# Bonding in Molecules

Atoms must 'stick' or bind to one-another in order to form molecules. In a molecule of water, H_2O, two hydrogen atoms are bonded to one oxygen atom. In the case of a water molecule the bonds are covalent bonds, a type of bond formed by one pair of electrons, shared between the atoms, which has a definite direction in space and so can be represented as a stick joining two atoms (depicted as balls) together (a ball-and-stick model). Each covalent bond binds two atoms together (usually) and so we have two such covalent bonds in water:
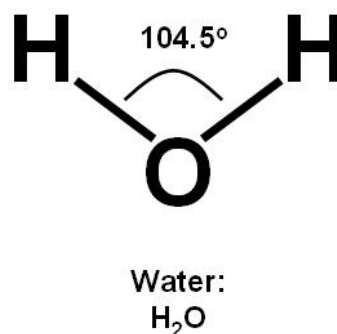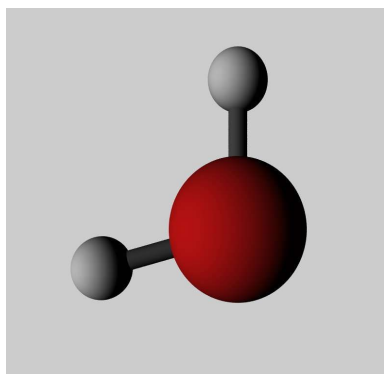
There are four main types of bond: **covalent bonds, ionic bonds, metallic bonds and hydrogen-bonds**, and several other weak intermolecular forces that act between molecules. Covalent, ionic and metallic bonds are strong and of the same general strength, though the exact strength varies according to the types of atom involved in the bond. hydrogen-bonds are weaker, and are sometimes grouped with weak intermolecular forces, however, the strongest hydrogen-bonds are as strong as the weakest covalent bonds.

All these various types of bond have one thing in common: they can all be described as chiefly due to the attractive force (the **Coulomb force**, see box below) between electric charges of opposite sign (opposite charges attract) although in the full quantum mechanical description of bonding things are never quite so simple.

Ionic Bonds

In ionic bonds, two atoms bond together because one of the atoms donates one or more electrons to the other atom, such that the atoms become ions. An ion is an atom or molecule that carries a net electric charge, positive (cation) or negative (anion). Electrons are negatively charged and atoms are neutral, so the atom that loses one or more electrons becomes a positively charged cation (gaining one unit of positive charge for each electron lost) and the atom that gains one or more electrons becomes a negatively charged anion (gaining one unit of negative charge for each electron gained). This is the simple case in a single ionic 'molecule' of say sodium chloride (common table salt) NaCl, in which sodium loses donates one electron to chlorine (which becomes a chloride, Cl^-, ion). To emphasise the charges this can be written: Na^+Cl^-. More than one atom/ion might be involved, for example, in calcium chloride ($CaCl_2$) the calcium atom loses two electrons, giving one to each of the two chlorine atoms to give $Ca^{2+}(Cl^-)_2$. Although such simple ionic molecules may exist in the gas phase, and transiently in solution, ionic substances usually involve millions of ions bonded together in a single crystal or **giant ionic lattice**. A single crystal of salt is such a lattice (and such crystals can be large).

This occurs because, unlike covalent bonds, ionic bonds are not directional and can not be represented as sticks. Instead, each cation is surrounded by several anions, binding to all of them by sharing its bond between them. likewise, each anion is surrounded by several cations.
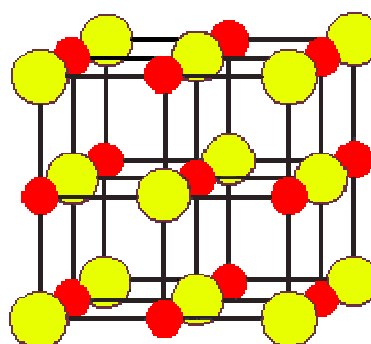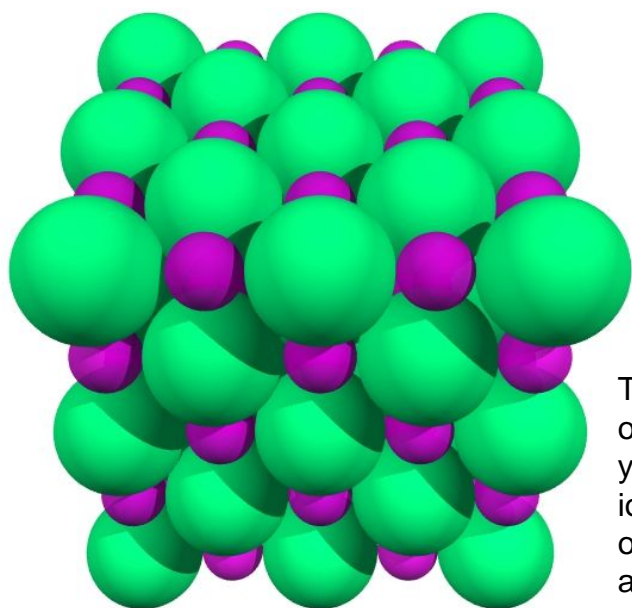
<u>The Coulomb force</u>:

$$\underline{F} = q\underline{E}(\underline{r}) \quad (1)$$

$$\underline{E}(\underline{r}) = \underline{F}/q \quad (2)$$

$$\underline{F} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r^2} \hat{r} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{|\underline{r}_2 - \underline{r}_1|^3}(\underline{r}_2 - \underline{r}_1) \quad (3)$$

$\dfrac{1}{4\pi\varepsilon_0}$ depends on choice of units and is the Coulomb (force) constant

$$\underline{F} = \frac{1}{4\pi\varepsilon_0} \sum_i \frac{q q_i}{r^2} \hat{r} = \frac{1}{4\pi\varepsilon_0} \sum_i \frac{q q_i}{|\underline{r} - \underline{r}_i|^3}(\underline{r} - \underline{r}_i) \quad (4)$$

Two representations of part of a giant ionic lattice of NaCl. The larger spheres (green on the left, yellow above) are the negatively charged chloride ions and the smaller spheres are the sodium ions. on the left is a space-filling representation. Ions and atoms are diffuse clouds of electric charge and have no definite surface, but become denser toward their centre. In the 'ball-and-stick' model, the lines are NOT bonds in the ionic case, simply lines to show the geometry!

Ionic bonding usually occurs between metals, like sodium and calcium, and non-metals, like chlorine, since metals tend to lose electrons (they are electropositive) and non-metals tend to gain electrons (they are electronegative). Although cations and anions vary in size, the cations are typically much smaller, as they are in the figures in this article.

The ions need not be simple, as ionic bonding can occur with complex ions. this happens in many salts of mineral acids, such as the oxygen containing or oxoacid salts, like sulphates, phosphates, nitrates and carbonates.
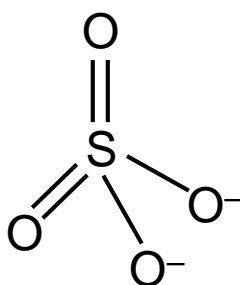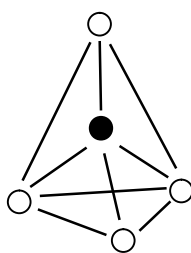
Left: the complex sulphate aoxoanion, SO_4^{2-} is tetrahedral. In reality, since all the oxygen atoms are equivalent, the charges are shared or delocalised across the whole molecule and each S-O bond then becomes 'one-and-a-half' bonds. A similar principle applies to other oxoanions.

Electron density maps

Another way to visualise ionic bonding is to look at an electron density contour map for a small slice through the lattice. These images are the results of actual measurements made by diffraction methods (such as electron diffraction). the lines in these maps are contours and can be given numbers indicated the value of electron density that they represent, however, for simplicity I have omitted the values so as to focus on the main features. However, in the centres of the ions (the groups of concentric circles are the ions) the electron density is higher in the centres (on the smaller circles).

On the next two pages are given the electron density maps obtained for calcium fluoride, CaF_2, sodium chloride, NaCl, and lithium fluoride, LiF. These are described in turn below.

Calcium fluoride. In this map we can see two calcium ions sandwiched between two rows of four fluoride ions (remember this is only one tiny part of the lattice). The calcium ions have very high electron density as shown by the close contours at its centre (both calcium ions and fluoride ions are small ions) due to the contraction of its outer layers as the increase in proton : electron ratio (by two upon ionisation from Ca to Ca^{2+}) increases the proton pull on each electron. Notice how circular the contours are, calcium fluoride is very strongly ionic.

Sodium chloride. Again the smaller ions are the sodium ions, Na^+, and the larger ions the chloride ions, Cl^-. Notice the squaring of the contours, which is due to distortion of the outer electron shell as some of the charge on the chloride is pulled back towards the sodium ion. We say that the bond is polarised.

Lithium fluoride. here the polarisation of the bonds is more pronounced and a significant amount of electron charge is pulled out and sitting between the anions and cations.
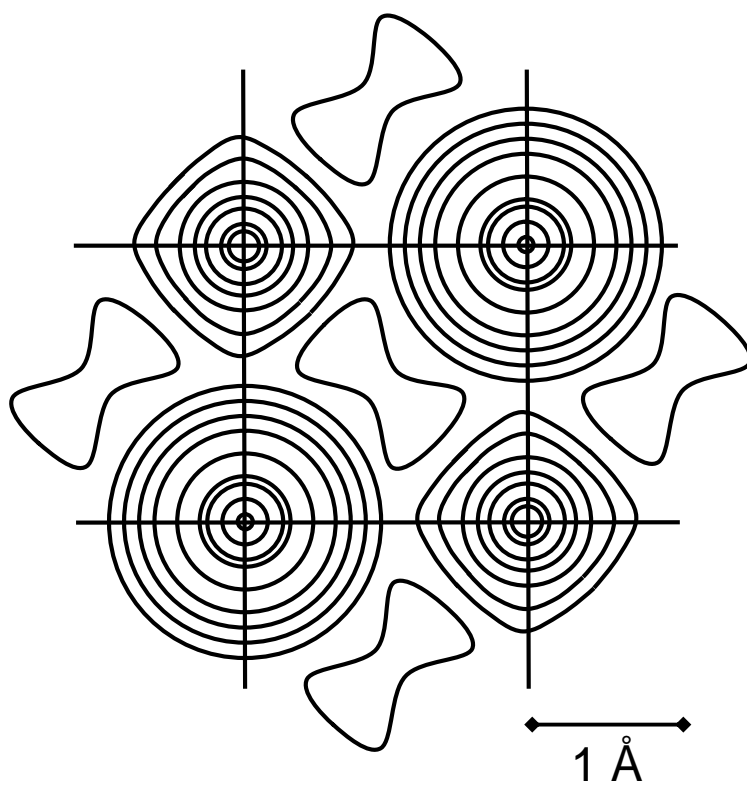
Electron density maps

CaF_2
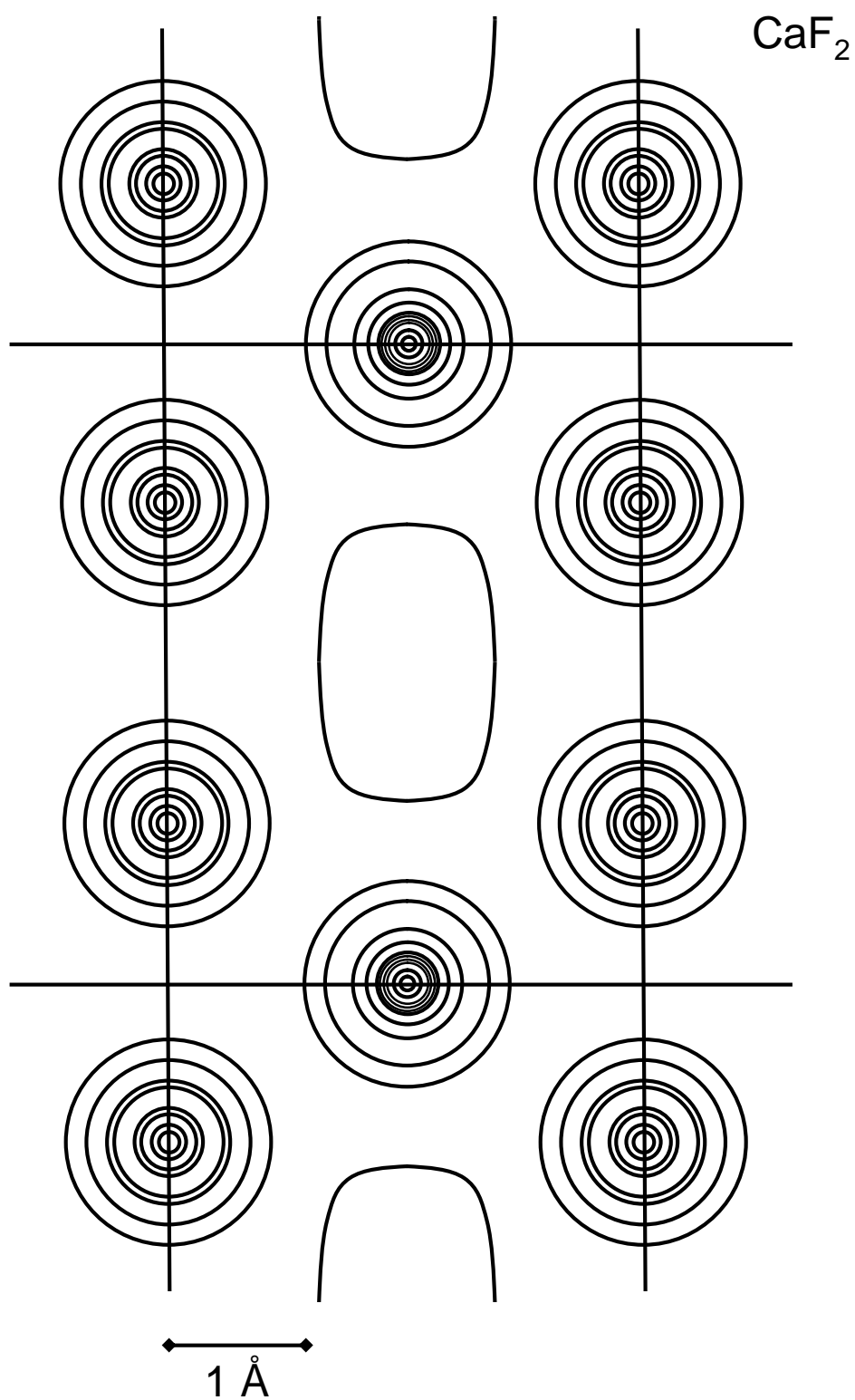
Electron density maps

NaCl

1 Å

LiF

1 Å
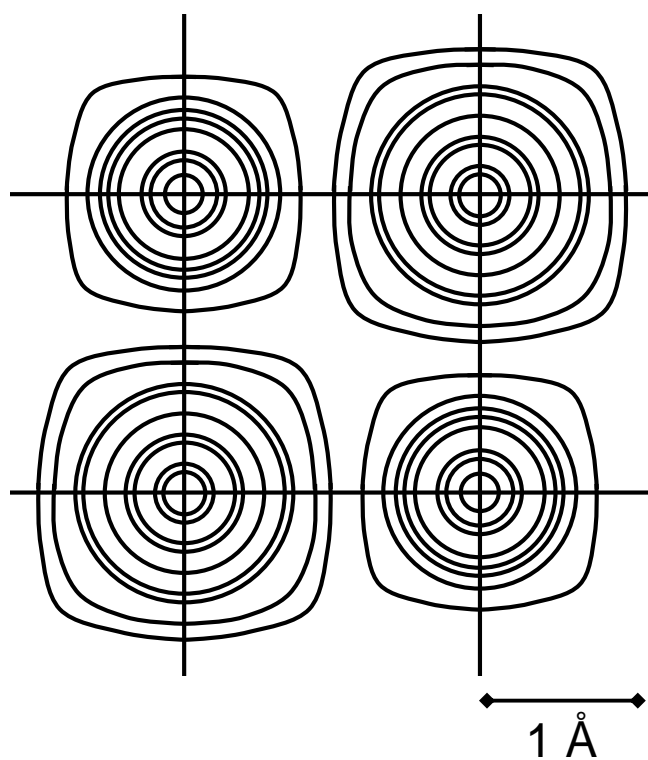
Bond Polarisation

As we have seen, ionic bonds are not 'pure' in the sense of being simple and complete electron transfers, but rather some of the electron charge may remain between the ions. Such a bond is said to be polarised. The cation is pulling back some of the electron charge toward itself until a balance is reached. Smaller cations with higher positive charge are more polarising since they have a higher positive charge density which exerts a stronger pull on the electron(s). Cations do not easily give up their electrons completely! If the anion is large, such that the distance between the outer electrons and the nucleus (or nuclei) is great, then the outer electrons are diffuse and easily distorted (being weakly bound to the anion nucleus). This is well-illustrated by lithium iodide, LiI, in which the small lithium ion exerts a strong pull on the diffuse electron cloud of the large iodide ion, significantly polarising the bond:

Li^+ ion I^- ion
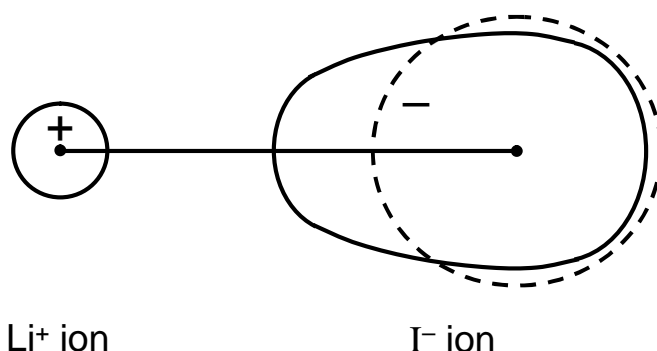
Polarisation in LiI, the iodide anion is no longer spherical, but has its electrons partly drawn towards the small Li^+ cation.

If the bond is strongly polarised, then it is no longer ionic, but the pair of electrons become essentially shared between the two atoms, and are localised in this mid-way region, forming a covalent bond!

There is a continuous spectrum from pure covalent bond (with the electron pair shared exactly equally by the two atoms, e.g. between two atoms of the same species, as in the hydrogen H_2 molecule for example) to polarised covalent (slightly ionic), to polarised ionic (slightly covalent) to (almost) pure ionic. (An ionic bond can never be pure, since there is always some distortion and polarisation, however slight, of the charge distribution).
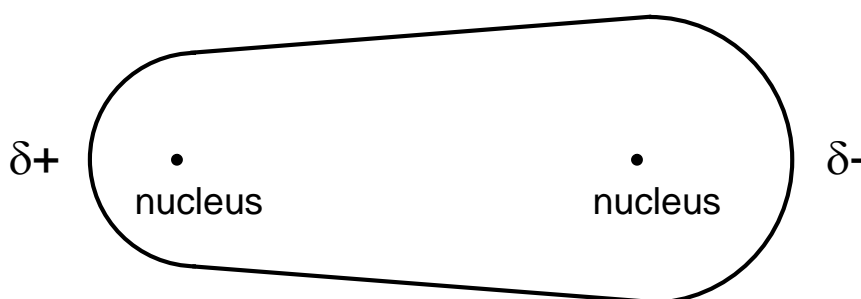
$\delta+$ nucleus   nucleus $\delta-$

Polarisation of a (predominantly) covalent bond. The electrons are still well-shared between the two nuclei, but the more electronegative nucleus gains more than its 'fair-share' and acquires a fractional negative charge ($\delta-$). E.g. H-Cl molecules ($\delta+$(H-Cl)$\delta-$ or $H^{\delta+}$-$Cl^{\delta-}$) in hydrogen chloride gas.

Covalent Bonds

First we consider covalent molecules made-up of two atoms only, so-called **diatomic molecules**. In a pure covalent bond, one pair of bonding electrons are equally shared between the two bonded atoms.

A covalent bond is formed by one pair of shared electrons between two atoms.

The bond can still be described in terms of electrostatic attraction (the Coulomb force) as the two positive nuclei of the atoms are attracted to the electrons between them and this attraction keeps the nuclei bound together (and overcomes their tendency to repel one-another as like-charges repel). Next we look at the quantum mechanical description of a covalent bond.

The H_2^+ molecular ion and the H_2 molecule

The simplest molecule is H_2^+, consisting of two protons and one electron. This makes a good starting point in understanding the quantum mechanics of the covalent bond as this molecular ion contains a covalent bond containing just one electron (a half-bond) holding two hydrogen nuclei (protons) together. We shall not go through all the mathematics here though some of the mathematical features of the problem are included below.

We need a coordinate system for our molecule. We shall use the centre of mass coordinate system, in which the origin of the coordinates is positioned at the centre of mass, which since the electron has negligible mass compared to the electron, is midway between the nuclei, on the axis of H--H bond.

First we have to find the classical Hamiltonian of the system, which is the sum of the total kinetic energy and the total potential energy. We then convert this into the quantum-mechanical Hamiltonian operator and use this to obtain the time-independent Schrödinger wave-equation (TISWE).

We will see that this wave equation is too complex too solve exactly. However we will use the **Born-Oppenheimer model**, in which we ignore the motion of the nuclei, since they are each about 2000 times heavier than an electron. We regard the nuclei as stationary point charges. This enables us to ignore the momentum of each nucleus. this simplifies the equation enough for an exact solution to be impossible, though still very difficult. (We know that H^{2+} has a well-defined bond length, so the nuclei do not move much relative to one-another, so our approximation is a reasonable one). However, a simpler method is to use an approximation method. We will not give the details here, but the **variational method** can be used. In this method we begin with an estimated wave-function, then use this to solve Schrodinger's equation by obtaining the minimum energy solution, which gives us the estimated ground state energy of the molecule. This can be compared to the experimental value for the H_2^+ bond energy of -2.791 eV, corresponding to a measured bond length of 1.06 angstroms (stronger bonds are shorter). (In this case, the entire solution can be compared to the exact calculated value, enabling us to validate the approximation, of course we usually can not do that for most systems that we approximate!). the bond energy is negative – atoms bond when they are able to lose energy in doing so, and they generally prefer to be in a low-energy state (though the really issue is really one of entropy).

The lower this energy, the stronger and more stable is the bond, since this energy (2.791 eV) must be added back to break the bond. (Note that we have given a single bond energy, but in chemistry bond energies are usually quoted in kJ per mole). We can say (a bit loosely) that *this is why particles bind together: because in doing so they lose energy and become more stable*.

The initial estimated wave-function used can be a simple combination of atomic orbitals, in this case we can begin with the simplest case and simply add two 1s-orbitals together to form a **molecular orbital (MO)**. This is the method of **linear combination of atomic orbitals (LCAO)**. This is reasonable, since in their ground state the two H atoms will have an electron in the 1s-orbital before combining to form H_2 (or one of them will in the case we combine it with H^+, a naked proton, to form H_2^+).

When this is done, it is found that the predicted ground state energy (of the electron) is too high, and the bond too weak and too long, with the electron concentration between the nuclei too low. The variational method is iterative, we modify the wave-function and recalculate the energy to see if a more realistic result is obtained. Two simple modifications improve the estimate considerably: 1) increasing the nuclear charge on each proton from 1 to 1.24 (sounds unreasonable, but maybe there was a problem in assuming the nucleus to be a point-charge); 2) we can modify our LCAO by forming a combination of the 1s and 2p atomic orbitals for each H atom (this would be a linear combination, that is a simple ratio of the two, mostly s with some p, which we can do as these are wave-functions and waves can be added linearly by the Principle of Superposition to form a new wave which is still a solution to the wave equation). in essence we are creating a hybrid orbital. This gives a much more accurate energy and bond-length.

The result is shown below. We actually obtain two solutions, one in which the energy is minimised, corresponding to the ground state, in which the electron forms a bond (a **bonding MO**) between the nuclei, formed by adding the 1s wavefunctions of the two atoms, with the electron density concentrated between the two nuclei; and one of maximum energy, in which the electron forms an **anti-bonding MO**, formed by subtracting the 1s wavefunction of one atom from that of the other, with the electron repelled from the region between the two nuclei. The former results in a bond, the latter does not.

Each orbital can hold two electrons, be it an atomic or molecular orbital. In H_2, there are two electrons and in the ground state they will both occupy the bonding molecular orbital. This increases the electron charge density between the two nuclei and strengthening and shortening the bond. However, there is an extra effect that means that the bond does not shorten/strengthen by as much as one might think: the two electrons also repel one-another by a Coulomb force (like charges repel). This repulsion is not strong enough to overcome the benefits of sharing the bonding MO, that benefit being that this state has lowest energy, but it does weaken the bonding slightly (and increase the energy of the state slightly, making the bond energy less negative). The end result is a covalent bond in H_2 which has an equilibrium length of 0.74 angstroms (with the nuclei oscillating slightly as the bond alternately lengthens and shortens). Variational theory can solve (approximately) the Born-Oppenheimer model with two electrons (H_2) with the electron repulsion switch off, and then this perturbation can be introduced as a **perturbation** (perturbation theory – another mathematical approximation method which tests the effects of additional factors or perturbations). the final answer is very close to the actual value, suggesting the validity of these methods. These approximation methods also allow us to construct a system by beginning with the main requirements and then adding in additional factors, which gives insight into the importance of various effects, such as electron repulsion).
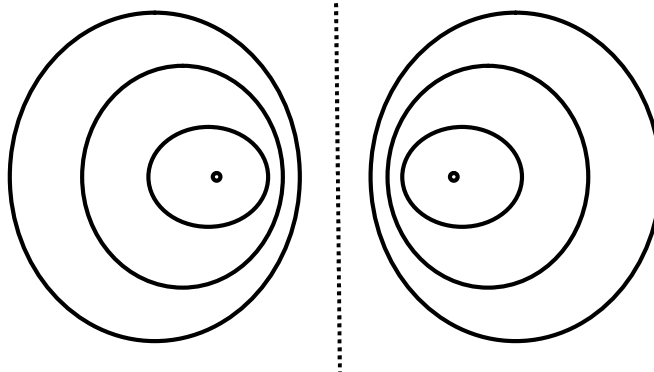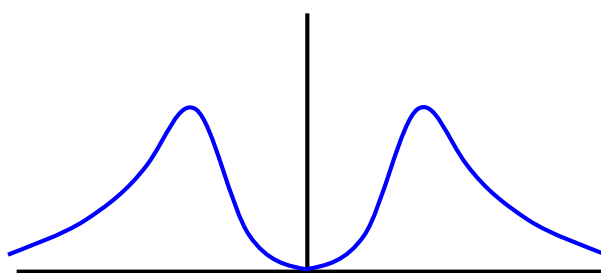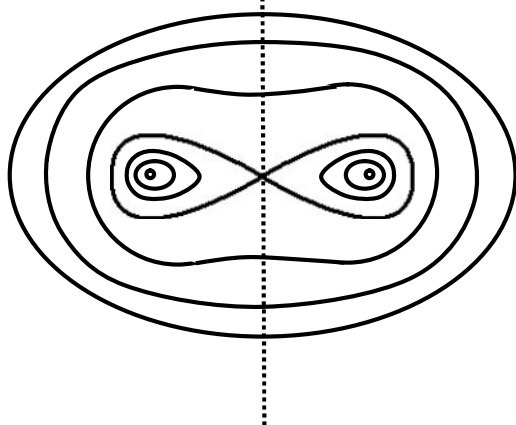
Electron density maps

H + H → H₂

H   H H_2

0.37Å
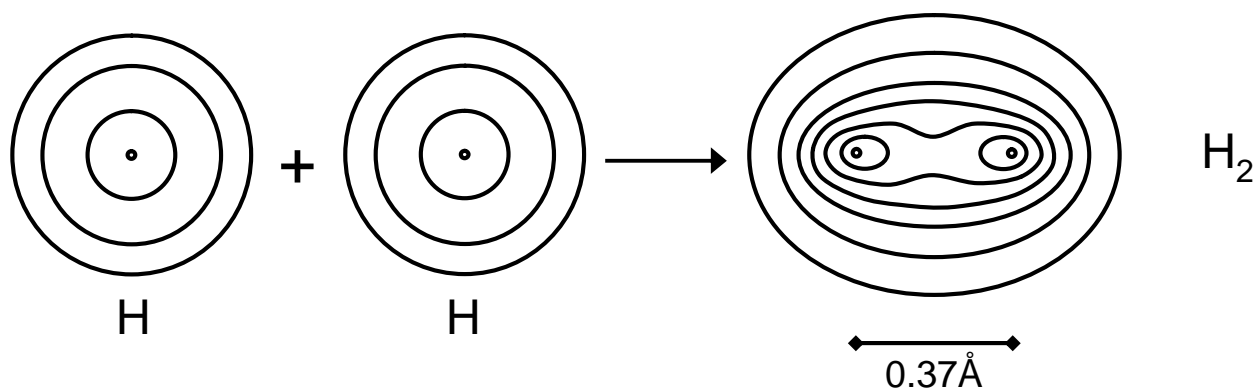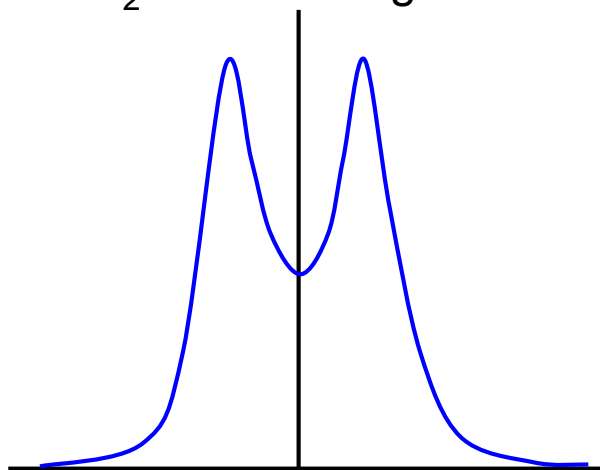
H_2^+ ion bonding MO

The H_2^+ ion is the simplest molecule, consisting of two protons and one electron.

H_2^+ ion anti-bonding MO

1. Find the Hamiltonian in the Born - Oppenheimer model :

Hamitonian, $H = $ (total kinetic energy) + (total potential energy)

Total kinetic energy $= \dfrac{\mathbf{p}_1^2}{2M} + \dfrac{\mathbf{p}_2^2}{2M} + \dfrac{\mathbf{p}_e^2}{2m}$

Where : $\mathbf{p}_1$ and $\mathbf{p}_2$ are the momenta (vectors) of the two protons and $\mathbf{p}_e$ is the momentum of the electron;

M is the mass of a proton and m the mass of an electron, and

$\mathbf{p}_1^2 = \mathbf{p}_1 \cdot \mathbf{p}_1 = (p_{1x})^2 + (p_{1y})^2 + (p_{1z})^2$

(and likewise for p22 and pe2 in the usual way for vectors).

Total potential energy V (due to the Coulomb potential) :

$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_e) = \dfrac{e^2}{4\pi\varepsilon_0} \left(-\dfrac{1}{|\mathbf{r}_1 - \mathbf{r}_e|} - \dfrac{1}{|\mathbf{r}_2 - \mathbf{r}_e|} + \dfrac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

Where :

$\mathbf{r}_1$ is the position vector of nucleus 1,

$\mathbf{r}_2$ is the position vector of nucleus 2

and $\mathbf{r}_e$ is the position vector of the electron,

in centre of mass coordinates;

e is the unit charge (magnitude of the charge on an electron or proton),

and ε_0 the permittivity of free space.

The classical hamiltonian, $H = $ kinetic energy + potential energy :

$$H = \dfrac{1}{2M}\left(\mathbf{p}_1^2 + \mathbf{p}_2^2\right) + \dfrac{1}{2m}(\mathbf{p}_e^2) + \dfrac{e^2}{4\pi\varepsilon^0} \left(\dfrac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \dfrac{1}{|\mathbf{r}_2 - \mathbf{r}_e|} - \dfrac{1}{|\mathbf{r}_2 - \mathbf{r}_e|} \right)$$

To obtain the quantum mechanical hamiltonian operator, $\hat{H}$, we replace each momentum in the classical Hamiltonian by the quantum mechanical momentum operator :

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

e.g. $\mathbf{p}_{1y}$ becomes $\hat{p}_{iy} = -i\hbar \frac{\partial}{\partial y_1}$

$\mathbf{p}_{ez}$ becomes $\hat{p}_{ez} = -i\hbar \frac{\partial}{\partial z_e}$

etc.

Thus the quantum machanical Hamiltonian operator is :

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) + V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_e)$$

The time - independent Schrödinger wave equation has 9 coordinates :

$$\hat{H}\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_e) = E\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_e)$$

2. Solve Schrödinger's Equation

This cannot be solved exactly - we must approximate.

The Born - Oppenheimer approximation assumes that $\mathbf{p}_1 = \mathbf{p}_2 = 0$, and so $\hat{p}_1$ and $\hat{p}_2$ are eliminated.

The Born - Oppenheimer model of H_2^+ and H_2 can be solved with variational methods (and perturbation theory).

Adding the second electron to H_2^+ to give H_2 follows the **Aufbau** or 'building-up' process in which each electrons are added, conceptually, to the orbitals one at a time, occupying the lowest energy levels first. If there are several energy levels of the same energy (degenerate levels) then the electrons will spread out to fill them singly initially, and the electron spins will be parallel in a so-called high-spin state (this principle is the same as that with atomic orbitals). In this case we have just the one bonding orbital (and a higher energy anti-bonding orbital) and so the second electron also fills the bonding orbital, but its spin is anti-parallel to the first (so the bonding MO contains one electron of spin-up and one of spin-down). This is necessary as electrons are fermions and so obey Fermi-Dirac statistics and the Pauli Exclusion Principle, which states that no two electrons can occupy the same state, so two electrons in the same orbital must differ, and the only way they can differ is in the direction of their spin.

Covalent bonding in polyatomic molecules

In a molecule consisting of more than two atoms, we need to consider linear combinations of atomic orbitals on all the atoms when obtaining molecular orbitals. For example in benzene, C_6H_6, six carbon atoms are bonded together in a hexagon and each carbon (C) atom is bonded to one hydrogen (H) atom. Since each C atom likes to share 4 pairs of electrons (receiving 4 from its bonding partners to complete its stable octet) this creates a problem, since to have 4 bonds on each C atom requires something like alternating single and double bonds (below, left). In practice this does not occur, after all if all the c atoms are equal why should double-bonds form between one set of alternating C atom pairs and not the others (below right:
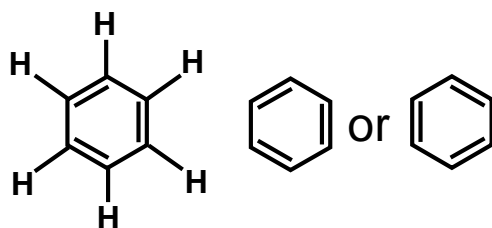

There is no reason for a preference, so instead the electrons share-out evenly, forming something more like 1½ bonds between each C atom:
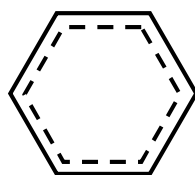

In fact, molecular orbital theory (backed by empirical measurements) suggests that all these half-bonds merge into a single group of molecular orbitals, a molecular band (a group of closely-spaced MOs (energy levels) that merge into a single **molecular band** or giant MO). The electrons are **delocalised** or 'smeared out' across the whole ring. Since each contributing orbital from each C atom contains just one electron in this delocalised ring, this MO is only half-full (of the other 3 valence electrons of each c atom, one is in the bond with the H atom and two are in the full bond between the adjacent 2 C atoms). When such a molecular band is not full, the electrons can jump up and down between the closely-spaced energy levels within the band, conducting electricity as waves of electrical energy.

Another way to visualise this is as electrons whizzing freely around the ring, carrying electric current (though the idea of waves of energy is probably more accurate).
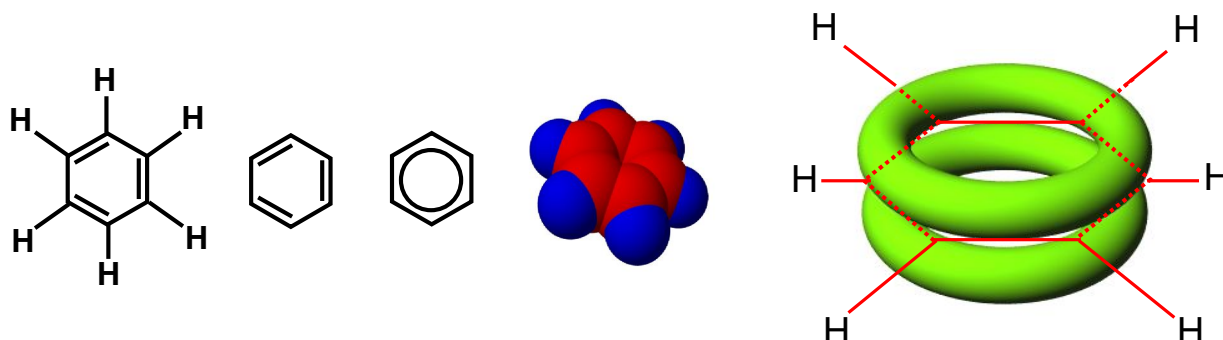
Above: different representations of benzene.

A similar thing happens in long chains of carbon atoms in which double and single bonds alternate between the atoms:
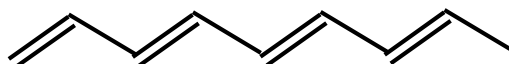
In these so-called **conjugated systems** (conjugated alkenes) the double bonds become 1½ bonds between each pair of atoms:


Again forming a delocalised molecular orbital (or band) that is half-full and so which can carry electric charge along the molecule.

In a large crystal, like a crystal of diamond, in which each C atom is covalently bonded to 4 other C atoms, the molecular orbitals delocalise across the whole crystal. In graphite, they delocalise across each sheet (the sheets being held together by weak intermolecular or van der Waals forces). In graphite the bands are not full and sheets of graphite conduct electricity.

In pure metallic bonding, as found in metals and many alloys, all the bonds between the atoms in the crystal are connected by these delocalised giant molecular orbitals and as the valence/bonding electron band is usually incomplete, the metal can conduct electricity from one end of the crystal to another. As large pieces of metal contain many crystals, this electrical energy is clearly passed from crystal to crystal too, e.g down a wire, if the metal has been drawn-out into a wire. (This is often thought of as electrons drifting or diffusing through the metal, but is perhaps more accurately thought of as waves of electron excitation passing through the crystal). To fully understand bonding in molecules like benzene, it is helpful to understand the different types of covalent bond, using a qualitative approach rather than MO theory. We do this in the next section.

Types of Covalent Bond

Sigma-bonds (σ-bonds) are covalent bonds that form between two atoms with the bonding electron concentrated directly between the two atomic nuclei. They may form, for example, between two spherical s-orbital electrons, an s-orbital and an end-on p-orbital, or two p-orbitals end-on to each other. The diagram below illustrates these types of σ-bond. The black dots indicate the positions of the atomic nuclei.

S   +   S   ⟶   σ-bond

S   +   p   ⟶   σ-bond

p   +   p   ⟶   σ-bond
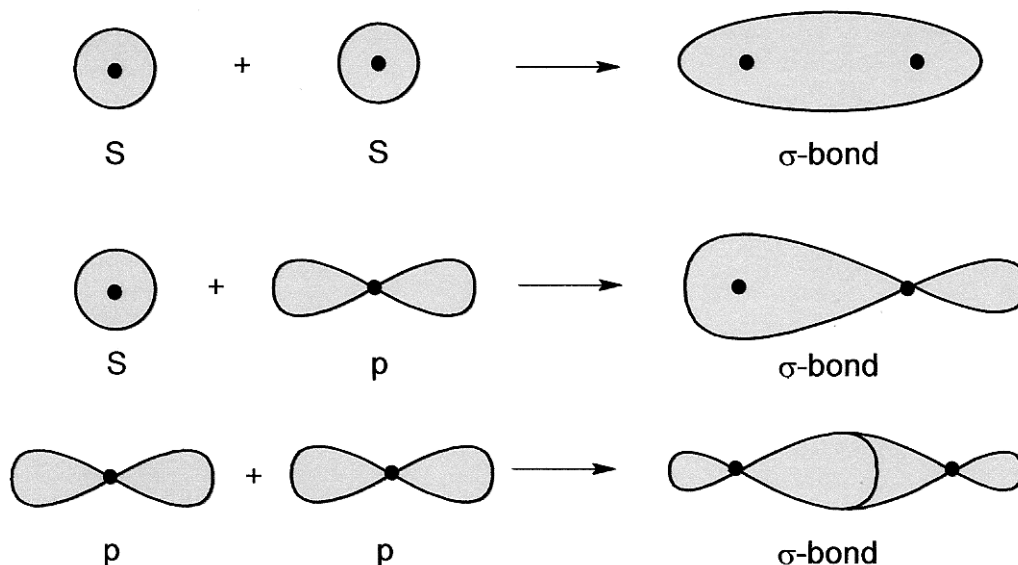
Pi-bonds (π-bonds) are covalent bonds that form when p-orbitals overlap side-on, such that there are regions of overlap above and below the axis joining the two nuclei, and it is in these off-axis regions that the electron density is concentrated.

p   +   p   ⟶   π-bond
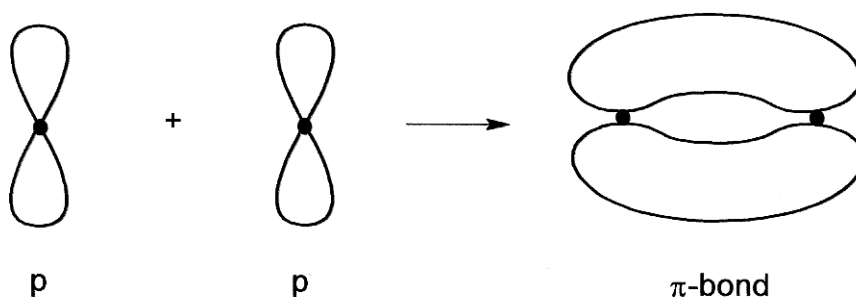
Sigma-bonds are stronger than pi-bonds, because the electron density in a sigma-bond is concentrated between the two positively charged nuclei, which are held together by their attraction to the intervening electrons. In a pi-bond, however, the electron density is not concentrated directly between the two positive nuclei and so they are less strongly bound. Sigma bonds form first, but a second bond in a double bond will usually be a pi-bond, since geometrically a pi-bond can accommodate a sigma-bond in-between its lobes (see the 'bonding in ethene' example).

The Electron Configuration in Carbon

What follows is a different qualitative approach for deriving approximations to the molecular orbitals: **atomic orbital hybridisation**.

When C is in its ground state it has the following electron configuration with 2 unpaired electrons:
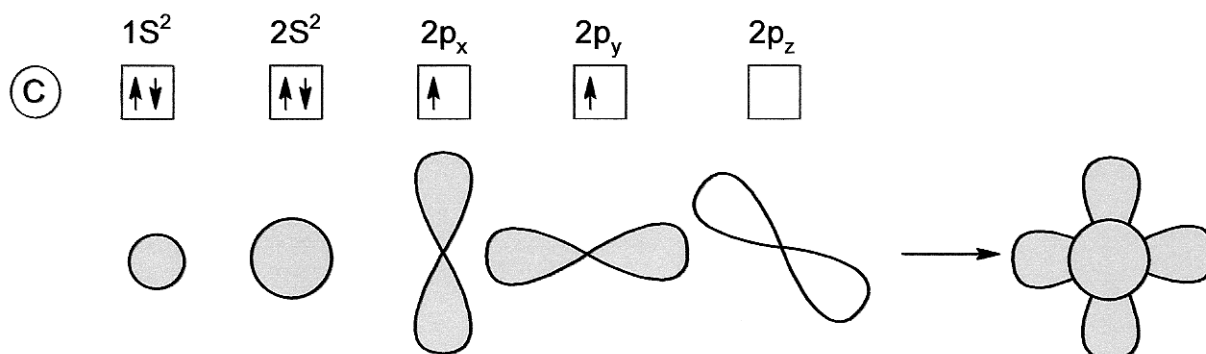

So how can C form 4 covalent bonds? When bonding C is in excited state with one 2s electron promoted to the 2p subshell:
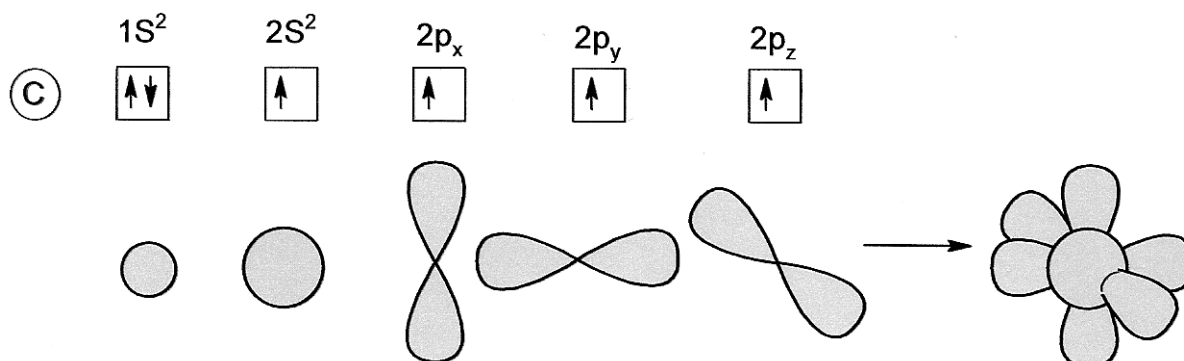
So how does C form 4 covalent bonds with a tetrahedral arrangement? Electron repulsion reconfigures the electron clouds, in fact the 2s and the three 2p orbitals hybridise to form 4 equivalent sp^3 hybrid orbitals separated by 109.5°:
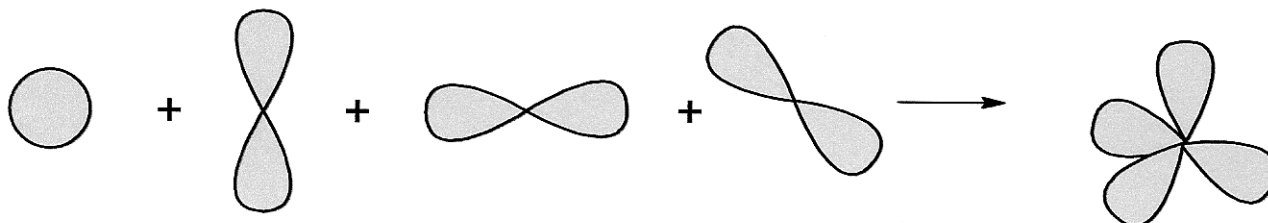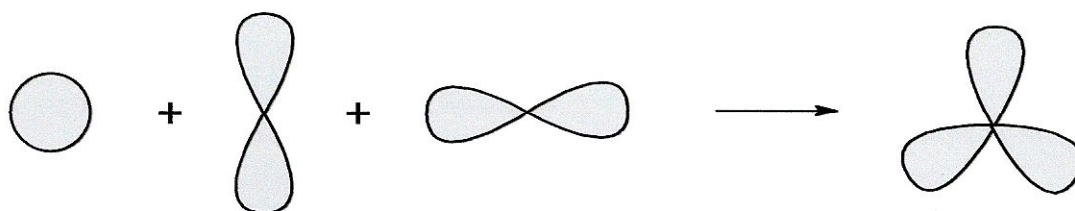
What about when C forms C=C bonds (is in ethene) or C to C triple bonds (as in ethyne)?
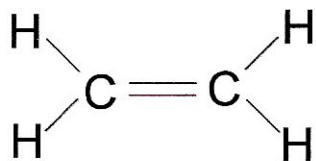
In ethene three of the bonding orbitals are equivalent and separated by 120°. The fourth contributes to the double bond.

When C is in its excited state, the 2s electron can hybridise with two of the 2p electrons, to form three equivalent sp^2 hybrid orbitals, separated from each other by 120°:


This leaves the remaining p orbital free to contribute to the C=C bond:

Unhybridised p-orbital in blue
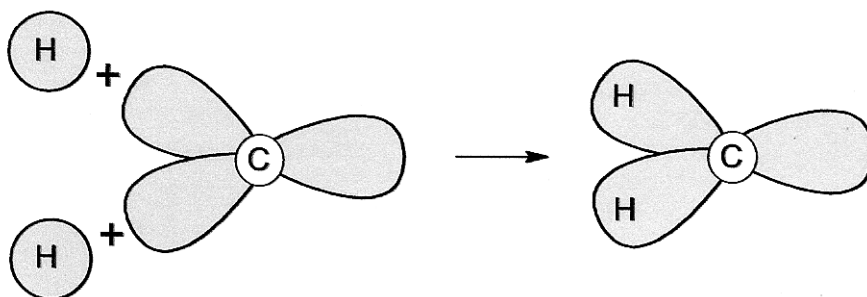
Three sp^2 hybrid orbitals
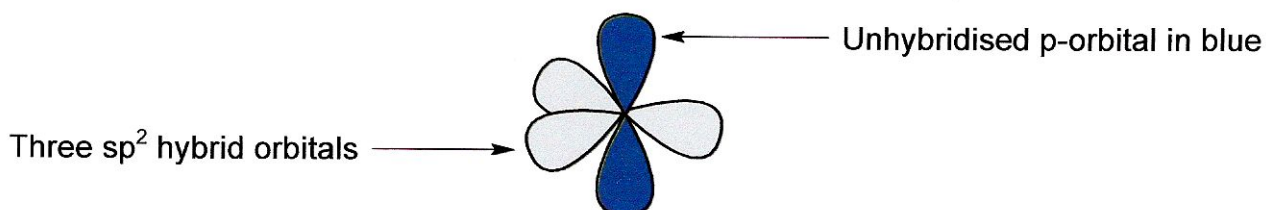
Similarly one 2s electron can hybridise with one 2p electron to form two equivalent sp hybrid orbitals (separated by 180°), allowing the two remaining non-hybridised 2p orbitals to contribute to the C to C double and triple bonds, as in ethyne for example:

Two unhybridised p-orbitals in blue
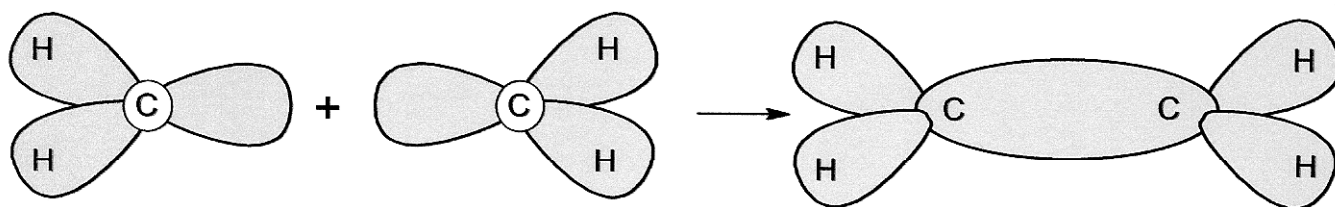
H—C≡C—H   Ethyne, C_2H_2
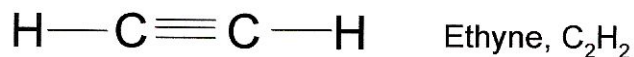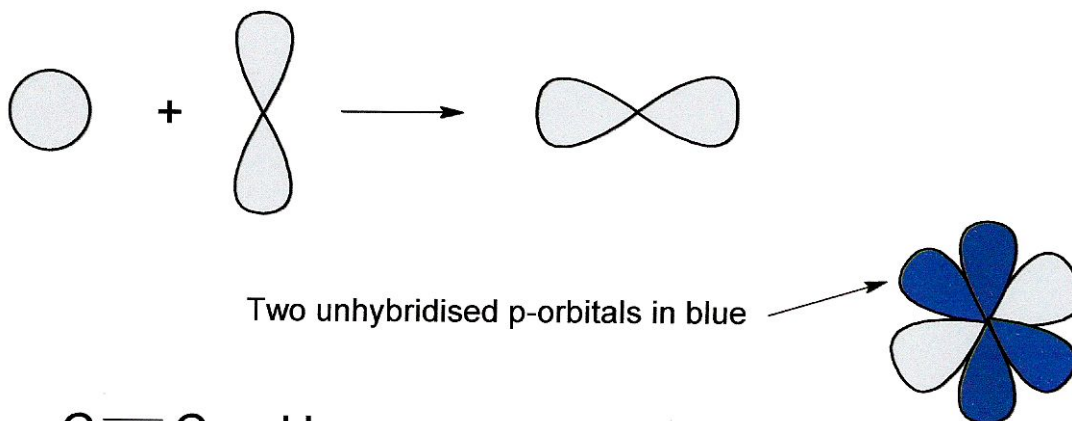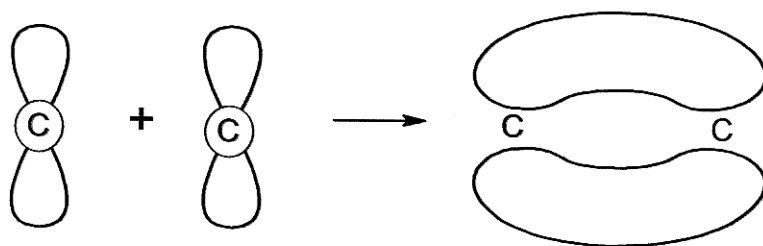
The Molecular Orbitals of Ethene:
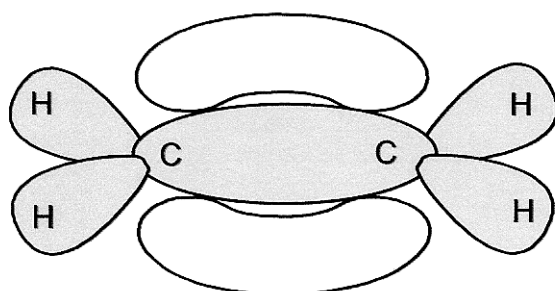
Formation of σ-bonds between H s-orbitals and C sp^2 hybrid orbitals:

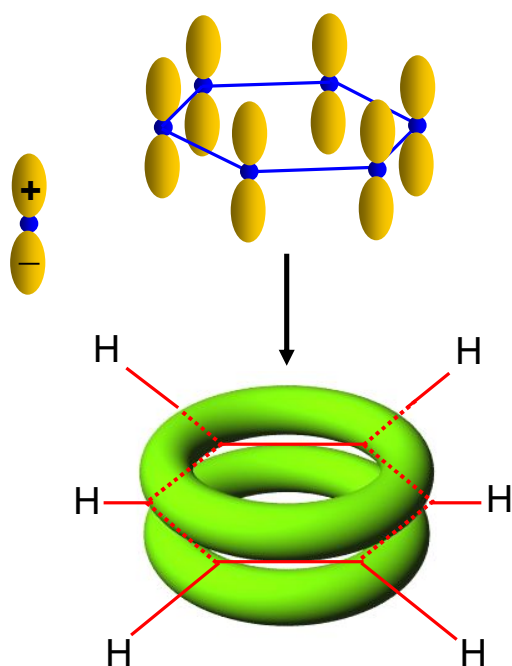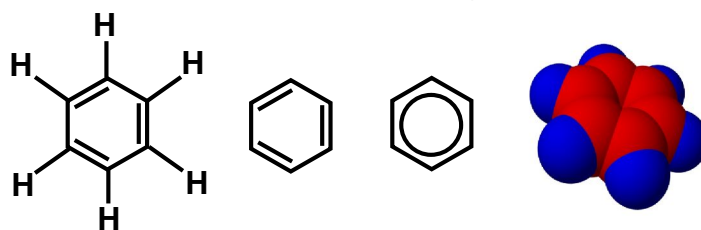Formation of σ-bonds between C sp^2 hybrid orbitals:

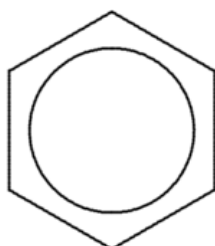Formation of π-bonds between C p-orbitals:

Bonding in benzene

Benzene (C_6H_6) is the most basic **arene** from which many other aromatic compounds are derived. Arenes are hydrocarbons with ring-systems containing **delocalised pi-electrons**. They are not to be confused with cycloalkanes or cycloalkenes which do not have delocalised electrons. **Aromatic compounds** are compounds that contain ring-systems of delocalised electrons and include the arenes and their derivatives. Aromatic compounds were so-named because many of these compounds have distinctive aromas.

There are different ways of representing the structure of benzene:

In benzene **six C atoms** are joined together in a symmetric hexagonal ring. Each of these 6 C atoms is joined to its two neighbours by σ-bonds between sp^2 hybid orbitals. The third lobe of each **sp^2 hybrid** orbital is σ-bonded to the 1s orbital of a H atom. This leaves one p orbital unaccounted for on each C atom. The lobes of this orbital are perpendicular to the plane of the ring, one above and the ring and one below. The lobes of these p-orbitals overlap sideways on to form π-bonds with those on the neighbouring C atoms. However, since each p-orbital contains a single electron, this means that there are only 6 electrons to form 6 covalent bonds between all the C atoms. Clearly this can not happen in the normal sense. There are not enough electrons to fill the resultant **molecular orbital**. The result is that the p-electrons become **delocalised**, so that they are free to move about the ring. The result is a **delocalised π-electron ring system**.

In exams, draw benzene using the skeletal formula on the right. Examiners may not like to see it drawn with alternating single and double bonds!

To summarise, there are different approaches or models of covalent bonding, of which the quantum mechanical calculations of the molecular orbital approach is the most accurate, the most universal (applying in principle to any molecule) and the most powerful for making predictions. You may also be familiar with 'dot-and-cross' models which enable us to predict bonding by assuming that atoms complete a stable octet (noble gas configuration of electrons in their outer or valence shells). This is a powerful tool for predicting bonding in many s and p-block compounds, but fails to explain why, for example, the O_2 molecule has two unpaired non-bonding electrons, or why some molecules are 'electron-deficient' such as certain compounds of boron and aluminium. Indeed, bonding in boron compounds is often very unusual and not explainable by these simpler approaches. All these anomalies can, in principle at least, be predicted by quantum-mechanical molecular orbital theory. However, all these approaches, include MO theory, require approximations.

In polyatomic molecules, Schrodinger's wave equation simply becomes too complex to solve exactly. however, the area of **computational chemistry** is developing increasingly reliable methods for using modern computers to make fairly accurate predictions of bonding. This approach ahs even succeeded in predicting the bonding in some large biological macromolecules, involving thousands of electrons and nuclei! Computational chemistry may use the LCAO approach, combining atom-like wave-functions to create MOs, or it may use quite different functions, such as Gaussian functions, to describe electron densities, still with accurate results and often with a reduction in computation. Electron spin must be incorporated, and instead of orbital wavefunctions, computational chemistry make use of **spinorbitals**, functions combining the orbital wave function and the spin wave function to give a more complete description of the electrons.

Metallic Bonding

Metallic bonding has been covered in the introductory article on metals. We shall review two different models of metallic bonds here. One approximate, but very useful, way to understand metallic bonding is illustrated below. We can think of a metal crystal as consisting of metal atoms in which the valence or bonding electrons have in some sense detached from the atoms, leaving behind the positively charged ion cores. These ion cores form a rigid **lattice**, in which their movement is greatly restricted, whilst the electrons form a '**sea of electrons**' surrounding the ion cores and binding them together by electrostatic attraction between the positive cores and the negative electrons. The electrons are free to move around the entire lattice, they are said to be **delocalised**. Their mobility can explain why metals conduct heat and electricity so well – the electrons are free to move, and since they carry both electric charge and thermal energy (as kinetic energy) they can carry these energies around the metal with them. In a sizeable piece of metal, there are many microscopic metal crystals fused together, but the electrons can move freely from crystal to crystal, and even from one piece of metal to another piece in physical contact. The electrons behave like a very sticky, very strong and highly viscous 'wet glue', holding the ions together. In a wire the metal has been pulled out into a long thread. This is possible because the metal ions can slide past one-another, whilst still embedded in the electron glue (rather like ball-bearings in toffee or very thick treacle). If we apply a voltage (potential difference) across the two ends of the wire then the electrons will drift from the negative terminal, which repels them (like charges repel) toward the positive terminal (unlike charges attract) and may enter other components of the circuit, flowing around it quite freely (but occasionally bumping into one-another or into nuclei and losing some of their kinetic energy as heat as the circuit heats up).

Note that in this model, the delocalised electrons set-up non-directional bonds – unlike covalent bonds we can not represent them as sticks, because the bonding acts in all directions. This is also why metals are not brittle – the ions can be moved around without breaking rigid and fixed 'stick-like' bonds and so metals are highly malleable (can be beat into any shape) and ductile (can be drawn into wires). Indeed, gold is the most malleable and can be squeezed into a sheet only one atom thick without breaking! (It is hard to conceptually visualise what happens to the individual metal crystals in such worked metals.)

1. Free or delocalised electron in 'electron sea'

2. Metal ions vibrate around fixed positions
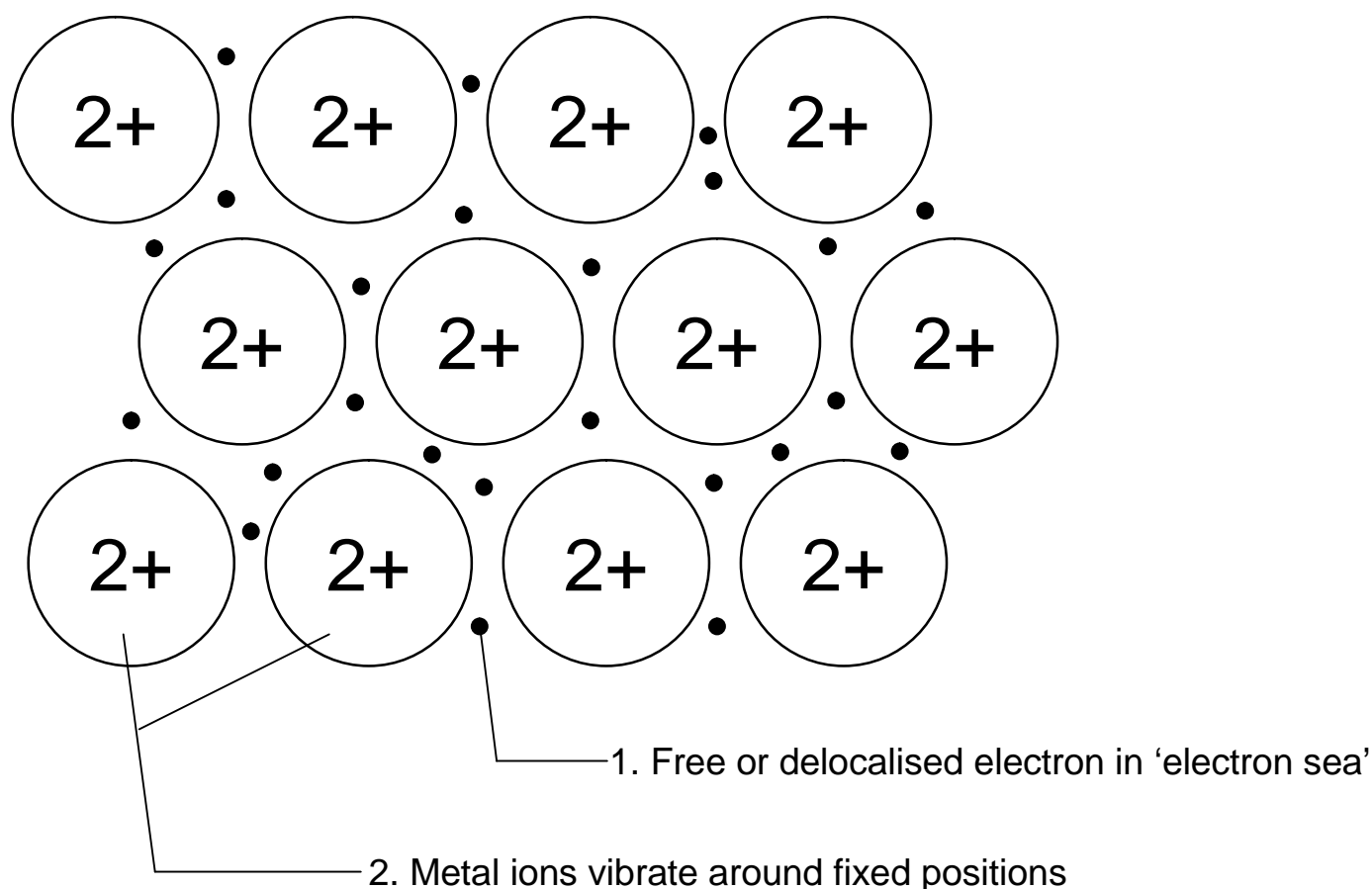
Above: a model of a metal with two valence electrons, such as calcium (Ca) or zinc (Zn). these two electrons become delocalised, leaving behind the 2+ ion cores in their fixed positions. Note: do not think of these ion cores too literally as 'ions' the electrons are still present and the metal contains atoms rather than ions proper.

The electron configuration of calcium is: [Ar] $4s^2$, and the metal loses these two electrons readily, forming a stable noble-gas octet (the argon configuration), The electron configuration of zinc is: [Ar] $3d10$ $4s^2$ and zinc tends to lose its two 4s electrons, leaving the complete (and therefore stable) 3d-shell intact.

A metal like sodium, which has only one valence electron to contribute to bonding has weaker metallic bonding than calcium, and so is a softer metal with a lower melting/boiling point. Iron, on the other hand, contributes three electrons per atom to the electron pool or sea and so is harder and stronger than calcium, with a higher meting/boiling temperature.

An alternative (or perhaps complementary) approach is to think in terms of **molecular orbitals**. The delocalised electrons are really occupying huge molecular orbitals which cover all the atoms in the crystal (if not the metal body). In this way, metallic bonding is really a special type of polyatomic (or multi-centre) covalent bonding. It is not too dissimilar to the metallic bonding in graphite, or to the delocalisation of electrons in benzene and conjugated alkenes, except that is occurs in three dimensions and over many more atoms.

What happens when we combine so many atomic orbitals into a molecular orbital? The result is a group of many molecular orbitals that are so similar in energy, so closely-spaced, that they form continuous bands. This is **band theory**. (See the article on metals for a fully description of band theory). If these bands are not full, as the valence band generally is not, then the electrons are free to move up and down within this band, by gaining or losing only small amounts of energy, and so these electrons can carry electrical charge and thermal energy, perhaps not so much by drifting through the metal under the guiding influence of a potential difference, but by oscillations or waves of energy that can pass from one end of the metal to the other.

A Unified Theory of Bonding?

We have now seen that ionic and covalent bonding are really opposite ends of a continuous spectrum. We have also seen that metallic bonding is really a special case of covalent bonding (though in some ways it is like ionic bonding, being non-directional). In reality, bonds formed between atoms in different molecules can have a variable amount of ionic, covalent and metallic character, although in some cases they are much more of one than the others.

This mixed nature of bonds can be represented on a triangular chart:

(Based on Fig. 5.11 of Mackay and Mackay, 1981)