

DP IB Chemistry: HL



14.1 More Structures & Shapes

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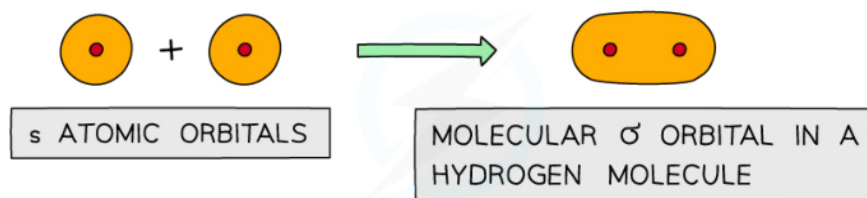
Your notes

14.1.1 Covalent Bonds

Sigma Bonds

Bond overlap in covalent bonds

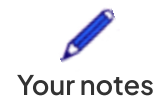
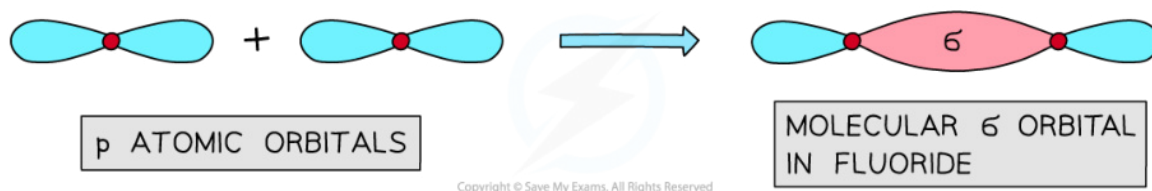
- A single **covalent bond** is formed when two nonmetals combine
- Each atom that combines has an **atomic orbital** containing a single unpaired electron
- When a covalent bond is formed, the **atomic orbitals** overlap to form a **combined orbital** containing two electrons
 - This new orbital is 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

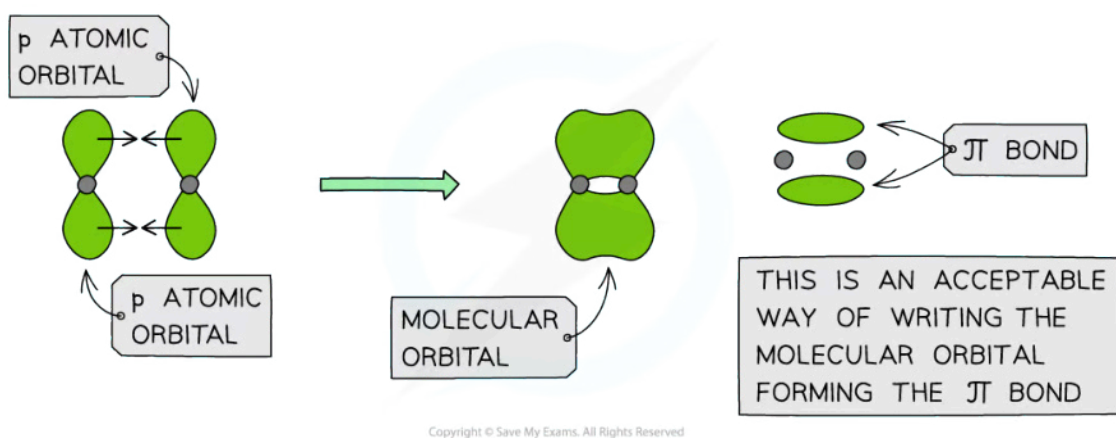


Your notes

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**

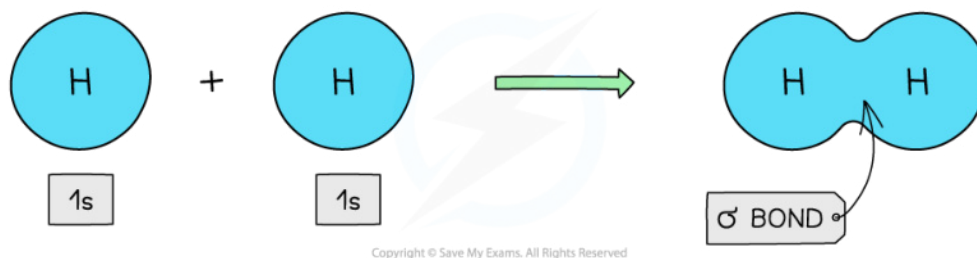


π orbitals are formed by the end-on overlap of p orbitals

Examples of sigma & pi bonds

Hydrogen

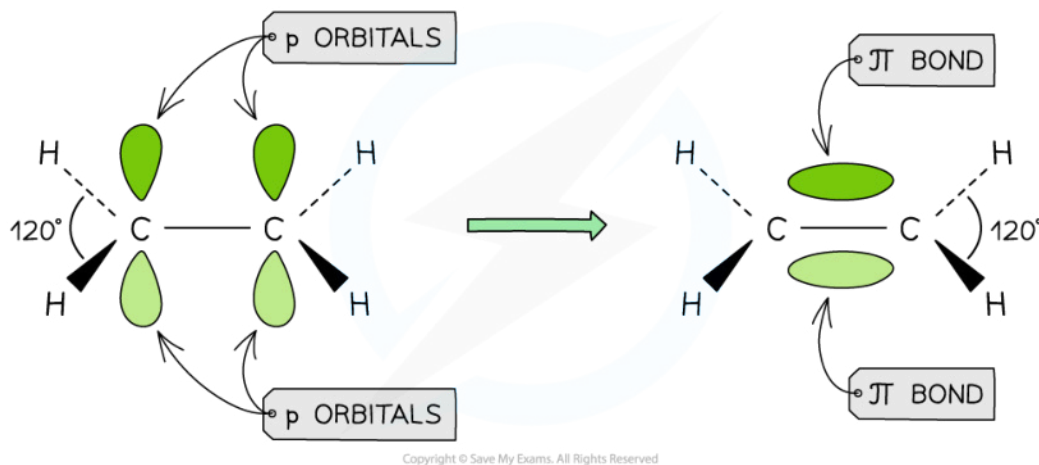
- The hydrogen atom has only one s orbital
- The s orbitals of the two hydrogen atoms will overlap to form a σ bond



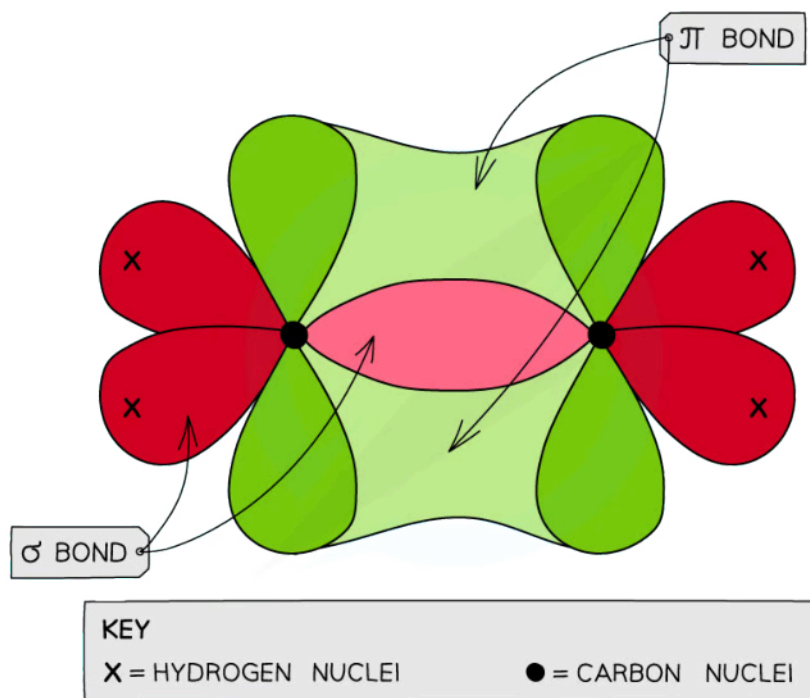
Direct overlap of the 1s orbitals of the hydrogen atoms results in the formation of a σ bond

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



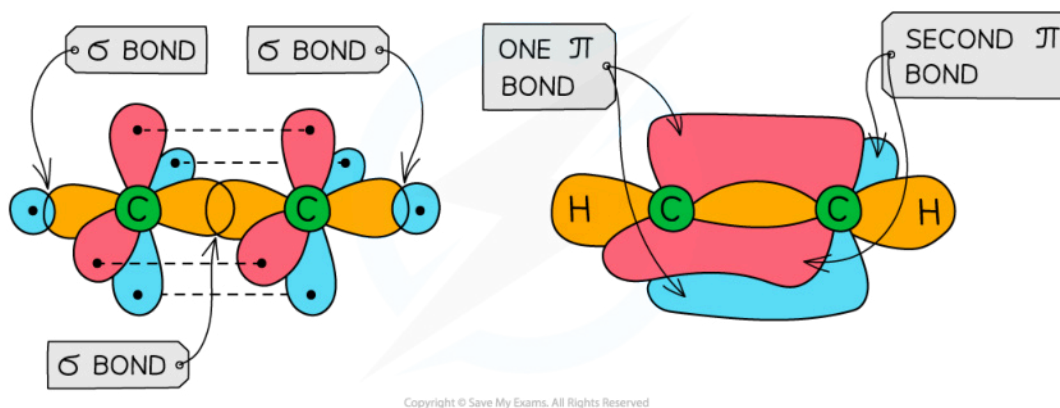
Each carbon atom in ethene forms two sigma bonds with hydrogen atoms and one σ bond with another carbon atom. The fourth electron is used to form a π bond between the two carbon atoms



Your notes

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



Your notes

Predicting the Type of Bonds

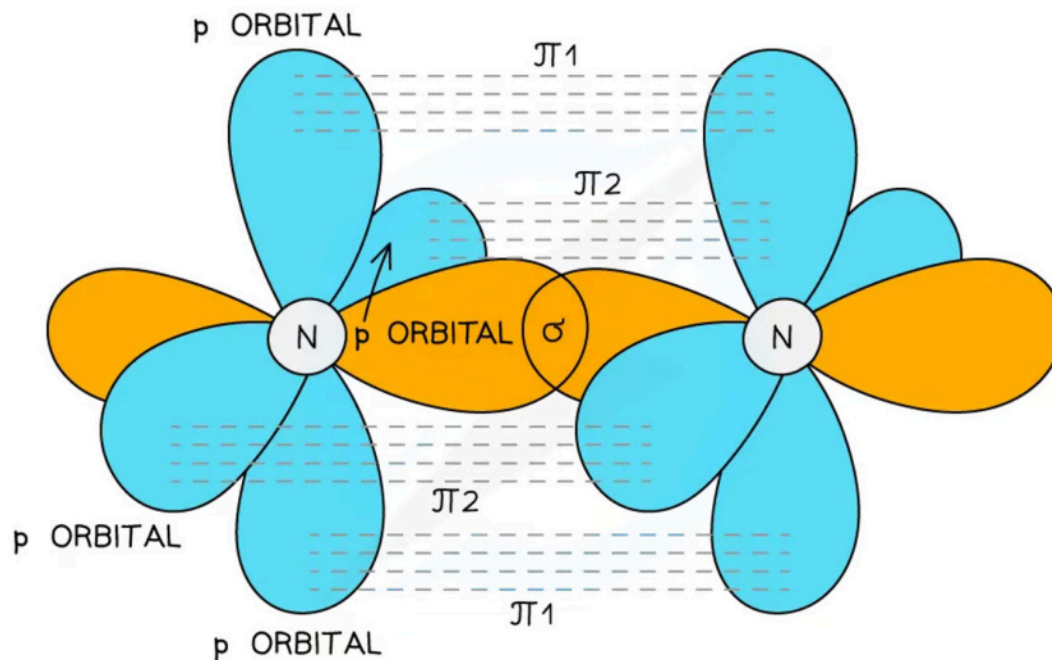
- Whether sigma (σ) or pi (π) bonds are formed can be predicted by consideration of the combination of atomic orbitals

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 $1s^2 2s^2 2p^3$
- 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**



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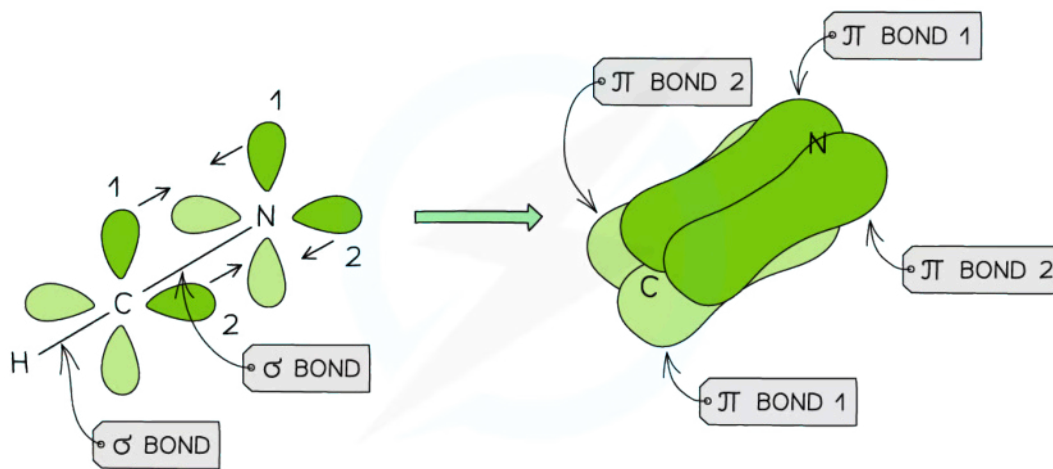
The triple bond is formed from two π bonds and one σ bond

- 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



Your notes



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



Your notes

14.1.2 More Lewis Structures

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 as H, Li, Be, B and Al
 - H can achieve a stable arrangement by gaining an electron to become $1s^2$, the same structure as the noble gas helium
 - Li does the same, but losing an electron and going from $1s^2 2s^1$ 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
$BeCl_2$	$Be + 2Cl =$ $2 + (2 \times 7) = 16$	$:\ddot{Cl}:Be:\ddot{Cl}:$
BF_3	$B + 3F =$ $3 + (3 \times 7) = 24$	$:\ddot{F}:B:\ddot{F}:$ $:\ddot{F}:$

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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



Your notes

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 $= \text{P} + 5\text{Cl} = 5 + (5 \times 7) = 40$
- 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 $= \text{S} + 4\text{F} = 6 + (4 \times 7) = 34$
- 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 $= \text{Cl} + 3\text{F} = 7 + (3 \times 7) = 28$
- 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 ClF₃

Triiodide ion, I₃⁻

- 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 I₃⁻

Six electron pairs

Sulfur hexafluoride, SF₆

- An example of a molecule with six bonding electron pairs is sulfur hexafluoride, SF₆
- 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:





Your notes

Lewis diagram for SF₆

Bromine pentafluoride, BrF₅

- The total number of valence electrons is = Br + 5F = 7 + (5 × 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 pair on the bromine
- The completed Lewis diagram looks like this:



Lewis diagram for BrF₅

Xenon tetrafluoride, XeF₄

- The total number of valence electrons is = Xe + 4F = 8 + (4 × 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 XeF₄



Your notes

14.1.3 Further VSEPR Theory

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)

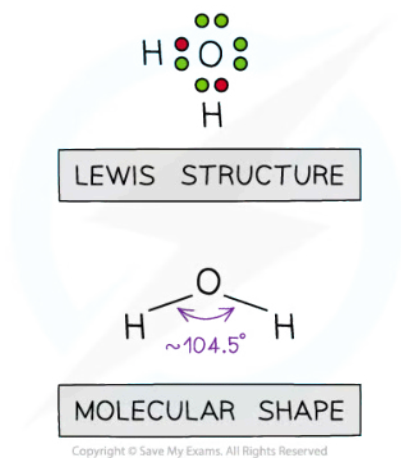


Diagram showing the Lewis structure of water and molecular shape from which the domain and molecular geometries may be determined

Five electron domains

Table showing the four molecular geometries associated with five electron domains



Your notes

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	

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*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



Your notes

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

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- SF_6 is a symmetrical molecule so the electron cloud charge is evenly spread with 90° 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° to the plane and the lone pairs are at 180°
 - 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 = $\text{Xe} + 2\text{F} = 8 + (2 \times 7) = 22$

- 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)



Your notes



Your notes

14.1.4 Formal Charge

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

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

or

$$\text{FC} = V - \frac{1}{2}B - N$$

- 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 .



1 TOTAL NUMBER OF VALENCE ELECTRONS = C + 4Cl = 4 + (4 × 7) = 32

2 DRAW THE SKELETAL POSITIONS

3 ADD THE BONDING PAIRS

ADD 24 LONE PAIR ELECTRONS

4 COMPLETED LEWIS STRUCTURE

4 BONDING PAIRS MEANS 32 - 8 = 24 ELECTRONS LEFT

LONE PAIRS

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Steps in drawing the Lewis structure for CCl₄

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

$$\text{FC for carbon} = (4) - \frac{1}{2}(8) - 0 = 0$$

$$\text{FC for chlorine} = (7) - \frac{1}{2}(2) - 6 = 0$$

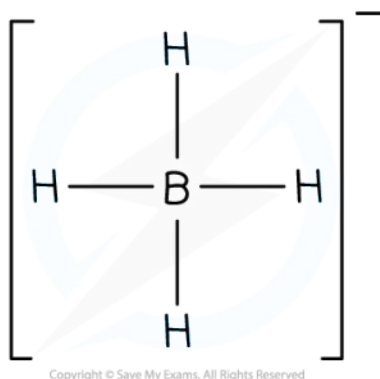
- Notice that formal charge is calculated for one of each type of atom and does not count the total number of atoms in the molecule

Worked example

What is the formal charge on boron in the BH₄⁻ 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 BH₄⁻

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

$$\text{FC}(\text{B}) = (3) - \frac{1}{2}(8) - 0 = -1$$

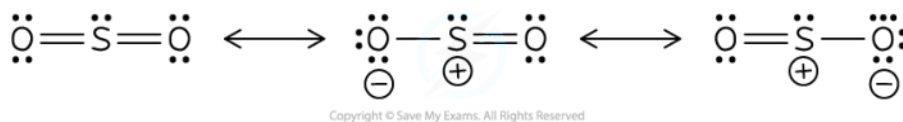


Your notes



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:

$$\text{FC on sulfur} = (6) - \frac{1}{2}(8) - (2) = 0$$

$$\text{FC on oxygen} = (6) - \frac{1}{2}(4) - (4) = 0$$

$$\text{Difference in FC} = \Delta\text{FC} = \text{FC}_{\text{max}} - \text{FC}_{\text{min}} = 0$$

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

$$\text{FC on sulfur} = (6) - \frac{1}{2}(6) - (2) = +1$$

$$\text{FC on left side oxygen} = (6) - \frac{1}{2}(2) - (6) = -1$$

$$\text{FC on right side oxygen} = (6) - \frac{1}{2}(4) - (4) = 0$$

$$\text{Difference in FC} = \Delta\text{FC} = \text{FC}_{\text{max}} - \text{FC}_{\text{min}} = 2$$

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

$$\text{FC on carbon} = (4) - \frac{1}{2}(8) - (0) = 0$$

$$\text{FC on oxygen} = (6) - \frac{1}{2}(4) - (4) = 0$$

$$\text{Difference in FC} = \Delta\text{FC} = \text{FC}_{\text{max}} - \text{FC}_{\text{min}} = 0$$

Structure II

$$\text{FC on carbon} = (4) - \frac{1}{2}(8) - (0) = 0$$

$$\text{FC on left oxygen} = (6) - \frac{1}{2}(6) - (2) = +1$$

$$\text{FC on right oxygen} = (6) - \frac{1}{2}(2) - (6) = -1$$

$$\text{Difference in FC} = \Delta\text{FC} = \text{FC}_{\text{max}} - \text{FC}_{\text{min}} = 2$$

Structure I is the preferred structure as the difference is zero



Your notes