The electronic structure of atoms

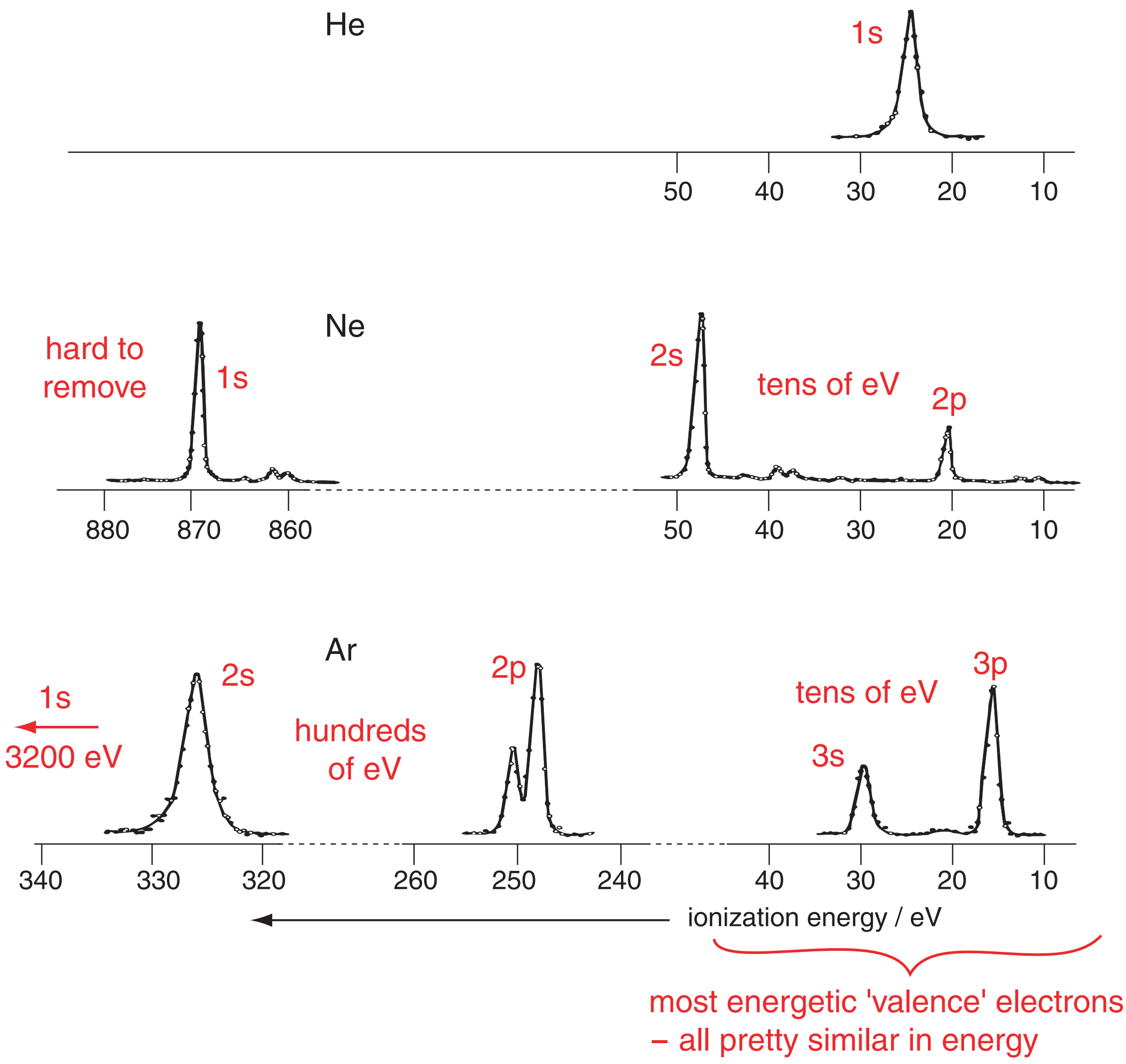
The chemical reactivity of any species be it atom, molecule or ion, is due to its electronic structure. For example, fluorine is incredibly reactive, forming compounds with all but three of the elements whereas the fluoride ion, with one extra electron making it isoelectronic with neon, is much less reactive and has a completely different chemistry.

Our goal in this part of the course is to gain an understanding of the electronic structure of molecules and to see how this helps in predicting the shapes of molecules and the outcome of chemical reactions. The simplest way to predict the energy levels that are present in a molecule is to combine the energy levels of the constituent atoms. Hence we first look at the electronic structure of the atom.

Energy levels and photoelectron spectroscopy

Information about the electronic structure of atoms can be gained from a technique called *photoelectron spectroscopy*. In this technique, the sample is bombarded with high energy X-ray photons of known energy which knock out electrons from the sample. By analyzing the energies of the emitted electrons, it is possible to deduce the energy they possessed in the atom.

Shown below are the photoelectron spectra of helium, neon and argon.



When helium atoms are bombarded with high energy X-ray photons, only electrons of one energy are emitted. This tells us that both the electrons in helium have the same energy. In the spectrum of neon, there are three main peaks – one around 870 eV which corresponds to the first shell electrons being removed and two peaks in the 20-50 eV region. This tells us that there are electrons with two different energies in the 2nd shell. In the argon spectrum, there is one peak around 3200 eV (not shown on the above spectrum), two main peaks in the hundred of eVs, and two in the tens of eV. The photoelectron spectra show that there are further subdivisions of energy levels within the main energy shells. You will probably already be familiar with these these energy levels and how they are denoted. The different peaks in the photoelectron spectra correspond to removing electrons from these different shells.

eg for Ar denote the electronic structure as

$1s^2 \quad 2s^2 \; 2p^6 \quad 3s^2 \; 3p^6$

small differences

large differences in energy

Whilst there is a huge difference in energy between different energy shells (*i.e.* between the 1s, 2s and 3s electrons), there is a much smaller energy difference between the subdivisions in each shell (*i.e* between the 2s and 2p or between the 3s and 3p electrons.

Orbitals and Quantum Numbers

The electrons in atoms are said to occupy different *orbitals*. We shall see exactly what an orbital is a little later, but for the moment we can think of it as an energy level. Any one orbital can accommodate two electrons. An atom has one 1s orbital and this can accommodate two electrons. Similarly, the 2s orbital can occupy two electrons. There are *three* 2p orbitals, all of equal energy and each can hold two electrons. Orbitals that have the same energy are described as *degenerate*. The d orbitals have a five-fold degeneracy so, for example, there are five 3d orbitals of the same energy.

In order to distinguish between atomic orbitals, we need to describe *three* things: which ‘shell’ it is in, whether it is an s, p, d, or f orbital and then which one of the three p orbitals or the five d orbitals or the seven f orbitals it is. Each of these things is expressed by a *quantum number*.

What shell we are referring to is denoted by the **principal quantum number**, n.

n takes integral values 1,2,3,4, and so on
For a one electron stsyem, the value of n alone determines the energy of the electron.

Whether we are referring to an s, p, d, or f (or g, h, *etc.*) is denoted by the **angular momentum quantum number**, l (sometimes called the *azimuthal* quantum number).

l can take integer values 0, 1, 2, ... but the particular value it takes depends on the value of n.

l takes integral values from 0 up to $(n - 1)$

The value of l determines the orbital angular momentum of the electron:

$$\text{angular momentum} = \hbar\sqrt{l(l+1)}$$

$$\text{where } \hbar = \text{Planck's constant}/2\pi$$

We can think of this angular momentum as being the momentum of the electron as it moves around the nucleus. We shall see later that orbitals with different values of l also have different shapes.

Each value of l has a different letter associated with it:

$l =$	0,	1,	2,	3,	4,	5,	. . .
	s	p	d	f	g	h,	. . .

When $n = 1$, the only value for $l = 0$. This is the 1s orbital.

When $n = 2$, l can be 0, or 1 which correspond to the 2s and 2p orbitals.

When $n = 3$, $l = 0$, 1, and 2 which correspond to the 3s, 3p and 3d orbitals.

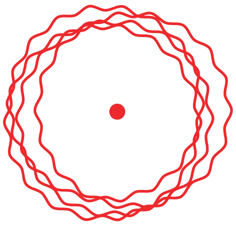
The third quantum number needed to label an orbital is the **magnetic quantum number**, m_l.

m_l takes integer values from $+l$ to $-l$ in integer steps.

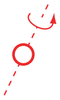
m_l tells us something about the orientation of the orbital.
(Specifically it tells us the component of the angular momentum on a particular axis.)

For an s orbital ($l = 0$):	$m_l = 0$ only	so just one s orbital for each value of n
For a p orbital ($l = 1$):	$m_l = +1, 0, -1$	so three p orbitals with the same value of n
For a d orbital ($l = 2$):	$m_l = +2, +1, 0, -1, -2$	so five d orbitals with the same value of n

The three quantum numbers, n, l and m_l define the orbital an electron occupies but if we are trying to label an electron, there is one further thing we need to know. We said earlier that the electron has angular momentum associated with it as it moves in its orbital. It also has its own *intrinsic* angular momentum. Whereas the *orbital* angular momentum might be thought of as the angular momentum the electron has as it moves about in the orbital, this intrinsic angular momentum might be thought of as the angular momentum the electron has due to it spinning about an internal axis (although bear in mind this is just an analogy).



orbital angular momentum



spin angular momentum

In an analogous manner to the orbital angular momentum which has its magnitude defined by l and its orientation defined by m_l, there are two quantum numbers for the spin angular momentum. The magnitude of the spin angular momentum is defined by the quantum number s and its orientation is defined by m_s.

The value of s for an electron is fixed: $s = \frac{1}{2}$. This means that *all electrons possess the same intrinsic angular momentum.*

The values m_s can take are integer steps from $+s$ to $-s$ which means the angular momentum can be oriented in one of two ways: $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. For historical reasons, we usually denote the spin of the electron by an arrow:

$$\uparrow \text{ for } m_s = +\tfrac{1}{2} \qquad \downarrow \text{ for } m_s = -\tfrac{1}{2}$$

[Note: this is exactly analogous to the spin of a nucleus in NMR. There the spin is given the symbol I. For ^{1}H, $I = \frac{1}{2}$ and this spin can be oriented in two ways, ↑ or ↓, corresponding to m_I values of $+\frac{1}{2}$ and $-\frac{1}{2}$. For deuterium, ^{2}H, $I = 1$, there are 3 ways $(2I + 1)$ of orienting the spin corresponding to m_I values of $+1$, 0 and -1.]

Summary

To specify the state of an electron in an atom (to be precise a one-electron atom or ion, see later) we need to specify four quantum numbers:

n (specifies the energy)

l (specifies the magnitude of the orbital angular momentum)

m_l (specifies the orientation of the orbital angular momentum)

these 3 quantum numbers define the orbital the electron is in

m_s (specifies the orientation of the spin angular momentum)

This tells us about the spin of the electron

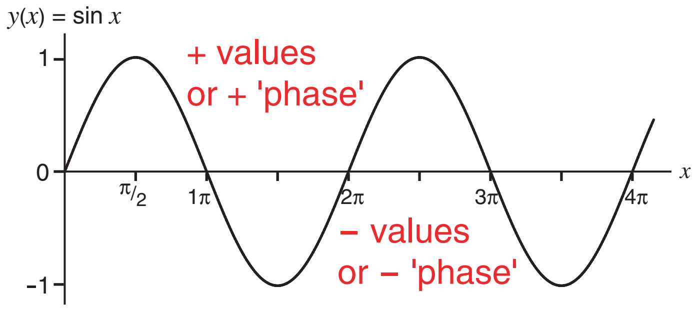
Note that there is no need to specify s since it is the same for all electrons ($s = \frac{1}{2}$).

It is a fundamental observation that no orbital (defined by n, l, and m_l) may contain more than two electrons, and if there are two, then they must have opposite spin ($m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$).

It therefore follows that any electron in an atom has a *unique set* of four quantum numbers. This is one form of the Pauli Principle.

A closer look at orbitals – wavefunctions

Many phenomena – such as the swinging of a pendulum or the change in the global population – can be described by mathematical functions. To describe the ripples on the surface of water, for example, we could use a function based on a sine wave; $y(x) = sin(x)$.



+ values
or + 'phase'

– values
or – 'phase'

A function is a mathematical tool that we can feed a number into and it will give out a new number. In this case, if we put in a value for x, say $(\pi/2)$, the sine function returns the value +1.

Quantum mechanics provides us with the best understanding of the electronic structure of atoms and molecules. The results from a quantum mechanical analysis reveal that the properties of an electron can also be described by a mathematical function called a *wavefunction*, given the Greek symbol ψ (psi).

ψ is a function of coordinates, for example x, y, & z
hence we write $\psi(x, y, z)$

We have seen that the properties of an electron depend on which particular orbital it occupies and that the orbital is defined by the quantum numbers n, l and m_l. An orbital is a wavefunction (specifically an orbital is a one-electron wavefunction, as we shall see later). A different function is needed for each orbital and each function is defined by the three quantum numbers n, l and m_l. We can write our wavefunction as:

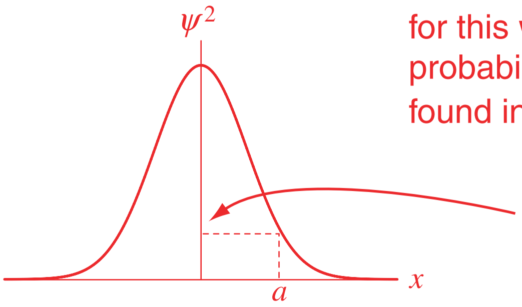
$$\psi_{n,l,m_l}(x, y, z)$$

which says that the wavefunction is a function of position coordinates x, y and z but that there are different wavefunctions defined by the quantum numbers n, l and m_l.

Once the wavefunction of the electron is known, it is possible to calculate useful information from it such as the position or momentum of the electron.

The Born Interpretation of the Wavefunction

One physical interpretation of the wavefunction, ψ , is that ψ^2 (or, more precisely ψ multiplied by its complex conjugate, ψ^*, since ψ can be a complex number) gives a measure of the probability of finding the electron at a given position.



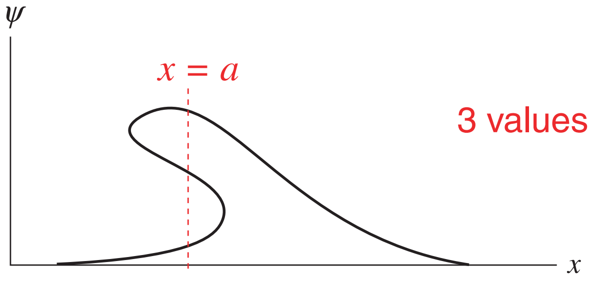
for this wavefunction, maximum probability of electron being found in region around $x = 0$

probability of being at $x = a$ (or technically between $x = a$ and $x = a + \delta x$)

The idea that we can only talk about the *probability* of finding the electron at a given position is in contrast to classical mechanics in which the position of an object can be specified precisely.

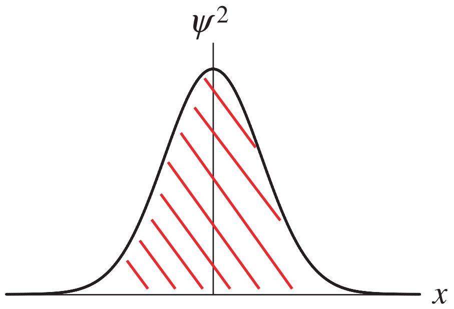
The Born interpretation imposes certain restrictions on just what is acceptable for a wavefunction:

- ψ must be single-valued, that is at any given value of x there can only be one value of ψ since there can only be one probability of finding an electron at any one point.

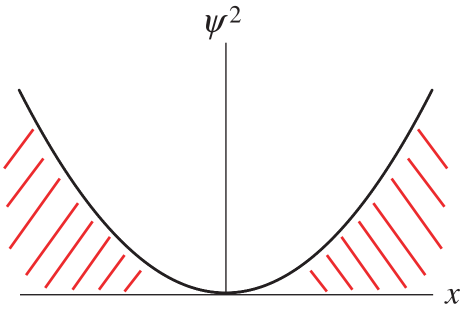


3 values of electron begin at x = a
Not allowed!

- ψ must not diverge; the total area under ψ^2 for all values of x must be finite since it is the probability of finding the electron anywhere.



shaded area = probability of
electron being found in all space



infinite area – no good!
must be finite

Each wavefunction has a given energy associated with it, for example the wavefunction for the 1s orbital has a different energy from the 2s etc. The way to calculate wavefunctions and the energies associated with them is to use Schrödinger's equation.

The Schrödinger Equation

In general, the Schrödinger Equation may be written:

$$\hat{H}\,\Psi = E\,\Psi$$

constant (the energy associated with the wave function)

same wavefunction

wavefunction

operator

To understand this equation, we need to be clear on the distinction between an operator and a function:

A FUNCTION is a device which converts a NUMBER to another number.

eg the function 'sine'; sin $\frac{\pi}{2}$ converts number $\frac{\pi}{2}$ ⟶ number +1

An OPERATOR is a device which converts a FUNCTION into another function.

eg $\dfrac{\mathrm{d}}{\mathrm{d}x}$ converts function sin$x$ ⟶ function cos$x$

$$\frac{\mathrm{d}\,\sin x}{\mathrm{d}x} = \cos x$$

The Hamiltonian operator, $\hat{H}$, is constructed so as to give us the energy associated with the wavefunction ψ.

'Solving' the Schrödinger equation means finding a suitable function, ψ, that when we operate on it using the operator $\hat{H}$ we get *the same function*, ψ , multiplied by a constant E. The constant E is the energy associated with the particular wavefunction, ψ.

The energy E is composed of both potential energy (*i.e.* 'stored up' energy for example by interaction with an electric field) and kinetic energy (*i.e.* due to its movement). The Hamiltonian operator contains parts to work out both these components.

For the hydrogen atom, the Hamiltonian operator is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 \qquad - \frac{e^2}{4\pi\varepsilon_0 r}$$

this part gives the kinetic energy associated with the electron

this part gives the potential energy associated with the electron

$$\nabla^2 \text{ (pronounced `del-squared')} = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

So the Schrödinger equation for the a hydrogen atom could be written:

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \frac{e^2\psi}{4\pi\varepsilon_0 r} = E\psi$$

where $\hbar$ = Planck's constant, h, divided by 2π
m_e = mass of the electron
ε_0 = vacuum permittivity
e = elementary charge
r = distance between nucleus and electron = $\sqrt{x^2 + y^2 + z^2}$.

Solving the Schrödinger Equation for the Hydrogen Atom

We can solve the Schrödinger equation exactly for the hydrogen atom. There is not one unique solution but a whole series of solutions defined by the quantum numbers we have already met. Each solution has a different mathematical form (these are listed for reference in the appendix).

In general, these solutions to the Schrödinger equation for a one-electron system may be denoted:

$$\Psi_{\underbrace{n,\, l,\, m_l}_{\text{quantum numbers}}}(x, y, z)$$

and its energy, E_n, is given by:

$$E_n = -\frac{m_e e^4}{8\,\varepsilon_0^2\, h^2} \times \frac{z^2}{n^2}$$

nuclear charge =1 for H atom

principal quantum number

a constant for the particular orbital defined by *n* only

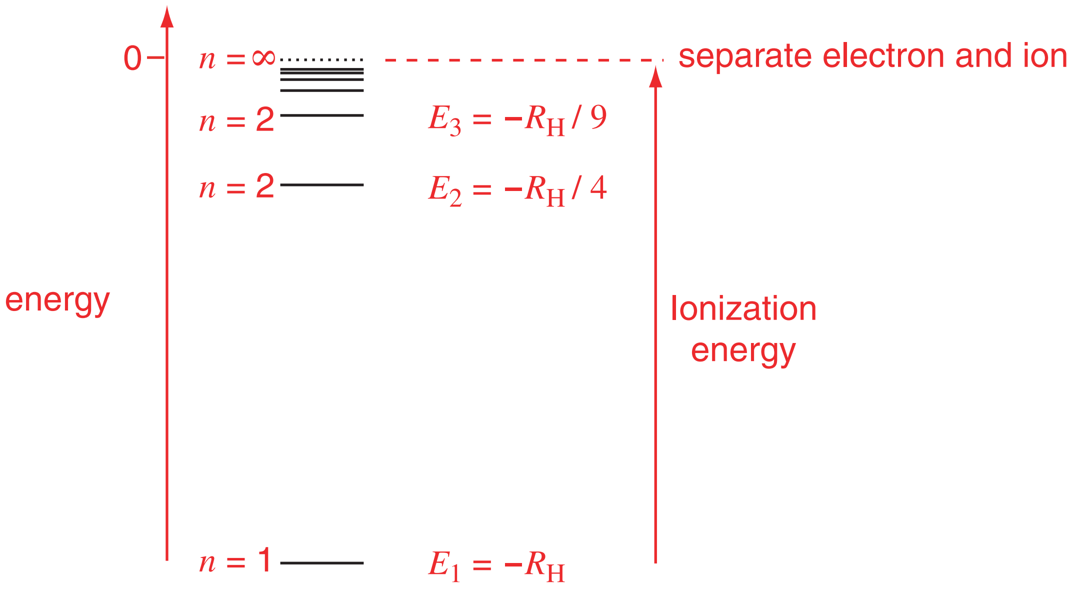
This is much more conveniently written as

$$E_n = -\,R_{\mathrm{H}} \times \frac{z^2}{n^2}$$

where R_{H} is the Rydberg constant whose value depends on the units used

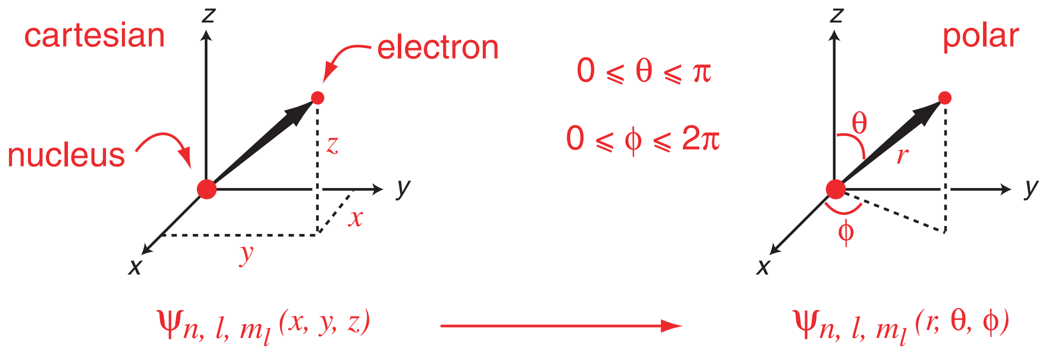
The first point to notice is that the energy of an orbital depends on n only. This means that the 2s and 2p orbitals have the same energy (that is, they are degenerate) and the 3s, 3p and 3d orbitals are also degenerate. We have already seen that this is not the case for multi-electron atoms where the 2s orbital is lower in energy than the 2p, for example.

The second point to notice is that the predicted energies are negative. As n gets larger, E_n tends towards zero. Zero energy corresponds to the electron being separated completely from the nucleus. The energy needed to promote the electron from the lowest energy level to zero energy is the ionization energy for the atom. The energy levels for the hydrogen atom, drawn to scale, can be represented:



Representing the Hydrogen Orbitals

Whilst it is possible to solve the Schrödinger equation exactly for a hydrogen atom, the actual mathematical form for the three-dimensional wavefunctions rapidly becomes complicated. In this course, we will use a variety of graphical means to represent the solutions. In order to do this, it is much more convenient to use polar coordinates rather than Cartesian coordinates to specify where the electron is relative to the nucleus.



One of the advantages in converting the wavefunction to polar coordinates is that ψ can then be written as the product of two functions, each of which can be represented separately.

$$\psi_{n,\,l,\,m_l}(r,\theta,\phi) = \underbrace{R_{n,\,l}(r)}_{\substack{\text{radial part of wavefunction}\\ \text{defined by } n \text{ and } l\\ \text{function of } r \text{ only}}} \times \underbrace{Y_{l,\,m_l}(\theta,\phi)}_{\substack{\text{angular part of wavefunction}\\ \text{defined by } l \text{ and } m_l\\ \text{function of } \theta \text{ and } \phi \text{ only}}}$$

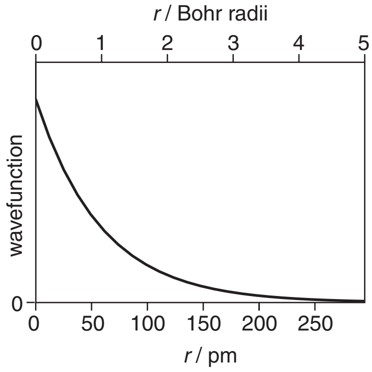
1s orbital

Shown below is a graph of the radial part of the 1s wavefunction as a function of the distance from the nucleus, r.

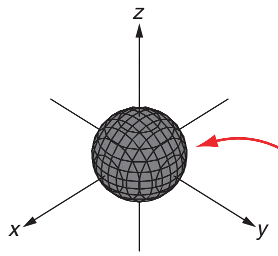
$\psi_{1s} \propto e^{-r}$

$(r \geqslant 0)$

$e^{-r} = \frac{1}{e^{r}}$

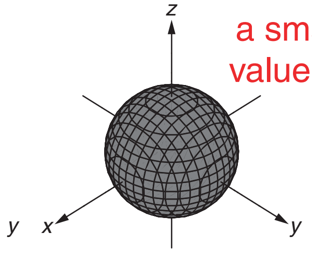


A 3-D plot shows how the wavefunction varies with angles θ and ϕ. For an s orbital, the wavefunction is independent of θ and ϕ and only depends on the radius from the nucleus. This means that all s orbitals are spherical.



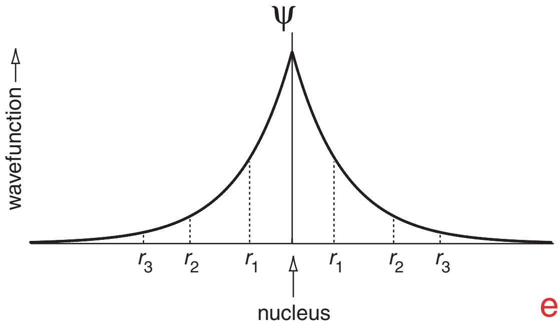
the surface shows
a particular value
of the wavefunction

surface with a
larger value of ψ



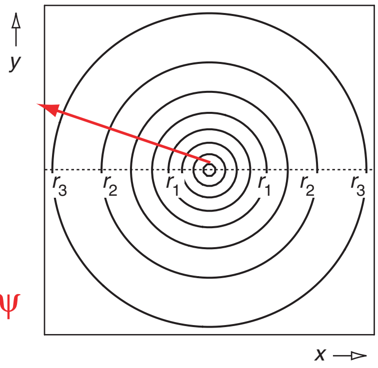
surface with
a smaller
value of ψ

One way to try and show how the value of the wavefunction varies at different positions is to draw a picture of a slice through the orbital in a given plane. A contour plot joins together regions of the same value of the wavefunction.

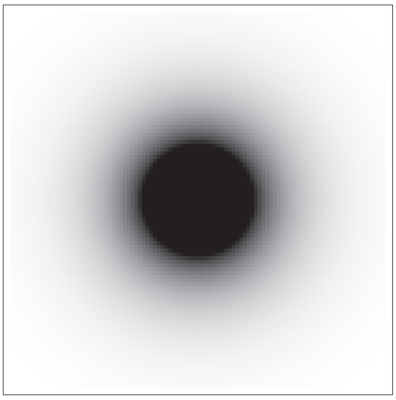


decreasing
values of ψ

equal values of ψ
along contours



Another way of representing the wavefunction is a *density plot*. Here, the more darkly shaded a region is, the greater the value of ψ.



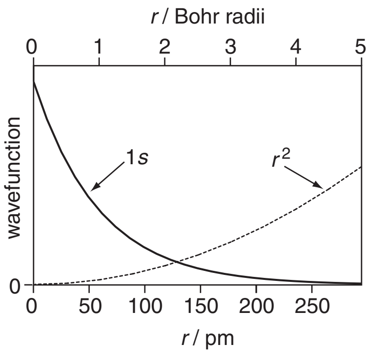
$\psi^2 \propto$ probability of
finding electron.

The darker the region,
the greater the probability

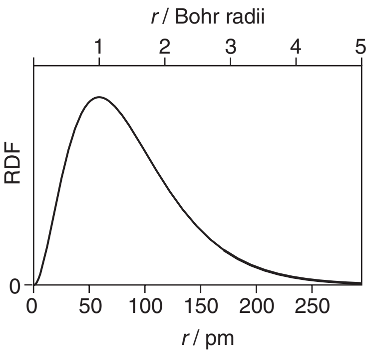
Finally, a further common way to represent the orbitals is to draw a graph showing the electron density at a set distance, r, from the nucleus, *summed over all angles*, θ and ϕ. This function known as the *Radial Distribution Function*, RDF, may be thought of as the sum of the electron density in a thin shell at a radius r from the nucleus. The volume of this shell goes up as r increases since the surface area of the shell increases.

$$\text{RDF} = [R(r)]^2 \times 4\pi r^2 \text{ i.e. } [R(r)]^2 \times \text{ surface area of sphere}$$

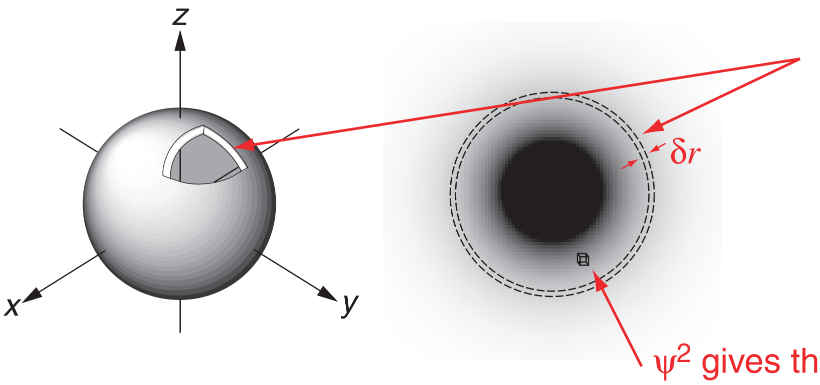
The graphs below show the wavefunction and the RDF for the 1s orbital.



product of ψ^2 x r^2
Hence reaches a maximum and then falls due to e^{-r} term



The radial distribution function and ψ^2 tell us different things. The RDF tells us the probability of finding an electron at a given radius, summed over all angles whereas ψ^2 tells us the probability of finding an electron at a given set of coordinates (either r, θ and ϕ or x, y, and z).



RDF gives probability of finding electron in a thin shell of thickness δr at radius r from the nucleus

ψ^2 gives the probability of finding electron in a tiny volume element δv at position x, y, z from the nucleus (or at position r, θ, ϕ)

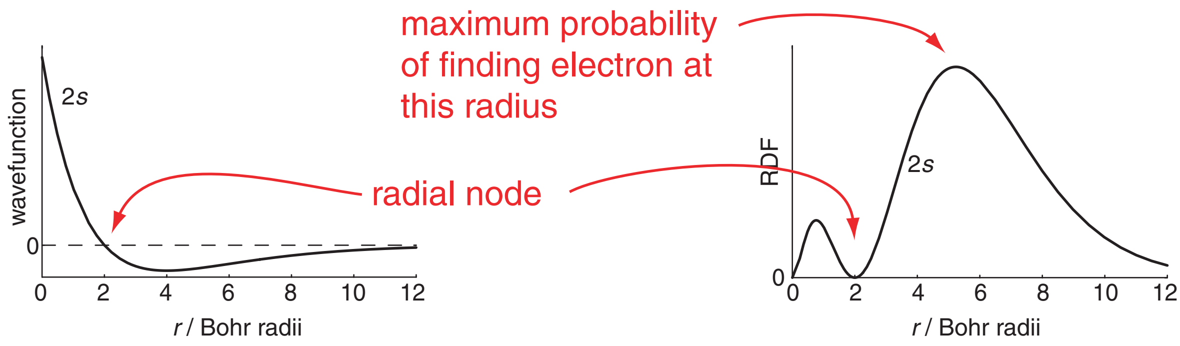
Note:

- ψ^2 for the 1s is greatest at the nucleus so this is the *position* (of tiny volume element) where is electron is most likely to be found.
- The Bohr radius, a_0, is the *radius* (tiny thin shell) at which the electron is most likely to be found.
- The radial distribution function is zero at the nucleus because of the r^2 term. (Essentially we are looking for the electron in a shell of zero volume.)

2s orbital

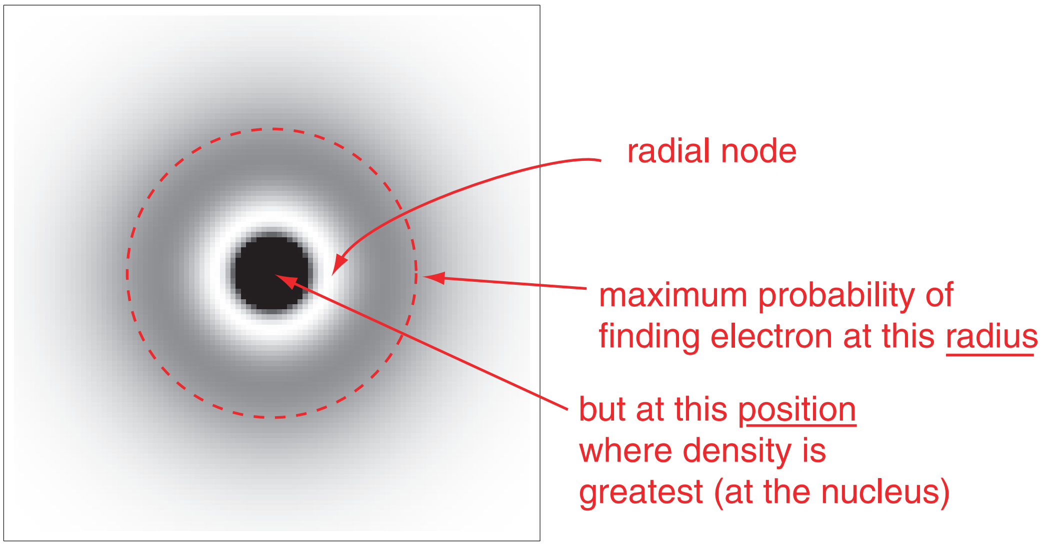
None of the wavefunctions for any s orbital contain any θ or ϕ terms; the value of ψ depends only on the distance from the nucleus, r. Consequently, *all* s orbitals have the same shape – they are all spherical.

However, the wavefunction for each s orbital is unique and each has a very different appearance. The wavefunction and the RDF for the 2s orbital are shown below.



Notice that the sign (or *phase*) of the wavefunction can be positive or negative. We shall see how this is important later, but this does not matter when we come to consider where the electron is since the probability of finding the electron is proportional to the *square* of the wavefunction.

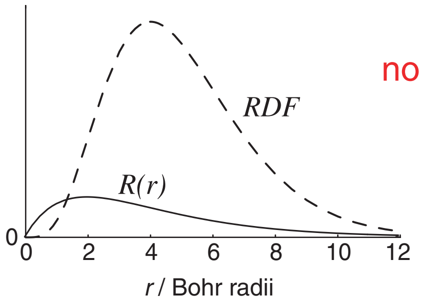
However, where the wavefunction changes sign from positive to negative, as it crosses the x-axis, there is a point at which $\psi = 0$. Such a position is called a *node*. This is clearly visible in the density plot, shown below.



[Note that the node is just a mathematical surface and therefore has no volume. It is meaningless to ask about the chance of finding an electron in any space with no volume. As soon as we specify a volume by saying it is a shell with a tiny thickness, there is then a *small* chance of finding the electron in that shell.]

2p orbitals

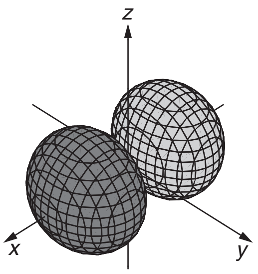
The radial part of the 2p orbitals does not depend on the value of m_l and so the radial parts for the p_x, p_y, and p_z are all the same.



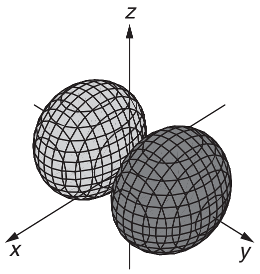
no radial nodes

The angular parts of p orbitals do depend on the value of m_l, which determines the way the orbital is oriented. This is best illustrated in the 3-D plots.

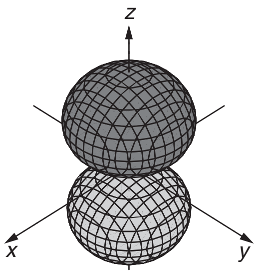
all p orbitals have one angular node



$2p_x$



$2p_y$



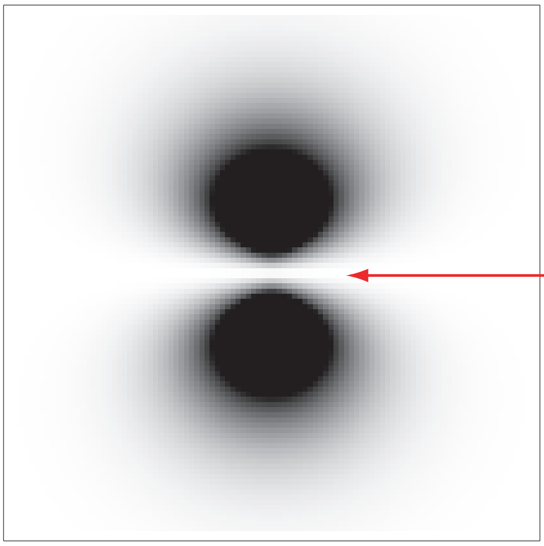
$2p_z$

angular node for φ = 90°
ie yz nodal plane

φ = 0°
xz plane

θ = 90°
xy plane

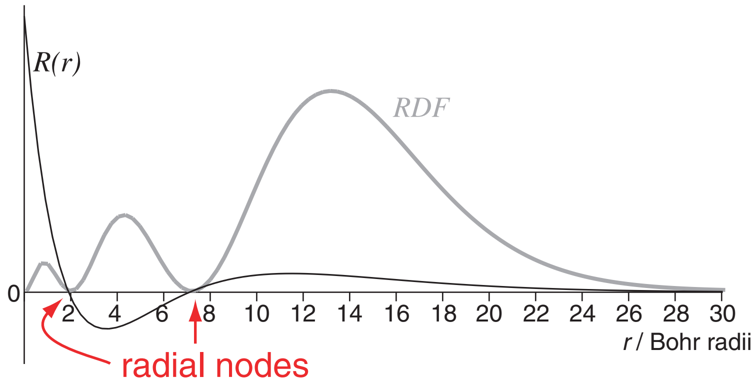
φ from x-axis
θ from z-axis

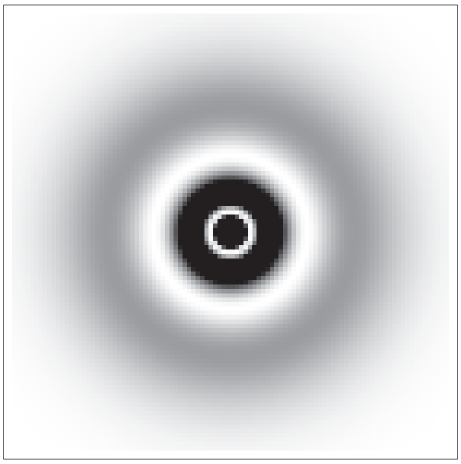


angular node

3s orbital

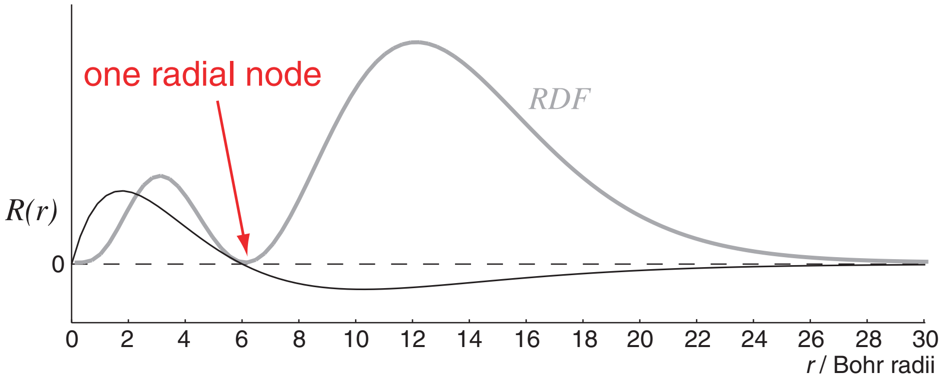
The radial part of the 3s orbital has two radial nodes.



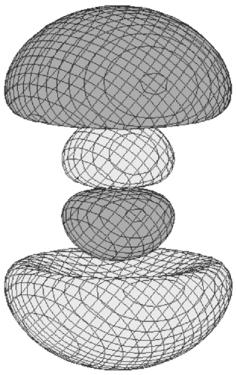


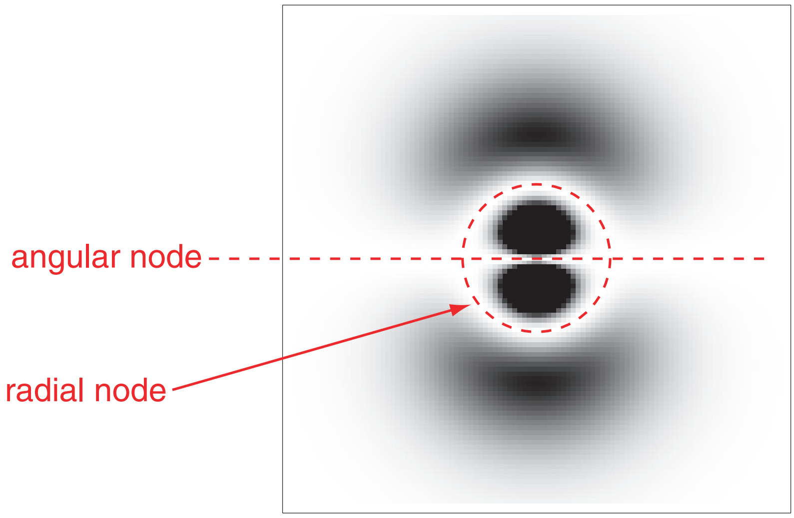
3p orbitals

In addition to the angular node common to all p orbitals, the 3p orbital also has a radial node.



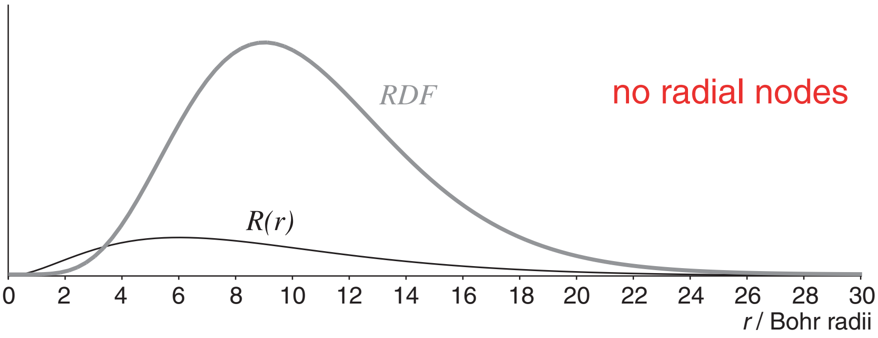
The radial and angular nodes of the 3p orbital are most clearly shown in the density and 3-D surface plots.

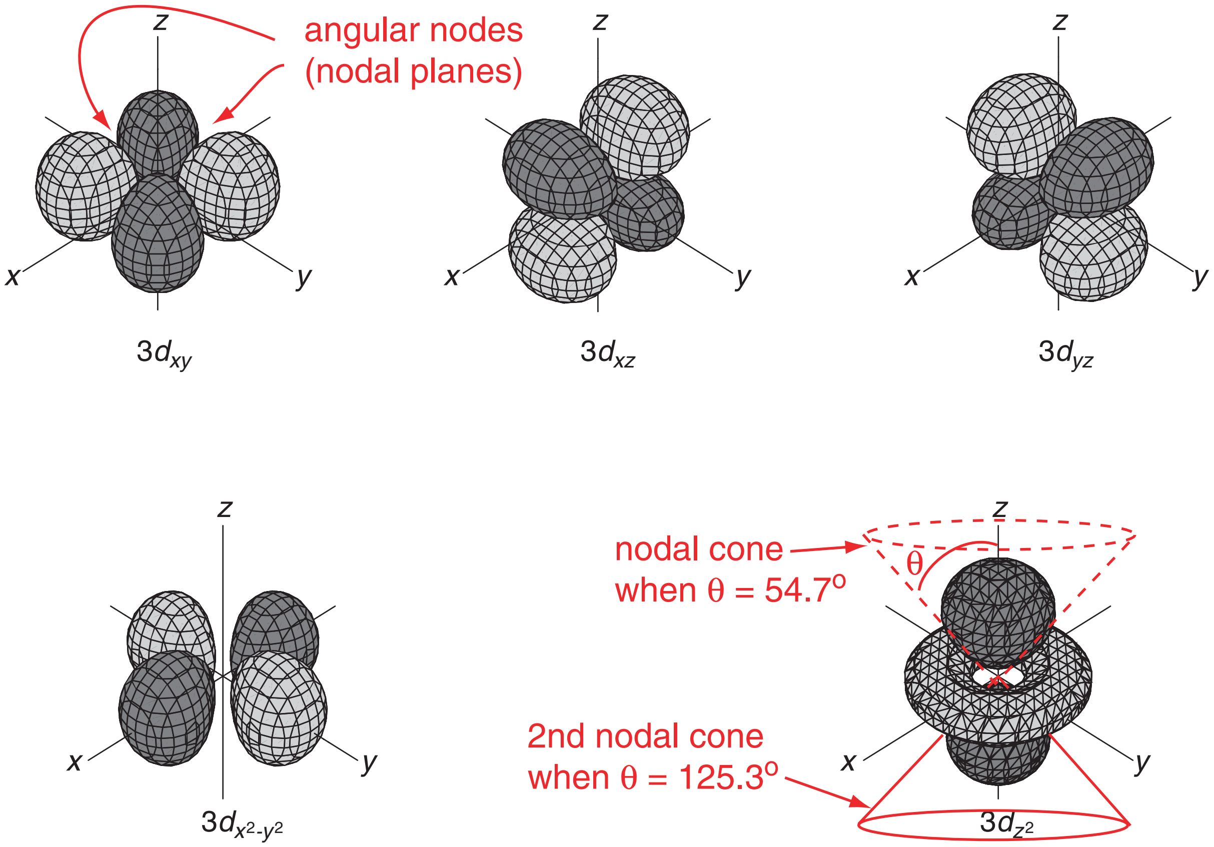




3d orbitals

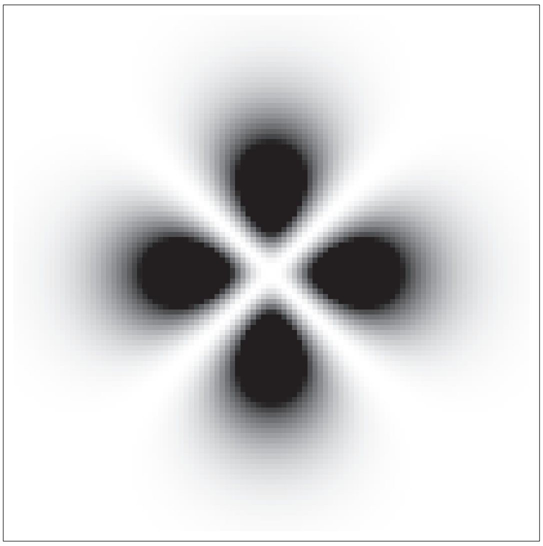
The radial parts of all five 3d orbitals are the same, but the angular parts depend on the values of m_l which determines the orientation of the orbital.



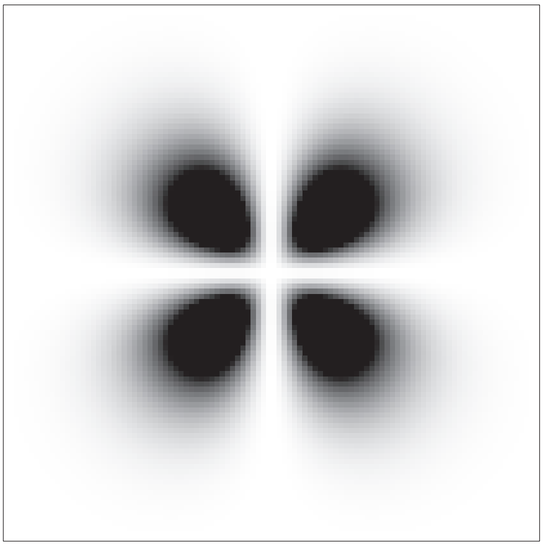


Each d orbital has two angular nodes. The angular nodes define planes for all the orbitals except the d_{z^2} for which the angular nodes are cones.

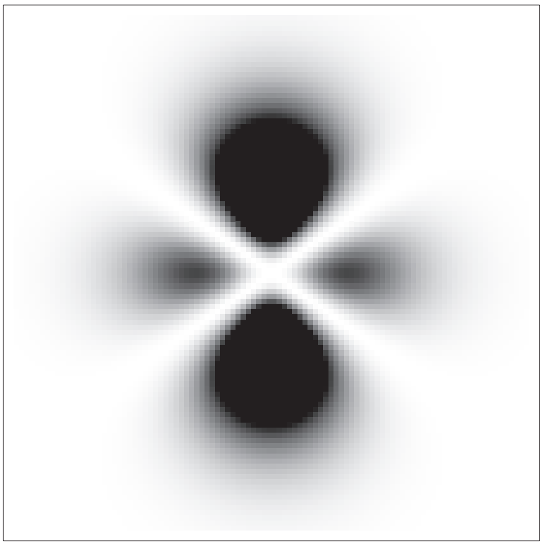
Shown below are the density plots for the 3d orbitals, taken through the specific planes.



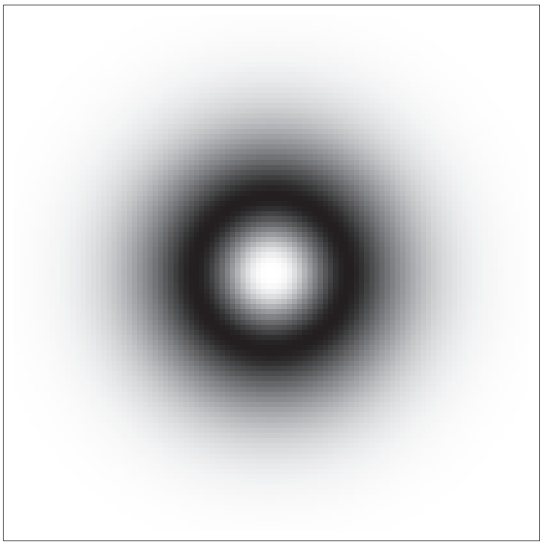
$d_{x^2-y^2}$ through xy plane



d_{xy} or d_{xz} or d_{yz}



d_{z^2} through xz pr yz plane



d_{z^2} through xy

Nodes

The total number of nodes in the hydrogen orbitals depends only on the principal quantum number, n.

total number of nodes = angular + radial = $n - 1$

Number of *angular* nodes = l i.e. all s orbitals have 0

p orbitals have 1

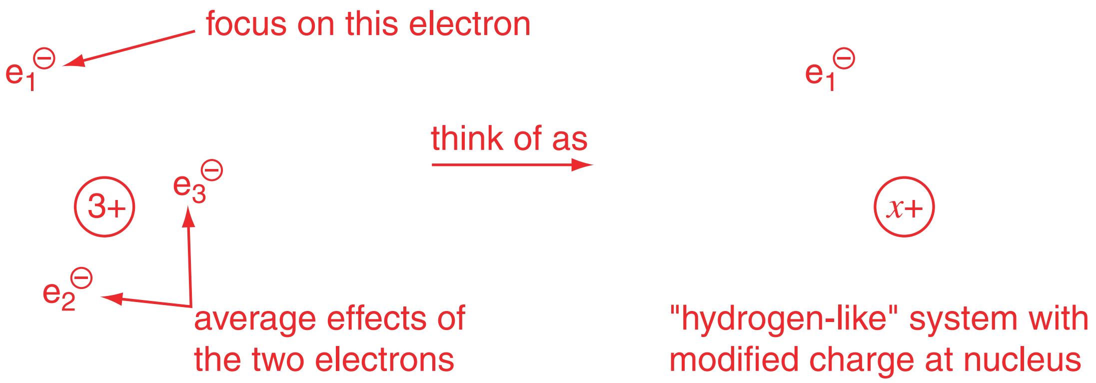
d orbitals have 2 etc

$\therefore$ Number of *radial* nodes = $n - 1 - l$

Building up multi-electron atoms using hydrogen orbitals

Whilst it is possible to solve the Schrödinger equation exactly for single electron systems this is not the case for multi-electron systems. For such systems, in addition to the attraction between the nucleus and electrons there is also repulsion between electrons. It is this added complication of electron-electron repulsion that makes it impossible to solve the Schrödinger equation for multi-electron systems. However, reasonably good approximations for the energies of the electrons in atoms can be made using the *orbital approximation*. This assumes that, from the point of view of one particular electron, the effect of all the other electrons can be averaged out to give a modified potential, centred on the nucleus.

As an example, take an atom of lithium which has three electrons. When working out the energy of the electron 1, we average out the effects of the other two electrons.



The orbital approximation assumes that the modified potential is spherically symmetric and centred on the nucleus. This means that the wavefunctions for each electron have the same form as those in hydrogen.

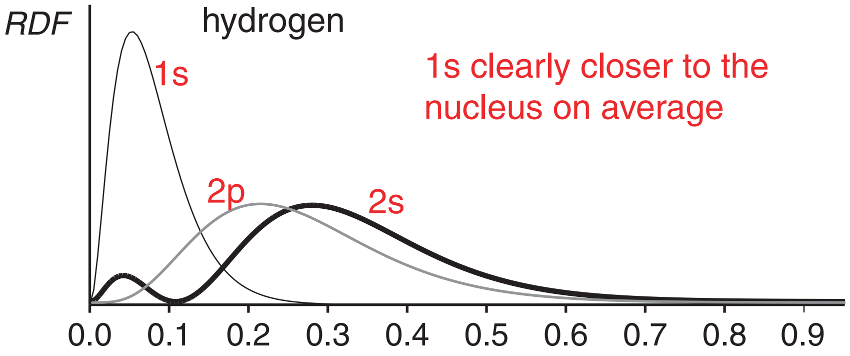
In the above example, electrons 2 and 3 are said to *screen* the effects of the nucleus from electron 1. Exactly how well electrons screen one another depends on which orbital they are in. For example, the 1s electrons in lithium screen off the nuclear charge felt by the electron in the 2s orbital rather well. In contrast, since the electron in the 2s orbital is on average further away from the nucleus than the 1s electrons, it has little effect on the nuclear charge experienced by the 1s electrons. This means the nuclear charge each electron experiences, the *effective nuclear charge*, Z_{eff}, is different for the different electrons.

1s electrons shield each other by about 30% of one proton's charge but are not really shielded by the 2s.

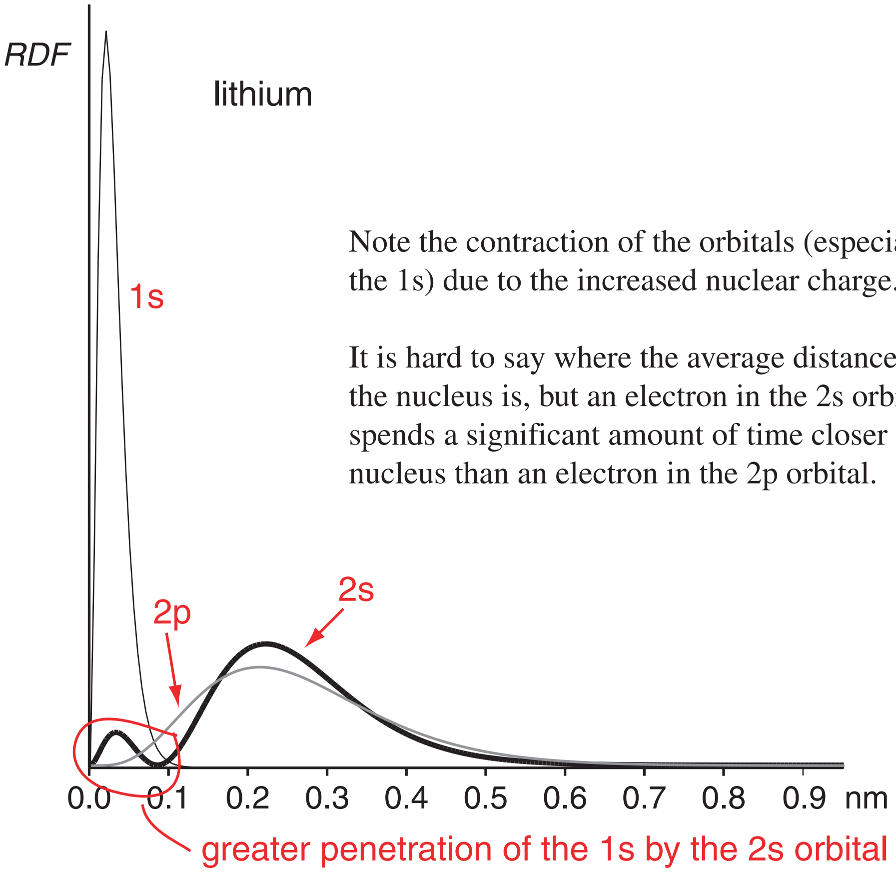
Instead of feeling a charge of +3, each 1s experiences a charge of about 2.7.

The two 1s electrons shield the 2s electron more fully; $Z_{\text{eff}}(2s)$ is around 1.3.

In hydrogen, the 2s and 2p orbitals have the same energy (as do the 3s, 3p and 3d *etc*). This is not obvious from looking at the radial distribution functions, but is perhaps not too surprising.



In multi-electron systems, such as lithium, orbitals which share the same principal quantum number but which differ in their orbital angular momentum quantum number are no longer degenerate. Inspection of the radial distribution functions for lithium 1s, 2s and 2p orbitals enables us to understand why the degeneracy is lost.

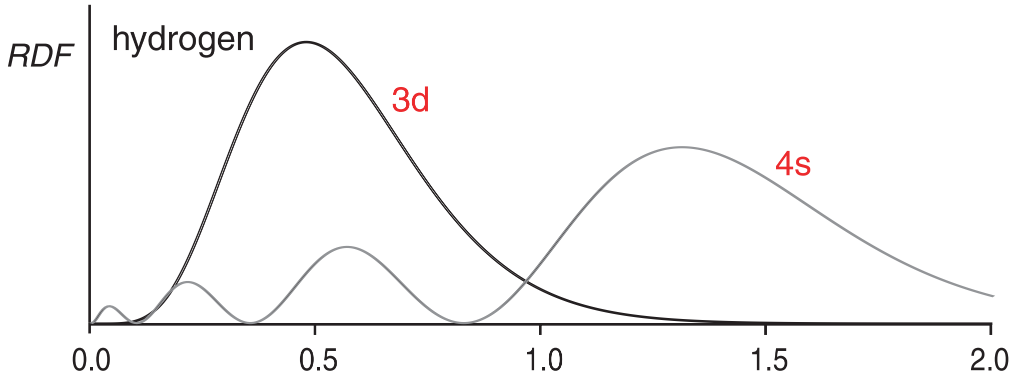


Note the contraction of the orbitals (especially the 1s) due to the increased nuclear charge.

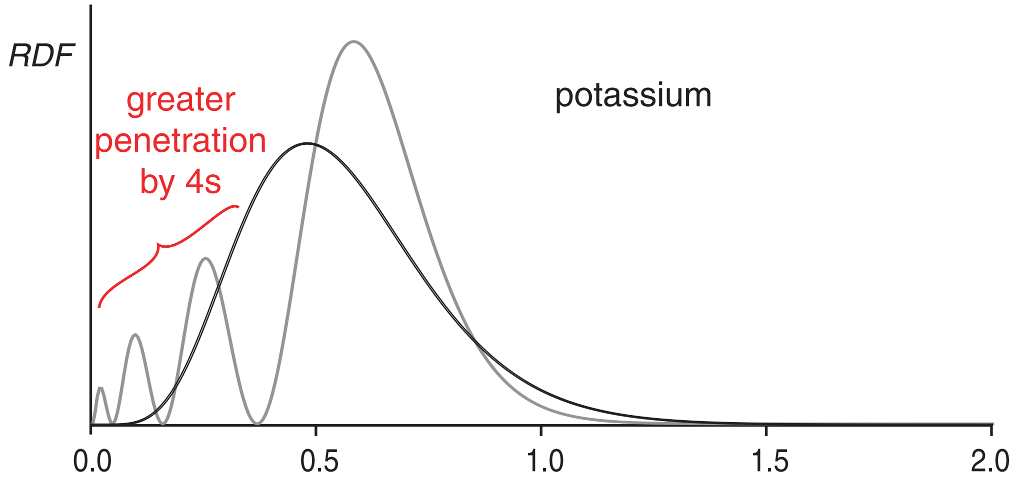
It is hard to say where the average distance from the nucleus is, but an electron in the 2s orbital spends a significant amount of time closer to the nucleus than an electron in the 2p orbital.

The 2s orbital is said to *penetrate* the 1s orbital to a greater extent than does the 2p orbital. This means it experiences more of the nuclear charge than the 2p orbital which in turn means that an electron in the 2s orbital has a slightly lower energy than the one in the 2p orbital. (Remember the greater the nuclear charge, the lower the energy: $E_n = -R_H Z^2/n^2$. Also the wavefunctions for s orbitals are all non-zero at the nucleus, in contrast to other orbitals.)

The effects of orbital penetration may become so pronounced that it becomes difficult to predict the energy order for orbitals in larger atoms. For example, in potassium and calcium, the 4s orbital is filled before the 3d orbital. Inspection of the radial distribution functions for the hydrogen 3d and 4s orbitals clearly indicates that if the electron is in the 4s orbital it is, on average, further from the nucleus.



However, in atoms like potassium, the greater nuclear charge contracts the orbitals and the penetration of the lower orbitals by the 4s orbital is sufficient to mean that this orbital is lower in energy than the 3d orbitals.



The exact ordering of energy levels in multi-electron atoms rapidly becomes complicated and impossible to predict:

For a hydrogen atom, the ordering of energy levels is:

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f \text{ etc.}$$

ie depends on n only

For lithium: $1s << 2s < 2p << 3s < 3p < 3d < 4s < 4p < 4d < 4f < 5s$ *etc.*

degeneracy now lost. Order still depends mainly on n but also on l.

For sodium: $1s << 2s < 2p << 3s < 3p < 4s < 3d < 4p < 5s$ *etc.*

4s lower than 3d (the same order as when fill up periodic table)

For potassium: $1s << 2s < 2p << 3s < 3p < 4s < 4p < 5s < 3d$ *etc.*

4s, 4p and 5s all lower than 3d

For Ca^+: $1s << 2s < 2p << 3s < 3p < 4s < 3d < 4p < 5s$ *etc.*

For Sc^{2+}: $1s << 2s < 2p << 3s < 3p < 3d < 4s < 4p < 5s$ *etc.*

K, Ca^+ and Sc^{2+} all isoelectronic but could not predict the ordering!

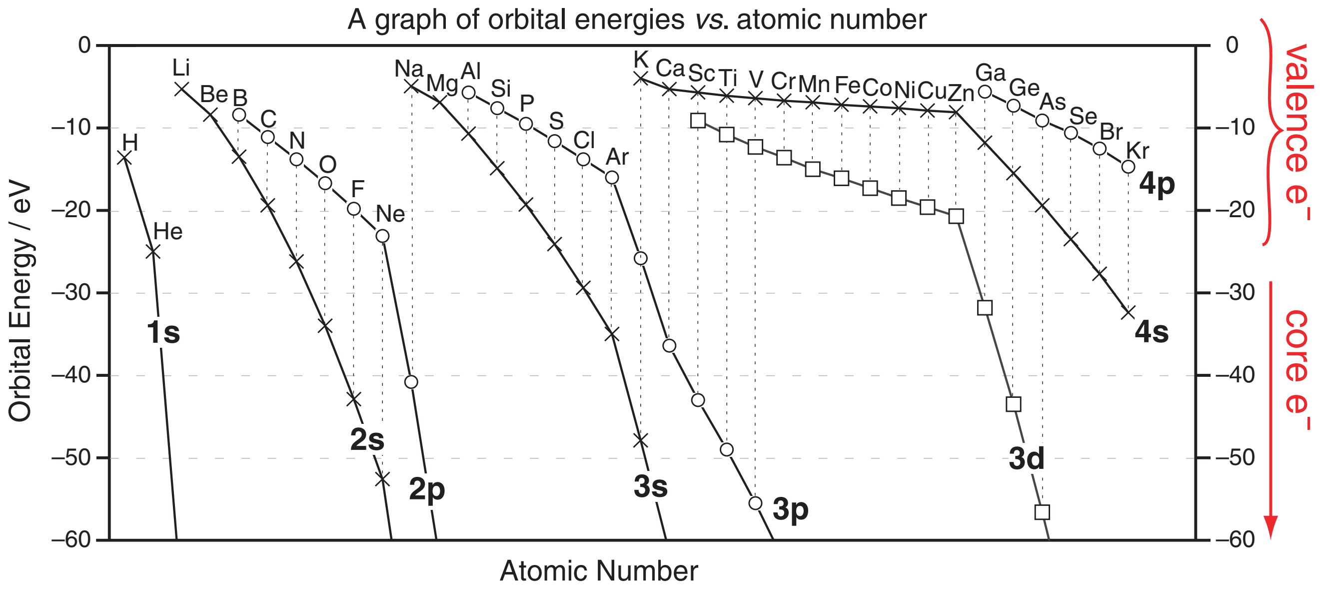
The energy of an atom with a particular electron configuration depends on the energies of *all* the electrons it contains. Removing or adding an extra electron changes the energy of *all* the electrons present. Because of this, it is meaningless to say that 'the 4s orbital is lower in energy than the 3d orbital'; whilst it might be true for one particular atom or ion, it may well change on the addition or subtraction of an extra proton or electron.

Orbital energies across the Periodic Table

Since electrons in the same shell do not shield each other very well (typically only by about 30-35%), the effective nuclear charge of the valence electrons increases as an extra proton and electron are added as we move across the periodic table.

element	Li	Be	B	C	N	O	F	Ne
Z_{eff} of valence electron	1.3	1.9	2.5	3.2	3.9	4.5	5.2	5.8

It is this increase in Z_{eff} together with the different degrees of penetration and shielding of the electrons present that explains the trends in orbital energies as we move across the periodic table.

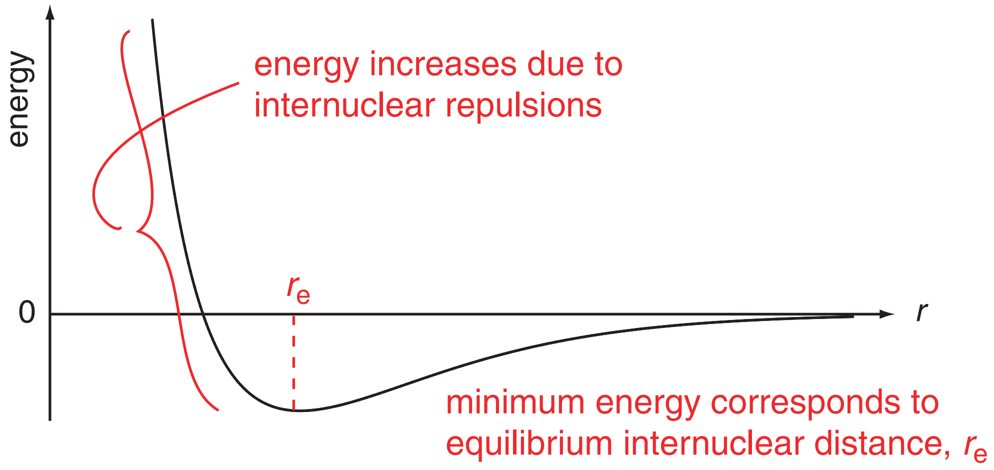


- orbital energy decreases across a period due to increased Z_{eff}
- Core electrons, i.e. electrons in shells lower than valence electrons, have very low energy and take little part in reactions.

The trends in the orbital energies are reflected in the ionization energies and electronegativities of the atoms (which increase with increasing Z_{eff}) and also in their atomic radii (which decrease with increasing Z_{eff}). These trends will be explored more fully in the *Chemistry of the Elements* course in the Easter term. We shall now see how these trends affect the chemical bonding between atoms.

Homonuclear Diatomics

As two hydrogen atoms approach each other, a bond is formed. What this means is that the H_2 molecule is lower in energy than two hydrogen atoms. Shown below is a graph showing how the energy of the system varies with the internuclear distance.

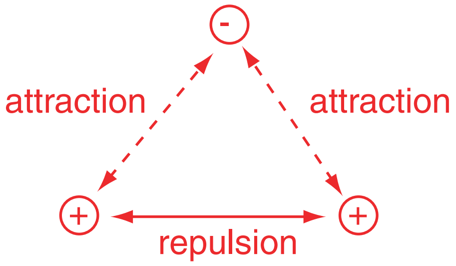


We want to work out where the electrons in molecules are and the energies they possess; we need to find the wavefunctions for the molecule.

Molecular orbitals

Solving the Schrödinger equation for a hydrogen atom gave a series of wavefunctions or atomic orbitals from which information about the electron could be deduced, such as its energy or the probability of finding it at a given position. We now want to find the wavefunctions for molecules – these are known as *molecular orbitals*.

The simplest 'molecule' is one which contains two protons and one electron – thea hydrogen molecular ion, H_2^+.



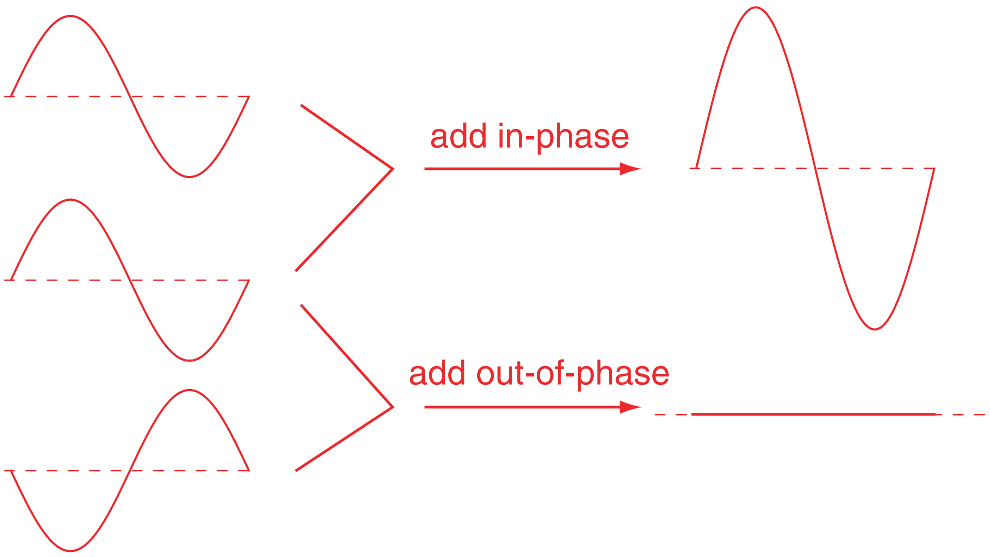
If we assume that the nuclei are a fixed distance apart, it is possible to calculate the molecular orbitals for this system exactly. However, the form of the molecular orbitals (MOs) may be visualised by combining the atomic orbitals of the constituent atoms. This method is called the *linear combination of atomic orbitals* (LCAO).

$$\text{MO} = c_1 \times \text{A.O.(atom 1)} + c_2 \times \text{A.O.(atom 2)}$$

where c_1 and c_2 are the orbital coefficients which express the proportions of A.O.s 1 and 2 in the molecular orbital. Quantum mechanics gives a way of calculating these coefficients.

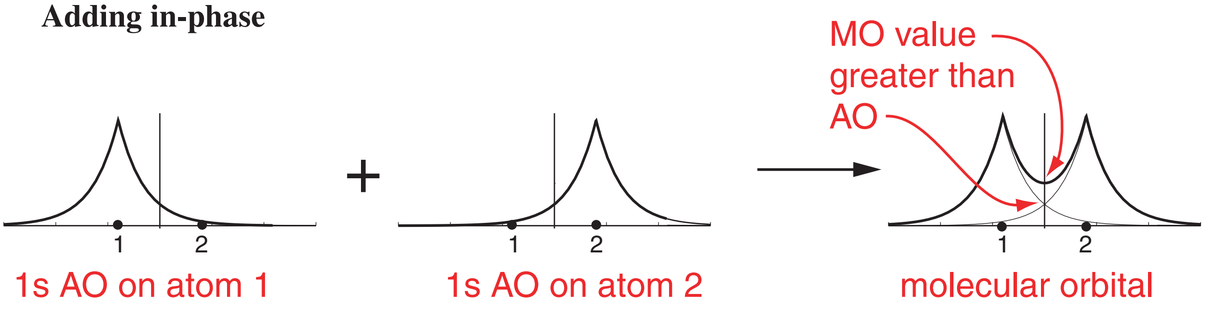
Combining wavefunctions

Sine waves can be combined in two different ways – either constructively or destructively.



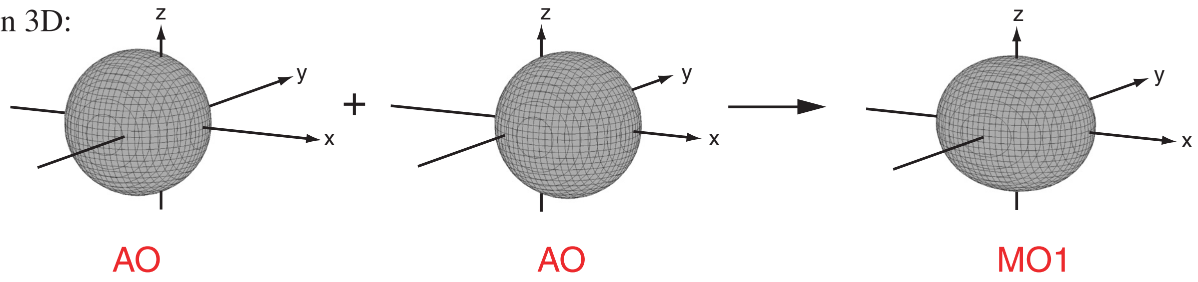
In an analogous manner, molecular orbitals result from combining constituent atomic orbitals in phase and out-of-phase.

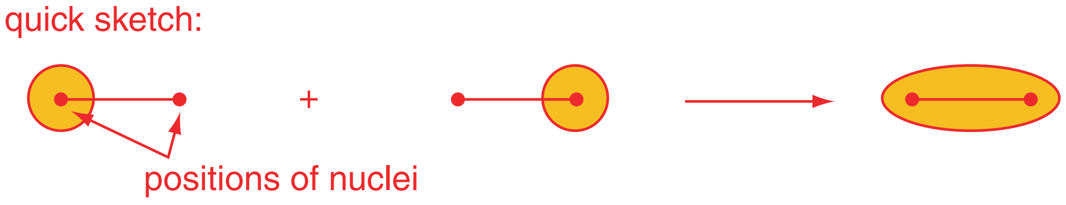
Adding in-phase



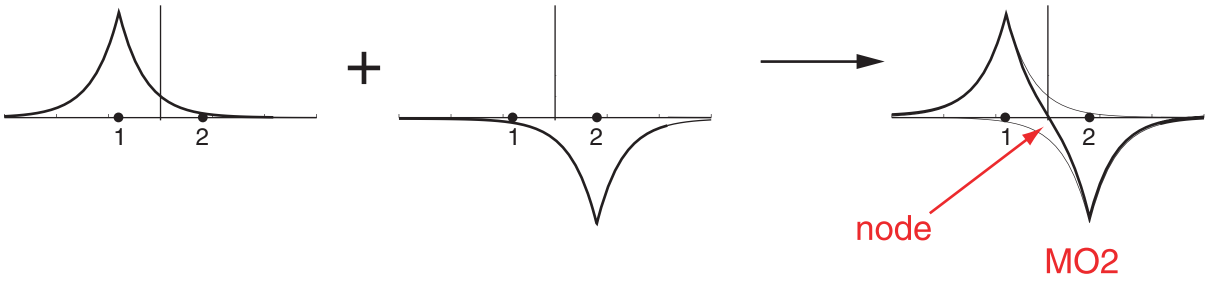
Note that in the region in between the nuclei, the value of the MO wavefunction is greater than that of the AO wavefunction. Since the square of the value of the wavefunction is proportional to the probability of finding the electron in this region, this means that it is more likely to find an electron in the internuclear region in the molecule H_2^+ than for the case of having a separate hydrogen atom $H^\bullet$ next to a proton H^+.

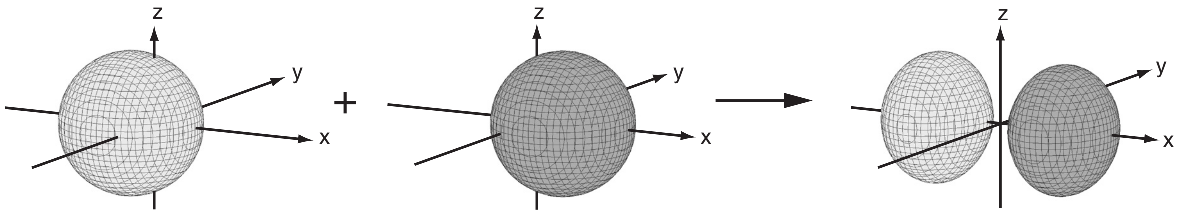
In 3D:

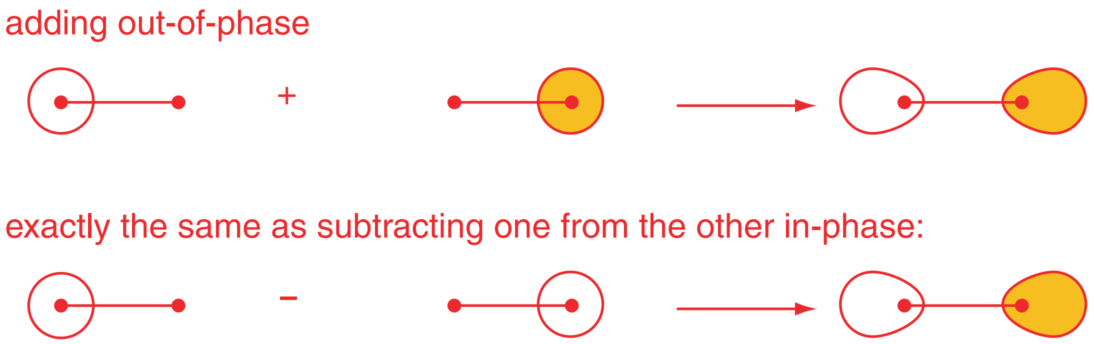




Adding out-of-phase

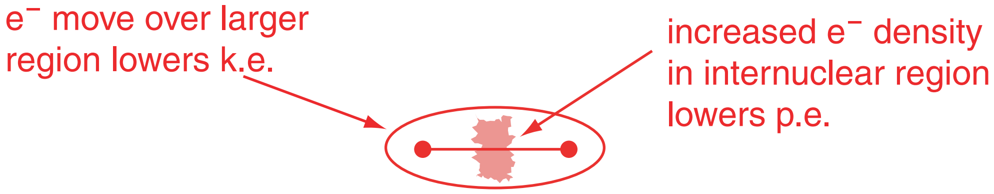






The resultant molecular orbitals are not of the same energy – the molecular orbital resulting from the *in-phase* combination (MO1) is *lower* in energy than the molecular orbital resulting from the out-of-phase combination (MO2). What is more, MO1 has a lower energy than the isolated AO whereas MO2 has a higher energy.

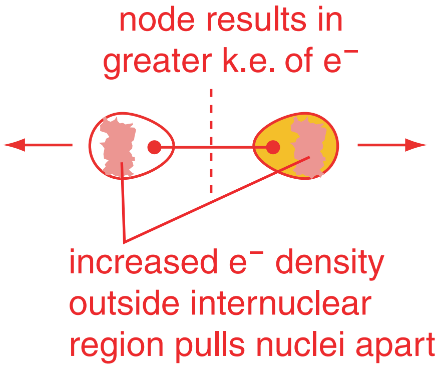
MO1 is lower in energy than the AO for two reasons. Firstly, when this orbital is occupied, there is increased electron density between the nuclei. The attraction from both nuclei leads to a lowering of the potential energy of the system. Secondly, an electron in MO1 is less constrained than it was when in the atom, *i.e.* it is more delocalized. This leads to a decrease in its kinetic energy.



Since this in-phase combination MO is lower in energy than the atomic orbitals and occupancy of this orbital gives rise to bonding, it is known as the *bonding molecular orbital*.

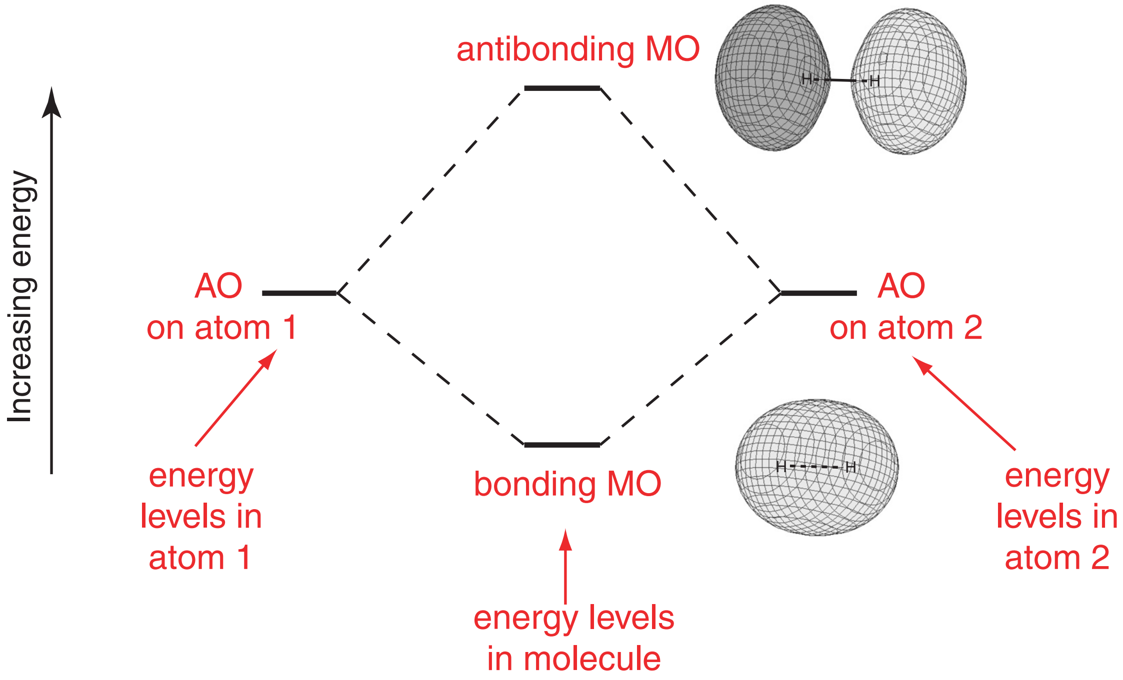
In contrast, MO2 is *higher* in energy than the AO. When this orbital is occupied, there is much more electron density outside the internuclear region than in between the nuclei. These electrons exert a force on the nuclei which moves them apart from each other. Eventually the nuclei would be completely separate from one another. The potential energy of the system with the electron in MO2 is therefore higher than in the separate species.

A second factor which contributes to the higher energy of MO2 is the fact that this orbital contains a node. This means that the kinetic energy of the electron in this orbital is greater than when it is in either the AO or MO1.



Since electrons in this out-of-phase combination MO leads to the species falling apart, it is known as an *antibonding molecular orbital*.

These results may be summarised using an energy level diagram:

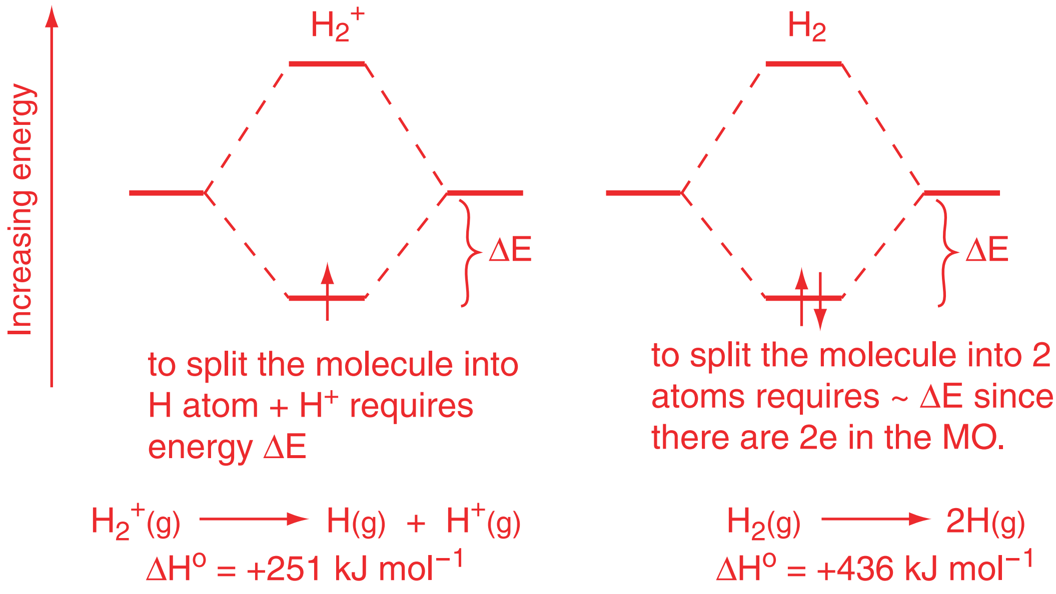


Important points to note

- Combining *two* atomic orbitals gives *two* molecular orbitals. (In general, combining n atomic orbitals gives n molecular orbitals.)
- One molecular orbital (the bonding MO) is lower in energy than the atomic orbitals, the other (the antibonding MO) is higher.

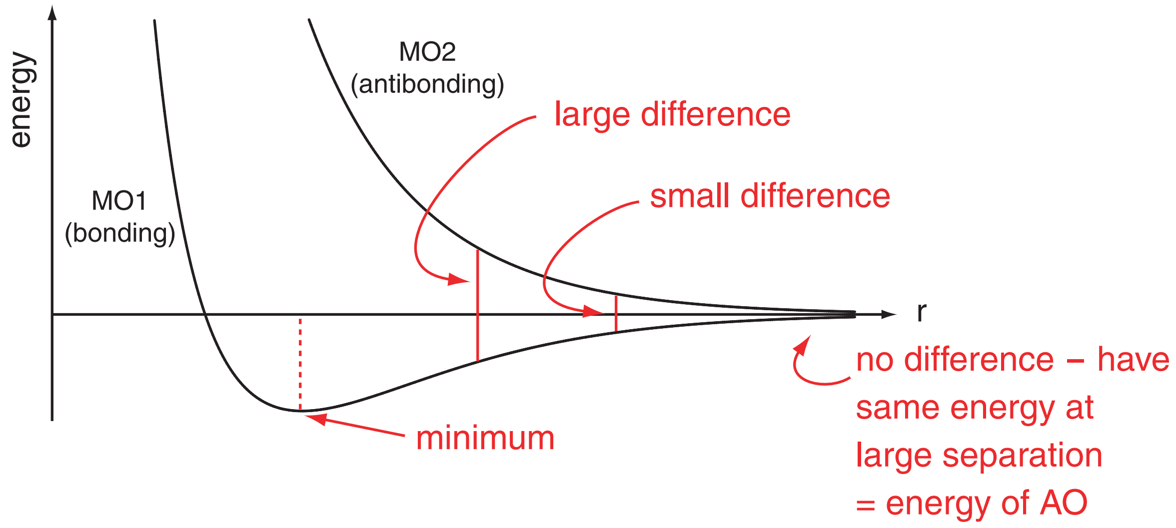
In an analogous manner to atomic orbitals, molecular orbitals describe the properties of electrons in molecules. Just as in atoms, electrons are fed into MOs, two spin paired electrons in each, working up from the MO lowest in energy.

We can use the energy level diagram to rationalize the stabilities of H_2^+ and H_2.

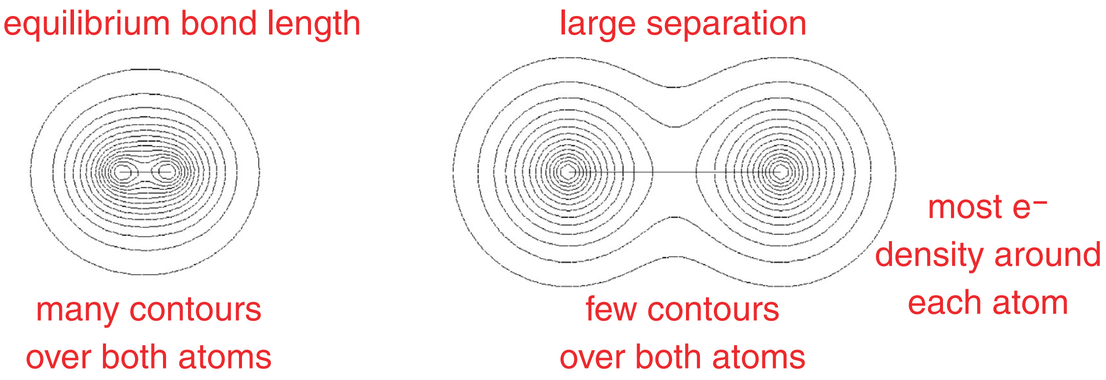


Since energy is required to split the H_2^+ molecule, we say there is a *bond* between the two species. The theory predicts the H_2 molecule to have a stronger bond than the H_2^+ molecule. We shall see that this is a general result – the more electrons in bonding MOs, the stronger the bond.

It is possible to calculate the energies of the bonding and antibonding molecular orbitals formed by combining two 1s orbitals in-phase and out-of-phase for any bond length. The results are shown below:

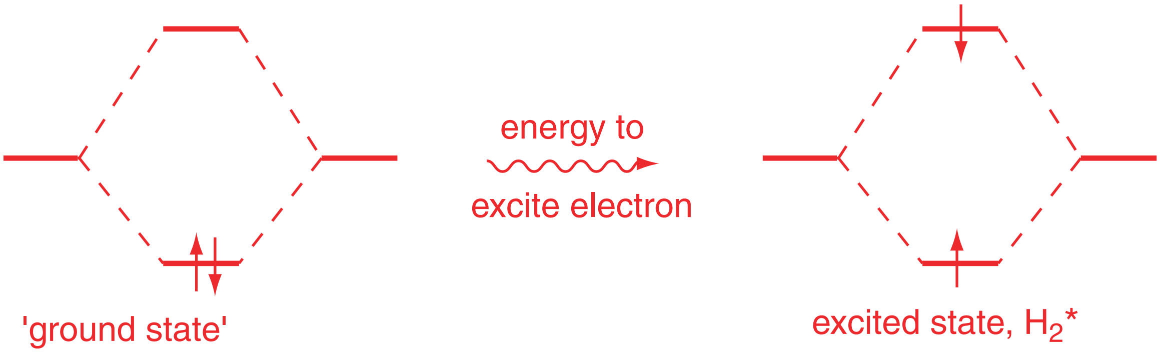


The first point to note is that the separation between the bonding and antibonding MOs decreases with increasing internuclear separation. This is because the further apart the atoms are, the less well their atomic orbitals interact. This may also be seen in the contour plots of the molecule.

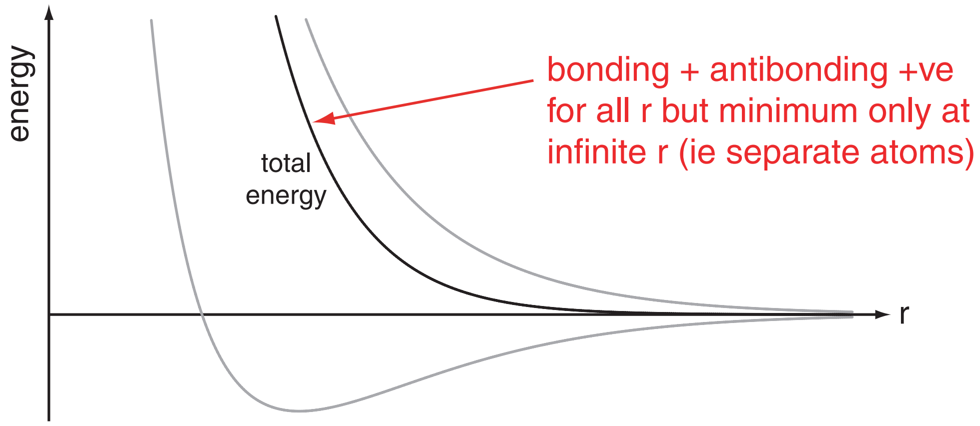


The second point to note is that whilst the energy curve for the bonding MO has an energy minimum, that for the antibonding MO does not. Thus, whilst there would be an equilibrium bond length if the only MO occupied was a bonding MO, if the only MO occupied was an antibonding MO, the molecule would minimize its energy by falling apart. We shall see that this is the important distinction between bonding and antibonding MOs.

If an electron is promoted from the bonding MO in H_2 to the antibonding MO, an excited H_2 molecule is formed.



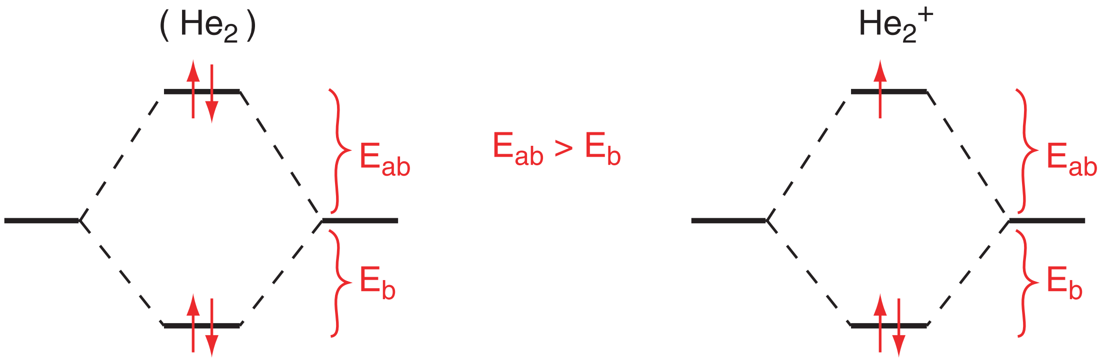
Whilst the energy of the electron in the bonding MO is lower than that of an electron in a hydrogen atom, the energy of the electron in the antibonding MO is higher. It turns out that antibonding MOs are in general raised slightly more in energy, relative to the component AOs, than bonding MOs are lowered. The total energy of the MOs (bonding MO + antibonding MO) with varying bond length is shown below.



The important point is, that with one electron in the bonding and one in the antibonding MOs, the total energy is always positive. At any point, the energy can decrease by increasing the bond length. Eventually, the bond breaks entirely to form two hydrogen atoms.

Electronically excited H_2 with one electron in the bonding MO and one in the antibonding MO is said to be unstable *with respect to two hydrogen atoms.*

We are now in a position to understand why He_2 does not exist. The interaction between two helium atoms involves the same orbitals as when two hydrogen atoms interact (only their energies will be different). The 1s atomic orbitals again interact to form the same MOs. The major difference is the number of electrons in the orbitals – each helium atom has *two* electrons which would mean *four* need to be accommodated in the MOs.



not stable – does not exist

$$He_2^+(g) \longrightarrow He(g) + He^+(g)$$
$$\Delta H^o = +290 \text{ kJ mol}^{-1}$$

Once more, the total energy of the system is greater than that of the two separate atoms which means that overall, energy would be released when He_2 breaks down to two helium atoms. In other words, He_2 is *unstable with respect to helium atoms and therefore does not exist*.

However, whilst He_2 does not exist, He_2^+ has been observed. If an electron is removed from the antibonding MO, the effects of the two electrons in the bonding MO outway the effect of the single electron in the antibonding MO and the species is stable with respect to dissociation.

A useful concept to consider when trying to work out if a bond forms is the *bond order*. The electrons in antibonding MOs cancel out the bonding gained by having electrons in bonding MOs, hence the difference between the number of electrons in bonding MOs and the number in antibonding MOs will tell us if the species is stable or not.

$$\textbf{Bond order} = \frac{1}{2} \times (\text{number of electrons in bonding MOs}) - (\text{number in antibonding MOs})$$

the factor of $\frac{1}{2}$ appears because we say that a *pair* of electrons makes up a *single* bond.

examples:

for H_2 2e in bonding, 0 in antibonding $\therefore$ bond order = $\frac{1}{2} \times (2 - 0) = 1$.

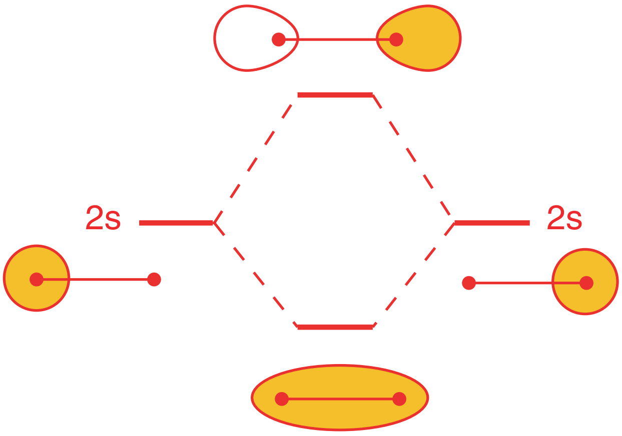
for He_2^+ 2e in bonding, 1 in antibonding $\therefore$ bond order = $\frac{1}{2} \times (2 - 1) = \frac{1}{2}$.

Combining other atomic orbitals

So far we have considered how 1s orbitals could combine but we can combine other atomic orbitals in a similar manner. Remember, we are using AOs to predict the form of MOs. Just as we can predict the energies of the atomic orbitals in hydrogen even though most of the time they are not occupied, we can predict the energies and shapes of MOs *whether or not they are occupied*.

When two atoms come together, the resulting MOs can be predicted by considering how the AOs on the constituent atoms may combine. We shall consider how the AOs with principal quantum number $n = 2$ combine.

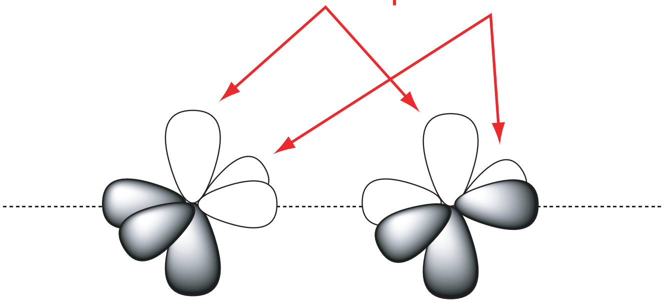
Two 2s orbitals combine in exactly the same way that two 1s orbitals combine:



(don't worry about the radial node)

However, when two p orbitals combine, we need to consider which direction they point in and how they can overlap.

these p orbitals are at 90° to the internuclear axis and so overlap side-on.



two of the orbitals (the p_z by convention) point along the internuclear axis. These overlap end-on.

The two $2p_z$ AOs that lie along the internuclear axis overlap end-on. The form of the resulting MOs formed from their combination may be shown like this:

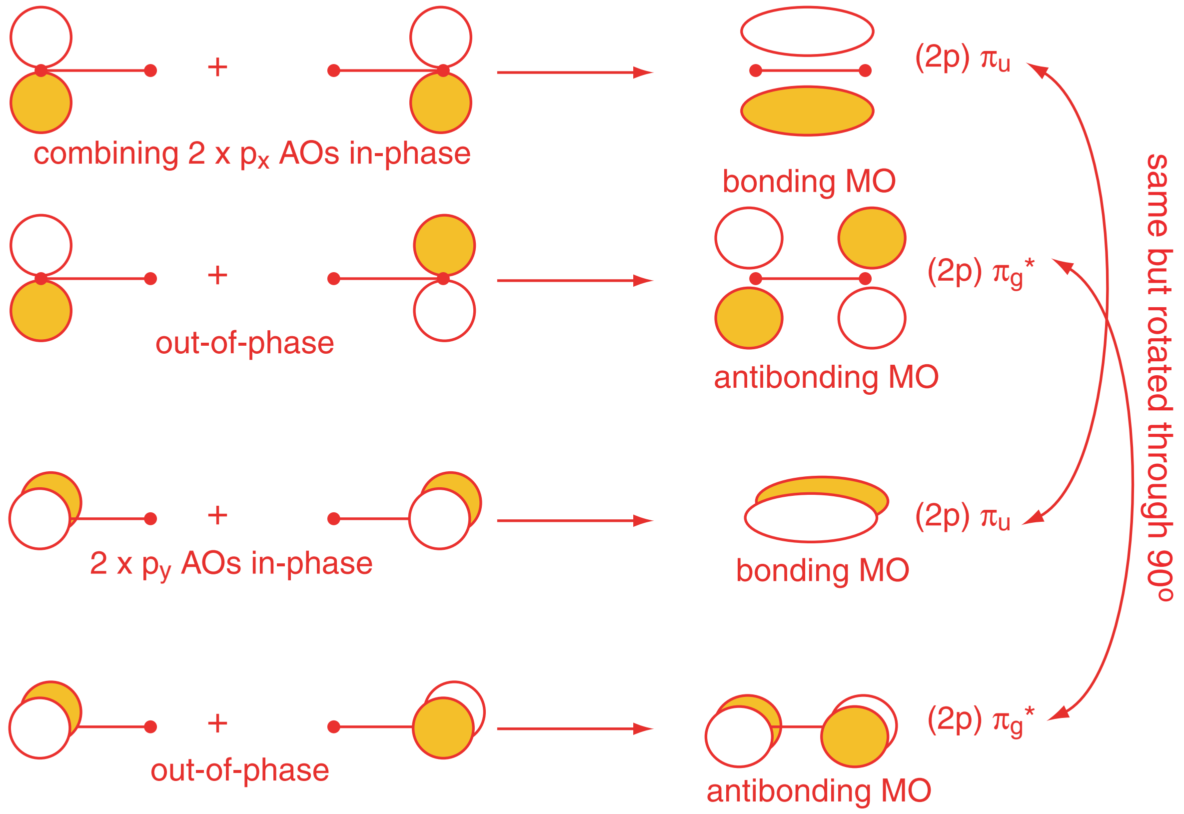
combining 2 x p_z AOs in-phase

bonding MO

combining 2 x p_z AOs out-of-phase

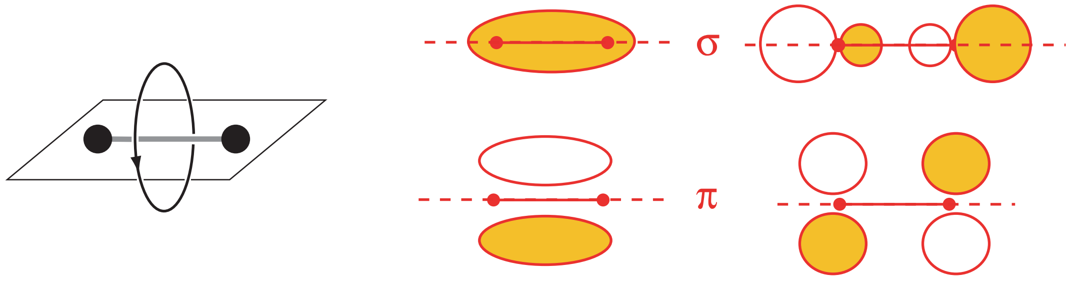
antibonding MO

The two $2p_x$ AOs and the $2p_y$ AOs are at right angles to the internuclear axis and combine side-on. The MOs formed from their combination may be shown like this:



Labelling molecular orbitals

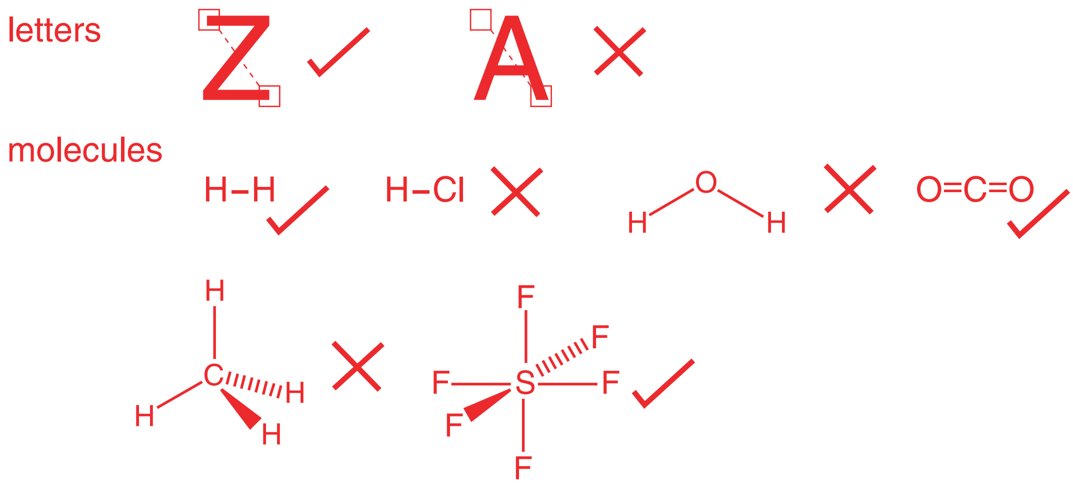
Molecular orbitals have labels which reflect the underlying symmetry they posses. The first label indicates the symmetry about the internuclear axis and depends on how the sign of the wavefunction changes about the internuclear axis:



If the MO is symmetrical about the internuclear axis and so does not change phase when traversing a path in a plane perpendicular to the internuclear axis, the orbital is given the label σ (sigma). If the internuclear axis contains a nodal plane, it is given the label π (pi). Thus the two MOs resulting from two s orbitals combining are both σ orbitals, as are the MOs resulting from combining the two p orbitals along the internuclear axis. When the p orbitals combine side on, molecular orbitals of π symmetry are formed.

The second label depends on how the sign of the wavefunction changes through the **centre of inversion**. An object is said to possess a centre of inversion if the following holds: start at any point and move in a straight line to the centre and then carry on exactly the same distance in the same direction – if the end point is equivalent to the start point, then the object possess a centre of inversion.

Examples



If the wavefunction does not change sign on passing through the centre of inversion, then the MO is called *even* and given the label **g** (from the German for even, *gerade*). If there is a change of sign, the MO is called *odd* and given the label **u** (from the German for odd, *ungerade*).

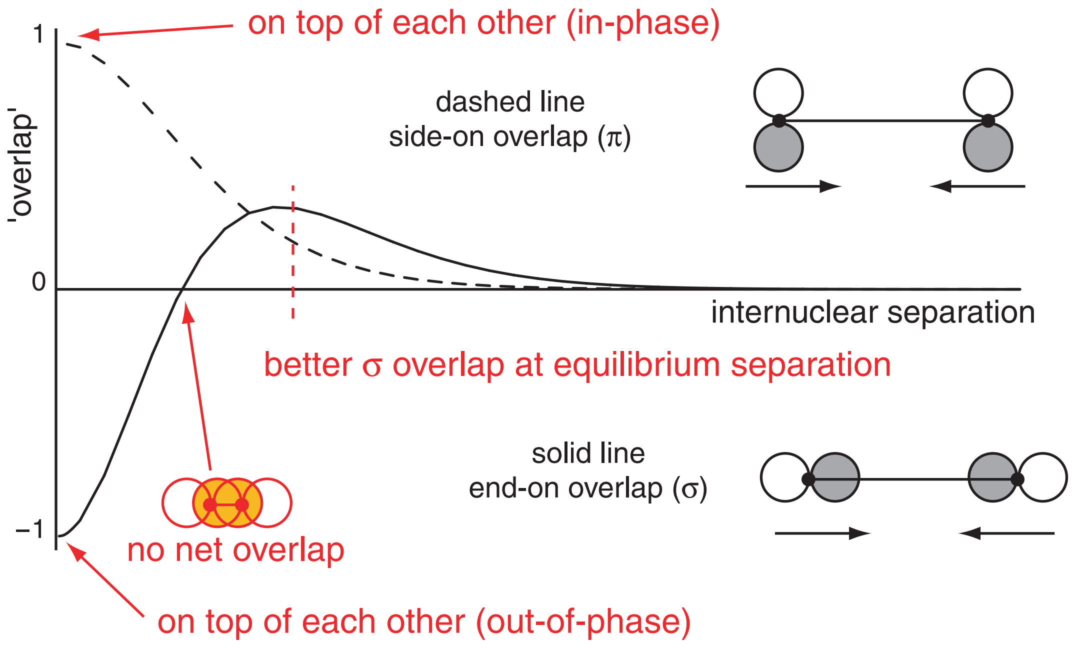
Note: This symmetry label only applies to molecules that possess a centre of inversion in the first place and so could be used for N_2 but not for CO, for example.

To distinguish between different MOs with the same symmetry, for example between the σ MOs obtained from the overlap of 1s, 2s or 2p orbitals, the atomic orbital from which they were formed is sometimes included in the label. If two different AOs formed the same MO, other labels might be used.

Finally, antibonding orbitals are sometimes labelled with a superscript asterisk. For example, the antibonding orbital formed from the out-of-phase interaction between two s orbitals is labelled the $1s\sigma^\star$ (read as ‘1 s sigma star’) orbital.

How well do the p orbitals overlap?

At typical bond lengths, the p orbitals on two atoms overlap more effectively *end-on* to give σ bonding and antibonding MOs than *side-on* to give π bonding and antibonding MOs. The graph below shows how the σ and π overlap between two p orbitals varies as the separation between them is decreased. Notice how the end-on overlap is initially net in-phase but if the two nuclei are forced together (much closer than their equilibrium separation) the net overlap is out-of-phase. At a certain separation there would be no net interaction between two.

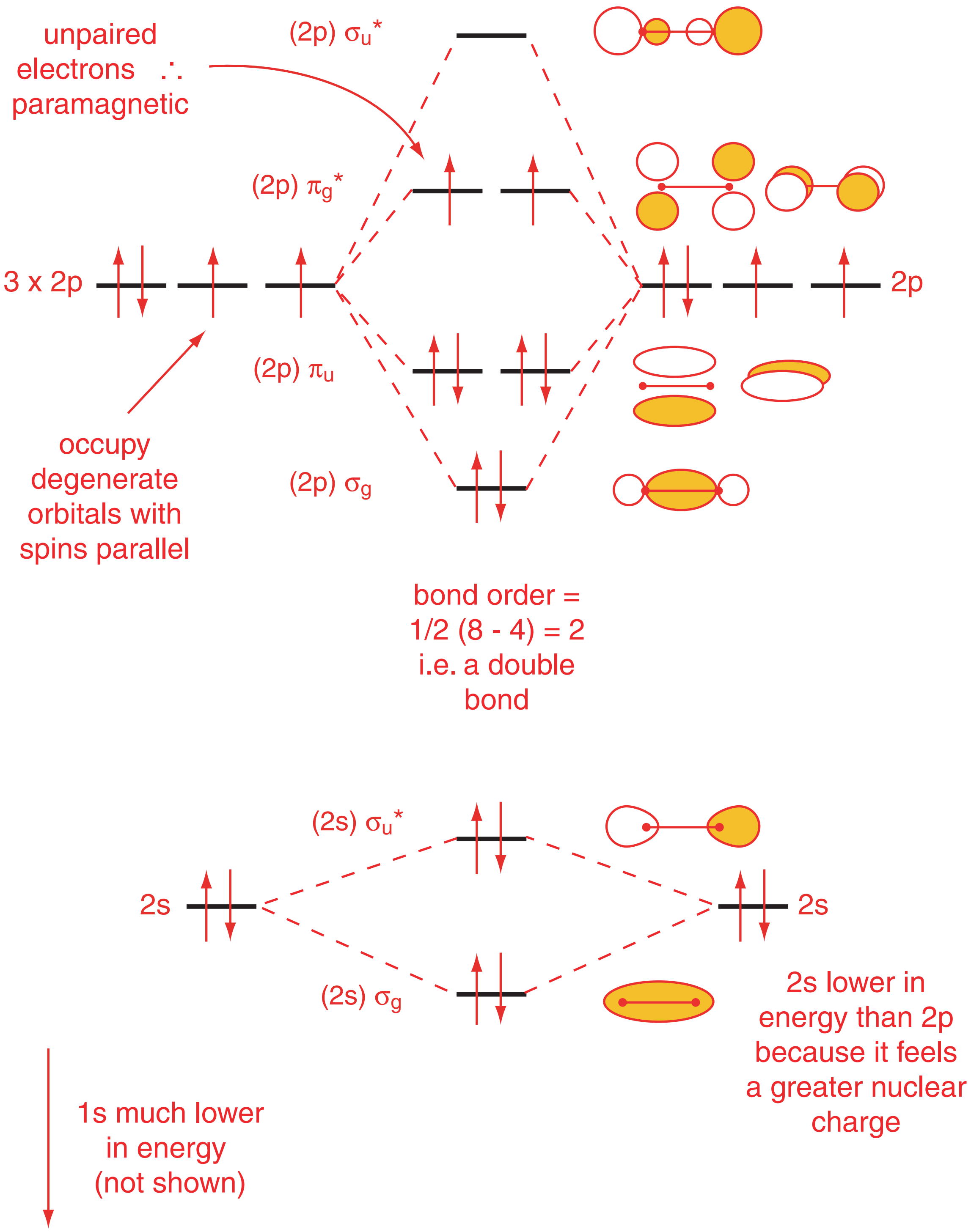


As a result of this greater overlap, the σ bonding MO formed from the end-on overlap of two p orbitals is lower in energy than the π bonding MOs formed from the side-on overlap. Similarly, the σ antibonding MO is higher in energy than the π antibonding MOs.

Constructing an energy level diagram for oxygen

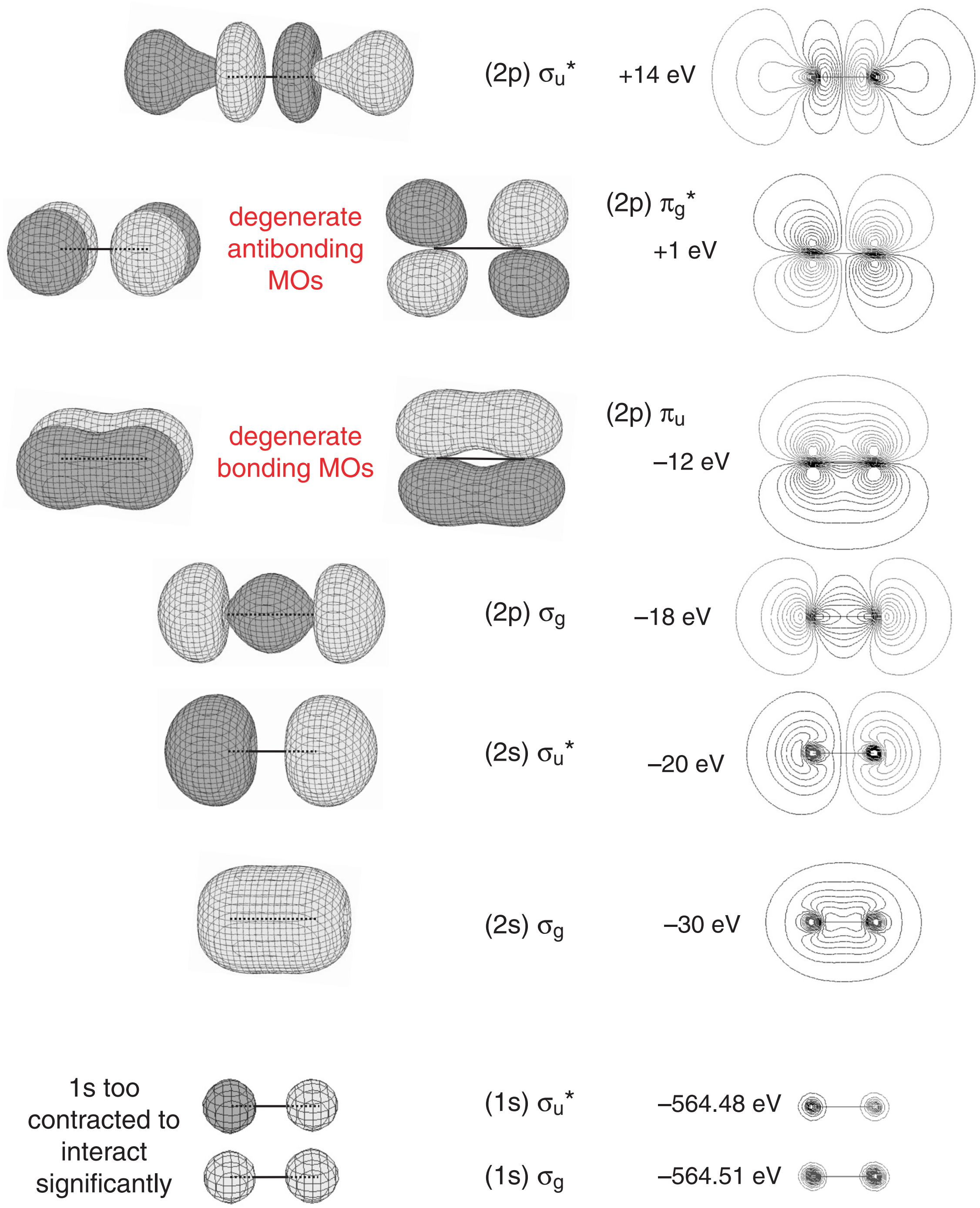
We are now in a position to construct an energy level diagram for a homonuclear diatomic molecule such as oxygen, O_2. For such a molecule, we only need to consider the overlap between the outermost orbitals (the valence orbitals) – in this case the 2s and 2p orbitals. Whilst the 1s AOs are occupied, they are far too contracted to interact significantly at the equilibrium bond length found in O_2 (see page 18).

MO energy level diagram for O_2



We can use the same MO energy level diagram for fluorine and neon. F_2 has two more electrons which must go into the antibonding (2p) $\pi_g^\star$ orbitals, thereby decreasing the bond order to 1. F_2 has no unpaired electrons and so is not paramagnetic. Ne_2 would have all the MOs filled and so have an equal number of bonding and antibonding MOs filled. Ne_2 would therefore have zero bond order which explains why it is not formed.

The shapes and approximate energies of the MOs for O_2



(2p) σ_u^* +14 eV

degenerate antibonding MOs

(2p) π_g^* +1 eV

degenerate bonding MOs

(2p) π_u –12 eV

(2p) σ_g –18 eV

(2s) σ_u^* –20 eV

(2s) σ_g –30 eV

1s too contracted to interact significantly

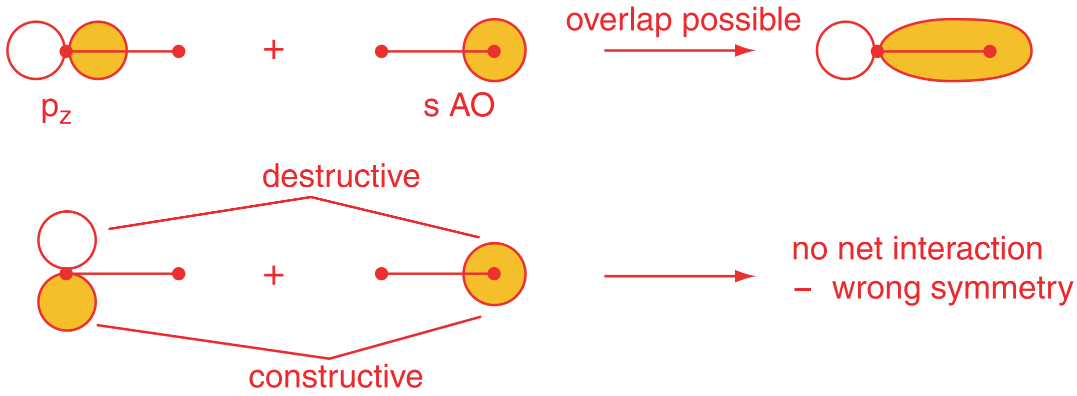
(1s) σ_u^* –564.48 eV

(1s) σ_g –564.51 eV

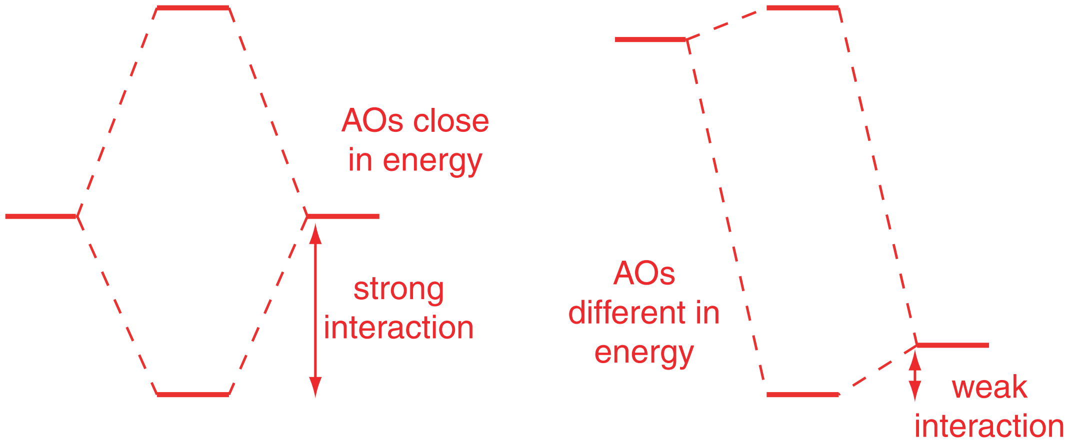
much lower in energy
essentially just 2 unchanged
1s AOs.

What determines how well AOs combine?

(1) The constituent atomic orbitals must have a suitable symmetry to interact:



(2) The constituent AOs must be close in energy for significant bonding or antibonding interactions to occur. Hence for a diatomic such as O_2, there is no significant interaction between the 1s AO of one atom and the 2s AO of the other, even though they have the correct symmetrry to interact.



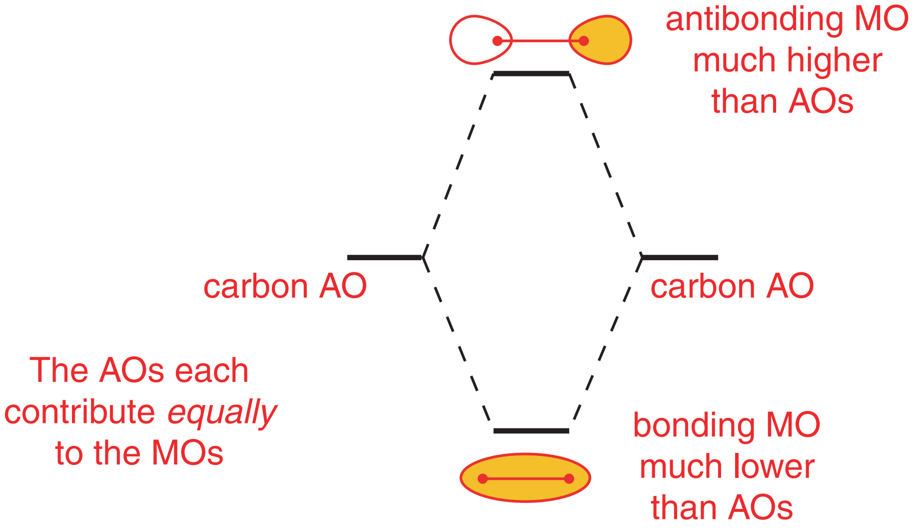
(3) Even if the orbitals are close in energy, the degree of overlap will vary depending on the sizes of the orbitals – the interaction between two large orbitals is less than that between two small orbitals:

$$1s - 1s > 2s - 2s > 3s - 3s \text{ etc}$$
$$2s - 2s > 2s - 3s > 2s - 4s \text{ etc}$$

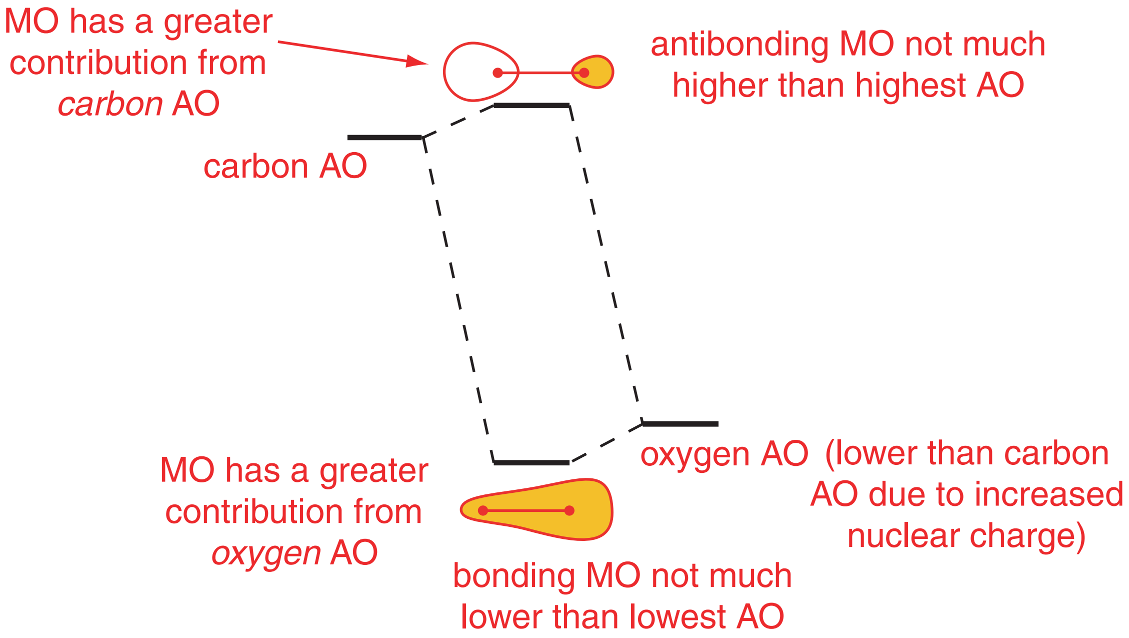
Heteronuclear Diatomics

In general, when two atomic orbitals of different energies combine, the resultant bonding MO is not lowered in energy, nor the resultant antibonding raised in energy, as much as when the two combining AOs have the same energy. What is more, the two AOs no longer contribute equally to the AOs

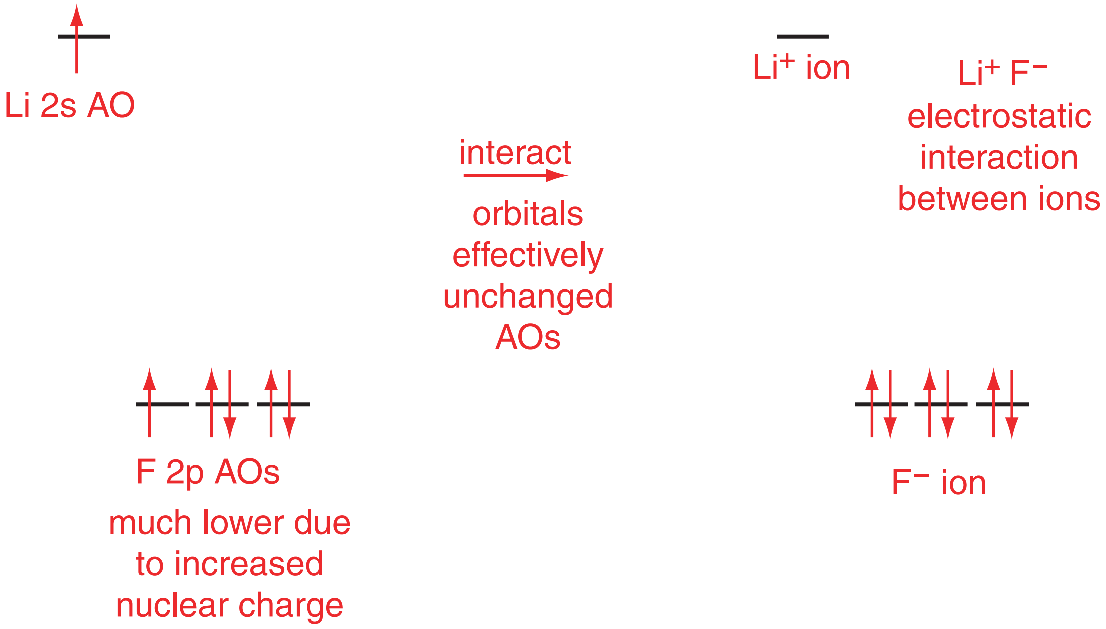
AOs with the same energy



AOs with different energy



Even though the C–O bonding MO might not be lowered by as much as the C–C bonding MO, this does not mean that a C–O bond is weaker than a C–C bond. As we shall see, the unequal sharing of electron density means that the bond also has considerable *ionic character* which also contributes to its bond strength. Consider the case when Li and F atoms come together. The orbitals are so far apart in energy that they do not interact to give molecular orbitals at all. The lithium electron ends up in what is effectively a fluorine atomic orbital.



- The lithium and fluorine species are not held together by electrons being *shared* between them but instead by the attraction between opposite charges. We can say there is an **ionic bond**.
- When two atoms contribute *equally* to form a MO, the electrons are shared between the two atoms in what is termed a **covalent bond**.
- When, as in a C–O bond, the electrons are shared *unequally* because of unequal contributions to the MOs, the bond will be polarised and may be said to have some **ionic character**.

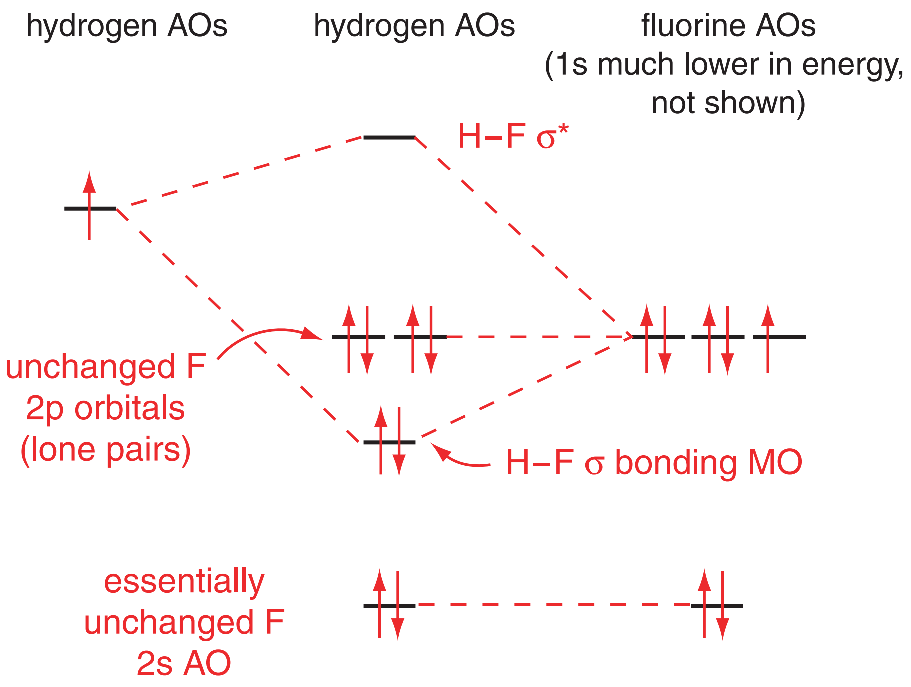
Example: The Molecular Orbitals of Hydrogen Fluoride

The first important point to consider when trying to predict the form of the MOs in HF is that the 1s orbital of fluorine is *much* lower in energy than the hydrogen 1s orbital (because of the much greater nuclear charge in fluorine) and as a result there is no interaction between the 1s orbitals. Because the fluorine 1s AO is so low in energy, it is *never* involved in bonding. Only electrons in the 2s and 2p orbitals of fluorine are involved in bonding which is why they are termed the *valence* electrons.

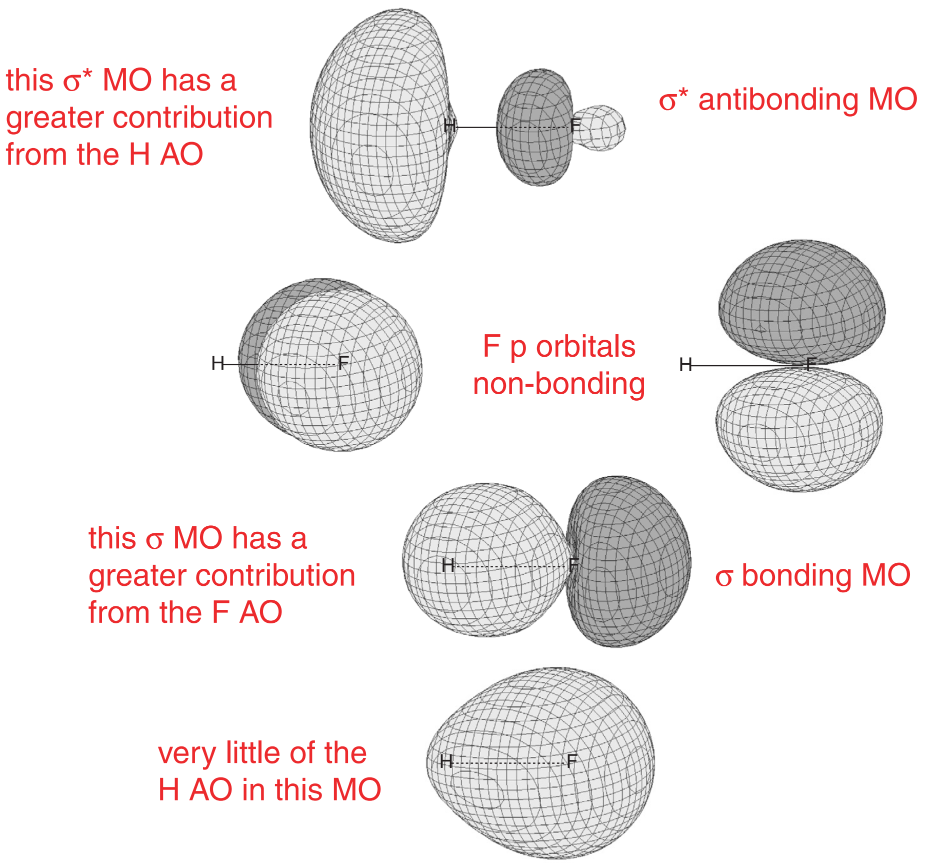
Not only is the fluorine 1s orbital much lower in energy than the hydrogen 1s orbital, so are the fluorine 2s and 2p orbitals (see graph on page 20). This is shown by the ionization energies :

To remove an e^- from 1s in hydrogen requires 13.6 eV
To ionize F (i.e. remove e^- from 2p orbital) requires 17.4 eV

This means that the strongest interaction when hydrogen and fluorine atomic orbitals combine to form MOs is between the H 1s and the F 2p. However, only the F $2p_z$ (which points along the internuclear axis) can interact because only this has the appropriate symmetry. The other two p orbitals remain unchanged. These unchanged p orbitals are referred to as **non-bonding** MOs; they are neither lower in energy than the starting AOs as bonding MOs would be, nor are they higher in energy as antibonding MOs would be.



Because of the difference in energy between the hydrogen 1s AO and the fluorine 2p AOs, the σ bonding MO has a greater contribution from the fluorine 2p AO than the hydrogen 1s AO. This is clearly shown in the diagrams of the molecular orbitals.

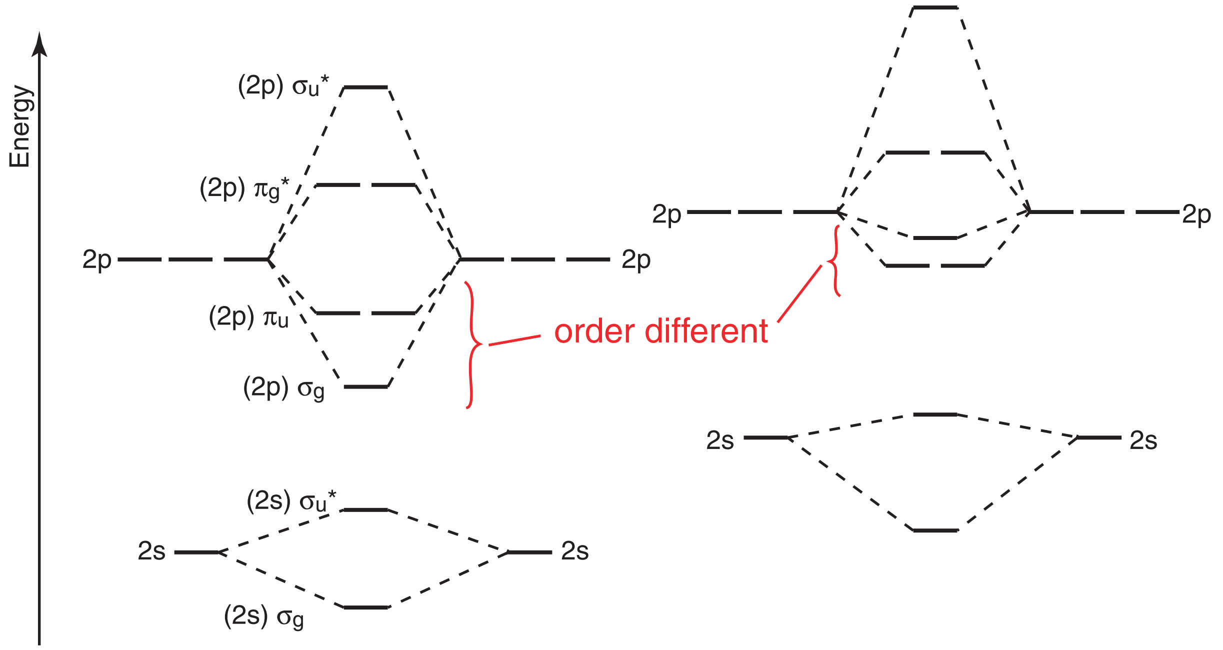


The energy level diagram and the MO pictures both show that most of the electrons in HF are concentrated around the fluorine atoms rather than the hydrogen atom. In other words, the HF bond is polarised towards the fluorine. (+) H—F (–)

More Complicated Mixing Between AOs

Homonuclear diatomics revisited – sp mixing

We have used the linear combination of atomic orbitals to predict the forms and relative energies for the molecular orbitals in H_2, O_2, F_2 and HF and the results agree well with experimental observations. However, the same method does not work so well for the homonuclear diatomic molecules before O_2, for example N_2. Experiment shows that the energy ordering of the molecular orbitals is different for these molecules.



MO diagram for O_2 MO diagram for N_2

In the model for homonuclear diatomics that we have used so far we have only considered the interactions between atomic orbitals of the same kind; for example how the 2s AOs interact with each other or how the 2p AOs interact. However, there is no reason to assume that the lowest energy MO is made up solely from a combination between the 2s orbitals only, for example, in H–F we have seen how an s orbital on one atom can interact with a p_z orbital from the other atom to form a σ bond.

We could generate more accurate MOs by considering how all the suitable AOs contribute to a given MO. Another way to obtain the same result is simply to allow the MOs initially formed from just two AOs to further combine.

combine AOs ⟶ first approximation MOs $\xrightarrow[\text{these further}]{\text{combine}}$ improved set of MOs

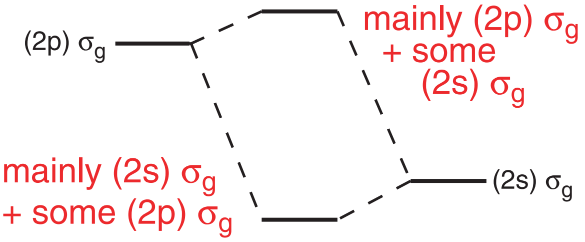
The rules for combining orbitals, that they should have the same symmetry and be of similar energy, can be used to see how the first approximation to the MOs might interact to produce a more accurate set.

which MOs have the same symmetry? Use the symmetry labels.

(2s) σ_g and (2p) σ_g can mix with each other as can the (2s) σ_u* and (2p) σ_u*

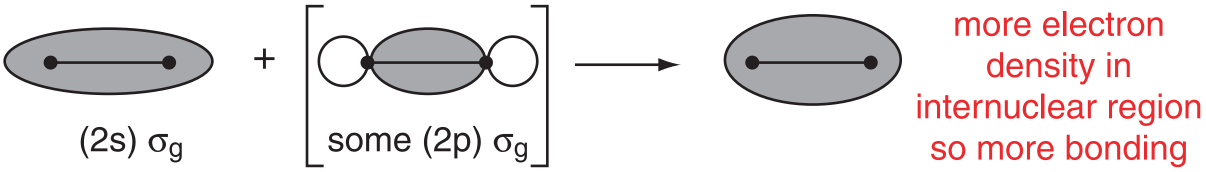
The extent to which the MOs can mix depends on how close they are in energy to each other. The two closest are the (2s) σ_g and the (2p) σ_g so these have the greatest interaction.

The MO energy level diagram shows that when the two orbitals combine, as usual, one is lowered in energy and one is raised. In this case the (2s) σ_g becomes more bonding and the (2p) σ_g becomes less bonding.

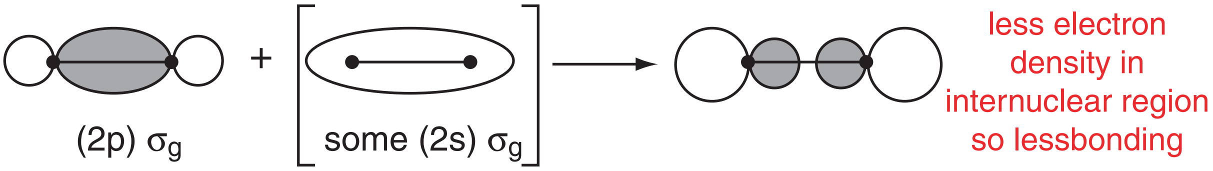


We can also show this interaction pictorially:

mixing the (2s) σ_g and (2p) σ_g orbitals in-phase

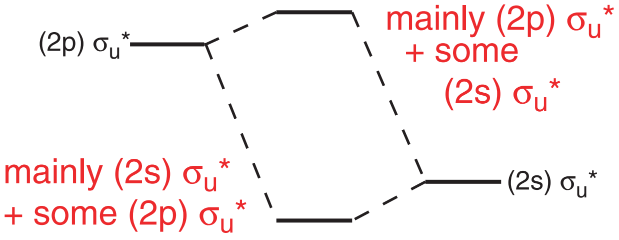


mixing the (2s) σ_g and (2p) σ_g orbitals out-of-phase

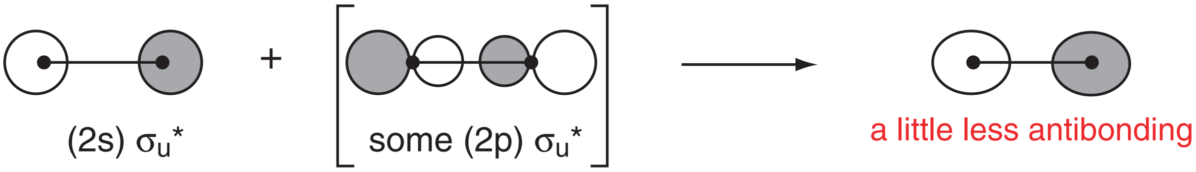


Similar interactions can take place between the (2s) σ_u^* and the (2p) σ_u^* although these interactions are not so marked because these orbitals are not so close in energy.

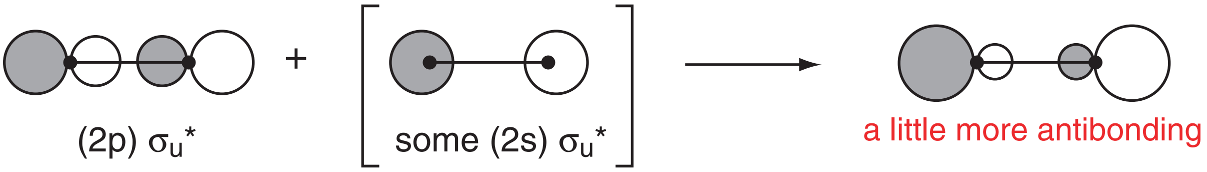
In this case the (2s) σ_u^* becomes less antibonding and the (2p) σ_u^* becomes more antibonding.



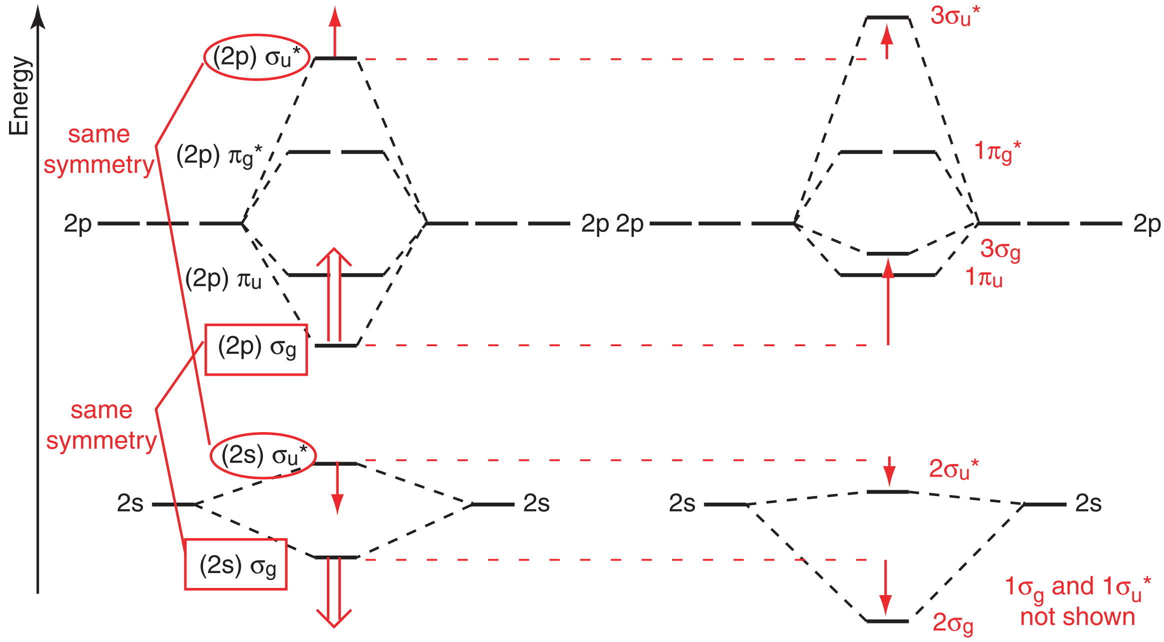
mixing the (2s) σ_u^* and (2p) σ_u^* orbitals in-phase



mixing the (2s) σ_u^* and (2p) σ_u^* orbitals out-of-phase



This process of refining the MOs by mixing the first approximation MOs is known as s-p mixing since here we are mixing the (2**s**)σ_g with the (2**p**)σ_g and the (2**s**)σ_u^* with the (2**p**)σ_u^*. The result is to slightly alter the ordering of the MOs:



Notice that the MOs can no longer be labelled using their AOs since they are now a *mixture* of orbitals; their label is determined by their symmetry only. The first MO of σ_g symmetry (not shown since *much* lower in energy, see page 33) is labelled '1σ_g', the second '2σ_g' and so on.

The final energy level diagram for N_2, such as is shown above, is consistent with the simple picture of nitrogen, *viz*. that it consists of a σ-bond, two π-bonds and has a lone pair on the end of each nitrogen atom.

The σ-bond corresponds to MO 2σ_g, the two π-bonds to the π_u MOs and the two lone pairs correspond to MO 2σ_u^* (which is actually weakly antibonding) and MO 3σ_g (which is actually weakly bonding). The only difference between the two pictures is that the simple structure suggests there is one lone pair on the end of each nitrogen atom, whereas the more sophisticated MO picture reveals that the essentially non-bonding MOs are actually delocalized equally over both nitrogen atoms, with most electron density outside the internuclear region, as suggested by the sketches on the previous page.

The degree to which s-p mixing takes place depends on how close in energy the combining orbitals are. The effects of s-p mixing are sufficiently strong to cause the (2p)σ_g to rise above the (2p)π_u orbitals for all the first row **homonuclear** diatomics up to and including nitrogen which means the order pictured above is used for all these diatomics. For O_2 and F_2, the (2s)σ_g and (2p)σ_g are far enough apart for no significant s-p mixing to take place and so the energy level diagram is the one we met earlier on page 32.

$$\underbrace{\mathrm{Li_2\ \ Be_2\ \ B_2\ \ C_2\ \ N_2}}_{\text{sp mixing significant}} \qquad \underbrace{\mathrm{O_2\ \ F_2}}_{\text{sp mixing not significant}}$$

Moving across the period, as the nuclear charge increases, both the 2s and 2p AOs become lower in energy, but the 2s orbital is lowered more because it is more penetrating (see the graph on page 20 and the preceeding explanation).

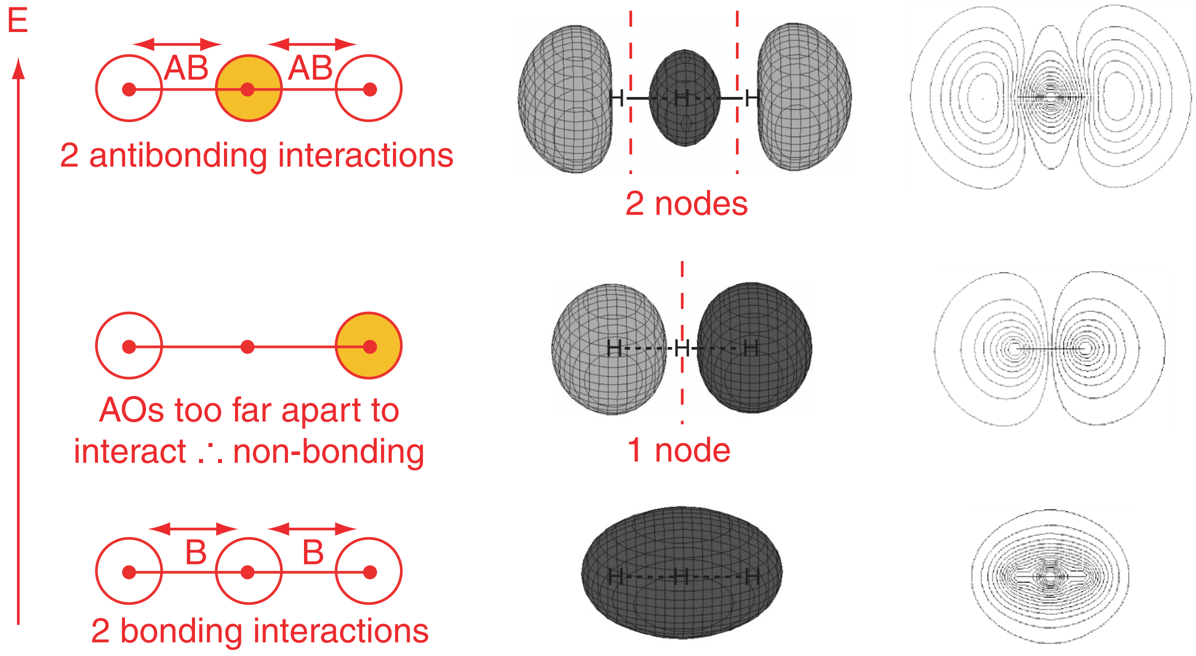
For **heteronuclear** diatomics, it is not generally possible to predict how significant the effects of s-p mixing will be without considerable computation.

Larger Molecules - the H_3^+ ion

So far the only molecules we have looked at have been comprised of just two atoms. As chemists, we are far more interested in larger molecules. It is important to understand, at least qualitatively, the form of the molecular orbitals for such larger molecules since, as we shall see in the next course, the orbitals dictate how a molecule reacts. In order to understand the principles of the bonding in larger molecules, we shall start with the simplest polyatomic species, the H_3^+ ion. Once again we shall use the Linear Combination of Atomic Orbitals method to predict the form of the molecular orbitals from the atomic orbitals of the component atoms.

The first step is to decide upon a geometry – we shall start by assuming a linear arrangement of the three atoms. It turns out that this is not the real shape of the H_3^+ ion, but it is a good starting point. We shall investigate the proper geometry later.

The forms of these molecular orbitals are shown below.

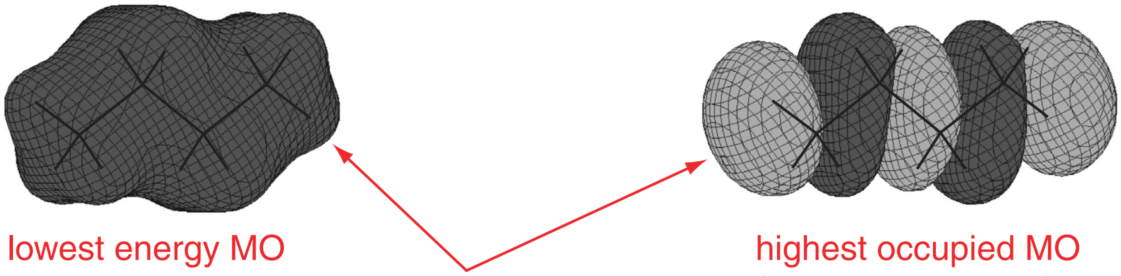


Important points:

- As usual, the number of orbitals are conserved – three AOs give three MOs.
- Each molecular orbital can still hold just two electrons. For example, whilst the non-bonding orbital might *look* like two 1s atomic orbitals, it is not. It is *one* orbital and can hold just two electrons, spin-paired as usual.
- In the H_3^+ ion, there are only two electrons and these are in the lowest energy MO, the bonding MO. These two electrons hold all three atoms together. The electrons in any orbital are said to be delocalised over all three atoms. This is rather different from our familiar picture of a bond being two electrons shared between two atoms!

Larger Molecules Still

In principle we could take any arrangement of atoms and calculate the molecular orbitals for them. However, because of the large number of orbitals involved, this procedure rapidly becomes too complicated without the aid of a computer. In the H_3^+ ion, the only orbitals we needed to consider for were the three 1s orbitals from the three atoms. If we wanted to calculate the MOs in butane, for example, (still a relatively small molecule) we would need to consider a total of 26 atomic orbitals (the 2s and 2p orbitals of each carbon and the 10 hydrogen 1s AOs). Combining 26 AOs gives 26 different molecular orbitals. Just as in the H_3^+ ion, each of these MOs is spread out over all the atoms, and each has a different energy.

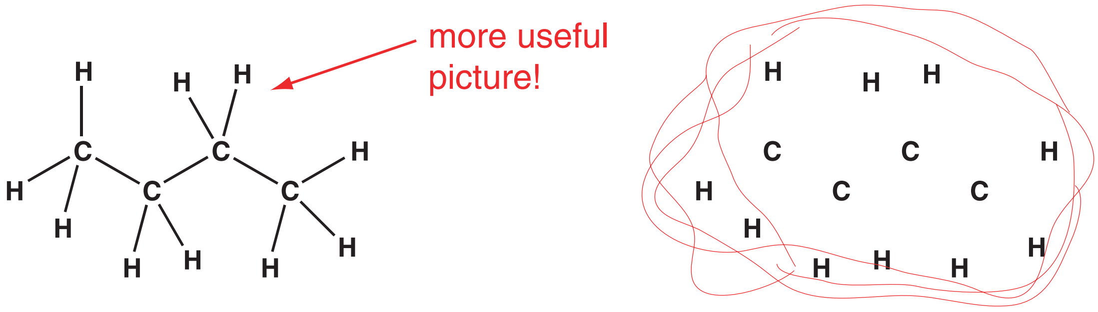


lowest energy MO

each MO can hold just 2 e⁻s.

highest occupied MO (many more nodes)

Occasionally chemists might have to use such a model, but most of the time it is inconvenient to think of the electrons as delocalised over the whole molecule in different molecular orbitals. It is usually far more useful to think of two atoms being bonded together by pair of electrons (although sometimes, especially in inorganic chemistry, this just is not possible). In butane, for example, we would say there are two electrons contributing to each C–C bond and each C–H bond.



more useful picture!

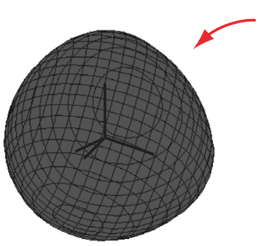
valence bond picture – we think of each line as representing a bond composed of 2e⁻s.

MO picture 13 MOs over all atoms, each MO holding 2e⁻s.

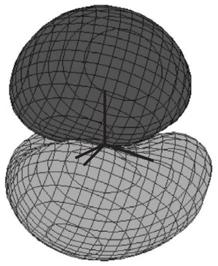
A convenient solution to this problem is to construct approximate molecular orbitals between any two atoms which are bonded. In butane, we would have a bonding (and antibonding) MO corresponding to each C–C and C–H bond. Unfortunately, the problem here is that the atomic orbitals which we must use to generate such MOs might not point in the correct direction to overlap efficiently. For example, in butane, the four atoms surrounding each carbon are at 109° to each other (the common tetrahedral structure) but the carbon 2p orbitals all lie at 90° to each other. A way round this is to use a procedure called *hybridization*.

Hybridization

Hybridization allows us to mix a number of atomic orbitals *on the same atom* to create hybrid atomic orbitals (HAOs) which point directly towards the atoms we wish to construct bonds with. To illustrate the principle of hybridization, we shall look at the bonding in methane. A molecular orbital description of methane has four occupied bonding molecular orbitals and four vacant antibonding MOs (this ignores the carbon 1s orbital which is too contracted to be of much use in the bonding). You are not expected to be able to generate these MOs, this is a topic that will be explored next year. The bonding MOs (each capable of holding two electrons) are delocalized over all five of the atoms and are of two different energies: one (comprised of the carbon 2s and the hydrogen 1s orbitals) is singly degenerate, the other three orbitals (comprised of the carbon 2p orbital and the hydrogen 1s orbitals) are degenerate. The form of these bonding MOs are shown below.

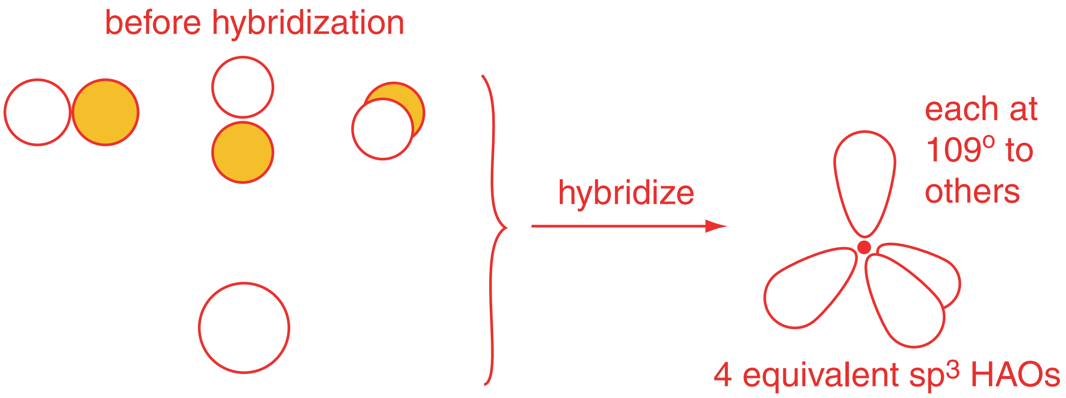


MO from carbon 2s and all 4 H 1s AOs in phase. Holds 2e⁻.

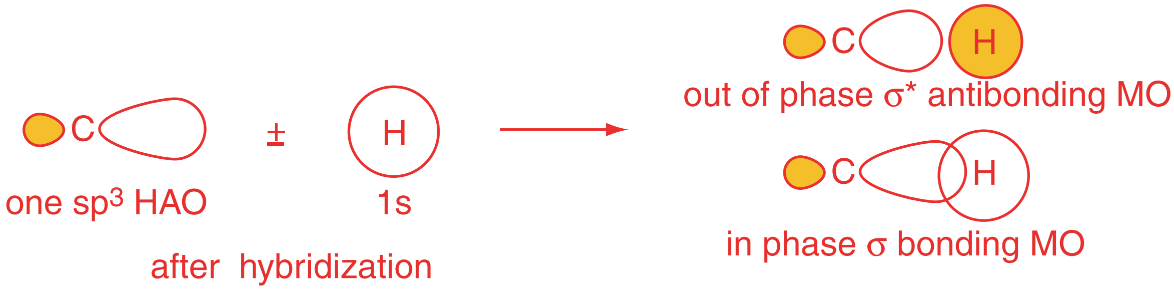


MO from carbon 2p and all 4 H 1s AOs in phase. There are 3 MOs like this.

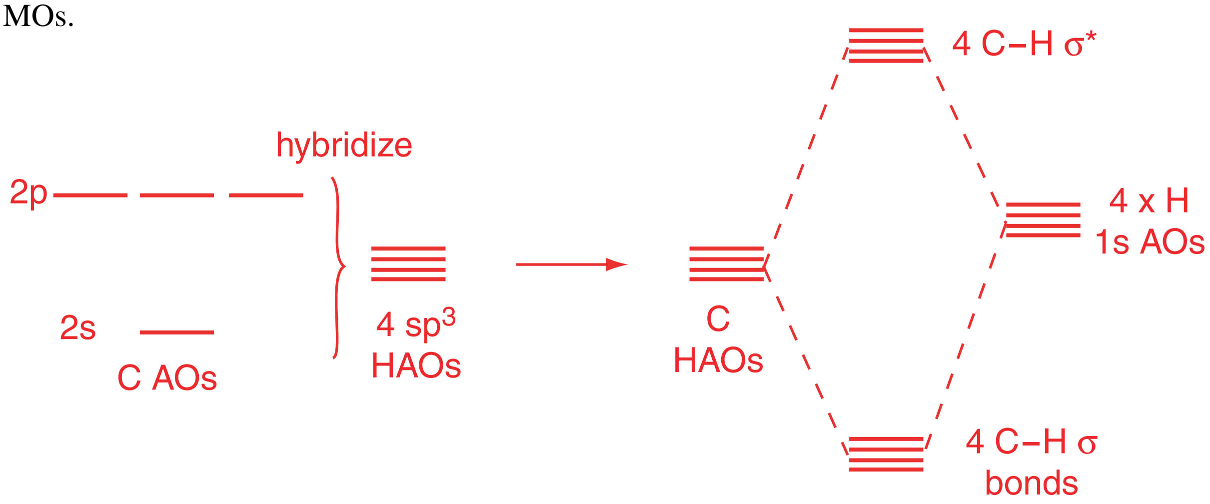
The carbon 2s and all three 2p atomic orbitals are all used to construct the four bonding molecular orbitals with the hydrogen 1s AOs but give the delocalized orbitals pictured above. In order to create a simpler scheme, we take the same carbon atomic orbitals (*i.e.* the 2s and all three 2p) and first combine them together to give four equivalent hybrid atomic orbitals.



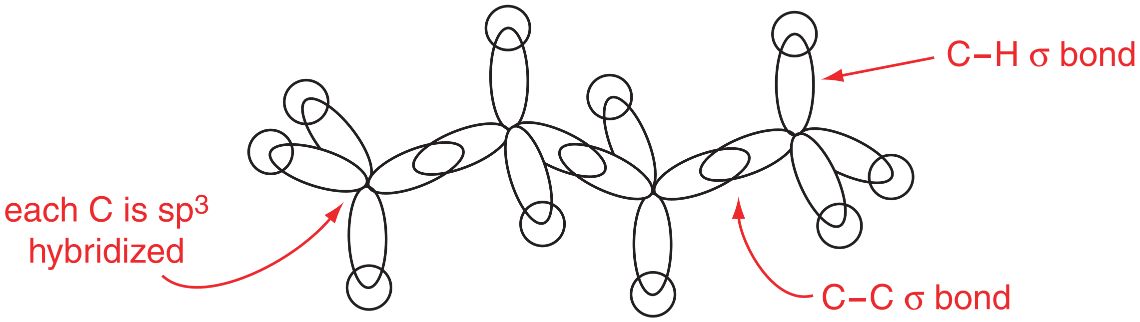
We no longer consider the carbon as having an s orbital and three p orbitals but four equivalent sp^3 hybrid atomic orbitals (HAO), each pointing to the corner of a regular tetrahedron. Each HAO can overlap with one of the hydrogen 1s atomic orbitals in-phase to give a bonding MO and out-of-phase to give an antibonding MO.



Each bonding and antibonding MO so formed is still symmetric about each C–H internuclear axis and so is given the σ label ($\sigma^\star$ for the antibonding MO). Using this approach, we would describe methane as having four equivalent occupied σ MOs and four equivalent vacant $\sigma^\star$ MOs.



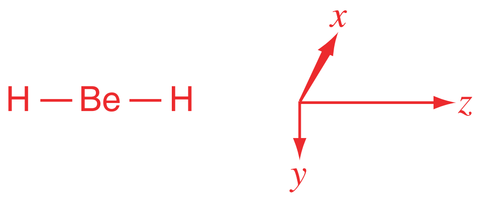
By considering butane in a similar fashion, we would say each carbon atom was sp^3 hybridized: two sp^3 HAO from neighbouring carbon atoms overlap to form a C–C σ bond (and vacant C–C $\sigma^\star$ orbital) and each remaining sp^3 HAO overlaps with a hydrogen 1s AO to form a C–H σ bond (and vacant C–H $\sigma^\star$ orbital). This is shown schematically in the figure below.



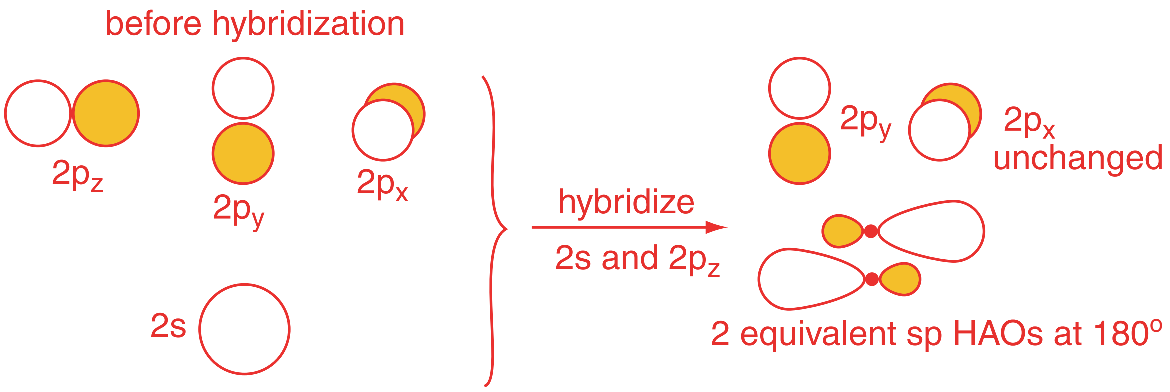
If the shape is known, so is the hybridization

Hybridization is simply a mathematical tool whose purpose is to generate modified atomic orbitals which point directly towards the atoms we wish to bond. In all cases, we do not use hybridization to predict the shapes of molecules, rather it is the other way round – we know the shape which the molecule adopts and hence can say how the orbitals must be hybridized in order to give that shape.

Examples: BeH$_2$

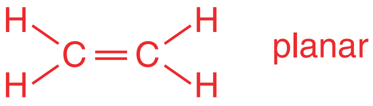


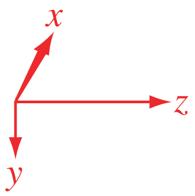
Both the 2s and 2p$_z$ atomic orbitals on the Be atom can be used to bond to the hydrogen atoms. The simplest way to consider the bonding is to first hybridize the Be 2s and 2p$_z$ orbitals to form two sp HAOs which point at 180° to each other.



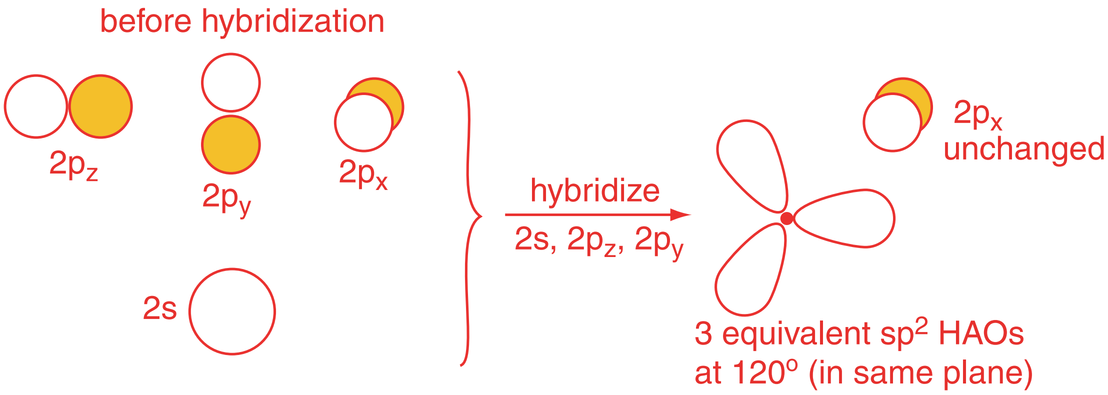
These HAOs can be used to overlap with the hydrogen orbitals.

Ethene

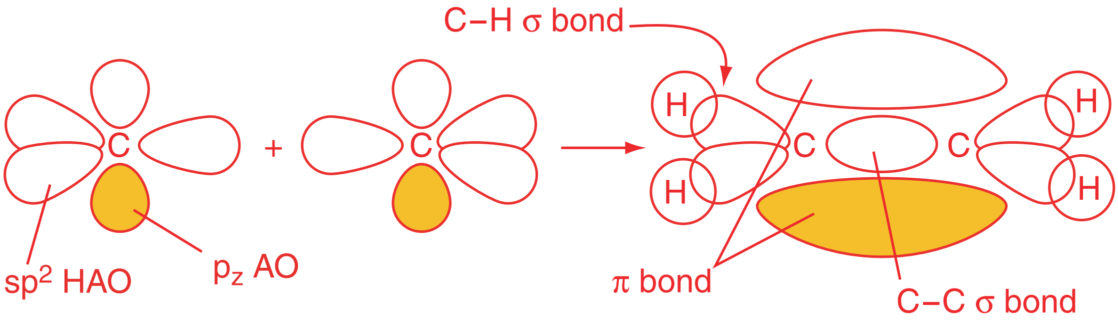




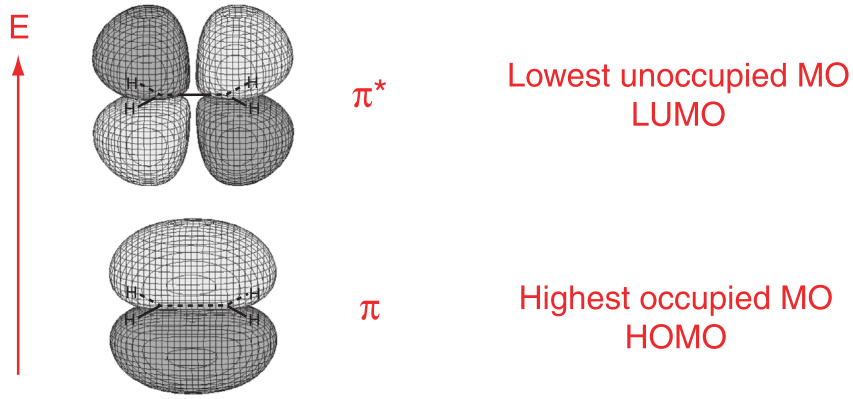
The simplest way to describe the bonding in ethene is to hybridize the carbon 2s, 2p$_z$ and 2p$_y$ AOs to give three equivalent sp^2 HAOs.



The HAOs and AOs then combine to give MOs.



The HOMO in ethene is the π bonding MO and the LUMO is the $\pi^\star$ antibonding MO.



Advantages of Hybridization

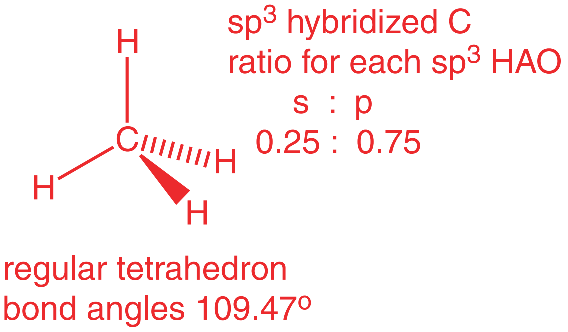
- Simplifies the bonding scheme.
- Gives more directional HAOs that point towards the bonding atoms or where we think of the lone pairs as pointing.
- Gives molecular orbitals in which the electrons are not delocalized over many atoms but instead the bonding electrons are localized in between two atoms and the lone pair electrons centred on one atom.
- More useful when trying to draw mechanisms (see later).

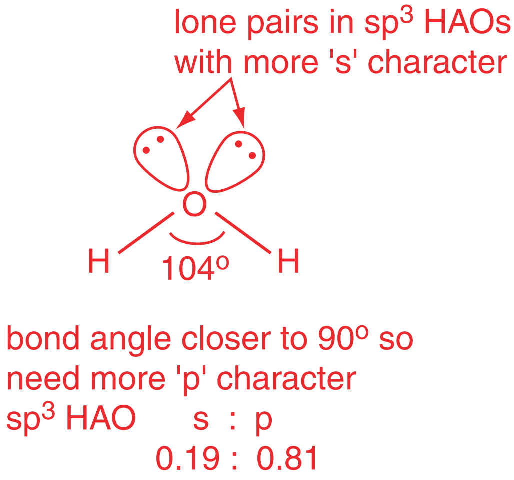
Disadvantages of Hybridization

- Simple hybridization does not give the best picture of the different energy levels within the molecule – further refinements are necessary.
- Encourages a localized view of electrons whereas in reality the electrons are spread over many atoms.

Other bond angles – H_2O

Mixing the s orbital with all three p orbitals gives four sp^3 HAOs which point at 109.47° to one another. Each HAOs has 1/4 ‘s character’ and 3/4 ‘p character’. In water, the H–O–H bond angle is 104°, *i.e.* less than the ideal tetrahedral angle of 109.47°. Since p orbitals point at 90° to each other, increasing the p character in the HAOs reduces the angle between them. This leads to HAOs made from non-integer ratios of s:p AOs.



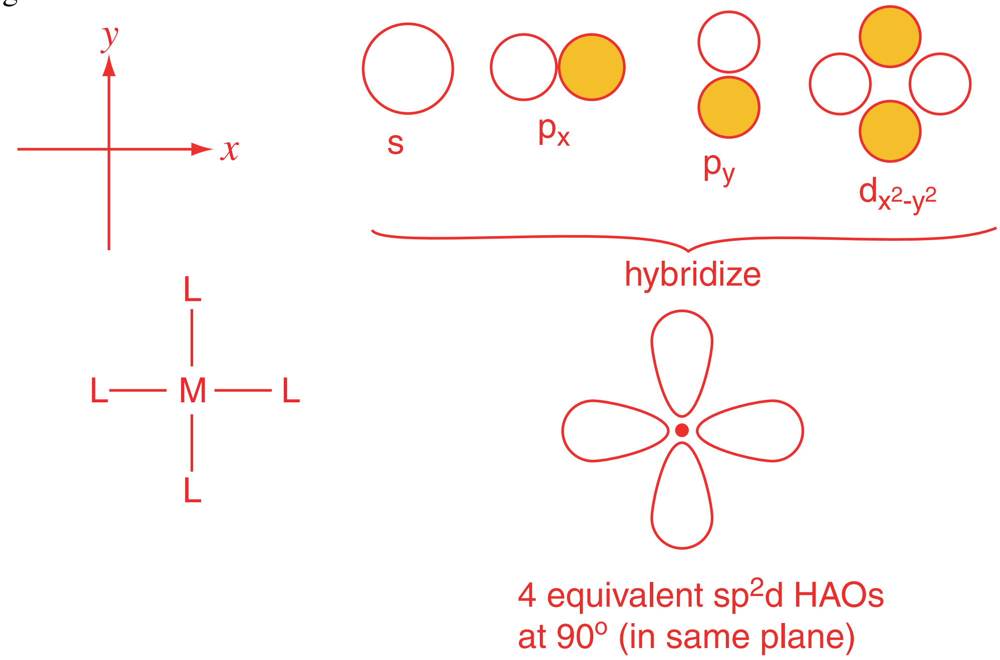


Hybridization using d orbitals

If there are d orbitals sufficiently low in energy to be used in bonding (*e.g.* in the transition metal structures), these too could be involved in forming hybrid atomic orbitals. For example, in the octahedral complex $Cu(H_2O)_6^{2+}$, we could use the s, p and d orbitals on the copper to form the six HAOs needed to bond to the water molecules. Forming *six* HAOs needs *six* AOs; to form HAOs pointing to the corners of an octahedron, the s orbital, all three p orbitals and the d_{z^2} and $d_{x^2-y^2}$ orbitals could be combined.

Note the three p orbitals and the d_{z^2} and $d_{x^2-y^2}$ orbitals all point along the axes towards the ligands. The d_{xy^2}, d_{xz^2} and d_{yz^2} point in between the axes and would not be suitable to interact with the ligands.

To bond to the four ligands in a square planar complex, we would need four HAOs in the same plane (*e.g.* in the x-y plane), pointing at 90°. To form the HAOs, we cannot use any AO in which both the x and y axes lie on nodal planes since such orbitals would have no net interaction with the ligand orbitals.



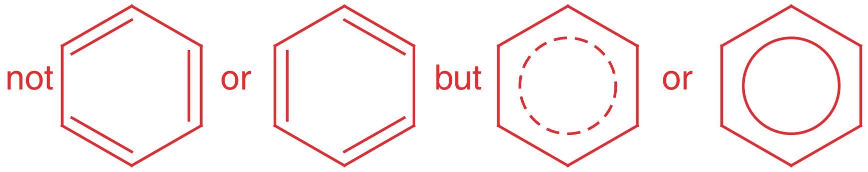
Summary of hybridization states

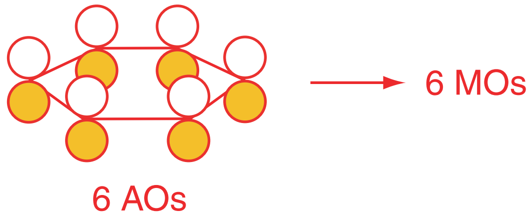
Geometry	Possible hybridization of central atom	Example
linear	sp	BeF_2
trigonal planar	sp^2	BF_3
tetrahedral	sp^3	CF_4
square planar	sp^2d or p^2d^2	$Pt(Cl)_2(NH_3)_2$
trigonal bipyramidal	sp^3d or spd^3	PF_5 ??
octahedral	sp^3d^2	SF_6 ??

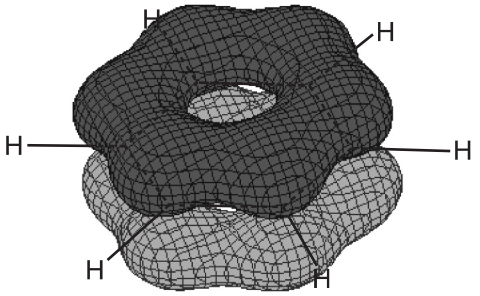
Where different hybridization schemes are possible, the most appropriate one depends on the energy match between the central atom AOs and the ligand AOs; often, for example, the s orbital on the central atom might be too low in energy to interact significantly.

Delocalized Systems - Conjugation

For certain molecules, the localized valence bond scheme may be inadequate. An example is benzene where each of the carbon-carbon bonds is neither a single bond nor a double bond but somewhere in between. To describe the bonding in such species, we usually have to resort back, at least in part, to the molecular orbital picture and form MOs where the electrons may be spread out over many atoms rather than localized between just two.



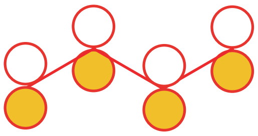




the lowest energy π MO
– holds just 2e⁻

The *six* 2p orbitals on benzene combine to give *six* molecular orbitals – the one illustrated above is the lowest in energy. As usual, each of these MOs can hold two electrons and therefore only the three lowest in energy MOs formed from combining these six p orbitals are occupied. We can still use the localized hybridization approach to describe the C–C and C–H single bond framework, but the π system is best described using the MO approach. This is the case for all molecules with conjugated π systems (alternate double and single bonds).

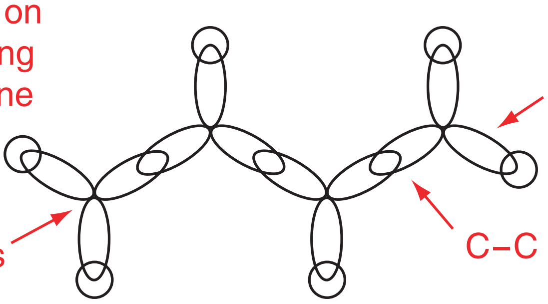
eg butadiene



p orbitals interact to give delocalized MOs

The σ bonding framework of the molecule is best considered using HAOs – each carbon is sp^2 hybridized leaving one p orbital which points out of the plane available for forming π MOs.

1 p orbital left on
each C pointing
out of the plane

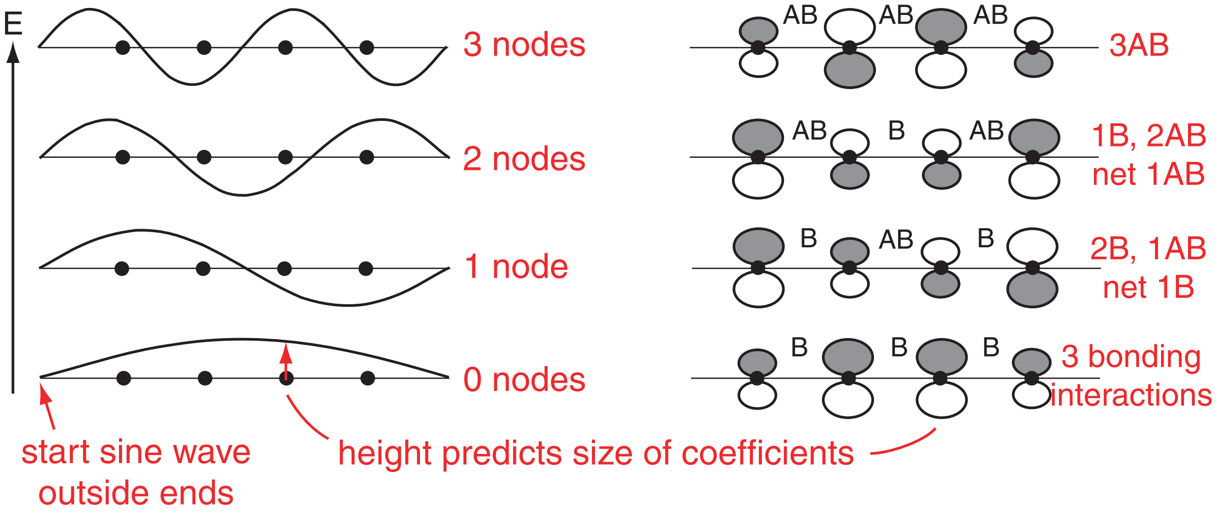


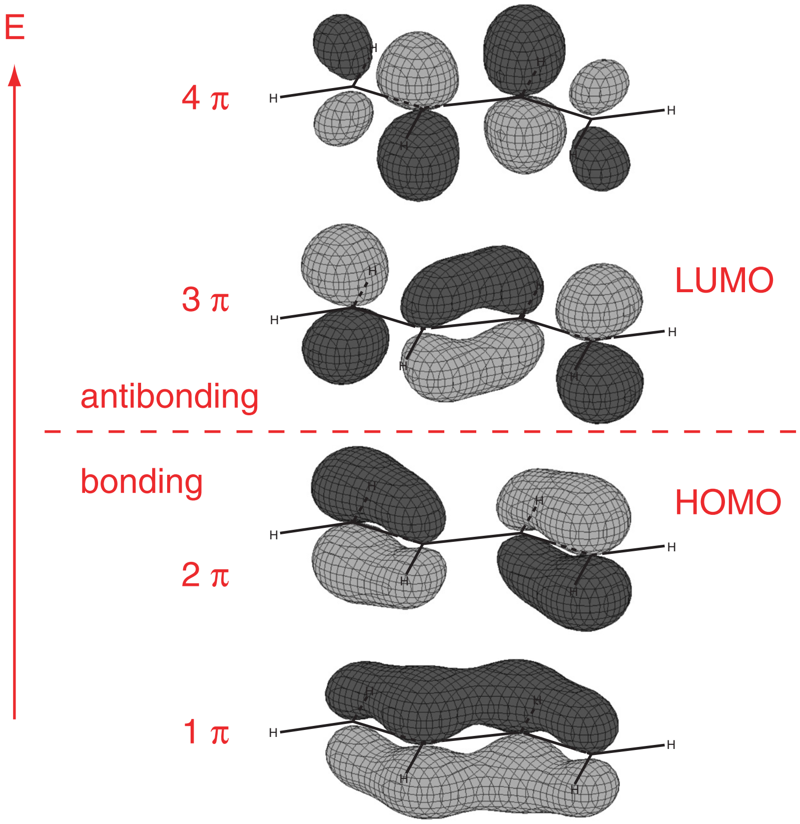
C–H σ bond

each carbon is
sp^2 hybridized

C–C σ bond

Combining n p orbitals gives n MOs. Since successively higher in energy MOs have more nodes, the form of the MOs resulting from combining the out-of-plane p orbitals may be predicted using a rule based on sine waves. We shall now construct the π MOs for butadiene from four p orbitals.

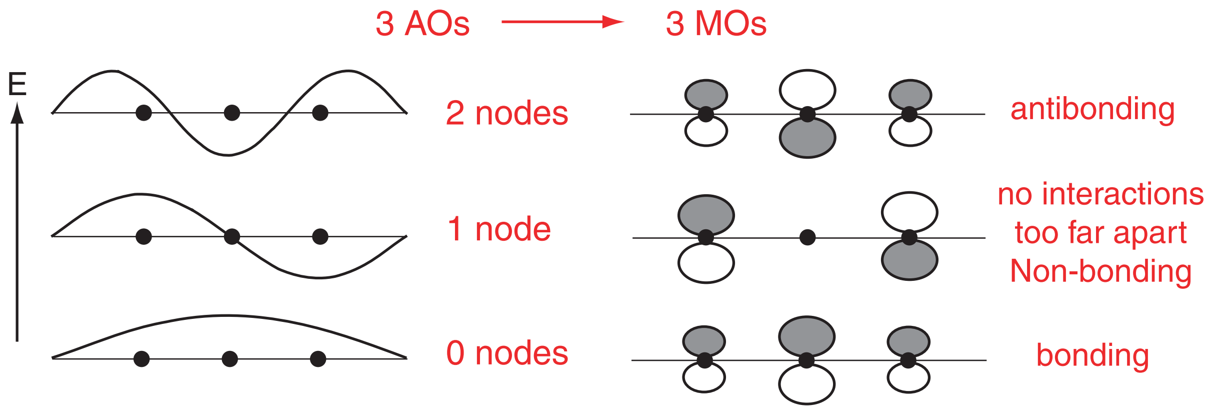




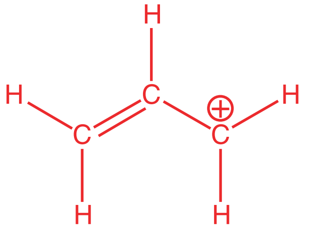
The four electrons in the π system fill up the two bonding MOs, 1π and 2π with two electrons in each. Both of these MOs lead to bonding interactions between carbon atoms 1 and 2 and between atoms 3 and 4. However, the bonding interaction between the two central carbon atoms in 1 is largely cancelled out by the antibonding interaction between these two atoms in 2π. The fact that there is still *some* double bond character about the central bond is because the coefficients are greater in MO 1π than in MO 2π and so the bonding interaction is not *fully* cancelled out.

still best representation, although
some double bond character
about the central 'single' bond

Three p orbitals in a line give three MOs

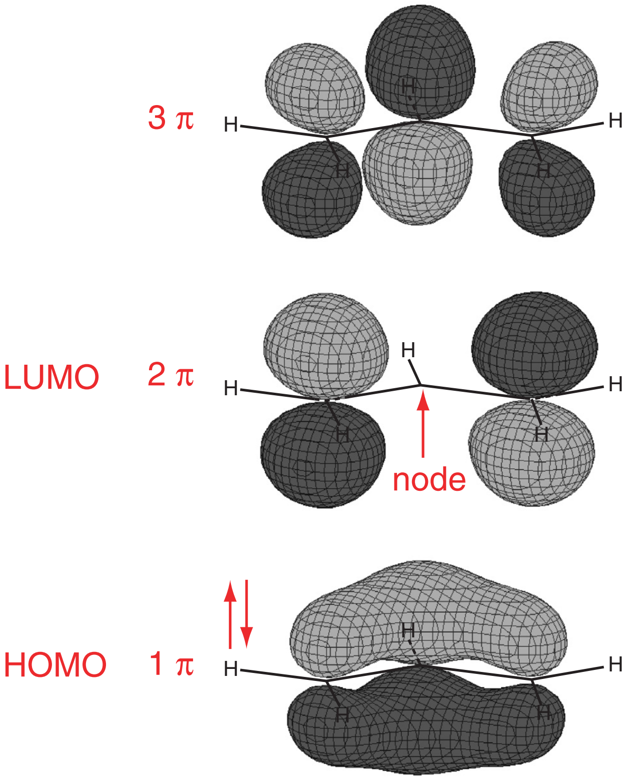


One such system that these MOs can be used for is the allyl cation.



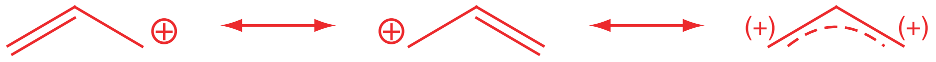
each carbon is sp^2 hybridized leaving one p orbital on each carbon to combine to give 3 π MOs.

only 2e$^-$ in π system

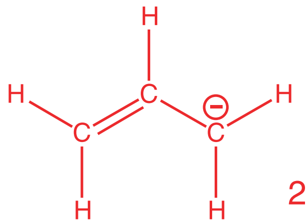


nucleophiles attack into LUMO on the ends

occupied MO shows most e$^-$ density on the central carbon, ∴ least on the ends



The same set of MOs may be used for the **allyl anion**.

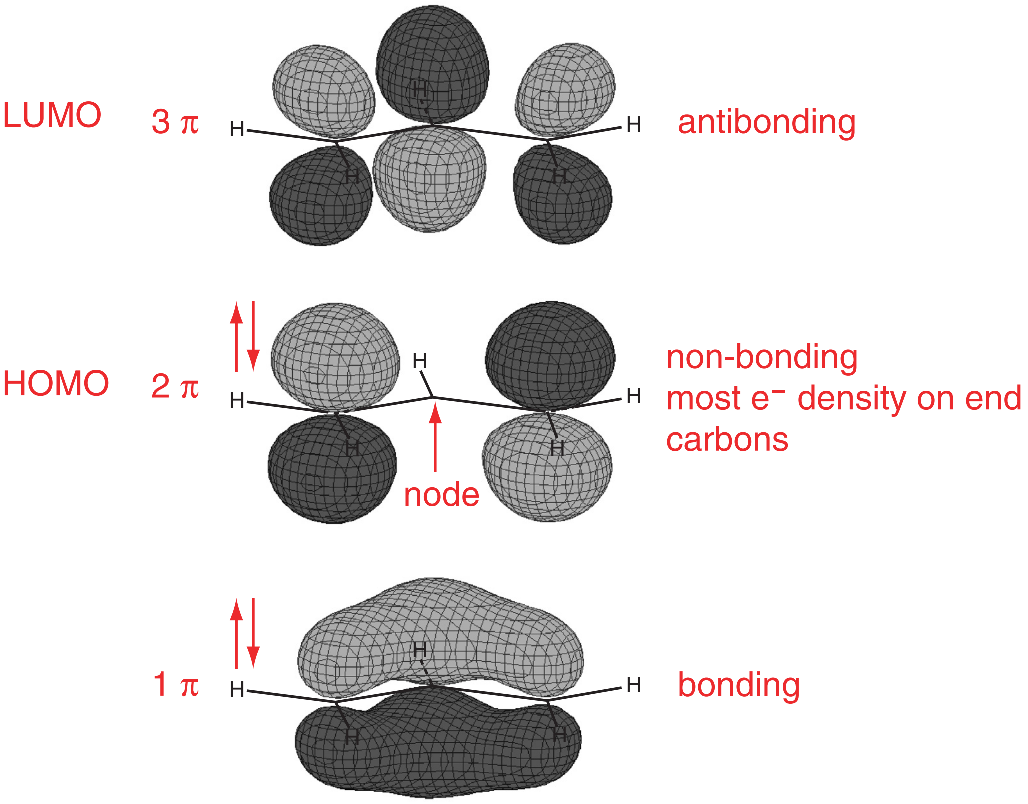


planar anion

2 more e⁻ than the cation

Each carbon is still hybridized sp^2 so the negative charge can be delocalized in the π system.

The same set of orbitals are filled but now there are *four* electrons in the π system. Two in the π bonding orbital and two in the π non-bonding orbital. In the allyl anion, most electron density is on the ends.

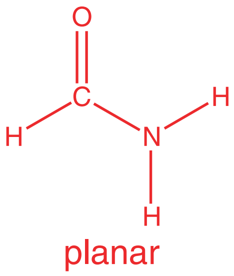


2 end carbons equivalent

The combining p orbitals do not need to be from the atoms of the same element.

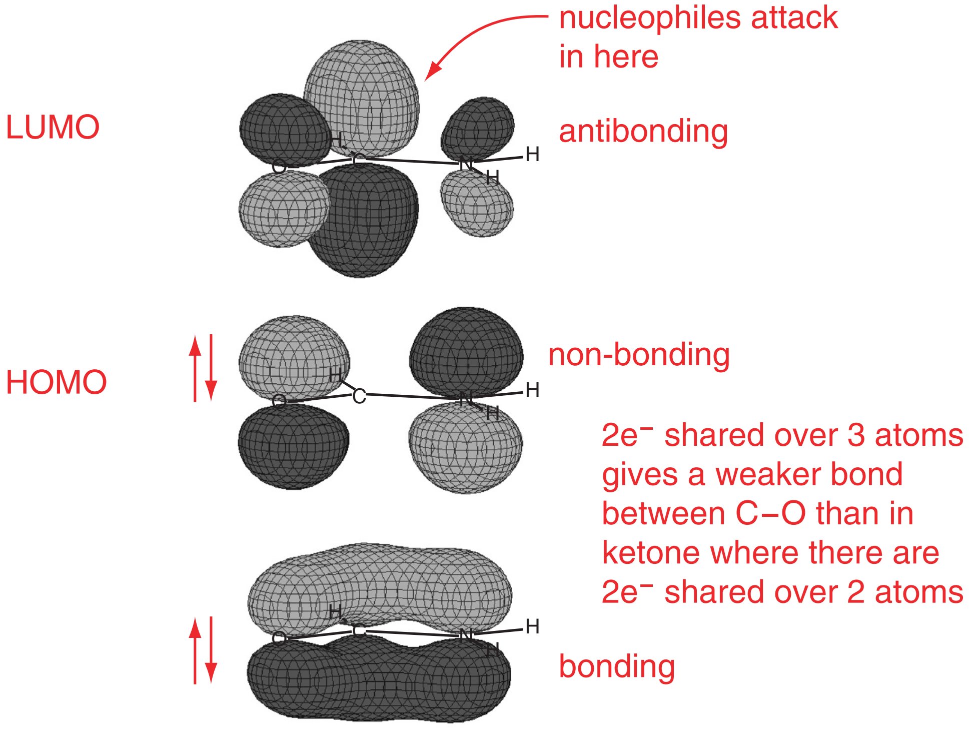
CO_2 could also be described using this scheme as could the carboxylate anion or the NO_2 group. The main difference in the bonding schemes is that AOs from different atoms have different energies which means that the form of the MOs will no longer symmetrical and the electrons density will not be shared evenly over the atoms.

As an example, consider formamide.



C, N and O all sp^2 hybridized
remaining p AOs give 3 π MOs

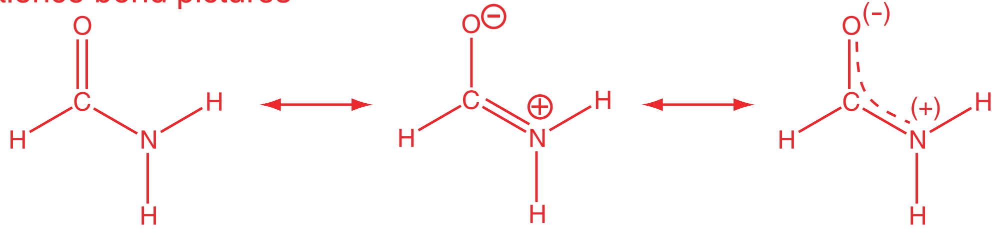
The carbon, nitrogen and oxygen atoms are all sp^2 hybridized. Each has a p orbital perpendicular to the plane of the molecule which can overlap with the others to give three MOs with the same form as for the allyl cation. However, in this scheme the oxygen p orbital is lower in energy than the nitrogen p orbital and lower still than the carbon p orbital.



$2e^-$ shared over 3 atoms gives a weaker bond between C–O than in ketone where there are $2e^-$ shared over 2 atoms

3 centre, $2e^-$ bond

Valence bond pictures



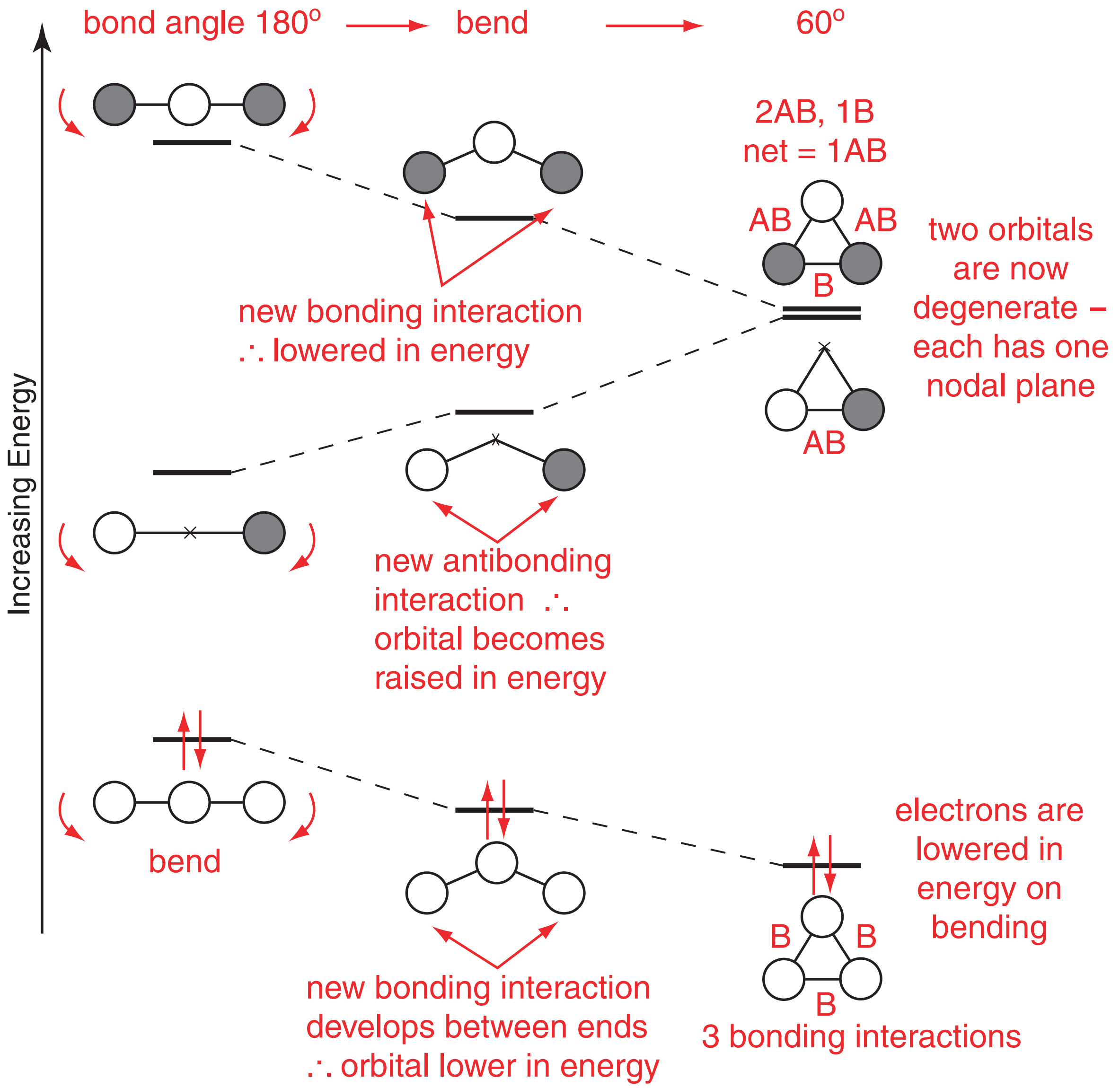
mainly like this

some degree of this

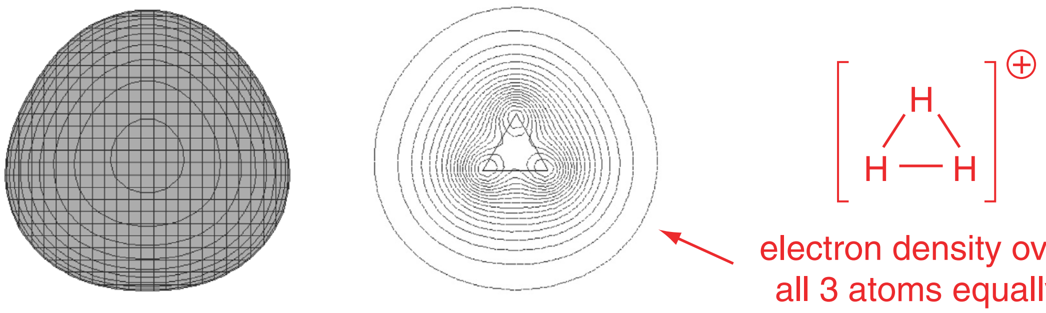
more realistic but awkward representation

Predicting structures by minimizing energies

In all of the examples we have looked at we have assumed the shape of the molecule and then looked at the molecular orbitals it would have. However it is possible (but complicated!) to theoretically predict from scratch the shape a molecule will adopt. In essence we simply assume a starting geometry for a molecule, work out its energy and then alter the geometry slightly and recalculate the energy again. We keep repeating this process until the energy of the molecule is at a minimum. This usually requires considerably computer power and is not something that can be simply worked out on paper. However, we can illustrate how the process works by returning to the very simple H_3^+ ion. Before we assumed the geometry of this ion to be linear but noted that this is not actually correct. On bending the molecule, the way the component atomic orbitals overlap changes and consequently so do the energies of the resultant molecular orbitals.



As is clear from above, the energy of the occupied orbital is lowered on bending. Hence the H_3^+ ion is more stable with the nuclei placed at the corners of an equilateral triangle. This ion has been detected, both in the laboratory and also in space and it does indeed adopt the triangular shape with bond length around 100 pm. The plots for the bonding MO are shown over.



The ‘bonding’ between any two atoms in this ion is same. We artificially draw lines in between the nuclei to represent the bonding but here these lines cannot represent a pair of electrons. The ion only has two electrons and these are delocalised over the whole structure. The bonding may be described as a three-centre, two-electron bond, similar to the bonding in the allyl cation.

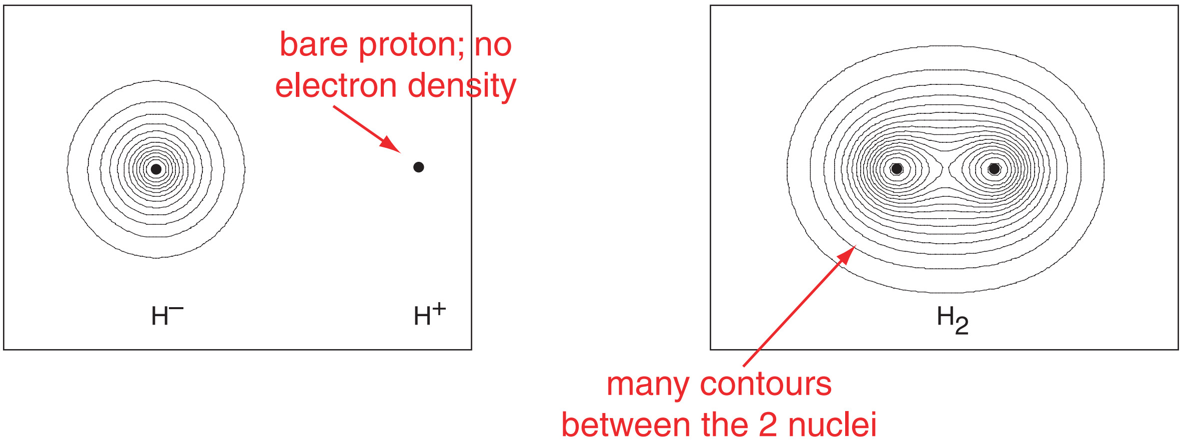
Reactions

Understanding the energies and shapes of molecular orbitals provides us with a means of rationalizing how molecules react. It is often the case that the highest energy electrons in one species may be lowered in energy by interacting with a second species. The shapes of the molecular orbitals give some insight into understanding how the two species interact.

The first ‘reaction’ we shall look at as a model, is the hypothetical reactions between a single proton, H^+, and a hydride ion, H^-, to produce H_2.

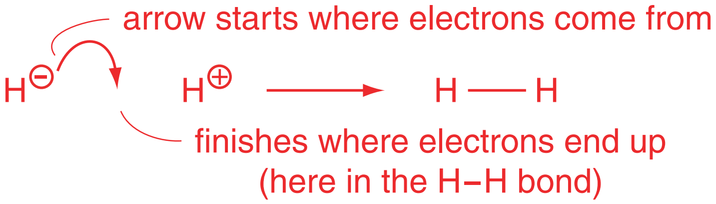
$$H^+ + H^- \longrightarrow H_2$$

The *initial* attraction between the two oppositely charged ions is electrostatic, but the interaction does *not* lead to an ionic bond but a covalent one where the two electrons are shared equally between the two nuclei. This is shown by the electron density contour maps:



Curly arrows

Chemists illustrate this redistribution of electrons by the use of *curly arrows*. A curly arrow represents the movement of a *pair* of electrons; they start where the electrons are in the reactants (here in the H^- ion) and show where the pair end up in the product (in this case between the two nuclei in the new bond).



We should compare this reaction between two ions with the reaction between two neutral hydrogen atoms. Each atom has just one electron associated with it so we do not use the normal curly arrows which are reserved for the movements of *pairs* of electrons; instead we use *half arrows* or *fish-hook arrows*.

You will not meet any further radical reactions involving the movements of single electrons this year but the comparison here is useful since it emphasises the meaning of the usual curly arrows and the fact that the hydride ion, H^-, with its overall negative charge, does indeed possess two electrons.

Formation of lithium borohydride

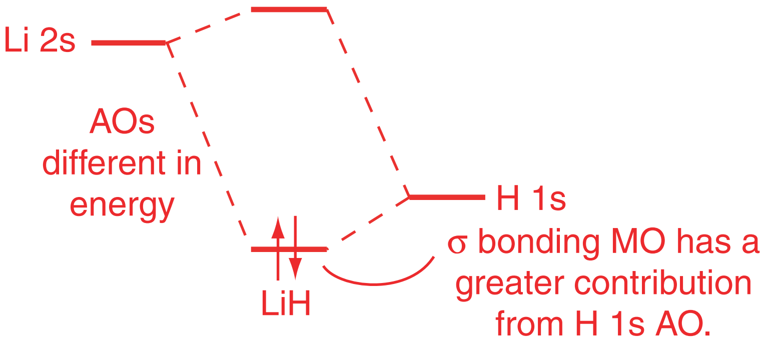
Let us consider the formation of lithium borohydride, $LiBH_4$, from lithium hydride and borane. The reaction readily takes place when borane gas (which actually exists as the dimer, B_2H_6) is bubbled through a mixture of lithium hydride, LiH, in ethoxyethane (ether) solvent. The reaction may be represented:

$$LiH + BH_3 \longrightarrow LiBH_4$$

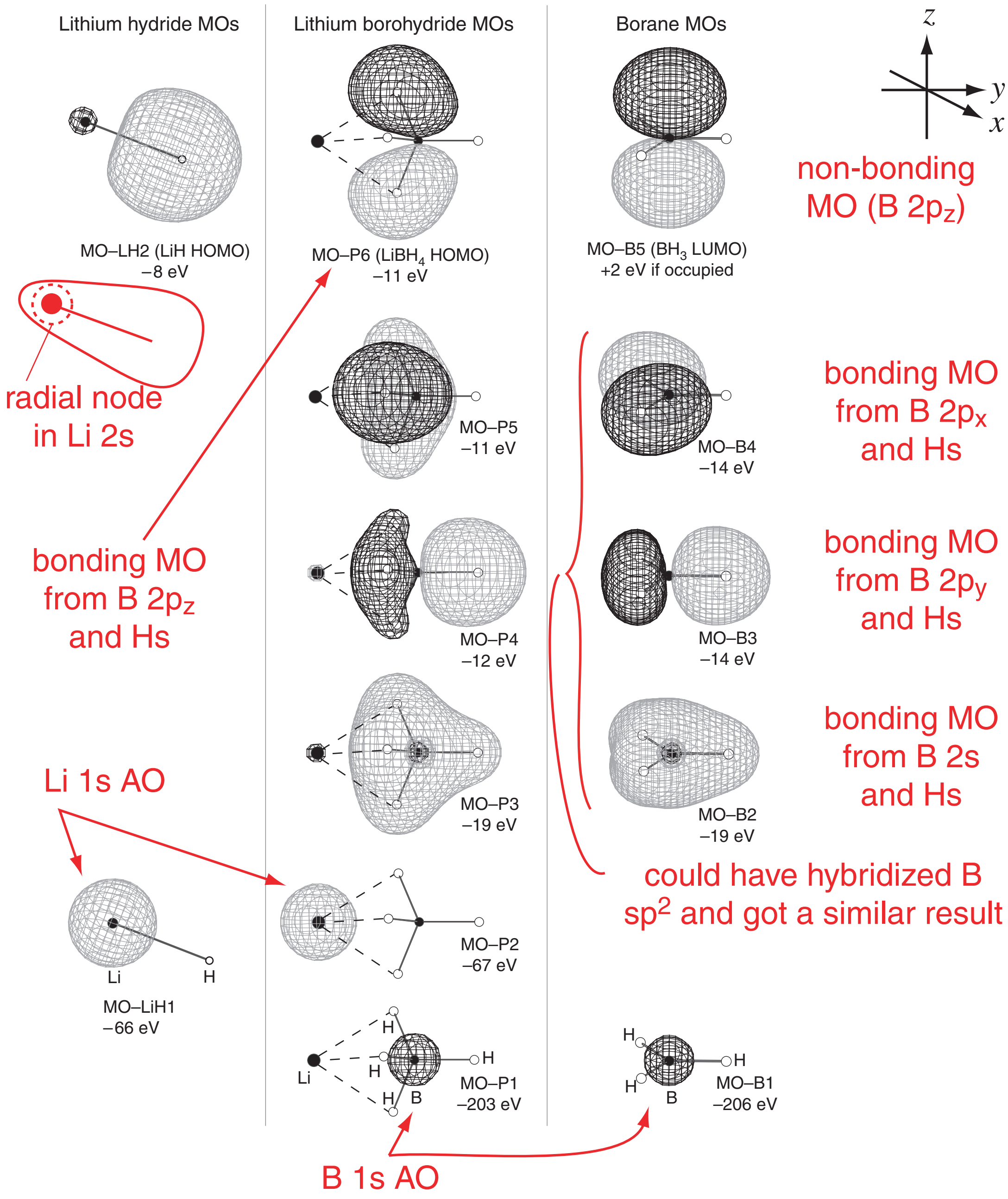
The molecular orbitals for the reactants and products are shown over the page, together with their approximate energies.

Let us first consider the MOs for LiH. The lowest energy orbital, MO-LH1, at −66 eV, is essentially just the 1s AO on lithium (it is just off the graph on page 20). This AO is too contracted and too low in energy to interact with the hydrogen atom in LiH or indeed any atoms in the product and so remains essentially unchanged during the reaction.

The Highest Occupied MO in LiH, MO-LH2, is a result of the interaction between the lithium 2s AO and the hydrogen 1s AO. Consulting the graph on page 20, we see that the hydrogen 1s AO is considerably lower in energy than lithium 2s AO hence the bonding MO formed (MO-LH2) has a greater contribution from the hydrogen atom than from the lithium atom. This is clearly seen in the orbitals's appearance.



The very lowest energy orbital in both BH_3 and $LiBH_4$ is the 1s atomic orbital on the boron at *ca.* −203 eV. It is considerably lower in energy than the lithium 1s since boron has a greater Z_{eff}. It too remains essentially unchanged during the reaction.

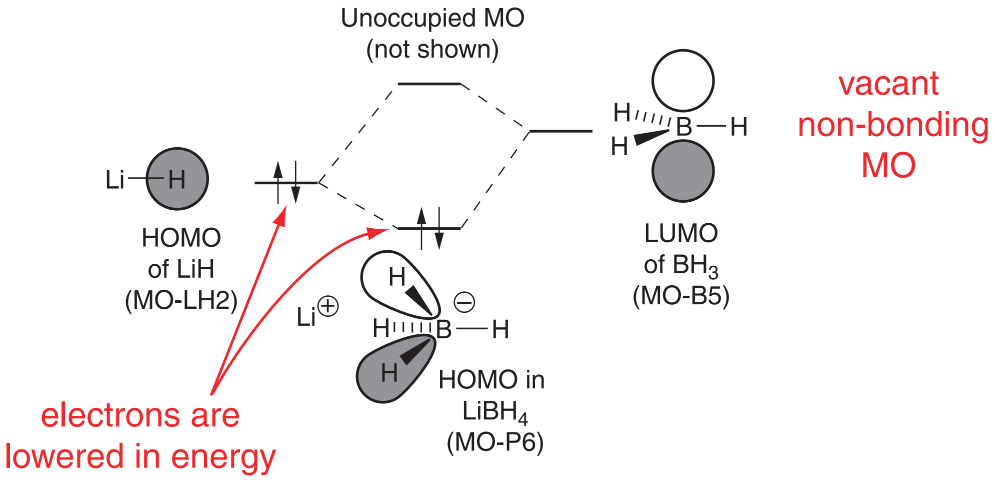


The MOs labelled MO-B2, B3 and B4 in BH_3 are all bonding between the boron and the hydrogen atoms. These are all delocalised MOs: MO-B2 is a combination of the boron 2s and the hydrogen 1s orbitals; MOs B3 and B4 are combinations of the boron $2p_y$ and $2p_x$ AOs with the hydrogen 1s orbitals. Because the three hydrogen atoms in planar BH_3 lie in the nodal plane of the boron's $2p_z$ orbital, there can be no net interaction between these orbitals. Thus MO-B5 is simply the (vacant) $2p_z$ AO of the boron.

Note that instead of using the boron 2s, $2p_x$ and $2p_y$ AOs separately to form delocalized bonding MOs with the hydrogens, we could have come up with a similar picture by considering the boron atom in BH_3 to be sp^2 hybridized. In either scheme, the Lowest Unoccupied MO in BH_3, the boron $2p_z$, remains exactly the same.

In the product, $LiBH_4$, MOs P3, P4 and P5 are essentially just modified versions of the orbitals B2, B3 and B4 in BH_3; they have the same approximate forms and energies even though they are now involved in bonding four hydrogen atoms in the product rather than just the three in the reactant, BH_3.

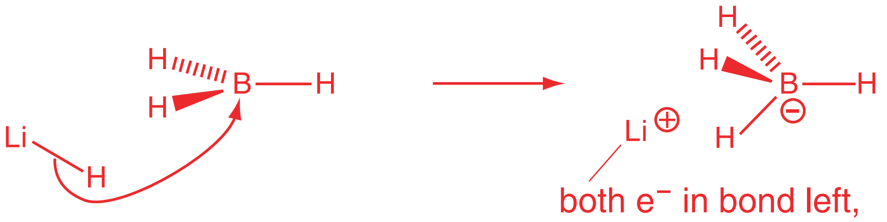
The highest energy electrons in the reactants, at −8 eV, were in MO-LH2 MO of the lithium hydride. The highest energy electrons in the product, at −11 eV, are in MO-P6. However, the form the HOMO in the $LiBH_4$ does not resemble the HOMO in LiH but is much closer in form to the LUMO in BH_3. MO-P6 is a bonding MO, consisting of a bonding interaction between the boron $2p_z$ with the hydrogens. We can show its formation from the interaction between the BH_3 LUMO and the LiH HOMO:



vacant non-bonding MO

electrons are lowered in energy

In BH_3 there are three pairs of electrons contributing to the three B–H bonds. In the product, $LiBH_4$, there are four pairs contributing to the four B–H bonds. The orbital interactions show that it is the electrons in the HOMO of the LiH (which are more associated with the hydrogen rather than the hydrogen) that end up contributing to the B–H bonding in the product (in MO-P6). We can use a curly arrow mechanism to sum up what happens during the interaction:



both e⁻ in bond left, leaving lithium as the +ve ion

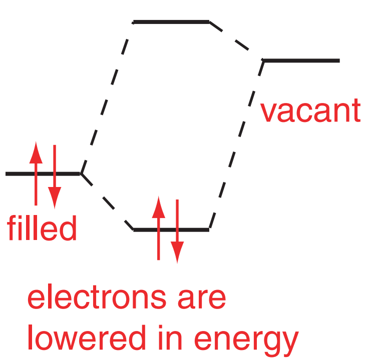
These arrows suggest that the electrons that were in the bond between the lithium and the hydrogen (but more associated with the hydrogen) end up contributing to a new bond between the boron and the hydrogen. This is consistent with what the MO interactions are telling us.

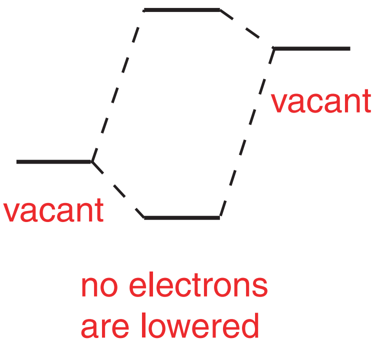
Summary

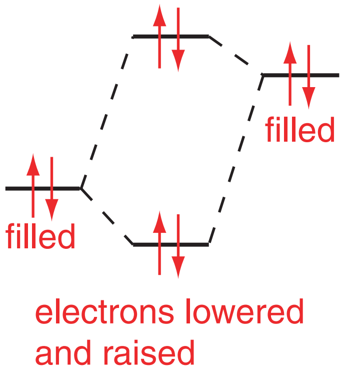
- The MOs for a product may be considered as arising from interactions between the MOs in the reactants.
- Many of the MOs remain virtually unchanged in the reactants and products.
- One of the most important interactions is that between the HOMO of one reactant and the LUMO of the other. This interaction will lead to a net lowering in energy of the most energetic electrons.
- A curly arrow mechanism helps to understand what has happened during the interaction.

HOMO-LUMO interactions

The interaction between a filled orbital from one species with a vacant orbital from a second always leads to a net lowering of energy of the electrons. This is not the case from interactions between two empty orbitals, or between two filled orbitals.

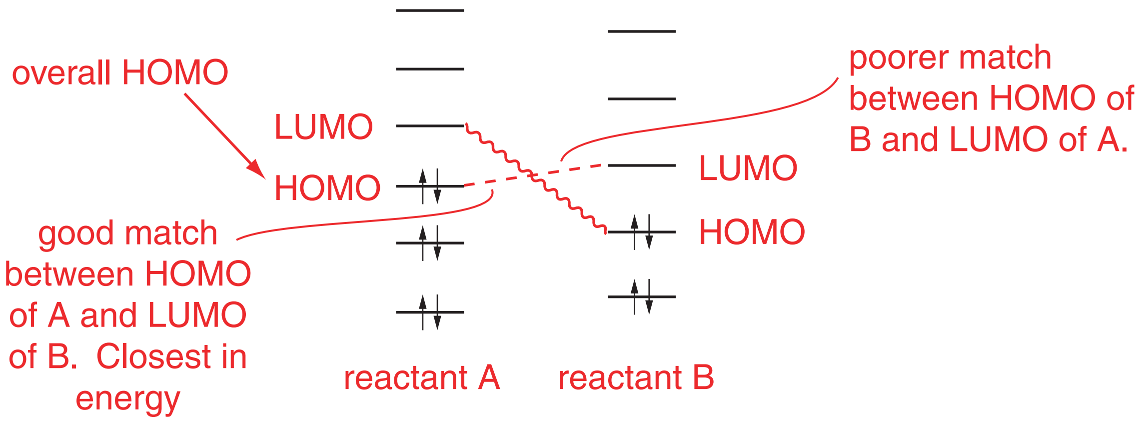




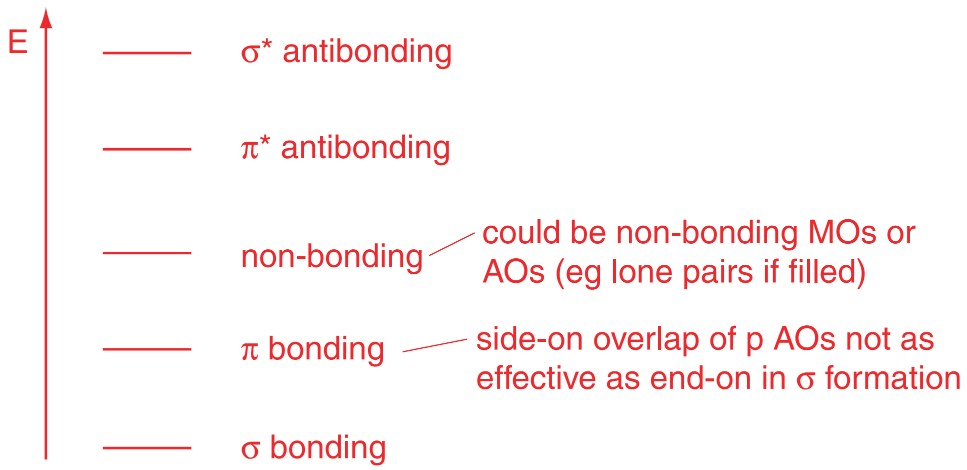


This lowering in energy of the electrons is a key driving force behind why the reaction takes place.

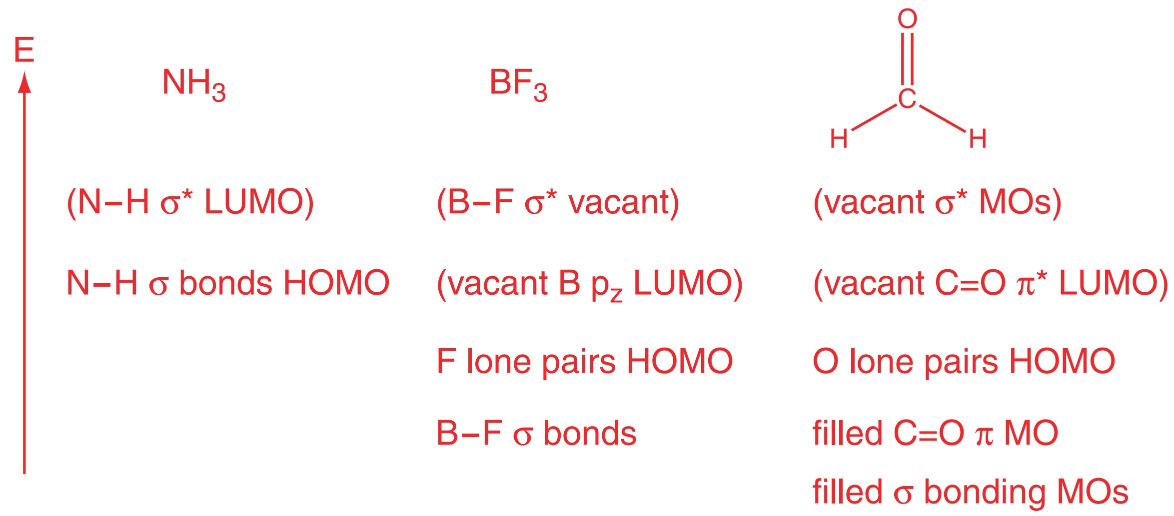
Often we can rationalize a reaction by focusing on the HOMO-LUMO interactions between the reactants. However, *two* HOMO-LUMO interactions are possible between two reactants; the HOMO of reactant A with the LUMO of reactant B and the HOMO of B with the LUMO of A. The *best* interaction will be between the orbitals which are closest in energy and this will be between whichever HOMO of A or B is higher in energy with the LUMO from the other reactant.



In order to help predict which orbitals are the HOMO and LUMO for any molecule, we shall use a simple ordering in terms of energy as a guide.



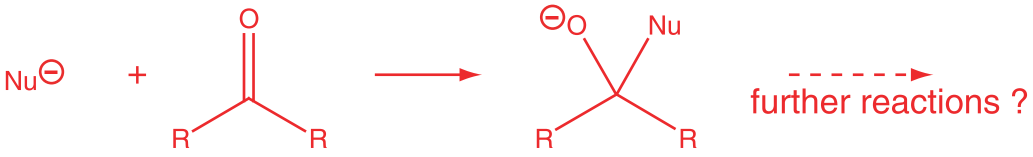
Examples



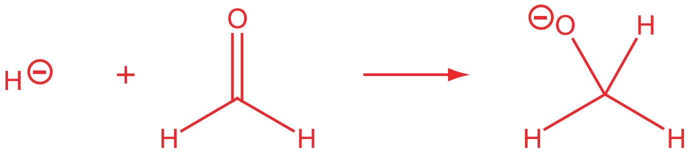
Nucleophilic addition to the carbonyl group

In this important class of reaction, a general nucleophile, Nu^-, attacks the carbonyl carbon, forming a new bond and simultaneously breaking the C–O π bond. The nucleophile might be hydroxide, cyanide (CN^-), a reducing agent such as $LiAlH_4$ (effectively adding H^-), or an alkyllithium reagent, R–Li (essentially adding R^-). The nucleophile need not necessarily be charged; NH_3 and H_2O are two such examples which can readily attack certain carbonyl groups. You will meet other examples later in the course.

All of the reactions be represented by the general equation:



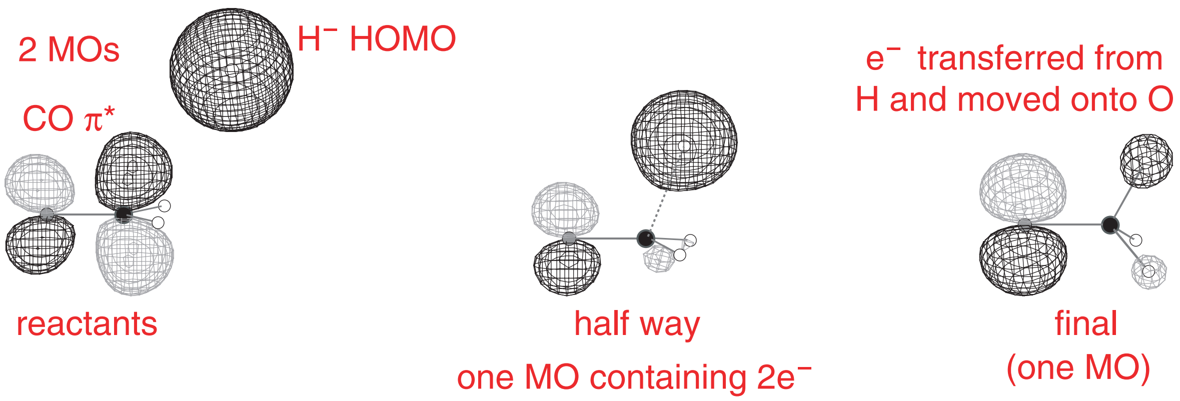
As an example, we shall consider the simplest possible interaction – that between a hydride ion and methanal:



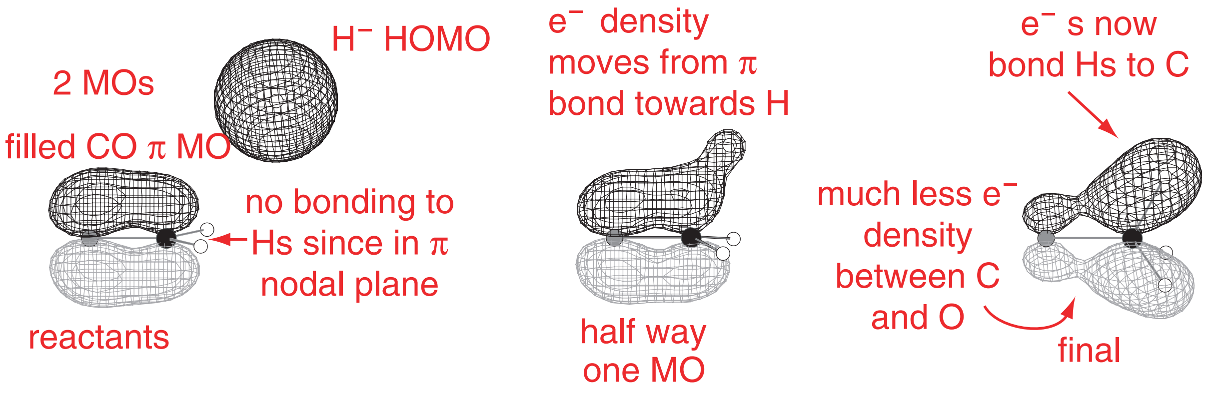
The carbonyl carbon bares a partial positive charge due to the influence of the electronegative oxygen atom attached to it. Hence there is an initial *electrostatic* attraction between the negatively charged hydride and the carbon. However, the two species do not just remain attracted to each other electrostically; bonds are broken and formed and electrons are redistributed.

All of the σ bonds present in the reactants remain essentially unchanged in the products – the 'action' involves the C–O π bond which disappears during the reaction. We can understand what takes place by considering the HOMO-LUMO interactions between the two species.

Consulting the graph on page 20 confirms that the very highest energy electrons are those in the HOMO of the hydride ion. These are higher in energy than the lone pairs of electrons on the carbonyl oxygen which represent the HOMOs for the methanal. The best interaction of the hydride HOMO is with the LUMO of the methanal, the $\pi^\star$ MO. This interaction is shown below.

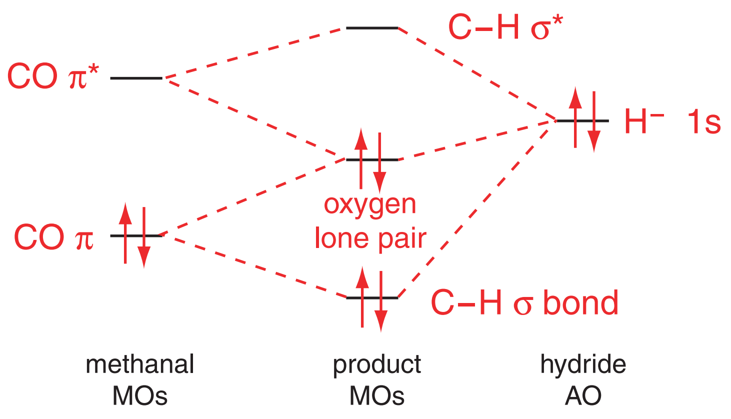


The orbitals show that electron density gradually disappears from the hydride and accumulates on the oxygen. This is one part of what we know happens during the reaction. The second thing we know takes place is that the π bond breaks. We can also look at the MOs to see what happens to the C–O π bond during the reaction.



During this interaction we see that the π electron density between the carbon and oxygen atoms decreases which corresponds to the C–O π bond breaking. What is more, whilst the carbon p orbital initially contributing to the π bond in methanal could not help bond to the hydrogen atoms, in the product this carbon p orbital does overlap with the hydrogens, contributing to the C–H bonding.

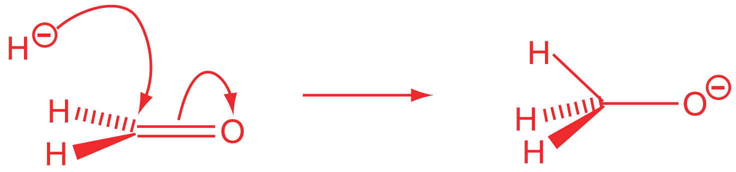
The interaction of the three orbitals – the carbonyl π and $\pi^\star$ and the hydride HOMO – gives rise to three new MOs in the product. A simple energy level diagram shows the interactions:



The important result is that overall, the energy of the electrons is lowered during the reaction which explains why it takes place.

Curly arrows

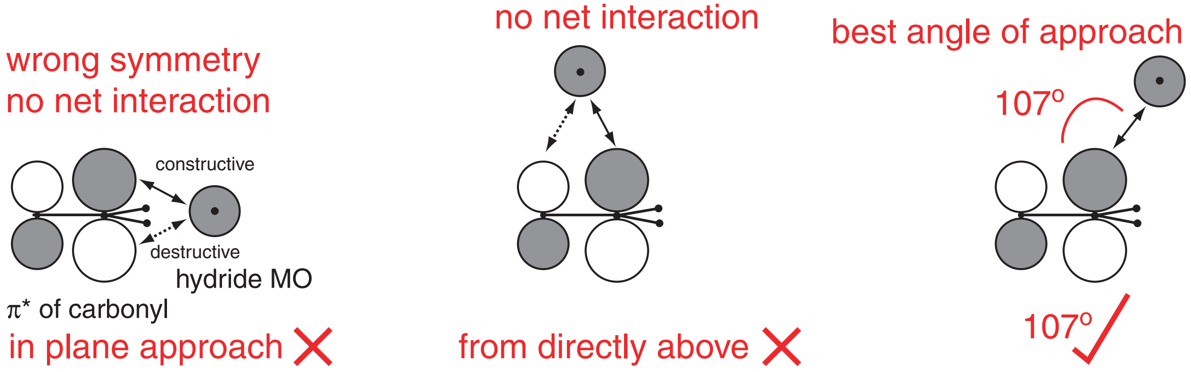
The key features of the reaction between methanal and hydride ion may be shown using a curly arrow mechanism.



The arrows show that the hydride ion attacks the carbonyl carbon and that a new bond forms between the carbon and the hydrogen. They also show that the π bond breaks and the electron density ends up on the oxygen.

Geometry of attack

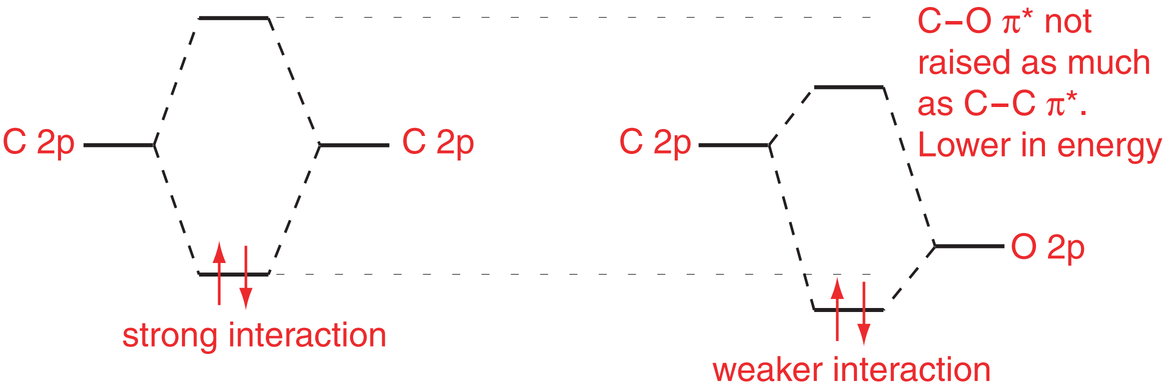
The orbitals also help us to rationalise the preferred angle from which an incoming nucleophile attacks a carbonyl group. There will be no net interaction if the nucleophile attacks from either directly above the carbonyl or in the same plane as the molecule. The most favourable angle, supported by experimental evidence, is somewhere in between these two extremes at approximately 107° from the carbonyl.



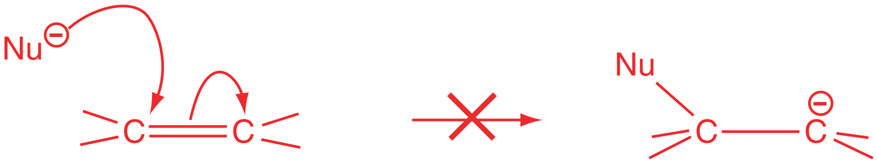
Other $\pi^\star$ orbitals; C=C *vs* C=O

Whereas nucelophiles readily attack into the C–O $\pi^\star$ of carbonyl groups, they do not usually react with alkenes by attacking into the C–C $\pi^\star$. One reason for this difference in behaviour is because, unlike the carbonyl, a C=C bond has no dipole moment. This means there is not the initial electrostatic attraction bringing the two species together. A second reason is because the C–C $\pi^\star$ is higher in energy than the C–O $\pi^\star$ and so there is a worse match between the HOMO of the nucleophile and the $\pi^\star$.

We can understand why the C–O $\pi^\star$ is lower in energy, and hence is more readily attacked than the C–C $\pi^\star$ by considering how each is formed from the overlap of 2p atomic orbitals. The poorer energy match between the carbon p orbital and the oxygen p orbital means there is a weaker interaction between these orbitals.



A final reason why nucleophiles do not attack alkenes in an analogous manner to the reaction with carbonyls, is that if the reaction did take place, a new bond would form between the carbon and the nucleophile and the C=C double bond would break *leaving the negative charge on the carbon*. This is nowhere near as favourable as the attack on a carbonyl where the negative charge ends up on the oxygen atom, the orbitals of which are considerably lower in energy than those of carbon (see graph on page 20).



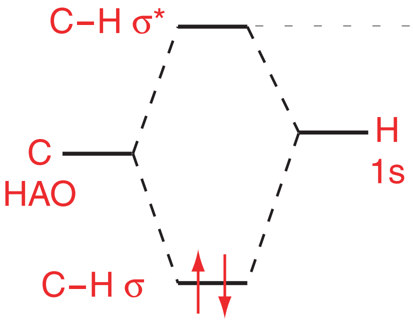
Nucleophilic substitution

The final type of reaction we are going to look at is a *Nucleophilic substitution* reaction where the incoming nucleophile attacks into a $\sigma^\star$ MO, thereby breaking a σ bond.

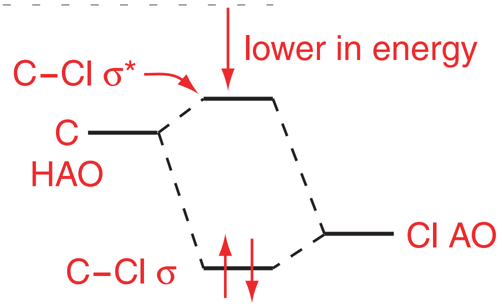
For example:

$$\mathrm{Nu^- + CH_3Cl \longrightarrow CH_3Nu + Cl^-}$$

Methyl chloride (chloromethane) has no π bonds and hence no π or $\pi^\star$ orbitals to attack into. The only bonds are C–H σ bonds and a C–Cl σ bond. The only vacant MOs the nucleophile can interact with are therefore the C–H $\sigma^\star$ MOs or the C–Cl $\sigma^\star$ MO. The question is, which $\sigma^\star$ is lower? We may answer this question by looking at the relative energies of the AOs which form these MOs.



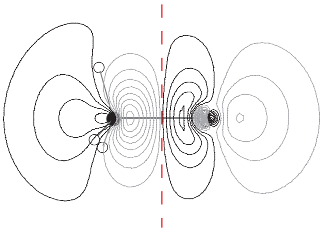
strong interaction



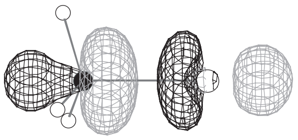
poor interaction

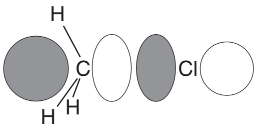
Whilst the carbon and hydrogen AOs are very similar in energy, there is a much poorer energy match between the carbon and chlorine AOs. What is more, there is a poor *size* match between the AOs (the valence AOs of the carbon are the 2s and 2p orbitals whereas those of the chlorine are the 3s and 3p). Taken together, these two factors mean that the interaction between the carbon and chlorine AOs is not as strong as that between the carbon and the hydrogen AOs and so the C-Cl $\sigma^\star$ MO is lower in energy than the C-H $\sigma^\star$.

Three different ways of representing the C-Cl $\sigma^\star$ MO are shown below.



node in between nuclei





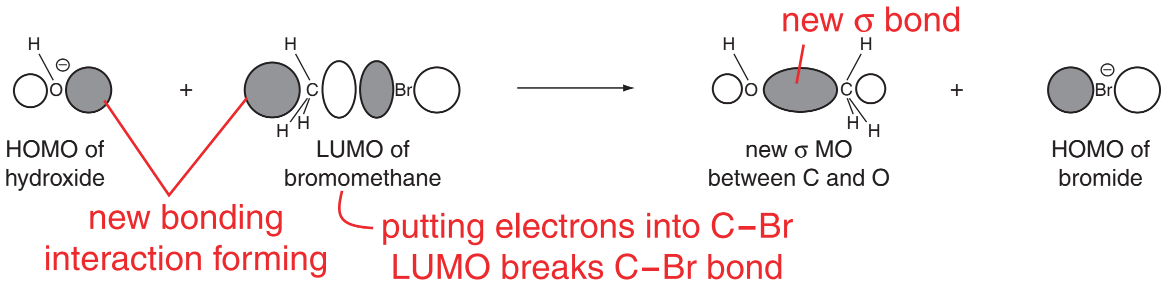
simple sketch

As an example of a nucleophilic substitution reaction, we shall consider the reaction between hydroxide ion and methyl bromide (bromomethane):

$$HO^- + CH_3Br \longrightarrow CH_3OH + Br^-$$

The highest energy electrons in the reactants are the non-bonding lone pairs on the hydroxide ion. For simplicity, we shall consider these lone pairs as residing in sp^3 AOs. One of the lone pairs interacts with the LUMO of the methyl bromide, the C–Br $\sigma^\star$.

Because of the difference in the electronegativities between carbon and bromine, the methyl bromide possesses a dipole moment, with the carbon atom slightly positively charged and the bromine slightly negatively charged. There is therefore an initial electrostatic attraction between the negatively charged hydroxide and the carbon atom. The best orbital interaction between the HOMO of the hydroxide and the LUMO of the methyl bromide is achieved if the nucleophile attacks the carbon from the opposite side to the bromine.

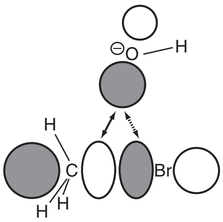


new σ bond

new bonding interaction forming

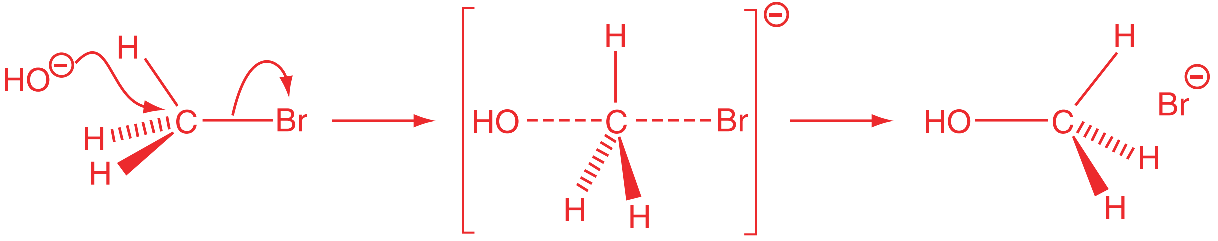
putting electrons into C–Br LUMO breaks C–Br bond

The hydroxide ion cannot approach the carbon from the side, since there would be poor overlap between the hydroxide HOMO and the LUMO of the methyl bromide, the C–Br $\sigma^\star$.



no net interaction also repulsion from e⁻ in C–Br σ bond

During the reaction, a new σ bond forms between the oxygen and the carbon and at the same time, the bond between the carbon and the bromine breaks. Eventually, the bromide ion leaves, carrying with it the negative charge. The curly arrow mechanism for the reaction may be represented:



transition state

The species in the middle in the square brackets is a *transition state*. It cannot be isolated and is just an arrangement of atoms through which the system passes during the reaction. In this structure, the three hydrogen atoms are in the same plane as the central carbon atom. In the product, the hydrogens all end up on the opposite side of the carbon from where they started in the reactant. We say that the carbon centre has undergone an *inversion* during the reaction.

This type of reaction and many others will be explored in more detail in the following course.

Appendix

The table gives the hydrogen atomic wavefunctions in their real forms for $n = 1, 2$ and 3. Each function is also multiplied by a normalization constant but this has been omitted for clarity; a_0 is the Bohr radius.

	$n = 1$	$n = 2$	$n = 3$
s	e^{-r/a_0}	$\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\left(27 - \frac{18r}{a_0} + \frac{2r^2}{a_0^2}\right) e^{-r/3a_0}$
p_z		$\left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos\theta$	$\left(\frac{r}{a_0}\right)\left(6 - \frac{r}{a_0}\right) e^{-r/3a_0} \cos\theta$
p_x		$\left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin\theta \cos\phi$	$\left(\frac{r}{a_0}\right)\left(6 - \frac{r}{a_0}\right) e^{-r/3a_0} \sin\theta \cos\phi$
p_y		$\left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin\theta \sin\phi$	$\left(\frac{r}{a_0}\right)\left(6 - \frac{r}{a_0}\right) e^{-r/3a_0} \sin\theta \sin\phi$
d_{z^2}			$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \left(3\cos^2\theta - 1\right)$
d_{xz}			$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \sin 2\theta \cos\phi$
d_{yz}			$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \sin 2\theta \sin\phi$
$d_{x^2-y^2}$			$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \sin^2\theta \cos 2\phi$
d_{xy}			$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \sin^2\theta \sin 2\phi$

Problems

1. The hydrogen atom orbitals can be characterised by the number of radial nodes and nodal planes in their wavefunctions. Examine the plots of the wavefunctions against r (given in the handout) and determine the number of radial nodes present in each type of orbital (1s, 2s, 2p, 3s, 3p and 3d). Make rough sketches of these plots and indicate on them where the nodes are (for present purposes, do not count it as node if the wavefunction goes to zero at the nucleus or at very large distances from the nucleus).

Now turn to the density plots and three-dimensional representations of the same orbitals, also shown in the handout. Examine these plots and determine the number of angular nodes present; make sketches showing where the planes are. Use these observations to find general formulae, expressed in terms of n (the principal quantum number) and l (the angular momentum quantum number), for (a) the number of radial nodes, (b) the number of angular nodes and (c) the total number of radial nodes and angular nodes.

By identifying the radial and angular nodes, suggest what orbitals the density plots on the cover of the hand out show. Each shows a cross section through the xz plane.

2. What orbitals would you expect to find in the shell with $n = 4$? By comparison with the plots given in the handout, sketch the form of the radial part of the wavefunction for an orbital with $n = 4$ and the highest value of l that is possible: start by considering how the wavefunction varies with the distance from the nucleus and then speculate about the three-dimensional shape of the orbital. Attempt a three-dimensional sketch of a possible form for the orbital, indicating where the angular nodes come.

3. (For the mathematically confident.)

In polar coordinates, the operator may be re-written:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\sin^2\theta\frac{\partial^2}{\partial\phi^2}$$

Whilst at first sight this looks rather formidable, when acting on the wavefunction for an s orbital which contain no angular parts, the expression becomes much more manageable. The full Schrödinger equation for the hydrogen 1s orbital is given by:

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_{1s}}{\partial r}\right)\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi_{1s} = E\psi_{1s}$$

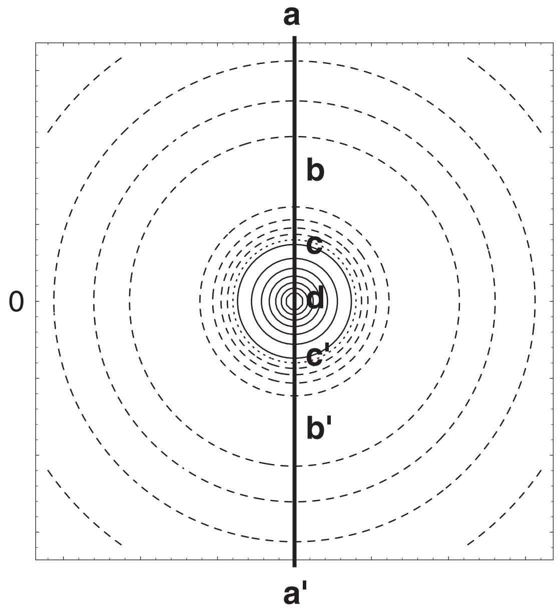
where $\psi_{1s} = \exp(-r/a_0)$

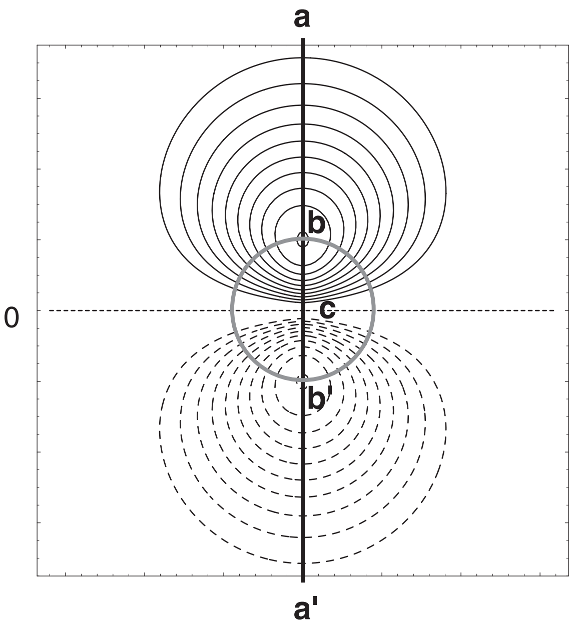
and a_0, the Bohr radius, is given by:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

Show that ψ_{1s} is indeed a solution to the Schrödinger equation by showing that the left hand side of the equation is equal to the right and hence determine the energy, E, associated with the 1s orbital. Compare your answer with that given on page 8.

4.





Shown above are contour plots for the 2s and $2p_z$ orbitals, taken through the *xz* plane with the nucleus at the centre of the plot. Each contour joins points with a specific value of the wavefunction. Where the wavefunction is positive, the contours are drawn solid — where the wavefunction is negative, the contours are dashed. The intervals between the values of the wavefunction depicted by the contours are constant: however, the *spacing* between the intervals for the positive values of the 2s AO are roughly four times the interval between the negative values.

(a) For the 2s AO, sketch a graph showing how the value of the wavefunction changes along the path along the *z*-axis from **a** to **a′**. Mark on your graph the positions **a**, **b**, **c**, **d**, **c′**, **b′**, and **a′**.

(b) For the $2p_z$ AO, sketch a graph showing how the value of the wavefunction changes along the path along the *z*-axis from **a** to **a′**. Mark on your graph the positions **a**, **b**, **c**, **b′**, and **a′**.

(c) Also for the $2p_z$ AO, sketch a graph showing how the value of the wavefunction changes along the grey circular path starting at **b** and moving in a clockwise direction. Plot your graph as a function of θ, where θ is the angle from the *z*-axis. (Position **b** corresponds to where $\theta = 0°$; position **b′** to where $\theta = 180°$.) What mathematical function does the your graph depict?

5. **(a)** State the nuclear charges for the atoms H, He and Li and write down their electronic configurations.

(b) For an atom with just one electron, the ionization energy of the electron when it is in an orbital with principal quantum number *n*, is given by $(R_H Z^2/n^2)$, where Z is the nuclear charge and R_H is the Rydberg constant (13.6 eV).

Calculate, in eV, the ionization energy of a 1s electron in hydrogen, He^+ and Li^{2+}.

(c) The ionization energy of a neutral He atom is 24.6 eV. To what effects do you attribute any difference between this value and those for H and He^+?

(d) Calculate the ionization energy for Li^{2+} when removing the electron from the 2s orbital.

(e) If the two 1s electrons in a neutral Li atom formed a perfect screen, the 2s electron would experience a nuclear charge of +1. For this case of perfect screening, what would you expect the ionization energy of the 2s electron to be?

(f) The experimental ionization energy for Li is 5.4 eV. To what factors do you attribute the dramatic fall in ionization energy on going from He to Li ?

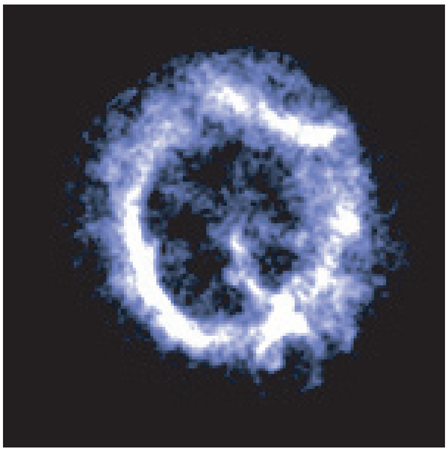
6. The hydrogen atom absorbs light from the visible/ultra-violet region of the spectrum when the electron is promoted from one orbital to another. Given that the energy (in units of hartrees) of the electron in orbital with principle quantum number n, E_n, is

$$E_n = -\frac{1}{2}\frac{Z^2}{n^2}$$

(where z is the nuclear charge), show that the energy of the photon needed to cause the electron in an orbital with principal quantum number i to move to a higher orbital with quantum number j is

$$\Delta E_{ij} = \frac{Z^2}{2}\left[\frac{1}{i^2} - \frac{1}{j^2}\right] \quad .$$

(a) Using this relationship, calculate, in hartrees, the energy of the series of transitions starting from the orbital with principle quantum number $n = 1$ and moving to successive higher levels with $n = 2, 3, 4, 5$, and 6 (*i.e.* 1 to 2, 1 to 3, 1 to 4 *etc*). Make a rough sketch of the resulting spectrum (absorption *vs.* energy), roughly to scale. The lines should appear to be converging – why is this and to what energy do the lines converge? What will happen to the electron at this convergence point?



(b) The picture shows an image of the supernova remnant ‘E0102-72’ located in a galaxy some 200,000 light years from Earth. The ring is about 30 light years across and contains more than a billion times the oxygen contained in the Earth’s oceans and atmosphere, and is at a temperature of many millions of degrees Kelvin. At such temperatures, any atoms are highly ionised and electronic transitions within these ions may be detected by telescopes such as *Chandra*. Analysis of the spectra recorded enable astronomers to determine the composition of such bodies.

Emission lines corresponding to electronic transitions from $n = 2, 3$ and 5 to $n = 1$ have been detected for the hydrogen-like ion O^{7+}.

(i) Calculate the energy in hartrees for these transitions.

(ii) Given that 1 hartree = 4.36×10^{-18} J, calculate the energy in Joules and hence the frequency and wavelength of light associated with each transition. What region of the electromagnetic spectrum do these lines appear in?

7. (For the mathematically confident.)
The table on page 64 gives the hydrogen atomic wavefunctions expressed using polar coordinates. Determine the value or values of the radius, r (expressed in units of the Bohr radius, a_0), at which the radial part goes to zero. Also, find the values of θ and ϕ at which the angular parts are zero. Which plane or planes do these values correspond to?

8. **(a)** Describe how two 1s atomic orbitals can be combined together to form bonding and antibonding molecular orbitals. Why is the bonding molecular orbital lower in energy, and the antibonding orbital higher in energy, than the atomic orbitals from which they are formed.

(b) When two AOs overlap, what factors determine by how much the energy of the bonding molecular orbital is lowered relative to the energy of the lowest energy AO?

9. **(a)** Using molecular orbital theory, explain carefully and concisely why there is no stable molecule He_2 whereas the ion, He_2^+ , can be detected.

(b) It is possible to promote an electron in helium from the 1s orbital to the 2s to give an electronically excited helium atom, He*. Explain why the collision between an excited helium atom and a helium atom in the ground state can give rise to a bound excited helium molecule, He_2^*.

10. The bond dissociation energies, in eV, of some homonuclear diatomics from the first row are given in the table:

Li_2	Be_2	B_2	C_2	N_2^+	N_2	O_2^+	O_2	F_2^+	F_2
1.14		3.0	6.4	8.9	9.9	6.8	5.2		1.3

(a) For each of the species listed above, give the arrangement of electrons in the molecular orbitals that you would expect (do not forget to include the effects of s-p mixing where appropriate). Which of the species would you predict to be paramagnetic?

(b) Find the bond order for each of the species listed above and make a plot the bond dissociation energy *vs.* bond order. Do you see any correlation between these two quantities? Why is there no entry in the table for Be_2? Using your plot, predict the bond dissociation energy of F_2^+.

11. Sketch the MO diagram for O_2, showing which molecular orbitals are occupied (ignore the 1s orbitals and electrons). Draw a similar diagram for NO and again indicate which orbitals are occupied (as O has a greater Z_{eff} than N, the 2p and 2s orbitals of O lie slightly below their counterparts in N).

On the basis of this diagram predict whether or not you would expect NO to be paramagnetic and compare the bond strength in NO with that in O_2. Sketch the form of the highest occupied molecular orbital (HOMO) in NO and state which atomic orbital is the major contributor to it.

12. Sketch an MO diagram for CN showing which molecular orbitals are occupied (ignore the 1s orbitals and electrons). Compare the arrangement of electrons in orbitals that you would expect for the ion CN^- with that expected for N_2. Why is CN^- described as being *isoelectronic* with N_2?

13. **(a)** For each of the following molecules state, with reasons, how you would expect the bond dissociation energy to compare between the neutral molecule (AB), the positive ion (AB^+) and the negative ion (AB^-): N_2, NO, O_2, C_2, F_2 and CN.

(b) Arrange the species O_2, O_2^+, O_2^-, and O_2^{2-} in order of increasing bond dissociation energy; give your reasoning.

14. Draw a diagram showing how the AOs on the metal and ligands might interact in a square planar complex to form multi-centre MOs (just consider the ligand as contributing one sp^3 HAO). Use your diagrams to explain how the metal in a square planar complex could be hybridized sp^2d or p^2d^2 but not sp^3.

15. How would you expect each of the following atoms to be hybridized?

(a) B in BF_3 (b) B in BH_4^- (c) C in CH_3^+ (d) C in CH_3^- (e) N in NH_3
(f) N in the planar molecule formamide $HCONH_2$ (g) Cu in $Cu(H_2O)_6^{2+}$
(h) Ni in the square planar complex $Ni(CN)_4^{2-}$ (i) P in PH_3 (H-P-H bond angle 94°)

16. How would you describe the hybridization of each of the carbon atoms in methyl methanoate? Which orbitals (AOs or HAOs) overlap to form the various bonds? Identify the orbital occupied by each bonding or lone pair electron.

17. Describe the σ and π bonding you would expect for the COO^- group in a carboxylate, $RCOO^-$; explain how your description leads to the conclusion that the two C–O bonds are equivalent. How would you describe the bonding between C and O? Explain why the bonds are intermediate in strength between those of a C–O single bond and a C–O double bond.

18. (Tripos question) Describe concisely what you understand by the terms bonding and antibonding molecular orbitals. What factors determine the energies of these orbitals?

The molecule BN has been observed in the gas phase and has been found to be paramagnetic and have a vibrational frequency which is considerably lower than that of N_2. Draw a molecular orbital diagram for BN and use it to explain these properties of BN.

How would you expect the bond vibration frequency in BO to compare to those in BN and N_2?

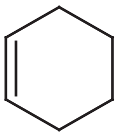
19. (Tripos question) Describe the molecular orbitals that you would expect to be formed from the overlap of three p orbitals which point out of the plane of a molecule if the atoms are arranged in a line. Use these orbitals to predict the atom or atoms which have the greatest π-electron density in the allyl anion and the allyl cation.

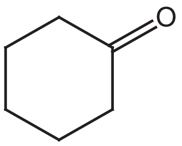
The azide anion, N_3^-, consists of a symmetrical linear arrangement of three nitrogen atoms. Assuming that the N atoms are sp hybridized, use a combination of σ-overlap between sp hybrids and π-overlap between out-of-plane p orbitals to draw a description of the bonding in N_3^-. Carefully describe the occupied orbitals.

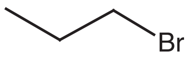
Would you expect N_3^- to be paramagnetic? Which atom or atoms have the greatest electron density?

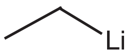
20. For each of the following molecules, identify the HOMO and LUMO.

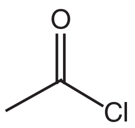
H_2O $H_3O^{\oplus}$ CH_4 $BH_4^{\ominus}$ $AlCl_3$ $H_3C{-}C{\equiv}N$



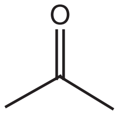




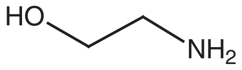


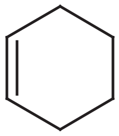


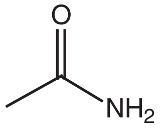
21. By identifying the HOMO for each, suggest where the following molecules would most easily be protonated in acid and draw a mechanism for each case.



$H_3C—C\equiv N$







22. At low temperatures in the gas phase, aluminium trichloride, $AlCl_3$, readily dimerizes to form Al_2Cl_6. By identifying the HOMO and LUMO in $AlCl_3$, draw a curly arrow mechanism for the reaction. Why does the reaction take place?

23. Draw a curly arrow mechanism for the reaction between BH_4^- and acetone (propanone). Why does this reaction take place?

24. Draw the curly arrow mechanism for the reaction between hydroxide ion and methyl iodide. Draw the transition state for the reaction. Suggest how the carbon is hybridized at each stage of the reaction (hint: consider the bond angles around it).