only with extreme reluctance, but the vast majority of atoms in the periodic table are much more stable in molecules than as free atoms. Here, for example, is methane: four hydrogen atoms arranged around a carbon in the shape of a tetrahedron.

Page

dash bond - away from you

these three atoms are on the plane of the paper

Also acceptable representations:

2 types of wedge:

methane - tetrahedral carbon - four bonds and no lone pair of electrons

red lines outlines the tetrahedron - black lines indicate covalent bonds

wedge bond - towards you

3 types of dash:

Molecules hold together because positively charged atomic nuclei are attracted to negatively charged electrons, and this fact allows electrons to act as 'glue' between the nuclei. The C and H nuclei of methane are of course positively charged, but the ten electrons (a total of six from C, four from the H atoms) bind those positive charges into a molecular structure.

Ammonia (NH_3) and water (H_2O) also have ten electrons in total, and we know that their molecular shapes are in fact just like that of methane, but with one or two hydrogen atoms removed.

redraw

if we include the lone pairs, both ammonia and water are approximately tetrahedral

ammonia - three bonds and one lone pair of electrons
- trigonal pyramidal

water - two bonds and two lone pairs of electrons

- bent

This tells us something important: it is the number of electrons which determines the shape of a molecule, and not just the number of atoms (or atomic nuclei). But what determines how electrons are arranged? Why do ten electrons give rise to a tetrahedron, for example?

Question: Why do ten electrons give rise to a tetrahedron?

Before we can answer this question, we need to simplify our discussion a bit and think about electrons not in molecules but in individual atoms. We can then approximate the electronic structure of molecules by considering how the component atoms combine. It is important to remember throughout this discussion, however, that molecules are only very rarely 'made' directly by joining atoms together. What we are going to present is an analysis of the structure of molecules, not a discussion of ways to build them.

Electrons have quantized energy levels:

The electron in an atom can only occupy energy levels with precisely determined values, in other words, the energy of an electron *orbiting* a proton (a hydrogen nucleus) is quantized. The electron can have only certain amounts of energy, and therefore the gaps between these energy levels (which give rise to the spectrum) likewise can only have certain well-defined values. Think of climbing a flight of stairs - you can jump up one, two, five, or even all the steps if you are energetic enough, but you cannot climb up half or two-thirds of a step. Likewise coming down, you can jump from one step to any other - lots of different combinations are possible but there is a finite number, depending on the number of steps.
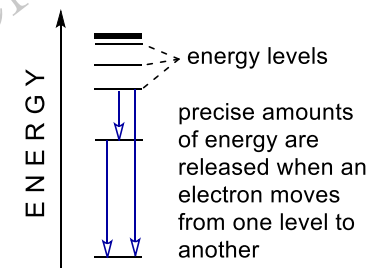
Why quantized energy levels?

To understand this, let us introduce a concept from nineteenth century physics - the experimentally observable fact that particles such as photons and electrons can also have the character of a wave as well as a particle. It's not obvious why the energy of a particle should be quantized, but it makes sense if you allow yourself to think of an electron as a wave.

Imagine a taut string - a piano wire or guitar string, for example - fixed at either end. You may well know that such a string has a fundamental frequency: if you make it vibrate by hitting or plucking it, it will vibrate in a way represented in the diagram on the right. This diagram shows a snapshot of the string; we could also represent a 'blurred' image of all the places you might find the string as it vibrates, such as you would get if you took a picture with a slow shutter speed.
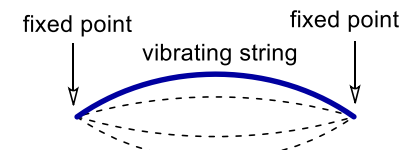
But this is not the only way the string can vibrate. An alternative possibility is shown on the right, where not only are the ends of the string stationary, but so is the point - known as a 'node' - right in the middle. The wavelength of the vibration in this string is half that of the one above, so the frequency is double. Musically this vibration will sound an octave higher and is known as the first harmonic of the first vibration we showed you, the fundamental. Third and fourth possibilities for 'allowed' vibrations are shown below, and again these correspond musically to further harmonics of the fundamental frequency.
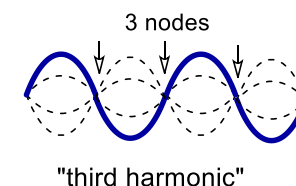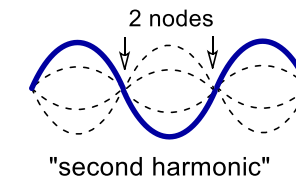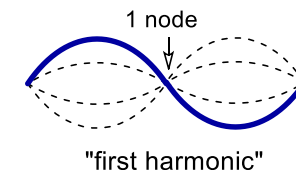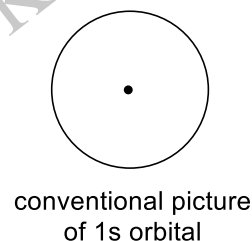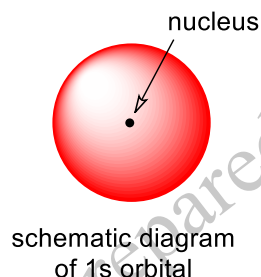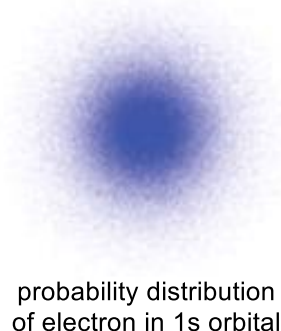
The vibrating string has no choice but to adopt one of these quantized frequencies - the frequency can take on only certain values because the fixed ends to the string means the wavelength has to be an exact divisor of the length of the string. Recall from your basic physics that frequencies are directly linked to energies: the energy levels of a vibrating string are thus quantized.

If you think of an electron as a wave, it becomes much easier to see why it can have only certain energy values. If you think of an electron orbiting a nucleus as a string looped back on itself, you can visualize from the diagrams on RHS why only certain wavelengths are possible. These wavelengths have associated frequencies and the frequencies have associated energies: we have a plausible explanation for the quantization of the energy of an electron.

energy levels

precise amounts of energy are released when an electron moves from one level to another

fixed point   fixed point

vibrating string

1 node

"first harmonic"

2 nodes

"second harmonic"

3 nodes

"third harmonic"
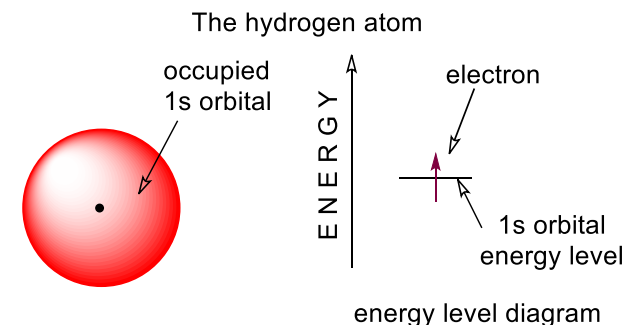
Electrons reside in atomic orbitals (AOs):

The popular image of an atom as a miniature solar system, with the electrons behaving like planets orbiting a star - the nucleus - works in some situations, but we are going to have to leave it behind. The problem with this view of the atoms is that electrons can never be precisely located, and instead must be thought of as 'smeared out' over the space available to them. The reason for this derives from Heisenberg's Uncertainty Principle, which tells us that we can never know exactly both the location and the momentum of any particle. If we know the energy of an electron (and with quantized energy levels we do), we know its momentum and therefore we cannot know exactly where it is.

As a consequence, we have to think of electrons in atoms (and in molecules) as having a probability of being in a certain place at a certain time, and the sum of all these probabilities gives a smeared out picture of the electron's habits, a bit like blurred pictures of the vibrating strings. Because an electron is free to move around an atom in three dimensions, not just two, the allowed 'vibrations' it can adopt are also three dimensional and are known as orbitals, or (because we are just considering electrons in a single atom for now) atomic orbitals. The shapes of these orbitals are determined by mathematical functions known as *wavefunctions*. The smeared out picture of the simple atomic orbital - the lowest energy state of an electron in a hydrogen atom - looks something like the picture on the left below. We have used shading to indicate the probability of finding an electron at any one point, but a more convenient way to represent an orbital is to draw a line (in reality a three-dimensional surface) encompassing the space where an electron spends, say, 95% of its time. This gives something like the picture on the right. This simplest possible orbita - the fundamental orbital of the H atom - is spherical, and is known as a 1s orbital. Higher energy atomic orbitals have different shapes.


nucleus

probability distribution
of electron in 1s orbital

schematic diagram
of 1s orbital

conventional picture
of 1s orbital

Werner Heisenberg
(1901-1976)
Nobel Prize in Physics, 1932

The hydrogen atom

It's useful to think of the atomic orbitals as a series of possible energy values for an electron, and to think of them as 'occupied' if there is an electron (or, as we shall later, two electrons) at that energy level, and 'unoccupied' if there isn't. In a hydrogen atom in its most stable state, there is only one electron, occupying the lowest energy 1s orbital. So our picture of the 1s orbital makes a good picture of what an H atom looks like too. We can also represent the 1s orbital as an energy level, and the electron which occupies it as a little arrow (which we will explain in a moment).

occupied
1s orbital

electron

ENERGY

1s orbital
energy level

energy level diagram

# Structure of molecules - electrons in atoms

What happens if you put more than one electron into the orbitals around an atom? According to Pauli Exclusion Principle, each orbital can hold two electrons - and only two, never any more. If you add an electron to the H atom, you get the hydride anion, H^-, which has two electrons around an H nucleus (a proton). Both of the electrons occupy the same spherical 1s orbital.
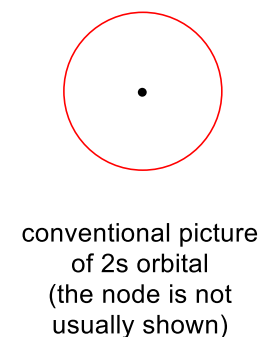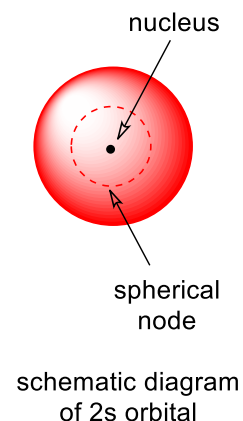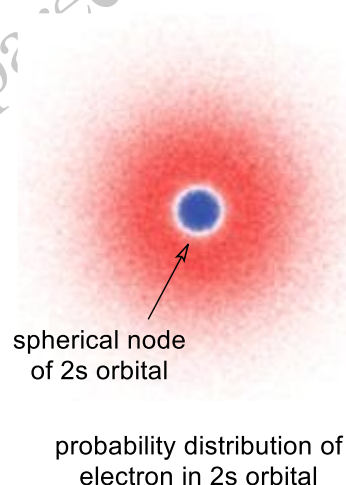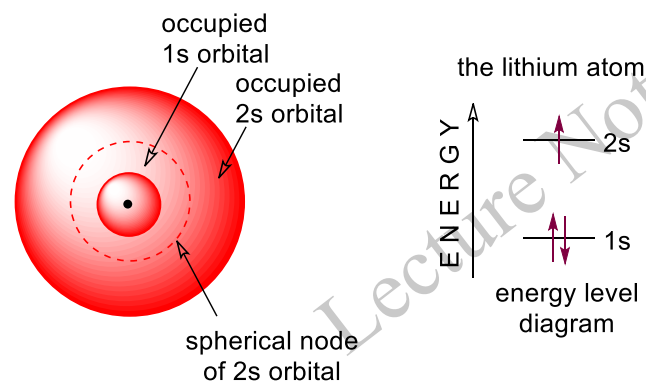
We can also represent the orbital occupancy as an energy level (the horizontal line) occupied by two electrons (the arrows). Why do we draw the electrons as arrows? Well, electrons have the property of spin, and the two electrons allowed in each orbital have to spin in opposite directions. The arrows are a reminder of these opposing spins.
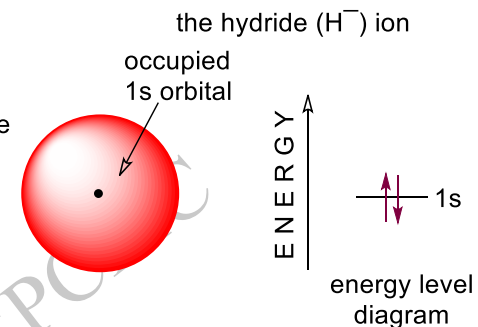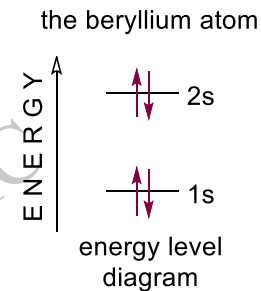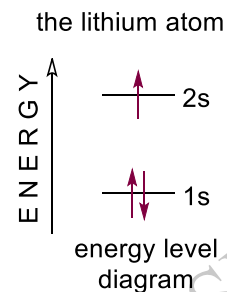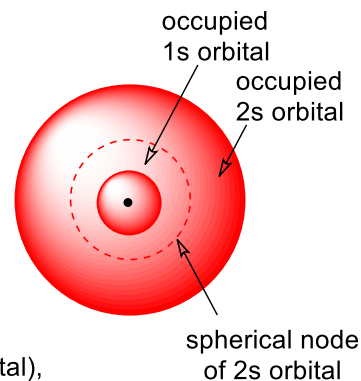
The same is true for the helium atom: its two electrons occupy the same orbital. However, the energy of that orbital (and all of the other possible orbitals) will be different from the orbital for hydrogen because it has double the nuclear charge of hydrogen and the electrons are more strongly attracted to the nucleus. We can represent the orbital occupancy like this, with the energy level lower than the one for H because of this stronger attraction.
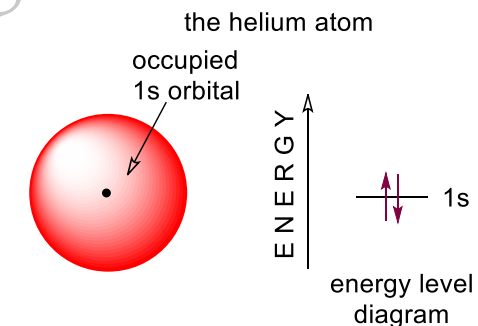
The next atom, lithium, has total three electrons. The lowest energy 1s orbital around the Li nucleus can contain two electrons, but two only, so the third electron has to go into a higher energy orbital - one of the energy levels whose existence was inferred from atomic absorption spectroscopy. You can think of this orbital as the three-dimensional equivalent of the first harmonic of the guitar string. Like the vibration of the string, this next orbital has a node. On the string the node was the point where no motion was observed. In an atom, a node is a point where the electron can never be found - a void separating the two parts of the orbital. For the orbital containing the third electron of the Li atom, this node is spherical - it divides the orbital into two parts which nestle one within another like the layers of an onion or the stone inside a peach. We call this orbital the 2s orbital.

the hydride (H^-) ion

occupied 1s orbital

ENERGY

1s

energy level diagram

the helium atom

occupied 1s orbital

ENERGY

1s

energy level diagram

occupied 1s orbital

occupied 2s orbital

spherical node of 2s orbital

the lithium atom

ENERGY

2s

1s

energy level diagram

spherical node of 2s orbital

probability distribution of electron in 2s orbital

nucleus

spherical node

schematic diagram of 2s orbital

conventional picture of 2s orbital (the node is not usually shown)

In a lithium atom the 1s orbital, close to the nucleus, is occupied by two electrons, while the 2s orbital, further from the nucleus, contains one. In beryllium, there is a second electron in the 2s orbital. As before the energy levels will change as the nuclear charge increases, so the orbital occupancy in Li and Be can be represented as shown in the adjacent diagram:.

occupied
1s orbital
occupied
2s orbital
spherical node
of 2s orbital

the lithium atom

ENERGY

2s
1s

energy level
diagram

the beryllium atom

ENERGY

2s
1s

energy level
diagram

When we get to boron, something a little different happens. It turns out that for an orbital with one node (such as the 2s orbital), the node *does not have to be* spherical. The node can alternatively be a plane. This alternative arrangement for an orbital with a single planar node gives us a new type of orbital, the 2p orbital. A 2p orbital looks something like the picture on the left below, in 'smeared out' form. It is often represented as the propeller shape in the middle, and it is conventionally drawn as the shape shown in the diagram to the right.

nucleus

nucleus

schematic diagram
of 2p orbital

conventional picture
of 2p orbital

probability distribution of
electron in 2p orbital
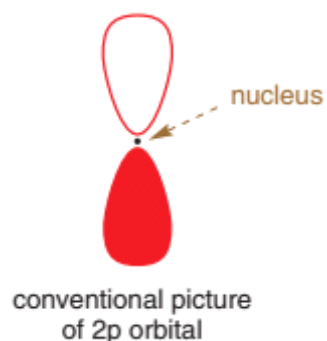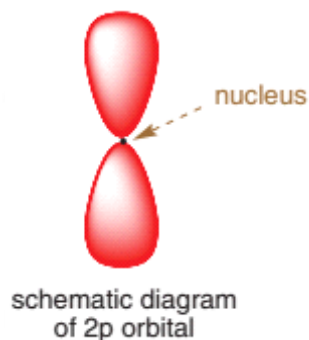
Unlike the 1s or 2s orbitals, the 2p orbital is directional - it points along an axis, and in three dimensions there are three possible orientations for the axis, each of which gives rise to a new 2p orbital (which we can call $2p_x$, $2p_y$ and $2p_z$ if we need to). The three 2p orbitals on any atom are of equal energy. We call such set of orbitals *degenrate orbitals*.

$2p_x$ z

$2p_y$ z

$2p_z$ z

x   y

x   y

x   y
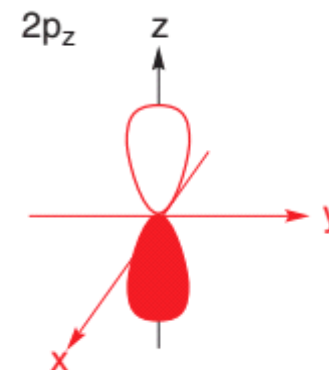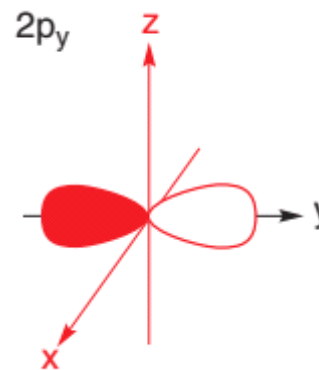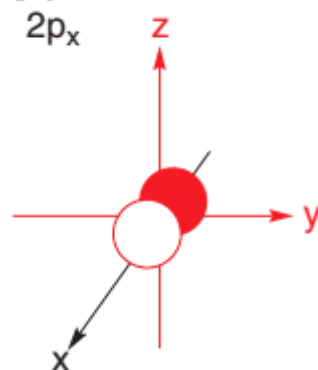
The planar node of the three 2p orbitals gives them just slightly more energy than a 2s orbital, with its spherical node. Boron atoms therefore have two electrons in the 1s orbital, two in the 2s orbital, and just one in one of the 2p orbitals. The orbital occupancy is shown in the energy level diagram on the right.

The next element, carbon, with one more (a sixth) electron, seems to have a choice - it can put its sixth electron paired with the fifth one, in the same 2p orbital, or it can put it into a new 2p orbital, with both electrons unpaired. In fact it chooses the latter: electrons are negatively charged and repel one another, so if there is a choice of equal energy orbitals they occupy
different orbitals singly until they are forced to start pairing up. The repulsion is never enough to force an electron to occupy a higher energy orbital, but when the orbitals are otherwise of identical energy, this is what happens. (Hund's Rule - an atom adopts the electronic configuration that has the greatest number of unpaired electrons in degenerate orbitals.)

the boron atom
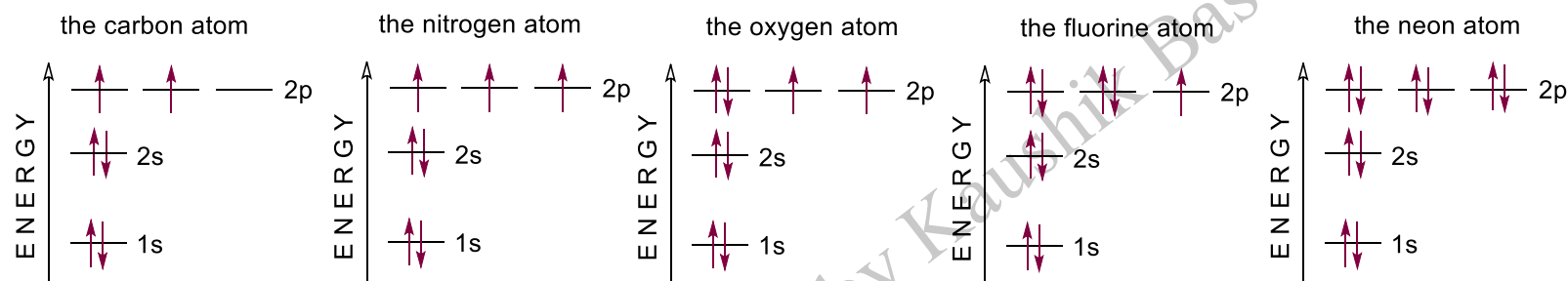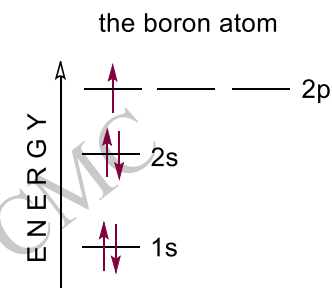
Not surprisingly therefore, the orbitals of atoms of the remainder of the elements of the first row of the periodic table are occupied as shown above. All the while the entire set of orbitals is *going down* in energy because the nucleus is attracting the electrons more strongly, but otherwise it is a simple matter of filling up the 2p orbitals first singly and then doubly. The relative energy ordering between 1s, 2s and 2p orbitals are the same. Interesting to note that for an one electron system such as H,the energy of the 2s and 2p orbitals are the same. Whenever a second electron is added into the system, however, this degenracy is lost and 2s becomes more stable AO than the 2p AOs.

With the ten electrons of neon, all the orbitals with one node are filled, and we say that neon has a 'closed shell'. A 'shell' is a group of orbitals of similar energy all with the same number of nodes (in this case all called '2' something - 2s or 2p - both AOs having one node, a sperical node for 2s and a nodal plane for the 2p AOs).

One important consequence of the lowering of AO energy as we move from Li to F is the progressive relative stabilisation of electrons in the AOs of atoms that are on the RHS of the periodic table. Basically, if we have an electron on the AOs of F, they will be closer to the nucleus than they would be if they were on B or C or N or even O. This implies that elecrons on AOs of F are more stabilised than they are on the AOs elements that are on the LHS of F in the periodic table. We will see that this leads to an important property - electronegativity.

as electronegativity increases, the energy of the orbital decreases
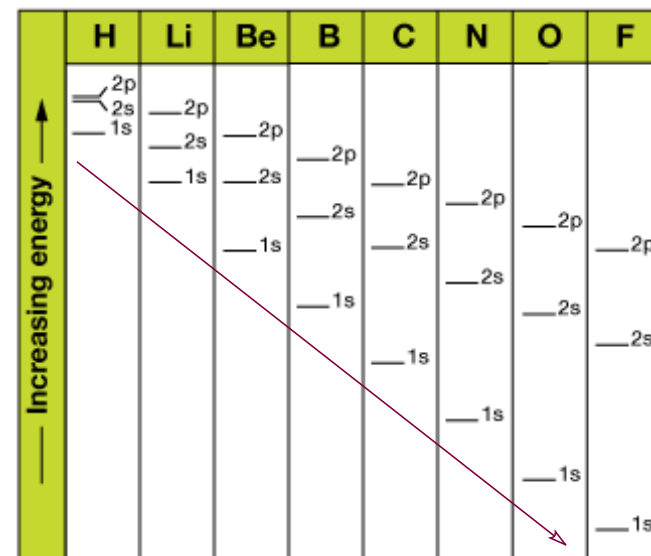
Look at the already familiar diagrams on the RHS:
they represent the first three vibrational frequencies
of a taut string. Now think about the motion of the
string itself:
in the first vibration, all of the string moves up and
down at the same time - each point on the string
moves by a different amount, but the direction moved
at every point is the same. The same is not true for the
second 'energy level' of the string - during a vibration
like this, the left-hand half of the string moves upwards while the right-hand half moves downwards - the two halves of the string are *out of phase* with one another,
and there is a change of phase at the node. The same is true of the third energy level - again, there is a change of phase at each node.
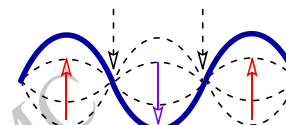
change of phase at the node   change of phase at each node
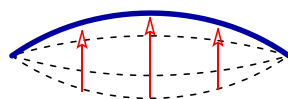
all the string moves
in the *same direction*
(upward)
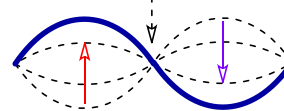
different parts of the string, separated by nodes,
move in *different directions* (upward & downward)

The same is true for orbitals. A nodal plane, such as that in the 2p orbitals, divides the orbital
into two parts with different phases, one where the phase of the wavefunction is positive and
one where it is negative. Consider the adjacent pictures. The two phases on either side of the
node (spherical node for 2s and nodal plane for 2p) are coloured differently. Blue and red:

But for a quick representation, these probability distributions are not suitable. In that case, the
phases are usually represented by shading - one half is shadedand the other half not.
You saw this in the representation of the 2p orbital before. Here it is again. The 2s orbital,
conventionally, is represented with out showing the node:
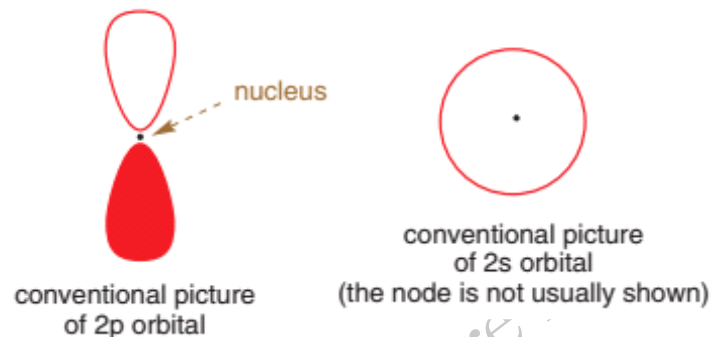
probability distribution of
electron in 2s orbital

probability distribution of
electron in 2p orbital

nucleus

conventional picture
of 2p orbital

conventional picture
of 2s orbital
(the node is not usually shown)

The phase of an orbital is arbitrary, in the sense that it doesn't matter which half you shade.
It's also important to note that phase is nothing to do with charge: both halves of a filled 2p
orbital contain electron density, so both will be negatively charged.

As it happens, the electron density at any point in the orbital is given by the square of the mathematical function (the wavefunction, ψ) which determines the
phase, so both positive and negative values of the wavefunction give positive electron densities.

So why is phase important? Well, in a moment we will see that, just as atoms add together to give molecules, we can add together the wavefunctions of atomic
orbitals to give molecular orbitals (MOs), which tell us where electrons are, and how much energy they have, in molecules. And when we add two
wavefunctions together, the result of that addition is dependent on the phase of the concerned orbitals.

We're about to develop the idea of orbitals in order to understand how electrons behave in molecules, but before we go on, we should just clarify a few points about orbitals that can sometimes lead to confusion.

1. Orbitals do not need to have electrons in them - they can be vacant (there doesn't have to be someone standing on a stair for it to exist). Helium's two electrons fill only the 1s orbital, but an input of energy - the intense heat in the sun, for example - will make one of them hop up into the previously empty 2s, or 2p, or 3s. . . etc. orbitals waiting to receive them. In fact, it was observing, from earth, the energy absorbed by this process which led to the first discovery of helium in the sun.

2. Electrons may be found anywhere in an orbital except in a node. In a p orbital containing one electron, this electron may be found on either side but never in the middle. When the orbital contains two electrons, one electron doesn't stay in one half and the other electron in the other half - both electrons could be anywhere (except in the node).

3. It is illogical to ask how an electron "passes over" from one lobe of a p orbital to the other lobe, as then it has through pass through the node, where, by definition, electron density has to be zero, i.e. electron cannot exist there at any time. Just as you accept the existence of two different phases in case of a standing wave, the electron can exsist in bothe lobes without actually passing over from one lobe to the other. Claerly, think9ing of electrons as particles leads to the logical fallacy. Electrons are waves too!

4. All these orbitals of an atom are superimposed on each other. The 1s orbital is not the middle part of the 2s orbital. The 1s and 2s orbitals are separate orbitals in their own rights and each can hold a maximum of two electrons but the 2s orbital does occupy some of the same space as the 1s orbital (and also as the 2p orbitals, come to that). Neon, for example, has ten electrons in total: two will be in the 1s orbital, two in the (much bigger) 2s orbital, and two in each of the three 2p orbitals. All these orbitals are superimposed on each other.

5. As we move across subsequent rows of the periodic table - starting with sodium - the 1s, 2s, and 2p orbitals are already filled with electrons, so we must start putting electrons into the 3s and 3p orbitals, then the 4s, 3d, and 4p orbitals. With d orbitals (and f orbitals, which start to be filled in the lanthanide series) there are yet further new arrangements of nodes. We won't be discussing these orbitals in detail but the principles are just the same as the simple arrangements we have described.