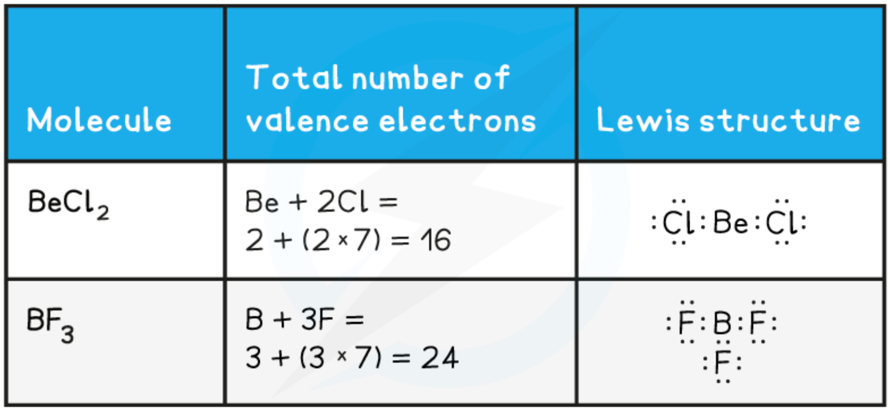
Octet Rule Exceptions

Incomplete octets

- We have seen previously that for elements below atomic number 20 the octet rule states that the atoms try to achieve 8 electrons in their valence shells, so they have the same electron configuration as a noble gas
- However, there are some elements that are exceptions to the octet rule, such a H, Li, Be, B and Al
  - H can achieve a stable arrangement by gaining an electron to become 1s2, the same structure as the noble gas helium
  - Li does the same, but losing an electron and going from $1s^22s^1$ to $1s^2$ to become a Li^+ ion
  - Be from group 2, has two valence electrons and forms stable compounds with just four electrons in the valence shell
  - B and Al in group 13 have 3 valence electrons and can form stable compounds with only 6 valence electrons

Table showing examples of incomplete octets



Molecule	Total number of valence electrons	Lewis structure
$BeCl_2$	Be + 2Cl = $2 + (2 \times 7) = 16$	:Cl:Be:Cl:
BF_3	B + 3F = $3 + (3 \times 7) = 24$	:F:B:F: :F:

Expansion of the octet

- Elements in period 3 and above have the possibility of having more than eight electrons in their valence shell
- This is because there is a d-subshell present which can accommodate additional pairs of electrons
- This is known as the expansion of the octet
- The concept explains why structures such as PCl_5 and SF_6 exist, which have 10 and 12 bonding pairs of electrons respectively, around the central atom

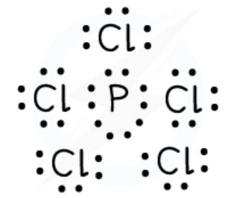
Credit: savemyexams.com

More Lewis Structures

Five electron pairs

Phosphorus pentachloride, PCl_5

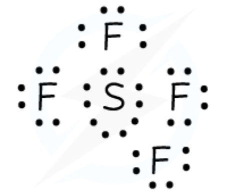
- An example of a molecule with five bonding electron pairs is phosphorus pentachloride, PCl_5
- The total number of valence electrons is = P + 5Cl = 5 + (5 x 7) = 40
- The number of bonding pairs is 5, which accounts for 10 electrons
- The remaining 30 electrons would be 15 lone pairs, so that each Cl has 3 lone pairs
- The completed Lewis diagram looks like this:



Lewis diagram for PCl_5

Sulfur tetrafluoride, SF_4

- The total number of valence electrons is = S + 4F = 6 + (4 x 7) = 34
- The number of bonding pairs is 4, which accounts for 8 electrons
- The remaining 26 electrons would be 13 lone pairs
- Fluorine cannot expand the octet so each fluorine would accommodate 3 lone pairs, accounting for 24 electrons, leaving one lone pair on the sulfur (sulfur has expanded the octet)
- The completed Lewis diagram looks like this:

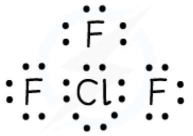


Lewis diagram for SF_4

Chlorine trifluoride, ClF_3

- The total number of valence electrons is = Cl + 3F = 7 + (3 x 7) = 28
- The number of bonding pairs is 3, which accounts for 6 electrons
- The remaining 22 electrons would be 11 lone pairs

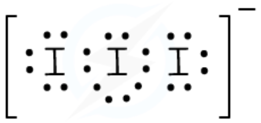
- Fluorine cannot expand the octet so each fluorine would accommodate 3 lone pairs, accounting for 18 electrons, leaving two lone pairs on the chlorine
- The completed Lewis diagram looks like this:



Lewis diagram for ClF_3

Triiodide ion, I_3^-

- The total number of valence electrons is = 3I + the negative charge = (3 x 7) + 1 = 22
- The number of bonding pairs is 2, which accounts for 4 electrons
- The remaining 18 electrons would be 9 lone pairs
- Iodine would accommodate 3 lone pairs, accounting for 12 electrons, leaving three lone pairs on the central iodine
- The completed Lewis diagram looks like this:

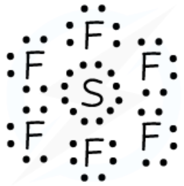


Lewis diagram for I_3^-

Six electron pairs

Sulfur hexafluoride, SF_6

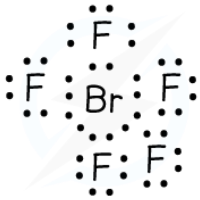
- An example of a molecule with six bonding electron pairs is sulfur hexafluoride, SF_6
- The total number of valence electrons is = S + 6F = 6 + (6 x 7) = 48
- The number of bonding pairs is 6, which accounts for 12 electrons
- The remaining 36 electrons would be 18 lone pairs, so that each F has 3 lone pairs, accounting for all electrons and no lone pairs
- The completed Lewis diagram looks like this:



Lewis diagram for SF_6

Bromine pentafluoride, BrF_5

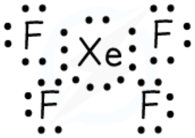
- The total number of valence electrons is = Br + 5F = 7 + (5 x 7) = 42
- The number of bonding pairs is 5, which accounts for 10 electrons
- The remaining 32 electrons would be 16 lone pairs
- Fluorine cannot expand the octet so each fluorine would accommodate 3 lone pairs, accounting for 30 electrons, leaving one lone pairs on the bromine
- The completed Lewis diagram looks like this:



Lewis diagram for BrF_5

Xenon tetrafluoride, XeF_4

- The total number of valence electrons is = Xe + 4F = 8 + (4 x 7) = 36
- The number of bonding pairs is 4, which accounts for 8 electrons
- The remaining 28 electrons would be 14 lone pairs
- Each fluorine would accommodate 3 lone pairs, accounting for 24 electrons, leaving two lone pairs on the xenon
- The completed Lewis diagram looks like this:



Lewis diagram for XeF_4

Further VSEPR Theory

Revisiting Valence Shell Electron Pair Repulsion Theory (VSEPR)

- When an atom forms a covalent bond with another atom, the electrons in the different bonds and the non-bonding electrons in the outer shell all behave as negatively charged clouds and repel each other
- In order to minimise this repulsion, all the outer shell electrons spread out as far apart in space as possible
- Molecular shapes and the angles between bonds can be predicted by the valence shell electron pair repulsion theory known by the abbreviation VSEPR theory
- VSEPR theory consists of three basic rules:

1. All electron pairs and all lone pairs arrange themselves as far apart in space as is possible.
2. Lone pairs repel more strongly than bonding pairs
3. Multiple bonds behave like single bonds

- These three rules can be used to predict the shape of any covalent molecule or ion, and the angles between the bonds
- The regions of negative cloud charge are known as domains and can have one, two or three pairs electrons

Molecular geometry versus domain geometry

- It is important to distinguish between molecular geometry and domain geometry in exam questions
  - Molecular geometry refers to the shape of the molecules based on the relative orientation of the atoms
  - Domain geometry refers to the relative orientation of all the bonding and lone pairs of electrons
- The Lewis structure for water enables us to see that there are four electron pairs around the oxygen so the domain geometry is tetrahedral
- However, the molecular geometry shows us there are two angled bonds so the shape is bent, angular, bent linear or V-shaped (when viewed upside down)

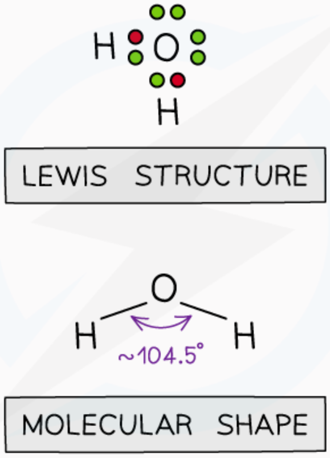
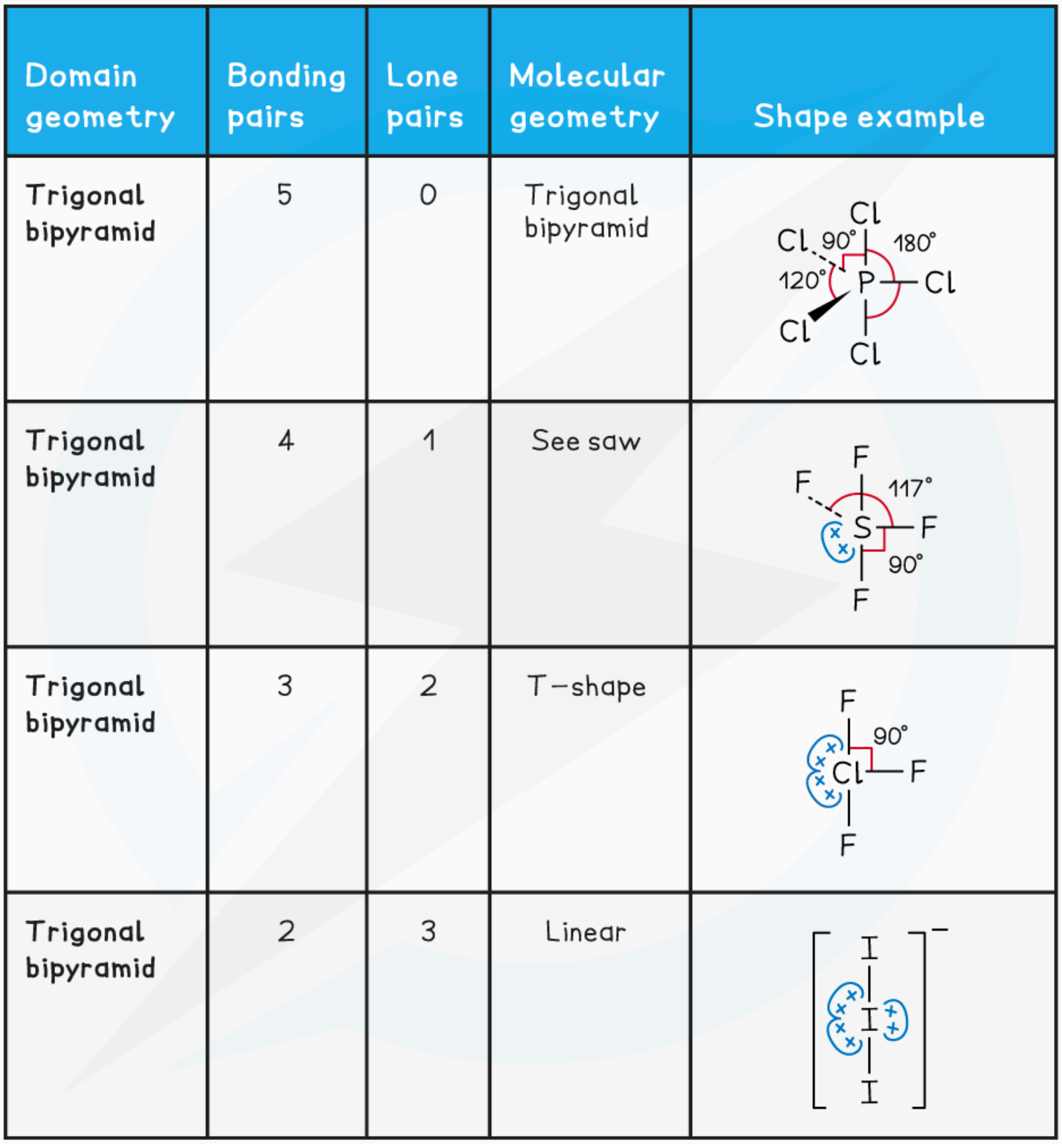


Diagram showing the Lewis structure of water and molecular shape from which the domain and molecular geometries may be determined

Five electron domains

Table showing the four molecular geometries associated with five electron domains



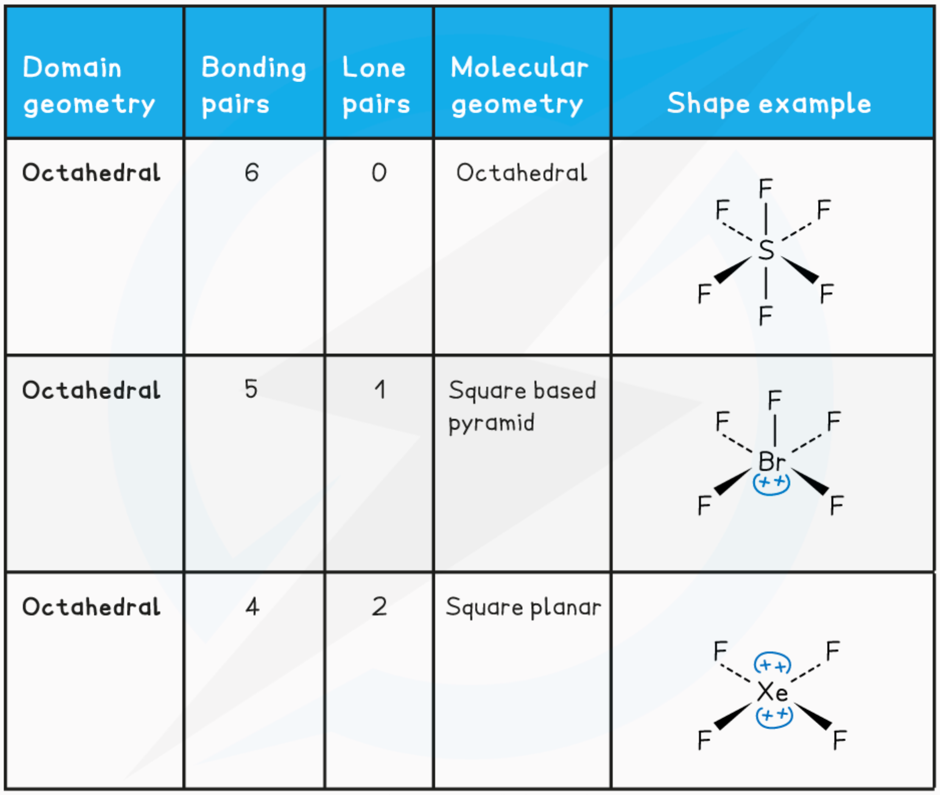
Domain geometry	Bonding pairs	Lone pairs	Molecular geometry	Shape example
Trigonal bipyramid	5	0	Trigonal bipyramid	
Trigonal bipyramid	4	1	See saw	
Trigonal bipyramid	3	2	T-shape	
Trigonal bipyramid	2	3	Linear	

*Trigonal or triangular may be used

- Notice that PCl_5 is a symmetrical molecule so the electron cloud charge is evenly spread
- This means that it will be a non-polar molecule as any dipoles from the P-Cl bonds would be cancelled out
- SF_4, ClF_3 are asymmetrical molecules having one or two lone pairs on one side of the central axis making the overall molecule polar

Six electron domains

Table showing the three molecular geometries associated with six electron domains



Domain geometry	Bonding pairs	Lone pairs	Molecular geometry	Shape example
Octahedral	6	0	Octahedral	SF_6
Octahedral	5	1	Square based pyramid	BrF_5
Octahedral	4	2	Square planar	XeF_4

- SF_6 is a symmetrical molecule so the electron cloud charge is evenly spread with 90_o between the bonds
- This means that it will be a non-polar molecule as any dipoles from the S-F bonds would be cancelled out
- XeF_4 is also non-polar despite having two lone pairs.
  - The bonding pairs are at 90_o to the plane and the lone pairs are at 180_o
  - The lone pairs are arranged above and below the square plane resulting in an even distribution of electron cloud charge
- BrF_5 is asymmetrical having a lone pair at the base of the pyramid making the overall molecule polar

Worked example

What is the domain geometry, molecular geometry and F-Xe-F bond angle of xenon difluoride, XeF_2?

Answer

- Count the valence electrons = Xe + 2F = 8 + (2 x 7) = 22
- There are two bonding pairs, accounting for 4 electrons, so 18 electrons remain

  - Each fluorine should have 3 lone pairs, accounting for 6 pairs or 12 electrons, which leaves 3 lone pairs on the xenon
  - Xenon therefore has 2 bonding pairs and 3 lone pairs making its domain geometry trigonal bipyramid and its molecular geometry linear
  - The bond angle will be 180° (having the same structure as the triiodide ion)

Resonance Structures

- The delocalization of electrons can explain the structures of some species that don't seem to fit with a Lewis structure
- Delocalized electrons are electrons in a molecule, ion or solid metal that are not associated with a single atom or one covalent bond
- The Lewis diagram for the nitrate (V) ion gives a molecule with a double and two single bonds
- There are three possible Lewis Structures
- These structures are called resonance structures
- However, studies of the electron density and bond length in the nitrate (V) ion indicate all the bonds are equal in length and the electron density is spread evenly between the three oxygen atoms
  - The bond length is intermediate between a single and a double bond
  - The actual structure is something in between the resonance structures and is known as a resonance hybrid

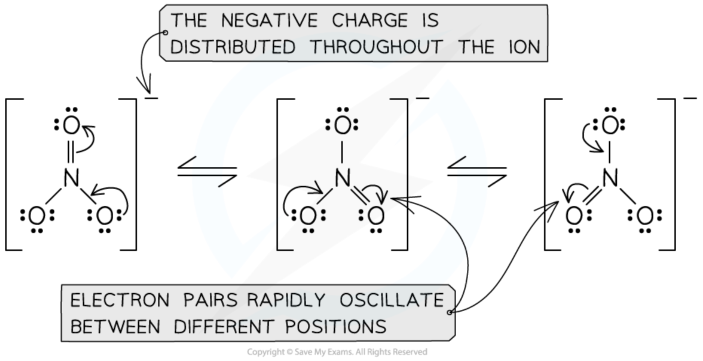
Resonance structures of the nitrate (V) ion

- To determine the Lewis structure of the nitrate (V) ion first count the number of valence electrons and then add one electron for the negative charge on the ion

Number of valence electrons = N + 3O +1

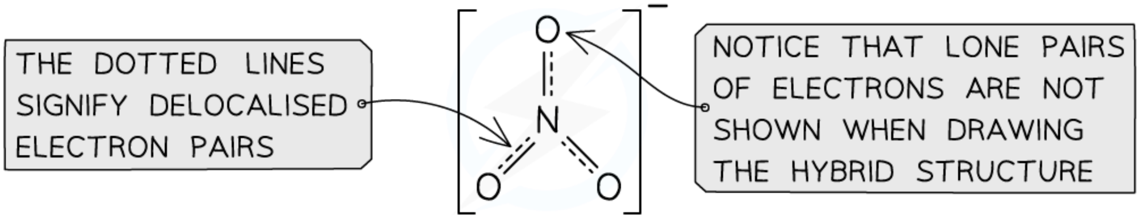
= 5 + (3 x 6) + 1 = 24 electrons

- Three structures are possible, consisting of a double bond and two singles:



Resonance structures in the nitrate ion

- Dotted lines are used to show the position of the delocalised electrons



THE DOTTED LINES SIGNIFY DELOCALISED ELECTRON PAIRS

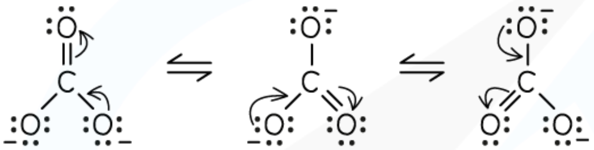
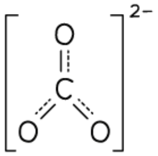
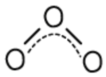
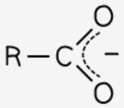
NOTICE THAT LONE PAIRS OF ELECTRONS ARE NOT SHOWN WHEN DRAWING THE HYBRID STRUCTURE

Resonance hybrid nitrate (V) ion

- The criteria for forming resonance hybrids structures is that molecules must have a double bond (pi bond) that is capable of migrating from one part of a molecule to another
- This usually arises when there are adjacent atoms with equal electronegativity and lone pairs of electrons that can re-arrange themselves and allow the double bonds to be in different positions
- Other examples that you should know about are the carbonate ion, benzene, ozone and the carboxylate anion

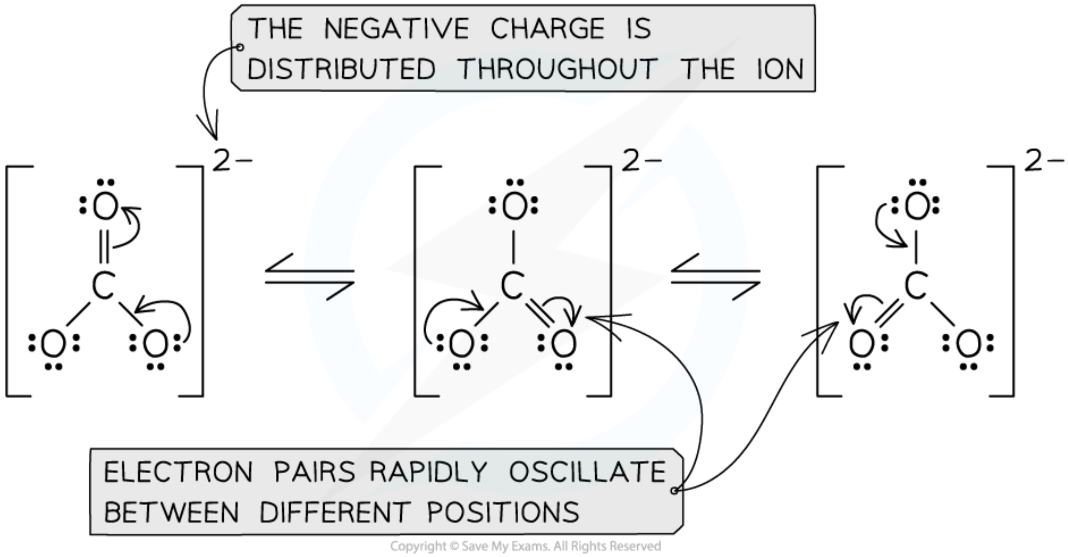
Resonance Hybrids Table

- Below are some other resonance structures and hybrids that you should know:

Species	Lewis resonance structures	Resonance hybrid
Carbonate ion, CO_3^{2-}		
Benzene, C_6H_6		
Ozone, O_3		
Carboxylate ion, $RCOO^-$		

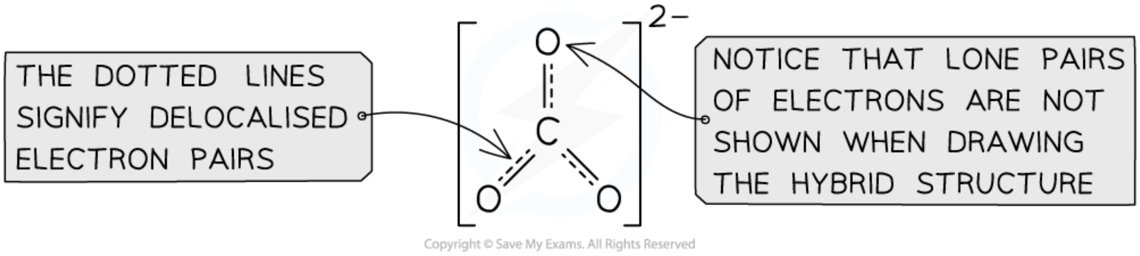
Delocalisation & Resonance

- The delocalisation of electrons can explain the structures of some species that don't seem to fit with a Lewis structure
- Delocalised electrons are electrons in a molecule, ion or solid metal that are not associated with a single atom or one covalent bond
- The Lewis diagram for the carbonate ion gives a molecule with a double and two single bonds
- There are three possible Lewis structures



The three resonance structures for the carbonate ion

- These structures are called resonance structures
- However, studies of the electron density and bond length in the carbonate ion indicate all the bonds are equal in length and the electron density is spread evenly between the three oxygen atoms
    - The bond length is intermediate between a single and a double bond
    - The actual structure is something in between the resonance structures and is known as a resonance hybrid



Resonance hybrid for the carbonate ion

- Dotted lines are used to show the position of the delocalised electrons

- The criteria for forming resonance hybrids structures is that molecules must have a double bond (pi bond) that is capable of migrating from one part of a molecule to another
- This usually arises when there are adjacent atoms with equal electronegativity and lone pairs of electrons that can re-arrange themselves and allow the double bonds to be in different positions

Conjugation & Bond Order

- Structures which have alternative single and double bonds are known as conjugated systems
- Electrons migrate between p-orbitals via adjacent sigma bonds
- The result is a sort of fractional bond, neither a single nor a double, so to accommodate this situation chemists use the concept of bond order:

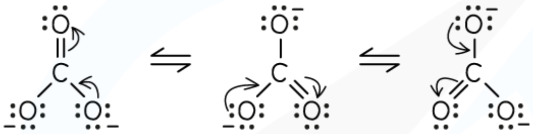
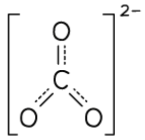
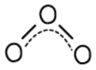
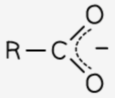
bond order = total number of bonding pairs ÷ total number of positions

- For example, in the case of the carbonate ion:

bond order in CO_3^{2-} = total number of CO_3^{2-} bonding pairs ÷ total number of positions = 4 ÷ 3 = 1.33

- Evidence for bond orders comes from measurements of bond lengths
    - A single C-O bond is 143 pm and a double C=O is 122 pm
    - The C-O bonds in the carbonate ion are all identical and 129 pm in length which is part way between a single and double
- Other examples that you should know about are benzene, ozone and the carboxylate anion

Resonance hybrids table

Species	Lewis resonance structures	Resonance hybrid
Carbonate ion, CO_3^{2-}		
Benzene, C_6H_6		
Ozone, O_3		
Carboxylate ion, $RCOO^-$		

Formal Charge

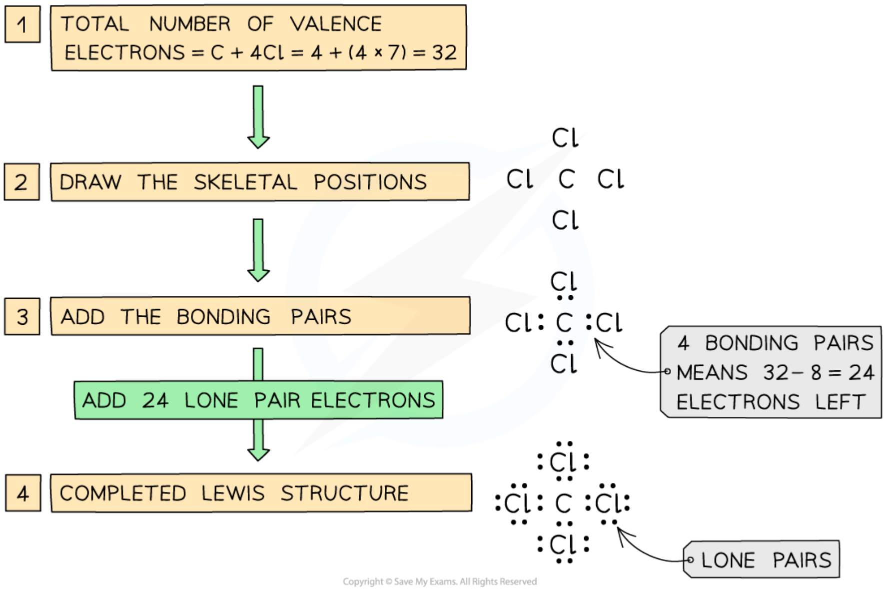
- A limitation of the model of covalent bonding is that when drawing Lewis structures for molecules, it is sometimes possible to come up with more than one structure while still obeying the octet rule
- This leads to the problem of deciding which structure is appropriate and is consistent with other information such as spectroscopic data on bond lengths and electron density
- One approach to determining which is the preferred structure is to determine the formal charge (FC) of all the atoms present in the molecule
- It is a kind of electronic book keeping involving the bonding, non-bonding and valence electrons
- Formal charge is described as the charge assigned to an atom in a molecule, assuming that all the electrons in the bonds are shared equally between atoms, regardless of differences in electronegativity
- The formula for calculating FC is

$$\text{FC} = (\text{number of valence electrons}) - [\tfrac{1}{2}(\text{number of bonding electrons}) - (\text{number of non-bonding electrons})]$$

or

$$\text{FC} = \text{V} - (\tfrac{1}{2}\text{B} - \text{N})$$

- The Lewis structure which is preferred is the one which:
  - the difference in FC of the atoms is closest to zero
  - has negative charges located on the most electronegative atoms
- The process of drawing a Lewis structure has been covered previously, but here is a reminder of how to draw the Lewis structure of tetrachloromethane, CCl_4,



Steps in drawing the Lewis structure for CCl_4

- To work our the formal charge of the C and Cl atoms in the structure simply apply the FC formula:

FC for carbon = (4) - ½(8) - 0 = 0

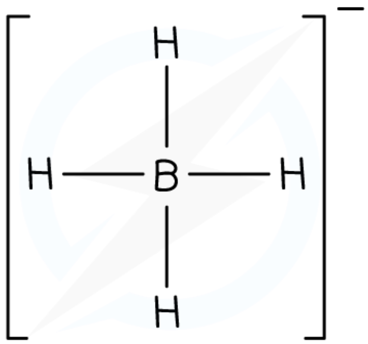
FC for chlorine = (7) - ½(2) - 6 = 0

- Notice that formal charge is calculated for one of each type of atom and does not count the total number of atoms in the molecule

Worked example

What is the formal charge on boron in the BH_4^- ion?
Answer

  - Boron is a group 13 element, so has 3 valence electrons. Hydrogen has one valence electron and the charge on the ion is -1, so there are 8 electrons in the diagram. The Lewis structure is therefore:



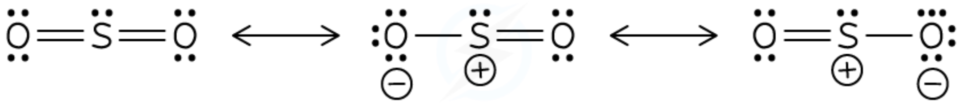
Lewis structure of BH_4^-

  - The number of bonded electrons is 8 and the number of non-bonded electrons is zero. So the formal charge on B is:

FC (B) = (3) - ½(8) - 0 = -1

Applying Formal Charge

- It is possible to draw three resonance structures for sulfur dioxide, SO_2:



The three resonance structures of sulfur dioxide

- The first structure is an illustration of the expansion of the octet as the sulfur has 10 electrons around it
- Formal charge can be used to decide which of the Lewis structures is preferred
- The FC on the first structure is as follows:

FC on sulfur = (6) - ½(8) -(2) = 0

FC on oxygen = (6) - ½(4) -(4) = 0

Difference in FC = ΔFC = FC_{max}- FC_{min} = 0

- The FC on the second (and third) structures is as follows:

FC on sulfur = (6) - ½(6) -(2) = +1

FC on left side oxygen = (6) - ½(2) -(6) = -1

FC on right side oxygen = (6) - ½(4) -(4) = 0

Difference in FC = ΔFC = FC_{max}- FC_{min} = 2

Worked example

What is the formal charge on the two resonance structures shown?

Resonance structures of carbon dioxide

Deduce which is the preferred structure.

Answer

Structure I

FC on carbon = (4) - ½(8) -(0) = 0

FC on oxygen = (6) - ½(4) -(4) = 0

Difference in FC = ΔFC = FC_{max}- FC_{min} = 0

Structure II

FC on carbon = (4) - ½(8) -(0) = 0

FC on left oxygen = (6) - ½(6) -(2) = +1

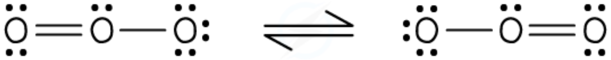
FC on right oxygen = (6) - ½(2) -(6) = -1

Difference in FC = ΔFC = $FC_{max} - FC_{min}$ = 2

Structure I is the preferred structure as the difference is zero

Ozone Revisited

- We have seen previously that ozone is a molecule with two resonance structures leading to a resonance hybrid



The two Lewis resonance structures for ozone

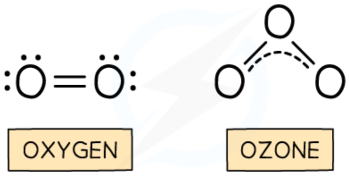
- The central oxygen atom has three electron domains and a lone pair, so the domain geometry is triangular planar and the molecular geometry is bent linear
- The presence of the lone pair repels the bonding pairs more strongly so the bond angle is reduced to 117°

The molecular structure of ozone

- The bond order for each bond in ozone is

bond order in O_3 = total number of O_3 bonding pairs ÷ total number of positions = 3 ÷ 2 = 1.5

- This gives a polar molecule with bonds that are weaker than the double bond in oxygen molecules



The structure of oxygen and ozone

- You would expect O-O bonds to be non-polar as the atoms have the same electronegativity; this is correct, but overall the molecule is polar due to the uneven distribution of electron cloud charge
- The formal charge on the Lewis structures show that the electrons are unevenly distributed

FC= (number of valence electrons) – [½(number of bonding electrons) – (number of non-bonding electrons)]

FC (oxygen A) = (6) - ½(2) - (6) = -1

FC (oxygen B) = (6) - ½(6) - (2) = +1

FC (oxygen C) = (6) - ½(4) - (4) = 0

Formal charges on the oxygens in ozone

Catalytic Depletion

- The bonding and structure of ozone is key to understanding how the catalytic depletion of ozone occurs in the stratosphere
- High energy UV radiation in the stratosphere breaks the oxygen-oxygen double bond creating oxygen atoms

$$O_2\ (g) \rightarrow O\cdot\ (g) + O\cdot\ (g)\quad \Delta H\ \text{+ve, UV light, } \lambda < 242\ \text{nm}$$

- These oxygen atoms have unpaired electrons - they are known as free radicals
- The free radicals are highly reactive and quickly attack oxygen molecules forming ozone in an exothermic reaction, which raises the temperature of the stratosphere

OZONE FORMATION $O\cdot\ (g) + O_2\ (g) \rightarrow O_3\ (g) \qquad \Delta H < 0$

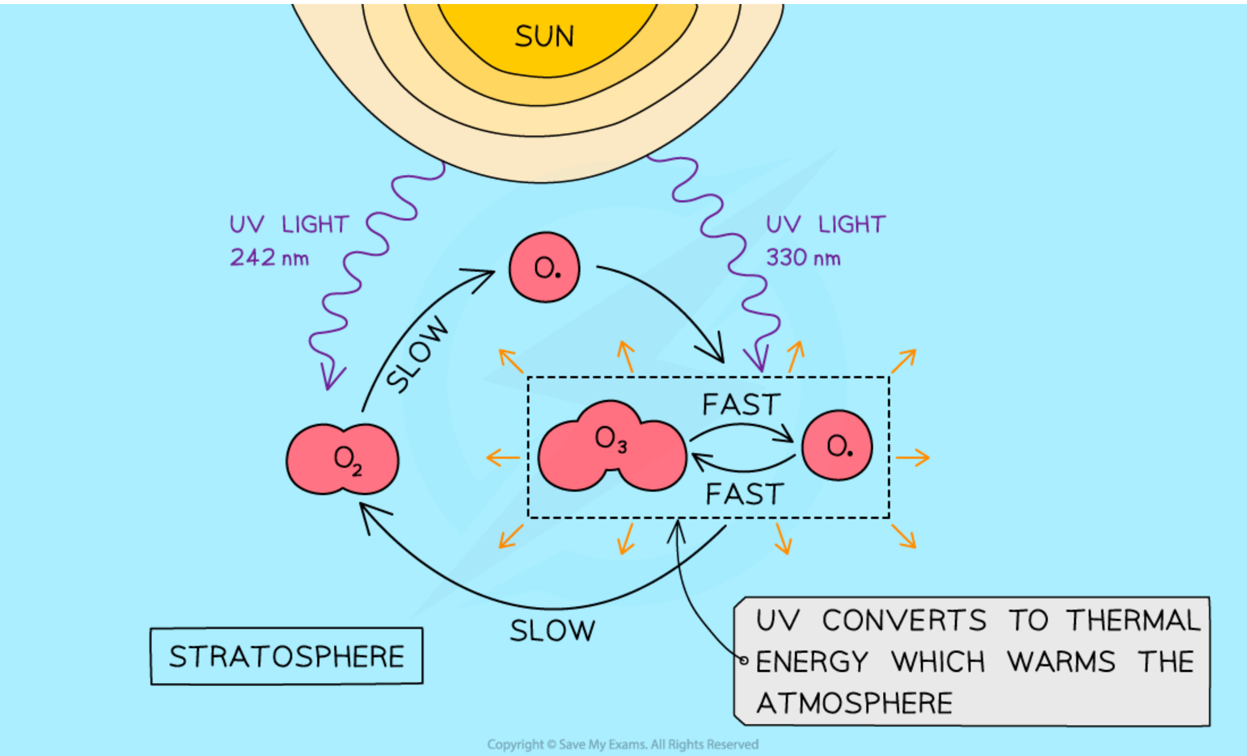
- Ozone requires less energy to break than oxygen
    - It produces an oxygen molecule and an oxygen free radical:

OZONE DEPLETION $O_3\ (g) \rightarrow O\cdot\ (g) + O_2\ (g)\ \Delta H$ +ve, UV light, $\lambda < 330$ nm

- The radical reacts with another ozone molecule making two molecules of oxygen in an exothermic reaction

OZONE DEPLETION O_3 (g) + O· (g) → $2O_2$ (g) $\Delta H < 0$

- The temperature in the stratosphere is maintained by the balance of ozone formation and ozone depletion in a process known as the Chapman Cycle
- It is not a closed system as matter and energy flow in and out, but it is what is called a steady state



The Chapman cycle

Catalytic Depletion

- The two main man made culprits that accelerate the depletion of ozone are nitrogen oxides and CFCs
- Nitrogen monoxide, NO, is produced from the high temperatures inside internal combustion engines
- If you count the valence electrons in nitrogen monoxide (5 + 6 =11), the odd number tells you it is a free radical as it has an unpaired electron
- The nitrogen monoxide reacts with ozone forming oxygen and a nitrogen dioxide radical

$$NO\cdot\ (g) + O_3\ (g) \rightarrow NO_2\cdot\ (g) + O_2\ (g)$$

- The nitrogen dioxide produced is also a free radical (it has 5 + 6 + 6= 17 electrons) and you can show the second step where it reacts with another molecule of ozone, producing oxygen and regenerating the NO· radical:

$$NO_2\cdot(g) + O_3(g) \rightarrow NO\cdot(g) + 2O_2(g)$$

- An alternative to the second step shows the $NO_2\cdot$ reacting with an oxygen radical to produce the same products but in a different stoichiometry

$$NO_2\cdot(g) + O\cdot(g) \rightarrow NO\cdot(g) + O_2(g)$$

- The nitrogen monoxide is regenerated so it has a catalytic role in the process
- Combining the two equations and cancelling out the $NO\cdot$ and $NO_2\cdot$ and you arrive at the overall depletion of ozone

$$O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$$

- A similar process happens with CFCs
- The C-Cl bond in the CFCs is weaker than the C-F bond and breaks more easily in the presence of UV light creating chlorine radicals

$$CCl_2F_2(g) + UV \rightarrow CClF_2\cdot(g) + Cl\cdot(g)$$

- The chlorine radicals attack ozone and are regenerated at the end of the cycle

$$Cl\cdot(g) + O_3(g) \rightarrow ClO\cdot(g) + O_2(g)$$

$$ClO\cdot(g) + O\cdot(g) \rightarrow Cl\cdot(g) + O_2(g)$$

- Once again a molecule of ozone has been destroyed by a catalytic free radical
- The net effect of these reactions is that these pollutants have created an imbalance in the natural ozone cycle leading to an overall depletion in stratospheric ozone
- CFCs are greatly damaging to stratospheric ozone and have been largely replaced by safer alternatives following the 1985 Montreal Protocol
- The depletion of ozone has allowed greater amounts of harmful UV light to reach the surface of the Earth
- UV light has been linked to greater incidence of skin cancer and cataracts as well as the destruction of phytoplankton and reduced plant growth

Exam Tip

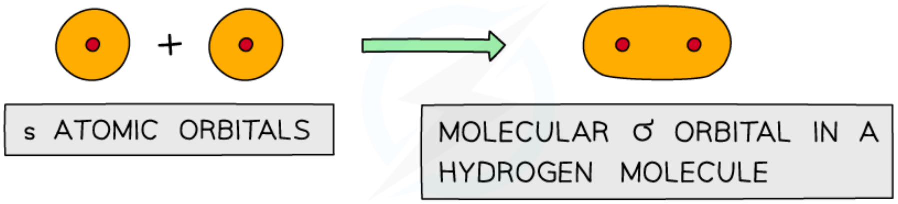
There are different conventions about showing radicals. Sometimes the dot is shown above the symbol of the element, sometimes to the left of the species and sometimes to the right.

In this course, radical dots are often ignored in exam mark schemes about ozone depletion, so you wouldn't be penalised if you omitted them or put them in different places. However, where the symbol for a radical is specified in the syllabus is in the halogenation of alkanes so you should include them there. The syllabus just states that radicals must be represented by a single dot.

Sigma Bonds

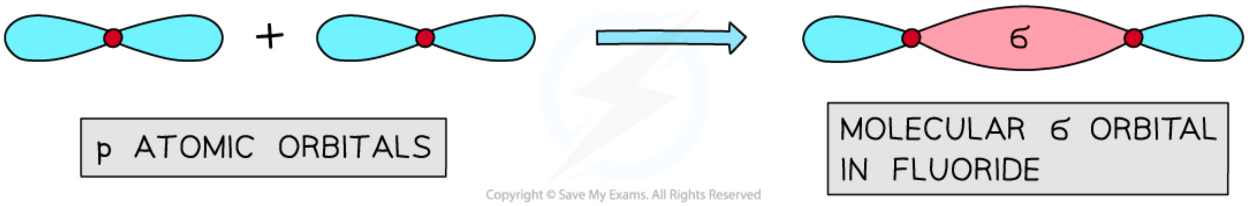
Bond overlap in covalent bonds

- A single covalent bond is formed when two nonmetals combine
- Each atom that combines has an atomic orbital containing a single unpaired electron
- When a covalent bond is formed, the atomic orbitals overlap to form a combined orbital containing two electrons
    - This new orbital is called the molecular orbital
- The greater the atomic orbital overlap, the stronger the bond
- Sigma (σ) bonds are formed from the head-on/ end-to-end overlap of atomic orbitals
- The electron density is concentrated between the two nuclei
- S orbitals overlap this way as well as p to p, and s with p orbitals



Sigma orbitals can be formed from the end-on overlap of s orbitals

Hydrogen fluoride has sigma bonds between s and p orbitals



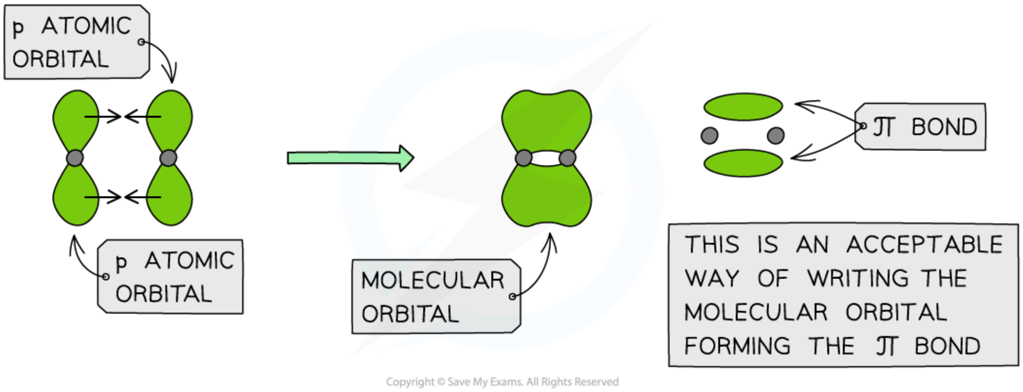
Fluorine has sigma bonds between p orbitals

- The electron density in a σ bond is symmetrical about a line joining the nuclei of the atoms forming the bond
- The pair of electrons is found between the nuclei of the two atoms
- The electrostatic attraction between the electrons and nuclei bonds the atoms to each other

Pi Bonds

π bonds

- Pi (π) bonds are formed from the sideways overlap of adjacent p orbitals
- The two lobes that make up the π bond lie above and below the plane of the σ bond
- This maximises overlap of the p orbitals
- A single π bond is drawn as two electron clouds one arising from each lobe of the p orbitals
- The two clouds of electrons in a π bond represent one bond containing two electrons

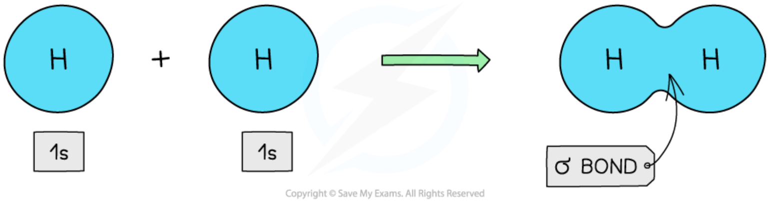


π orbitals are formed by the end-on overlap of p orbitals

Examples of sigma & pi bonds

Hydrogen

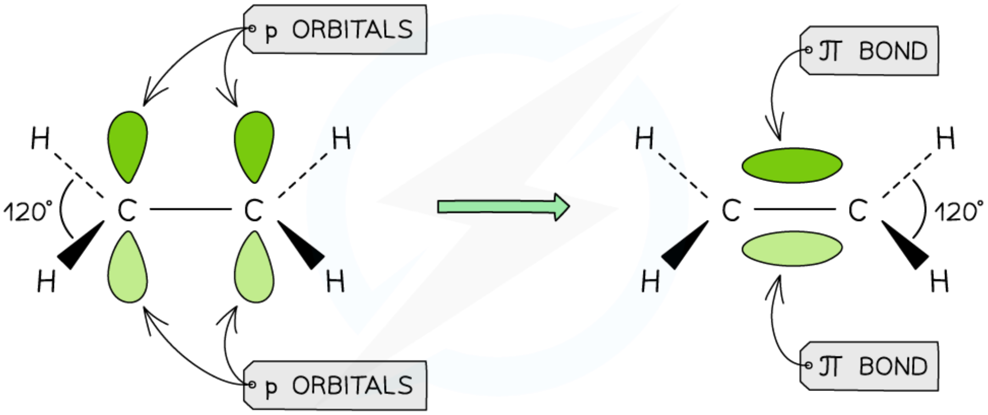
- The hydrogen atom has only one s orbital
- The s orbitals of the two hydrogen atoms will overlap to form a σ bond



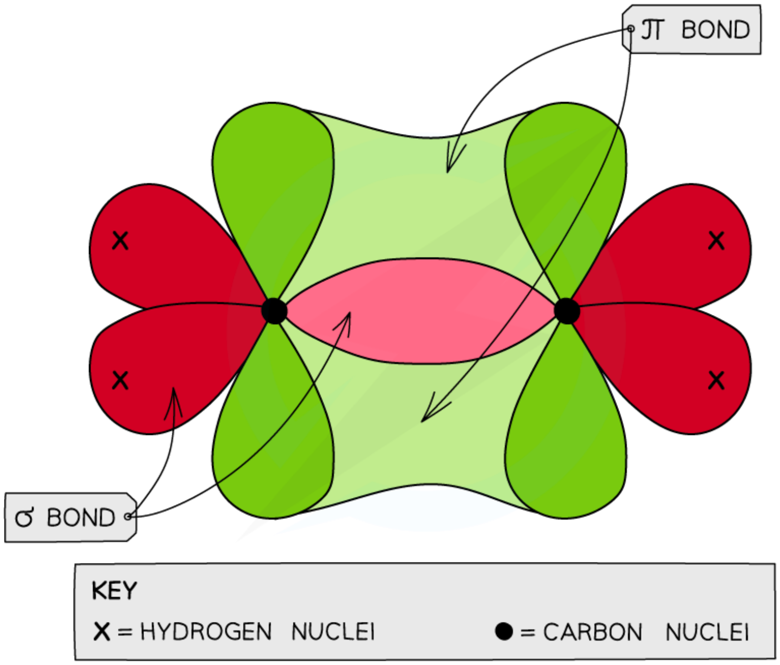
Direct overlap of the 1s orbitals of the hydrogen atoms results in the formation of a σ bond

Ethene

- Each carbon atom uses three of its four electrons to form σ bonds
- Two σ bonds are formed with the hydrogen atoms
- One σ bond is formed with the other carbon atom
- The fourth electron from each carbon atom occupies a p orbital which overlaps sideways with another p orbital on the other carbon atom to form a π bond
- This means that the C-C is a double bond: one σ and one π bond



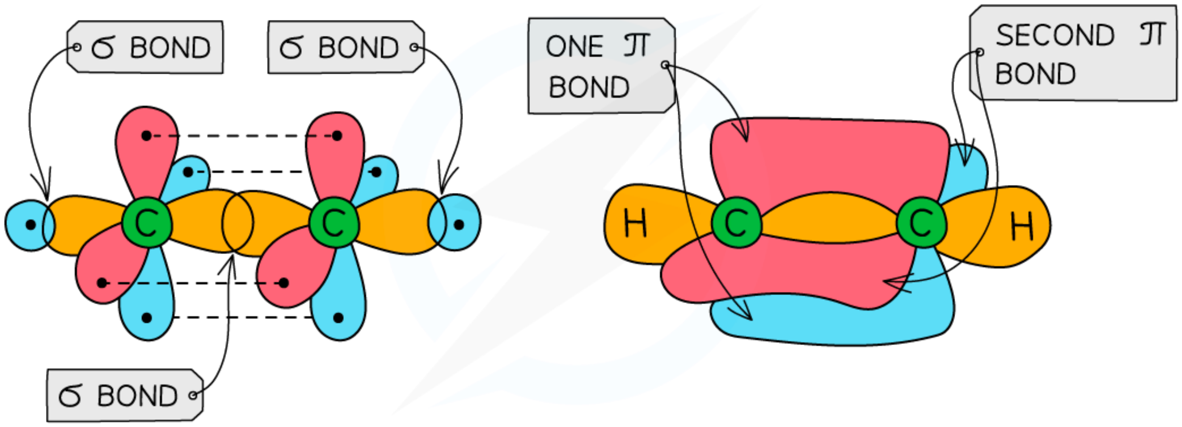
Overlap of the p orbitals results in the forming of a π bond in ethene



Each carbon atom in ethene forms two sigma bonds with hydrogen atoms and one σ bond with another carbon atom. The fourth electron is used to form a π bond between the two carbon atoms

Ethyne

- This molecule contains a triple bond formed from two π bonds (at right angles to each other) and one σ bond
- Each carbon atom uses two of its four electrons to form σ bonds
- One σ bond is formed with the hydrogen atom
- One σ bond is formed with the other carbon atom
- Two electrons are used to form two π bonds with the other carbon atom



Ethyne has a triple bond formed from two π bonds and one σ bond between the two carbon atoms

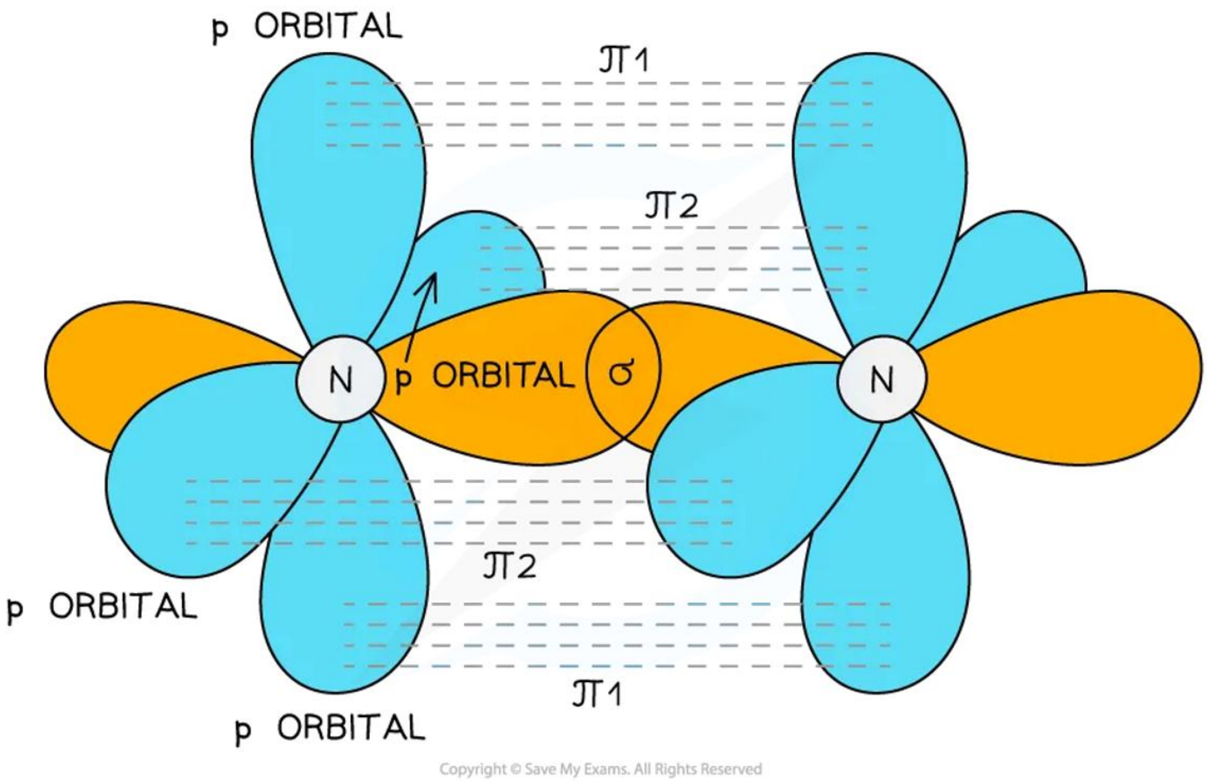
Predicting the Type of Bonds

- Whether sigma (σ) or pi (π) bonds are formed can be predicted by consideration of the combination of atomic orbitals

Worked example

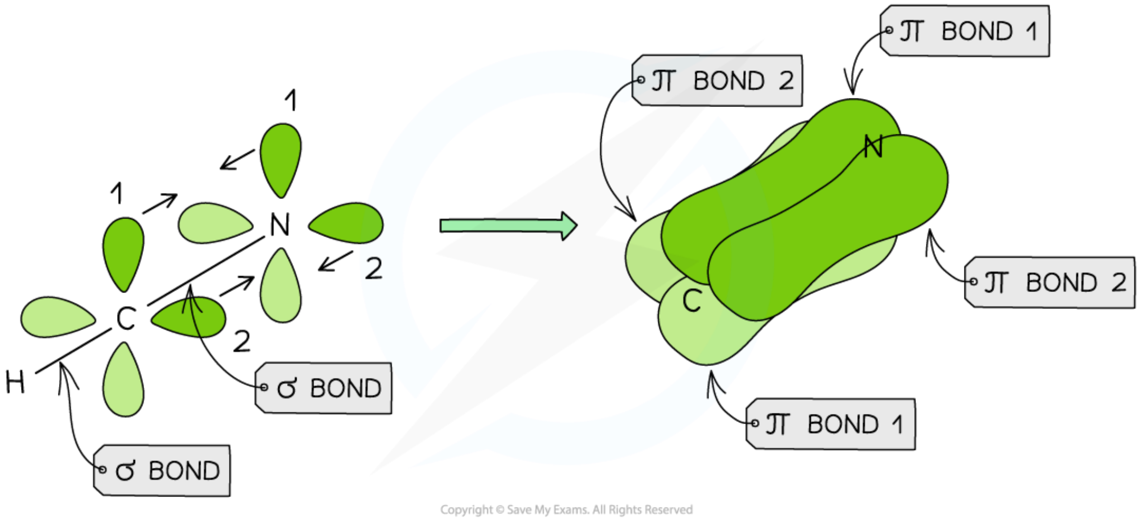
What type of molecular orbitals are found in nitrogen, N_2, and hydrogen cyanide, HCN?
Answer

- ○ Nitrogen contains a triple bond and a lone pair on each nitrogen atom
- ○ Nitrogen atoms have the electronic configuration $1s^22s^22p^3$
- ○ The triple bond is formed from a σ bond and the overlap of two sets of p orbitals on the nitrogen atoms to form two π bonds
- ○ These π bonds are at right angles to each other



The triple bond is formed from two π bonds and one σ bond

- ○ Hydrogen cyanide contains a triple bond
- ○ One σ bond is formed between the H and C atom
- ○ A second σ bond is formed between the C and N atom
- ○ The remaining two sets of p orbitals of nitrogen and carbon will overlap to form two π bonds at right angles to each other

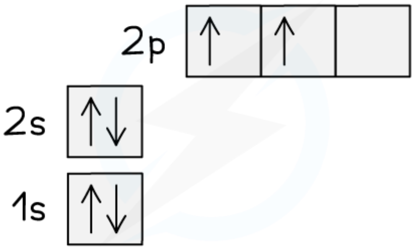


Hydrogen cyanide has a triple bond formed from a σ bond and the overlap of two sets of p orbitals of nitrogen

Hybrid Orbitals

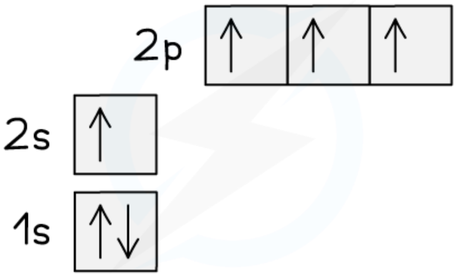
Hybridisation

- The ground state of the electrons in a carbon atom is $1s^2 2s^2 2p^2$
- This can be represented using a spin diagram as shown:



Orbital spin diagram for carbon in the ground state

- This electronic structure would imply that carbon forms two covalent bonds using the unpaired 2p electrons
- Since the 2s electrons are paired there would be no reason for them to be involved in bonding
- However studies of carbon compounds show that carbon typically forms four covalent bonds that are all equal in energy
- This puzzle has been explained using the theory of bond hybridisation
- A half full p-subshell has a slightly lower energy than a partially filled one. The difference in energy between the 2s and 2p subshells is small, so an electron can fairly easily be promoted from the 2s to the 2p giving the new arrangement:

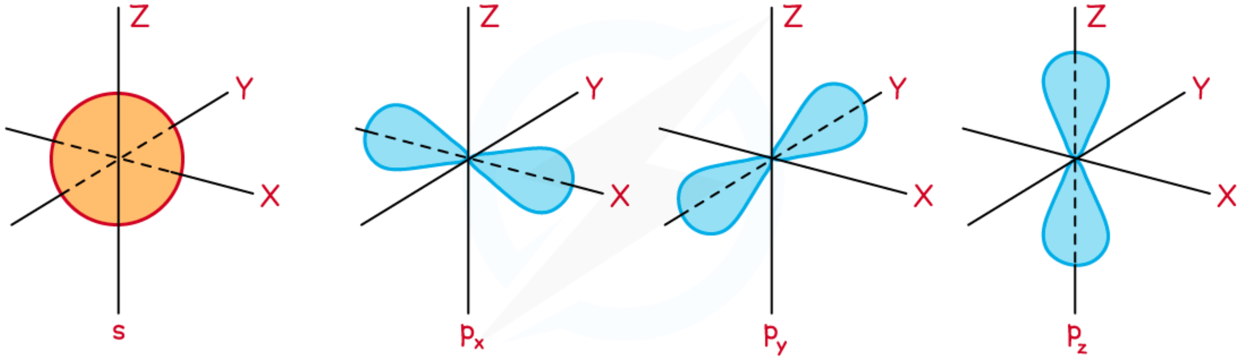


Orbital spin diagram for carbon in the excited state

- The 2s and 2p subshells blend together and form four new hybrid orbitals (called sp^3 orbitals, after the merger of an s and 3 p orbitals)
- This would give four unpaired electrons of equal energy, capable of forming four covalent bonds.

Orbital spin diagram for carbon showing sp3 hybrid orbitals

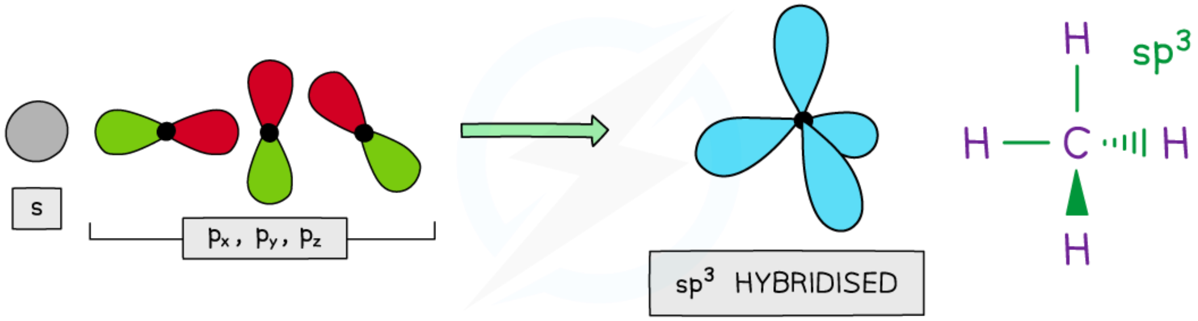
- The theory of Quantum mechanics shows that the shape of a 1s orbital is spherical and a p orbital is dumbbell or figure-of-eight shaped
- There are three p orbitals all at right angles to each other, known as p_x, p_y and p_z



The shape of s and p orbitals

sp3 hybridisation

- Four hybrid orbitals are produced when the 2s and three 2p orbitals blend together
- These hybrids have ¼ s character and ¾ p character so they have a club shape reminiscent of an enlarged p orbital
- The four sp3 hybrid orbitals space themselves out at 109.5° forming a tetrahedron
- This is the resolution of the structure seen when carbon forms single bonds, such as would be found in methane

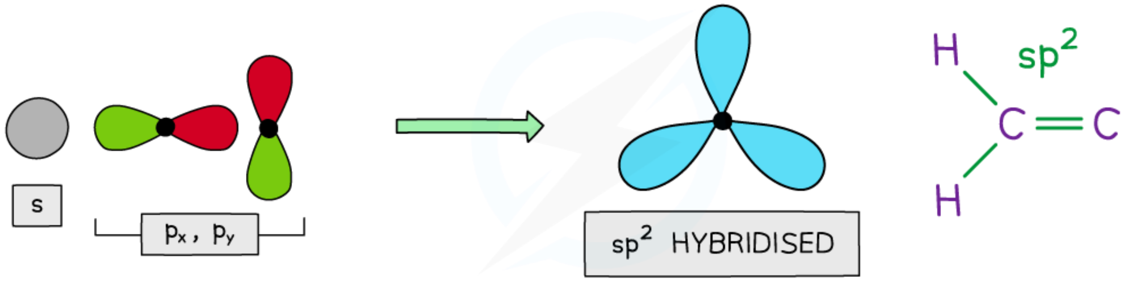


4 x sp^3 hybrid orbitals

- The sp^3 orbitals merge with the s orbitals in hydrogen forming four equal sigma bonds
- It is not just bonding pairs of electrons that are accommodated in hybrid orbitals - lone pairs can also be present
- The domain geometry of ammonia is tetrahedral due to sp^3 hybrid orbitals where three bonding pairs and one lone pair are found

sp^2 hybridisation

- Three hybrid orbitals are produced when the 2s and two 2p orbitals blend together
- These hybrids have ⅓ s character and ⅔ p character
- The three sp^2 hybrid orbitals space themselves out at 120° forming a trigonal planar geometry
- This is the resolution of the structure seen when carbon forms two single bonds and a double bond with itself in alkenes

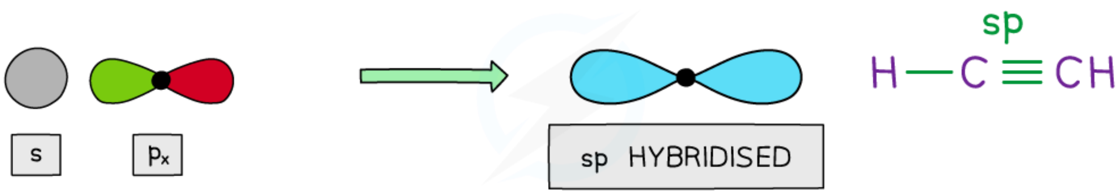


3 x sp^2 hybrid orbitals

- In the case of carbon, the sp^2 orbitals merge with the s orbitals in hydrogen and the sp^2 of an adjacent carbon, forming three equal sigma bonds
- The double bond is created by the side-to-side overlap of the unhybridised p-orbitals
- This bonding arrangement can also occur between a double bonded carbon and oxygen so is typically seen in the carbonyl group

sp hybridisation

- Two hybrid orbitals are produced when the 2s and one 2p orbital blend together
- These hybrids have ½ s character and ½ p character
- The two sp hybrid orbitals space themselves out at 180° forming linear geometry
- This is the resolution of the structure seen when carbon forms one single bonds and a triple bond with itself in alkynes



2 x sp hybrid orbitals

- In the case of carbon, the sp orbital merges with the s orbital in hydrogen and the sp of an adjacent carbon, forming two equal sigma bonds
- The triple bond is created by the side-to-side overlap of two pairs of the unhybridised p-orbitals, set at right angles to each other

Identifying Hybridisation

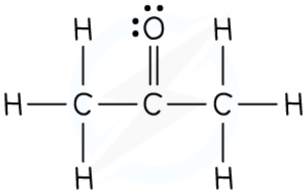
- You can predict the hybridisation present in molecules based on Lewis structures, electron domains, molecular geometries by applying the principles outlines in the previous section

Worked example

Identify the domain geometry, molecular geometry and hybridisation in the underlined atom in a) $CH_3\underline{C}OCH_3$ b) $\underline{P}H_3$ c) $\underline{NO}_2$

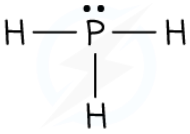
Answer

a) CH_3COCH_3



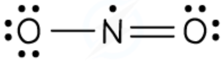
The Lewis structure shows that there are three electron domains around the central carbon, so the domain geometry is trigonal planar. There are two single bonds and one double bond, so the molecular geometry is also trigonal planar, and the carbon must have sp^2 hybridisation.

b) PH_3



The Lewis structure shows that there are four electron domains around the phosphorus, so the domain geometry is tetrahedral. There are three single single bonds and a lone pair, so the molecular geometry is trigonal pyramid. Four domains means the phosphorus must have sp^3 hybridisation.

c) NO_2



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The Lewis structure shows that there are three electron domains around the nitrogen, so the domain geometry is trigonal planar. There is one single bonds and one double bond, so the molecular geometry is bent linear, and the nitrogen must have sp^2 hybridisation

Exam Tip

You may be wondering why the unpaired electron lies on the nitrogen rather than on a oxygen in the Lewis structure for NO_2. This is easily demonstrated by considering the formal charges and electronegativity. The preferred Lewis structure has negative charges located on the most electronegative atoms.

FC (N) = V – ½B – N = (5) – ½(6) – 1 = +1

FC (single bonded O) = (6) – ½(2) – 6 = -1

FC (double bonded O) = (6) – ½(4) – 4 = 0

Oxygen and nitrogen have electronegativity of 3.4 and 3.0, respectively (Table 8 in the Data booklet), so placing the electron on the nitrogen means it has a positive FC instead of the oxygen.