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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Structure 2.2
The Covalent Model

Booklet 4 · Higher Level · Understandings 2.2.13 – 2.2.16

Expanded octets, formal charge, sigma and pi bonds, and hybridization

Complete revision notes & memory points · Higher Level

How the level tags work in this booklet

HL Every understanding in this booklet is **Additional Higher Level** material. SL students do not need this booklet: Booklets 1–3 contain everything examined at SL in Structure 2.2.

SL + HL Used only for short reminders of earlier, common material that this booklet builds on.

Inside this booklet

1. What the syllabus actually asks of you
2. 2.2.13 — Expanded octets: five and six electron domains
3. 2.2.14 — Formal charge
4. 2.2.15 — Sigma and pi bonds
5. 2.2.16 — Hybridization
6. Bringing it all together
7. Key points to memorise
8. Check yourself
9. Answers

1 What the syllabus actually asks of you

This final booklet of Structure 2.2 takes the covalent model beyond the octet rule and beyond simple dot-and-cross diagrams. It deals with central atoms that hold more than eight electrons, gives you a way to choose between competing Lewis formulas, and then explains *how* a covalent bond forms, in terms of atomic orbitals overlapping. Everything here builds on Booklets 1 (Lewis formulas), 2 (VSEPR and polarity) and 3 (resonance and benzene).

Understanding	What it says	What you must be able to do	Level
2.2.13 Expanded octets	Some atoms can form molecules in which they have an expanded octet of electrons.	Represent Lewis formulas for species with five and six electron domains around the central atom. Deduce the electron-domain geometry and the molecular geometry of these species using VSEPR.	HL
2.2.14 Formal charge	Formal charge values can be calculated for each atom in a species and used to determine which of several possible Lewis formulas is preferred.	Apply formal charge to determine a preferred Lewis formula from different Lewis formulas for a species.	HL
2.2.15 Sigma and pi bonds	Sigma (σ) bonds form by the head-on combination of atomic orbitals, with electron density concentrated along the bond axis. Pi (π) bonds form by the lateral combination of p orbitals, with electron density concentrated on opposite sides of the bond axis.	Deduce the presence of sigma and pi bonds in molecules and ions. Include both organic and inorganic examples.	HL
2.2.16 Hybridization	Hybridization is the concept of mixing atomic orbitals to form new hybrid orbitals for bonding.	Analyse the hybridization and bond formation in molecules and ions. Identify the relationships between Lewis formulas, electron domains, molecular geometry and type of hybridization. Predict the geometry around an atom from its hybridization, and vice versa. Only **sp, sp^2 and sp^3** need to be covered, with organic and inorganic examples.	HL

Linking questions, Nature of Science and TOK attached to 2.2.13 – 2.2.16

- **Structure 3.1:** how does the ability of some atoms to expand their octet relate to their position in the periodic table? → section 2.1
- **Structure 3.1, Reactivity 3.2:** what are the different assumptions made in the calculation of formal charge and of oxidation states for atoms in a species? → section 3.6
- **Nature of Science:** using formal charge in some situations and oxidation numbers in others is an application of Occam's razor → section 3.6
- **Nature of Science:** hybridization is a model, validated by how well it explains observed geometries → section 5.7
- **TOK:** to what extent does the use of language and imagery ("orbitals", "mixing") enhance or mask our understanding of what is represented? → section 5.7

What you need from earlier booklets and the data booklet

- SL + HL How to draw a Lewis formula and count valence electrons (Booklet 1); how to count electron domains and apply VSEPR for two to four domains (Booklet 2); resonance and delocalization (Booklet 3).
- **Data booklet:** electronegativity values (Section 9), needed to decide between Lewis formulas with equal formal charges; bond enthalpies (Section 12), which show that a π bond is weaker than a σ bond.
- **Memorise:** the formal charge formula, the five- and six-domain geometries and their names, and the link between number of domains and hybridization.

2 Structure 2.2.13 — Expanded octets HL

2.1 Which atoms can hold more than eight electrons?

The octet rule (Booklet 1) works very well for elements in period 2. A central atom from **period 3 or below**, however, can sometimes accommodate **more than eight** electrons in its valence shell — five or six electron domains instead of four. This is an **expanded octet**. Phosphorus forms PCl_5 (10 electrons around P), sulfur forms SF_6 (12 around S), and even the noble gas xenon forms XeF_4 (12 around Xe).

This answers the Structure 3.1 linking question. Two features of the periodic table explain it:

- **Available d orbitals.** From the third shell onwards, each shell has a d sublevel (3d, 4d, 5d) whose energy is fairly close to that of the s and p orbitals of the same shell. Electrons can be promoted into these empty d orbitals, so more than four electron pairs can be accommodated. The second shell has **no 2d sublevel**, so C, N, O and F can never exceed an octet: phosphorus forms PCl_5, but nitrogen cannot form NCl_5.
- **Atomic size.** Larger atoms have room for five or six neighbours around them. Expanded octets are most common when the surrounding atoms are small and highly electronegative, such as F, O and Cl.

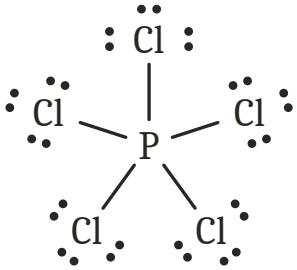
The d-orbital explanation is the one used in the IB course and in the Pearson text. More advanced bonding models suggest that d orbitals contribute less than this simple picture implies, and that the size of the central atom and the electronegativity of the surrounding atoms are the key factors. For IB answers, use the d-orbital explanation.

The two exceptions to the octet rule, side by side

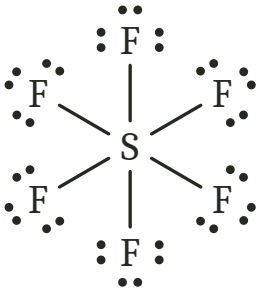
- **Incomplete octet** (Booklet 1): small atoms such as **Be and B** (and Al) form stable molecules with fewer than eight electrons, e.g. $BeCl_2$ (4) and BF_3 (6).
- **Expanded octet** (this booklet): atoms of elements in **period 3 and below** can have more than eight, using d orbitals in their valence shell, e.g. PCl_5 (10) and SF_6 (12).

2.2 Lewis formulas with five and six electron domains

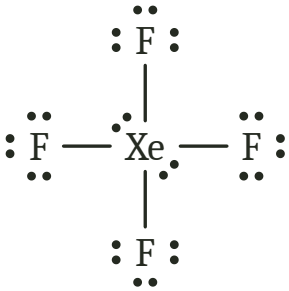
The method is the same as in Booklet 1, except that you **stop trying to limit the central atom to eight**. Count the valence electrons, join each outer atom to the central atom, complete the octets of the **outer** atoms first, and then place any remaining electrons on the central atom as lone pairs.



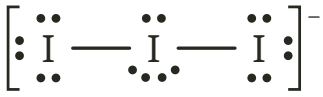
PCl_5
5 + (5 × 7) = 40 e · 5 bonds, 0 lone pairs



SF_6
6 + (6 × 7) = 48 e · 6 bonds, 0 lone pairs



XeF_4
8 + (4 × 7) = 36 e · 4 bonds, 2 lone pairs



I_3^-
(3 × 7) + 1 = 22 e · 2 bonds, 3 lone pairs on central I

Worked example — XeF_4: how many lone pairs on the central atom?

1. Count: 8 + (4 × 7) = 36 valence electrons = 18 pairs.

2. Bonds: four Xe–F single bonds use 4 pairs; 14 pairs remain.

3. Outer atoms first: each F needs three lone pairs to complete its octet: 4 × 3 = 12 pairs. 2 pairs remain.

4. Central atom: the last 2 pairs go on Xe as lone pairs. Xe has 4 bonding + 2 lone pairs = **6 electron domains** (12 electrons).

The quick check: lone pairs on the central atom = (total valence pairs − bonds − lone pairs on outer atoms). The same steps for SF_4 (34 e, 17 pairs) give four bonds, twelve outer lone pairs and **one** lone pair on S, so five domains.

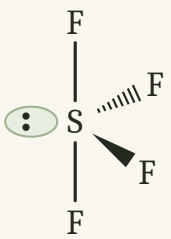
2.3 Five electron domains: triangular bipyramidal

Five domains arrange themselves in a **triangular bipyramid** (also called *trigonal bipyramidal*; both names earn the mark). Three positions lie in a plane around the central atom — the **equatorial** positions, 120° apart — and two lie above and below that plane — the **axial** positions, at 90° to the equatorial plane and 180° to each other. Unlike every shape you met at SL, the five positions are **not equivalent**.

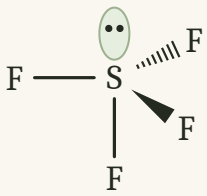
Where do the lone pairs go? Always equatorial.

A lone pair repels more strongly than a bonding pair, and the strongest repulsions are those at 90°. A lone pair in an **equatorial** position has only **two** neighbours at 90° (the two axial bonds). In an **axial** position it would have **three** (all the equatorial positions). So lone pairs occupy equatorial positions, which keeps the number of 90° lone pair–bond repulsions to a minimum.

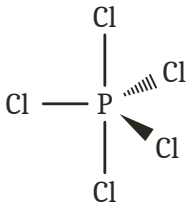
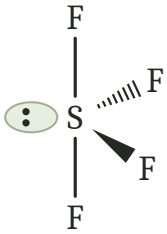
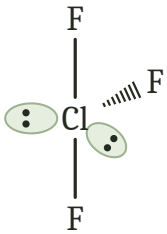
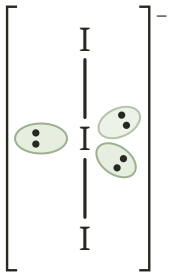
The general rule for predicting five-domain shapes is to choose the arrangement with the fewest 90° lone pair–lone pair interactions first, and then the fewest 90° lone pair–bonding pair interactions.



lone pair equatorial ✓
two 90° lone pair–bond repulsions



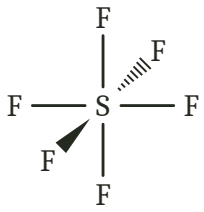
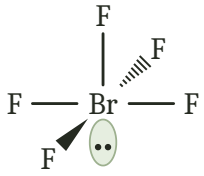
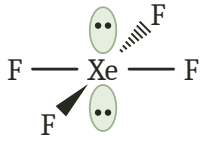
lone pair axial ×
three 90° lone pair–bond repulsions

Bonding / lone pairs	Shape	Molecular geometry	Bond angles	Examples	Polar?
5 / 0		**triangular bipyramidal**	90°, 120°, 180°	PCl_5, PF_5, AsF_5	no
4 / 1		**see-saw** (unsymmetrical tetrahedron)	< 90°, < 120°	SF_4, SeF_4, IF_4^+	yes
3 / 2		**T-shaped**	< 90°	ClF_3, BrF_3, ICl_3	yes
2 / 3		**linear**	180°	I_3^-, XeF_2, KrF_2	no

In see-saw and T-shaped molecules the lone pairs push the bonds closer together, so the angles are slightly **less** than 90° and 120°. In the linear species the three equatorial lone pairs are spread symmetrically, so the angle stays at exactly 180°.

2.4 Six electron domains: octahedral

Six domains arrange themselves in an **octahedron**, with all angles 90°. All six positions are equivalent, so the first lone pair can go anywhere. A second lone pair goes **opposite** the first (180° away) to keep the two lone pairs as far apart as possible.

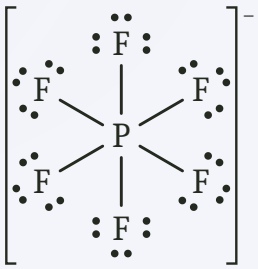
Bonding / lone pairs	Shape	Molecular geometry	Bond angles	Examples	Polar?
6 / 0		**octahedral**	90°	SF_6, PF_6^-, PCl_6^-, TeF_6	no
5 / 1		**square pyramidal**	< 90°	BrF_5, IF_5, $XeOF_4$	yes
4 / 2		**square planar**	90°	XeF_4, ICl_4^-, BrF_4^-	no

The octahedral arrangement is also common in transition element complexes such as $[Fe(H_2O)_6]^{3+}$ (Booklet 1 and Structure 3.1). Xenon tetrafluoride forms stable colourless crystals; its square planar structure was confirmed by NMR spectroscopy and X-ray crystallography in 1963.

Worked example — predict the shape and bond angles of PF_6^- and ClF_3

PF_6^-: 5 + (6 × 7) + 1 = 48 electrons. Six P–F bonds; each F has three lone pairs (36 electrons); none remain for P. Six bonding domains, no lone pairs: **octahedral, 90°**.

ClF_3: 7 + (3 × 7) = 28 electrons. Three Cl–F bonds (6 e) and 3 × 6 = 18 e on the F atoms leave 4 electrons: **two lone pairs on Cl**. Five domains, triangular bipyramidal electron-domain geometry; both lone pairs equatorial, so the molecule is **T-shaped**, with F–Cl–F angles slightly **less than 90°**.



2.5 The complete VSEPR summary

Domains	Electron-domain geometry	Bonding	Lone pairs	Molecular geometry	Angle	Example
2	linear	2	0	linear	180°	CO_2
3	triangular planar	3	0	triangular planar	120°	BF_3
		2	1	bent (V-shaped)	< 120°	SO_2
4	tetrahedral	4	0	tetrahedral	109.5°	CH_4
		3	1	trigonal pyramidal	107°	NH_3
		2	2	bent (V-shaped)	104.5°	H_2O
5	**triangular bipyramidal**	5	0	triangular bipyramidal	90°, 120°	PCl_5
		4	1	see-saw	< 90°, < 120°	SF_4
		3	2	T-shaped	< 90°	ClF_3
		2	3	linear	180°	XeF_2, I_3^-
6	**octahedral**	6	0	octahedral	90°	SF_6
		5	1	square pyramidal	< 90°	BrF_5
		4	2	square planar	90°	XeF_4

2.6 Polarity of molecules with five and six domains

The rule from Booklet 2 still applies: a molecule is polar if its bond dipoles do not cancel. With **identical outer atoms and no lone pairs** (PCl_5, SF_6) the dipoles cancel. Lone pairs make a molecule polar **only if** they destroy the symmetry: XeF_2 and XeF_4 are non-polar because their lone pairs are arranged symmetrically, while SF_4, ClF_3 and BrF_5 are polar. Different outer atoms can also break the symmetry: $SBrF_5$ is polar, but PCl_3F_2, with both F atoms axial, is non-polar because the two axial dipoles cancel and so do the three equatorial ones.

Examiner traps in 2.2.13

- Placing lone pairs in axial positions in a five-domain molecule. They go **equatorial**.
- Saying a period 2 element (N, O, F) can expand its octet. It has no 2d sublevel.
- Forgetting the lone pairs on the outer halogen atoms when drawing the Lewis formula of PCl_5 or SF_6.
- Calling XeF_4 "tetrahedral" (from its four atoms) or "octahedral" (its electron-domain geometry). Its molecular geometry is **square planar**.
- Assuming any molecule with lone pairs on the central atom is polar. XeF_2, XeF_4 and I_3^- are symmetrical.

3 Structure 2.2.14 — Formal charge HL

3.1 Why we need a tie-breaker

For some species, the Lewis formula method gives more than one structure that seems acceptable. This happens especially with central atoms that can expand their octet. Sulfur dioxide, for example, can be drawn obeying the octet rule (one S=O and one S–O, with resonance between them, as in Booklet 2), or with an expanded octet on S (two S=O bonds). All of these have the same skeleton and the same shape — bent, about 117–119° — but which electron arrangement best represents the molecule? **Formal charge** is the tool that decides.

3.2 The idea and the formula

Formal charge treats every covalent bond as if it were **purely covalent**, with the electrons shared **equally**, ignoring electronegativity. It counts how many electrons "belong" to each atom in the Lewis formula and compares this with the number of valence electrons in the free atom. Each atom is assigned:

- **half** of the electrons in each of its bonds (one electron per shared pair, even for a coordination bond), and
- **all** of the electrons in its own lone pairs.

The formula to memorise

$$FC = V - (\tfrac{1}{2}B + L)$$

V = number of valence electrons in the free atom (from its group); B = number of **bonding** electrons around the atom (two per bond, so ½B is simply the **number of bonds**); L = number of **lone-pair** electrons on the atom.

Three rules for choosing the preferred structure

1. The formal charges in a structure must add up to the **overall charge** on the species: zero for a neutral molecule, the ionic charge for an ion. Use this to check your arithmetic.
2. The preferred structure is the one with formal charges **closest to zero** on all atoms. Low formal charges mean that less charge separation has taken place in forming the structure.
3. If two structures are equally good by rule 2, the preferred one places any **negative** formal charge on the **more electronegative** atom (data booklet, Section 9).

3.3 Worked examples

Worked example 1 — sulfur dioxide, SO_2

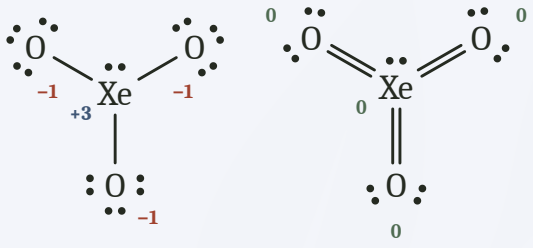


(i) octet structure (ii) expanded octet on S

Atom	(i) one S=O, one S–O	(ii) two S=O
S	3 bonds, 1 lone pair: 6 − (3 + 2) = **+1**	4 bonds, 1 lone pair: 6 − (4 + 2) = **0**
O (double bond)	2 bonds, 2 lone pairs: 6 − (2 + 4) = **0**	6 − (2 + 4) = **0**
O (single bond)	1 bond, 3 lone pairs: 6 − (1 + 6) = **−1**	(the second O is also double bonded) **0**
Sum	0 ✓	0 ✓

Structure (ii), with every formal charge zero, is **preferred**. In reality all resonance structures contribute to the true structure, but the one with the lowest formal charges contributes most.

Worked example 2 — xenon trioxide, XeO_3

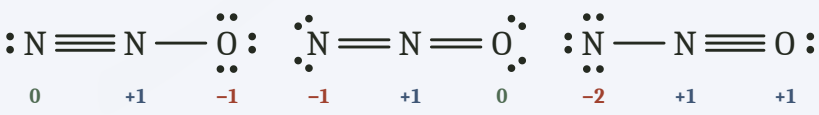


(i) three single bonds (ii) three double bonds

(i) Xe: 3 bonds, 1 lone pair: 8 − (3 + 2) = **+3**; each O: 6 − (1 + 6) = **−1**; sum = 3 − 3 = 0. (ii) Xe: 6 bonds, 1 lone pair: 8 − (6 + 2) = **0**; each O: 6 − (2 + 4) = **0**.

Structure (ii) is **preferred**. Either way Xe has four electron domains (three bonding + one lone pair), so XeO_3 is trigonal pyramidal.

Worked example 3 — dinitrogen monoxide, N_2O (skeleton N–N–O)

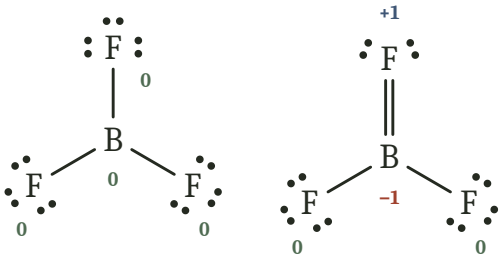


(i) (ii) (iii)

Structure (iii) has the largest formal charges (−2 and two +1), so it is the least favoured. Structures (i) and (ii) both have charges of magnitude 1, so rule 2 cannot separate them. Rule 3 decides: (i) places the −1 on **oxygen** (3.4), which is more electronegative than nitrogen (3.0), so **(i) is preferred**.

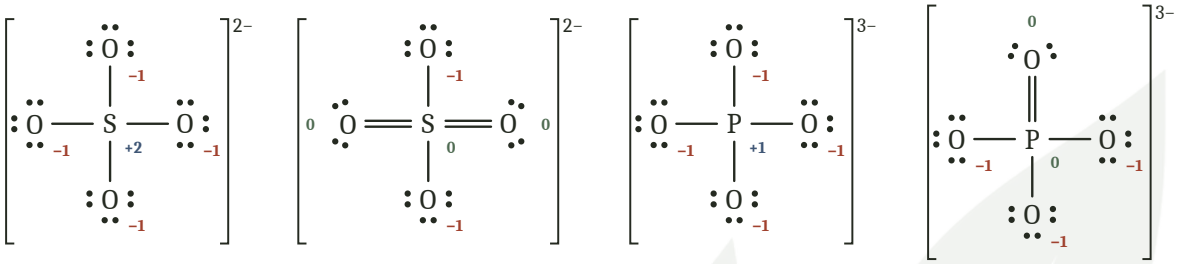
3.4 Formal charge and the exceptions to the octet rule

Why is BF_3 happy with an incomplete octet? Giving boron an octet by forming a B=F double bond produces formal charges of −1 on B and **+1 on F**, the most electronegative element of all. The structure with three single bonds has every formal charge zero, so it is preferred, even though boron has only six electrons.



preferred: all formal charges 0 — not preferred: +1 on F

Sulfate and phosphate. The same calculation favours structures with an expanded octet on the central atom:



SO_4^{2-} octet: S +2 — SO_4^{2-} expanded: S 0 — preferred — PO_4^{3-} octet: P +1 — PO_4^{3-} one P=O: P 0 — preferred

In the preferred sulfate structure the two double bonds can be placed in six different ways, so sulfate is a resonance hybrid and all four S–O bonds are found experimentally to be identical. The formal charges always sum to the ionic charge: −2 for sulfate and −3 for phosphate.

3.5 The limits of formal charge

Formal charge ignores electronegativity, so it does not give the full picture. Carbon monoxide is a good warning. Its best Lewis formula, C≡O with a lone pair on each atom, gives carbon a formal charge of −1 and oxygen +1 — the "wrong" way round by electronegativity — yet it is the only structure in which both atoms have an octet, and it correctly predicts the very strong triple bond. Similarly, ozone, O_3, which contains only one element, is polar: the central O carries a formal charge of +1 and the end atoms share −1 between them through resonance, and the molecule is bent.



carbon monoxide — one resonance structure of ozone

3.6 Formal charge and oxidation state: two opposite models

This answers the Structure 3.1 / Reactivity 3.2 linking question. Both quantities share out the electrons in a structure, but they make opposite assumptions:

	Formal charge	Oxidation state (Structure 3.1)
Assumption	every bond is **purely covalent**: bonding electrons are shared **equally**	every bond is **ionic**: bonding electrons are transferred completely to the **more electronegative** atom
C in CO_2	4 − (4 + 0) = **0**	**+4**
N in NH_4^+	5 − (4 + 0) = **+1**	**−3**
Used for	choosing the preferred Lewis formula	tracking electron transfer in redox reactions

Neither model gives the real charge on an atom, which lies somewhere between the two. Both are useful in the right circumstances.

> **Nature of Science — Occam's razor**
>
> Choosing formal charge in one situation and oxidation numbers in another applies the principle of **Occam's razor**: the simplest explanation that does the job is usually the most appropriate, because it maximises the explanatory power of the theory. Chemists do not insist on one "true" model; they use the simplest model that answers the question being asked.

> **Examiner traps in 2.2.14**
>
> - Using the total number of bonding electrons for B without halving it. Each bond contributes **one** electron to the atom.
> - Forgetting that a coordination bond still contributes one electron to each atom for formal charge.
> - Formal charges that do not add up to the overall charge. Always check the sum.
> - Confusing formal charge with oxidation state, or with the real charge on the atom.
> - Choosing between equal-magnitude structures without using electronegativity.

4 Structure 2.2.15 — Sigma and pi bonds HL

4.1 Bonds as overlapping orbitals

VSEPR predicts angles of 109.5° and 120°, yet atomic orbitals are spherical (s) or dumb-bell shaped at 90° to each other (p). To explain the angles, we need a picture of what happens to the orbitals when a bond forms. In simple terms, a covalent bond forms when two atomic orbitals, each containing one electron, **overlap** and combine to form a new **molecular orbital** at a lower energy, which holds the shared pair. There are two ways the orbitals can overlap, giving two types of covalent bond.

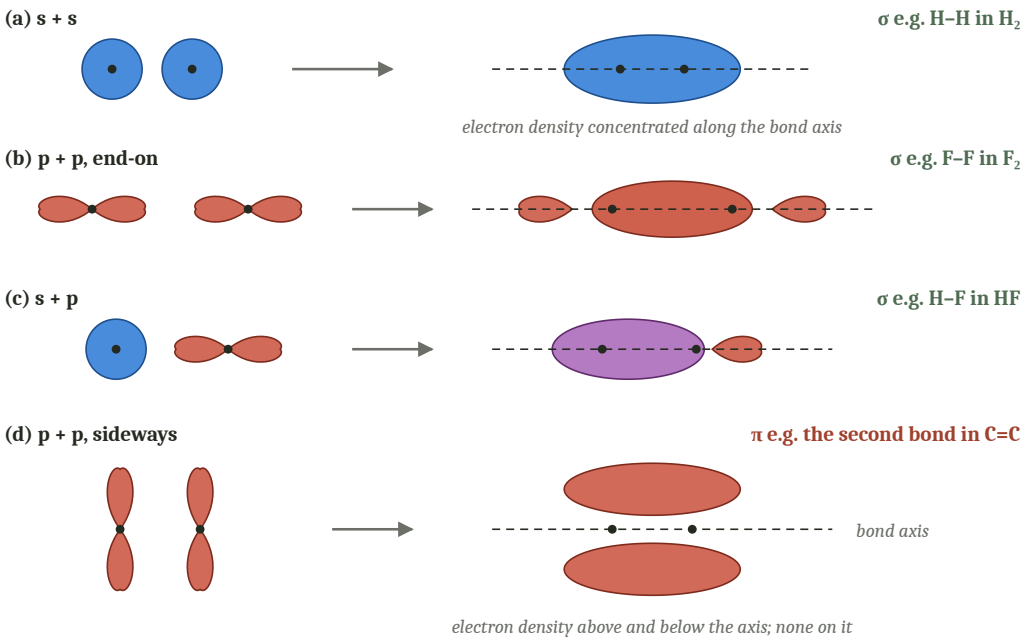


Figure 1 — Sigma bonds form by head-on overlap (a)–(c); a pi bond forms by sideways overlap of parallel p orbitals (d).

Definitions — learn the guide wording

- **Sigma (σ) bond** — formed by the **head-on** combination of atomic orbitals, with the electron density concentrated **along the bond axis** (the line joining the two nuclei). It can form from s, p or hybrid orbitals.
- **Pi (π) bond** — formed by the **lateral** (sideways) combination of **p orbitals**, with the electron density concentrated in two regions **on opposite sides** of the bond axis. Although it has two lobes, a π bond is **one** bond containing one pair of electrons.

4.2 Which orbitals form which bond

Orbitals that combine	Type of bond	Examples
s and s	σ	H–H in H_2
s and p	σ	H–Cl in HCl, H–F in HF
p and p, head-on	σ	Cl–Cl in Cl_2, F–F in F_2
hybrid and s	σ	C–H in CH_4, N–H in NH_4^+
hybrid and hybrid	σ	C–C in C_2H_6; one of the bonds in C=C and C≡C
p and p, sideways	π	the second bond in C=C (C_2H_4) and C=O; the second and third bonds in C≡C (C_2H_2) and N≡N

Any overlap of a hybrid orbital with another orbital (s, p or hybrid) always forms a σ bond, because hybrid orbitals point directly at the neighbouring atom.

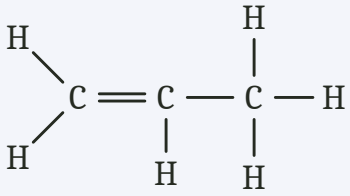
4.3 Counting σ and π bonds

The rule

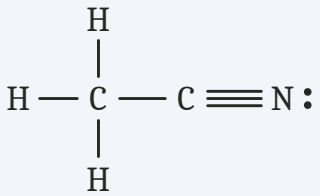
A **single bond** is always one σ bond. A **double bond** is one σ bond + one π bond. A **triple bond** is one σ bond + two π bonds. A π bond can only form alongside a σ bond, so π bonds occur only in multiple bonds.

Species	Bonds present	σ	π
N_2	N≡N	1	2
CO_2	two C=O	2	2
HCN	C–H, C≡N	2	2
C_2H_4 (ethene)	four C–H, C=C	5	1
C_2H_2 (ethyne)	two C–H, C≡C	3	2
CO_3^{2-}	three C–O (one π delocalized over all three)	3	1
C_6H_6 (benzene)	six C–C, six C–H; π electrons delocalized	12	3 (delocalized)

Worked example — propene, $CH_3CH{=}CH_2$, and ethanenitrile, CH_3CN



Propene: six C–H (6 σ), one C–C (1 σ), one C=C (1 σ + 1 π). Total: **8 σ, 1 π**.



Ethanenitrile: three C–H (3 σ), one C–C (1 σ), one C≡N (1 σ + 2 π). Total: **5 σ, 2 π**. Always draw the full structural formula first, so that no bond is missed.

4.4 Why a π bond is weaker than a σ bond — and why it matters

In a σ bond the shared pair lies directly between the two nuclei, where the overlap is greatest. In a π bond the electron density lies above and below the axis, **further from the nuclei**, and the sideways overlap is less effective. The electrostatic attraction is therefore weaker, so a π bond is **weaker than a σ bond**. The data booklet shows this: C=C (614 kJ mol^{-1}) is less than twice C–C (2 × 346 = 692 kJ mol^{-1}), so the π part contributes only about 268 kJ mol^{-1}.

- **Reactivity.** The π electrons are more exposed and more easily broken. This is why alkenes undergo addition reactions much more readily than alkanes, and why the region of π electron density attracts **electrophiles** (Reactivity 3.4).
- **No rotation.** Rotating one end of a C=C bond would twist the p orbitals out of alignment and break the π bond. So there is **no free rotation about a double bond**, which is why cis–trans isomers, such as those of 1,2-dichloroethene in Booklet 2, exist as separate compounds (Structure 3.2). Free rotation is possible about a single σ bond.

Examiner traps in 2.2.15

- Counting a double bond as two σ bonds, or a triple bond as three π bonds.
- Saying a π bond has "two bonds" because it has two lobes. It is one bond, one pair of electrons.
- Saying π bonds can form from s orbitals or hybrid orbitals. They form only from the sideways overlap of **p** orbitals.
- Describing a σ bond as "a single bond" without saying how it forms: head-on overlap, electron density along the axis.
- Forgetting C–H bonds when counting σ bonds in organic molecules.

5 Structure 2.2.16 — Hybridization HL

5.1 The problem: carbon forms four identical bonds

In its ground state, carbon ($1s^2\ 2s^2\ 2p^2$) has only **two** singly occupied orbitals, so we might expect it to form only two bonds. In almost all its compounds, however, carbon forms **four**. The first step in explaining this is **excitation**: one 2s electron is promoted to the empty 2p orbital, giving four singly occupied orbitals. The energy needed for this is more than repaid by the energy released when two extra bonds form.

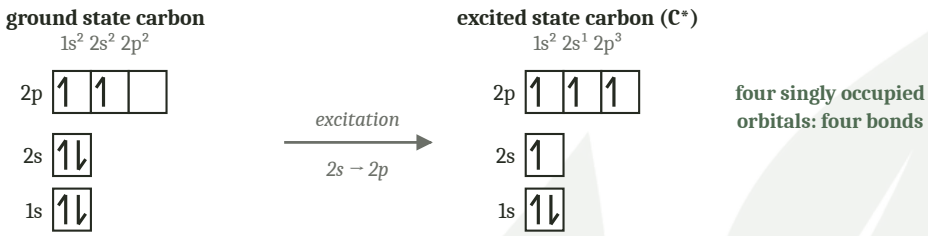


Figure 2 — Excitation of carbon: a 2s electron is promoted to the empty 2p orbital.

But excitation alone does not explain methane. The four orbitals now available are **not** the same — one 2s and three slightly higher-energy 2p orbitals at 90° to each other — so we would expect one C–H bond to differ from the other three, and angles of 90°. In fact all four C–H bonds in CH_4 are identical and the angles are 109.5°.

5.2 Hybridization: mixing atomic orbitals

Definition — learn the guide wording

Hybridization is the concept of **mixing atomic orbitals** within an atom to form new **hybrid orbitals** for bonding. The hybrid orbitals are identical to one another, have energies intermediate between those of the orbitals that mixed, and have new shapes and orientations that allow greater overlap, and so stronger bonds.

A useful analogy: mixing one bucket of white paint with three buckets of red gives four identical buckets of pink. Each sp^3 orbital similarly has a share of s and p character — more p than s. The number of hybrid orbitals formed always equals the number of atomic orbitals mixed.

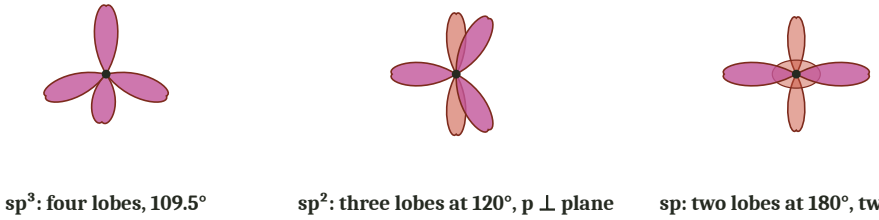
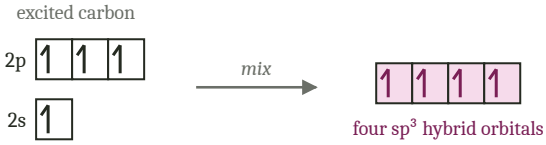


Figure 3 — Hybrid orbitals (magenta) and the unhybridized p orbitals left over (red).

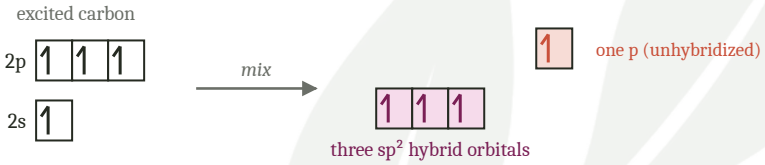
5.3 sp^3 hybridization — four electron domains, tetrahedral



One s and three p orbitals mix to form **four sp^3 hybrid orbitals**. They point to the corners of a **tetrahedron**, at **109.5°**, and each overlaps head-on with an orbital of another atom, forming four **σ bonds**. Examples: CH_4, C_2H_6 (each C), diamond, NH_4^+.

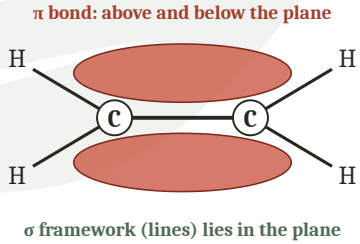
Lone pairs can occupy hybrid orbitals too. In NH_3 the nitrogen is sp^3 hybridized: three sp^3 orbitals form N–H σ bonds and the fourth holds the lone pair. In H_2O the oxygen is sp^3 hybridized, with two of its four sp^3 orbitals holding lone pairs. This is why the hybridization follows the **number of electron domains**, not the number of bonded atoms.

5.4 sp^2 hybridization — three electron domains, triangular planar



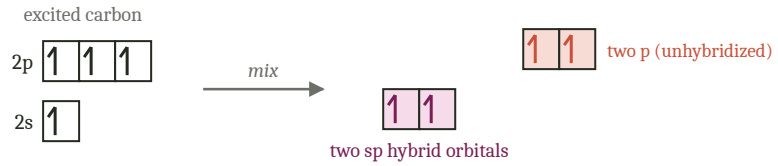
One s and two p orbitals mix to form **three sp^2 hybrid orbitals** in a plane at **120°**; one p orbital is left **unhybridized**, at 90° to that plane. The sp^2 orbitals form σ bonds; the leftover p orbital can overlap sideways with a p orbital on a neighbouring atom to form a **π bond**.

Ethene, C_2H_4: each carbon is sp^2. On each C, two sp^2 orbitals overlap with H 1s orbitals (two C–H σ bonds) and the third overlaps with an sp^2 orbital of the other C (the C–C σ bond). The two unhybridized p orbitals, one on each C, overlap sideways above and below the plane to form the **π bond**. So the double bond is one σ + one π, and all six atoms lie in one plane.



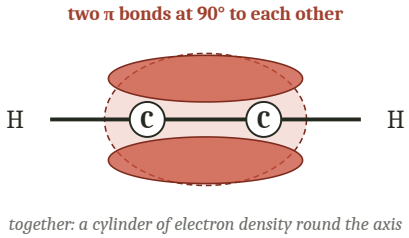
Other sp^2 examples: BF_3, the carbon in HCHO and in CO_3^{2-}, N in NO_3^-, S in SO_2 (two bonds and a lone pair: three domains), and each carbon in graphite, graphene and benzene.

5.5 sp hybridization — two electron domains, linear



One s and one p orbital mix to form **two sp hybrid orbitals** at **180°**; two p orbitals are left unhybridized, at 90° to each other and to the bond axis. The sp orbitals form two σ bonds; the two p orbitals can form **two π bonds**.

Ethyne, C_2H_2: each carbon is sp. One sp orbital forms the C–H σ bond and the other forms the C–C σ bond. The two pairs of un-hybridized p orbitals overlap sideways to form two π bonds at 90° to each other, which merge into a **cylinder** of electron density around the C–C axis. The triple bond is one σ + two π. This exposed electron density makes ethyne susceptible to attack by electrophiles.



Other sp examples: $BeCl_2$, the carbon in CO_2 and HCN, and the C and N of the C≡N group.

5.6 Predicting hybridization — and geometry from hybridization

The relationship to learn

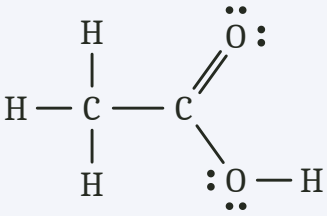
number of electron domains ↔ electron-domain geometry ↔ hybridization

2 domains ↔ linear ↔ sp · 3 domains ↔ triangular planar ↔ sp^2 · 4 domains ↔ tetrahedral ↔ sp^3

To find the hybridization of any atom: draw the Lewis formula, count the electron domains on that atom (lone pairs + bonds of any order, each counting one), and read off the hybridization. Working the other way, an atom known to be sp^2 must have three domains in a triangular planar arrangement.

Species	Atom	Domains	Electron-domain geometry	Molecular geometry	Hybridization
CO_2	C	2	linear	linear	sp
HCN	C	2	linear	linear	sp
NO_3^-	N	3	triangular planar	triangular planar	sp^2
SO_2	S	3	triangular planar	bent	sp^2
NH_4^+	N	4	tetrahedral	tetrahedral	sp^3
NH_3	N	4	tetrahedral	trigonal pyramidal	sp^3
H_2O	O	4	tetrahedral	bent	sp^3

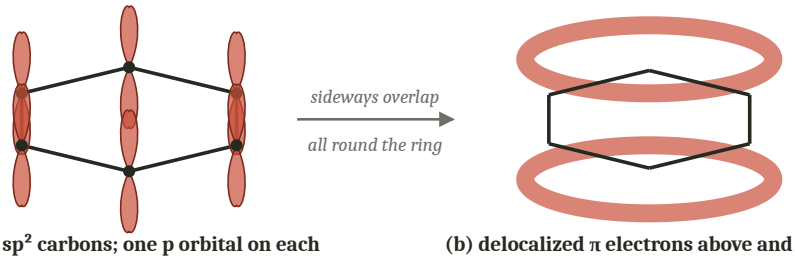
Worked example — the hybridization of every non-hydrogen atom in ethanoic acid, CH_3COOH



- **CH_3 carbon:** four single bonds, 4 domains → **sp^3**, tetrahedral, ≈ 109.5°.
- **Carboxyl carbon:** C–C, C=O and C–O, 3 domains → **sp^2**, triangular planar, ≈ 120°.
- **Carbonyl oxygen (C=O):** one double bond + two lone pairs, 3 domains → **sp^2**.
- **Hydroxyl oxygen (O–H):** two single bonds + two lone pairs, 4 domains → **sp^3**, bent, ≈ 104.5°.

An atom that forms a π bond cannot be sp^3, because it needs an unhybridized p orbital for the sideways overlap.

Hybridization in benzene and the carbon allotropes



(a) six sp^2 carbons; one p orbital on each **(b) delocalized π electrons above and below**

Figure 4 — Benzene: six sp^2 carbons form a planar σ framework; their p orbitals overlap all round the ring, delocalizing the π electrons above and below the plane.

Each carbon in benzene is **sp^2** hybridized and forms three σ bonds at 120° (two C–C and one C–H), making the molecule planar. Each carbon has one unhybridized p electron in a p orbital perpendicular to the ring. Instead of pairing up into three separate π bonds, the six p orbitals overlap in both directions, forming a **delocalized π system** in two doughnut-shaped regions above and below the ring. This is the orbital picture behind the resonance hybrid of Booklet 3: six identical C–C bonds and extra stability. The same idea describes graphite and graphene (sp^2, delocalized π electrons, electrical conductivity), while diamond is sp^3 with only σ bonds (Booklet 2).

Cyclohexane vs benzene. Cyclohexane, C_6H_{12}, has only single bonds. Each carbon is sp^3 with bond angles of about 109.5°, which a flat hexagon (120°) cannot accommodate, so the ring is **puckered**. Benzene's sp^2 carbons need 120° angles, which a flat hexagon gives exactly, so benzene is **planar**.

5.7 A model, not a mechanism

Nature of Science and TOK — what is an orbital, really?

Hybridization has a sound mathematical foundation: it corresponds to combining wave functions to produce new wave functions in quantum mechanics. Because that mathematics is complex, it is usually presented as an imaginary "mixing" process. The model is justified by how well it explains geometries that are consistent with observation. Orbitals themselves are not physical objects; they are descriptions of where an electron is likely to be found. Words such as "mixing", "lobes" and "overlap", like "buckets of paint", are convenient images. They can help understanding, but they can also mislead if taken literally — a good example of language shaping, and sometimes masking, what a scientific model actually says.

Molecules with five or six domains (PCl_5, SF_6) would need hybrid orbitals that include d orbitals. These are beyond the IB course: only sp, sp^2 and sp^3 are required.

Examiner traps in 2.2.16

- Deducing hybridization from the number of **atoms** bonded instead of the number of **electron domains**. NH_3 has three bonded atoms but four domains: sp^3, not sp^2.
- Counting a double bond as two domains when deciding hybridization. The C in CO_2 has two domains: sp.
- Saying the unhybridized p orbital in an sp^2 carbon "forms a σ bond". It forms the **π** bond.
- Describing hybridization as electrons "mixing". It is **orbitals** that mix.
- Giving sp^3d or other d-containing hybrids in an IB answer. Only sp, sp^2 and sp^3 are required.

6 Bringing it all together HL

One chain of reasoning for any species

Count valence electrons → Lewis formula, allowing an expanded octet for period 3+ central atoms → if several Lewis formulas are possible, choose the one with **formal charges closest to zero → count domains** on each central atom → **electron-domain geometry** and **molecular geometry** (2–6 domains) → **hybridization** (2–4 domains) → **σ and π bonds** → polarity, reactivity and isomerism.

Species	Domains (central atom)	Molecular geometry	Hybridization	σ / π	Polar?
$BeCl_2$	2	linear	sp	2 / 0	no
HCN	2 (C)	linear	sp	2 / 2	yes
HCHO	3 (C)	triangular planar	sp^2	3 / 1	yes
SO_3	3	triangular planar	sp^2	3 / 3 (expanded) *	no
CH_4	4	tetrahedral	sp^3	4 / 0	no
H_2O	4	bent	sp^3	2 / 0	yes
PCl_5	5	triangular bipyramidal	—	5 / 0	no
SF_4	5	see-saw	—	4 / 0	yes
XeF_4	6	square planar	—	4 / 0	no

* For SO_3, formal charge favours the structure with three S=O double bonds (S has 12 electrons, all formal charges zero), giving 3 σ and 3 π bonds. The octet-only structure would have one S=O (3 σ, 1 π). Either way S has three domains and is sp^2, and the molecule is triangular planar and non-polar.

7 Key points to memorise

Everything below is either wording that examiners look for, or knowledge you must carry into the exam yourself.

A Definitions — near-verbatim

- **Expanded octet:** more than eight electrons in the valence shell of a central atom; possible for elements in period 3 and below, which have d orbitals in their valence shell.
- **Formal charge:** FC = V − (½B + L); the charge an atom would have if all bonding electrons were shared equally.
- **Sigma (σ) bond:** head-on combination of atomic orbitals; electron density concentrated along the bond axis.
- **Pi (π) bond:** lateral combination of p orbitals; electron density concentrated on opposite sides of the bond axis.
- **Hybridization:** the mixing of atomic orbitals to form new, identical hybrid orbitals for bonding.

B Five and six domains

- 5 domains, triangular bipyramidal: 5/0 triangular bipyramidal (90°, 120°); 4/1 see-saw; 3/2 T-shaped; 2/3 linear. **Lone pairs go equatorial.**
- 6 domains, octahedral: 6/0 octahedral (90°); 5/1 square pyramidal; 4/2 square planar. **Two lone pairs go opposite each other.**
- Non-polar despite lone pairs: XeF_2, I_3^-, XeF_4. Polar: SF_4, ClF_3, BrF_5.

C Formal charge rules

- ½B = number of bonds; L = lone-pair electrons. Sum of formal charges = overall charge.
- Preferred structure: formal charges closest to zero; then negative charge on the more electronegative atom.
- Formal charge assumes equal sharing (pure covalent); oxidation state assumes complete transfer (ionic). Neither is the real charge.

D σ, π and hybridization in one table

Domains	Geometry	Hybrid	Unhybridized p	Typical bonding	Examples
4	tetrahedral, 109.5°	sp^3	none	σ bonds only	CH_4, NH_3, H_2O, diamond
3	triangular planar, 120°	sp^2	one	σ + one π (double bond)	C_2H_4, BF_3, benzene, graphite
2	linear, 180°	sp	two	σ + two π (triple bond, or two double bonds)	C_2H_2, CO_2, HCN, $BeCl_2$

Single = 1σ · double = 1σ + 1π · triple = 1σ + 2π. π bonds are weaker than σ bonds and prevent rotation about a double bond.

E Command terms — what each one is actually asking for

- **Deduce** (a shape) — Lewis formula, domain count, electron-domain geometry, then molecular geometry and angle.
- **Apply** (formal charge) — calculate the formal charge on *every* atom in *each* structure, then state which is preferred and why.
- **Compare** (σ and π) — how each forms (head-on vs sideways), where the electron density lies, and relative strength.
- **Identify** (σ and π bonds) — give the numbers of each.
- **Analyse / Explain** (hybridization) — which orbitals mix, how many hybrid orbitals form, their geometry, and which bonds they form.

8 Check yourself

Cover the answers on the next pages. Marks are shown in brackets where a question is written in exam style. All questions in this booklet are Higher Level.

1. Explain why phosphorus can form PCl_5 but nitrogen cannot form NCl_5. **[2]**
2. Deduce the Lewis formula, the electron-domain geometry, the molecular geometry and the bond angle(s) of: (a) SeF_4 (b) ICl_4^- (c) BrF_3 (d) IF_5 (e) PCl_6^- (f) KrF_2
3. Explain why the lone pair in SF_4 occupies an equatorial rather than an axial position. **[2]**
4. Which molecule has an octahedral electron-domain geometry but a square planar molecular geometry?
   A SF_6 B XeF_4 C SF_4 D BrF_5
5. State whether each molecule is polar, with a reason: (a) SF_6 (b) ClF_3 (c) XeF_2 (d) PCl_3F_2, with both F atoms axial.
6. Calculate the formal charge on each atom in: (a) NH_4^+ (b) CO (c) XeF_4
7. Draw two Lewis formulas for the sulfate ion, SO_4^{2-}: one in which every atom obeys the octet rule, and one in which sulfur has 12 electrons. Use formal charges to deduce the preferred structure. **[3]**
8. Use formal charge to explain why BF_3 is an exception to the octet rule. **[2]**
9. Three Lewis formulas can be drawn for the cyanate ion, OCN^-, with the skeleton O–C–N: $[O{=}C{=}N]^-$, $[O{-}C{\equiv}N]^-$ and $[O{\equiv}C{-}N]^-$. Calculate the formal charges on each atom in each structure, and deduce which is preferred. **[4]**
10. State the formal charge and the oxidation state of carbon in CO_2, and explain why they differ. **[3]**
11. Which combinations of orbitals form a σ bond? I. a hybrid orbital and an s orbital II. two p orbitals overlapping sideways III. an s orbital and a p orbital
    A I and II only B I and III only C II and III only D I, II and III
12. State the numbers of σ and π bonds in: (a) propyne, $CH_3C{\equiv}CH$ (b) propenenitrile, $CH_2{=}CHCN$ (c) trans-but-2-ene-1,4-dioic acid, HOOC–CH=CH–COOH
13. Compare the formation of the σ and π bonds between the carbon atoms in ethene. **[2]**
14. Explain why a carbon–carbon π bond is weaker than a carbon–carbon σ bond, and why there is no free rotation about a C=C double bond. **[3]**

15. State the hybridization of the atom named in each: (a) C in HCHO (b) B in BH_4^- (c) S in SO_3 (d) Be in $BeCl_2$ (e) N in NH_3 (f) each C in CH_3CN

16. Explain, in terms of hybridization, why all four C–H bonds in methane are identical and at 109.5°. **[3]**

17. Cyclohexane, C_6H_{12}, has a puckered ring, whereas benzene, C_6H_6, is planar. Explain this difference with reference to bond angles and hybridization. **[3]**

18. Consider methanamide, $HCONH_2$. (a) Draw its Lewis formula. (b) State the numbers of σ and π bonds. (c) State the hybridization of the carbon and nitrogen atoms. **[5]**

19. Explain how hybridization accounts for the bonding in the triple bond of propyne. **[3]**

9 Answers

1. Phosphorus is in period 3, so its valence shell (n = 3) has empty 3d orbitals available, allowing more than eight electrons around it **[1]**. Nitrogen is in period 2; the second shell has no d sublevel, so nitrogen cannot exceed an octet **[1]**.

2. (a) SeF_4: 34 e, 4 bonds + 1 lone pair; triangular bipyramidal; **see-saw**; < 90° and < 120° (b) ICl_4^-: 36 e, 4 bonds + 2 lone pairs; octahedral; **square planar**; 90° (c) BrF_3: 28 e, 3 bonds + 2 lone pairs; triangular bipyramidal; **T-shaped**; < 90° (d) IF_5: 42 e, 5 bonds + 1 lone pair; octahedral; **square pyramidal**; < 90° (e) PCl_6^-: 48 e, 6 bonds; octahedral; **octahedral**; 90° (f) KrF_2: 22 e, 2 bonds + 3 lone pairs; triangular bipyramidal; **linear**; 180°. In each Lewis formula every F or Cl has three lone pairs.

3. Lone pairs repel more strongly than bonding pairs, and repulsions at 90° are the most significant **[1]**. In an equatorial position the lone pair has only two bonding pairs at 90°, compared with three in an axial position, so repulsion is minimised **[1]**.

4. **B.** Six domains, two of them lone pairs, opposite each other.

5. (a) non-polar: octahedral, six identical S–F dipoles cancel (b) polar: T-shaped, dipoles do not cancel (c) non-polar: linear, the two Xe–F dipoles cancel (d) non-polar: the two axial P–F dipoles cancel each other and the three equatorial P–Cl dipoles cancel each other.

6. (a) N: 5 − (4 + 0) = +1; each H: 1 − (1 + 0) = 0; sum +1 (b) C: 4 − (3 + 2) = −1; O: 6 − (3 + 2) = +1; sum 0 (c) Xe: 8 − (4 + 4) = 0; each F: 7 − (1 + 6) = 0.

7. Octet structure: four S–O single bonds; S +2, each O −1 **[1]**. Expanded structure: two S=O and two S–O; S 0, the two double-bonded O 0, the two single-bonded O −1 **[1]**. The expanded structure has formal charges closer to zero, so it is preferred **[1]**.

8. With three B–F single bonds, every atom has a formal charge of zero **[1]**. Giving boron an octet with a B=F double bond would give B −1 and F +1, placing a positive formal charge on the most electronegative element, so the incomplete octet structure is preferred **[1]**.

9. $[O{=}C{=}N]^-$: O 0, C 0, N −1 **[1]**. $[O{-}C{\equiv}N]^-$: O −1, C 0, N 0 **[1]**. $[O{\equiv}C{-}N]^-$: O +1, C 0, N −2 **[1]**. The third is least favoured. The first two have charges of the same magnitude, but $[O{-}C{\equiv}N]^-$ places the negative charge on the more electronegative atom, oxygen (3.4 vs 3.0), so it is preferred **[1]**.

10. Formal charge 4 − (4 + 0) = 0 **[1]**; oxidation state +4 **[1]**. Formal charge assumes the bonding electrons are shared equally; oxidation state assumes they are transferred completely to the more electronegative oxygen atoms **[1]**.

11. **B.** Sideways overlap of p orbitals forms a π bond.

12. (a) 6 σ, 2 π (four C–H, one C–C, one C≡C) (b) 6 σ, 3 π (three C–H, C=C, C–C, C≡N) (c) 11 σ, 3 π (two O–H, two C–O, two C=O, two C–C, one C=C, two C–H).

13. The σ bond forms by head-on overlap of sp^2 hybrid orbitals, with electron density along the axis between the two carbon nuclei **[1]**. The π bond forms by sideways overlap of the two unhybridized p orbitals, with electron density above and below the plane of the molecule **[1]**.

14. In a π bond the electron density lies above and below the bond axis, further from the nuclei, and the sideways overlap is less effective than head-on overlap **[1]**, so the attraction between the nuclei and the shared pair is weaker **[1]**. Rotation about C=C would twist the p orbitals out of alignment and break the π bond, so it cannot occur without breaking a bond **[1]**.

15. (a) sp^2 (b) sp^3 (c) sp^2 (d) sp (e) sp^3 (three bonds + one lone pair) (f) CH_3 carbon sp^3; C≡N carbon sp.

16. One 2s electron of carbon is promoted to the empty 2p orbital, giving four unpaired electrons **[1]**. The 2s and three 2p orbitals mix to form four identical sp^3 hybrid orbitals **[1]**, which point to the corners of a tetrahedron at 109.5° and each overlaps with an H 1s orbital to form four identical σ bonds **[1]**.

17. In cyclohexane each carbon is sp^3 hybridized, with bond angles of about 109.5° **[1]**; a flat hexagon would require 120°, so the ring puckers to relieve the strain **[1]**. In benzene each carbon is sp^2 hybridized with 120° bond angles, which a flat hexagon provides exactly, and the delocalized π system requires the p orbitals to be parallel, so the ring is planar **[1]**.
18. (a) H–C(=O)–NH_2, with two lone pairs on O and one lone pair on N **[2]**. (b) 5 σ (C–H, C=O, C–N, two N–H) and 1 π **[1]**. (c) C: three domains, sp^2 **[1]**; N: three bonds + one lone pair, four domains, sp^3 by VSEPR **[1]**. (In reality the nitrogen in an amide is nearly planar because its lone pair is partly delocalized, but for IB answers use the domain count.)
19. Each carbon of the C≡C is sp hybridized: one 2s and one 2p orbital mix to form two sp orbitals at 180° **[1]**. One sp orbital on each carbon overlaps head-on to form the C–C σ bond (the other forms a σ bond to H or to the CH_3 carbon) **[1]**. The two remaining unhybridized p orbitals on each carbon overlap sideways to form two π bonds at 90° to each other **[1]**.

Structure 2.2 is complete

- **Booklet 1** — covalent bonds, Lewis formulas, multiple bonds, coordination bonds (2.2.1–2.2.3).
- **Booklet 2** — VSEPR, bond and molecular polarity, covalent networks (2.2.4–2.2.7).
- **Booklet 3** — intermolecular forces, physical properties, chromatography; HL resonance and benzene (2.2.8–2.2.12).
- **Booklet 4** — HL expanded octets, formal charge, σ and π bonds, hybridization (2.2.13–2.2.16).
- Next in the course: **Structure 2.3 — the metallic model**, then Structure 2.4 (the bonding triangle). Links forward: Structure 3.1 (transition element complexes, oxidation states), Structure 3.2 (cis–trans isomers, infrared spectroscopy), Reactivity 3.4 (electrophilic addition and substitution).

These notes are a free resource, shared for any IB student who finds them useful.

If a particular idea here still isn't clicking, specialist one-to-one support in Physics, Chemistry and Maths from a past A Level examiner is available at iBLaurel — call or message **+44 7404 710097**, or use the contact form at **www.iBLaurel.com**.

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