

Advanced Bonding Theories

CHEM 50 · Dr. Karmach

By the end of this unit, you can...

- Assign sp , sp^2 , or sp^3 hybridization to a central atom from its number of electron domains
- Count sigma and pi bonds in a molecule from its Lewis structure
- Build the molecular-orbital occupation of a second-period diatomic and compute its bond order
- Predict paramagnetism or diamagnetism from a molecular-orbital diagram

Today's route

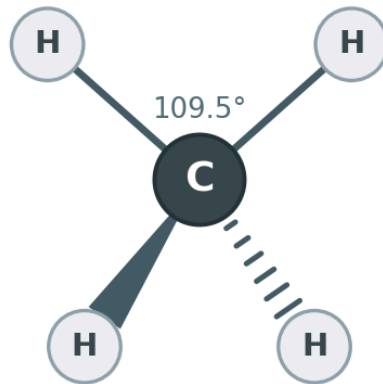
1. Hybridization
2. Sigma & Pi Bonds
3. Molecular Orbitals & Bond Order
4. MO Diagrams & Magnetism

1 • Hybridization

Assign sp , sp^2 , sp^3 , sp^3d , or sp^3d^2 hybridization to a central atom by counting its electron domains.

Four identical bonds

methane — natural gas
four identical C-H bonds



same length · same strength · one shape, tetrahedral

Natural gas is methane. Its carbon makes four bonds of equal length and strength, spread evenly in space, yet carbon's electrons began in two different kinds of orbitals.

Domain counts from VSEPR

**2 domains: linear, 180° · 3: trigonal planar, 120° · 4: tetrahedral, 109.5°
5: trigonal bipyramidal, 120° and 90° · 6: octahedral, 90° · domains = bonded atoms + lone pairs, a
multiple bond counted once**

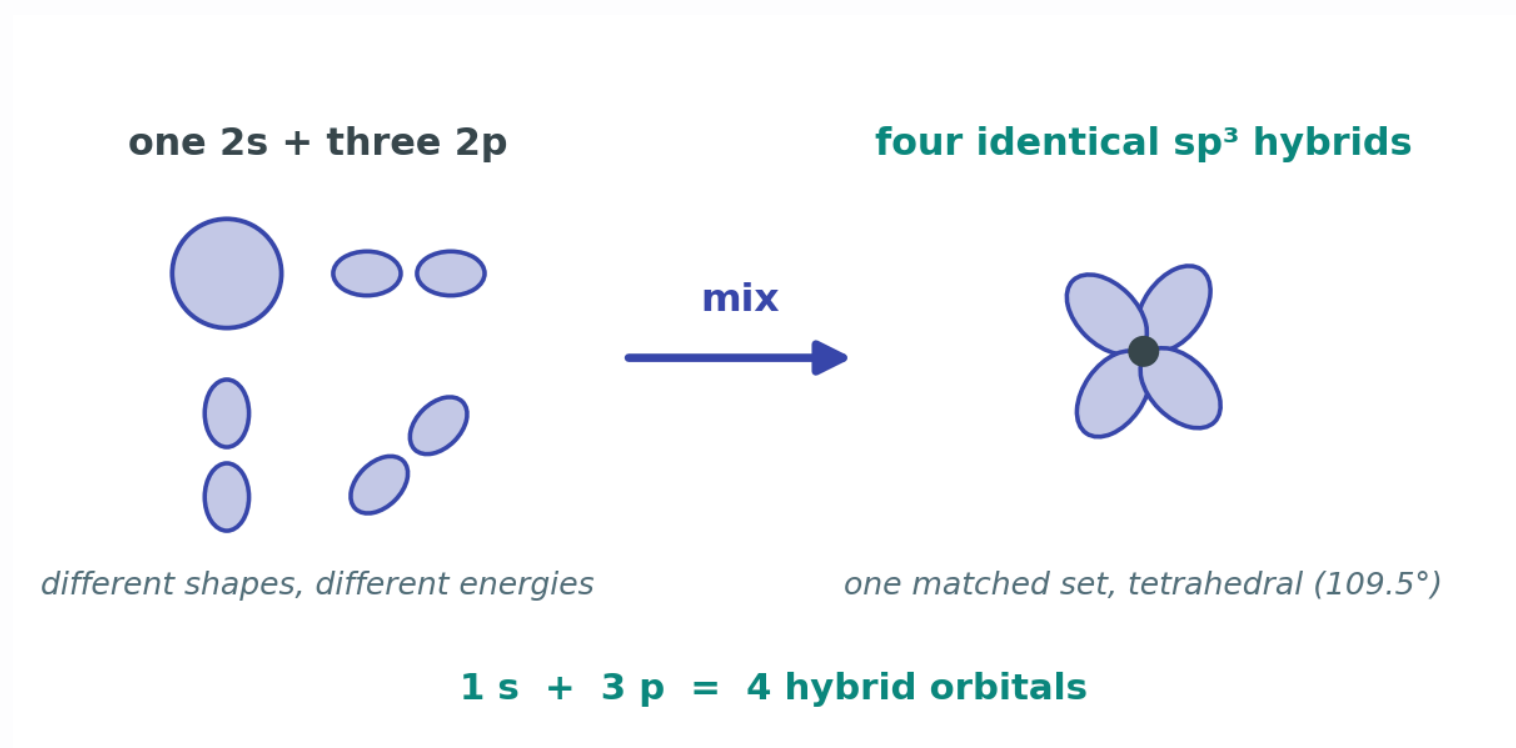
VSEPR counts the electron domains on a central atom and spreads them apart. The three p orbitals point 90° apart, so they cannot aim along 109.5° or 120° . Hybridization starts from the same count.

Electron domains set the hybridization

2 domains → mix 2 orbitals · 3 domains → mix 3 · 4 domains → mix 4
the mixed orbitals are hybrids: equal in energy, each aimed at one domain

A central atom mixes its valence orbitals into new, equivalent **hybrid orbitals**. The number it makes equals its number of electron domains, and each hybrid points at one domain.

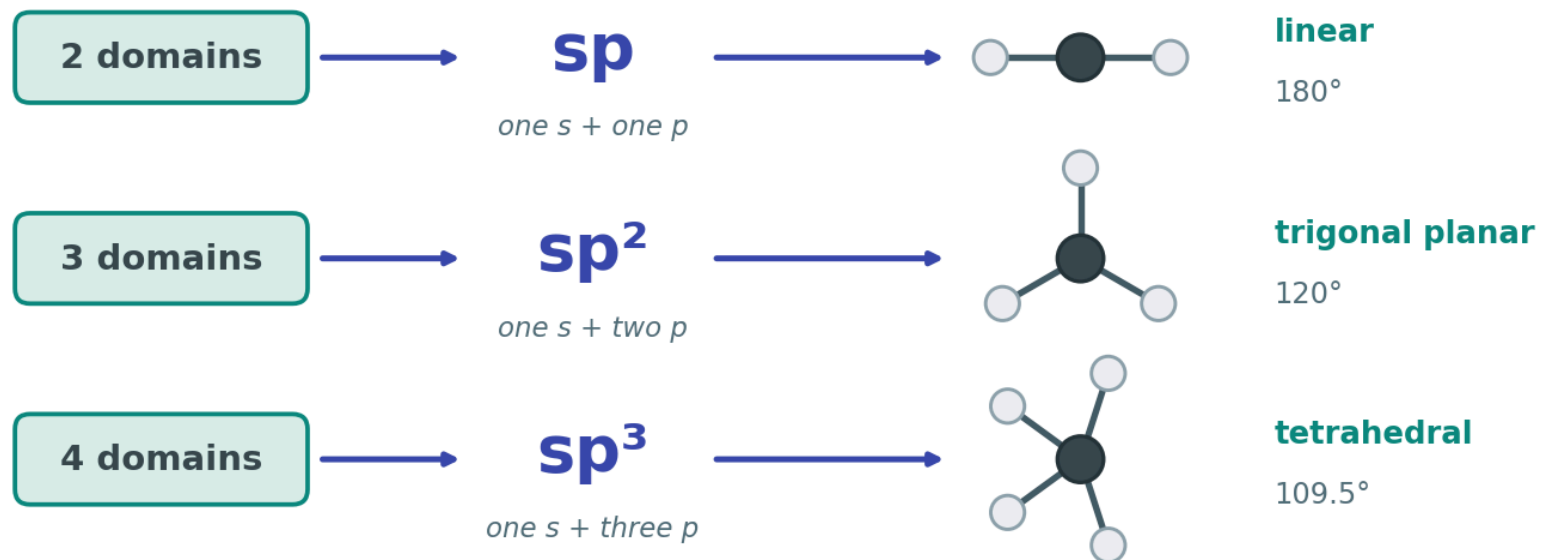
One s and three p become four alike



Pure s and p orbitals would give 90° bonds; real methane is 109.5° . So carbon mixes its one 2s and three 2p into four identical sp^3 orbitals, aimed at a tetrahedron's corners.

Two, three, or four domains

Electron domains set the hybridization



Each domain count mixes that many orbitals into one matched set: two make sp , three make sp^2 , four make sp^3 . The set points where VSEPR placed the domains: linear, trigonal planar, tetrahedral.

A lone pair is a domain

H₂O: 2 bonds + 2 lone pairs = 4 domains → sp³
bonded atoms: 2 · lone pairs on O: 2 · total electron domains: 4

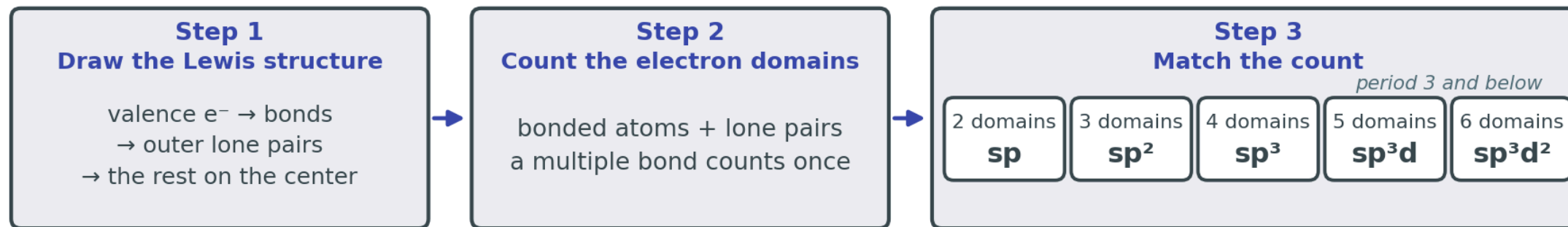
Every region of electron density around the central atom is a domain: a bond or a lone pair. Both take a hybrid orbital. Count bonds and lone pairs together.

memory hook: count the domains, not the bonds
a lone pair takes a hybrid just as a bond does · a double or triple bond is still one domain

The method

1. **Draw the Lewis structure** and find the central atom.
2. **Count the electron domains.** A lone pair counts; a multiple bond counts once.
3. **Match the count:** 2 $\rightarrow$ sp, 3 $\rightarrow$ sp², 4 $\rightarrow$ sp³, 5 $\rightarrow$ sp³d, 6 $\rightarrow$ sp³d².

Find the lone pairs, count every domain once, then match.



✗ skipping lone pairs · ✗ a double bond counted twice



Worked example 1: methane, CH₄



central atom: C · bonded atoms: 4 H · lone pairs on C: 0

Methane's carbon bonds to four hydrogen atoms with no lone pairs left over. Assign the hybridization of the carbon: count its domains, then match.

✓ Worked example 1: solution



central atom: C · bonded atoms: 4 H · lone pairs on C: 0

Step 1 · Draw the Lewis structure and find the central atom

Step 2 · Count the electron domains

4 bonded groups + 0 lone pairs = 4 domains

every bond is a single bond: four separate domains

Step 3 · Match the count

4 domains → sp^3

mix one 2s + three 2p → four equivalent sp^3 hybrids, tetrahedral

 **Sense check:** Four matched hybrids point at a tetrahedron's corners, 109.5° apart: methane's real shape.

Step 1

no lone pairs on C

Step 2

$4 + 0 = 4$

sp

sp^2

$sp^3 \cdot \text{C}$

sp^3d

sp^3d^2



Worked example 2: ammonia, NH_3



central atom: N · bonded atoms: 3 H · lone pairs on N: 1

Nitrogen bonds to three hydrogens and keeps one lone pair. Assign the hybridization of the nitrogen.

✓ Worked example 2: solution



central atom: N · bonded atoms: 3 H · lone pairs on N: 1

Step 1 · Draw the Lewis structure and find the central atom

Step 2 · Count the electron domains

3 bonded groups + 1 lone pair = 4 domains

the lone pair is a domain: counting only the 3 bonded atoms would miss it

Step 3 · Match the count

4 domains → sp^3

three sp^3 hybrids hold bonds · the fourth holds the lone pair

 **Sense check:** Same sp^3 as methane, four domains, even though one hybrid holds a lone pair instead of a bond.

Step 1	1 lone pair on N	→	Step 2	3 + 1 = 4	→	sp	sp ²	sp³ · N	sp ³ d	sp ³ d ²	× 3 bonded atoms only → sp ²
--------	------------------	---	--------	-----------	---	----	-----------------	---------------------------	-------------------	--------------------------------	---



Guided example: hydrogen selenide, H_2Se



central atom: Se · bonded atoms: 2 H

Only the formula is given. Assign the hybridization of the selenium, naming each method step as it runs: the lone pairs on Se come from the valence electrons.

✓ Guided example: solution



central atom: Se · bonded atoms: 2 H

Step 1 · Draw the Lewis structure and find the central atom

$$6 + 2(1) = 8 \text{ valence } e^- \cdot 8 - 2 \text{ bonds} \times 2 = 4 \text{ left for Se}$$

Se brings 6, each H brings 1 · H holds no lone pairs · $4 e^- = 2$ lone pairs on Se

Step 2 · Count the electron domains

Step 3 · Match the count

$$2 \text{ bonded atoms} + 2 \text{ lone pairs} = 4 \text{ domains} \rightarrow sp^3$$

both lone pairs take a hybrid · one 4s + three 4p → four sp^3 hybrids

 **Sense check:** Same count as the oxygen in water: two bonds, two lone pairs, sp^3 . The formula shows neither lone pair; the valence count finds both.



Your turn: boron trifluoride, BF_3



central atom: B · bonded atoms: 3 F · lone pairs on B: 0

step	result
count the electron domains	3 bonded + 0 lone pairs = _____ domains
match the count	_____

Fill in the domain count, then the hybridization.

3 domains $\rightarrow$ sp^2

mix one 2s + two 2p $\rightarrow$ three equivalent sp^2 hybrids, trigonal planar (120°)

 **Sense check:** Boron carries only six valence electrons here: three bonds, no lone pair, three domains, sp^2 .



⚠ Where this goes wrong

Counting only the bonded atoms. Water has two bonds, so its oxygen looks like sp . But the two lone pairs are domains too: $2 + 2 = 4$, sp^3 . Every lone pair takes a hybrid orbital.

Reading the superscript as a domain count. Four domains is not sp^4 . The superscripts count the p orbitals mixed in: one s + three p = sp^3 . There is no fourth p orbital to add.

Skipping hybridization altogether. Pure s and p orbitals would bond at 90° . Methane, BF_3 , and CO_2 bond at 109.5° , 120° , and 180° . Mixing the orbitals is what points them at the measured geometry.



Practice 1

NI_3 : nitrogen triiodide
central atom: N · bonded atoms: 3 I

What is the hybridization of the central nitrogen atom?

- A. sp^2 : three iodines bonded to the nitrogen
- B. sp^3 : three bonds and one lone pair on the nitrogen
- C. sp^4 : one s orbital plus three p orbitals, four in all
- D. Unhybridized: nitrogen bonds through pure s and p orbitals

✓ Practice 1 answer: B

NI_3 : 3 bonds + 1 lone pair = 4 domains $\rightarrow \text{sp}^3 \rightarrow \text{answer B}$

$5 + 3(7) = 26$ valence e^- · 3 bonds use 6 and 9 I lone pairs use 18 · 2 left = 1 lone pair on N

🧠 **Sense check:** Nitrogen here matches ammonia: three bonds, one lone pair, four domains, sp^3 . The lone pair counts.

Step 1

26 e^- : 1 lone pair on N

Step 2

$3 + 1 = 4$

sp

sp^2

$\text{sp}^3 \cdot \text{N}$

sp^3d

sp^3d^2

✗ A: 3 I only $\rightarrow \text{sp}^2$

Worked example 3: carbon dioxide, CO₂



central atom: C · two double bonds · lone pairs on C: 0

Carbon sits between two oxygens, joined by a double bond on each side. A common first attempt: two double bonds, count two domains each, four total. Assign the hybridization of the carbon.

✓ Worked example 3: solution



central atom: C · two double bonds · lone pairs on C: 0

A common first attempt

two double bonds, two domains each = 4 domains → sp^3 ?
counting each line of a double bond separately ✗

Step 1 · Draw the Lewis structure and find the central atom

Step 2 · Count the electron domains

Step 3 · Match the count

1 double bond + 1 double bond = 2 domains → sp
each double bond is one domain · two sp hybrids, linear (180°)

 **Sense check:** Two domains sit 180° apart. A double bond adds electrons, not a direction.

Step 1 two C=O, no lone pairs on C

Step 2 1 + 1 = 2

sp · C

sp^2

sp^3

sp^3d

sp^3d^2

✗ each C=O as 2 → sp^3

Take-home: a multiple bond is one domain

CO₂: O=C=O → 2 domains → sp
two double bonds, each one domain, not four ✓

counting each double bond as two → 4 domains → sp³
the classic error: a double or triple bond is one region of electrons ✗

A double or triple bond crowds more electrons between the same two atoms, but it stays one domain. Count regions of electron density, not lines.



Practice 2

$\text{CH}_3\text{-CH=O}$: acetaldehyde

a classmate's labels: CH_3 carbon sp^3 · carbonyl carbon sp · O sp^2 · the O keeps two lone pairs

Three atoms in acetaldehyde carry labels. Which label is wrong, and what should it be?

- A. The CH_3 carbon: sp^2 , its three hydrogens make three domains
- B. The oxygen: sp^3 , the double bond counted twice plus two lone pairs make four domains
- C. The carbonyl carbon: sp^2 , one H, one C, and one O make three domains
- D. None of them: a carbon joined by a double bond is sp , as in CO_2

✓ Practice 2 answer: C

CH₃ carbon: 3 H + 1 C = 4 → sp³ ✓ · carbonyl carbon: H + C + O = 3 domains → sp²,
 not sp · O: 1 double bond + 2 lone pairs = 3 → sp² ✓
 a double bond is one domain · the wrong label is the carbonyl carbon → answer C

 **Sense check:** Count regions, not lines. A carbon with three neighbors is sp² whatever the bond orders; only two neighbors and no lone pair make sp.

Step 1 no lone pairs on C · 2 on O

Step 2 C 4 · C=O C 3 · O 3

sp

sp² · C=O C, O

sp³ · CH₃ C

sp³d

sp³d²

✗ D: C=O carbon as sp, like CO₂

Five and six domains: sp^3d and sp^3d^2

5 domains $\rightarrow sp^3d$: one s + three p + one d · 6 domains $\rightarrow sp^3d^2$: one s + three p + two d

sp^3d aims at a trigonal bipyramid (120° and 90°) · sp^3d^2 aims at an octahedron (90°) · lone pairs still count as domains

Four hybrids use up one s and three p. A fifth or sixth domain needs d orbitals. The $n = 2$ shell has none: C, N, O, and F stop at sp^3 .

5 or 6 domains: central atoms from period 3 and below only
the atoms that expand their octets · the VSEPR frames · single bonds and lone pairs only

 Worked example 4: dichlorobromate ion, BrCl_2^- 

central atom: Br (period 4) · bonded atoms: 2 Cl · valence electrons: $7 + 2(7) + 1 = 22$

Bromine bonds to two chlorine atoms, and the ion is linear. Assign the hybridization of the bromine: find its lone pairs, count its domains, then match.

✓ Worked example 4: solution



central atom: Br (period 4) · bonded atoms: 2 Cl · valence electrons: 22

Step 1 · Draw the Lewis structure and find the central atom

$$22 - 2 \text{ bonds} \times 2 - 2 \text{ Cl} \times 6 = 6 \text{ left for Br}$$

the 1– charge adds one electron · three lone pairs on each Cl use 12 · 3 lone pairs on Br

Step 2 · Count the electron domains

Step 3 · Match the count

$$2 \text{ bonded groups} + 3 \text{ lone pairs} = 5 \text{ domains} \rightarrow \text{sp}^3\text{d}$$

10 e[–] on Br, allowed in period 4 · one 4s + three 4p + one 4d → five hybrids, trigonal bipyramidal

 **Sense check:** The three lone pairs take the equatorial hybrids and the two Cl sit on the axis: a linear ion. Read as 2 domains, it would wrongly be sp.

Step 1 22 e[–]: 3 lone pairs on Br

Step 2

$$2 + 3 = 5$$

sp

sp²

sp³

sp³d · Br

sp³d²

✗ linear read as 2 → sp

 Worked example 5: hexachlorostannate ion, SnCl_6^{2-} 

central atom: Sn (period 5) · bonded atoms: 6 Cl · valence electrons: $4 + 6(7) + 2 = 48$

Tin bonds to six chlorine atoms, and the ion carries a 2– charge. Assign the hybridization of the tin.

✓ Worked example 5: solution



central atom: Sn (period 5) · bonded atoms: 6 Cl · valence electrons: 48

Step 1 · Draw the Lewis structure and find the central atom

$$48 - 6 \text{ bonds} \times 2 - 6 \text{ Cl} \times 6 = 0 \text{ left for Sn}$$

the 2– charge adds two electrons to the 46 from the atoms · lone pairs on Sn: 0

Step 2 · Count the electron domains

Step 3 · Match the count

$$6 \text{ bonded groups} + 0 \text{ lone pairs} = 6 \text{ domains} \rightarrow sp^3d^2$$

12 electrons on Sn, allowed in period 5 · one 5s + three 5p + two 5d → six hybrids, octahedral

 **Sense check:** Six hybrids point at an octahedron's corners, every neighbor 90° away. The charge changed the electron count, not the rule: count the domains, then match.





Practice 3



central atoms: Xe in XeF_3^+ · N in FNO (skeleton F-N-O)

What are the hybridizations of the central atoms in XeF_3^+ and FNO, respectively?

- A. sp^3d^2 and sp^2
- B. sp^2 and sp^2
- C. sp^3d and sp^3
- D. sp^3d^2 and sp^3
- E. sp^3d and sp^2

✓ Practice 3 answer: E

XeF_3^+ : 3 bonded F + 2 lone pairs = 5 domains $\rightarrow sp^3d$ · FNO: 2 bonded atoms + 1 lone pair = 3 domains $\rightarrow sp^2 \rightarrow$ answer E

XeF_3^+ : $8 + 3(7) - 1 = 28$ valence e^- · 3 bonds use 6, 9 F lone pairs use 18 · 4 left = 2 lone pairs on Xe
FNO: $5 + 7 + 6 = 18$ · F-N and N=O use 6 · 5 lone pairs on F and O use 10 · 2 left = 1 lone pair on N

 **Sense check:** Count each center on its own. The charge sets the electron total; the double bond adds electrons to N but no domain, while N's lone pair adds one.

Step 1 Xe: 2 lone pairs · N: 1

Step 2 Xe $3 + 2 = 5$ · N $2 + 1 = 3$

sp

sp^2 · N

sp^3

sp^3d · Xe

sp^3d^2

✗ A: 1+ charge added $\rightarrow sp^3d^2$



Practice 4: sulfur and oxygen with fluorine

SF₆: sulfur hexafluoride · OF₂: oxygen difluoride

SF₆: central S (period 3), 6 F, $6 + 6(7) = 48$ valence e⁻ · OF₂: central O (period 2), 2 F, $6 + 2(7) = 20$ valence e⁻

Sulfur and oxygen share a group, and here each bonds only to fluorine. What hybridization do the sulfur in SF₆ and the oxygen in OF₂ use, respectively?

- A. S sp³d², O sp³: six bonds on S; two bonds + two lone pairs on O
- B. S sp³d², O sp: six bonds on S; only the two F count on O
- C. S sp³, O sp³: S capped at four, like O; two bonds + two lone pairs on O
- D. S sp³, O sp: S capped at four, like O; only the two F count on O

✓ Practice 4 answer: A

SF_6 : 6 bonded atoms + 0 lone pairs = 6 domains $\rightarrow \text{sp}^3\text{d}^2$ · OF_2 : 2 bonded atoms + 2 lone pairs = 4 domains $\rightarrow \text{sp}^3 \rightarrow$ answer A

SF_6 : six S-F bonds use 12 e^- and 18 F lone pairs use 36, none left on S · OF_2 : bonds and F lone pairs use 16 of 20, 4 left = 2 lone pairs on O

 **Sense check:** Same group, different limits. S in period 3 reaches six domains; O in period 2 has no d orbitals and stops at four, which is why OF_6 does not exist.

Step 1 S: none left · O: 2 lone pairs

Step 2 $\text{S } 6 + 0 = 6$ · $\text{O } 2 + 2 = 4$

sp

sp^2

sp^3 · O

sp^3d

sp^3d^2 · S

✗ B: O from its 2 F only $\rightarrow \text{sp}$



Practice 5: the tetrafluorobromate ion

BrF_4^- : tetrafluorobromate ion

central atom: Br (period 4) · bonded atoms: 4 F · charge: 1–

The bromine and all four fluorines lie in one plane. What is the hybridization of the bromine atom?

- A. sp^2 : a flat ion, like a trigonal planar atom
- B. sp^3 : four fluorines bonded to the bromine
- C. sp^3d : four bonds and one lone pair on the bromine
- D. sp^3d^2 : four bonds and two lone pairs on the bromine

✓ Practice 5 answer: D

BrF_4^- : 4 bonded F + 2 lone pairs = 6 domains $\rightarrow \text{sp}^3\text{d}^2 \rightarrow$ answer D

$7 + 4(7) + 1 = 36$ valence e^- · 4 bonds use 8 and 12 F lone pairs use 24 · 4 left = 2 lone pairs on Br · 12 e^- on Br, allowed in period 4

 **Sense check:** The two lone pairs sit opposite each other in an octahedral frame, so the four F form a square plane. Six domains, six hybrids: sp^3d^2 .

Step 1 36 e^- : 2 lone pairs on Br

Step 2 4 + 2 = 6

sp

sp^2

sp^3

sp^3d

sp^3d^2 · Br

✗ C: charge subtracted $\rightarrow \text{sp}^3\text{d}$

Practice 6: xenon trioxide

XeO_3 : xenon trioxide

central atom: Xe (period 5) · bonded atoms: 3 O · each Xe-O drawn as a single bond

Which row is fully correct for the xenon atom (electron geometry | molecular shape | hybridization)?

- A. trigonal planar | trigonal planar | sp^2
- B. tetrahedral | tetrahedral | sp^3
- C. tetrahedral | trigonal pyramidal | sp^3
- D. tetrahedral | trigonal pyramidal | sp^2

✓ Practice 6 answer: C

XeO_3 : 3 bonded O + 1 lone pair = 4 domains $\rightarrow$ tetrahedral | trigonal pyramidal | sp^3
 $\rightarrow$ answer C

$8 + 3(6) = 26$ valence e^- · 3 bonds use 6 and 9 O lone pairs use 18 · 2 left = 1 lone pair on Xe

 **Sense check:** One domain count sets both the electron geometry and the hybridization; only the shape leaves out the lone pair. Xe sits in period 5, yet four domains need only sp^3 .

Step 1 26 e^- : 1 lone pair on Xe

Step 2 $3 + 1 = 4$

sp

sp^2

$\text{sp}^3 \cdot \text{Xe}$

sp^3d

sp^3d^2

✗ D: 3 O only $\rightarrow \text{sp}^2$

Practice 7: 1,2-butadiene



carbons C1 to C4 from the left · no lone pairs on any carbon

With carbons numbered from the left, what are the hybridizations of C1, C2, C3 and C4, in that order?

- A. sp^2 , sp^2 , sp^2 , sp^3
- B. sp^2 , sp , sp^2 , sp^3
- C. sp^2 , sp^3 , sp^2 , sp^3
- D. sp^3 , sp^3 , sp^3 , sp^3

✓ Practice 7 answer: B

C1: $2 + 1 = 3 \rightarrow sp^2$ · C2: $1 + 1 = 2 \rightarrow sp$ · C3: $1 + 1 + 1 = 3 \rightarrow sp^2$ · C4: $3 + 1 = 4 \rightarrow sp^3 \rightarrow$ answer B

C1: 2 H + C2 · C2: C1 + C3, no H · C3: H + C2 + C4 · C4: 3 H + C3 · each double bond is one domain

 **Sense check:** Count each atom on its own. The middle carbon matches the carbon of CO₂: two double bonds, two domains, sp, linear.

Step 1 no lone pairs on any C → Step 2 C1 3 · C2 2 · C3 3 · C4 4 → sp · C2 sp² · C1, C3 sp³ · C4 sp³d sp³d² X C: C2 counted as 4 → sp³



Check yourself

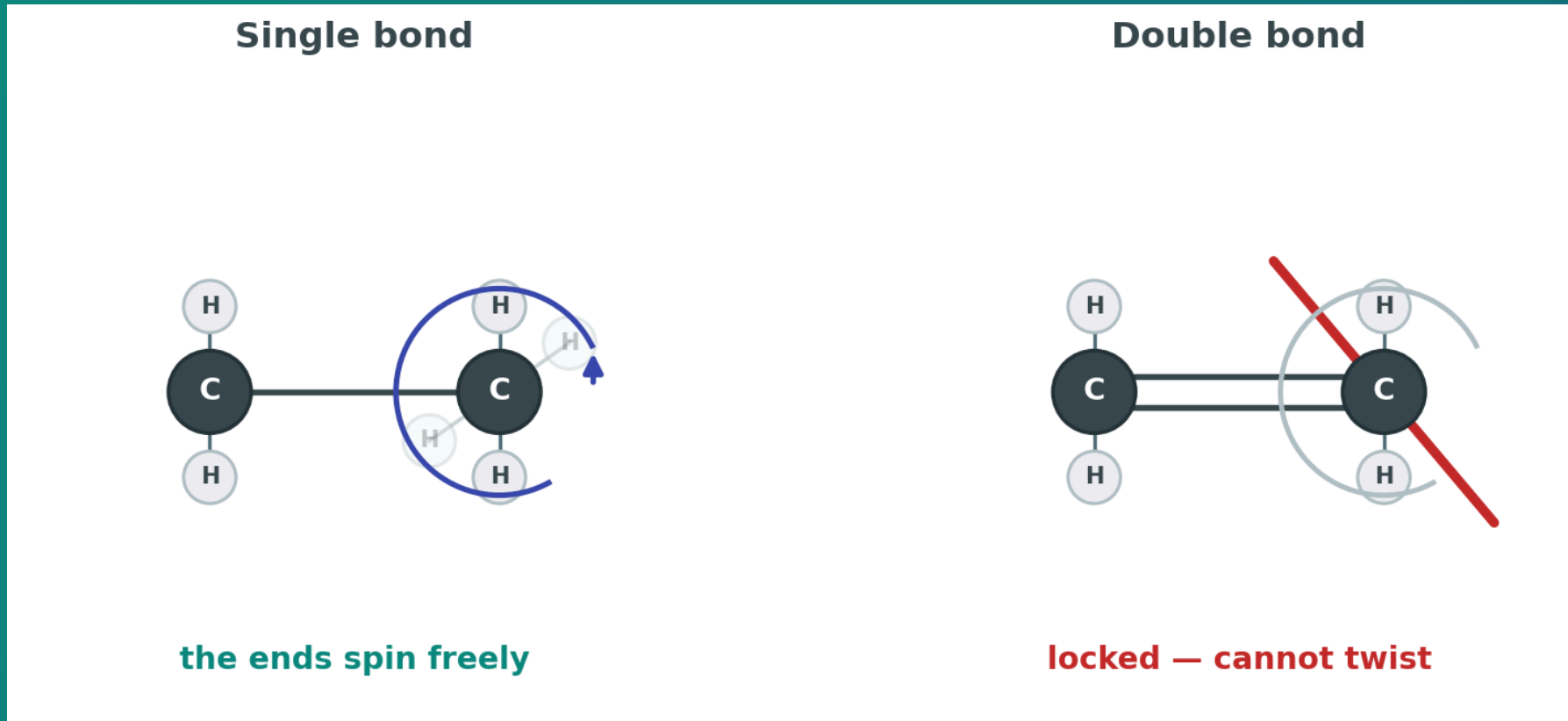
1. Sulfur dioxide, SO_2 , has a central sulfur with two bonding groups and one lone pair. How many domains, and what hybridization?
2. Why can a period-3 atom reach six electron domains while a period-2 atom stops at four? Name the hybridization at each limit.

Each hybrid orbital either overlaps end-to-end to form one **sigma bond** or holds a lone pair. The extra lines of a double or triple bond are **pi bonds**, built from the p orbitals an sp or sp^2 atom leaves unmixed. Sorting every bond into sigma and pi builds straight on the hybridization counted here.

2 · Sigma & Pi Bonds

Count the sigma and pi bonds in a molecule from its Lewis structure, using that every bond is one σ and each extra line of a double or triple bond is a π .

Bonds that turn and bonds that don't



The ends of a single bond spin freely, like a wheel on an axle. A double bond is locked. That rigidity fixes a molecule's shape.

What a Lewis structure already shows

H-O-H: 2 lines · 2 bonded pairs · N≡N: 3 lines · 1 bonded pair

each line is one shared electron pair · N≡N puts $3 - 1 = 2$ extra lines between the same two atoms

Each line in a Lewis structure is one shared electron pair. Lines and bonded pairs match only when every bond is single. A double or triple adds extra lines between two atoms.

Every bond is one sigma

The first line is σ ; every extra line is π



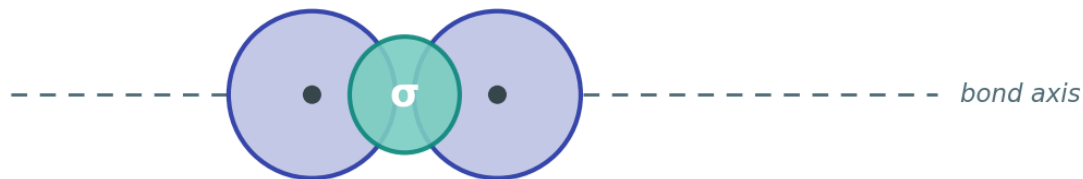
 σ (on the axis)

 π (off the axis)

Two kinds of bond form between atoms: sigma and pi. The first bond between any two atoms is always a σ . Every extra line of a double or triple bond is a π .

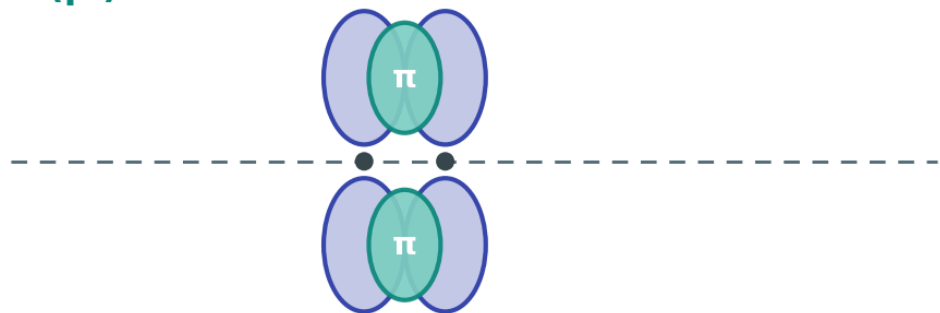
Sigma and pi: two kinds of overlap

σ (sigma) bond



end-on overlap — the shared region lies ON the axis

π (pi) bond



side-by-side overlap — shared regions sit ABOVE and BELOW the axis

A sigma bond overlaps end-on, along the bond axis. A pi bond overlaps side-on, above and below it. The σ framework is built from hybrid orbitals.

Why a double bond cannot twist

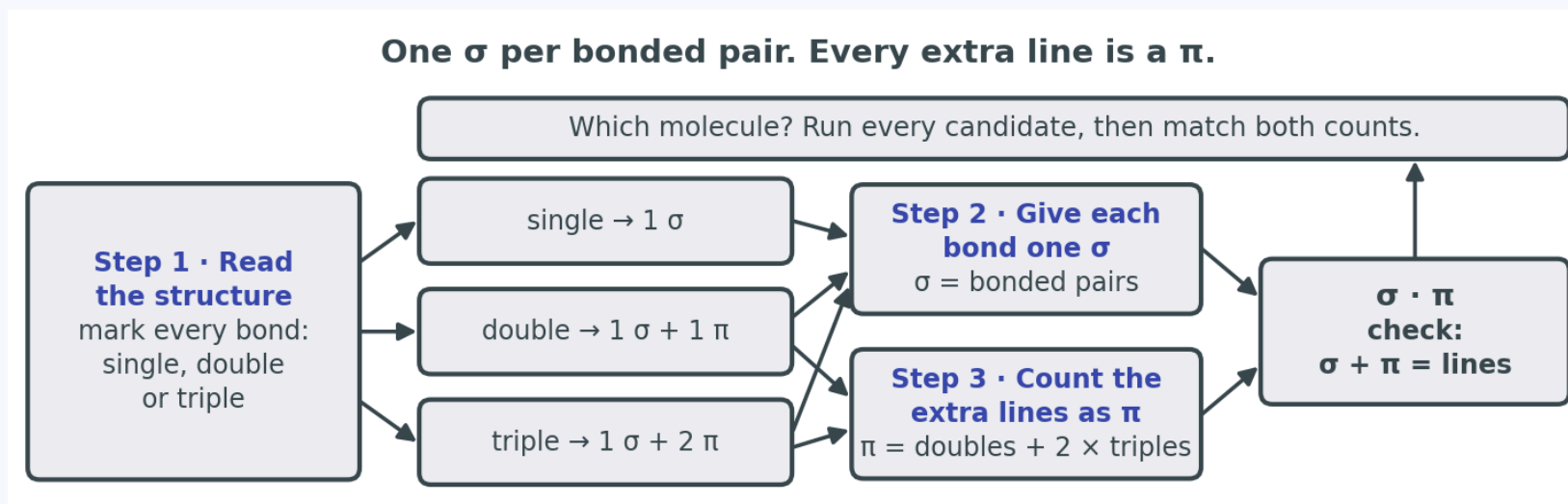
single bond → free rotation · double bond → locked

the σ lies on the axis, so the ends turn · a π sits off the axis, and twisting would tear it

A σ bond's overlap lies on the axis, so the ends spin freely. A π bond's overlap sits off the axis, and twisting would tear it. So a double bond holds its shape.

The method

1. **Read the structure.** Mark every bond: single, double, or triple.
2. **Give each bond one σ .** Every bonded pair has one σ .
3. **Count the extra lines as π ,** then total. A double adds 1 π ; a triple adds 2 π .





Worked example 1: methane

Step 1 • Read the structure

CH₄: four C-H single bonds

given: the Lewis structure of CH₄ • wanted: total σ and π

Methane has four single bonds and no double or triple bonds. Count the σ and the π .

✓ Worked example 1: solution

CH_4 : four C-H single bonds

given: the Lewis structure of CH_4 · wanted: total σ and π

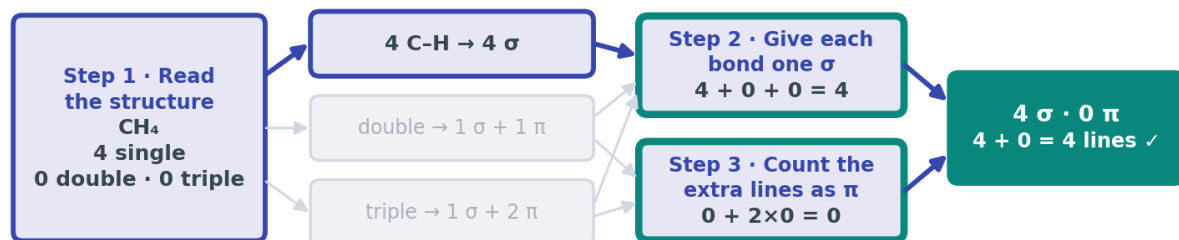
Step 2 · Give each bond one σ

Step 3 · Count the extra lines as π

$$\sigma: 4 + 0 + 0 = 4 \quad \cdot \quad \pi: 0 + 2 \times 0 = 0$$

four C-H bonds, one σ each · π comes only from the extra lines of a double or triple

 **Sense check:** Four bonds, four σ , zero π . A molecule of only single bonds carries only σ bonds.



Worked example 2: ethylene

Step 1 • Read the structure

$\text{H}_2\text{C}=\text{CH}_2$: four C-H bonds and one C=C double
given: the Lewis structure of C_2H_4 • wanted: total σ and π

Ethylene has one double bond. A common first attempt: count the double as two σ . Find the σ and the π .

✓ Worked example 2: solution

$\text{H}_2\text{C}=\text{CH}_2$: four C-H bonds and one C=C double
given: the Lewis structure of C_2H_4 · wanted: total σ and π

A common first attempt

count the C=C as two $\sigma \rightarrow 4 + 2 = 6 \sigma$?
that reads both lines of the double as σ : only one σ fits along the axis ✕

🧠 **Sense check:** Two σ cannot share one axis. The C=C holds one σ , and its second line is a π .

✓ Worked example 2: solution

$\text{H}_2\text{C}=\text{CH}_2$: four C-H bonds and one C=C double
given: the Lewis structure of C_2H_4 · wanted: total σ and π

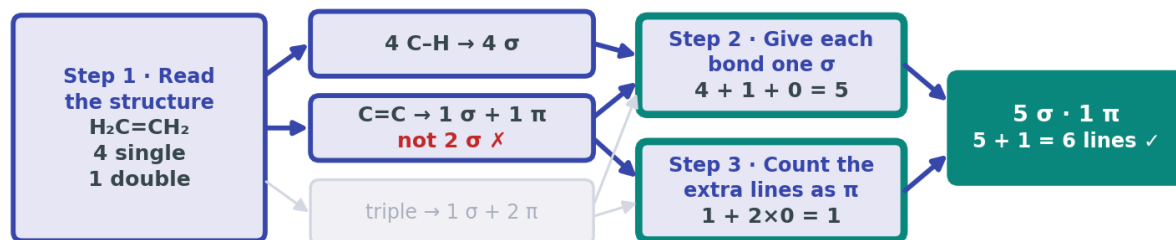
Step 2 · Give each bond one σ

Step 3 · Count the extra lines as π

$$\sigma: 4 + 1 + 0 = 5 \quad \cdot \quad \pi: 1 + 2 \times 0 = 1$$

every bonded pair gives one σ · the double's second line is the one π

🧠 **Sense check:** Five σ and one π . The double bond splits into one σ and one π , never two σ .



Take-home: a double bond is not two σ



one σ lies on the axis · the second line is the π · a triple is $1 \sigma + 2 \pi$

The two lines of a double bond are not two σ bonds. The first line is the σ ; the second is a π .

memory hook: one σ per bond, the rest are π

count the bonded pairs for σ · every extra line of a double or triple is a π

Your turn: carbon dioxide

O=C=O: two C=O double bonds
each double bond splits into one σ and one π

bond	σ	π
first C=O	_____	_____
second C=O	_____	_____
total	_____	_____

Give each double bond one σ and one π , then total.

$\sigma: 1 + 1 = 2 \cdot \pi: 1 + 1 = 2$
two doubles $\rightarrow$ 2 σ and 2 π $\cdot$ CO₂ has 2 σ and 2 π

⚠ Where this goes wrong

Counting every line as a σ . A double or triple looks like two or three σ . Only one σ fits along the axis. Ethylene is 5 σ and 1 π , not $4 + 2 = 6$ σ with no π .

Dropping the σ inside a multiple bond. Reading the double as pure π forgets the σ on the axis. Ethylene's double is 1 σ + 1 π , so 5 σ and 1 π , not 4 σ and 2 π .

Counting a double bond as 2 σ . A double bond is one σ plus one π , never two σ . Counting 2 σ turns ethylene's 5 σ into 6 σ , still with its 1 π .



Practice 1

$\text{H}_2\text{C}=\text{O}$: two C-H bonds and one C=O double
formaldehyde · count every bond, single and double

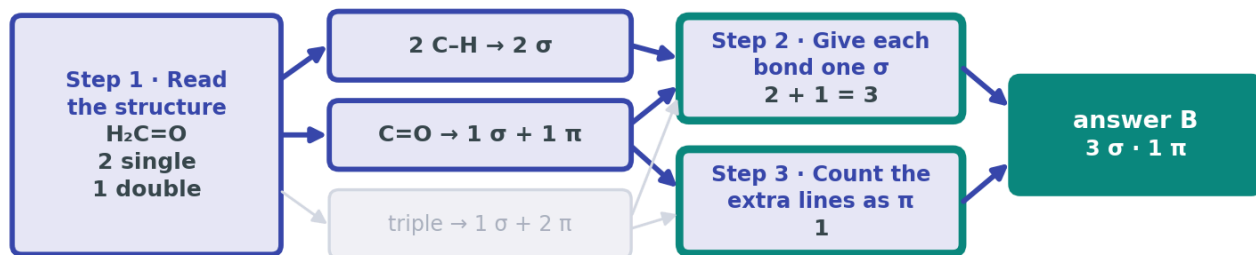
Counting every bond, how many σ and how many π does formaldehyde contain?

- A. σ : 4 · π : 0
- B. σ : 3 · π : 1
- C. σ : 2 · π : 2
- D. σ : 4 · π : 1

✓ Practice 1 answer: B

$\text{H}_2\text{C}=\text{O} \rightarrow 2 + 1 = 3 \sigma$ and $1 \pi \rightarrow$ answer B
 $2 \text{ C-H} + 1 \sigma$ in the $\text{C}=\text{O}$ · the double's second line is the π

🧠 **Sense check:** Three σ and one π . The double contributes one of each; the two C-H bonds add the other two σ .





Worked example 3: acetylene

Step 1 • Read the structure

$\text{H}-\text{C}\equiv\text{C}-\text{H}$: two C-H bonds and one $\text{C}\equiv\text{C}$ triple
given: the Lewis structure of C_2H_2 • wanted: total σ and π

Acetylene has a triple bond. Count the σ and the π .

✓ Worked example 3: solution

H-C≡C-H: two C-H bonds and one C≡C triple
given: the Lewis structure of C₂H₂ · wanted: total σ and π

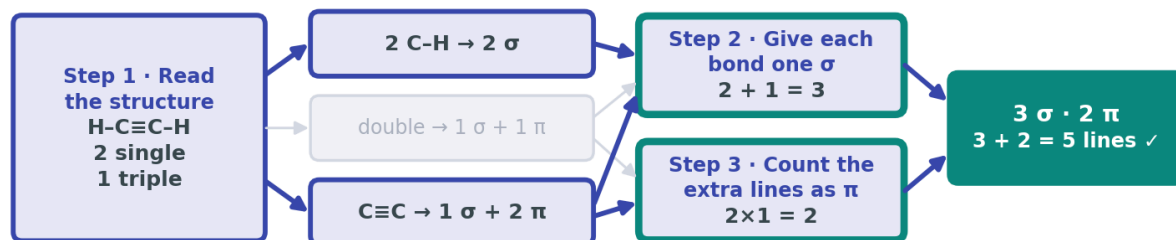
Step 2 · Give each bond one σ

Step 3 · Count the extra lines as π

$$\sigma: 2 + 1 = 3 \quad \cdot \quad \pi: 2 \times 1 = 2$$

the triple counts as one σ · it adds two π, and its σ is already counted

🧠 **Sense check:** Three σ and two π. The triple bond is one σ and two π; the two C-H bonds add the other two σ.





Practice 2

$\text{HC}\equiv\text{C}-\text{CH}=\text{O}$: propynal

wanted: total σ and π

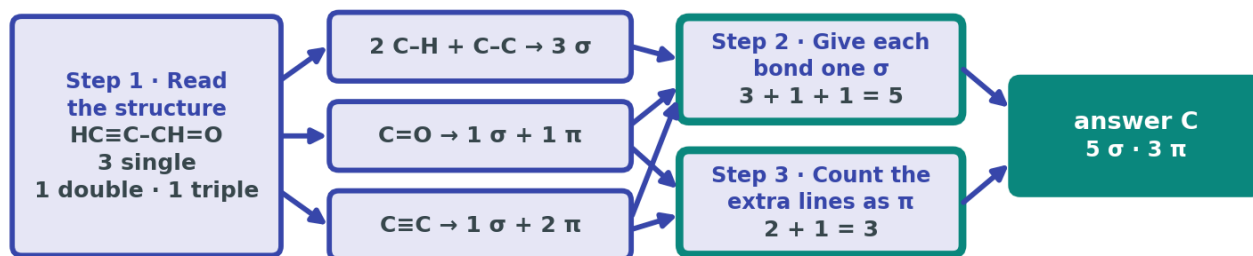
Counting every bond, how many σ and how many π does propynal contain?

- A. σ : 8 · π : 0
- B. σ : 3 · π : 5
- C. σ : 5 · π : 3
- D. σ : 8 · π : 3

✓ Practice 2 answer: C

2 C-H + C-C = 3 single · C≡C and C=O add one σ each: $3 + 1 + 1 = 5 \sigma$ · π : $2 + 1 = 3$
 $\rightarrow$ answer C
 one σ per bonded pair · the triple adds 2 π , the double 1 π

 **Sense check:** Five σ and three π . Three single bonds plus one σ in each multiple bond make five; the triple adds two π and the double one.





Guided example: matching a σ and π count



given: three Lewis structures · wanted: the one molecule with exactly 4 σ and 2 π

Formic acid, acetonitrile and cyanamide. Run the three method steps on each molecule. Then keep the one that matches both counts.

✓ Guided example: solution



given: three Lewis structures · wanted: the one molecule with exactly 4 σ and 2 π

Step 1 · Read the structure

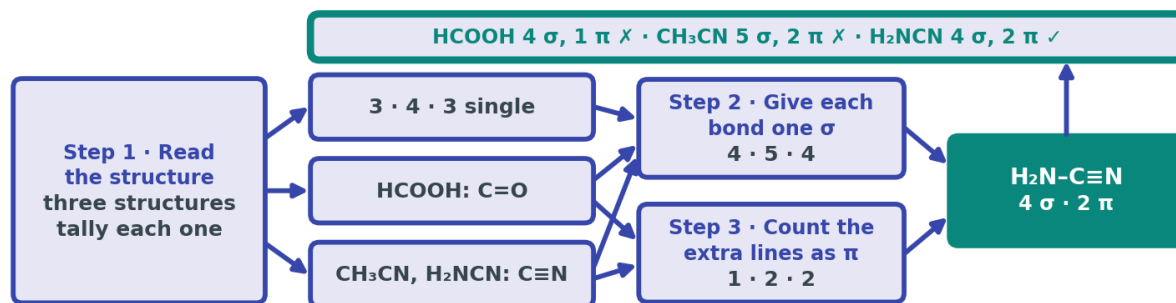
Step 2 · Give each bond one σ

Step 3 · Count the extra lines as π

$$\sigma: 3 + 1 = 4 \cdot 4 + 1 = 5 \cdot 3 + 1 = 4 \cdot \pi: 1 \cdot 2 \times 1 = 2 \cdot 2 \times 1 = 2$$

formic acid 4 σ , 1 π · acetonitrile 5 σ , 2 π · cyanamide 4 σ , 2 π

 **Sense check:** Only cyanamide, $\text{H}_2\text{N}-\text{C}\equiv\text{N}$, matches both counts. Formic acid matches only the σ ; acetonitrile only the π .



Practice 3

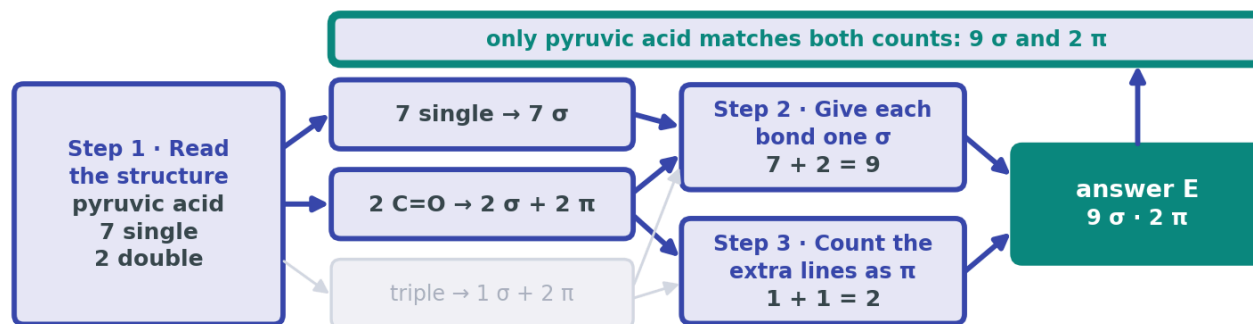
Which molecule has exactly 9 σ bonds and 2 π bonds?

- A. acetone, $\text{CH}_3\text{-C(=O)-CH}_3$
- B. propargyl alcohol, $\text{HC}\equiv\text{C-CH}_2\text{-OH}$
- C. methyl acetate, $\text{CH}_3\text{-C(=O)-O-CH}_3$
- D. methyl propiolate, $\text{HC}\equiv\text{C-C(=O)-O-CH}_3$
- E. pyruvic acid, $\text{CH}_3\text{-C(=O)-C(=O)-O-H}$

✓ Practice 3 answer: E

pyruvic acid: 7 single + 2 C=O $\rightarrow \sigma: 7 + 2 = 9 \cdot \pi: 1 + 1 = 2 \rightarrow$ answer E
 single: 3 C-H, 2 C-C, C-O, O-H $\cdot$ C₃H₄O₃ has 10 atoms and no ring: $10 - 1 = 9$ bonded pairs ✓

🧠 **Sense check:** Both counts must match. Three choices have 9 σ and two have 2 π ; only pyruvic acid has both.





Practice 4

$\text{H}_2\text{N}-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{H}$: glycine
the simplest amino acid in proteins

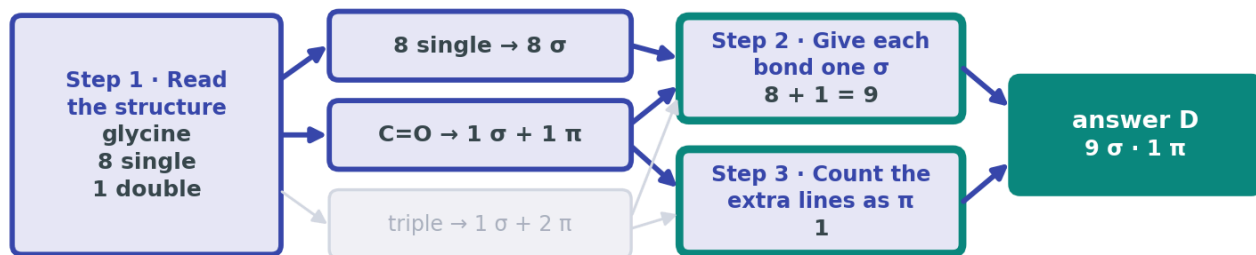
How many σ bonds and how many π bonds are in one glycine molecule?

- A. σ : 10 · π : 0
- B. σ : 8 · π : 2
- C. σ : 9 · π : 0
- D. σ : 9 · π : 1
- E. σ : 10 · π : 1

✓ Practice 4 answer: D

8 single + 1 σ in the C=O = 9 σ · π : 1 → answer D
 single: 2 N-H, N-C, 2 C-H, C-C, C-O, O-H · the C=O's second line is the π

🧠 **Sense check:** Nine σ and one π . Nine bonded pairs give nine σ ; the only extra line is the C=O's π .





Practice 5

$\text{CH}_2=\text{C}(\text{C}\equiv\text{N})-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_3$: ethyl cyanoacrylate
the bonding agent in instant glue

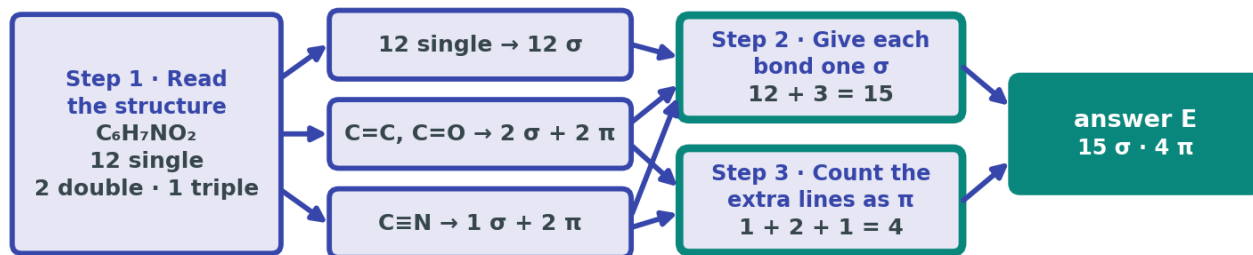
What are the total σ and π bond counts for ethyl cyanoacrylate?

- A. σ : 19 · π : 0
- B. σ : 12 · π : 7
- C. σ : 13 · π : 2
- D. σ : 19 · π : 4
- E. σ : 15 · π : 4

✓ Practice 5 answer: E

12 single + 3 multiple (one σ each) = 15 σ · π : 1 + 2 + 1 = 4 → answer E
 single: 2 C-H, C-CN, C-C(=O), C-O, O-C, 2 C-H, C-C, 3 C-H · multiple: C=C, C $\equiv$ N, C=O

🧠 **Sense check:** Fifteen σ and four π . C₆H₇NO₂ has 16 atoms and no ring, so 16 – 1 = 15 bonded pairs, one σ each.





Practice 6



the acid in vinegar · the bond asked about joins the C=O carbon to the OH oxygen

Which orbital overlaps make up the C-O single bond in acetic acid?

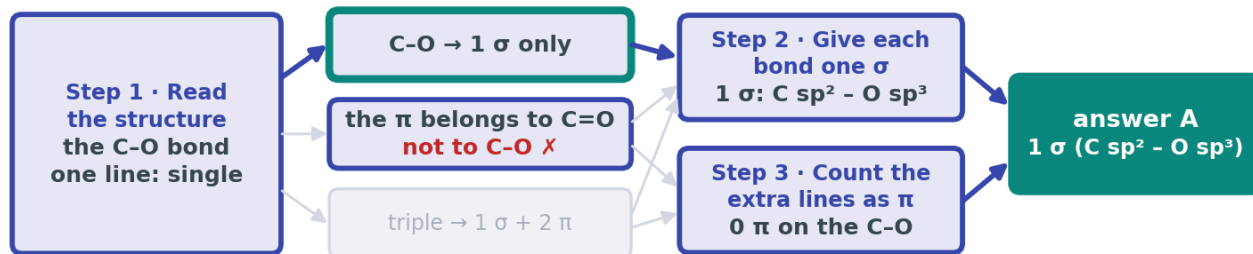
- A. $\sigma (\text{C } sp^2 - \text{O } sp^3)$
- B. $\sigma (\text{C } sp^3 - \text{O } sp^3)$
- C. $\sigma (\text{C } sp^2 - \text{O } sp)$
- D. $\sigma (\text{C } sp^2 - \text{O } sp^2) + \pi (\text{C } 2p - \text{O } 2p)$

✓ Practice 6 answer: A

C: $3 + 0 = 3$ domains $\rightarrow sp^2$ · O: $2 + 2 = 4$ domains $\rightarrow sp^3 \rightarrow$ answer A

C: CH_3 , $=O$ and OH , no lone pair · OH oxygen: 2 bonds, 2 lone pairs · one σ (C sp^2 - O sp^3)

🧠 **Sense check:** Two hybrids meet end-on to make the σ . The carbon's leftover 2p forms the π of the $C=O$, not of the $C-O$.





Check yourself

1. In HCN ($\text{H}-\text{C}\equiv\text{N}$): how many σ and how many π ? Give each bond one σ , then count the extra lines.
2. Why can a single bond rotate while a double bond cannot? Name the bond that would have to break.

A σ bond allows rotation; a π bond fixes a shape. Counting them reads a fixed Lewis structure. **Molecular-orbital theory** goes further: atomic orbitals combine into bonding and antibonding levels, and how they fill gives a **bond order**: the measure a Lewis structure cannot express.

3 · Molecular Orbitals & Bond Order

Build the molecular-orbital picture of a second-period diatomic, count its bonding and antibonding electrons, and take the bond order as $(\text{bonding} - \text{antibonding}) \div 2$: the number that says how strong the bond is and whether the molecule can exist at all.

The air's unreactive gas

Nitrogen gas holds itself together tightly



three shared pairs — a triple bond

the main gas in every breath — about 78% of the air

so tightly bonded it barely reacts; splitting it takes lightning or furnace heat

Nitrogen is most of the air, yet it barely reacts. Its two atoms are locked together by a triple bond that takes lightning or furnace heat to break.

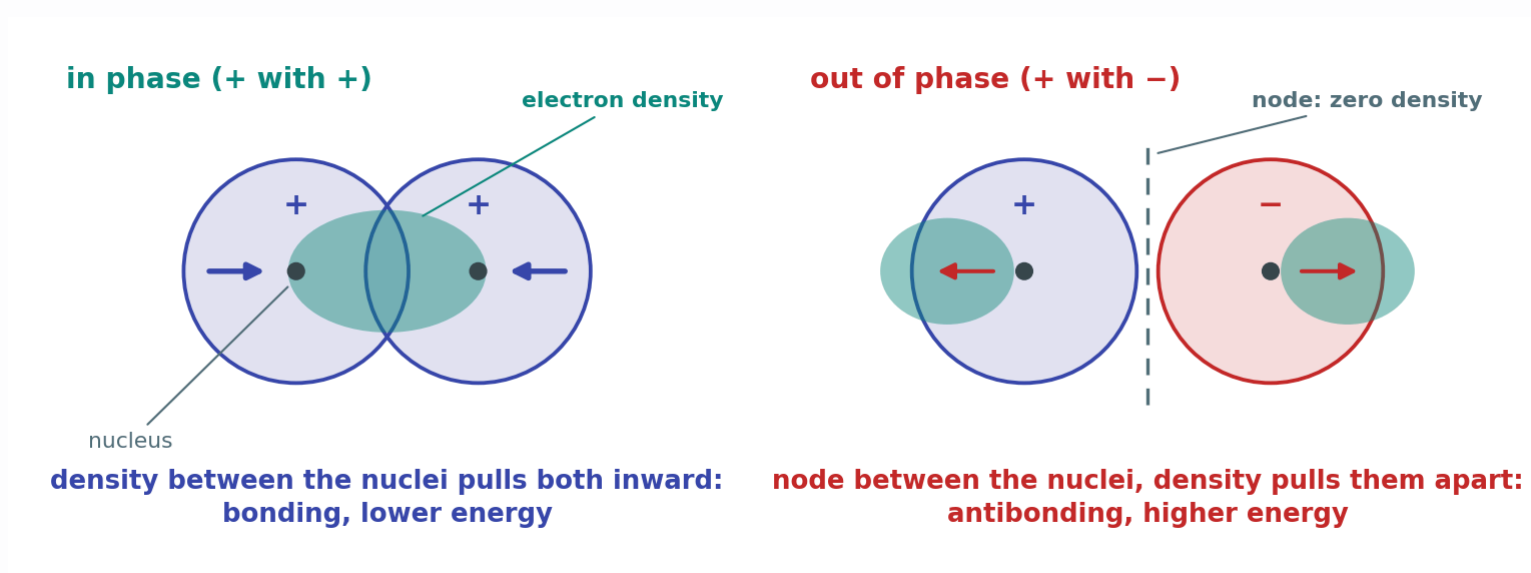
Bond order in a Lewis structure



1 shared pair · 2 shared pairs · 3 shared pairs → bond order 1, 2, 3

A Lewis structure shows bond order: the number of electron pairs two atoms share. Molecular orbital theory counts the same pairs from bonding and antibonding electrons. It also finds half bonds.

Why a molecule holds together



H_2 : 2 bonding, 0 antibonding $\rightarrow$ bond order = $(2 - 0)/2 = 1$

bonding wins $\rightarrow$ the molecule exists

He_2 : 2 bonding, 2 antibonding $\rightarrow$ bond order = $(2 - 2)/2 = 0$

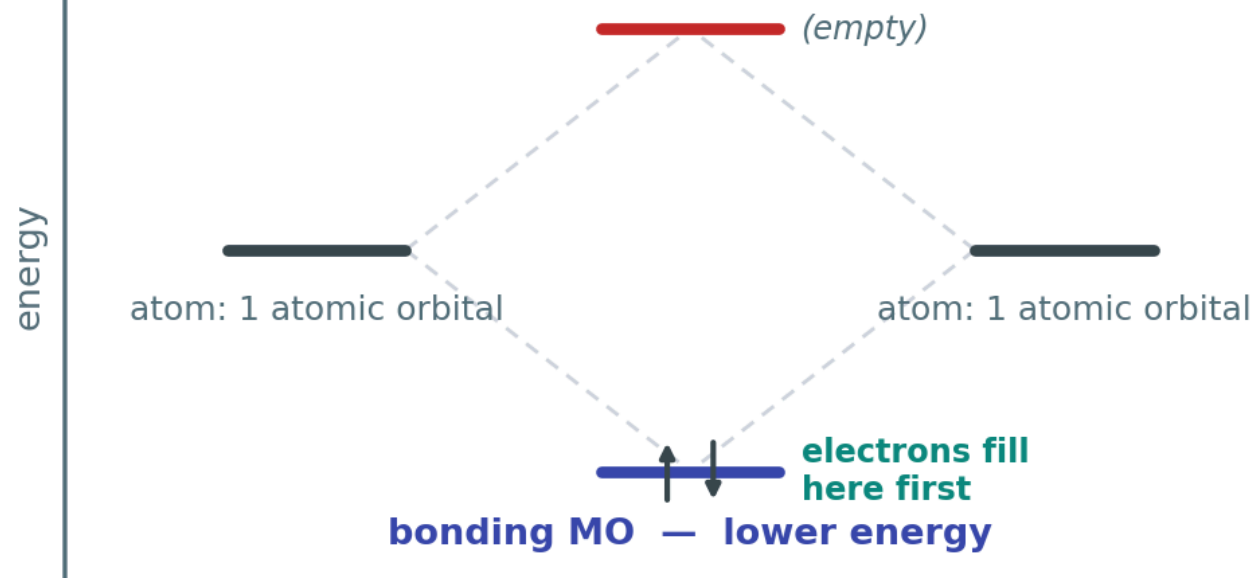
bonding and antibonding cancel $\rightarrow$ no stable molecule

Bonding must beat antibonding; bond order counts the surplus, in pairs.

How molecular orbitals form

Two atomic orbitals make one bonding + one antibonding MO

antibonding MO* — higher energy

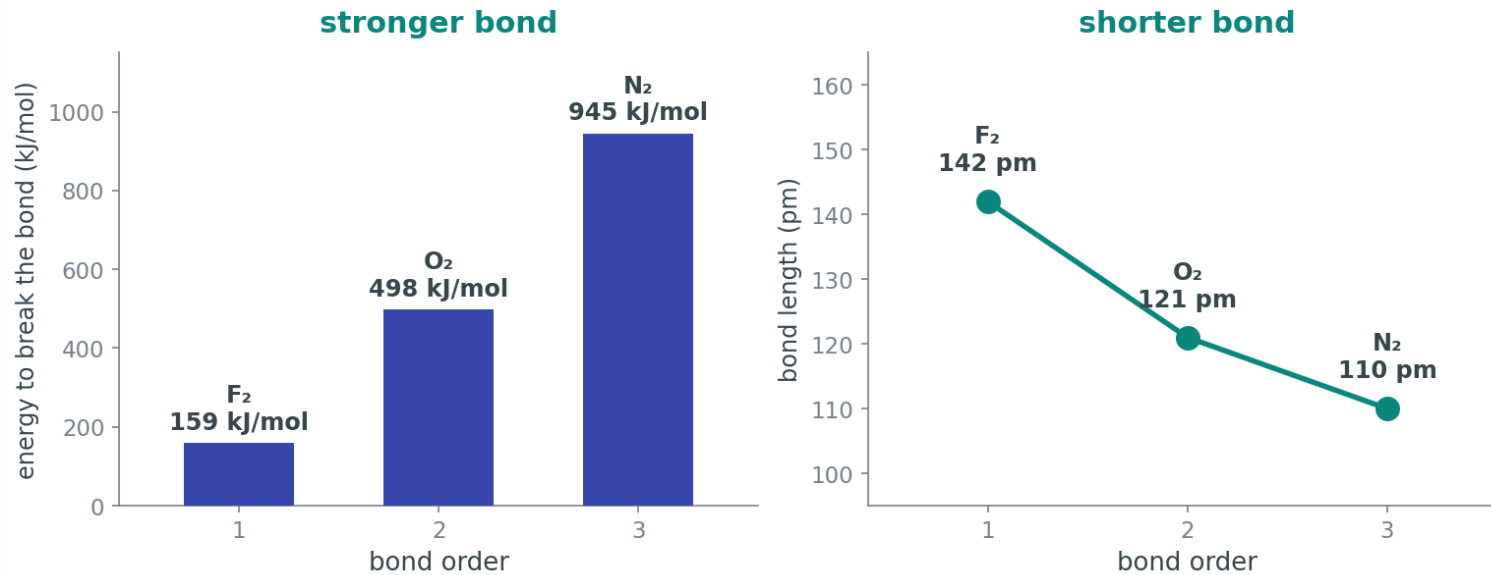


Two atomic orbitals, one from each atom, combine into two molecular orbitals: a bonding MO at lower energy and an antibonding MO (starred) at higher energy. Electrons fill the lowest first.

Bond order measures the bond

bond order = (bonding electrons – antibonding electrons) ÷ 2
the net number of bonding pairs · memory hook: a star means subtract, then halve for pairs

Higher bond order → stronger and shorter bond



The formula counts the net bonding pairs. A higher bond order means a stronger, shorter bond. A bond order of zero means the atoms do not stay bonded.

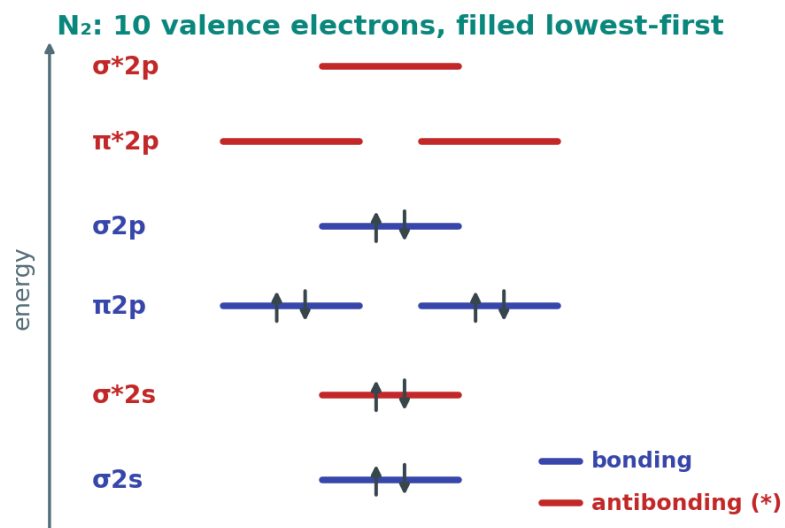


The method

1. **Fill the orbitals lowest-first:** valence electrons into the MOs.
2. **Count bonding and antibonding** electrons.
3. **Bond order = (bonding – antibonding) ÷ 2.**
4. **Read the bond:** higher order, stronger and shorter.

Worked example 1: the bond order of N₂

bond order = (bonding – antibonding) ÷ 2
given: N₂, 10 valence electrons · wanted: the bond order



The molecular orbitals of N₂ are filled with its 10 valence electrons. Count the bonding and antibonding electrons, then find the bond order.

✓ Worked example 1: solution

bond order = (bonding – antibonding) ÷ 2

N₂: 10 valence electrons in the molecular orbitals

Step 1 • Fill the orbitals lowest-first

Step 2 • Count bonding and antibonding

Step 3 • Bond order = (bonding – antibonding) ÷ 2

$$\text{bond order} = \frac{8 - 2}{2} = 3$$

Step 4 • Read the bond

🧠 **Sense check:** Bond order 3: a triple bond. That is the strong, short bond that makes nitrogen gas so hard to pull apart. ✓



Worked example 2: the bond order of O₂

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

given: O₂, 12 valence electrons · wanted: the bond order

Oxygen has 12 valence electrons, two more than nitrogen. Fill the orbitals, count each kind, and find the bond order.

✓ Worked example 2: solution

bond order = (bonding – antibonding) ÷ 2

O₂: 12 valence electrons in the molecular orbitals

Step 1 • Fill the orbitals lowest-first

Step 2 • Count bonding and antibonding

Step 3 • Bond order = (bonding – antibonding) ÷ 2

$$\text{bond order} = \frac{8 - 4}{2} = 2$$

Step 4 • Read the bond

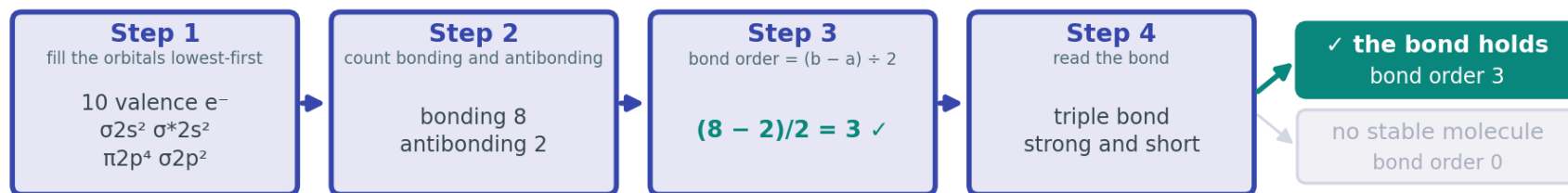
 **Sense check:** Bond order 2: a double bond, weaker and longer than nitrogen's triple bond. Four antibonding electrons cancel four of the bonding ones. ✓

✓ Worked examples 1 and 2: the route

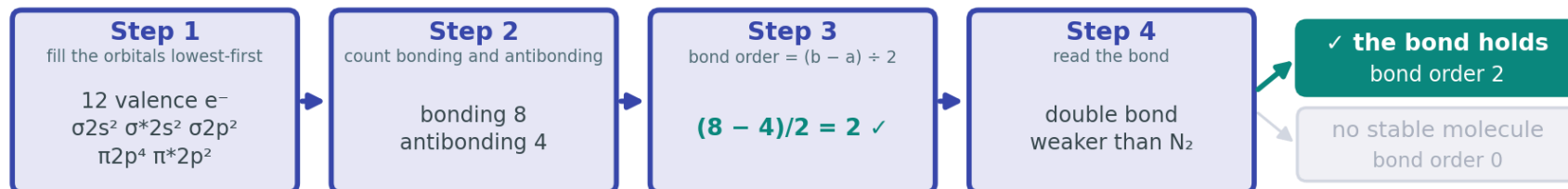
$$\text{N}_2: (8 - 2)/2 = 3 \quad \cdot \quad \text{O}_2: (8 - 4)/2 = 2$$

found: N_2 10 valence electrons, bond order 3 · O_2 12 valence electrons, bond order 2

nitrogen, N_2



oxygen, O_2



🧠 **Sense check:** Same four steps, same verdict: both bonds hold. O_2 's two extra electrons go into antibonding $\pi^* 2p$ and cost one bond. ✓

Your turn: the bond order of F₂

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

given: F₂ · bonding 8, antibonding 6 · wanted: the bond order

F₂ fills every bonding orbital and all but one antibonding orbital.

$$\text{bond order} = \frac{\text{---} - \text{---}}{2} = \text{---}$$

Fill in the bonding and antibonding counts, then compute.

$$\text{bond order} = \frac{8 - 6}{2} = 1$$

 **Sense check:** Bond order 1: a single bond. Six antibonding electrons cancel six of eight bonding: one net pair. ✓



Guided example: neon, Ne₂

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

given: Ne₂, two neon atoms with 8 valence electrons each · wanted: the bond order

Run all four method steps in order and name each move as you make it. Decide whether Ne₂ holds together.

✓ Guided example: solution

Step 1 · Fill the orbitals lowest-first

Step 2 · Count bonding and antibonding



$2 \times 8 = 16$ valence electrons · bonding $2 + 2 + 4 = 8$ · antibonding $2 + 4 + 2 = 8$

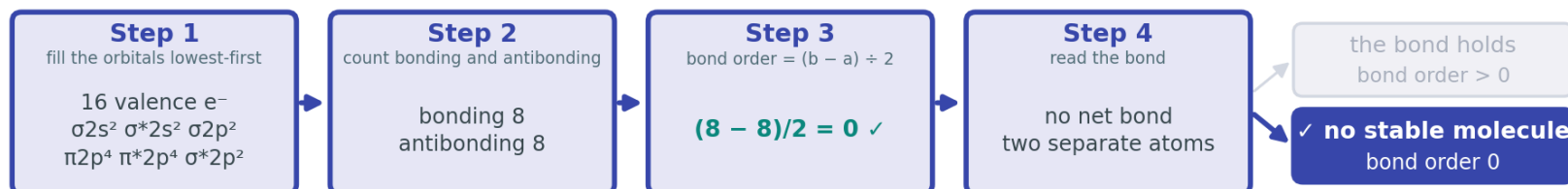
Step 3 · Bond order = (bonding – antibonding) ÷ 2

Step 4 · Read the bond

$$\text{bond order} = \frac{8 - 8}{2} = 0$$

 **Sense check:** Bond order 0: no net bond. Neon stays as separate atoms, the same verdict as He₂. ✓

neon, Ne₂



⚠ Where this goes wrong

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

N₂: bonding 8, antibonding 2 · correct bond order = 3

Forgetting to divide by two. $8 - 2 = 6$ is the surplus of bonding electrons, not the bond order. Bond order counts PAIRS, so halve it: $(8 - 2)/2 = 3$.

Adding the antibonding electrons. Antibonding electrons cancel bonding ones, so subtract. Adding gives $(8 + 2)/2 = 5$, a bond order larger than any real diatomic.

Subtracting in the wrong order. $(2 - 8)/2 = -3$. A negative bond order has no meaning. Bonding electrons come first: $(8 - 2)/2 = 3$.

Counting every electron. $8 + 2 = 10$ is the total number of valence electrons, not the difference. Bond order uses bonding minus antibonding, then $\div 2$.



Practice 1

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

Li_2 : bonding 2, antibonding 0 · Be_2 : bonding 2, antibonding 2 · B_2 : bonding 4, antibonding 2

Three second-period diatomics are listed with their molecular-orbital electron counts. Which one is predicted not to exist as a stable molecule?

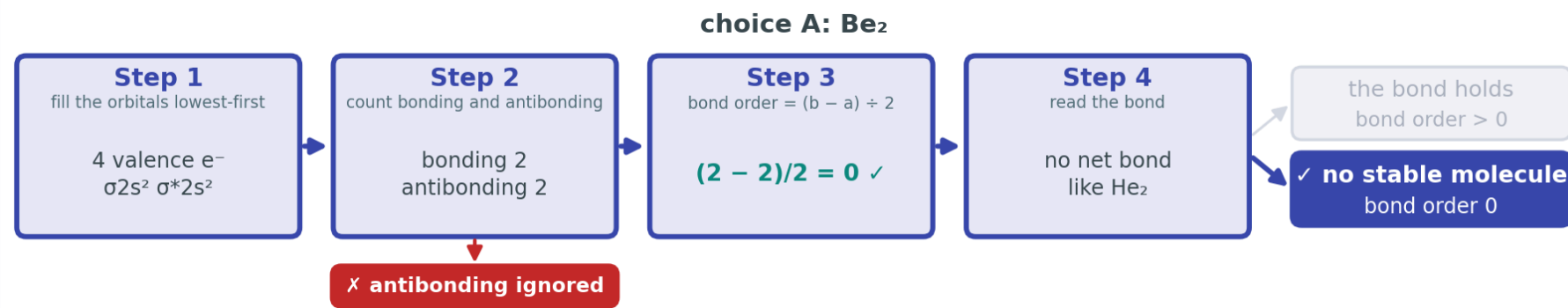
- A. Be_2
- B. Li_2
- C. B_2
- D. None of them: each has bonding electrons

✓ Practice 1 answer: A

$\text{Li}_2: (2 - 0)/2 = 1 \cdot \text{Be}_2: (2 - 2)/2 = 0 \cdot \text{B}_2: (4 - 2)/2 = 1$
 bond order 0 means no net bond: Be_2 does not hold together

$$\text{Be}_2: \text{bond order} = \frac{2 - 2}{2} = 0 \rightarrow \text{answer A}$$

🧠 **Sense check:** Be_2 repeats the He_2 pattern: equal bonding and antibonding counts, bond order 0, no molecule. ✓





Worked example 3: the bond order of O_2^+

$$\text{bond order} = (\text{bonding} - \text{antibonding}) \div 2$$

given: O_2^+ · bonding 8, antibonding 3 · wanted: the bond order

Remove one electron from O_2 and it leaves an antibonding orbital, giving O_2^+ : 8 bonding, 3 antibonding. A common first attempt: $8 - 3 = 5$. Test it.

✓ Worked example 3: solution

bond order = (bonding – antibonding) ÷ 2
given: O₂⁺ · bonding 8, antibonding 3 · wanted: the bond order

$$\text{bonding} - \text{antibonding} = 8 - 3 = 5 \times$$

Step 1 · Fill the orbitals lowest-first

Step 2 · Count bonding and antibonding

Step 3 · Bond order = (bonding – antibonding) ÷ 2

$$\text{bond order} = \frac{8 - 3}{2} = 2.5$$

Step 4 · Read the bond

 **Sense check:** Bond order 2.5: fractional, and real. Taking away an antibonding electron strengthens the bond, so O₂⁺ has a shorter, stronger bond than O₂. ✓

Take-home: bond order counts pairs

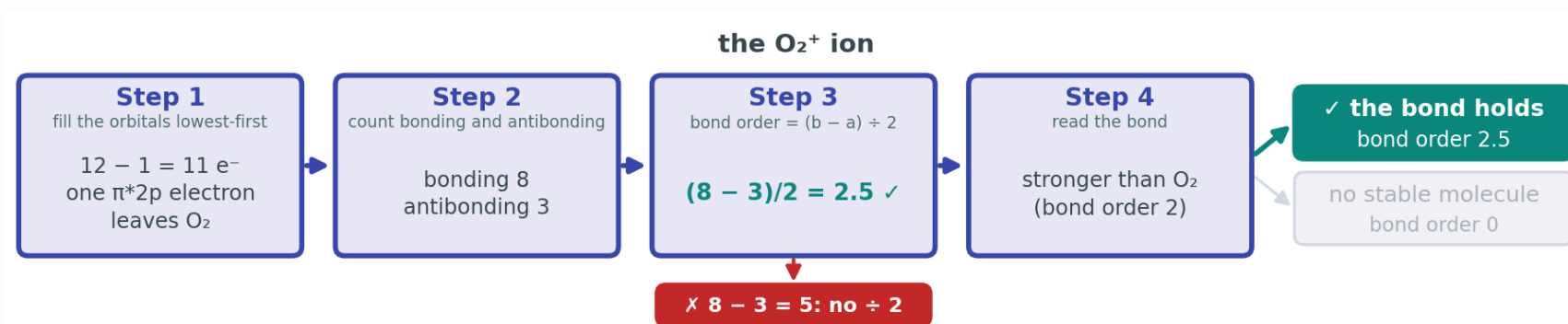
bonding – antibonding = the surplus of bonding electrons

$8 - 3 = 5$ electrons $\times$ · not a bond order

bond order = (bonding – antibonding) $\div$ 2

$(8 - 3)/2 = 2.5$ $\checkmark$ · the surplus counted in pairs

A bond is a shared PAIR of electrons. The surplus of bonding electrons must be halved to count pairs. The $\div 2$ is never optional.





Practice 2

**N_2 : bonding 8, antibonding 2 · N_2^+ : one electron fewer
wanted: the bond order of N_2^+**

Nitrogen gas loses one electron to form N_2^+ . What is the bond order of N_2^+ ?

- A. 3.5
- B. 2.5
- C. 5
- D. 3

✓ Practice 2 answer: B

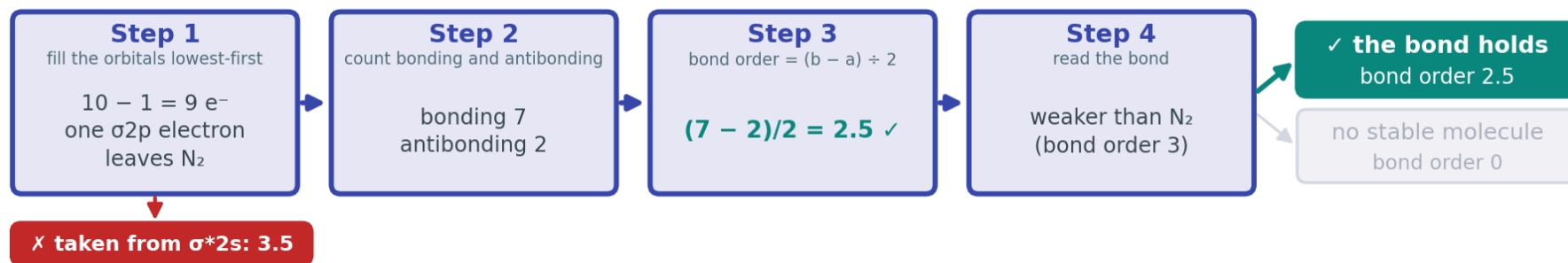


10 – 1 = 9 valence electrons · bonding 8 – 1 = 7, antibonding 2

$$\text{bond order} = \frac{7 - 2}{2} = 2.5 \rightarrow \text{answer B}$$

 **Sense check:** Losing a bonding electron weakens the bond: N_2^+ at 2.5 sits below N_2 at 3. O_2^+ moved the other way because its electron left an antibonding orbital. ✓

the N_2^+ ion





Practice 3



wanted: the bond order

What bond order does molecular orbital theory predict for Ne_2^{2+} ?

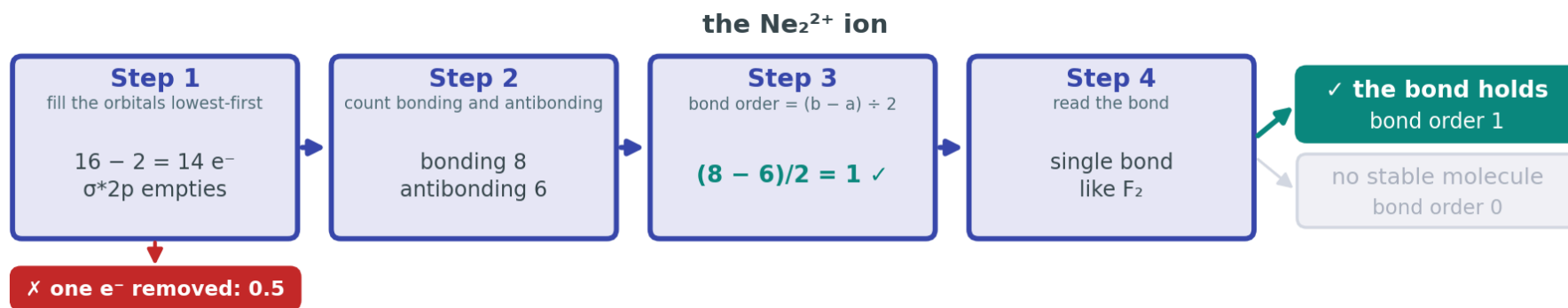
- A. 0.5
- B. 2
- C. 0
- D. 1

✓ Practice 3 answer: D

Ne_2^{2+} : $2 \times 8 - 2 = 14$ valence electrons · $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p^2 \pi 2p^4 \pi^* 2p^4$
bonding $2 + 2 + 4 = 8$, antibonding $2 + 4 = 6$ · $\sigma^* 2p$ is empty

$$\text{bond order} = \frac{8 - 6}{2} = 1 \rightarrow \text{answer D}$$

 **Sense check:** Taking two electrons off Ne_2 empties $\sigma^* 2p$, so the bond order rises from 0 to 1: a single bond, like F_2 , which has the same 14 electrons. ✓





Practice 4



valence molecular orbitals, filled lowest-first · wanted: the bond order

The valence molecular orbitals of B_2^+ are filled as shown. What is its bond order?

- A. 1
- B. 0.5
- C. 2.5
- D. 1.5

✓ Practice 4 answer: B



bonding: $\sigma 2s + \pi 2p = 2 + 1 = 3$ · antibonding: $\sigma^* 2s = 2$

$$\text{bond order} = \frac{3 - 2}{2} = 0.5 \rightarrow \text{answer B}$$

A forgot to halve: $3 - 2 = 1$. C added the antibonding electrons: $(3 + 2)/2 = 2.5$. D left the antibonding electrons out: $3/2 = 1.5$.

🧠 **Sense check:** Bond order 0.5: half a bond. B_2 has bond order 1, and losing one bonding $\pi 2p$ electron halves it. ✓



Practice 5

cyanide ion, CN^-

wanted: the bond order · the π bonds in its Lewis structure

What bond order does molecular orbital theory give CN^- , and how many π bonds does its Lewis structure show?

- A. Bond order 3; 0 π bonds
- B. Bond order 2.5; 2 π bonds
- C. Bond order 6; 2 π bonds
- D. Bond order 3; 3 π bonds
- E. Bond order 3; 2 π bonds

✓ Practice 5 answer: E

CN^- : $4 + 5 + 1 = 10$ valence electrons, the same count as N_2
 $\sigma 2s^2 \sigma^* 2s^2 \pi 2p^4 \sigma 2p^2$ · bonding 8, antibonding 2 · Lewis structure $[:\text{C}\equiv\text{N}:]^-$

$$\text{bond order} = \frac{8 - 2}{2} = 3; \text{C}\equiv\text{N} = 1 \sigma + 2 \pi \rightarrow \text{answer E}$$

A counted all three lines of $\text{C}\equiv\text{N}$ as σ : 3 σ , 0 π . B ignored the charge: CN has $4 + 5 = 9$, $(7 - 2)/2 = 2.5$. C forgot to halve: $8 - 2 = 6$. D read the triple bond as pure π and dropped its σ .

🧠 **Sense check:** MO bond order 3 matches the Lewis triple bond: one σ on the axis plus two π . ✓

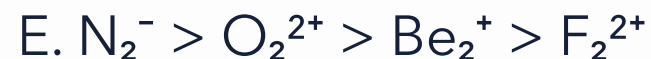
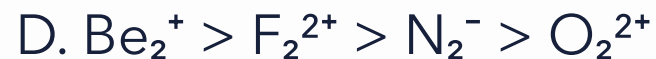
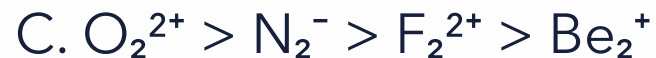
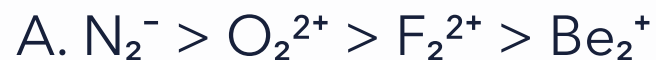


Practice 6



wanted: the order of decreasing bond order

Using molecular orbital theory, arrange these four species in order of decreasing bond order.



✓ Practice 6 answer: C

valence electrons: O_2^{2+} $12 - 2 = 10$ · N_2^- $10 + 1 = 11$ · F_2^{2+} $14 - 2 = 12$ · Be_2^+ $4 - 1 = 3$

bond order: $(8 - 2)/2 = 3$ · $(8 - 3)/2 = 2.5$ · $(8 - 4)/2 = 2$ · $(2 - 1)/2 = 0.5$

$3 > 2.5 > 2 > 0.5$: $\text{O}_2^{2+} > \text{N}_2^- > \text{F}_2^{2+} > \text{Be}_2^+ \rightarrow \text{answer C}$

A ignored the charges: neutral N_2 $3 > \text{O}_2$ $2 > \text{F}_2$ $1 > \text{Be}_2$ 0 . B ranked by electron count, $12 > 11 > 10 > 3$. D listed increasing bond order, the reverse. E moved each charge the wrong way: N_2^- as 9 electrons gives $(7 - 2)/2 = 2.5$, O_2^{2+} as 14 gives $(8 - 6)/2 = 1$, Be_2^+ as 5 gives $(3 - 2)/2 = 0.5$, F_2^{2+} as 16 gives $(8 - 8)/2 = 0$.

 **Sense check:** More electrons do not mean more bond. F_2^{2+} has the most, but four of them sit in antibonding orbitals. ✓



Check yourself

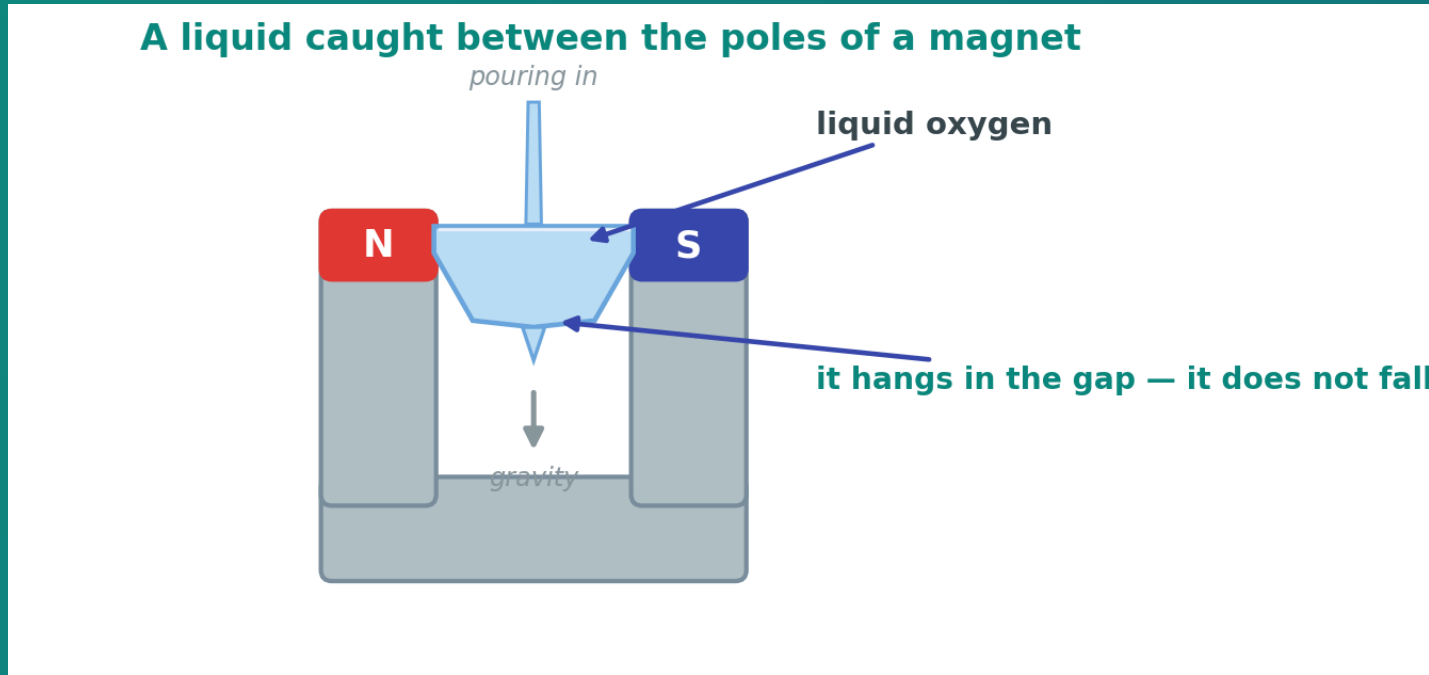
1. C_2 has 8 valence electrons: 6 fill bonding orbitals and 2 fill antibonding. Find the bond order, and say whether C_2 is held more or less tightly than N_2 .
2. A molecule has equal numbers of bonding and antibonding electrons. What is its bond order, and can the molecule exist?

The same electron filling that sets the bond order also decides magnetism. A molecule with unpaired electrons in its orbitals is pulled toward a magnet. O_2 's two antibonding electrons are unpaired, which is why liquid oxygen clings to a magnet.

4 · MO Diagrams & Magnetism

Fill the molecular-orbital diagram of a second-period diatomic, then read its bond order and whether it is paramagnetic or diamagnetic from the filled diagram.

A liquid that clings to a magnet



Pour liquid oxygen between a magnet's poles and it bridges the gap, held there against gravity. The plain dot picture of oxygen gives no hint of this.

What a Lewis structure already shows

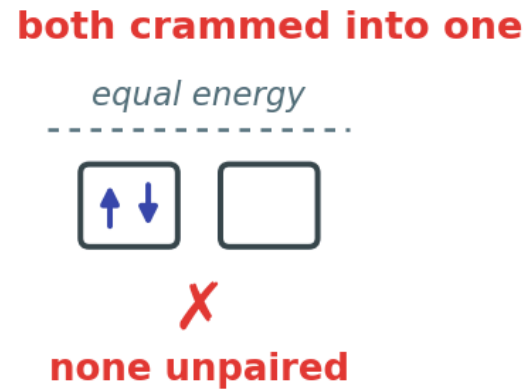
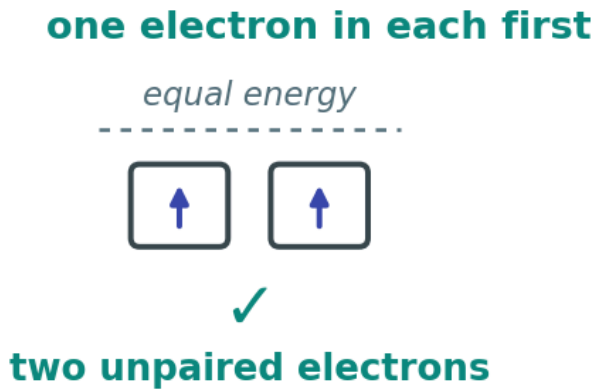
O=O with two lone pairs on each O

2 bonding pairs + 4 lone pairs = 6 pairs = 12 valence electrons · not one drawn alone

A Lewis structure counts each bond as a shared pair and draws every electron paired. Molecular orbitals keep that count as the bond order, and they can find an electron left alone.

Molecular orbitals fill like atomic ones

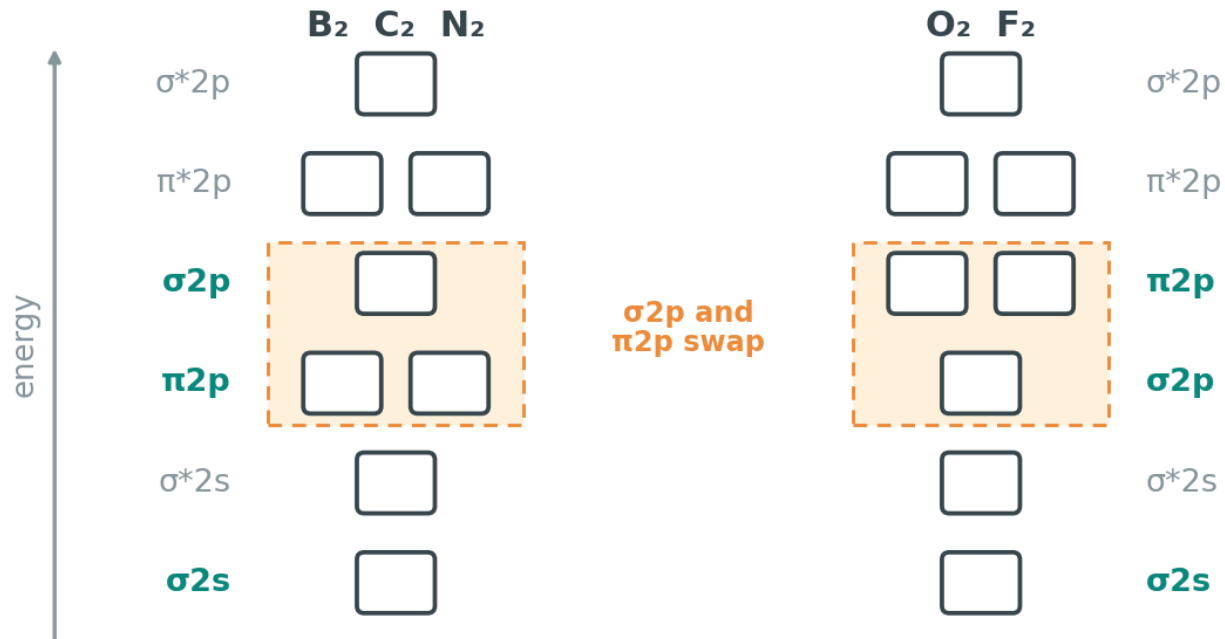
Equal-energy orbitals take one electron each before any pairs



Molecular orbitals fill by the same rules as an atom's: lowest first, opposite spins per orbital, one electron in every equal-energy orbital before pairing. A leftover unpaired electron makes the molecule magnetic.

The molecular-orbital ladder

The valence-MO ladder — teal bonding, grey antibonding



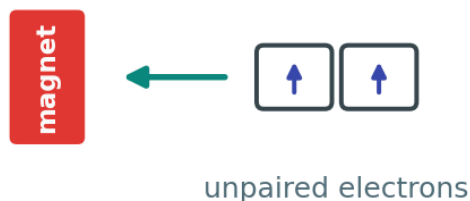
Only the boxed pair changes order; every other level and the filling rules stay the same

Each set pairs a lower bonding orbital with a higher antibonding one. The two π orbitals share one energy: a degenerate pair. Only the $\sigma 2p$ and $\pi 2p$ order changes.

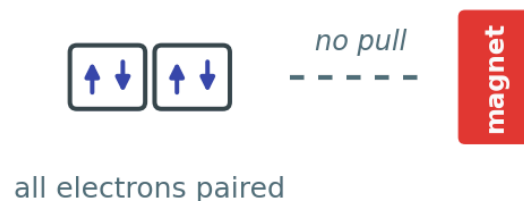
Reading magnetism from the diagram

One unpaired electron is enough to make a molecule magnetic

paramagnetic — pulled in



diamagnetic — not pulled



Every electron spins and acts as a tiny magnet. Paired electrons spin opposite ways and cancel. An unpaired electron leaves a net magnet for the field to grab: paramagnetic. All paired: diamagnetic, not pulled.

memory hook: unpaired means paramagnetic, pulled into the field

hear the di in diamagnetic as two: every electron sits in a pair, nothing for the field to grab



The method

1. **Count the valence electrons.**
2. **Fill from the bottom up:** opposite spins per orbital, one electron in each equal-energy orbital before pairing.
3. **Read the magnetism:** any unpaired electron, paramagnetic; none, diamagnetic.
4. **Bond order** = (bonding – antibonding) $\div$ 2.



Worked example 1: nitrogen, N₂

Step 1 • Count the valence electrons

N₂: each N contributes 5 valence electrons

$2 \times 5 = 10$ valence electrons to place

Nitrogen sits early in the second period, so its $\pi 2p$ pair lies below $\sigma 2p$. Fill the diagram, then read the magnetism and the bond order.

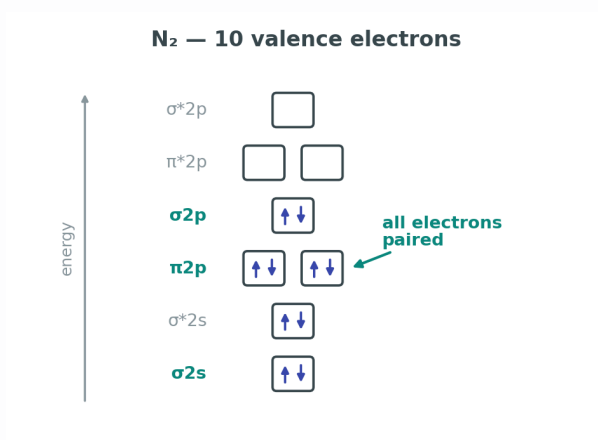
✓ Worked example 1: filling the diagram

N_2 : 10 valence electrons

$2 \times 5 = 10$ to place

Step 2 • Fill the MOs from the bottom up

Fill upward: $\sigma 2s$, $\sigma^* 2s$, the degenerate $\pi 2p$ pair, then $\sigma 2p$. Every filled orbital holds a pair.



Sense check: Every filled orbital holds a pair, so the N_2 diagram is ready to read for magnetism and bond order.

✓ Worked example 1: reading it

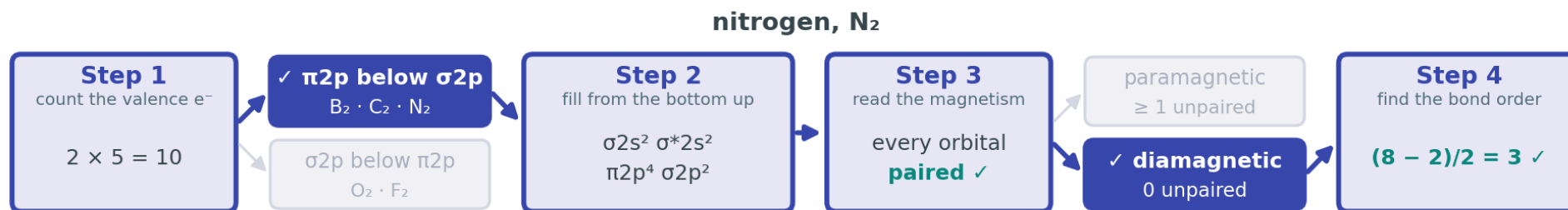
N_2 : 10 valence electrons, diagram filled
 $\sigma 2s$, $\sigma^* 2s$, the $\pi 2p$ pair, then $\sigma 2p$ · every orbital paired

Step 3 · Read the magnetism

Step 4 · Find the bond order

$\text{N}_2 \rightarrow$ diamagnetic · bond order = $(8 - 2)/2 = 3$
 0 unpaired electrons · 8 bonding – 2 antibonding, halved · a triple bond

🧠 **Sense check:** Both results come off the same diagram: N_2 carries a triple bond and no unpaired electrons, so it is diamagnetic.



Worked example 2: oxygen, O₂

Step 1 • Count the valence electrons

O₂: each O contributes 6 valence electrons

$$2 \times 6 = 12 \text{ valence electrons to place}$$

Oxygen sits later in the period, so σ_{2p} drops below π_{2p} . The last two electrons reach the degenerate π^*_{2p} pair. A common first attempt pairs them in one orbital. Fill the diagram and read the magnetism.

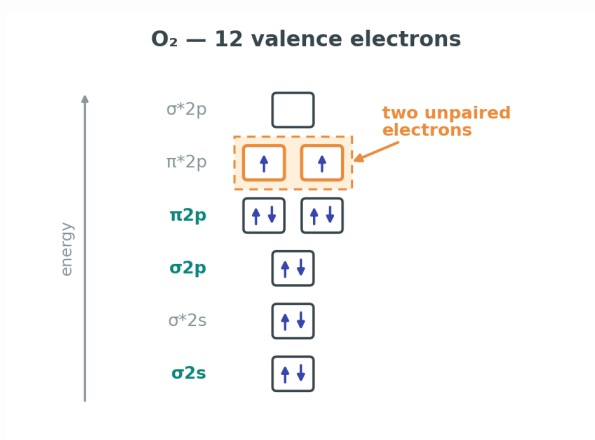
✓ Worked example 2: filling the diagram

O₂: 12 valence electrons

$$2 \times 6 = 12 \text{ to place}$$

Step 2 · Fill the MOs from the bottom up

Hund's rule puts one electron in each π^*2p orbital before either pairs.



🧠 **Sense check:** Each π^*2p orbital takes one electron; read the diagram for magnetism and bond order.

✓ Worked example 2: reading it

O_2 : 12 valence electrons, diagram filled
 $\sigma 2p$ below $\pi 2p$ · the last two electrons reach the $\pi^* 2p$ pair

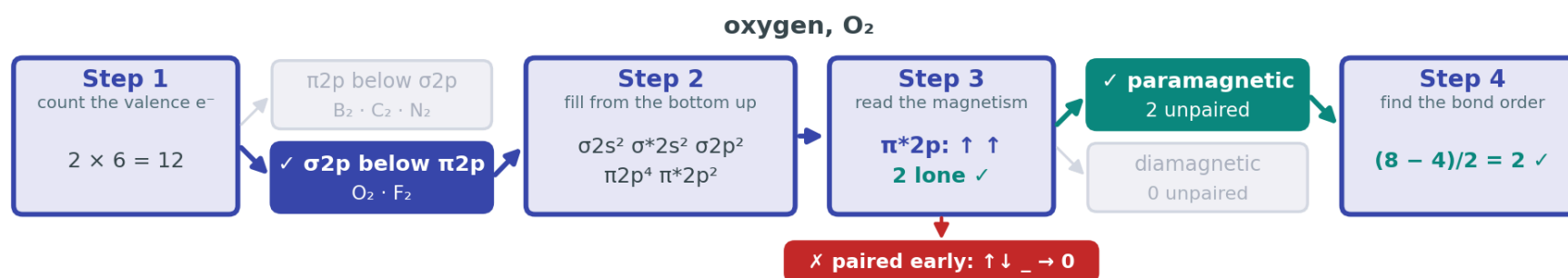
A common first attempt

Step 3 · Read the magnetism

Step 4 · Find the bond order

$O_2 \rightarrow$ paramagnetic · bond order = $(8 - 4)/2 = 2$
 2 unpaired electrons · 8 bonding – 4 antibonding, halved · a double bond

 **Sense check:** The dot structure pairs every electron and predicts no magnetism. The diagram keeps the last two apart, so O_2 is paramagnetic: the liquid clings to a magnet.



Take-home: fill a degenerate pair one at a time

✓ Hund: one electron in each π^*2p orbital
2 unpaired · O_2 is paramagnetic

✗ paired early: both crammed into one π^*2p orbital
0 unpaired · wrongly predicts diamagnetic

Two electrons entering an equal-energy pair take one orbital each before either pairs. That single choice is why O_2 is paramagnetic, the result a dot structure misses.



Guided example: diboron, B₂

Step 1 • Count the valence electrons

B₂: each B contributes 3 valence electrons

$2 \times 3 = 6$ valence electrons to place

Boron sits early in the second period. Pick its orbital order, then run Steps 2 to 4 and name each move as you make it. Find the magnetism and the bond order.

✓ Guided example: solution

B₂: 6 valence electrons

2 × 3 = 6 to place · boron sits early: n2p lies below σ2p

A common first attempt

✗ oxygen's order: σ2s² σ*2s² σ2p² → 0 unpaired

σ2p placed below n2p · electrons 5 and 6 pair there · wrongly predicts diamagnetic

Step 2 · Fill the MOs from the bottom up

Step 3 · Read the magnetism

Step 4 · Find the bond order

σ2s² σ*2s² n2p² → paramagnetic · bond order = (4 – 2)/2 = 1

2 + 2 + 2 = 6 placed · n2p: ↑ ↑, 2 unpaired · σ2p stays empty

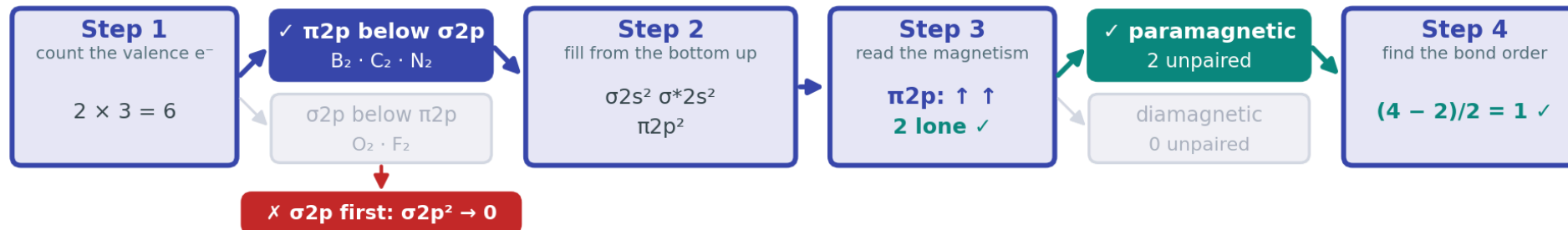
 **Sense check:** B₂ is in fact paramagnetic: the magnet test shows n2p lies lowest for boron. ✓

✓ Guided example: the route

B_2 : $2 \times 3 = 6$ valence electrons

given: B_2 · found: 2 unpaired, paramagnetic · bond order 1

diboron, B_2



 **Sense check:** The order fork decides the magnetism. Boron's $\pi 2p$ -first order keeps the last two electrons apart; $\sigma 2p$ first would pair them and miss the magnet test.

Your turn: fluorine, F_2

F_2 has 14 valence electrons, two more than O_2 . Those two complete the π^*2p pair. Fill the blanks, then name the magnetism.

quantity	value
electrons in the π^*2p pair	4 (both orbitals full)
unpaired electrons	_____
bonding – antibonding	8 – _____
bond order	_____
magnetism	_____

$F_2 \rightarrow$ diamagnetic · bond order = $(8 - 6)/2 = 1$
 π^*2p full: 0 unpaired · 8 bonding – 6 antibonding, halved

⚠ Where this goes wrong

Pairing the degenerate electrons. Forcing O_2 's last two electrons into one π^*2p orbital leaves none unpaired and wrongly calls O_2 diamagnetic. Hund's rule puts one in each orbital first: 2 unpaired, paramagnetic.

Reading magnetism from the dot structure. The $O=O$ dot structure pairs every electron and predicts diamagnetic. Magnetism is read off the filled MO diagram, where the two π^*2p electrons stay unpaired.

Forgetting to halve the bond order. For O_2 , bonding minus antibonding is $8 - 4 = 4$. Bond order counts electron pairs: $(8 - 4)/2 = 2$, not 4.

Adding the antibonding electrons. Antibonding electrons weaken the bond. Bond order is $(8 - 4)/2 = 2$, not $(8 + 4)/2 = 6$. They subtract, never add.



Practice 1

superoxide ion, O_2^- : 13 valence electrons

O_2 plus 1 more electron, into π^*2p

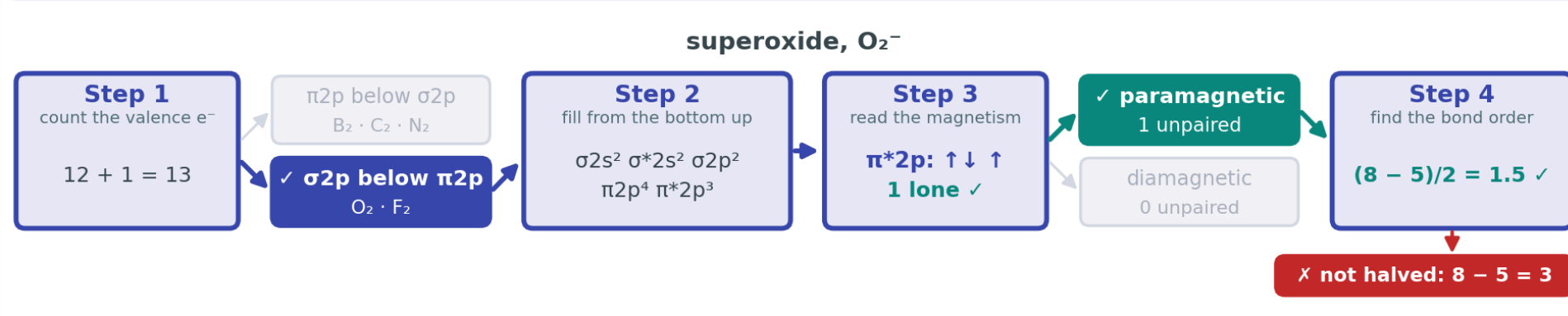
Give the bond order and the magnetic behavior of the superoxide ion.

- A. Bond order 1.5; paramagnetic
- B. Bond order 1.5; diamagnetic
- C. Bond order 3; paramagnetic
- D. Bond order 6.5; paramagnetic

✓ Practice 1 answer: A

$\text{O}_2^- \rightarrow$ bond order 1.5, paramagnetic $\rightarrow$ answer A
 π^*2p holds 3 electrons: one orbital paired, one single $\cdot (8 - 5)/2 = 1.5$

🧠 **Sense check:** An odd electron count guarantees at least one unpaired electron. The extra antibonding electron drops the bond order below O_2 's 2.





Worked example 3: the O_2^+ ion

Step 1 • Count the valence electrons

O_2^+ : O_2 with one electron removed

$12 - 1 = 11$ valence electrons to place

An electron leaves from the highest occupied orbital, a π^*2p . Fill the diagram, then read the magnetism and the bond order.

✓ Worked example 3: solution

O_2^+ : 11 valence electrons

$12 - 1 = 11$ to place

Step 2 · Fill the MOs from the bottom up

Step 3 · Read the magnetism

$\text{O}_2^+ \rightarrow$ paramagnetic

1 unpaired electron · still pulled toward a magnet

Step 4 · Find the bond order

Removing an antibonding electron leaves 8 bonding and 3 antibonding.

bond order = $(8 - 3)/2 = 2.5$

8 bonding – 3 antibonding, halved · stronger than O_2

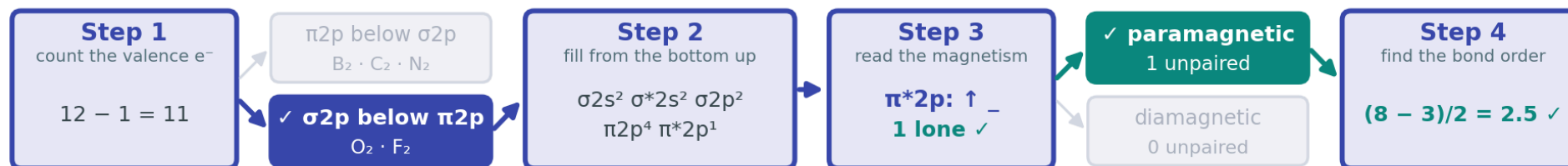
 **Sense check:** Pulling an electron from an antibonding orbital raises the bond order from 2 to 2.5. One electron stays unpaired, so O_2^+ is paramagnetic.

✓ Worked example 3: the route

O_2^+ : $12 - 1 = 11$ valence electrons

given: O_2 minus one electron · found: 1 unpaired, paramagnetic · bond order 2.5

the O_2^+ ion



 **Sense check:** O_2^+ runs the same $\sigma 2p$ -first order as O_2 , one electron short. Only the $\pi^* 2p$ count changes, and with it both results: 1 unpaired, bond order up from 2 to 2.5.



Practice 2



wanted: the molecular orbital that holds an unpaired electron

Which molecular orbital of Be_2^- holds an unpaired electron?

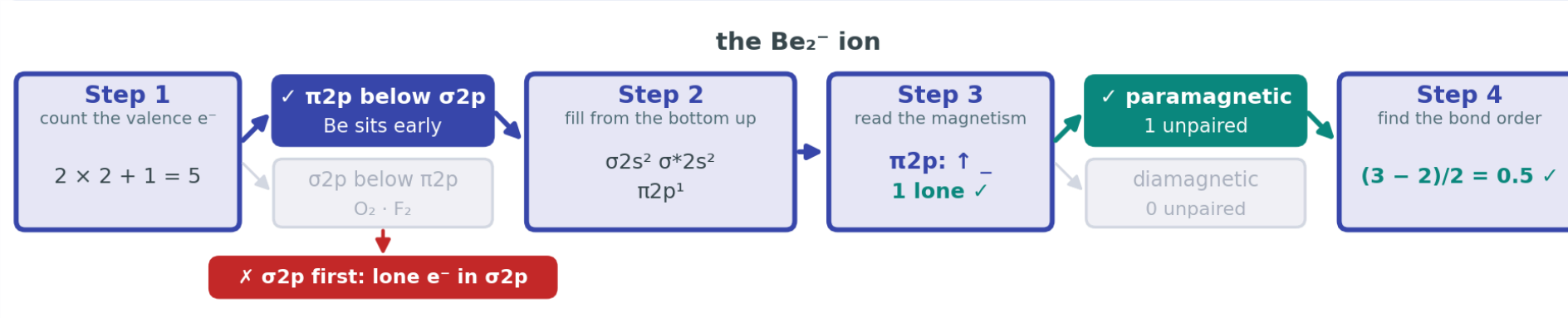
- A. σ^*2s
- B. $\pi 2p$
- C. $\sigma 2p$
- D. None: every electron is paired

✓ Practice 2 answer: B



beryllium sits early: $\pi 2p$ below $\sigma 2p$ · the 5th electron enters the $\pi 2p$ pair alone · 1 unpaired

🧠 **Sense check:** An odd count of 5 leaves one electron alone. It enters a bonding orbital: bond order $(3 - 2)/2 = 0.5$, up from Be_2 's 0. ✓





Practice 3



wanted: the paramagnetic one · the higher bond order

Of F_2^- and the acetylide ion C_2^{2-} , which one is paramagnetic, and which one has the higher bond order?

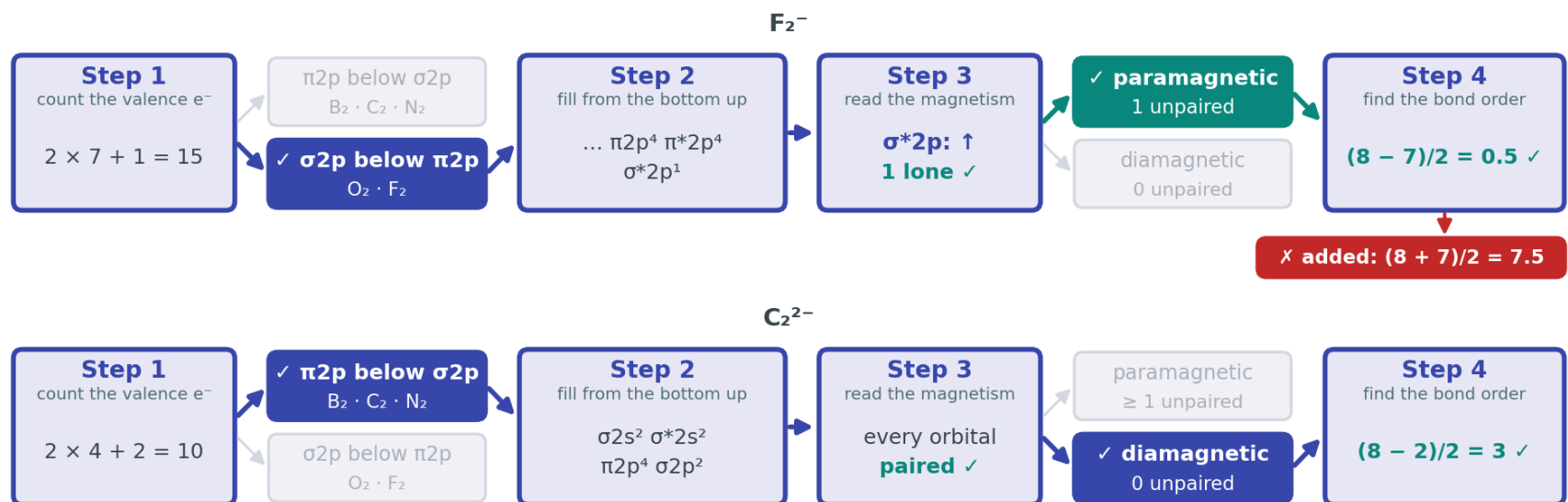
- A. C_2^{2-} is paramagnetic; C_2^{2-} has the higher bond order
- B. F_2^- is paramagnetic; F_2^- has the higher bond order
- C. C_2^{2-} is paramagnetic; F_2^- has the higher bond order
- D. F_2^- is paramagnetic; C_2^{2-} has the higher bond order

✓ Practice 3 answer: D

F_2^- paramagnetic, bond order 0.5 · C_2^{2-} diamagnetic, bond order 3 → answer D

F_2^- : $2 \times 7 + 1 = 15$ · π^*2p full, the 15th electron alone in σ^*2p · $(8 - 7)/2 = 0.5$ · C_2^{2-} : $2 \times 4 + 2 = 10$, all paired · $(8 - 2)/2 = 3$

 **Sense check:** Count the charge before filling: the 2– adds two electrons to C_2 , the – adds one to F_2 , past the full π^*2p into σ^*2p . An odd count always leaves an electron unpaired. ✓



 Practice 4

$\text{B}_2^{2+} \cdot \text{N}_2^{2+} \cdot \text{O}_2^{2-} \cdot \text{C}_2^{2+}$
wanted: the paramagnetic species

Which of these species is paramagnetic?

- A. B_2^{2+}
- B. N_2^{2+}
- C. O_2^{2-}
- D. C_2^{2+}

✓ Practice 4 answer: D

$$\text{C}_2^{2+}: 2 \times 4 - 2 = 6 \cdot \sigma 2s^2 \sigma^* 2s^2 \pi 2p^2 \rightarrow \text{answer D}$$

the two $\pi 2p$ electrons take one orbital each · 2 unpaired · paramagnetic

A took both electrons from $\sigma^* 2s$, leaving $\sigma 2s^2 \pi 2p^2$. They leave the highest filled orbital, $\pi 2p$: B_2^{2+} has $2 \times 3 - 2 = 4$, only the 2s orbitals filled, all paired. B applied the charge backwards, $2 \times 5 + 2 = 12$, O_2 's count with two unpaired. N_2^{2+} loses 2: $2 \times 5 - 2 = 8$, $\pi 2p$ full, all paired. C dropped the charge and filled neutral O_2 , which is paramagnetic. O_2^{2-} has $2 \times 6 + 2 = 14$: both antibonding π orbitals full, 0 unpaired.

 **Sense check:** An even count can still leave electrons unpaired. The last two C_2^{2+} electrons enter the degenerate $\pi 2p$ pair, so Hund's rule keeps them apart. ✓



Practice 5



wanted: the valence MO configuration, lowest energy first

Which is the correct valence molecular-orbital configuration of B_2^- , written from lowest to highest energy?

- A. $\sigma 2s^2 \sigma^* 2s^2 \pi 2p^3$
- B. $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p^2 \pi 2p^1$
- C. $\sigma 2s^2 \sigma^* 2s^2 \pi 2p^2 \sigma 2p^1$
- D. $\sigma 2s^2 \sigma^* 2s^2 \pi 2p^1$

✓ Practice 5 answer: A

$$\text{B}_2^-: 2 \times 3 + 1 = 7 \cdot \sigma 2s^2 \sigma^* 2s^2 \pi 2p^3 \rightarrow \text{answer A}$$

boron sits early: $\pi 2p$ below $\sigma 2p$ · the $\pi 2p$ pair holds 3 of its 4 places

B used the oxygen ordering, $\sigma 2p$ below $\pi 2p$. Boron sits early in the period, so the $\pi 2p$ pair fills before $\sigma 2p$. C let the $\pi 2p$ pair take only 2, as if it were one orbital. It is two orbitals and holds 4. D applied the charge backwards: $2 \times 3 - 1 = 5$ electrons.

 **Sense check:** Seven is an odd count: one $\pi 2p$ electron stays unpaired, so B_2^- is paramagnetic, bond order $(5 - 2)/2 = 1.5$. ✓

 Practice 6

wanted: the species that matches O_2 in bond order and in magnetism

Which species has the same bond order and the same magnetic behavior as O_2 ?



✓ Practice 6 answer: C

N_2^{2-} : $2 \times 5 + 2 = 12 \cdot \sigma 2s^2 \sigma^* 2s^2 \pi 2p^4 \sigma 2p^2 \pi^* 2p^2 \rightarrow \text{answer C}$
 bond order $(8 - 4)/2 = 2 \cdot 2$ unpaired in $\pi^* 2p \cdot \text{O}_2$: bond order 2, paramagnetic

A applied the charge backwards, $2 \times 7 - 2 = 12$, O_2 's count. F_2^{2-} gains 2: $2 \times 7 + 2 = 16$, every antibonding orbital full, $(8 - 8)/2 = 0$. B matched the magnetism only: C_2^- has $2 \times 4 + 1 = 9$, 1 unpaired in $\sigma 2p$, but $(7 - 2)/2 = 2.5$. D matched the bond order only: B_2^{2-} has $2 \times 3 + 2 = 8$, $(6 - 2)/2 = 2$, all paired.

 **Sense check:** N_2^{2-} holds 12 electrons, the same count as O_2 . The $\sigma 2p$ and $\pi 2p$ order differs, but both diagrams end with one electron in each $\pi^* 2p$ orbital. ✓

Check yourself

1. N_2^- has 11 valence electrons, one more than N_2 , and the extra one enters π^*2p . How many electrons are unpaired, and what is the bond order?
2. C_2 has 8 valence electrons. Give its bond order, and state whether it is paramagnetic or diamagnetic.

Magnetism and bond order both come from how electrons pack into orbitals. The next unit turns to how whole molecules pack against one another: the intermolecular forces that set boiling points, and the gas laws that describe those particles once the attractions between them become negligible.

Can you...?

- ☐ assign sp , sp^2 , or sp^3 hybridization to a central atom from its number of electron domains?
- ☐ count sigma and pi bonds in a molecule from its Lewis structure?
- ☐ build the molecular-orbital occupation of a second-period diatomic and compute its bond order?
- ☐ predict paramagnetism or diamagnetism from a molecular-orbital diagram?

If any box stays empty, the practice site has a drill for it. 🧪