

Year 2, Organic Chemistry, Chapter 02:

Hybridised Atomic Orbitals in the formation of π bonds

*Resonance/Delocalisation/Stability/Conjugation and Hyperconjugation/the Inductive and Mesomeric Effects/Activation and Deactivation all involve the **sharing** of electrons. Sometimes electron density is **increased** (e.g. '+M' or '+I') and at other times electron density (e.g. '-M' or '-I') is **decreased**. The phrases "electron donating" and "electron withdrawing" are technically incorrect. In molecular species electrons are neither donated nor withdrawn, they are SHARED and ELECTRON DENSITY is thereby altered.*

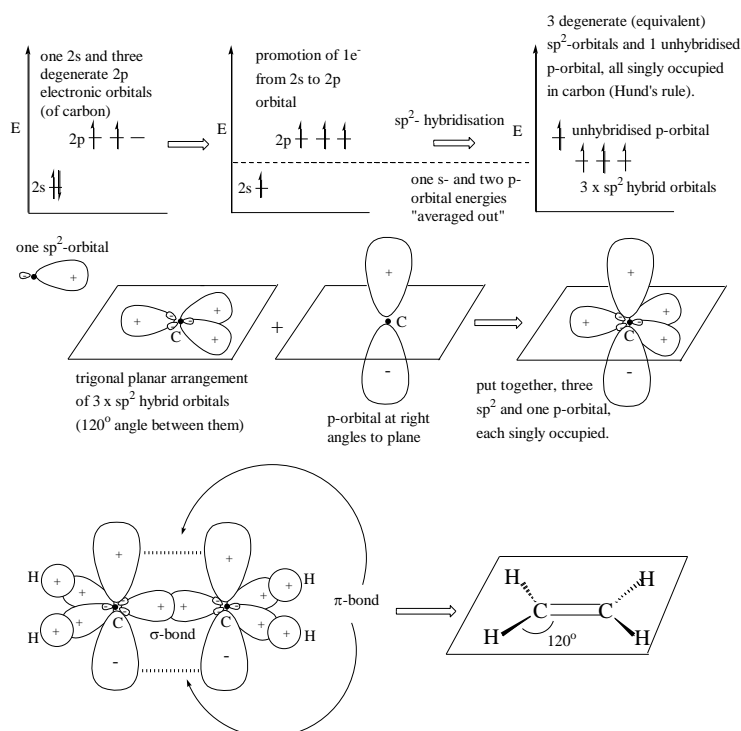
- I mentioned the phrase "unhybridised 'p' orbitals" quite a lot when we were talking about double and triple bonds last year, and now it is time for us to talk about "hybridisation".
- When the appropriate atomic orbitals are available, hybridisation is not needed. When the appropriate orbitals are **not** available, then **atomic orbitals need to be HYBRIDISED to form the necessary molecular orbitals**.
- Let me start (almost at the beginning of our Second Year) by telling you that in one sense there are no such things as electrons "orbiting" nuclei as the moon orbits the earth. We use that concept quite validly at GCSE and First Year 'A' Level because **an electron can be thought of as a minutely tiny particle that has to be somewhere in the space associated with its nucleus**, therefore to portray it as though it were the moon orbiting the earth is not untrue and it is *moderately* realistic. However, in reality, an electron **actually is also a wave** – **an electron is simultaneously both a particle and a wave**¹ and it is by making use of the mathematics of wave functions that the great Physicists/Mathematicians of the first half of the last century such as Bohr/Heisenberg/ Pauli/ Schrodinger/Dirac/et alii² (and most of them were only in their thirties) came up with the idea that **an "orbital" is a volume of space in which an electron is most likely to be found**. The probability referred to here is a **statistical** probability, and the concept of probability had to be applied to atomic theory in order to accommodate the principle of uncertainty pointed out by Werner Heisenberg.
 - An **ATOMIC orbital** (such as an s/p/d/f/etc orbital) is thus a volume of space in which an electron *in an atom* is most likely to be found, but an atom cannot form molecular bonds of equal energy and equal length by using electrons in atomic orbitals that possess different levels of energy (such as those in s/p/d/f/etc orbitals), therefore in order to form *molecular bonds* of equal energy and equal length, an atom must first hybridise its standard atomic orbitals into hybridised atomic orbitals (such as s¹p¹/s¹p²/and s¹p³). Therefore
 - a **HYBRID atomic orbital** (as we shall see) is a cross or a "hybrid" between two different types of standard atomic orbitals, and it is a volume of space in which an electron in a hybridised atomic orbital *in an atom* is most likely to be found, and finally
 - a **MOLECULAR orbital** is a volume of space in which the two bonding electrons that constitute a covalent bond *in a molecule* are most likely to be found.

¹ The great British father and son duo, JJ and GP Thomson both won Nobel Laureates (just as the two Braggs did) – JJ for proving that an electron is a particle (1906) and GP (1937) for proving that an electron is a wave!

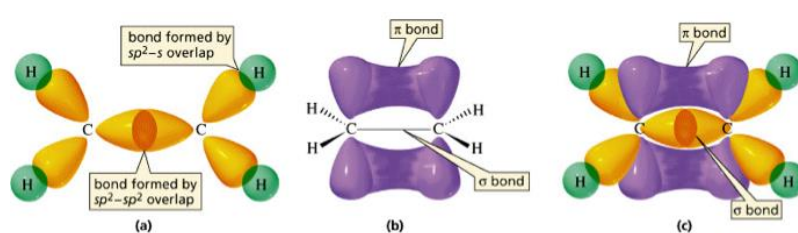
² If you are interested in the history of the discoveries involved, you might want to read Marcus Chown's very interesting book "The Magic Furnace". The furnaces here are the stars where all the elements were 'cooked' from Hydrogen atoms, and it was the great Fred Hoyle and William Fowler ("Nucleosynthesis in Massive Stars and Supernovae") who, in the 1950s, developed the theory that the heavy elements were formed in massive stars and supernovae.

A) Hybridisation and Hybrid Atomic Orbitals

- In the diagram below I show you how Dr N Chatterton of London Metropolitan University shows the formation of sp^2 (or s^1p^2) orbitals to form the Ethene molecule. A double bond consists of a σ bond and a π bond, and a molecular π bond is formed by the overlap of two unhybridised 'p' orbitals, one on each of the two bonding atoms. (The word “*degenerate*” in Chemistry is used to indicate that all the species involved have the same amount of energy.)



- The diagram below is taken from Prof Stephen Lower's excellent virtual Chemistry textbook on <http://www.chem1.com/acad/webtext/virtualtextbook.html>



- As you can see, in Ethene,
 - the molecular σ bond between the two C atoms (the bond that is formed in the direct line connecting the nuclei of the two bonding atoms) is created by the overlap of one atomic hybridised sp^2 orbital from each of the two bonded C atoms, and
 - the molecular σ bond between each of the C atoms and each of the H atoms is formed by the overlap of a hybridised atomic sp^2 orbital from the C atom and the s orbital from the H atom, and
 - the molecular π bond is formed by the overlap of the two unhybridised atomic 'p' orbitals, one on each of the two bonded C atoms (the π bond lying in the plane above and below the σ bond).
- That is it! At 'A' Level that is all that you need to know about hybridisation as background to the formation of multiple bonds and the formation of delocalised π rings in Arenes.

- OK, now let us talk about Molecular Orbitals.

B) Molecular Orbitals (MOs)

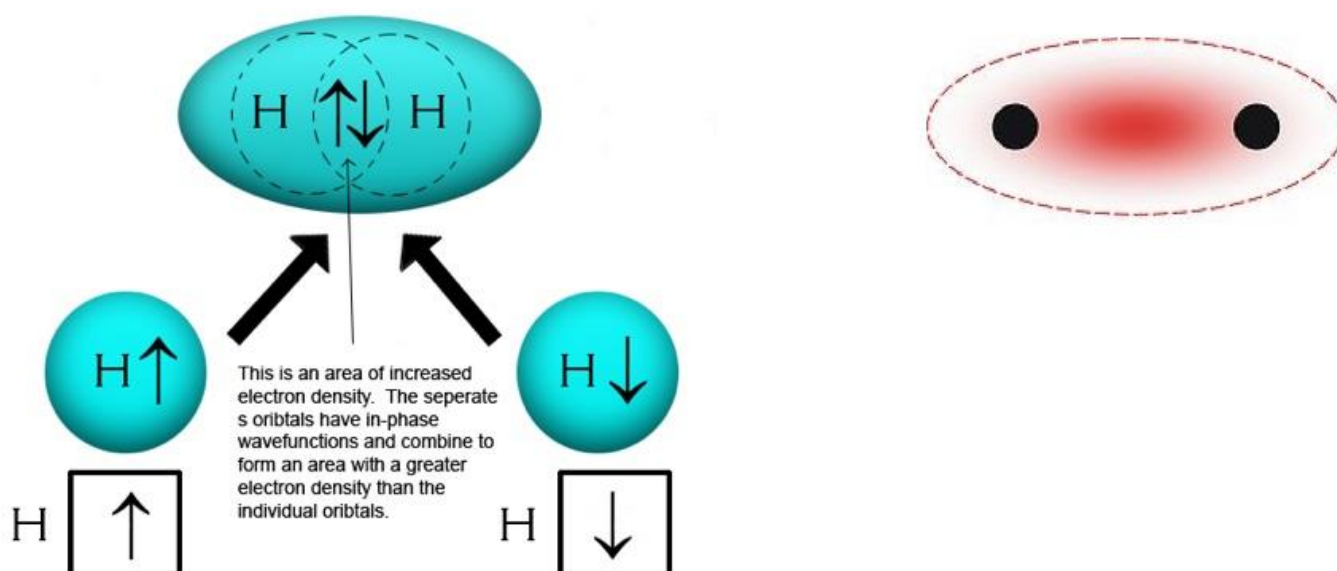
- All that you need to know about Molecular orbitals is summed up in the following quotation

*.... (the) different (s, p, d, f, atomic) orbitals arise in the first place from the interaction of the electron with the **single** central electrostatic force field associated with the positive nucleus of just one atom. An outer-shell electron in a **bonded** atom will be under the influence of a force field emanating from **TWO** positive nuclei, so we would expect the orbitals in the bonded atoms to have a somewhat different character from those in free atoms.*

Professor Stephen Lower, Simon Fraser University.

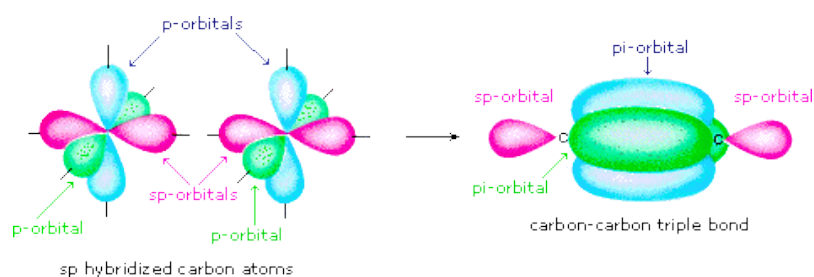
- A **molecular/covalent bond** is formed by the overlap of **two half-filled atomic orbitals**. (NB “half-filled” means that the atomic orbital has only one electron in it. Fully-filled orbitals have two electrons in them.)
- When two atoms bond together they form **molecular orbitals** for the electrons that they share, and when the atoms bind together they form either
 - a single bond called a sigma “ σ ” bond, or
 - a double bond that consists of one σ bond and one pi “ π ” bond, or
 - a triple bond that consists of one sigma bond and two pi bonds.

Sigma (or “ σ ”) bonds



Source: Prof Stephen Lower, Simon Fraser University

- When two atoms are joined together by a covalent bond, then it is natural for the strongest/the most immediate/the most direct bond between the two atoms to be formed first of all – and **the strongest/the most immediate/the most direct bond will be the one that lies on the straight line that connects the nuclei of the two atoms of the elements involved**. Thus, irrespective of the nature of the two orbitals that are overlapping i.e. irrespective of whether they are s/p/d/f or whatever orbitals³, **the bond formed in the line connecting the nuclei of the atoms of the elements involved is called a “sigma” or “ σ ” bond**. A sigma bond is just one bond. It is a single bond, and it is a molecular bond.
- A sigma bond is the bond that is formed along the line connecting the nuclei of two bonded atoms and can be formed from any type of atomic orbital (‘s’ / ‘p’ / ‘d’ / ‘f’ / hybridised / unhybridised / *whatever* orbital). For example, a Hydrogen, H₂, molecule is formed by the overlap of a half-filled ‘1s’ atomic orbital from one of the H atoms, and a ‘1s’ half-filled atomic orbital from the other H atom.
- A sigma, σ , bond may also be formed from a mixture of atomic orbitals e.g. as in CH₄. To form the four C–H bonds, the C atom uses **four sp^3** [i.e. an s^1p^3 (1 + 3 = 4)] hybridised atomic orbitals, while the H atom uses its ‘1s’ orbital, and together each ‘1s’ and each ‘ sp^3 ’ **atomic** orbital makes up **one molecular orbital**.



Source: William Reusch of Michigan University

Pi (or “ π ”) bonds

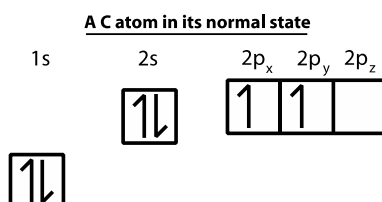
- There may however be bonds formed that do NOT lie on the line connecting the nuclei of the atoms of the elements involved in the compound (*e.g. they may lie in the area above and below the line connecting the two nuclei*) – and **when this type of bond occurs, it is called a “pi” or “ π ” bond**.
- To form
 - one covalent bond **TWO** electrons must be shared by the two bonding atoms, and to form
 - a *double* bond (as in a diatomic molecule such as O₂) **TWO PAIRS** of electrons (i.e. four electrons) must be shared by the two bonding atoms, and
 - to form a triple bond (as in Carbon Monoxide, CO) **THREE PAIRS** of electrons (i.e. six electrons) must be shared by the two bonding atoms.
- In some circumstances one of the bonding atoms contributes *both* the electrons in a bond (and this happens in *one* of the three bonds in Carbon Monoxide) and then this is called a ‘dative bond’ or a ‘coordinate’ bond. This happens also in the Ammonium ion, NH₄⁺.

³ They could also be sp^1 , sp^2 or sp^3 , etc orbitals (all these being “hybridised” orbitals). If a C atom forms bonds with four other atoms, then it does so via four s^1p^3 (or sp^3) hybridised orbitals (and 1+3=4). If a C atom forms bonds with three other atoms, then it does so via three s^1p^2/sp^2 hybridised orbitals (and 1+2=3). If a C atom forms bonds with two other atoms, then it does so via two $s^1p^1/sp^1/sp$ hybridised orbitals (and 1+1=2).

- However, (ignoring dative bonds for the moment), a second condition for the forming of any covalent bond is that **there must be an overlap of half-filled orbitals – one half-filled orbital from each of the two bonding electrons.**

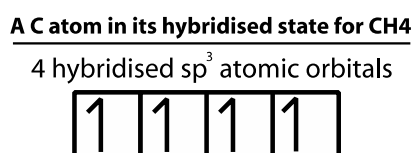
Methane, CH₄

- At first sight it is **not** easy to see how a molecule such as Methane, CH₄, can be formed according to these rules. After all, a C atom has only two half-filled orbitals and yet it forms **four bonds** when it forms the molecule CH₄!



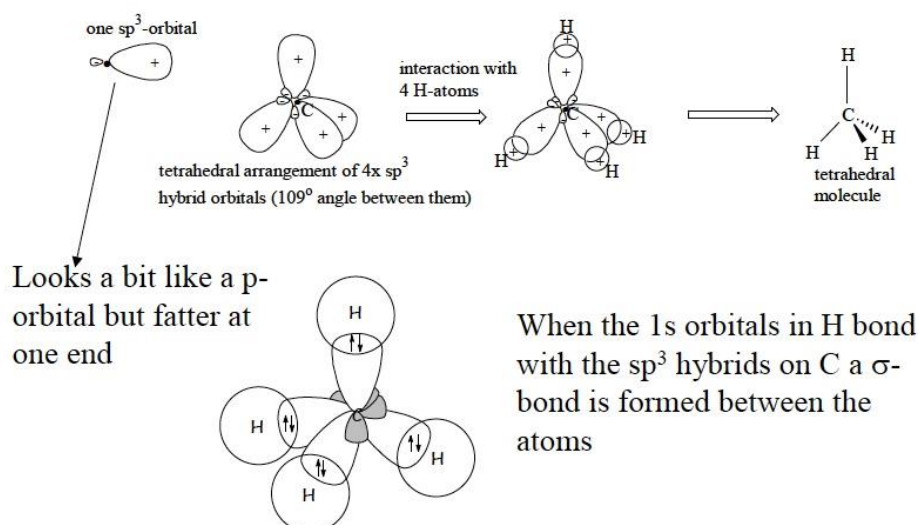
and in this configuration it has only two half-filled orbitals available for bonding.

- The answer is that it therefore merges its 2s orbital and its three 2p orbitals together (1 + 3 = 4) to form **four s¹p³ or sp³ hybridised half-filled orbitals** as follows



and now it can use one of each of these four half-filled orbitals to form four σ bonds – one σ bond with each of the four H atoms in CH₄. (Please note that in CH₄, while the C atom is using an sp³ atomic orbital to form a molecular bond with each H atom, each H atom is using a '1s' atomic orbital to form that bond with the Carbon atom's sp³ orbital.)

Hybrid orbitals: bonding in CH₄

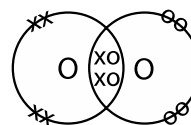
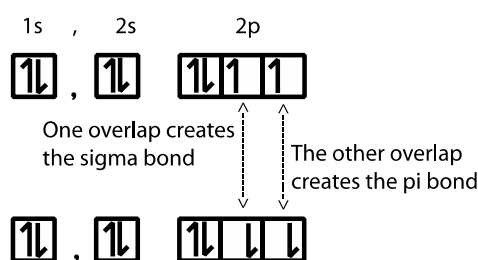


Source: Dr N Chatterton, London Metropolitan University

- OK, let us now see what we have to do to get a π bond – and the answer is that **you do NOT need to hybridise any atomic orbitals to get a π bond**. In fact, **it is essential that there should be an unhybridised ‘p’ orbital to create a π bond**. Let us look at how Oxygen solves the problem.

An O₂ Molecule

- I hope that you will remember that the electron configuration of an ${}_8\text{O}$ atom is $1s^2, 2s^2 2p^4$.
- For the two Oxygen atoms, the arrow and box-orbital representation is shown below. Each of the two half-filled orbitals in the O atoms has here been drawn slightly differently in order to show that **when the half-filled orbitals in each of the two atoms overlap, then TWO bonds are created, i.e. a double bond is created!** (NB The diagram below is not correct, but at this stage of the game I do not want to make it too complicated.) Could you please notice that in forming a molecule, the two O atoms have used their *atomic* orbitals to create *molecular* σ and π orbitals and molecular sigma and pi bonds.
- That is basically how an Oxygen molecule is formed. (NB We have not had to create any hybridised orbitals because there were already two half-empty unhybridised **atomic** orbitals which could overlap to form two **molecular** bonds. In the diagram below the **sigma** bond and the pi bond are the **molecular** orbitals. Greek words are used for the names of **molecular** orbitals, while Latin words are used to name **atomic** orbitals.)

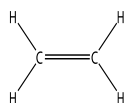


Dot-and-cross diagram showing the double bond

- OK, what about an **Ethene**, C₂H₄, molecule?
- Well that does need hybridisation (**but NOT for the π bond**). As we noted on page 4, a C atom has only two half-filled orbitals, and in C₂H₄, each C atom bonds with three other atoms and every C atom (*and indeed every Group IV atom*) has to form four bonds. So how does the C atom fulfil all those requirements?

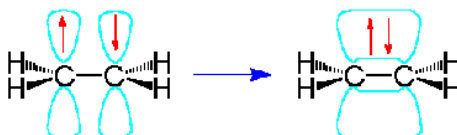
Ethene, C₂H₄

- Last year I taught you how to create Lewis and bond-line structures, so if we now do the Lewis structure for Ethene, then we will see that the total number of valence electrons for C₂H₄ is $[(2 \times 4) + (4 \times 1)] = 12$, and if we draw the following Lewis structure



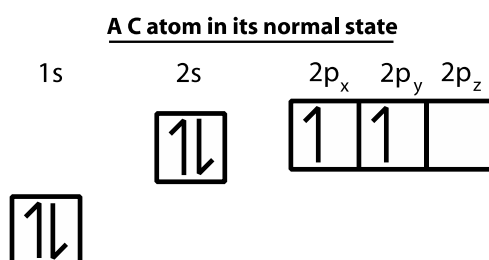
then we have used all the 12 electrons and each C atom has a full outer shell of 8 electrons and each H atom has a full outer shell of 2 electrons – therefore the structure is a *satisfactory* one.

- However, we have not solved the problem of how the C atom creates four bonds out of two half-filled orbitals.
- In Ethene, each C atom bonds with three other atoms and the hybridisation rules are that
 - there must be one half-filled orbital for each atom to which the atom is bonding (and here we are examining the C atoms), and
 - for every double bond (and we know from our Lewis structure that there is a double bond in Ethene) **an unhybridised 'p' orbital must be used to form the π bond**
 therefore we know that the C atom must create three sp^2 (s^1p^2) hybridised orbitals and leave one 'p' orbital unhybridised.
- We then get the following structure.



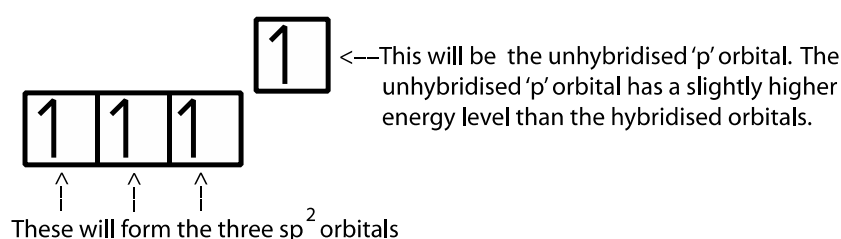
Source: Florida State University

- The molecular σ bond between a C atom and each one of its H atoms is formed by the overlap of an unhybridised 's' atomic orbital from the H atom and a hybridised atomic ' sp^2 ' orbital on the C atom. That takes care of two of the four bonds on a C atom.
- The third hybridised ' sp^2 ' atomic orbital on each C atom is used to create a molecular σ bond between the two C atoms, while the unhybridised 'p' atomic orbital on the C atom is used to create the molecular π bond. (NB Molecular orbitals are created in the formation of molecular bonds.)
- The normal way of drawing the bond-line diagram of an Ethene molecule (C_2H_4) is shown above.
- Please note that (i) in the bond line diagram of Ethene, there is a σ bond between each one of the two Carbon atoms and each of its Hydrogen atoms, and that (ii) **the double bond between the two Carbon atoms consists of both one σ bond and one π bond.**
- *I will say that again. **ALL** Group IV elements must have four bonds, therefore in an Ethene molecule, the overlap of two half-filled hybridised ' sp^2 ' orbitals (one from each of the two Carbon atoms) creates a σ bond between them, and **simultaneously** the overlap of two half-filled **unhybridised** 'p' orbitals creates a π bond— and the existence of the σ bond and the π bond constitutes the double bond between the two C atoms. **Whenever there is a DOUBLE bond, then one of the two bonds has to be a σ (sigma) bond and one of them is a π (pi) BOND!** I will say that a third time, **whenever there is a DOUBLE bond, then one of the two bonds has to be a σ (sigma) bond and one of them is a π (pi) BOND!***
- Understanding how π bonds are constructed is unbelievably important in Organic Chemistry, so let us remind ourselves of what we have already noted, namely that in the box-orbital representation of Carbon (i.e. in ${}_6C : 1s^2, 2s^2 2p^2$) there are only *TWO half-filled* '2p' orbitals viz.



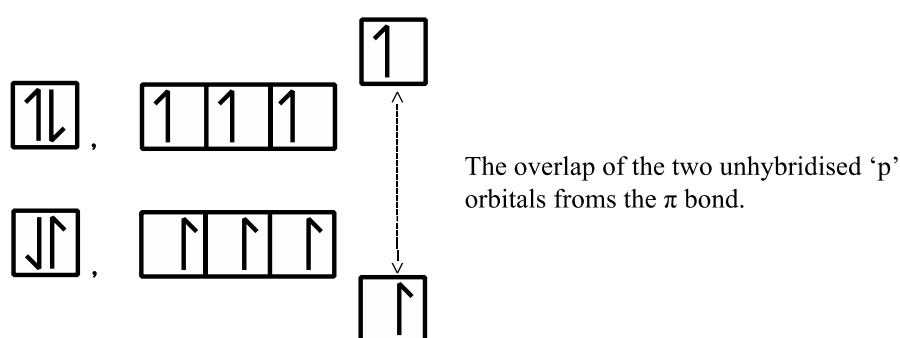
- In this state, since Carbon has only two half-filled '2p' orbitals, it should be able to form only **TWO** bonds – but in order to achieve the stability of the Noble Gas configuration, Carbon (a Group IV element) needs to form **FOUR** bonds⁴ and therefore (in forming Ethene where each C atom has **four** bonds but is connected to only **three** other atoms) Carbon promotes one of its '2s' electrons from '2s' to '2p' (as is shown below) thus creating **four** half-filled atomic orbitals. Three of the orbitals in the n=2 shell now become altered into three hybridised sp^2 orbitals and there is one unhybridised 'p' orbital *and this configuration of four half-filled orbitals now allows the C atom to form the **FOUR** bonds that it needs to form Ethene (C_2H_4)*.⁵
- The box-orbital diagram is a representation of a Carbon atom in Ethene in which one electron has been promoted from the '2s' orbital to the '2p' orbital (after which four orbitals will exist in the n=2 shell, viz. **one unhybridised 'p' orbital and three hybridised sp^2 orbitals**).

A C atom in which one 2s atom has been promoted from 2s to 2p to now form three $3sp^2$ orbitals



- I would like you to notice that (*in the formation of Ethene*), on the excited Carbon atoms there are THREE 'hybridised' sp^2 orbitals (each one of which will be used to form a σ bond) and one **unhybridised 'p' orbital** (which will be used to form a π bond) – **and it is the overlap of the two unhybridised 'p' orbitals (one on EACH of the two C atoms in Ethene) that will form the π bond!** **THAT is the message that I am trying to get across here.**

ETHENE



One of the hybridised sp^2 orbitals forms the sigma bond between the two C atoms, and the other sp^2 hybridised orbitals form the sigma bond with the H atoms.

- The above is just a vague representation of reality and is nothing more than that. It should not be taken as "gospel".

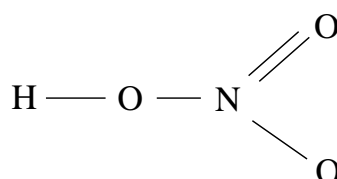
⁴ **ALL** Group IV elements must have four bonds.

⁵ When a C atom promotes a '2s' electron to '2p', the C atom then enters into an "excited" state.

- OK, what about something even more complicated like HNO_3 ? Actually, the answer is that if we stick to the procedure then we will get the answer. So let us do just that.

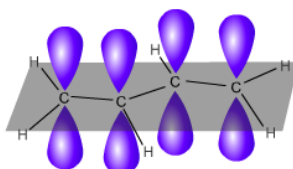
HNO_3

- For the Lewis structure for HNO_3 we need first to calculate the total number of valence electrons, therefore $[(1 \times 1) + (1 \times 5) + (3 \times 6)] = 24$, and if we put in all the single bonds then we will have used up 8 electrons and then if we complete the octets on the peripheral atoms (including the H atom) then that will use up another 16 electrons (which = 24), but the central N atom does not have an octet therefore we have to take one of the lone pairs on one of the O atoms (but not from the O atom bonded to the H atom) and put that between the O and the N atom and now we have a *satisfactory* Lewis structure.⁶



- N has three half-filled orbitals, but to create four bonds (one of them being a double bond) it creates three sp^2 (s^1p^2) hybridised orbitals and leaves one 'p' orbital unhybridised – and then uses the unhybridised 'p' orbital to form the double bond.
- **OK, there cannot be a single one of you who now does not know how a double bond is formed, and that for a double bond to be formed, an unhybridised 'p' orbital MUST be used.**
- Let me make one last point, and then I am going to move on to the Inductive and the Mesomeric effect.
- The unhybridised 'p' orbital stands at 90° to the plane of the other bits of the molecule, and it is the closeness of the two areas of the dumb-bell shapes of the 'p' orbitals in a double bond that allows them to overlap – and it is this feature that is so important in Resonance/Delocalisation/Conjugation/and Hyperconjugation.
- Let me remind you what happened in Butadiene in Chapter 1, and then I shall move on to the Inductive and Mesomeric Effects in Chapter 3.
- The four electrons in the four unhybridised 'p' orbitals in the four C atoms are shared equally by all the four C atoms. **The electrons are delocalised.** They are not held firmly between any two bonded C atoms. They 'wander' (an anthropomorphism) randomly above and below the horizontal plane that contains the four C atoms.

Delocalisation in Butadiene



⁶ You will have noticed that I have now on two occasions used the adjective “satisfactory” about my resulting Lewis structures. That is because they are “satisfactory” **but not correct** because as can be seen the resulting structure is not ‘fair’ in its treatment of the O atoms, therefore to be even-handed, nature will create a **delocalised resonance** structure for HNO_3 .