

Anglo-Chinese School (Independent)

Year 6 (2023) IBDP Chemistry HL



TOPIC 4 Chemical bonding and structure

14.1 Further aspect of covalent bonding and structure

Larger structures and more in-depth explanations of bonding systems often require more sophisticated concepts and theories of bonding.

14.2 Hybridization

Hybridization results from the mixing of atomic orbitals to form the same number of new equivalent hybrid orbitals that can have the same mean energy as the contributing atomic orbitals.

ØNature of science:

Principle of Occam's razor—bonding theories have been modified over time. Newer theories need to remain as simple as possible while maximizing explanatory power, for example the idea of formal charge. (2.7)

Understandings:

- Covalent bonds result from the overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi bond (π) is formed by the sideways overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.
- Formal charge (FC) can be used to decide which Lewis (electron dot) structure is preferred from several. The FC is the charge an atom would have if all atoms in the molecule had the same electronegativity. FC = (Number of valence electrons)-½(Number of bonding electrons)-(Number of non-bonding electrons). The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.
- Exceptions to the octet rule include some species having incomplete octets and expanded octets.
- Delocalization involves electrons that are shared by/between all atoms in a molecule or ion as opposed to being localized between a pair of atoms.
- Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone.

Applications and skills:

- Prediction whether sigma (σ) or pi (π) bonds are formed from the linear combination of atomic orbitals.
- Deduction of the Lewis (electron dot) structures of molecules and ions showing all valence electrons for up to six electron pairs on each atom.
- Application of FC to ascertain which Lewis (electron dot) structure is preferred from different Lewis (electron dot) structures.
- Deduction using VSEPR theory of the electron domain geometry and molecular geometry with five and six electron domains and associated bond angles.
- Explanation of the wavelength of light required to dissociate oxygen and ozone.#
- Description of the mechanism of the catalysis of ozone depletion when catalysed by CFCs and NO_x.#
- •

Refer to page 343 of Chemistry Course Companion: An environment perspective: Catalysis of ozone depletion.

Guidance:

- The linear combination of atomic orbitals to form molecular orbitals should be covered in the context of the formation of sigma (σ) and pi (π) bonds.
- Molecular polarities of geometries corresponding to five and six electron domains should also be covered.

S Theories of bonding and structure (Refer to page 330 of Chemistry Course Companion)

14.2 Hybridization

Solution Nature of science:

The need to regard theories as uncertain—hybridization in valence bond theory can help explain molecular geometries, but is limited. Quantum mechanics involves several theories explaining the same phenomena, depending on specific requirements. (2.2)

Understandings:

• A hybrid orbital results from the mixing of different types of atomic orbitals on the same atom.

Applications and skills:

- Explanation of the formation of sp3, sp2 and sp hybrid orbitals in methane, ethene and ethyne.
- Identification and explanation of the relationships between Lewis (electron dot) structures, electron domains, molecular geometries and types of hybridization.

Guidance:

• Students need only consider species with sp³, sp² and sp hybridization.

4.3.5 Hybridization Theory

Valence bond theory (VBT) and molecular orbital theory (MOT) are basic chemistry theories that were developed to explain chemical bonding using quantum mechanics.

In VBT, a covalent bond is formed by the overlap of half-filled valence atomic orbitals of two atoms. These atomic orbitals contain one unpaired electron each. The overlapping of the atomic orbitals result in in the formation of a bonding orbital with electrons localized between the two atoms. In VBT, it is assumed that when the atoms interact they retain their own respective atomic orbitals but the overlapping atomic orbitals can differ. The two types of overlapping orbitals are sigma and pi; which will be elaborated in a later the section. The diagram below shows the formation of a σ bond when two 1s orbitals from 2 H atoms overlap.



http://www.sparknotes.com/chemistry/organic1/orbitals/section1.rhtml

In MOT however, the overlap of atomic orbitals results in the formation of new orbitals known as molecular orbitals. The electrons are assigned to these molecular orbitals, and associated with the whole molecule rather than individual atoms.



http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.rhtml

The figure above shows the formation of the molecular orbitals for H₂ molecule. The two 1s orbitals on the hydrogen atoms combine to form two new molecular orbitals. One combination results in a bonding molecular orbital (σ), which is of lower energy, and the other combination forms an anti-bonding molecular orbital (σ ^{*}) which is of higher energy.



http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.rhtml

A molecular orbital is a new orbital created from the combination of atomic orbitals used to make a bond. Hence, covalent bonds are formed by the overlapping of atomic orbitals.

1. Types of Bonds

- A Lewis structure is a simple model showing how the valence electrons are distributed in a molecule or a polyatomic ion. But the MOT helps to visualize the difference between a sigma (σ) and a pi (π) bond.
- For atomic orbitals to overlap and form molecular orbitals
- ✓ they must be relatively close in energy;
- \checkmark and the symmetry of the atomic orbitals must be identical.
- When X number of atomic orbitals combine, it will form x number of new molecular orbitals. There are 3 possible combinations:
 - ✓ bonding orbital: sigma (σ) or pi (π) orbital
 - ✓ anti-bonding orbital: sigma^{*} (σ^*) or pi^{*} (π^*) orbital
 - ✓ non-bonding situation.

(See table 2 on page 335 of Chemistry Course Companion for the different possible combinations of atomic orbitals.)

- There are two main ways atomic orbitals can overlap to make a new bond:
 - ✓ Head on (or end-on) overlap resulting in a sigma (σ) bond.
 - ✓ Sideways overlap resulting in a pi (π) bond.

(a) Sigma (σ) bond

- Sigma (σ) bond is formed from the head on (axial) overlap of orbitals.
- In σ bond, the bonding electrons are localized symmetrically along the inter-nuclear axis of the bonding atoms.
- The electron density in a σ -bond is found mainly in the space between the two nuclei.
- There are three different types of σ -Bond.



iii. $\mathbf{p} - \mathbf{p}$ overlap (eg Cl₂)



Note that a bonding molecular orbital can only hold 2 electrons (like an atomic orbital), and hence a σ -bond is made up of a doubly-filled σ -orbital.

(b) Pi (π) bond

- Pi (π) bond is formed from the sideways overlap of parallel p orbitals. It is much weaker than a σ bond.
- The π bond electron cloud consists of two lobes, one above and one below the internuclear axis of the bonding atoms.
- Each π bond (a molecular orbital) can contain a maximum of one pair of electrons only.
- The electron density for a π -bond is found above and below the plane of the nuclei.



(c) Double Bonds

- π bonds are used to make multiple bonds.
- A double bond consists of a σ bond and a π bond.



electrons in each of the two O atoms i.e. in the $2p_x$ and $2p_y$ orbitals.

The two singly occupied p-orbitals, the p_x and p_y orbitals, at 90° to each other, are shown below for the two O atoms approaching each other.



- As they approach, two of these p-orbitals (the p_y orbitals) first overlap along the internuclear axis to form a σ bond.
- The other two p-orbitals (the p_x orbitals) then overlap sideways to form a π bond as the two atoms approach even closer.



- As shown in the diagram above, the sideways overlap of the two p_x orbitals requires the two atoms to be very close to each other, therefore the double bond is shorter than a single bond (just one σ bond). Note that a π bond is only formed after a σ bond is formed.
- Note that the third pair of p-orbitals at 90° to the other two pairs (not shown above) also approach sideways but do not merge because they already have two electrons each.

Double bond = σ + π

(d) Triple Bonds

• To form a triple covalent bond, the atom at each end of the bond must have three valence orbitals, each containing one electron, to overlap with one another. Each atom contributes three valence orbitals and three valence electrons to form the triple bond.

Example:
$$N_2 (N \equiv N)$$



- Three singly occupied p-orbitals, the p_x , p_y and p_z orbitals are at 90° to each other.
- As the two N atoms approach, their p_y orbitals first overlap end-on to form a σ bond.
- As the two atoms come closer to each other, the two p-orbitals (the p_x and p_z orbitals) then overlap sideways to form two π bonds.



• As shown in the diagram above, the sideways overlap of the two p_x orbitals and two p_z orbitals requires the two atoms to be very close to each other, therefore the triple bond is shorter than a single bond (just one σ bond) and double bond (1 σ bond & 1 π bond).

I rible bond = $\sigma + \pi + \pi$

2. Differences between the σ bond and the π bond

σ bond	π bond
Head on overlap of the orbitals of two atoms	Sideways overlap of the parallel <i>p</i> orbitals of two atoms
The electron density is localized symmetrically along the inter- nuclear axis of two bonded carbon atoms.	The electron density in the π bond appears as two lobes, one above and one below the inter-nuclear axis of the two bonded atoms
Stronger	Weaker
Free to rotate	Restricted to rotation

Note: In large atoms, π bonds are not favourable because, being removed from the line between the centres of the atoms, the π bond rapidly weakens as the size of the atom increases. E.g. C=C double bond exists but Si=Si double bond does not exist.

3. Types of Hybridization

- **Hybridization** is a term used to describe the mixing of atomic orbitals to generate a set of new hybrid orbitals that are equivalent. Hybridization is a mathematical procedure.
- A **hybrid orbital** results from the mixing of different types of atomic orbitals on the same atom.

Models, theories, assumptions and deductions (Refer to page 345 of Chemistry Course Companion)

- There are **three** types of hybridization:
- ✓ **sp**³ **hybridization** (e.g. methane, CH₄)
- ✓ **sp² hybridization** (e.g. ethene, C₂H₄)
- ✓ **sp hybridization** (e.g. ethyne, C₂H₂)
- Rules of Hybridization :
 - ♦ Only orbitals of similar energy level can be mixed to form hybrid orbitals.
 - ♦ The number of hybrids formed equals the number of atomic orbitals mixed.
 - All hybrid orbitals formed are similar in nature but with different orientation in space.
- The three types of hybridization will be explained using carbon as the example. Carbon has **four electrons in its valence shell** and it needs to share these four electrons to make covalent bonds.

(a) sp³ hybridization

- One 2s and three 2p orbitals undergo hybridization to form four equivalent hybrid orbitals, each containing ¼ s and ¾ p character. These hybrid orbitals are directed towards the corners of a **regular tetrahedron**, such that the repulsion between electrons occupying these orbitals is minimized.
- This type of orbitals is called sp³ hybrid orbitals.
- The bond angle around each C atom is approximately 109.5°.



Examples of sp³ hybridization : Methane (CH₄)

Each hybrid orbital overlaps with 1s orbital of a H atom, forming C – H bond



> The bond formed from the head-on overlap of the sp³ orbital and 1s orbital is known as **sigma bond** (σ **bond**).



- Shape : tetrahedral
- Electron pairs have the maximum separation of 109.5°





Other examples of sp³ hybridization: Ammonia (NH₃) & Water (H₂O)

(b) sp² hybridization

- Three orbitals of C (2s, 2p_x, 2p_y) are 'mixed' to form three equivalent sp² hybrid orbitals which are coplanar and at 120° to each other.
- Each of the sp² hybridized orbital has a large lobe and a smaller lobe.
- The 2p_z orbital of C remains unchanged.



> 2 sp² hybridized C atoms form a σ bond with each other by the head on overlap of one sp² hybrid orbital from each C atom.

- > The remaining sp² hybrid orbitals of the C atoms form σ bond to 4 H atoms through head-on overlapping with the 1s orbitals of H atoms.
- > The remaining $2p_z$ orbitals on each C atom overlap sideways to form a pi bond.
- > Carbon-Carbon double bond is formed from one σ bond and one π bond.



Shape : flat molecule with inter-bond angles of 120° and pi electron cloud above and below the plane of atoms





Another example of sp² hybridization :

Boron chloride (BCl₃)



(c) sp hybridization

Example of sp hybridization : C₂H₂

• The 2 orbitals of C (2s, 2p_x) are 'mixed' to form 2 equivalent sp hybrid orbitals which are linear and at 180° to each other.



- Each C atom has two sp hybrid orbitals. One sp hybrid orbital of each of the two carbon atom overlaps head on with each other to form a σ bond.
- The other sp hybrid orbital then overlaps with the singly occupied 1s orbital of hydrogen to form another σ bond.
- The two 2p un-hybridized p orbitals then overlap sideways to form 2 π bonds given rise to a triple bond between the two carbon atoms. Hence C₂H₂ has a linear structure.



Formation of C₂H₂ molecule by *sp* hybridisation http://www.sciencehq.com/chemistry/hybridisation-2.html

In summary,

No. of electron domains	Hybridization	Molecular Geometry	Shape of Molecule	Example
2	sp	Linear	Linear	CO ₂ BeCl ₂
3	sp²	Trigonal planar	Trigonal planar	BF ₃ SnCl ₂ NO ₂ -
4			Tetrahedral	CH₄
	sp³	Tetrahedral	Trigonal Pyramidal	NH ₃
			Bent (V-shaped)	H₂O

No. of electron domains	Hybridization	Molecular Geometry	Shape of Molecule	Example
			Trigonal bipyramid	PCI ₅
5	sp³d	Trigonal bipyramid	Seesaw	SF₄
			T-shaped	CIF₃
		Octahedral	Octahedral	SF ₆
6	sp ³ d ²		Square Pyramidal	IF ₅
				ICl4 ⁻

4.3.6 Delocalization of electrons (Resonance)

Resonance involves using two or more Lewis structures to represent a particular molecule or ion. A **resonance structure** is one of two or more alternative Lewis structures for a molecule or ion that cannot be described fully with one Lewis structure alone.

In **delocalization**, electrons are shared by **more than two atoms** in a molecule or ion as opposed to being localized between a pair of atoms.

 π electrons are electrons found in the π bonds. Delocalized π electrons are electrons of a molecule that are not associated with a single atom or to a covalent bond. Delocalization of π electrons is a result of the interaction of p orbitals on more than two atoms. Delocalized π electrons are contained within an orbital that extends over several adjacent atoms.

A. Carbonate ion, CO₃²⁻

- According to VSEPR theory, the carbonate ion contains two types of C-O bonds; one of them is a double bond and the other two are single bonds. In other words, two of the C-O bonds in carbonate ion are predicted to be the same length, while the other C=O is different. Therefore, the C-O double bond should be shorter than the two C-O single bonds.
- These predictions are contradicted by the experimental facts: all three C-O bonds in carbonate ion are the same length. This discrepancy is explained by the delocalization of electrons or the resonance theory.





• Whenever there are two or more valid Lewis structures for the same compound, the true structure of the molecule is best represented as a "hybrid" of the individual structures.



Carbonate Ion as a Resonance Hybrid

• Resonance structures are also observed in nitrates, nitrites and ozone. Try to determine the resonance hybrid for each.

B. Benzene, C₆H₆

 In benzene, each carbon atom is sp² hybridized. It forms 3 coplanar covalent bonds with 2 other carbon atoms and 1 hydrogen atom. The remainder electron is in a 2p orbital perpendicular to the plane of atoms.



- Six C atoms are joined in a ring. They all lie in the same plane, with bond angles corresponding to 120°.
- Each p orbital overlaps equally with each of its neighbors resulting in six p electrons completely delocalized in a two-lobed cloud over and under the ring of carbon atoms.



Extensive π electrons delocalisation gives benzene its extra stability

- All six carbon-carbon bonds are identical; they are neither single nor double.
- Benzene is planar and symmetrical.
- Representation of the benzene ring:



Two Kekulé structures of benzene showing resonance

• None of the two structures above adequately represent benzene, so it is simply written as



(benzene showing the delocalized nature of its π electrons.)

• The circle represents the delocalized π electrons.

C. Carboxylate ion, RCOO⁻

• The C atom in the carboxylate group (formed from a carboxylic acid molecule) is sp² hybridized. The p orbital of carbon can overlap with the p orbital of either oxygen to form a double bond as shown below:



• In the actual structure, delocalization of the negative charge will occur resulting in a more stable anion (i.e. resonance hybrid of the 2 forms).

D. Graphite

• Graphite is an example of a molecular solid in which layers of atoms are held together with dispersion forces. In each layer, the carbon atoms are sp² hybridized and bonded to three other carbon atoms.



http://www.everyscience.com/Chemistry/Inorganic/Carbon/a.1189.php

E. Conjugated system

- Conjugated double bonds in a molecule mean that the single and double bonds **alternate**. This enables the electrons to be delocalized over the whole system and so be shared by many atoms. This means that the delocalized electrons may move around the whole system.
- Consider the molecule buta-1,3-diene:



- The interaction of the two double bonds with each other will produce a delocalized system of pi electrons over all four atoms. This is known as *conjugation*. Conjugation in this context literally means "joining together".
- All the p-orbitals will overlap sideways and a system of delocalized pi bonds is formed. See diagrams below.



- The delocalization of electrons in compounds with alternating single and multiple bonds may lower the overall energy of the molecule and increase its stability.
- The double bonds do not have to be always between carbon atoms. All of the following molecules contain conjugated double bonds, although in the last case, the conjugation does not extend over the whole molecule:

$$CH_{2} = C - C = C - C = CH_{2}$$

$$H + H + H$$

$$CH_{2} = C - C = C - C = O$$

$$H + H + H$$

$$CH_{3} - CH_{2} - C = C - C = CH_{2}$$

$$H + H + H$$

• The largest conjugated systems are found in graphite, graphene, conductive polymers, and carbon nanotubes.

F. Bond Order

- **Bond order** is the number of chemical bonds between a pair of atoms.
- For example,
 - ✓ in diatomic nitrogen N≡N, the bond order is 3,
 - ✓ in ethyne H−C≡C−H the bond order between the two carbon atoms is 3, and the C−H bond order is 1.
- Bond order gives an indication of the stability of a bond.
- In molecules that have resonance structures, the bond order does not need to be an integer.
- Compounds with resonance structures often have chemical bonds that are not easily described as single, double, or triple bonds.
- To describe the bond order, bond length, and bond energy of these bonds, the number of resonance structures and bonding pairs must be taken into account.
- Consider the nitrite ion, NO₂⁻, which has two equivalent resonance structures.



Because neither resonance structure represents the actual electron arrangement, the nitrogen–oxygen bonds in this ion are not single bonds (bond order = 1) or double bonds (bond order = 2). Instead, NO₂⁻ has two equivalent NO bonds where three pairs of bonding electrons are distributed over two equivalent NO bond locations. The best way to describe the bonding in the resonance hybrid is with a fractional bond order:

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each NO bond order in NO_2^- = \frac{\text{total number of NO bonding pairs}}{\text{number of NO bond locations}} = \frac{3}{2} = 1.5
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 The NO bonds in the nitrite ion have a bond order that is intermediate between a single and a double bond. The bond length and bond energy of the NO bonds in the nitrite ion are also intermediate between average NO single and double bond lengths and bond energies.

Bond	Bond Length (pm)	Bond Energy (kJ/mol)
N—O	136	143
NO in NO ₂ -	125	174
N=O	115	201

• In benzene, where the delocalized molecular orbitals contain 6 π electrons over six carbons essentially yielding half a π bond together with the sigma bond for each pair of carbon atoms, giving a calculated bond order of 1.5.

4.3.7 Formal charge

- Resonance structures are all the possible Lewis structures for a molecule. Formal charge (FC) is a technique to identify which Lewis structure is the more correct structure. The most correct Lewis structure will be the structure where the formal charges are evenly distributed throughout the molecule and where the atoms have FC values closest to zero. The sum of all the formal charges should equal the total charge of the molecule.
- Hence, the formal charge of the atoms present in the molecule or ion can be used to determine the most appropriate structure.
- A **formal charge** (FC) is the charge assigned to an atom in a molecule, assuming that electrons in a chemical bond are shared equally between atoms, regardless of relative electronegativity.

Formal charge (FC) = (no. of valence electrons) – $\frac{1}{2}$ (no. of bonding electrons) – (no. of non-bonding electrons)

- If there are a number of possible Lewis structures that all obey the octet rule, the most reasonable one will be:
 - ✓ the one with FC difference (Δ FC = FC_{max} FC_{min}) closest to zero, and
 - \checkmark the one that has the negative charges located on the most electronegative atoms.
- The figures below show two Lewis structures for carbon dioxide, CO₂.



- Since △FC for Lewis structure A is closest to zero, it is the most reasonable representation of CO₂.
- The FC considerations can also be applied to species with incomplete octet of electrons (BF₃) or with expanded octets of electrons (SO₄²⁻).
 [See page 331 and 338 344 of Chemistry Course Companion.]
- For a neutral molecule, the sum of the FCs = 0.
- For a polyatomic ion, the sum of the FCs = charge on the ion.

S Different interpretations of 'charge'. (Refer to page 331 of Chemistry Course Companion)

Models and theories of structure and bonding. (Refer to page 344 of Chemistry Course Companion)

4.3.8 Ozone (O₃)

- Ozone is a colourless and odourless gas made of oxygen.
- The molecules of ozone contain three oxygen atoms (O_3) . It is a very reactive gas, and is toxic even at low concentrations. It occurs naturally in small amounts in the Earth's upper atmosphere, and in the air of the lower atmosphere after a lightning storm.



Resonance forms of ozone, O₃

- Ozone is much more reactive than O_2 . It is a very powerful oxidizing agent, second among elements only to fluorine.
- Ozone is a V-shaped molecule with a bond angle of 116.8° and the two O O bond lengths are equal i.e. 128 pm.
- The bond order for the O O bond in ozone is calculated as follows: Each bond order in $O_3 =$ <u>total number of O – O bonding pairs</u> = <u>3</u> = 1.5 itions 2

- Photodissociation
 - ✓ The Sun emits radiation over a wide range of wavelengths. The shorter-wavelength and higher-energy radiations in the ultraviolet range of the spectrum are energetic enough to cause chemical changes.
 - ✓ The rupture of a chemical bond resulting from absorption of a photon by a molecule is called photodissociation. Photodissociation does not form ions. The bond cleavage leaves half the bonding electrons with each of the two atoms forming two neutral particles.
 - The equation below shows the photodissociation of an oxygen molecule.

$$O_2(g) \xrightarrow{h_V} 2O_{\bullet}(g)$$

✓ Ozone also undergoes dissociation in the presence of UV radiation from the sun i.e.

$$O_3(g) \xrightarrow{n_V} O_2(g) + O_2(g)$$

- ✓ Both the bonds in oxygen and ozone can be broken by UV radiation.
- \checkmark The bond order in ozone is 1.5 but that in oxygen is 2. Hence the double bond in O = O is stronger and radiation of a shorter wavelength is required to break the bond in oxygen.
- \checkmark Using E = hv and given that the average bond enthalpy of an ozone and oxygen molecule are 362 kJ mol⁻¹ and 498 kJ mol⁻¹ respectively, the wavelength of the UV radiation required to break the O - O bond in ozone and the O = O double bond in oxygen can be calculated.
- \checkmark Refer to page 343 of Chemistry Course Companion for the wavelength of light required to dissociate oxygen and ozone.
- ✓ The mechanism of the catalysis of ozone depletion will be discussed in Topic 6 Kinetics.