4 Structure of molecules

Introduction

You may recognize the model above as DNA, the molecule that carries the genetic instructions for making all life on earth. The helical shape of DNA was discovered in 1953, and the detailed arrangement of atoms in the DNA molecule determines whether it is a recipe for an ant, an antelope, an antirrhinum, or anthrax.
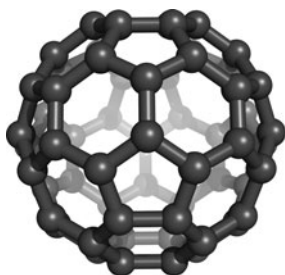
You may also have recognized this molecule as buckminsterfullerene, a soccer-ball shaped allotrope of carbon. Buckminsterfullerene, named after the architect of the geodesic dome (which it resembles), was first identified in 1985 and earned its discoverers the Nobel Prize for chemistry in 1996.

Now, our question is this: how did you recognize these two compounds? You recognized their *shapes*. Molecules are not simply a jumble of atoms: they are atoms held together in a defined three-dimensional shape. A compound's properties are determined not only by the atoms it contains, but also by the spatial arrangement of these atoms. Graphite and diamond—the two other allotropes of carbon—are both composed only of carbon atoms and yet their properties, both chemical and physical, are completely different because those carbon atoms are arranged very differently. Graphite has carbon atoms arranged in sheets of hexagons; diamond has them arranged in a tetrahedral array.

Graphite

Diamond
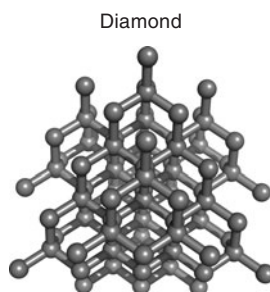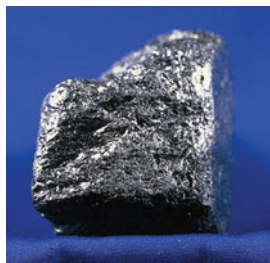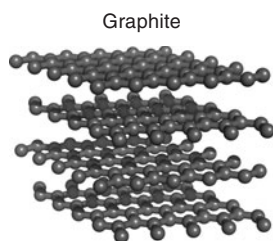
We know what shapes molecules have because we can see them—not literally of course, but by methods such as atomic force microscopy (AFM). AFM reveals the shape of pentacene, the molecule we w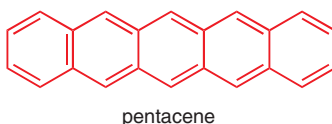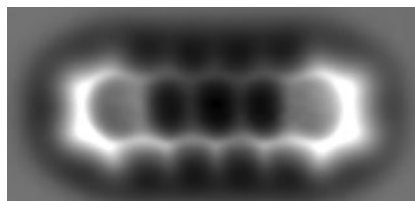ould usually draw as the structure below, to be as shown on the left. This is the closest we can get to actually 'seeing' the atoms themselves.

Interactive structures of buckminsterfullerene, graphite, diamond, and pentacene

pentacene

Most analytical techniques reveal the shapes of molecules less directly. X-ray diffraction gives information about the arrangement of atoms in space, while the other spectroscopic methods you met in Chapter 3 reveal details of the composition of molecules (mass spectroscopy) or the connectivity of the atoms they contain (NMR and IR).

From methods such as these, we know what shapes molecules have. This is why we urged you in Chapter 2 to make your drawings of molecules realistic—we can do this because we know what is realistic and what isn't. But now we need to tackle the question of *why* molecules have the shapes they do. What is it about the properties of their constituent atoms which dictates those shapes? We will find that the answer not only allows us to explain and predict structure, but also allows us to explain and predict reactivity (which forms the topic of Chapter 5).

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

tetrahedral methane
four bonds and no lone pairs

Interactive structures of methane, ammonia, and water

Molecules hold together because positively charged atomic nuclei are attracted to negatively charged electrons, and this fact allows electrons to act as 'glue' between the nuclei. The C and H nuclei of methane are of course positively charged, but the ten electrons (a total of six from C, four from the H atoms) bind those positive charges into a molecular structure. Ammonia (NH_3) and water (H_2O) also have ten electrons in total, and we know that their molecular shapes are in fact just like that of methane, but with one or two hydrogen atoms removed.

tetrahedral ammonia
three bonds and one lone pair

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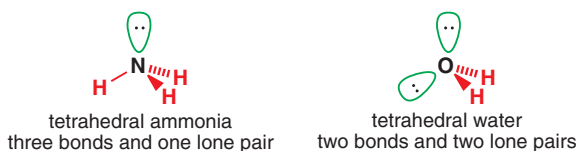
This tells us something important: it is the number of *electrons* which determines the shape of a molecule, and not just the number of *atoms* (or atomic nuclei). But what determines how electrons are arranged? Why do ten electrons give rise to a tetrahedron, for example?

Before we can answer this question, we need to simplify our discussion a bit and think about electrons not in molecules but in individual atoms. We can then approximate the electronic structure of *molecules* by considering how the component atoms combine. It is important to remember throughout this chapter, however, that molecules are only very rarely 'made' directly by joining atoms together. What we are going to present is an analysis of the structure of molecules, not a discussion of ways to build them (to which we will devote much of the later part of this book). Much of what we will cover was worked out in the decades around 1900, and it all came from experimental observation. Quantum theory explains the details, and you can read much more about it in a textbook of physical chemistry. Our aim here is to give you enough of an understanding of the theory to be able to use sound principles to predict and explain the structure of organic molecules.

So, first, some evidence.

Atomic emission spectra

Many towns and streets are lit at night by sodium vapour lamps, which emit an intense, pure yellow-orange glow. Inside these lights is sodium metal. When the light is switched on, the sodium metal is slowly vaporized. As an electric current is passed through the sodium vapour, an orange light is emitted—the same colour as the light you get when you put a small amount of a sodium compound on a spatula and place it in a Bunsen flame. Given sufficient energy (from the electric current or from a flame) sodium always emits this same wavelength of light, and it does so because of the way the electrons are arranged in a sodium atom. The energy supplied causes an electron to move from a lower energy state to a higher energy, or *excited*, state, and as it drops down again light is emitted. The process is a bit like a weight-lifter lifting a heavy weight—he can hold it above his head with straight arms (the excited state) but sooner or later he will drop it and the weight will fall to the ground, releasing energy with a crash, if not a broken toe. This is the origin of the lines in the atomic spectra not only for sodium but for all the elements. The flame or the electric discharge provides the energy to promote an electron to a higher energy level and, when this electron returns to its ground state, this energy is released in the form of light.

If you refract the orange sodium light through a prism, you see a series of very sharp lines, with two particularly bright ones in the orange region of the spectrum at around 600 nm. Other elements produce similar spectra—even hydrogen, and since a hydrogen atom is the simplest atom of all, we shall look at the atomic spectrum of hydrogen first.

Electrons have quantized energy levels

The absorption spectrum for hydrogen was first measured in 1885 by a Swiss schoolmaster, Johann Balmer, who also noticed that the wavelengths of the lines in this spectrum could be predicted using a mathematical formula. You do not need to know the details of his formula at this stage, instead let's think about the implications of the observation that a hydrogen atom, with just one electron, has a spectrum of discrete lines at precise wavelengths. It means

■ You met the idea of using energy to move from a lower state to a higher state, and the re-emission of that energy, in the context of NMR in Chapter 3. Here we are talking about much larger differences in energy, and consequently much shorter wavelengths of emitted light.

Two elements, caesium and rubidium, were discovered by Robert Bunsen in 1860 and 1861 after studying atomic emission spectra of this type. They are named after the presence of a pair of brightly coloured lines in their spectra—caesium from the Latin *caesius* meaning bluish grey and rubidium from the Latin *rubidus* meaning red.

■ You can find details of Balmer's formula in a textbook of physical chemistry.

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

We mentioned an electron 'orbiting' a hydrogen nucleus in the last paragraph deliberately, because that is one way of thinking about an atom—as a miniature (10^{-23} scale!) solar system with the nucleus as the sun and the electrons as planets. This model breaks down when we look at it in detail (as we shall see shortly), but for the moment we can use it to think about why electrons must exist in quantized energy levels.

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

Imagine a taut string—a piano wire or guitar string, for example—fixed at either end. You may well know that such a string has a fundamental frequency: if you make it vibrate by hitting or plucking it, it will vibrate in a way represented in the diagram on the right.

This diagram shows a snapshot of the string; we could also represent a 'blurred' image of all the places you might find the string as it vibrates, such as you would get if you took a picture with a slow shutter speed.

But this is not the only way the string can vibrate. An alternative possibility is shown on the right, where not only are the ends of the string stationary, but so is the point—known as a 'node'—right in the middle. The wavelength of the vibration in this string is half that of the one above, so the frequency is double. Musically this vibration will sound an octave higher and is known as the first harmonic of the first vibration we showed you, the fundamental. Third and fourth possibilities for 'allowed' vibrations are shown below, and again these correspond musically to further harmonics of the fundamental frequency.

Even if you have not met this idea in music or physics before, we hope that you can see that the vibrating string has no choice but to adopt one of these quantized frequencies—the frequency can take on only certain values because the fixed ends to the string means the wavelength has to be an exact divisor of the length of the string. And as we have seen before, frequencies are directly linked to energies: the energy levels of a vibrating string are quantized.

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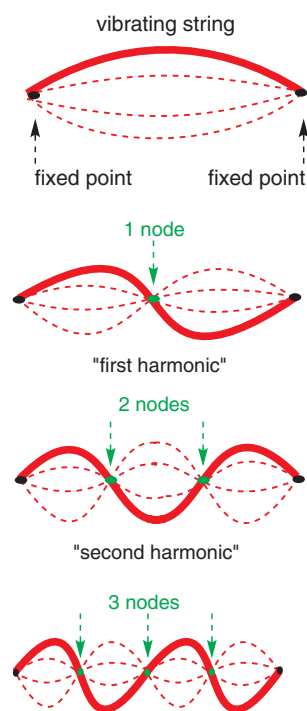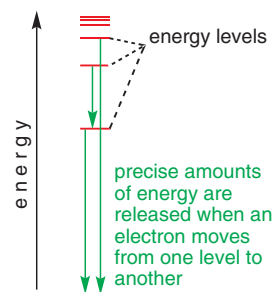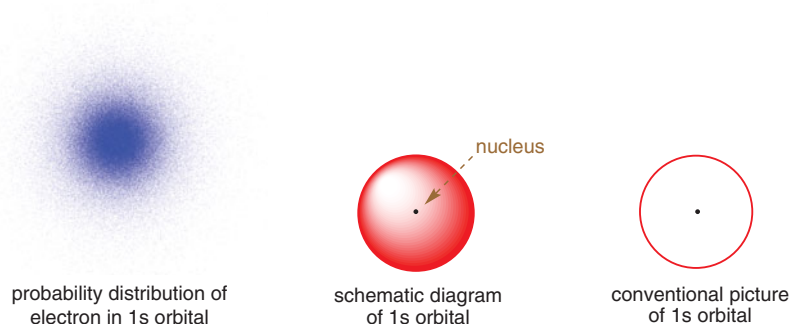
Electrons occupy atomic orbitals

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

As a consequence, we have to think of electrons in atoms (and in molecules) as having a **probability** of being in a certain place at a certain time, and the sum of all these probabilities gives a smeared out picture of the electron's habits, a bit like blurred pictures of the vibrating strings. Because an electron is free to move around an atom in three dimensions, not just two, the allowed

energy levels

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

energy

vibrating string

fixed point   fixed point

1 node

"first harmonic"

2 nodes

"second harmonic"

3 nodes

The vibration analogy was first seen by the Danish physicist Niels Bohr, and we hope you can see how it helps to explain why orbitals can only have certain energies. The analogy only works so far—we will have to leave it behind soon—but it can be used to visualize some other aspects of orbitals too, such as nodes and signs of wavefunctions.

'vibrations' it can adopt are also three dimensional and are known as orbitals, or (because we are just considering electrons in a single atom for now) **atomic orbitals**. The shapes of these orbitals are determined by mathematical functions known as **wavefunctions**. The smeared out picture of the simple atomic orbital—the lowest energy state of an electron in a hydrogen atom—looks something like the picture on the left below. We have used shading to indicate the probability of finding an electron at any one point, but a more convenient way to represent an orbital is to draw a line (in reality a three-dimensional surface) encompassing the space where an electron spends, say, 95% of its time. This gives something like the picture on the right. This simplest possible orbital—the fundamental orbital of the H atom—is spherical, and is known as a **1s orbital**. Higher energy atomic orbitals have different shapes, as you will see soon.

probability distribution of
electron in 1s orbital

schematic diagram
of 1s orbital

conventional picture
of 1s orbital

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

the hydrogen atom

What happens if you put more than one electron into the orbitals around an atom? Well, for reasons we can't go into here, each orbital can hold two electrons—and only two, never any more. If you add an electron to the H atom, you get the hydride anion, H^-, which has two electrons around an H nucleus (a proton). Both of the electrons occupy the same spherical 1s orbital.

This is known as the *Pauli exclusion principle*.

the hydride (H^-) ion
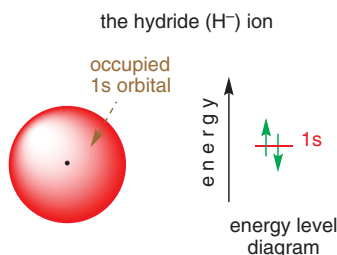
■ We talked about spinning *nuclei* in the context of NMR (p. 53). Electron spin is analogous, but different—you can't observe electrons by NMR, for example, and instead they can be observed by a technique known as electron spin resonance or ESR.

We can also represent the orbital occupancy as an energy level (the horizontal line) occupied by two electrons (the arrows). Why do we draw the electrons as arrows? Well, electrons have the property of spin, and the two electrons allowed in each orbital have to spin in opposite directions. The arrows are a reminder of these opposing spins.

The same is true for the helium atom: its two electrons occupy the same orbital. However, the energy of that orbital (and all of the other possible orbitals) will be different from the orbital for hydrogen because it has double the nuclear charge of hydrogen and the electrons are more strongly attracted to the nucleus. We can represent the orbital occupancy like this, with the energy level lower than the one for H because of this stronger attraction.

the helium atom

occupied
1s orbital

energy level
diagram
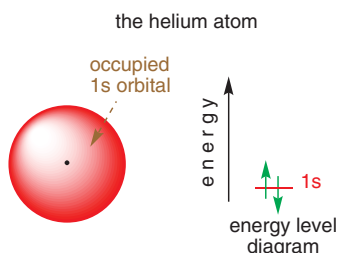
s and p orbitals have different shapes

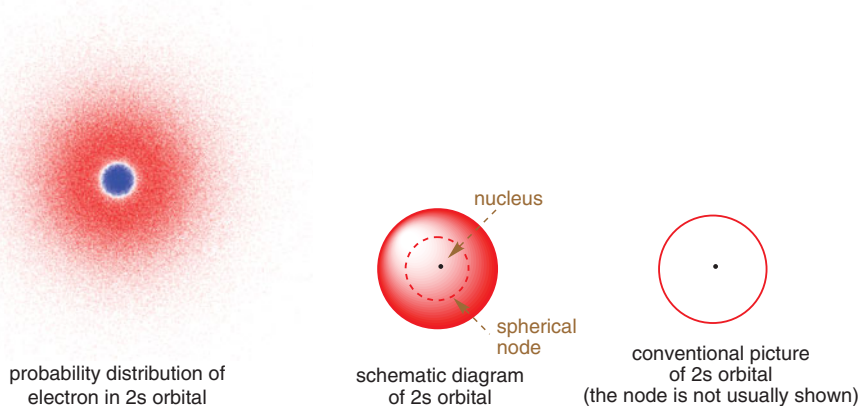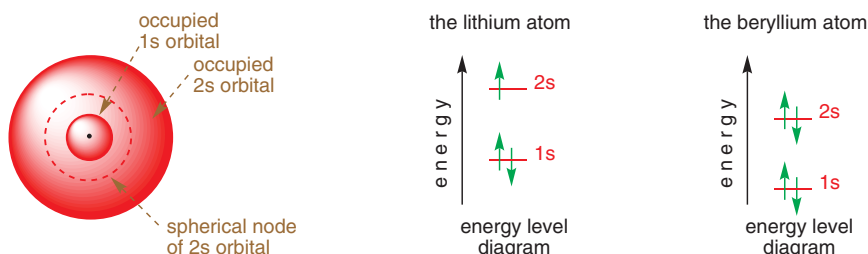So far, so good. Now, lithium. The lowest energy 1s orbital around the Li nucleus can contain two electrons, but two only, so the third electron has to go into a higher energy orbital—one of the energy levels whose existence was inferred from atomic absorption spectroscopy. You can think of this orbital as the three-dimensional equivalent of the first harmonic of the guitar string. Like the vibration of the string, this next orbital has a node. On the string the node was the point where no motion was observed. In an atom, a node is a point where the electron can never be found—a void separating the two parts of the orbital. For the orbital containing the third electron of the Li atom, this node is spherical—it divides the orbital into two parts which nestle one within another like the layers of an onion or the stone inside a peach. We call this orbital the 2s orbital—'2' because we have moved up to an orbital with a node (like the first harmonic) and 's' because the orbital is still spherical. The 's' did not originally stand for 'spherical', but as all 's' orbitals are spherical it's fine to remember it that way.

nucleus

spherical
node

probability distribution of
electron in 2s orbital

schematic diagram
of 2s orbital

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

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

occupied
1s orbital

occupied
2s orbital

spherical node
of 2s orbital

the lithium atom

energy level
diagram

the beryllium atom
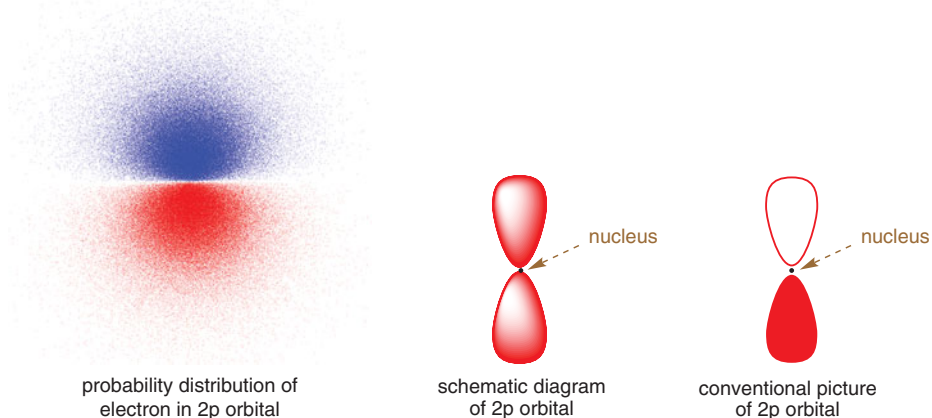
energy level
diagram

When we get to boron, something a little different happens. It turns out that for an orbital with one node (such as the 2s orbital), the node does not have to be *spherical*. The node can

alternatively be a *plane*. This alternative arrangement for an orbital with a single planar node gives us a new type of orbital, the 2p orbital. A 2p orbital looks something like the picture on the left below, in 'smeared out' form. It is often represented as the propeller shape in the middle, and it is conventionally drawn as the shape shown in the diagram to the right.

■ We will explain shortly why only half of the picture of the p orbital on the right has been filled in.

| probability distribution of electron in 2p orbital | schematic diagram of 2p orbital | conventional picture of 2p orbital |

Three-dimensional representations of the shapes of atomic orbitals

Unlike the 1s or 2s orbitals, the 2p orbital is directional—it points along an axis, and in three dimensions there are three possible orientations for the axis, each of which gives rise to a new 2p orbital (which we can call $2p_x$, $2p_y$ and $2p_z$ if we need to).


the boron atom
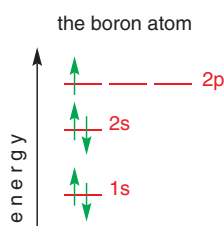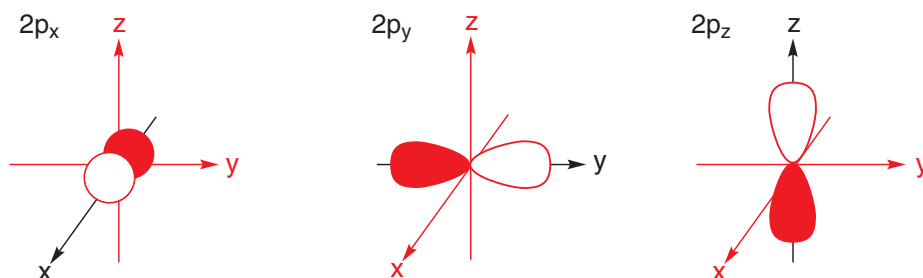
This is known as **Hund's rule**. An atom adopts the electronic configuration that has the greatest number of unpaired electrons in degenerate orbitals. Whilst this is all a bit theoretical in that isolated atoms are not found very often, the same rule applies to electrons in degenerate orbitals in molecules, as you will see soon.

The planar node of the three 2p orbitals gives them just slightly more energy than a 2s orbital, with its spherical node. Boron atoms therefore have two electrons in the 1s orbital, two in the 2s orbital, and just one in one of the 2p orbitals. The orbital occupancy is shown in the energy level diagram on the left. You can imagine what shape each of the orbitals has: we won't need to show a picture of them all superimposed.

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

Not surprisingly therefore, the orbitals of atoms of the remainder of the elements of the first row of the periodic table are occupied as shown below. All the while the entire set of orbitals is going down in energy because the nucleus is attracting the electrons more strongly, but otherwise it is a simple matter of filling up the 2p orbitals first singly and then doubly. With the ten electrons of neon, all the orbitals with one node are filled, and we say that neon has a 'closed shell'. A 'shell' is a group of orbitals of similar energy all with the same number of nodes (in this case all called '2' something—2s or 2p).

the carbon atom   the nitrogen atom   the oxygen atom   the fluorine atom   the neon atom
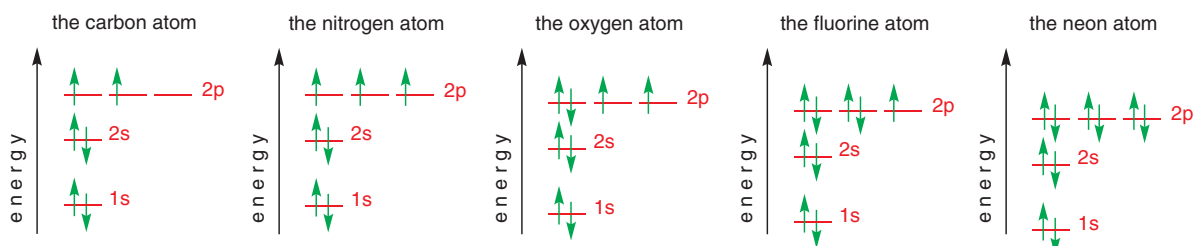
The phase of an orbital

Look at the diagrams below, which are the same as the ones on p. 83: they represent the first three vibrational frequencies of a string. Now think about the motion of the string itself: in the first vibration, all of the string moves up and down at the same time—each point on the string moves by a different amount, but the direction moved at every point is the same. The same is not true for the second 'energy level' of the string—during a vibration like this, the left-hand half of the string moves upwards while the right-hand half moves downwards— the two halves of the string are out of phase with one another, and there is a change of phase at the node. The same is true of the third energy level—again, there is a change of phase at each node.

change of phase at the node   change of phase at each node

all the string moves   different parts of the string, separated by nodes,
in the same direction   move in different directions
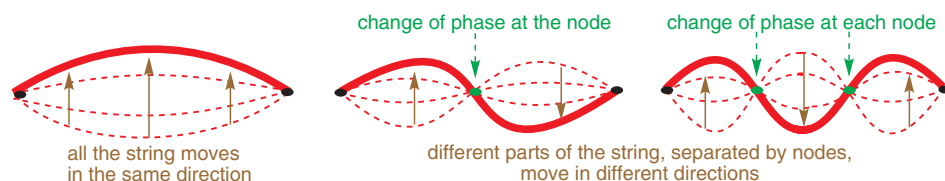
The same is true for orbitals. A nodal plane, such as that in the 2p orbitals, divides the orbital into two parts with different phases, one where the phase of the wavefunction is positive and one where it is negative. The phases are usually represented by shading—one half is shaded and the other half not. You saw this in the representation of the 2p orbital above. The phase of an orbital is arbitrary, in the sense that it doesn't matter which half you shade. It's also important to note that phase is nothing to do with charge: both halves of a filled 2p orbital contain electron density, so both will be negatively charged.

So why is phase important? Well, in a moment we will see that, just as atoms add together to give molecules, we can add together the wavefunctions of atomic orbitals to give molecular orbitals, which tell us where electrons are, and how much energy they have, in molecules.

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

s, p, d, f

Why 2s, 2p...? These letters hark back to the early days of spectroscopy and refer to the appearance of certain lines in atomic emission spectra: 's' for 'sharp' and 'p' for 'principal'. Later you will meet d and f orbitals, which have other arrangements of nodes. These letters came from 'diffuse' and 'fundamental'. The letters s, p, d, and f matter and you must know them, but you do not need to know what they originally stood for.

Four short clarifications about orbitals before we go on

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

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

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

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

(much bigger) 2s orbital, and two in each of the three 2p orbitals. All these orbitals are superimposed on each other.

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

🖱 Three-dimensional representations of d and f orbitals

Molecular orbitals—diatomic molecules

Now for electrons in molecules. Just as the behaviour of electrons in atoms is dictated by the **atomic orbitals** they reside in, so electrons in molecules behave in ways dictated by the **molecular orbitals** which contain them. We think of molecules as being built from atoms (even if that is not actually how you would usually make them), and likewise we can think of molecular orbitals as being built up from a combination of atomic orbitals.

■ This way of building up molecular from atomic orbitals is known as the **linear combination of atomic orbitals** or **LCAO**.

As atomic orbitals are wavefunctions, they can be combined in the same way that waves combine. You may be already familiar with the ideas of combining waves either *constructively* (in phase) or *destructively* (out of phase):

combine ↓ in phase   combine ↓ out of phase

constructive overlap   destructive overlap
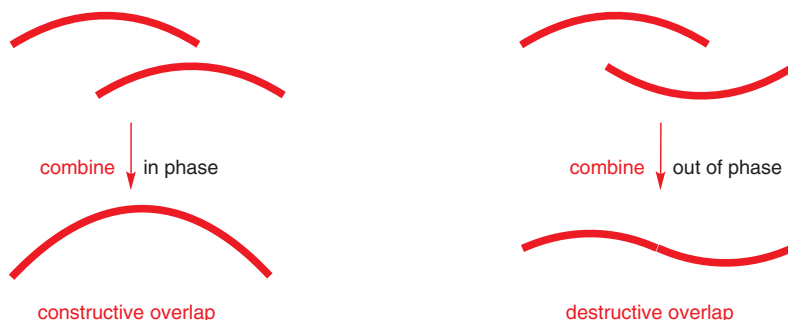
Atomic orbitals can combine in the same ways—in phase or out of phase. Using two 1s orbitals drawn as circles (representing spheres) with dots to mark the nuclei and shading to represent phase, we can combine them in phase (that is, we add them together), resulting in an orbital spread over both atoms, or out of phase (by subtracting one from the other). In this case we get a molecular orbital with a nodal plane down the centre between the two nuclei, where the wavefunctions of the two atomic orbitals exactly cancel one another out and with two regions of opposite phase.

generates a **bonding** molecular orbital   generates an **antibonding** molecular orbital
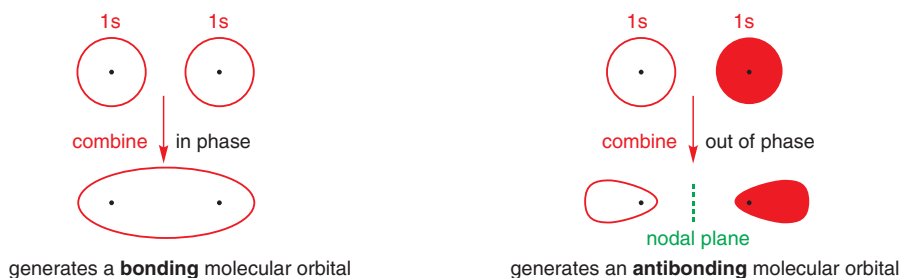
The resulting orbitals belong to both atoms—they are *molecular* rather than atomic orbitals. Now, imagine putting electrons into the first of these orbitals (the bonding orbital). Remember, you can put zero, one, or two electrons into an orbital, but no more. The diagram of the orbital shows that the electrons would spend most of their time in between the two atomic nuclei. Being negatively charged, the electrons will exert an attractive force on each of the nuclei, and would hold them together. We have a chemical bond! For this reason the in-phase molecular orbital is called a **bonding orbital**.

The out-of-phase molecular orbital offers no such attractive possibility—in fact putting electrons into the out-of-phase molecular orbital works against bonding. These electrons are mainly to be found anywhere *but* between the two nuclei, where there is a node. The exposed positively charged nuclei repel each other, and that is why this orbital is known as an **antibonding molecular orbital**.

The combination of the atomic 1s orbitals to give the two new molecular orbitals can also be shown on a molecular orbital energy level diagram. The two atomic orbitals are shown on the left and the right, and the molecular orbitals which result from combining them in and out of phase are shown in the middle. The diagram as a whole is a sort of 'before and after' diagram—the situation before the interaction between the orbitals is shown on the left and the right, and after the interaction is shown in the middle. Notice that the bonding orbital is lower in energy than the constituent 1s orbitals, and the antibonding orbital is higher.
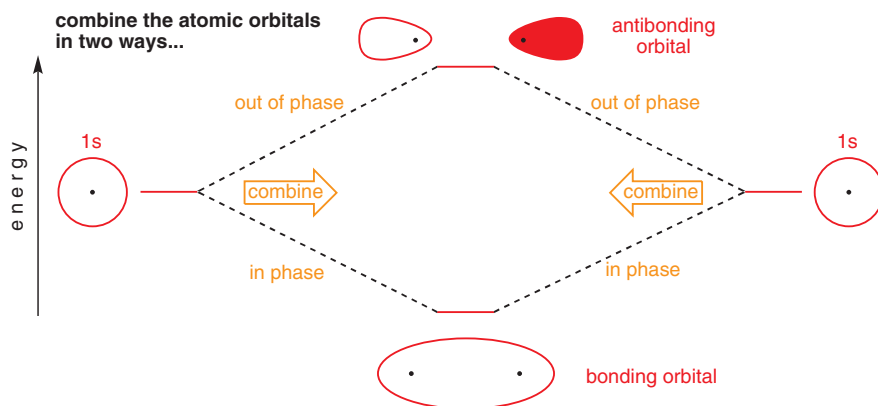
Interactive molecular orbitals for hydrogen

Now we can actually put the electrons into the orbitals, just as we did on p. 84 when we were building up the picture of atomic orbitals. Each hydrogen atom has one electron and so the resulting hydrogen molecule (shown in the middle) contains two electrons. Always fill up orbitals from the lowest energy first, putting a maximum of two electrons into each orbital, so both of these electrons go into the bonding orbital. The antibonding orbital remains empty. The electrons therefore spend most of their time in between the nuclei, and we have a plausible explanation for the existence of a chemical bond in the H_2 molecule.
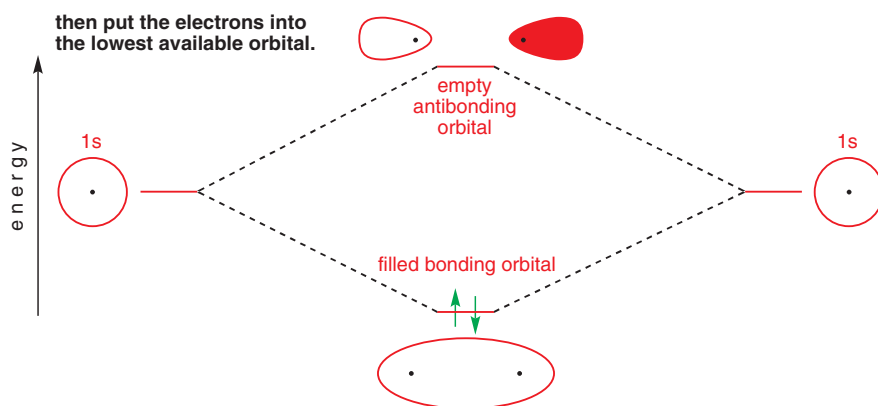
Diagrams such as these are central to the way we can use molecular orbital theory (MO theory) to explain structure and reactivity, and you will in future meet many more of them. So before we go on it is worth clarifying several points about this one:

- *Two* atomic orbitals (AOs) combine to give *two* molecular orbitals (MOs). You always get the same number of MOs out as you put AOs in.
- Adding the wavefunctions (combining them in phase) of the two AOs makes the bonding orbital; subtracting them (combining them out of phase) makes the antibonding orbital.

- Since the two atoms are the same (both H), each AO contributes the same amount to the MOs (this will not always be the case).

- The bonding MO is *lower* in energy than the AOs.

- The antibonding MO is *higher* in energy than the AOs.

- Each hydrogen atom initially had one electron. The spin of these electrons is unimportant.

- The two electrons end up in the MO lowest in energy—the bonding MO.

- Just as with AOs, each MO can hold two electrons as long as the electrons are spin-paired (shown by opposing arrows). You do not need to be concerned with the details of spin-pairing at this stage, just with the result that any orbital may contain no more than two electrons.

- The two electrons between the two nuclei in the bonding MO hold the molecule together—they are the chemical bond.

- Since these two electrons are lower in energy in the MO than they were in the AOs, the molecule is more stable than its constituent atoms; energy is given out when the atoms combine.

- Or, if you prefer, we must put in energy to separate the two atoms again and to break the bond.

From now on, we will always represent molecular orbitals in energy order—the highest-energy MO at the top (usually an antibonding MO) and the lowest in energy (usually a bonding MO and the one in which the electrons are most stable) at the bottom.

Before you leave this section, let's recap how we got to the MO diagram of H_2. It's worth working through these steps to check you can draw your own MO diagram before you leave this section.

1. Draw two H atoms along with the 1s atomic orbitals which contain the electron, one on either side of the page.

2. Sketch the result of adding and of subtracting the wavefunctions of these two 1s orbitals to show the bonding and antibonding MOs. These go one above the other (high energy antibonding orbital on top) in between the AOs.

3. Count up the total number of electrons in the atoms going in to the molecule, and put that number of electrons into the MOs, starting at the bottom and building upwards, two in each orbital.

Breaking bonds

The diagram we have studied shows the most stable ground state of a hydrogen molecule, in which the electrons have the lowest possible energy. But what happens if an electron is promoted up from the lowest energy level, the bonding MO, to the next lowest energy level, the antibonding MO? Again, an energy level diagram helps.
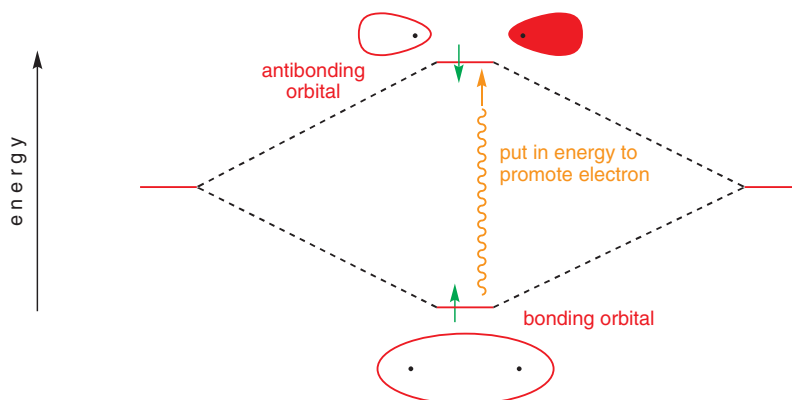
Now the electron in the antibonding orbital cancels out the bonding of the electron in the bonding orbital. Since there is no overall bonding holding the two atoms together, they can drift apart as two separate atoms with their electrons in 1s AOs. In other words, promoting an electron from the bonding MO to the antibonding MO breaks the chemical bond. This is difficult to do with hydrogen molecules but easy with, say, bromine molecules. Shining light on Br_2 causes it to break up into bromine atoms.

Why hydrogen is diatomic but helium is not

Like H atoms, He atoms have their electrons in 1s orbitals, so we can construct an energy level diagram for He_2 in a similar way. But there is one big difference: each helium atom has two electrons so now both the bonding MO and the antibonding MO are full! Any bonding due to the electrons in the bonding orbital is cancelled out by the electrons in the antibonding orbital, and the He_2 molecule falls apart. He_2 does not exist.
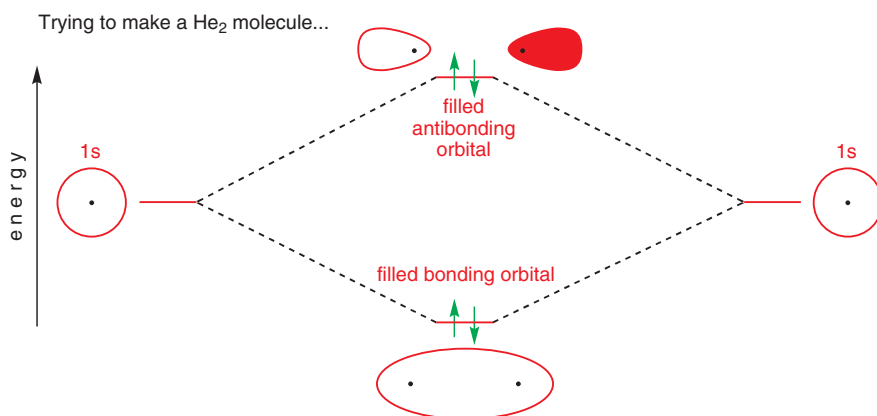
Bond order

Only if there are more electrons in bonding MOs than in antibonding MOs will there be any bonding between two atoms. In fact, we define the number of bonds between two atoms as the bond order (dividing by two since *two* electrons make up a chemical bond).

$$\text{bond order} = \frac{(\text{no. of electrons in bonding MOs}) - (\text{no. of electrons in antibonding MOs})}{2}$$

Hence the bond orders for H_2 and He_2 are

$$\text{bond order } (H_2) = \frac{2-0}{2} = 1, \quad \text{i.e. a single bond}$$

$$\text{bond order } (He_2) = \frac{2-2}{2} = 0, \quad \text{i.e. no bond}$$

Forming bonds using 2s and 2p atomic orbitals: σ and π orbitals

Atoms in the row of the periodic table running from Li to F have electrons in 2s and 2p orbitals, and as all molecules of interest to organic chemists contain at least one such atom we now need to think about how 2s and 2p orbitals interact. We also need to introduce you to a useful piece of terminology that is used to describe the *symmetry* of molecular orbitals.

We can do all of this by thinking about the bonding in another ubiquitous diatomic gas, N_2. N atoms have electrons in 1s, 2s, and 2p orbitals, so we need to consider interactions between pairs of each of these orbitals in turn.

1s orbitals we have already dealt with. Combining 2s orbitals is essentially just the same; they form bonding and antibonding orbitals just as 1s orbitals do and with similar shapes too, but higher energies, because the 2s orbitals are higher in energy that the 1s orbitals. The 2s orbitals are also bigger than 1s orbitals, and because of their 'onion skin' form, the exact nature of the MOs they give rise to is more complex than those which come from 1s AOs, but you can represent them in sketches in just the same way:
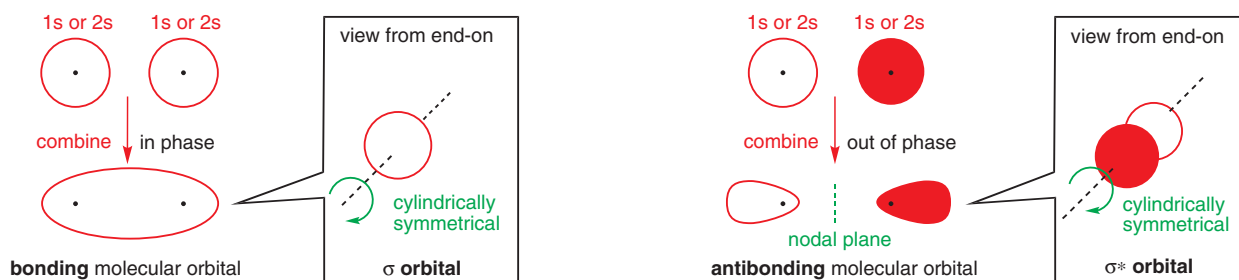

The bonding orbitals formed from 1s–1s and 2s–2s interactions have another important feature in common: they are all *cylindrically symmetrical*. In other words, if you look at the molecular orbital end-on, you can rotate it around the axis between the two atoms by any amount and it looks identical. It has the symmetry of a cigar, a carrot, or a baseball bat. Bonding orbitals with cylindrical symmetry like this are known as σ (sigma) orbitals, and the bonds which result from putting two electrons into these orbitals are known as σ bonds. The single bond in the H_2 molecule is therefore a σ bond.

The antibonding orbitals which result from combining these AOs are also cylindrically symmetrical and are called σ* orbitals, with the * denoting their antibonding character.

Now for the 2p orbitals. As described on p. 86 each atom has three mutually perpendicular 2p atomic orbitals. In a diatomic molecule, such as N_2, these 2p orbitals must combine in two different ways—one p orbital from each atom (shown in red here) can overlap end-on, but the other two p orbitals on each atom (shown in black) must combine side-on.
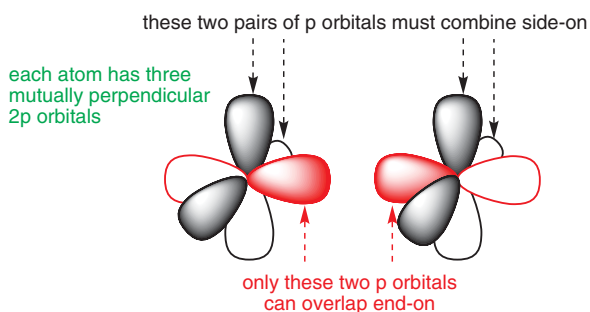
We'll deal with the end-on overlap first. This is what happens if we combine the two 2p orbitals out of phase: as with the 2s orbitals, we have a node between the atoms, and any electron in this MO would spend most of its time not between the nuclei—as you can guess, this is an antibonding orbital.
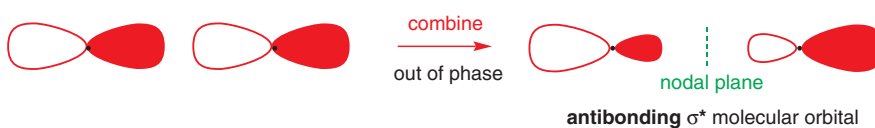
If we combine the orbitals in phase, this is what we get.

bonding σ molecular orbital
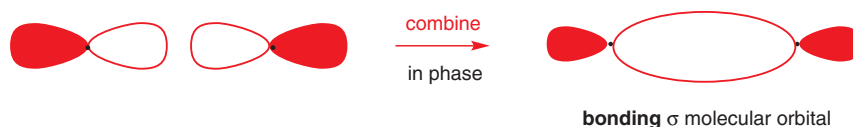
There is a nice rich area of electron density between the nuclei, and somewhat less outside, so overall filling this orbital with electrons would lead to an attraction between the atoms and a bond would result.

Both of these MOs have cylindrical symmetry and are therefore designated σ and σ* orbitals, and a bond formed by filling the MO made from interacting two 2p orbitals end-on is called a σ bond.
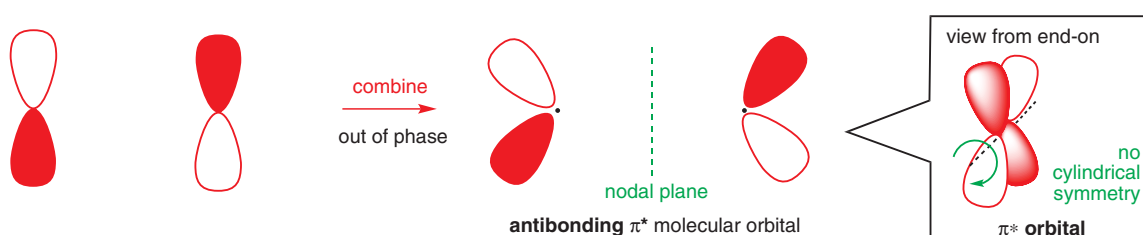
> ● σ **bonds can be made from s or p atomic orbitals, provided they form a cylindrically symmetrical molecular orbital.**

Each atom presents its other two 2p orbitals for side-on overlap. This is what the antibonding MO formed by out-of-phase combination of two side-on p orbitals looks like:

antibonding π* molecular orbital

And this is the bonding, in-phase combination
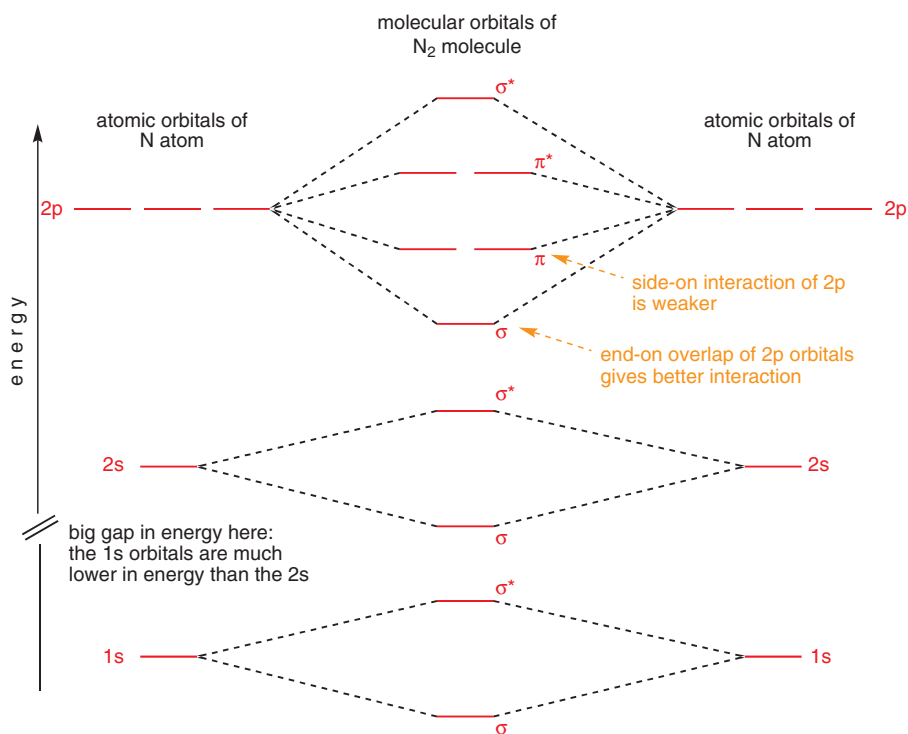

bonding π molecular orbital
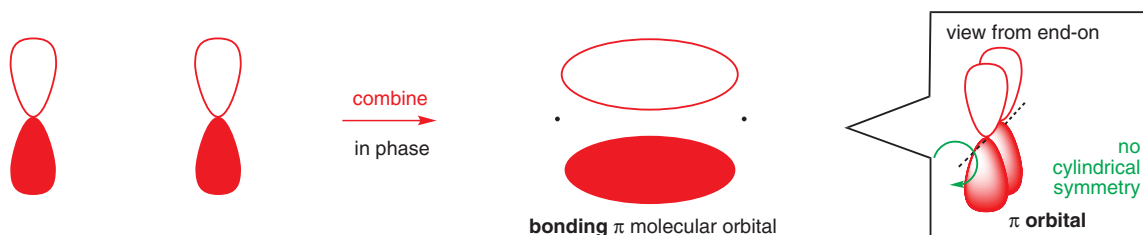
These MOs do not have cylindrical symmetry—in fact you have to rotate them 180° about the axis between the nuclei before you get back something looking like what you started with but with opposite phase—and as a result the symmetry of these orbitals is given the symbol π: the bonding orbital is a π orbital and the antibonding orbital is a π* orbital. Bonds which are formed by filling π orbitals are called π bonds, and you'll notice that because of the π symmetry the electron density in these bonds does not lie directly between the two nuclei but rather to either side of the line joining them.

Since an atom has three mutually perpendicular 2p orbitals, two of which can interact side-on in this way, there will exist a pair of degenerate (equal in energy) mutually perpendicular π orbitals and likewise a pair of degenerate mutually perpendicular π* orbitals. (The third p orbital interacts end-on, forming a σ orbital and a σ* orbital, of course).

The two sorts of MOs arising from the combinations of the p orbitals are, however, not degenerate—more overlap is possible when the AOs overlap end-on than when they overlap side-on. As a result, the 2p–2p σ orbital is lower in energy than the 2p–2p π orbitals.

We can now draw an energy level diagram to show the combinations of the 1s, 2s, and 2p AOs to form MOs, labelling each of the energy levels with σ, σ*, π, or π* as appropriate.

■ Because it can be difficult to represent exactly the result of adding and subtracting p orbitals, you will often see π and π* orbitals represented in diagrams simply as their 'uncombined' p orbitals—the structures on the left above. For an example, see p. 105.

molecular orbitals of
N_2 molecule

atomic orbitals of
N atom

atomic orbitals of
N atom

σ*

π*

2p ——— 2p

π

side-on interaction of 2p
is weaker

σ

end-on overlap of 2p orbitals
gives better interaction

energy

σ*

2s ——— 2s

σ

big gap in energy here:
the 1s orbitals are much
lower in energy than the 2s

σ*

1s ——— 1s

σ

Now for the electrons. Each nitrogen atom contributes seven electrons to the molecule, so we have to fill this stack of orbitals with 14 electrons, starting at the bottom. The result is:

■ The 2sσ, 2pσ, and 2pπ orbitals fall very close in energy: for a more detailed discussion of their relative energies, consult an inorganic chemistry textbook.

σ*

empty antibonding orbitals

π*

2p ——— 2p

π

two π bonds

filled bonding orbitals

σ

one σ bond

energy

σ*   filled antibonding orbital

2s ——— 2s

σ   filled bonding orbital

big gap in energy here:
the 1s orbitals are much
lower in energy than the 2s

bonding and
antibonding
cancel out

σ*   filled antibonding orbital

1s ——— 1s
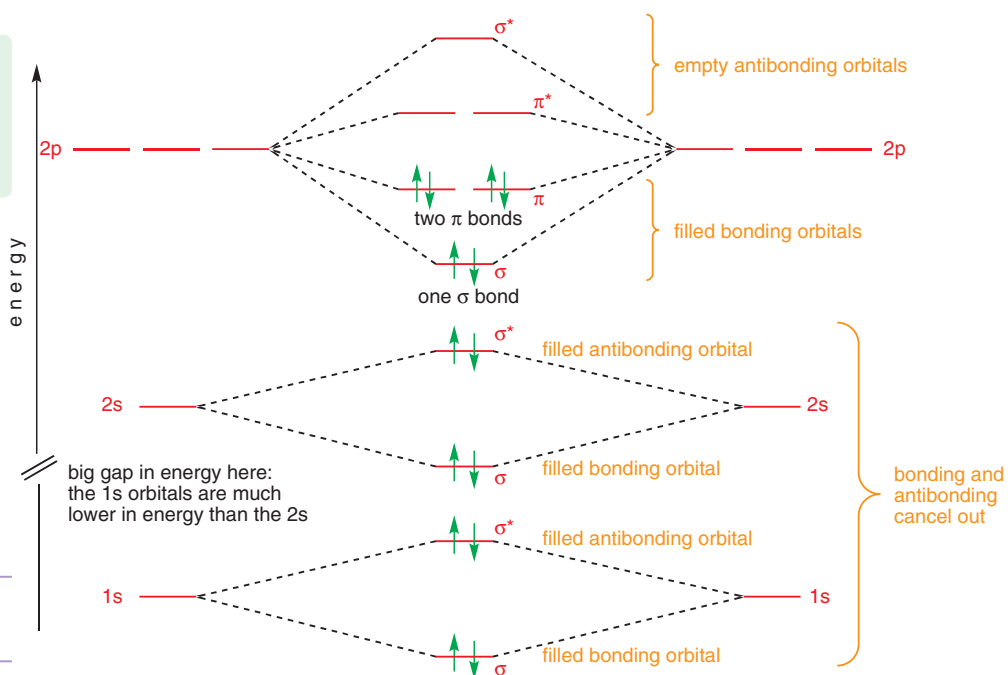
🖱 Interactive molecular orbitals
for nitrogen

σ   filled bonding orbital

The σ and σ* MOs formed from interactions between the two 1s orbitals, and the two 2s orbitals are all filled: no overall bonding results because the filled bonding and antibonding orbitals cancel each other out. All the bonding is done with the remaining six electrons. They fit neatly into a σ bond from two of the p orbitals and two π bonds from the other two pairs.

The electrons in the σ bond lie between the two nuclei, while the electrons in the two π bonds lie in two perpendicular clouds flanking the central σ bond.

σ bond   π bond   π bond

N nucleus

N nucleus   N nucleus

N nucleus   N nucleus

N nucleus

N nucleus

all three bonds superimposed:
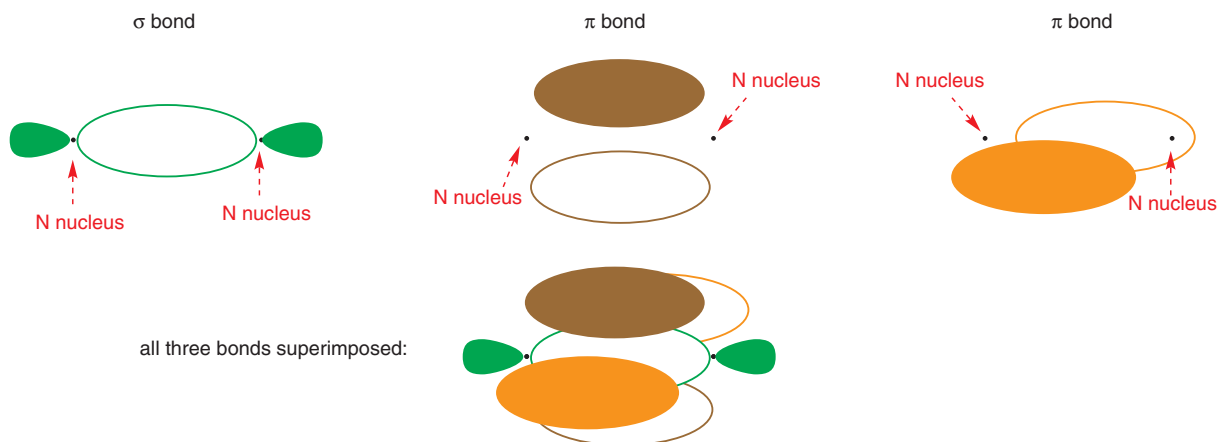
Calculating the bond order in N_2 is easy—a total of ten bonding electrons and four anti-bonding electrons gives a credit of six, or a bond order of three. N_2 has a triple-bonded structure.

We can't, however, ignore the electrons that are not involved in bonding: there are eight of them altogether. These non-bonding electrons can be thought of as being localized on each of the N atoms. The four 1s electrons are low-energy inner shell electrons that are not involved in the chemistry of N_2, while the four 2s electrons provide the non-bonded lone pairs located one on each N atom. In the structure shown here we have drawn them in: you don't have to draw lone pairs of every molecule that has them, but sometimes it can be useful to emphasize them—for example if they are taking part in a reaction scheme.

2s electrons form non-bonding lone pairs

one σ bond

:N $=$ N:

two π bonds
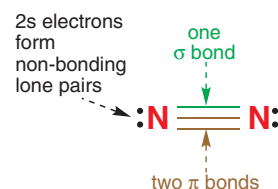
Bonds between different atoms

Up to now we have only considered combining two atoms of the same element, which makes things simpler because the same orbitals on each of the two atoms have the same energy. But when the two atoms are different two things change. The first is obvious—the number of electrons contributed by each atom is different. This is easy to accommodate since it just affects the total number of electrons we need to put into the MO diagram when we fill up the energy levels. So, for example, if you were constructing an MO diagram for NO, the gas nitric oxide (NO, a rather remarkable biological messenger in the human body) rather than N_2, you simply put in a total of 15 rather than 14 electrons because O contributes eight electrons and N seven.

Nitric oxide, NO

Nitric oxide was for a long time known only as one of the villains of urban air pollution, being formed during the combustion of petroleum and other fossil fuels. In the last 20 years, however, it has become evident that it is much more than that—one unexpected role, which earned its discoverers the Nobel Prize in physiology in 1998, is as a biological messenger, managing the contraction of smooth vessels and hence regulating blood flow.

The second thing that changes when you have two different atoms bonded together is the relative energies of the AOs being combined. It may seem natural to assume that a 2p orbital has the same energy whatever atom it finds itself in, but of course the difference is that an electron in a 2p (or any other) orbital feels an attraction to the nucleus which depends on the nuclear charge. The greater the number of protons in the nucleus, the greater the attraction, and hence the more tightly held, more stable, and lower in energy the electron becomes.

This is the origin of *electronegativity*. The more electronegative an atom is, the more it attracts electrons, the lower in energy are its AOs, and so any electrons in them are held more tightly.

As you move across each row of the periodic table, therefore, electronegativity increases as the energy of each orbital drops. From Li (electronegativity 0.98) across to C (2.55), and on to N (3.04), O (3.44), and F (3.98), the elements steadily become more electronegative and the AOs lower in energy.

So our diagram of the orbitals of NO actually looks like this.
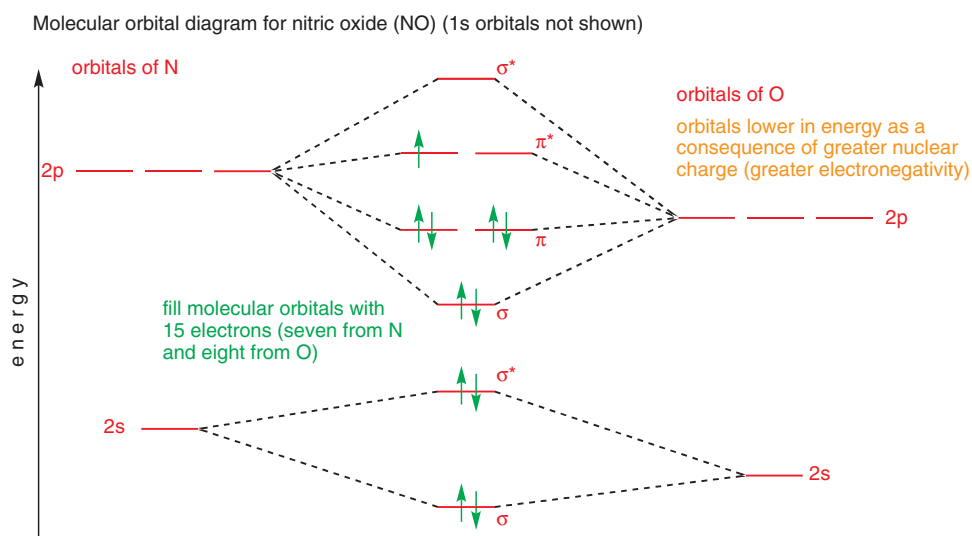
Molecular orbital diagram for nitric oxide (NO) (1s orbitals not shown)

We have shown only the 2s and 2p orbitals as the 1s orbitals are much lower in energy, and as you saw in the diagram of N_2 on p. 94 their bonding and antibonding interactions cancel each other out.

The orbitals on O are lower in energy than the orbitals on N, but they still interact just fine. However, there is one interesting consequence: if you look at each bonding orbital, you will see that it is closer in energy to the contributing orbital on O than the contributing orbital on N. Likewise, each antibonding orbital is closer in energy to the contributing orbital on N than the contributing orbital on O. The result is that the MOs are unsymmetrical, and while all the bonding orbitals have a greater contribution from the oxygen AOs, all the antibonding orbitals have a greater contribution from the nitrogen AOs. Overall the diagram shows eight electrons in bonding orbitals and three electrons in antibonding orbitals, so the overall electron distribution is skewed (polarized) towards O, just as you would expect from a comparison of the electronegativities of N and O.

The eight electrons in bonding orbitals and three electrons in antibonding orbitals means that NO has a bond order of 2½. It also has an unpaired electron—it is a radical. We can't easily represent half a bond in valence bond terms, so we usually draw NO with a double bond, representing four bonding electrons. The remaining seven electrons can be shown as three lone pairs and one unpaired electron. Where do we put them? Well, our MO diagram tells us that the unpaired electron occupies an orbital closer in energy to N than to O, so we put that on N.

N and O differ only slightly in electronegativity (electronegativity of N 3.04; O 3.44): their orbitals are quite close in energy and form stable covalent bonds. But we also need to consider what happens when two atoms forming a bond differ hugely in electronegativity. We can take sodium (electronegativity 0.93) and chlorine (electronegativity 3.16) as our example. We know from observation that the product of reacting these two elements (don't try this at home) is the ionic solid Na^+Cl^-, and the MO energy level diagram tells us why.

The AOs we need to consider are the 3s and 3p orbitals of Na (all its lower energy 1s, 2s, and 2p orbitals are filled, so we can ignore those, as we did with the 1s orbitals of N_2 and NO above) and the 3s and 3p orbitals of Cl (again, the 1s, 2s, and 2p orbitals are all filled). Here is the diagram, with the Na orbitals much higher in energy than the Cl orbitals.
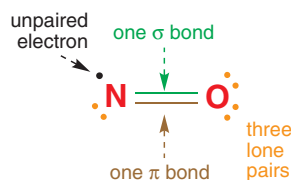
■ We have here the beginnings of an explanation for both the structure and reactivity of polarized bonds. In Chapter 6 we will revisit the idea that a carbonyl C=O bond is polarized towards O, but that the asymmetry of the antibonding π^* orbital leads to attack on the C=O group at C.
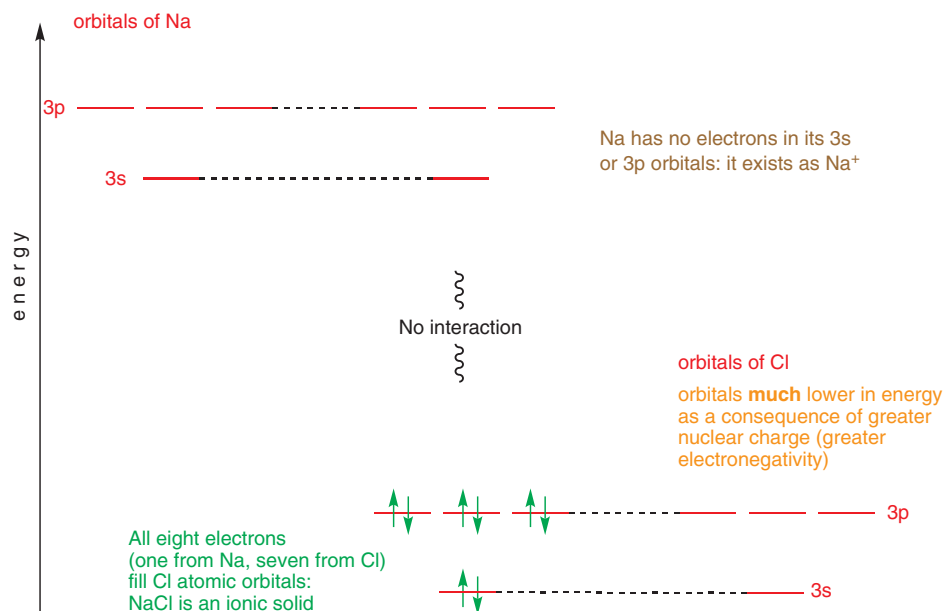

■ We haven't considered what happens in the second row of the periodic table yet, but it will come as no surprise to you to learn that the electronic structure of the elements of Na to Cl arises from filling 3s and 3p orbitals. You might like to think about what shape these orbitals have: a textbook on inorganic chemistry will tell you more.

Trying to construct a molecular orbital diagram for NaCl

orbitals of Na

3p

3s

Na has no electrons in its 3s or 3p orbitals: it exists as Na^+

energy

No interaction

orbitals of Cl

orbitals **much** lower in energy as a consequence of greater nuclear charge (greater electronegativity)

3p

All eight electrons (one from Na, seven from Cl) fill Cl atomic orbitals: NaCl is an ionic solid
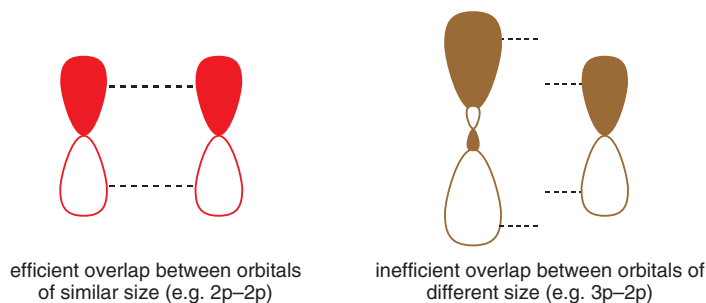
3s

But these AOs are too far apart in energy to combine to form new MOs and no covalent bond is formed. The orbitals which get filled are simply the 3s and 3p orbitals of the Cl atom. The electrons available to fill these orbitals are the seven provided by Cl plus the one from Na: we end up with Na^+ and Cl^-. The ionic bonding in NaCl is due simply to the attraction between two oppositely charged ions—there is no orbital overlap.

These three different cases where the two combining orbitals differ greatly in energy, only a little, or not at all are summarized below.

Energies of AOs both the same	AO on atom B is a little lower in energy than AO on atom A	AO on atom B is a lot lower in energy than AO on atom A
large interaction between AOs	less interaction between AOs	AOs are too far apart in energy to interact
bonding MO much lower in energy than AOs	bonding MO is lowered by a small amount relative to AO on atom B	the filled orbital on the same energy as the AO on atom B
antibonding MO is much higher in energy than the AOs	antibonding MO is raised in energy by a small amount relative to AO on atom A	the empty orbital on the cation has same energy as the AO on atom A
both AOs contribute equally to the MOs	the AO on B contributes more to the bonding MO and the AO on A contributes more to the antibonding MO	Only one AO contributes to each MO
electrons in bonding MO are shared equally between the two atoms	electrons in bonding MO are shared between atoms but are associated more with B than A	electrons in the filled orbital are located only on atom B
bond between A and B would classically be described as purely covalent	bond between A and B is covalent but there is also some electrostatic (ionic) attraction between atoms	bond between A and B would classically be described as purely ionic
easiest to break bond into two radicals (homolytic fission)	easiest to break bond into two ions, A^+ and B^-, although it is also possible to give two radicals	compound already exists as ions A^+ and B^-
heterolytic fission of the bond is possible and could give either A^+ and B^- or A^- and B^+ (this point is discussed more fully in Chapters 24 and 37)		

Other factors affecting degree of orbital interaction

Having similar energies is not the only criterion for good interaction between two AOs. It also matters how the orbitals overlap. We have seen that p orbitals overlap better in an end-on fashion (forming a σ bond) than they do side-on (forming a π bond). Another factor is the size of the AOs. For best overlap, the orbitals should be the same size—a 2p orbital overlaps much better with another 2p orbital than it does with a 3p or 4p orbital.

efficient overlap between orbitals
of similar size (e.g. 2p–2p)

inefficient overlap between orbitals of
different size (e.g. 3p–2p)

A third factor is the symmetry of the orbitals—two AOs must have the appropriate symmetry to combine. Thus a $2p_x$ orbital cannot combine with a $2p_y$ or $2p_z$ orbital since they are all perpendicular to each other (they are orthogonal). Depending on the alignment, there is either no overlap at all or any constructive overlap is cancelled out by equal amounts of destructive overlap. Likewise, an s orbital can overlap with a p orbital only end-on. Sideways overlap leads to equal amounts of bonding and antibonding interactions and no overall gain in energy.

these two p orbitals cannot
combine because they are
perpendicular to each other

here any constructive overlap is
cancelled out by equal amounts
of destructive overlap

however, s and p orbitals
can overlap end-on
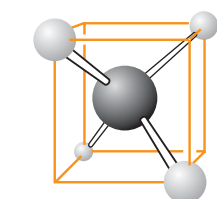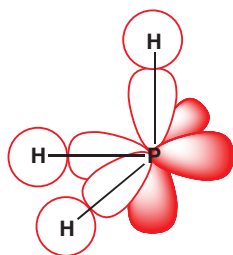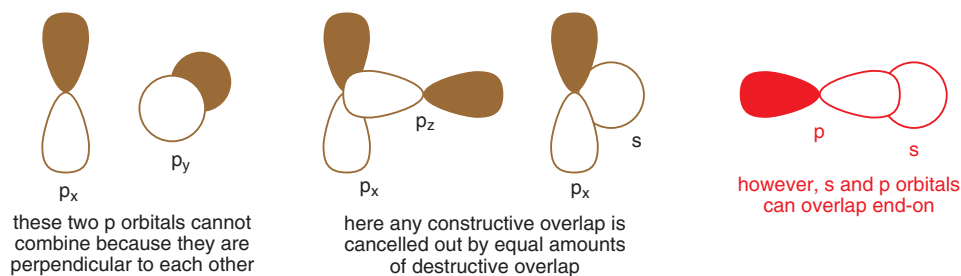
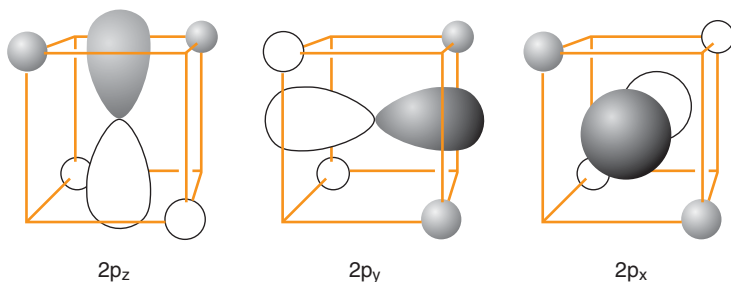## Molecular orbitals of molecules with more than two atoms

We now need to look at ways of combining more than two atoms at a time. For some molecules, such as H_2S and PH_3, which have all bond angles equal to 90°, the bonding should be straightforward—the 3p orbitals (which are at 90°) on the central atom simply overlap with the 1s orbitals of the hydrogen atoms.

Now, you might imagine it would be similar for ammonia, NH_3, since N lies above P in the periodic table. The trouble is, we know experimentally that the bond angles in ammonia, as in water and methane, are not 90°, but instead 104°, 107°, and 109°, respectively. All the covalent compounds of elements in the row Li to Ne raise this difficulty. How can we get 109° angles from orbitals arranged 90° apart?

To see what has to happen, we'll start with a molecule of methane enclosed in a cube. It is possible to do this since the opposite corners of a cube describe a perfect tetrahedron. The carbon atom is at the centre of the cube and the four hydrogen atoms are at four of the corners.

Now let's consider each of the carbon's 2s and 2p AOs in turn. The carbon's 2s orbital can overlap with all four hydrogen 1s orbitals at once with all the orbitals in the same phase.

a molecule of methane
enclosed in a cube

Each of the 2p orbitals points to a pair of opposite faces of the cube. Once more all four hydrogen 1s orbitals can combine with each p orbital, provided the hydrogen AOs on the opposite faces of the cube are of opposite phases.

the carbon 2s AO can overlap with all four hydrogen 1s AOs at once

2p$_z$ 2p$_y$ 2p$_x$

the hydrogen 1s orbitals can overlap with the three 2p orbitals

The three MOs generated in this way are degenerate, and this gives us four bonding orbitals. Along with four associated antibonding orbitals this gives us a total of eight MOs, which is correct since there were eight AOs (C gave us 2s and $3 \times 2p$, while $4 \times H$ gave us $4 \times 1s$).
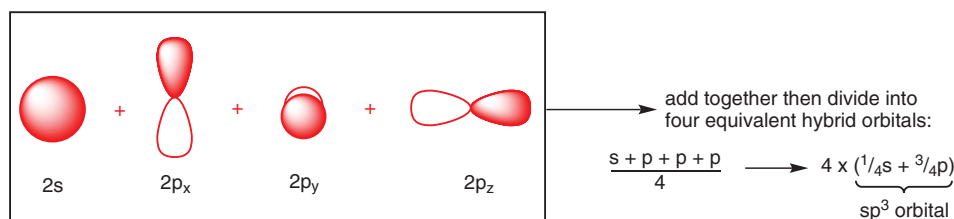
Using this approach, it is possible to construct a complete MO picture of methane—and indeed for very much more complex molecules than methane. There is experimental evidence too that these pictures are correct. But the problem is this: the four filled, bonding orbitals of methane are *not* all the same (one came from the interaction with the C 2s orbital and three from the C 2p orbitals). But we also know from experimental observations all four C–H bonds in methane *are* the same.

Something seems to be wrong, but there is in fact no contradiction. The MO approach tells us that there is one MO of one kind and three of another but the electrons in them are shared out over all five atoms. No one hydrogen atom has more or fewer electrons than any other—they are all equivalent. Techniques that tell us the structure of methane do not tell us where bonds are; they simply tell us where the atoms are located in space—*we* draw in bonds connecting atoms together. Certainly the *atoms* form a regular tetrahedron but exactly where the electrons are is a different matter entirely. So, do we have to give up the idea that methane has four bonds, each made of two electrons, linking the C with an H? If we choose to, then for every reaction, even of the simplest molecules, we are going to need to calculate, by computer, a full set of MOs and all of their interactions.

That would be using physics to do chemistry. It might be accurate but it would kill creativity and invention. So here is an alternative: we keep our tried and tested practical picture of molecules made from discrete bonds, each containing a pair of electrons, but we make it compatible with MO theory. To do this we need a concept known as *hybridization*.

Hybridization of atomic orbitals

To get a picture of methane with four equivalent pairs of electrons we need to start with four equivalent AOs on C, which we don't have. But we can get them if we combine the carbon 2s and 2p orbitals first to make four new orbitals, each composed of one-quarter of the 2s orbital and three-quarters of one of the p orbitals. The new orbitals are called sp³ (that's said *s-p-three*, not *s-p-cubed*) hybrid orbitals to show the proportions of the AOs in each. This process of mixing is called *hybridization*. The hybrid orbitals are mathematically equivalent to the 2s and 2p orbitals we started with, and they have the advantage that when we use them to make MOs the orbitals correspond to bonding pairs of electrons.
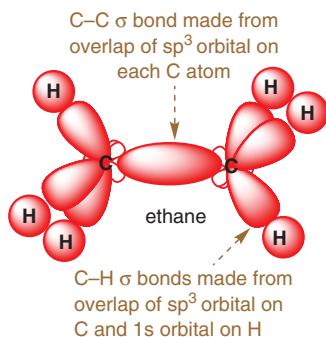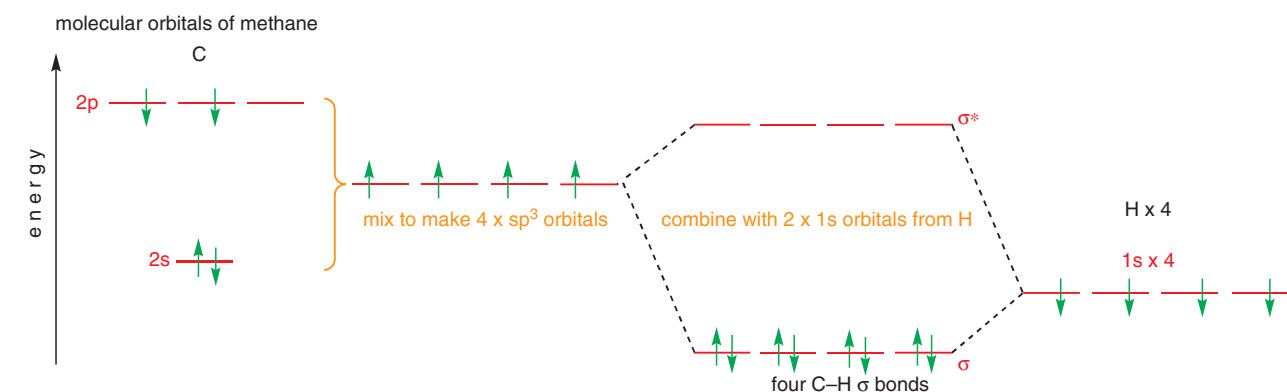

2s 2p$_x$ 2p$_y$ 2p$_z$

add together then divide into four equivalent hybrid orbitals:

$$\frac{s + p + p + p}{4} \longrightarrow 4 \times (\tfrac{1}{4}s + \tfrac{3}{4}p)$$

sp³ orbital

What do the four hybrid orbitals look like? Each sp³ orbital takes three-quarters of its character from a p orbital and one-quarter from an s orbital. It has a planar node through the nucleus like a p orbital but one lobe is larger than the other because of the extra contribution of the 2s orbital: the symmetry of the 2s orbital means that adding it to a 2p orbital will increase the size of the wavefunction in one lobe, but decrease it in the other.
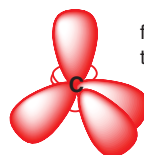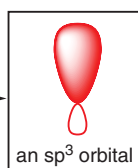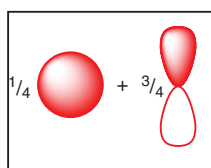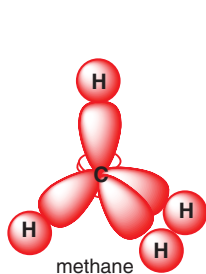
methane

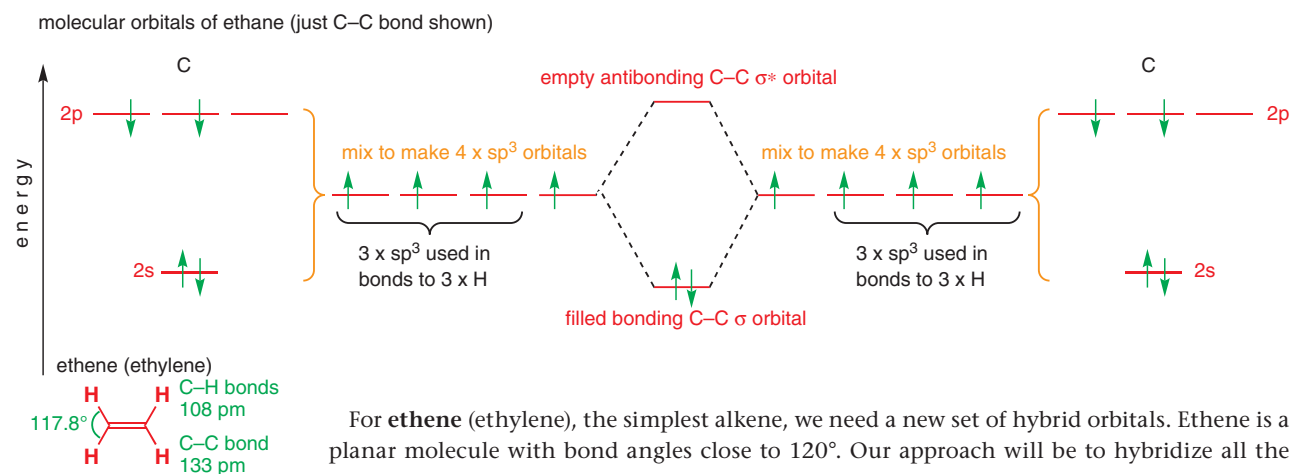four sp³ on one C atom point to the corners of a tetrahedron

¼ + ¾ → an sp³ orbital

The four sp³ orbitals point to the corners of a tetrahedron and we build up a molecule of methane by overlapping the large lobe of each sp³ orbital with the 1s orbital of a hydrogen atom, as shown in the margin. Each overlap forms an MO (2sp³ + 1s) and we can put two electrons in each to form a C–H σ bond. There will of course also be an antibonding MO, σ* (2sp³ – 1s) in each case, but these orbitals are empty. Overall, the electrons are spatially distributed exactly as they were in our previous model, but now we can *think of them* as being located in four bonds.

molecular orbitals of methane

C–C σ bond made from overlap of sp³ orbital on each C atom

ethane

C–H σ bonds made from overlap of sp³ orbital on C and 1s orbital on H

The great advantage of this method is that it can be used to build up structures of much larger molecules quickly and without having to imagine that the molecule is made up from isolated atoms. Take **ethane**, for example. Each carbon uses three sp³ AOs orientated towards the three hydrogen atoms, leaving one sp³ orbital on each carbon atom for the C–C bond.

In the MO energy level diagram we now have both C–H bonding σ and antibonding σ* orbitals (made from combining sp³ orbitals on C with 1s orbitals on H) and also a C–C bonding σ and antibonding σ* orbital, made from two sp³ orbitals on C. The diagram below just shows the C–C bond.

molecular orbitals of ethane (just C–C bond shown)

ethene (ethylene)

117.8°   C–H bonds 108 pm
C–C bond 133 pm

For **ethene** (ethylene), the simplest alkene, we need a new set of hybrid orbitals. Ethene is a planar molecule with bond angles close to 120°. Our approach will be to hybridize all the

orbitals needed for the C–H framework and see what is left over. In this case we need three equivalent bonds from each carbon atom (one to make a C–C bond and two to make C–H bonds). T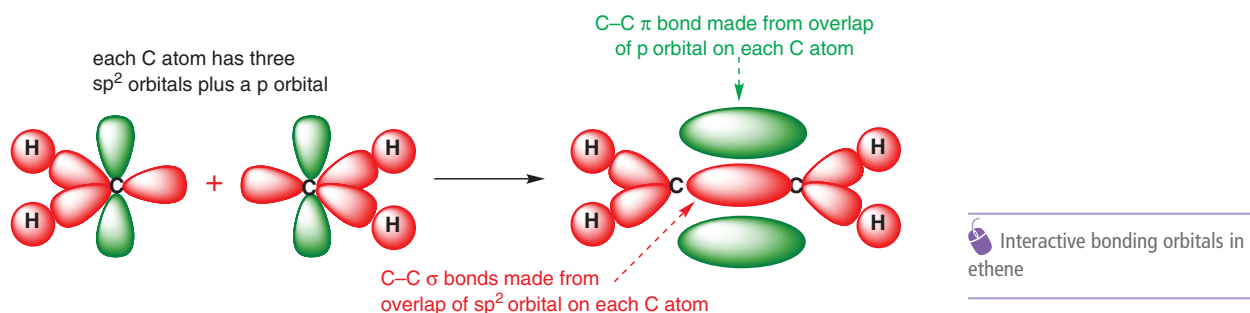herefore we need to combine the 2s orbital on each carbon atom with two p orbitals to make the three bonds. We could hybridize the 2s, $2p_y$, and $2p_z$ orbitals (that is, all the AOs in the plane) to form three equal sp^2 orbitals, leaving the $2p_z$ orbital unchanged. These sp^2 hybrid orbitals will have one-third s character and only two-thirds p character.

2s $2p_y$ $2p_z$

add together then divide into three equivalent hybrid orbitals:

$$\frac{s + p + p}{3} \longrightarrow 3 \times \underbrace{(^1/_3 s + {}^2/_3 p)}_{sp^2 \text{ orbital}}$$

plus remaining $2p_x$ orbital

$2p_x$
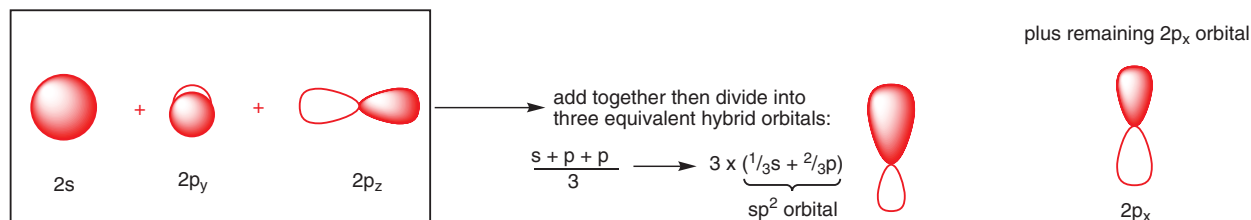
The three sp^2 hybrid AOs on each carbon atom can overlap with three other orbitals (two hydrogen 1s AOs and one sp^2 AO from the other carbon) to form three σ MOs. This leaves the two $2p_x$ orbitals, one on each carbon, which combine to form the π MO. The skeleton of the molecule has five σ bonds (one C–C and four C–H) in the plane and the central π bond is formed by two $2p_x$ orbitals above and below the plane.

each C atom has three sp^2 orbitals plus a p orbital

C–C π bond made from overlap of p orbital on each C atom

C–C σ bonds made from overlap of sp^2 orbital on each C atom

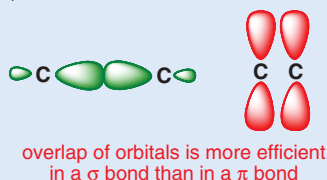Interactive bonding orbitals in ethene

This is the first MO picture we have constructed with a C=C double bond, and it is worth taking the time to think about the energies of the orbitals involved. We'll again ignore the C–H bonds, which involve two of the sp^2 orbitals of each C atom. Remember, we mixed two of the three 2p orbitals in with the 2s orbital to make $3 \times sp^2$ orbitals on each C atom, leaving behind one unhybridized 2p orbital.

Now, first we need to generate the σ and σ* orbitals by interacting one sp^2 orbital on each atom. Then we need to deal with the two p orbitals, one on each C, which interact side-on. The unhybridized p orbitals are a bit higher in energy than the sp^2 orbitals, but they interact less well (we discussed this on p. 93) so they give a π orbital and a π* orbital whose energies are *in between* the σ and σ* orbitals. Each C atom donates two electrons to these orbitals (the other two electrons are involved in the two bonds to H), so the overall picture looks like this. Two AOs give two MOs.
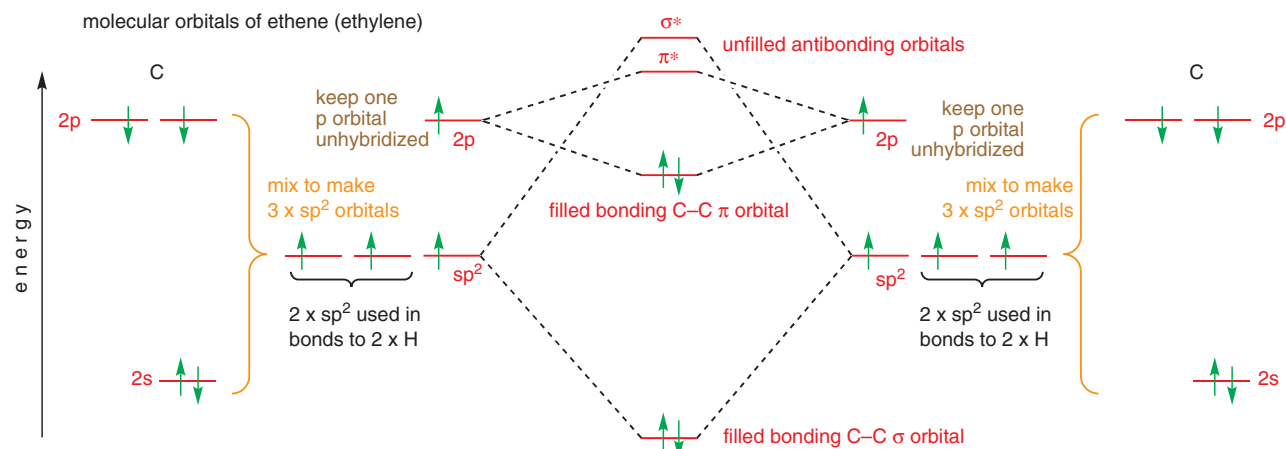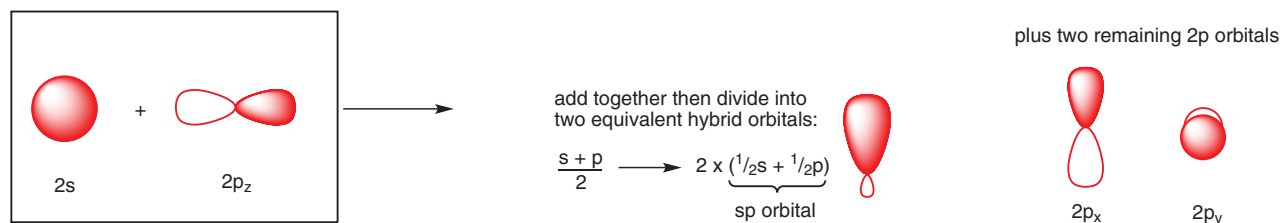
The fact that the sideways overlap of the p orbitals to form a π bond is not as effective as the head-on overlap of the orbitals to form a σ bond means that it takes less energy to break a C—C π bond than a C—C σ bond (about 260 kJ mol^{-1} compared to about 350 kJ mol^{-1}).
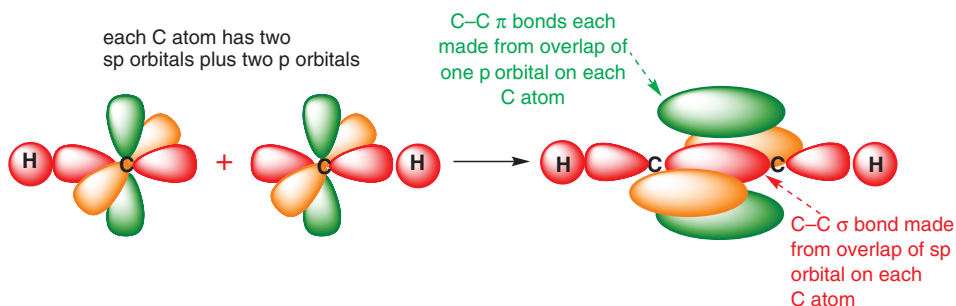

overlap of orbitals is more efficient
in a σ bond than in a π bond

ethyne (acetylene)

H ════ H

Ethyne (acetylene) has a C≡C triple bond. Each carbon bonds to only two other atoms to form a linear CH skeleton. Only the carbon 2s and $2p_x$ have the right symmetry to bond to the two atoms at once so we can hybridize these to form two sp hybrids on each carbon atom, leaving the $2p_y$ and $2p_z$ to form π MOs with the 2p orbitals on the other carbon atom. These sp hybrids have 50% each s and p character and form a linear carbon skeleton.

plus two remaining 2p orbitals

add together then divide into
two equivalent hybrid orbitals:

$$\frac{s + p}{2} \longrightarrow 2 \times \underbrace{(^{1}/_{2}s + {}^{1}/_{2}p)}_{\text{sp orbital}}$$

2s $2p_z$

$2p_x$ $2p_y$

We could then form the MOs as shown below. Each sp hybrid AO overlaps with either a hydrogen 1s AO or with the sp orbital from the other carbon. The two sets of p orbitals combine to give two mutually perpendicular π MOs.

each C atom has two
sp orbitals plus two p orbitals

C–C π bonds each
made from overlap of
one p orbital on each
C atom

C–C σ bond made
from overlap of sp
orbital on each
C atom

🖱 Interactive bonding orbitals in
ethyne

Hydrocarbon skeletons are built up from tetrahedral (sp^3), trigonal planar (sp^2), or linear (sp) hybridized carbon atoms. Deciding what sort of hybridization any carbon atom has, and hence what sort of orbitals it will use to make bonds, is easy. All you have to do is count up the atoms bonded to each carbon atom. If there are two, that carbon atom is linear (sp hybridized), if there are three, that carbon atom is trigonal (sp^2 hybridized), and if there are four, that carbon atom is tetrahedral (sp^3 hybridized). Since the remaining unhybridized p orbitals are used to make the π orbitals of double or triple bonds, you can also work out hybridization state just by counting up the number of π bonds at each carbon. Carbon atoms with no π bonds are tetrahedral (sp^3 hybridized), those with one π bond are trigonal (sp^2 hybridized), and those with two π bonds are linear (sp hybridized).

There's a representative example on the left. This hydrocarbon (hex-5-en-2-yne) has two linear sp carbon atoms (C2 and C3), two trigonal sp^2 carbon atoms (C5 and C6), a tetrahedral sp^3 CH$_2$ group in the middle of the chain (C4), and a tetrahedral sp^3 methyl group (C1) at the end of the chain. We had no need to look at any AOs to deduce this—we needed only to count the bonds.

hex-5-en-2-yne
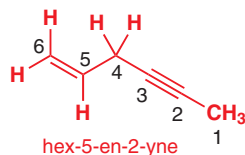
We can hybridize any atoms

We can use the same ideas with any sort of atom. The three molecules shown on the next page all have a tetrahedral structure, with four equivalent σ bonds from the central tetrahedral sp^3

atom, whether this is B, C, or N, and the same total number of bonding electrons—the molecules are said to be **isoelectronic**. The atoms contribute different numbers of electrons so to get the eight bonding electrons we need we have to add one to BH_4 and subtract one from NH_4—hence the charges in BH_4^- and NH_4^+. In each case the central atom can be considered to be sp^3 hybridized, using an sp^3 orbital to bond to each of the four H atoms, each resulting σ bond being made up of two electrons.

Compounds of the same three elements with only three bonds take more thinking about. Borane, BH_3, has only three pairs of bonding electrons (three from B and three from the three H atoms). Since the central boron atom bonds to only three other atoms we can therefore describe it as being sp^2 hybridized. Each of the B–H bonds results from the overlap of an sp^2 orbital with the hydrogen 1s orbital. Its remaining p orbital is not involved in bonding and must remain empty. Do not be tempted by the alternative structure with tetrahedral boron and an empty sp^3 orbital. You want to populate the lowest energy orbitals for greatest stability and sp^2 orbitals with their greater s character are lower in energy than sp^3 orbitals. Another way to put this is that, if you have to have an empty orbital, it is better to have one with the highest possible energy since it has no electrons in it and so it doesn't affect the stability of the molecule.
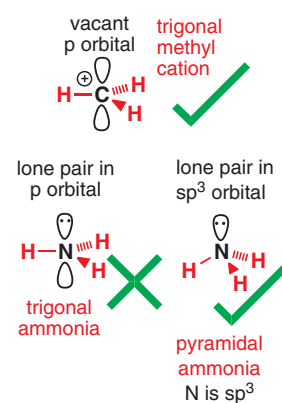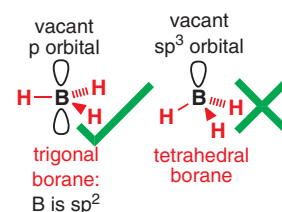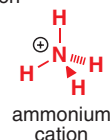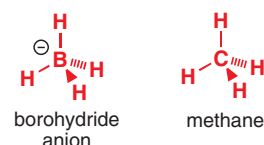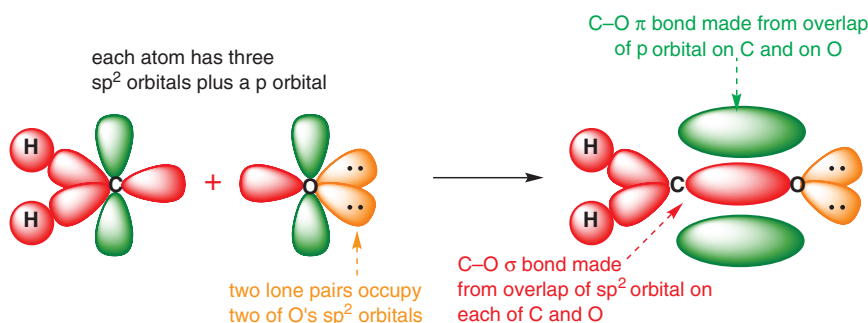
Borane is isoelectronic with the methyl cation, CH_3^+ or Me^+. All the arguments we have just applied to borane also apply to Me^+ so it too is sp^2 hybridized with a vacant p orbital. This will be very important when we discuss the reactions of carbocations in Chapters 15 and 36.

Now what about ammonia, NH_3? Ammonia is *not* isoelectronic with borane and Me^+! It has a total of eight electrons—five from N and three from $3 \times H$. As well as three N–H bonds, each with two electrons, the central nitrogen atom also has a lone pair of electrons. We have a choice: either we could hybridize the nitrogen atom sp^2 and put the lone pair in the p orbital or we could hybridize the nitrogen sp^3 and have the lone pair in an sp^3 orbital.

This is the opposite of the situation with borane and Me^+. The extra pair of electrons *does* contribute to the energy of ammonia so it prefers to be in the lower-energy orbital, sp^3, rather than pure p. Experimentally the H–N–H bond angles are all 107.3°. Clearly, this is much closer to the 109.5° sp^3 angle than the 120° sp^2 angle. But the bond angles are not exactly 109.5°, so ammonia cannot be described as pure sp^3 hybridized. One way of looking at this is to say that the lone pair repels the bonds more than they repel each other. Alternatively, you could say that the orbital containing the lone pair must have slightly more s character while the N–H bonding orbitals must have correspondingly more p character.
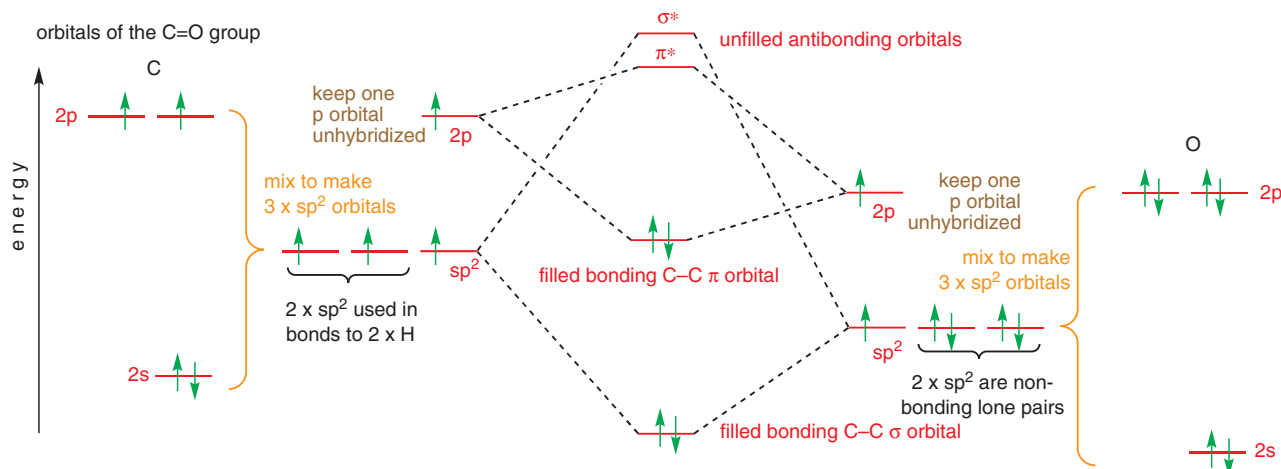
The carbonyl group

The C=O double bond is the most important functional group in organic chemistry. It is present in aldehydes, ketones, acids, esters, amides, and so on. We shall spend several chapters discussing its chemistry so it is important that you understand its electronic structure from this early stage. We'll use the simplest carbonyl compound, methanal (formaldehyde), as our example. As in alkenes, the carbon atom needs three sp^2 orbitals to form σ bonds with the two H atoms and the O atom. But what about oxygen? It needs only to form one σ bond to C, but it needs two more hybrid orbitals for its lone pairs: the oxygen atom of a carbonyl group is also sp^2 hybridized. A p orbital from the carbon and one from the oxygen make up the π bond, which also contains two electrons. This is what the bonding looks like:

borohydride anion

methane

ammonium cation

vacant p orbital

vacant sp^3 orbital

trigonal borane: B is sp^2

tetrahedral borane

vacant p orbital

trigonal methyl cation

lone pair in p orbital

lone pair in sp^3 orbital

trigonal ammonia

pyramidal ammonia N is sp^3

each atom has three sp^2 orbitals plus a p orbital

two lone pairs occupy two of O's sp^2 orbitals

C–O σ bond made from overlap of sp^2 orbital on each of C and O

C–O π bond made from overlap of p orbital on C and on O

How do we know the O has its lone pairs in sp^2 orbitals? Well, whenever carbonyl compounds form bonds using those lone pairs—hydrogen bonds, for example—they prefer to do so in a direction corresponding to where the lone pairs are expected to be.

🖱 Interactive bonding orbitals in formaldehyde

For the MO energy diagram, we'll again just consider the bonding between C and O. First, we hybridize the orbitals of both atoms to give us the $3 \times sp^2$ orbitals and $1 \times p$ orbital we need. Notice that we have made the AOs at O lower in energy than the AOs at C because O is more electronegative. Once we have accounted for the non-bonding sp^2 orbitals at O and the two C–H bonds, we allow the two remaining sp^2 orbitals to interact and make a σ and a σ* orbital, and the two p orbitals to make a π and a π* orbital.

orbitals of the C=O group

The fact that oxygen is more electronegative than carbon has two consequences for this diagram. Firstly it makes the energy of the orbitals of a C=O bond lower than they would be in the corresponding C=C bond. That has consequences for the reactivity of alkenes and carbonyl compounds, as you will see in the next chapter.

The second consequence is polarization. You met this idea before when we were looking at NO. Look at the filled π orbital in the MO energy level diagram. It is more similar in energy to the p orbital on O than the p orbital on C. We can interpret this by saying that it receives a *greater contribution* from the p orbital on O than from the p orbital on C. Consequently the orbital is distorted so that it is bigger at the O end than at the C end, and the electrons spend more time close to O. The same is true for the σ bond, and the consequent polarization of the C=O group can be represented by one of two symbols for a dipole—the arrow with the cross at the positive end or the pair of δ+ and δ– symbols.
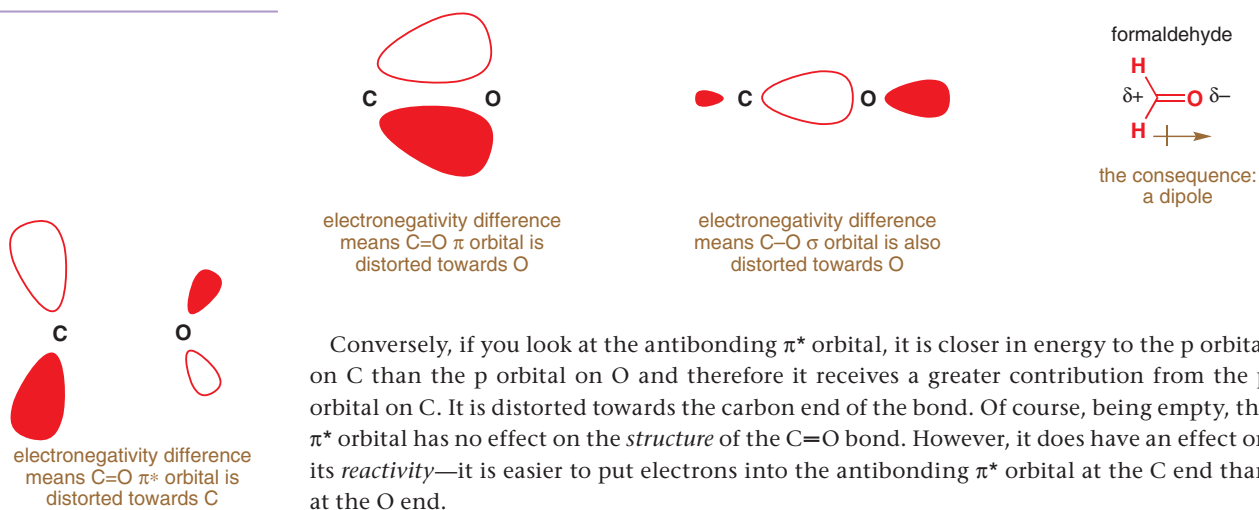
> ■ Alkenes have *nucleophilic* π bonds while carbonyl compounds have *electrophilic* π bonds. If you are not yet familiar with these terms, you will meet them in Chapter 5.

> ➡ We will develop this idea in Chapter 6.

electronegativity difference means C=O π orbital is distorted towards O

electronegativity difference means C–O σ orbital is also distorted towards O

formaldehyde

the consequence: a dipole

electronegativity difference means C=O π* orbital is distorted towards C

Conversely, if you look at the antibonding π* orbital, it is closer in energy to the p orbital on C than the p orbital on O and therefore it receives a greater contribution from the p orbital on C. It is distorted towards the carbon end of the bond. Of course, being empty, the π* orbital has no effect on the *structure* of the C=O bond. However, it does have an effect on its *reactivity*—it is easier to put electrons into the antibonding π* orbital at the C end than at the O end.

Rotation and rigidity

To end this chapter, we deal with one more question which MOs allow us to answer: how flexible is a molecule? The answer depends on the molecule of course, but more importantly it depends on the type of bond. You may be aware that many alkenes can exist in two forms, *cis* and *trans*, also called *Z* and *E* (see Chapter 17). These two forms are not usually easy to interconvert—in other words the C=C double bond is very rigid and cannot rotate.

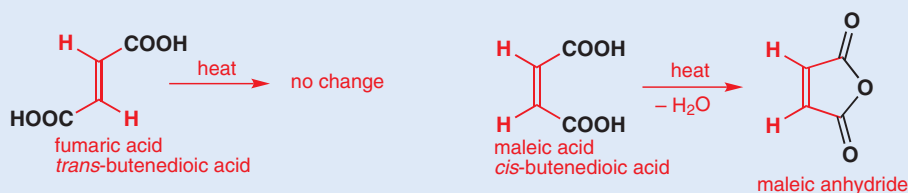*trans (E)* but-2-ene   do not interconvert   *cis (Z)* but-2-ene

If we look at the bonding in but-2-ene we can see why. The π bond is made up of two parallel p orbitals. To rotate about the π bond requires those orbitals to lose their interaction, pass through a state in which they lie perpendicular, and finally line up again. That transitional, perpendicular state is very unfavourable because all of the energy gained through π bonding is lost. Alkenes are rigid and do not rotate.
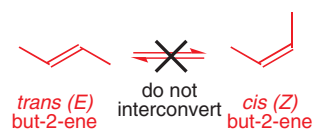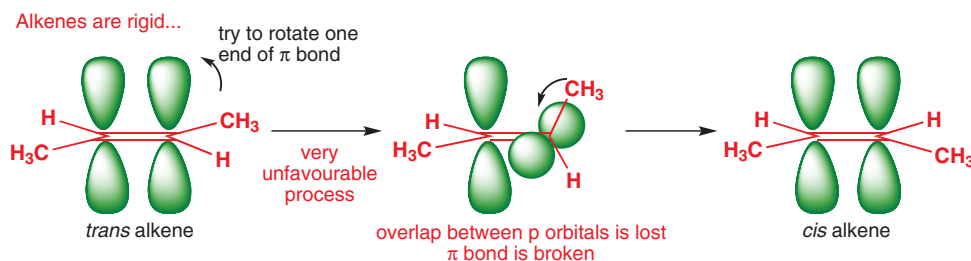
It is in fact possible to interconvert *cis* and *trans* alkenes, but it requires a considerable amount of energy—around 260 kJ mol⁻¹. One way to break the π bond is to promote an electron from the π orbital to the π* orbital. If this were to happen, there would be one electron in the bonding π orbital and one in the antibonding π* orbital, and hence no overall bonding. The energy required to do this corresponds to light in the ultraviolet (UV) region of the spectrum. Shining UV light on an alkene can break the π bond (but not the σ bond) and allows rotation to occur.

Alkenes are rigid...

try to rotate one end of π bond

trans alkene — very unfavourable process → overlap between p orbitals is lost π bond is broken → *cis* alkene
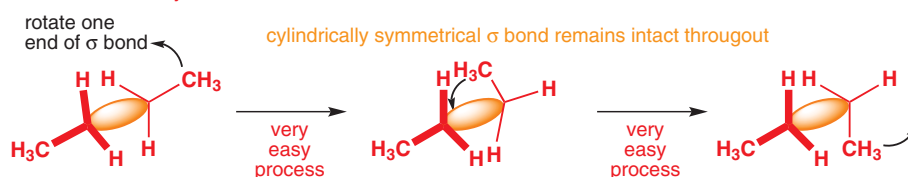
Alkene isomers

Maleic and fumaric acids were known in the nineteenth century to have the same chemical composition and the same functional groups, and yet they were different compounds—why remained a mystery. That is, until 1874 when van't Hoff proposed that free rotation about double bonds was restricted. This meant that, whenever each carbon atom of a double bond had two different substituents, isomers would be possible. He proposed the terms *cis* (Latin meaning 'on this side') and *trans* (Latin meaning 'across or on the other side') for the two isomers. The problem was: which isomer was which? On heating, maleic acid readily loses water to become maleic anhydride so this isomer must have both acid groups on the same side of the double bond.

fumaric acid
trans-butenedioic acid — heat → no change

maleic acid
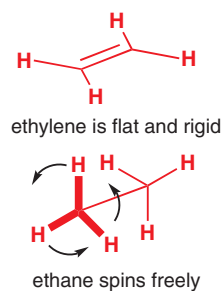*cis*-butenedioic acid — heat − H₂O → maleic anhydride

Compare that situation with butane. Rotating about the middle bond doesn't break any bonds because the σ bond is, by definition, cylindrically symmetrical. Atoms connected only by a σ bond are therefore considered to be rotationally free, and the two ends of butane can spin relative to one another.

■ In fact not all orientations about a σ bond are equally favourable. We come back to this aspect of structure, known as *conformation*, in Chapter 16.

Alkanes rotate freely...

rotate one end of σ bond

cylindrical symmetrical σ bond remains intact througout

very easy process → very easy process →

The same comparison works for ethylene (ethene) and ethane: in ethylene all the atoms lie in a plane, enforced by the need for overlap between the p orbitals. But in ethane, the two ends of the molecule spin freely. This difference in rigidity has important consequences throughout chemistry, and we will come back to it in more detail in Chapter 16.

ethylene is flat and rigid

ethane spins freely

Conclusion

We have barely touched the enormous variety of molecules, but it is important that you realize at this point that these simple ideas of structural assembly can be applied to the most complicated molecules known. We can use AOs and combine them into MOs to solve the structure of very small molecules and to deduce the structures of small parts of much larger molecules. With the additional concept of conjugation in Chapter 7 you will be able to grasp the structure of any organic compound. From now on we shall use terms like AO and MO, 2p orbital, sp^2 hybridization, σ bond, energy level, and populated orbital without further explanation. If you are unsure about any of them, refer back to this chapter.

Looking forward

We started the chapter with atomic orbitals, which we combined into molecular orbitals. But what happens when the orbitals of *two molecules* interact? This is what happens during chemical reactions, and it's where we are heading in the next chapter.

Further reading

An excellent introduction to orbitals and bonding is *Molecular Orbitals and Organic Chemical Reactions: Student Edition* by Ian Fleming, Wiley, Chichester, 2009.

Check your understanding

To check that you have mastered the concepts presented in this chapter, attempt the problems that are available in the book's Online Resource Centre at **http://www.oxfordtextbooks.co.uk/orc/clayden2e/**