

# 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

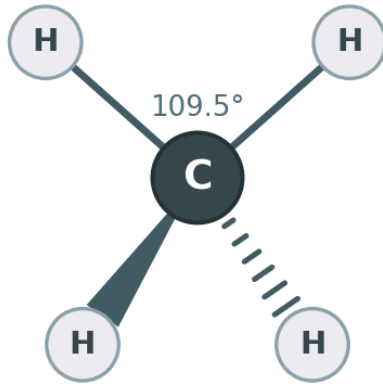
1. Hybridization
2. Sigma & Pi Bonds
3. Molecular Orbitals & Bond Order
4. MO Diagrams & Magnetism

# 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,  $180^\circ$  · 3: trigonal planar,  $120^\circ$  · 4: tetrahedral,  $109.5^\circ$   
5: trigonal bipyramidal,  $120^\circ$  and  $90^\circ$  · 6: octahedral,  $90^\circ$  · 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  $90^\circ$  apart, so they cannot aim along  $109.5^\circ$  or  $120^\circ$ . Hybridization starts from the same count.

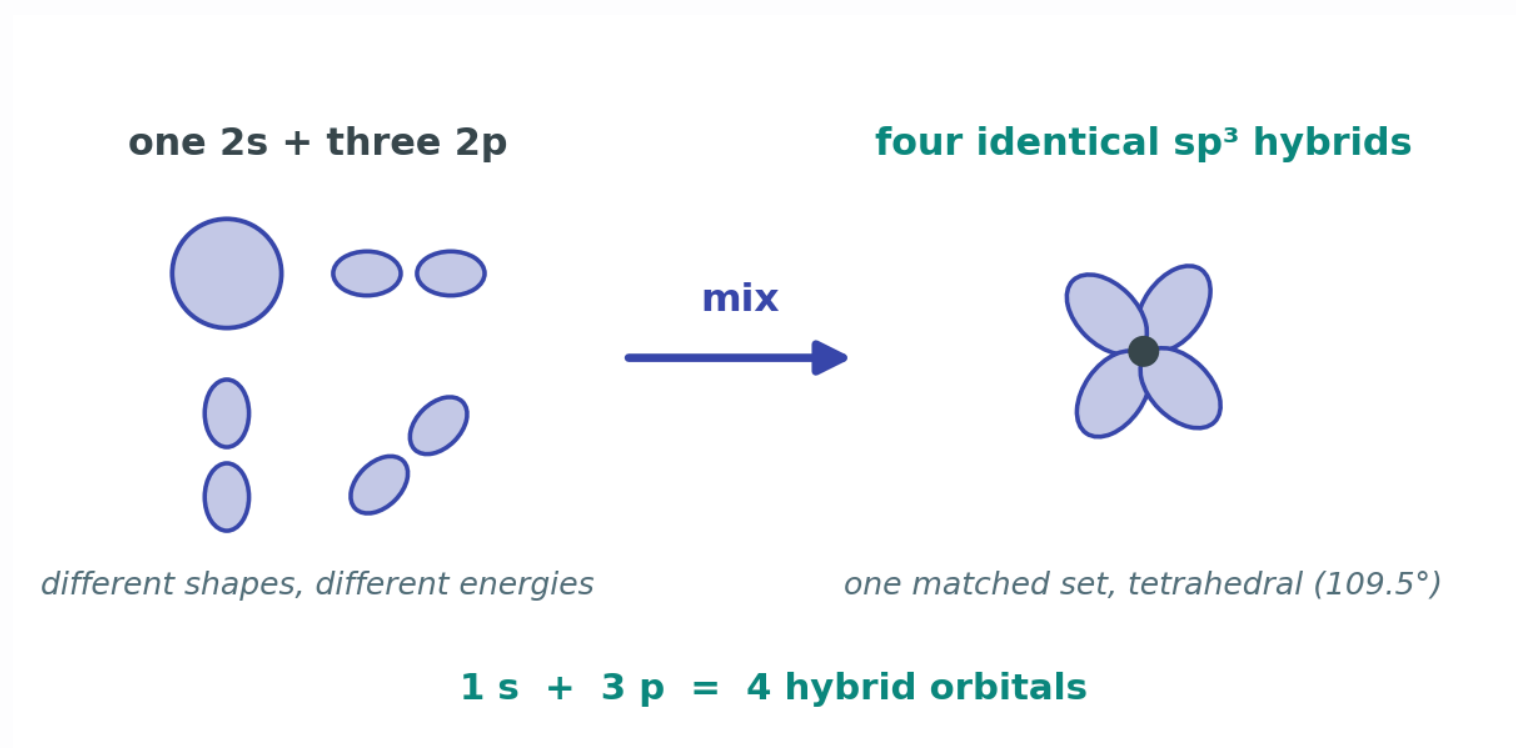
# Electron domains set the hybridization

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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.

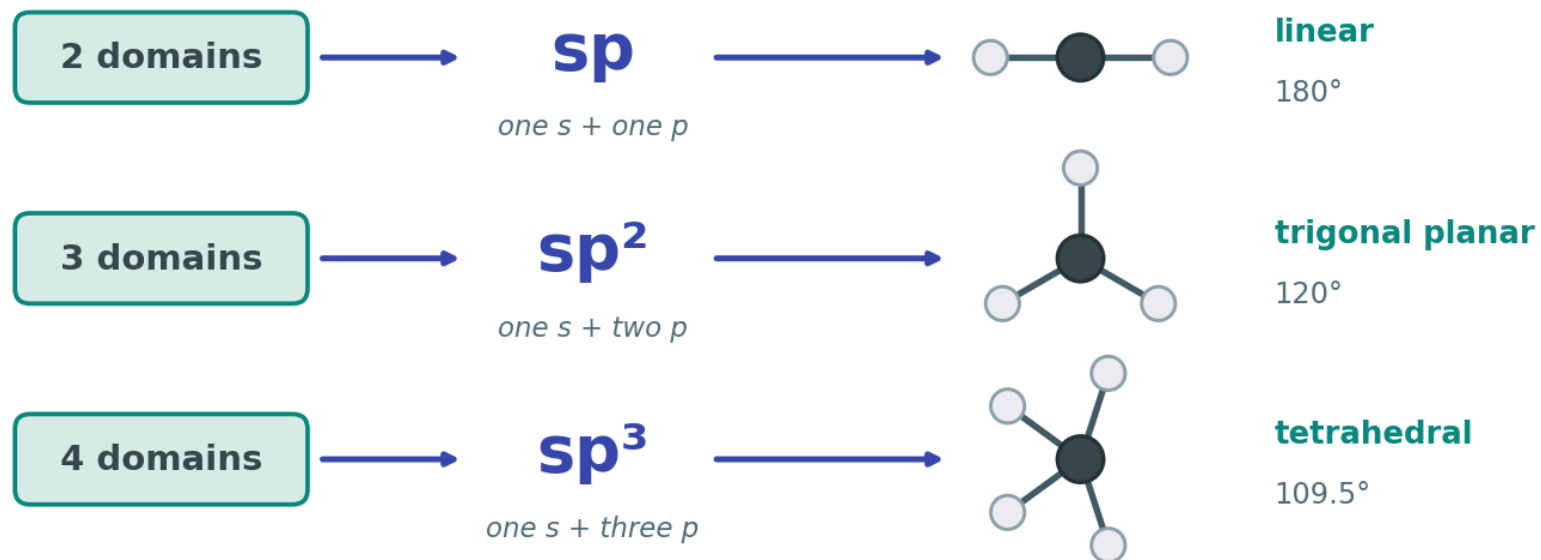
# One s and three p become four alike



Pure s and p orbitals would give  $90^\circ$  bonds; real methane is  $109.5^\circ$ . 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

**H<sub>2</sub>O: 2 bonds + 2 lone pairs = 4 domains → sp<sup>3</sup>**  
**bonded atoms: 2 · lone pairs on O: 2 · total electron domains: 4**

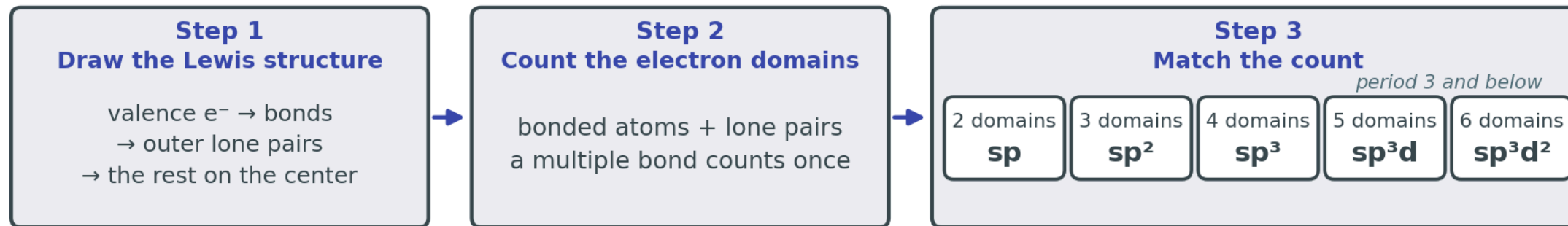
Every region of electron density around the central atom is a domain: a bond or a lone pair. Both take a hybrid orbital. Count bonds and lone pairs together.

**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  $\rightarrow$  sp<sup>2</sup>, 4  $\rightarrow$  sp<sup>3</sup>, 5  $\rightarrow$  sp<sup>3</sup>d, 6  $\rightarrow$  sp<sup>3</sup>d<sup>2</sup>.

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



**✗ skipping lone pairs · ✗ a double bond counted twice**

 **Worked example 1: methane, CH<sub>4</sub>**

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,  $109.5^\circ$  apart: methane's real shape.





## Worked example 2: ammonia, $\text{NH}_3$



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

$sp$

$sp^2$

$sp^3$  · N

$sp^3d$

$sp^3d^2$

✗ 3 bonded atoms only →  $sp^2$



## Guided example: hydrogen selenide, H<sub>2</sub>Se



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, $\text{BF}_3$



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  $\rightarrow$   $\text{sp}^2$**

**mix one 2s + two 2p  $\rightarrow$  three equivalent  $\text{sp}^2$  hybrids, trigonal planar ( $120^\circ$ )**

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



## ⚠ 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  $90^\circ$ . Methane,  $BF_3$ , and  $CO_2$  bond at  $109.5^\circ$ ,  $120^\circ$ , and  $180^\circ$ . Mixing the orbitals is what points them at the measured geometry.



## Practice 1

**$\text{NI}_3$ : nitrogen triiodide**  
central atom: N · bonded atoms: 3 I

What is the hybridization of the central nitrogen atom?

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

## ✓ Practice 1 answer: B

$\text{NI}_3$ : 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,  $\text{sp}^3$ . The lone pair counts.

Step 1

26  $e^-$ : 1 lone pair on N

Step 2

$3 + 1 = 4$

sp

$\text{sp}^2$

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

$\text{sp}^3\text{d}$

$\text{sp}^3\text{d}^2$

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

## Worked example 3: carbon dioxide, CO<sub>2</sub>



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 ( $180^\circ$ )

 **Sense check:** Two domains sit  $180^\circ$  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

**CO<sub>2</sub>: O=C=O → 2 domains → sp**  
two double bonds, each one domain, not four ✓

**counting each double bond as two → 4 domains → sp<sup>3</sup>**  
**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

**CH<sub>3</sub>-CH=O: acetaldehyde**

**a classmate's labels: CH<sub>3</sub> carbon sp<sup>3</sup> · carbonyl carbon sp · O sp<sup>2</sup> · the O keeps two lone pairs**

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

- A. The CH<sub>3</sub> carbon: sp<sup>2</sup>, its three hydrogens make three domains
- B. The oxygen: sp<sup>3</sup>, the double bond counted twice plus two lone pairs make four domains
- C. The carbonyl carbon: sp<sup>2</sup>, 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<sub>2</sub>

## ✓ Practice 2 answer: C

CH<sub>3</sub> carbon: 3 H + 1 C = 4 → sp<sup>3</sup> ✓ · carbonyl carbon: H + C + O = 3 domains → sp<sup>2</sup>,  
 not sp · O: 1 double bond + 2 lone pairs = 3 → sp<sup>2</sup> ✓  
 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 sp<sup>2</sup> 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

sp<sup>2</sup> · C=O C, O

sp<sup>3</sup> · CH<sub>3</sub> C

sp<sup>3</sup>d

sp<sup>3</sup>d<sup>2</sup>

✗ D: C=O carbon as sp, like CO<sub>2</sub>

## 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 ( $120^\circ$  and  $90^\circ$ ) ·  $sp^3d^2$  aims at an octahedron ( $90^\circ$ ) · 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,  $\text{BrCl}_2^-$** 

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<sup>–</sup> 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<sup>–</sup>: 3 lone pairs on Br

Step 2

$$2 + 3 = 5$$

sp

sp<sup>2</sup>

sp<sup>3</sup>

sp<sup>3</sup>d · Br

sp<sup>3</sup>d<sup>2</sup>

✗ linear read as 2 → sp

 **Worked example 5: hexachlorostannate ion,  $\text{SnCl}_6^{2-}$** 

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

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

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  $\text{XeF}_3^+$  · N in FNO (skeleton F-N-O)

What are the hybridizations of the central atoms in  $\text{XeF}_3^+$  and FNO, respectively?

- A.  $\text{sp}^3\text{d}^2$  and  $\text{sp}^2$
- B.  $\text{sp}^2$  and  $\text{sp}^2$
- C.  $\text{sp}^3\text{d}$  and  $\text{sp}^3$
- D.  $\text{sp}^3\text{d}^2$  and  $\text{sp}^3$
- E.  $\text{sp}^3\text{d}$  and  $\text{sp}^2$

## ✓ Practice 3 answer: E

$\text{XeF}_3^+$ : 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

$\text{XeF}_3^+$ :  $8 + 3(7) - 1 = 28$  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  $\rightarrow sp^3d^2$



## Check yourself

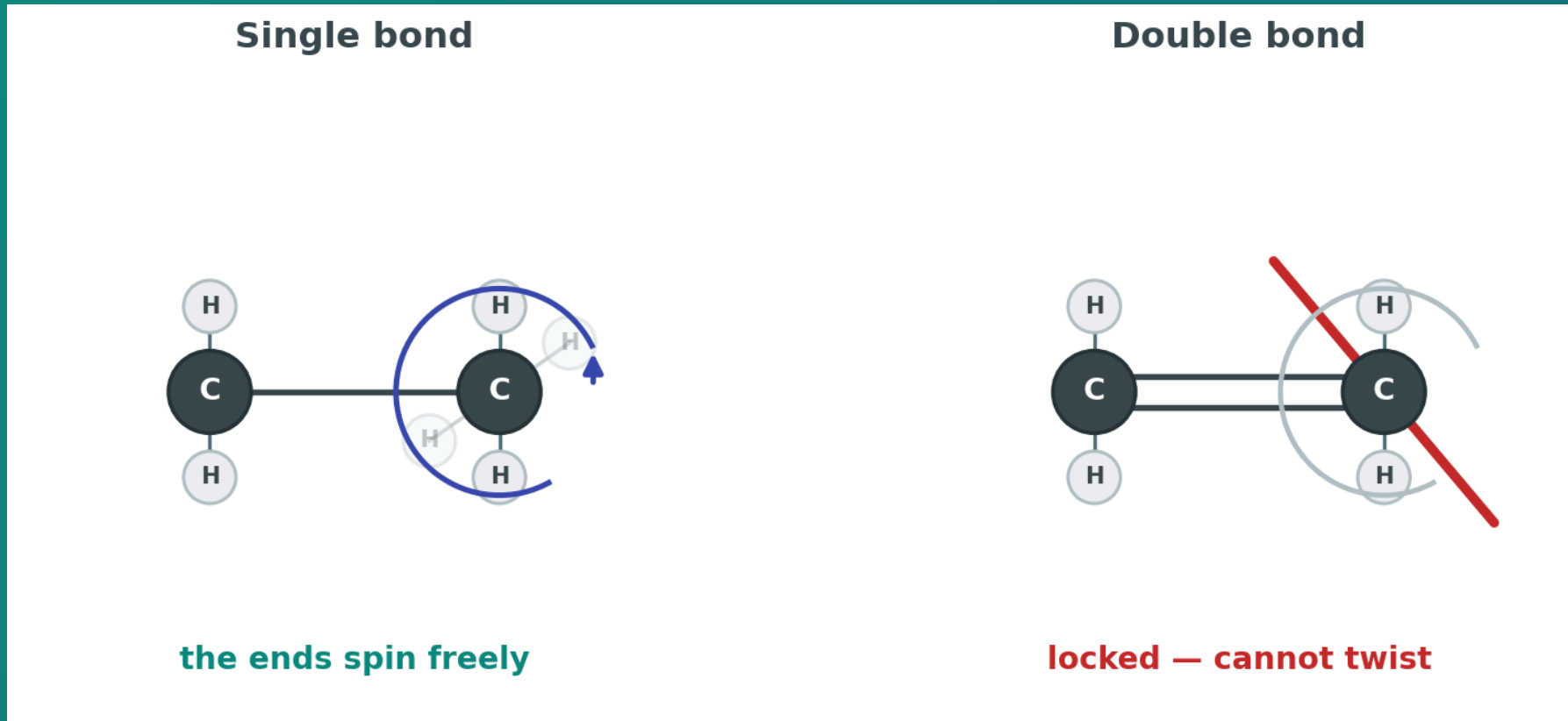
1. Sulfur dioxide,  $\text{SO}_2$ , has a central sulfur with two bonding groups and one lone pair. How many domains, and what hybridization?
2. Why can a period-3 atom reach six electron domains while a period-2 atom stops at four? Name the hybridization at each limit.

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  $\text{sp}^2$  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  $\sigma$  and each extra line of a double or triple bond is a  $\pi$ .

# 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

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**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  $\sigma$ ; every extra line is  $\pi$



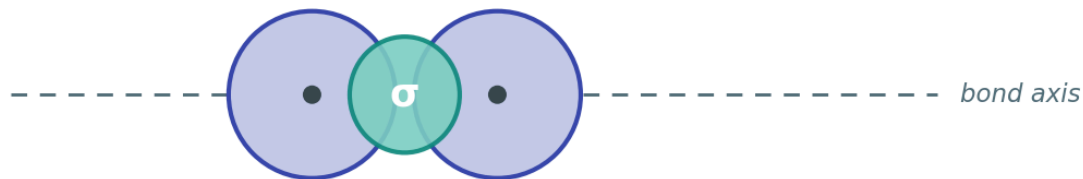
  $\sigma$  (on the axis)

  $\pi$  (off the axis)

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

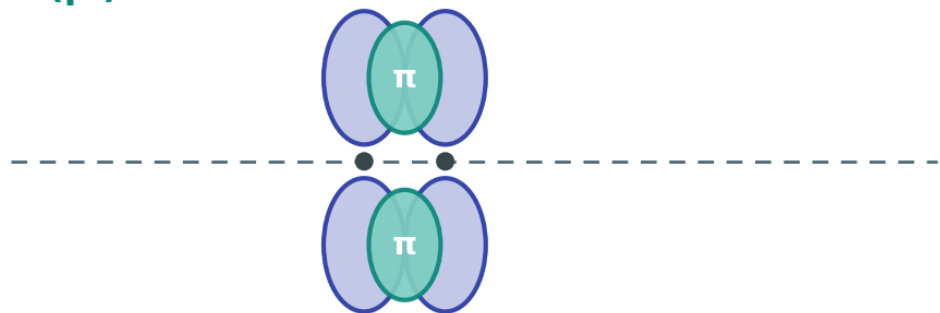
# Sigma and pi: two kinds of overlap

## $\sigma$ (sigma) bond



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

## $\pi$ (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  $\sigma$  framework is built from hybrid orbitals.

# Why a double bond cannot twist

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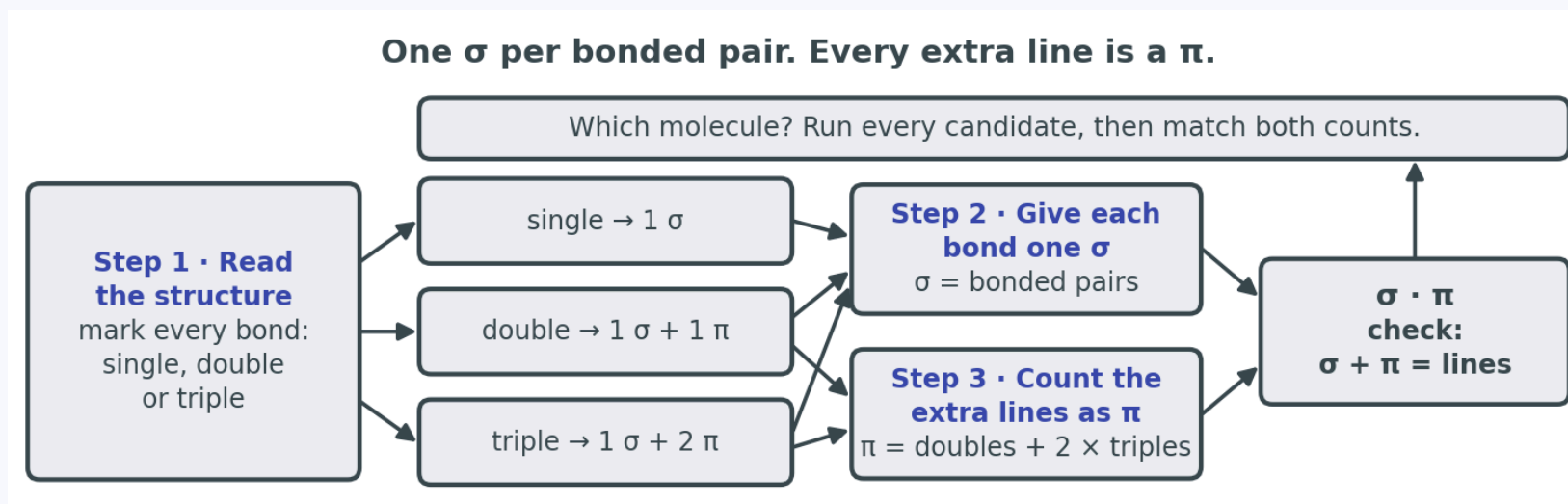
**single bond → free rotation · double bond → locked**

**the  $\sigma$  lies on the axis, so the ends turn · a  $\pi$  sits off the axis, and twisting would tear it**

A  $\sigma$  bond's overlap lies on the axis, so the ends spin freely. A  $\pi$  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  $\sigma$ .** Every bonded pair has one  $\sigma$ .
3. **Count the extra lines as  $\pi$ ,** then total. A double adds 1  $\pi$ ; a triple adds 2  $\pi$ .





## Worked example 1: methane

### Step 1 • Read the structure

**CH<sub>4</sub>: four C-H single bonds**

**given: the Lewis structure of CH<sub>4</sub> • wanted: total  $\sigma$  and  $\pi$**

Methane has four single bonds and no double or triple bonds. Count the  $\sigma$  and the  $\pi$ .

## ✓ Worked example 1: solution

$\text{CH}_4$ : four C-H single bonds

given: the Lewis structure of  $\text{CH}_4$  · wanted: total  $\sigma$  and  $\pi$

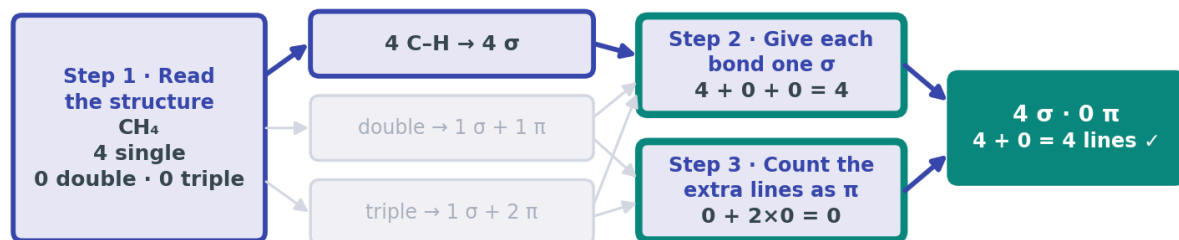
**Step 2 · Give each bond one  $\sigma$**

**Step 3 · Count the extra lines as  $\pi$**

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

four C-H bonds, one  $\sigma$  each ·  $\pi$  comes only from the extra lines of a double or triple

 **Sense check:** Four bonds, four  $\sigma$ , zero  $\pi$ . A molecule of only single bonds carries only  $\sigma$  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  $\text{C}_2\text{H}_4$  • wanted: total  $\sigma$  and  $\pi$

Ethylene has one double bond. A common first attempt: count the double as two  $\sigma$ . Find the  $\sigma$  and the  $\pi$ .

## ✓ 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  $\text{C}_2\text{H}_4$  · wanted: total  $\sigma$  and  $\pi$

### A common first attempt

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

🧠 **Sense check:** Two  $\sigma$  cannot share one axis. The C=C holds one  $\sigma$ , and its second line is a  $\pi$ .

## ✓ 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  $\text{C}_2\text{H}_4$  · wanted: total  $\sigma$  and  $\pi$

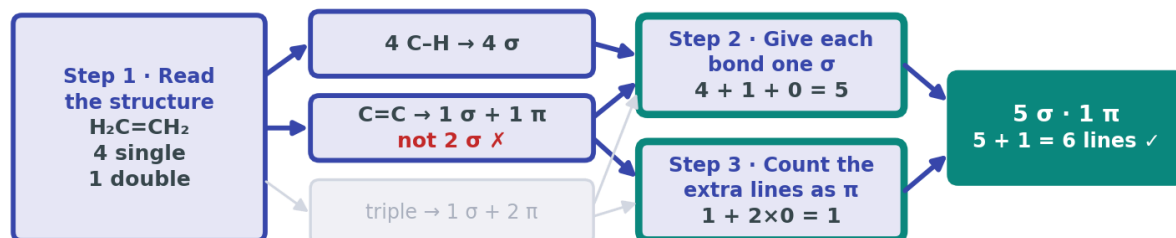
Step 2 · Give each bond one  $\sigma$

Step 3 · Count the extra lines as  $\pi$

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

every bonded pair gives one  $\sigma$  · the double's second line is the one  $\pi$

🧠 **Sense check:** Five  $\sigma$  and one  $\pi$ . The double bond splits into one  $\sigma$  and one  $\pi$ , never two  $\sigma$ .



## Take-home: a double bond is not two $\sigma$



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

The two lines of a double bond are not two  $\sigma$  bonds. The first line is the  $\sigma$ ; the second is a  $\pi$ .

**memory hook: one  $\sigma$  per bond, the rest are  $\pi$**

**count the bonded pairs for  $\sigma$  · every extra line of a double or triple is a  $\pi$**

## Your turn: carbon dioxide

**O=C=O: two C=O double bonds**  
each double bond splits into one  $\sigma$  and one  $\pi$

| bond       | $\sigma$ | $\pi$ |
|------------|----------|-------|
| first C=O  | _____    | _____ |
| second C=O | _____    | _____ |
| total      | _____    | _____ |

Give each double bond one  $\sigma$  and one  $\pi$ , then total.

**$\sigma: 1 + 1 = 2 \cdot \pi: 1 + 1 = 2$**   
**two doubles  $\rightarrow$  2  $\sigma$  and 2  $\pi$   $\cdot$  CO<sub>2</sub> has 2  $\sigma$  and 2  $\pi$**

## ⚠ Where this goes wrong

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

**Dropping the  $\sigma$  inside a multiple bond.** Reading the double as pure  $\pi$  forgets the  $\sigma$  on the axis. Ethylene's double is 1  $\sigma$  + 1  $\pi$ , so 5  $\sigma$  and 1  $\pi$ , not 4  $\sigma$  and 2  $\pi$ .

**Counting a double bond as 2  $\sigma$ .** A double bond is one  $\sigma$  plus one  $\pi$ , never two  $\sigma$ . Counting 2  $\sigma$  turns ethylene's 5  $\sigma$  into 6  $\sigma$ , still with its 1  $\pi$ .



## 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

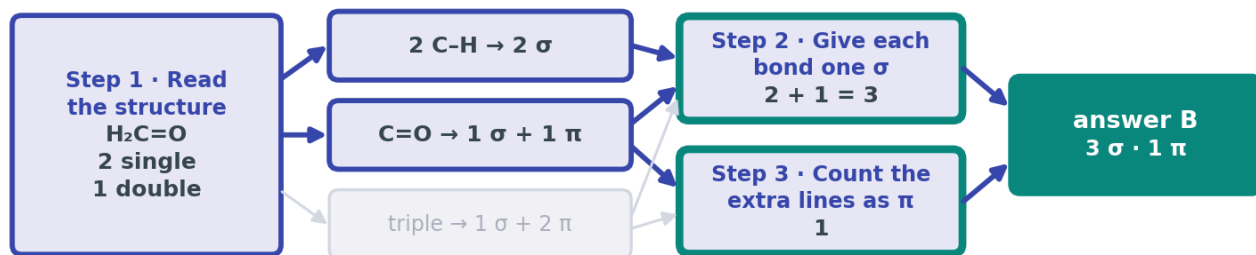
Counting every bond, how many  $\sigma$  and how many  $\pi$  does formaldehyde contain?

- A.  $\sigma$ : 4 ·  $\pi$ : 0
- B.  $\sigma$ : 3 ·  $\pi$ : 1
- C.  $\sigma$ : 2 ·  $\pi$ : 2
- D.  $\sigma$ : 4 ·  $\pi$ : 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  $\pi$

🧠 **Sense check:** Three  $\sigma$  and one  $\pi$ . The double contributes one of each; the two C-H bonds add the other two  $\sigma$ .





## 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  $\text{C}_2\text{H}_2$  • wanted: total  $\sigma$  and  $\pi$

Acetylene has a triple bond. Count the  $\sigma$  and the  $\pi$ .

## ✓ Worked example 3: solution

H-C≡C-H: two C-H bonds and one C≡C triple  
given: the Lewis structure of C<sub>2</sub>H<sub>2</sub> · wanted: total σ and π

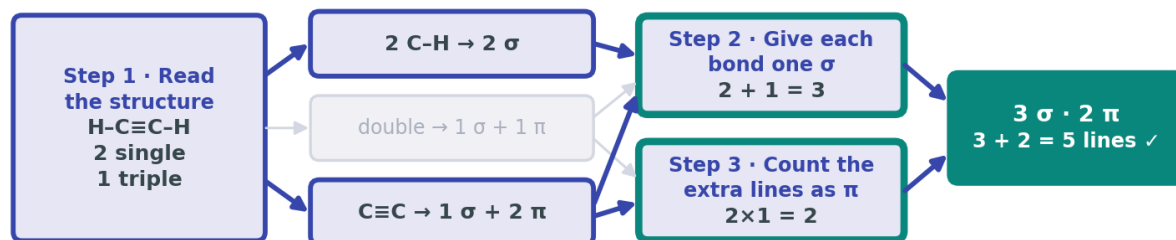
Step 2 · Give each bond one σ

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  $\sigma$  and  $\pi$

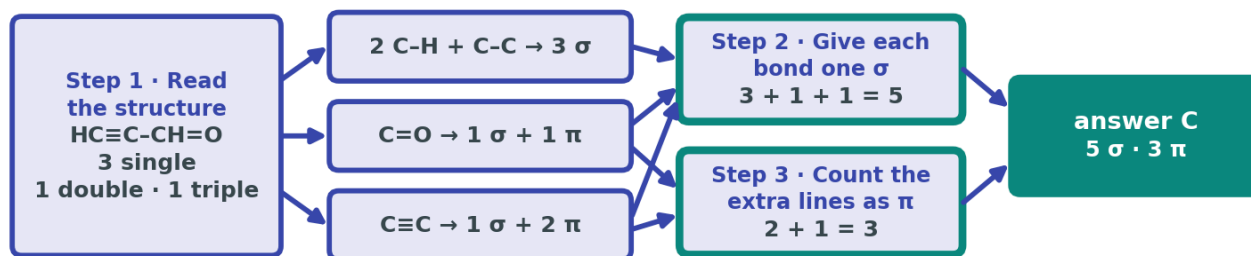
Counting every bond, how many  $\sigma$  and how many  $\pi$  does propynal contain?

- A.  $\sigma$ : 8 ·  $\pi$ : 0
- B.  $\sigma$ : 3 ·  $\pi$ : 5
- C.  $\sigma$ : 5 ·  $\pi$ : 3
- D.  $\sigma$ : 8 ·  $\pi$ : 3

## ✓ Practice 2 answer: C

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

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





## Guided example: matching a $\sigma$ and $\pi$ count



given: three Lewis structures · wanted: the one molecule with exactly 4  $\sigma$  and 2  $\pi$

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  $\sigma$  and 2  $\pi$

Step 1 · Read the structure

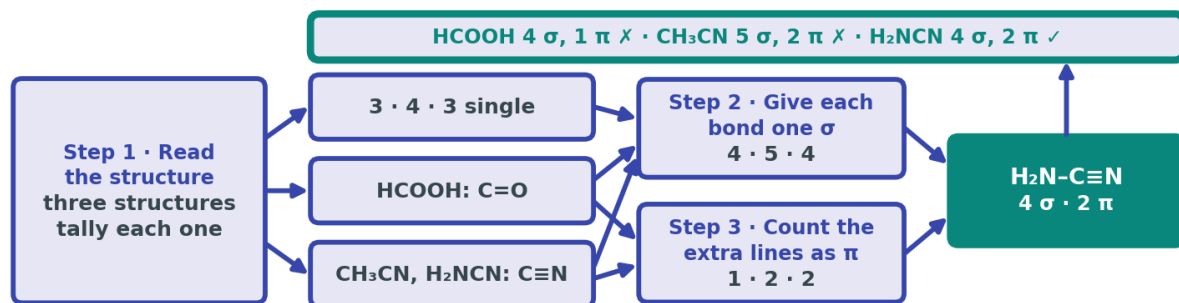
Step 2 · Give each bond one  $\sigma$

Step 3 · Count the extra lines as  $\pi$

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

formic acid 4  $\sigma$ , 1  $\pi$  · acetonitrile 5  $\sigma$ , 2  $\pi$  · cyanamide 4  $\sigma$ , 2  $\pi$

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



## Practice 3

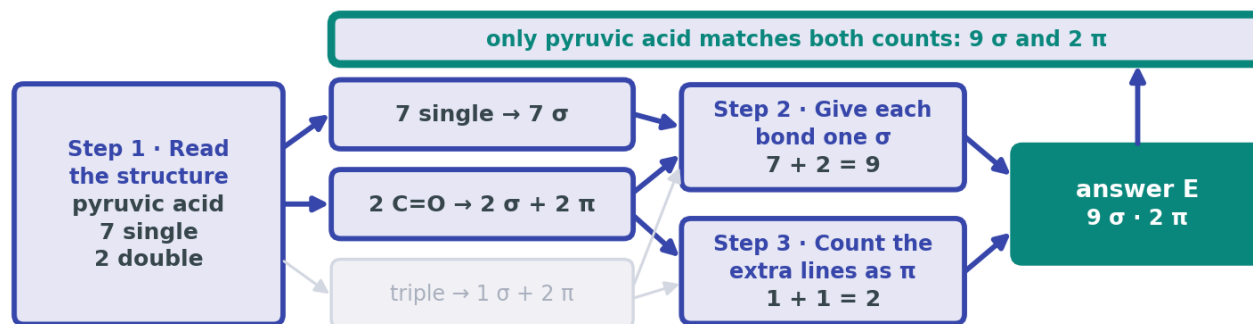
Which molecule has exactly 9  $\sigma$  bonds and 2  $\pi$  bonds?

- 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  $\cdot$  C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> has 10 atoms and no ring:  $10 - 1 = 9$  bonded pairs ✓

🧠 **Sense check:** Both counts must match. Three choices have 9  $\sigma$  and two have 2  $\pi$ ; only pyruvic acid has both.





## Check yourself

1. In HCN ( $\text{H}-\text{C}\equiv\text{N}$ ): how many  $\sigma$  and how many  $\pi$ ? Give each bond one  $\sigma$ , 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  $\sigma$  bond allows rotation; a  $\pi$  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

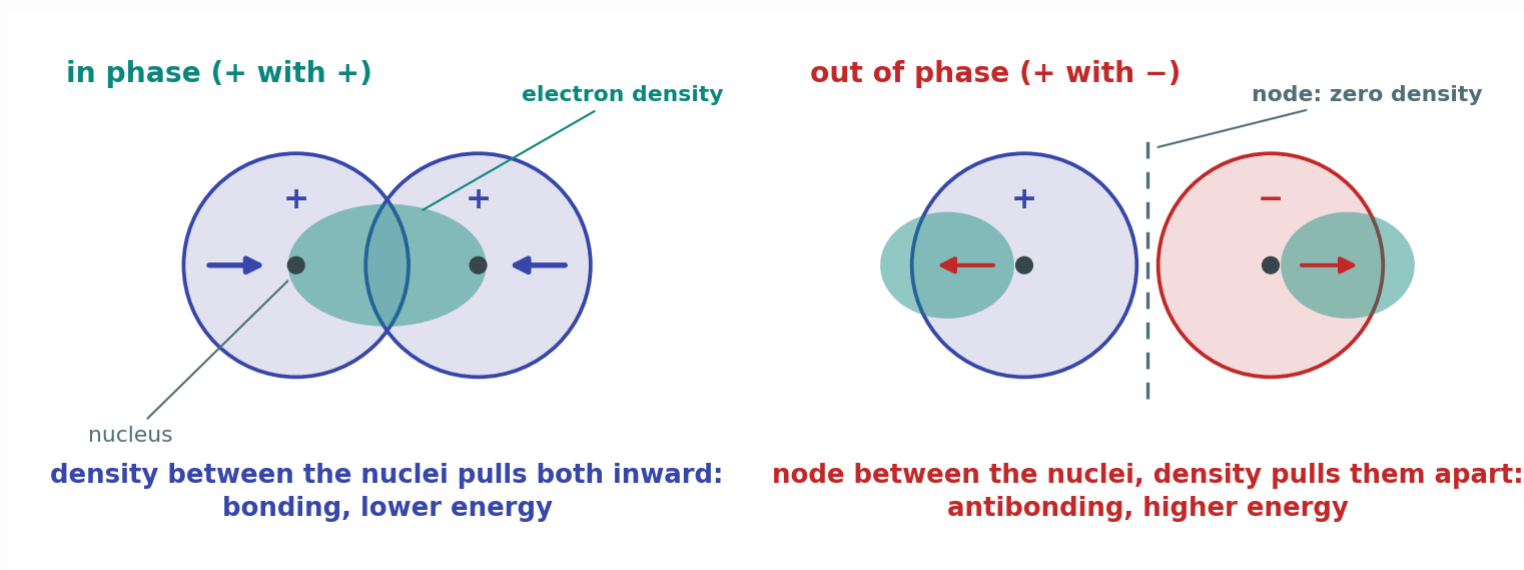
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1 shared pair · 2 shared pairs · 3 shared pairs → bond order 1, 2, 3

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



$\text{H}_2$ : 2 bonding, 0 antibonding  $\rightarrow$  bond order =  $(2 - 0)/2 = 1$

bonding wins  $\rightarrow$  the molecule exists

$\text{He}_2$ : 2 bonding, 2 antibonding  $\rightarrow$  bond order =  $(2 - 2)/2 = 0$

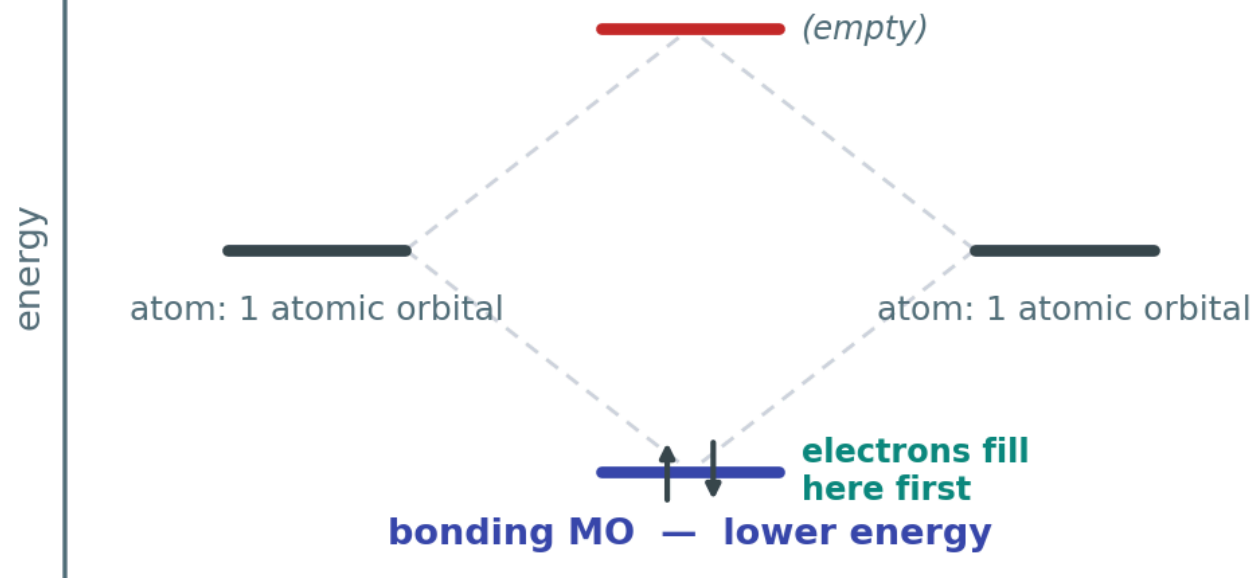
bonding and antibonding cancel  $\rightarrow$  no stable molecule

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**

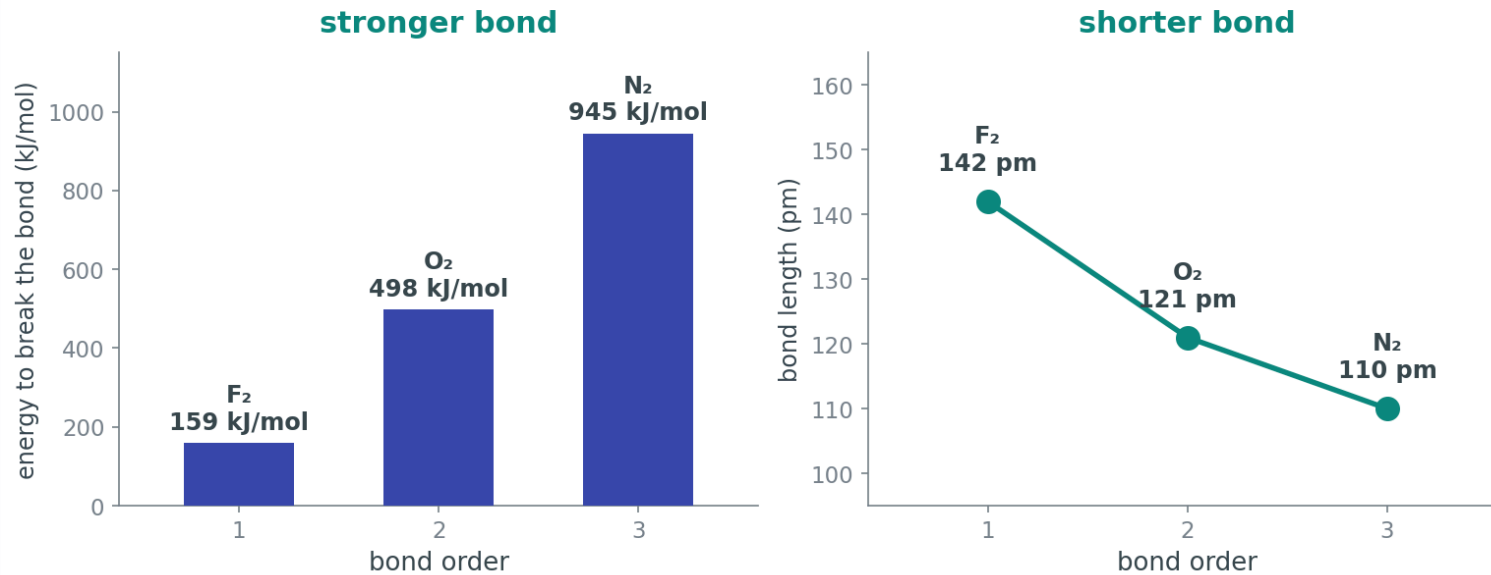


Two atomic orbitals, one from each atom, combine into two molecular orbitals: a bonding MO at lower energy and an antibonding MO (starred) at higher energy. Electrons fill the lowest first.

# 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.

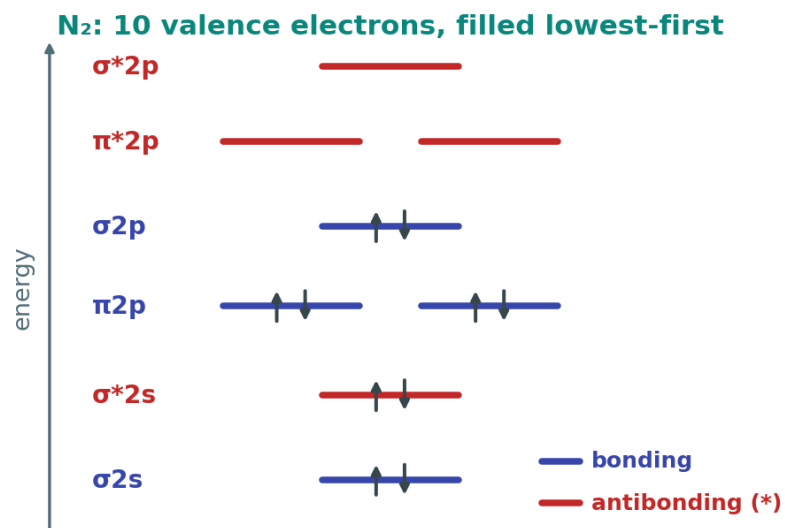


## The method

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 N<sub>2</sub>

bond order = (bonding – antibonding) ÷ 2  
given: N<sub>2</sub>, 10 valence electrons · wanted: the bond order



The molecular orbitals of N<sub>2</sub> 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

N<sub>2</sub>: 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 O<sub>2</sub>

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

given: O<sub>2</sub>, 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

O<sub>2</sub>: 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

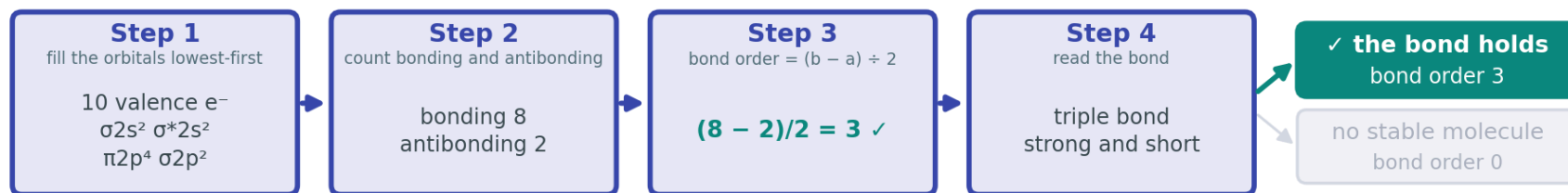
 **Sense check:** Bond order 2: a double bond, weaker and longer than nitrogen's triple bond. Four antibonding electrons cancel four of the bonding ones. ✓

## ✓ Worked examples 1 and 2: the route

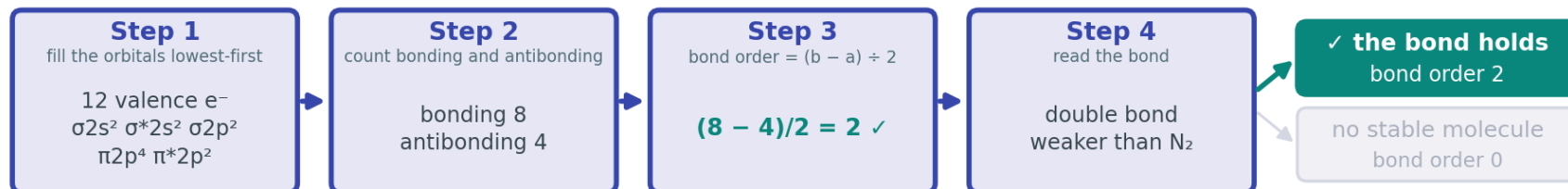
$$\text{N}_2: (8 - 2)/2 = 3 \cdot \text{O}_2: (8 - 4)/2 = 2$$

found:  $\text{N}_2$  10 valence electrons, bond order 3 ·  $\text{O}_2$  12 valence electrons, bond order 2

### nitrogen, $\text{N}_2$



### oxygen, $\text{O}_2$



🧠 **Sense check:** Same four steps, same verdict: both bonds hold.  $\text{O}_2$ 's two extra electrons go into antibonding  $\pi^* 2p$  and cost one bond. ✓

## Your turn: the bond order of F<sub>2</sub>

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

given: F<sub>2</sub> · bonding 8, antibonding 6 · wanted: the bond order

F<sub>2</sub> 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, Ne<sub>2</sub>

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

given: Ne<sub>2</sub>, 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 Ne<sub>2</sub> 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  $2 + 4 + 2 = 8$

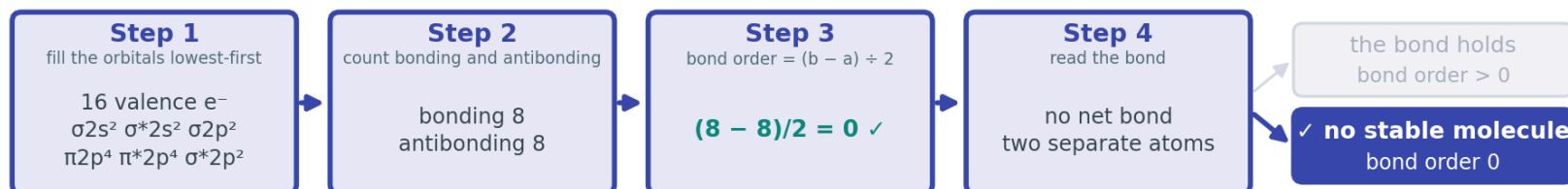
**Step 3 · Bond order = (bonding – antibonding) ÷ 2**

**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 He<sub>2</sub>. ✓

neon, Ne<sub>2</sub>



## ⚠ Where this goes wrong

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

N<sub>2</sub>: 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

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

$\text{Li}_2$ : bonding 2, antibonding 0 ·  $\text{Be}_2$ : bonding 2, antibonding 2 ·  $\text{B}_2$ : 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?

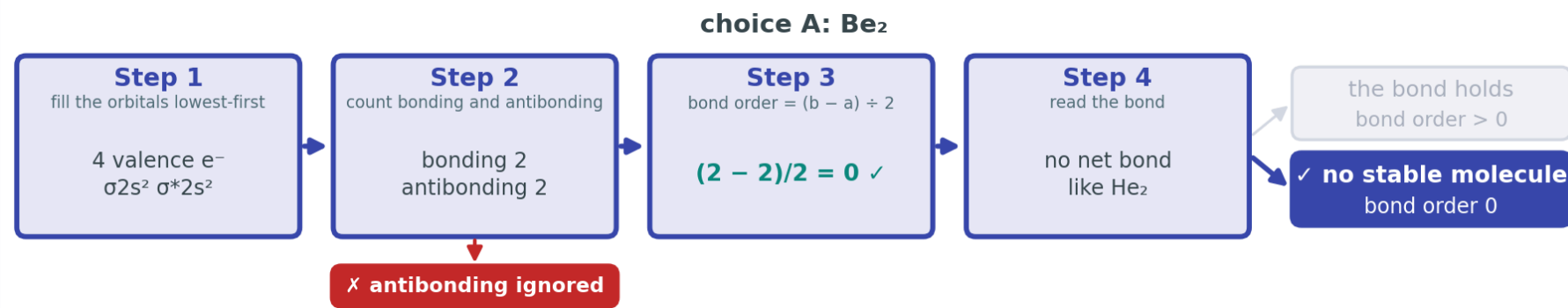
- A.  $\text{Be}_2$
- B.  $\text{Li}_2$
- C.  $\text{B}_2$
- D. None of them: each has bonding electrons

## ✓ 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:  $\text{Be}_2$  does not hold together

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

🧠 **Sense check:**  $\text{Be}_2$  repeats the  $\text{He}_2$  pattern: equal bonding and antibonding counts, bond order 0, no molecule. ✓





## Worked example 3: the bond order of $\text{O}_2^+$

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

given:  $\text{O}_2^+$  · bonding 8, antibonding 3 · wanted: the bond order

Remove one electron from  $\text{O}_2$  and it leaves an antibonding orbital, giving  $\text{O}_2^+$ : 8 bonding, 3 antibonding. A common first attempt:  $8 - 3 = 5$ . Test it.

## ✓ Worked example 3: solution

bond order = (bonding – antibonding) ÷ 2  
given: O<sub>2</sub><sup>+</sup> · 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 O<sub>2</sub><sup>+</sup> has a shorter, stronger bond than O<sub>2</sub>. ✓

# Take-home: bond order counts pairs

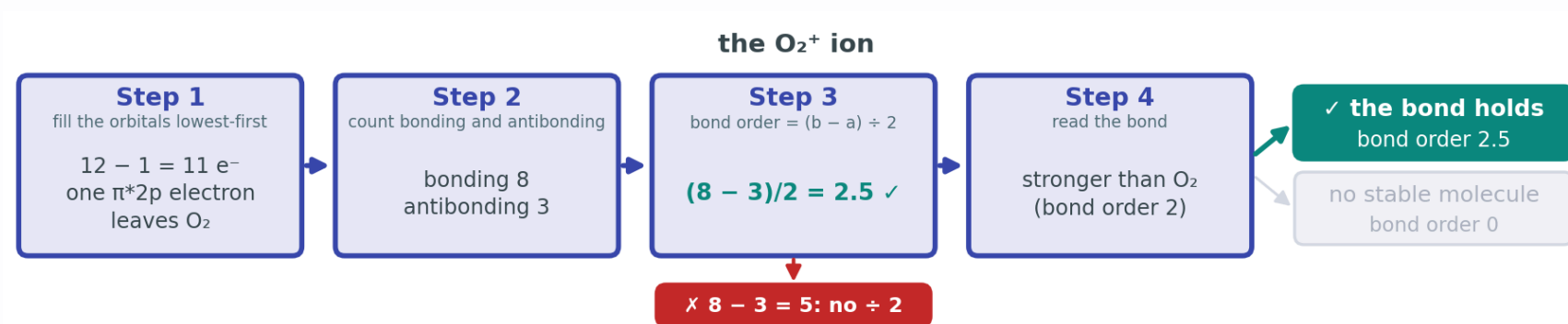
bonding – antibonding = the surplus of bonding electrons

$8 - 3 = 5$  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

**$\text{N}_2$ : bonding 8, antibonding 2 ·  $\text{N}_2^+$ : one electron fewer  
wanted: the bond order of  $\text{N}_2^+$**

Nitrogen gas loses one electron to form  $\text{N}_2^+$ . What is the bond order of  $\text{N}_2^+$ ?

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

## ✓ Practice 2 answer: B

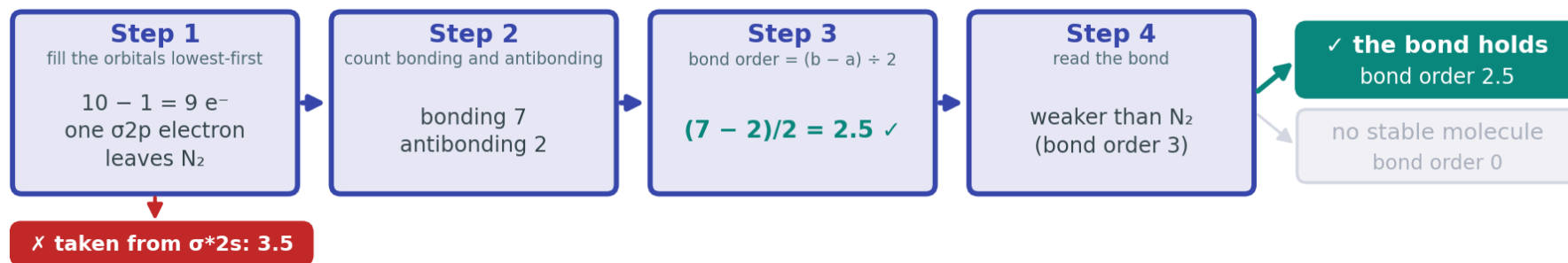


10 – 1 = 9 valence electrons · bonding 8 – 1 = 7, antibonding 2

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

 **Sense check:** Losing a bonding electron weakens the bond:  $\text{N}_2^+$  at 2.5 sits below  $\text{N}_2$  at 3.  $\text{O}_2^+$  moved the other way because its electron left an antibonding orbital. ✓

the  $\text{N}_2^+$  ion





## Practice 3



wanted: the bond order

What bond order does molecular orbital theory predict for  $\text{Ne}_2^{2+}$ ?

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

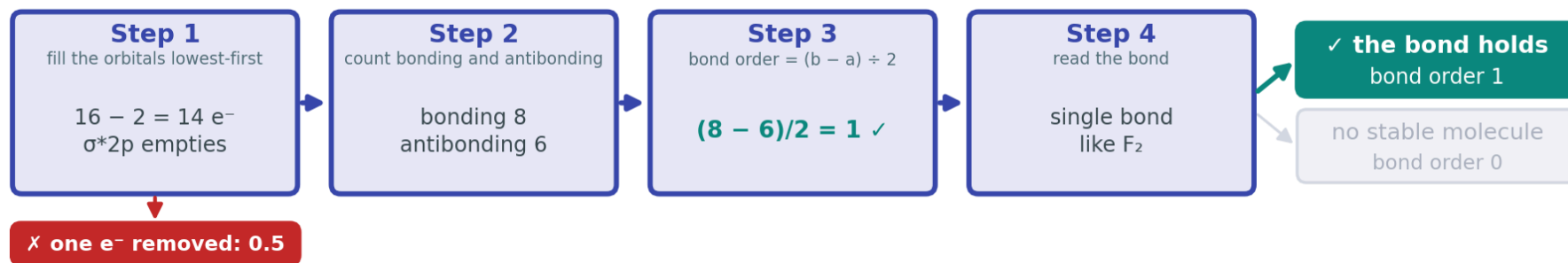
## ✓ Practice 3 answer: D

$\text{Ne}_2^{2+}$ :  $2 \times 8 - 2 = 14$  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  $\text{Ne}_2$  empties  $\sigma^* 2p$ , so the bond order rises from 0 to 1: a single bond, like  $\text{F}_2$ , which has the same 14 electrons. ✓

the  $\text{Ne}_2^{2+}$  ion





## Check yourself

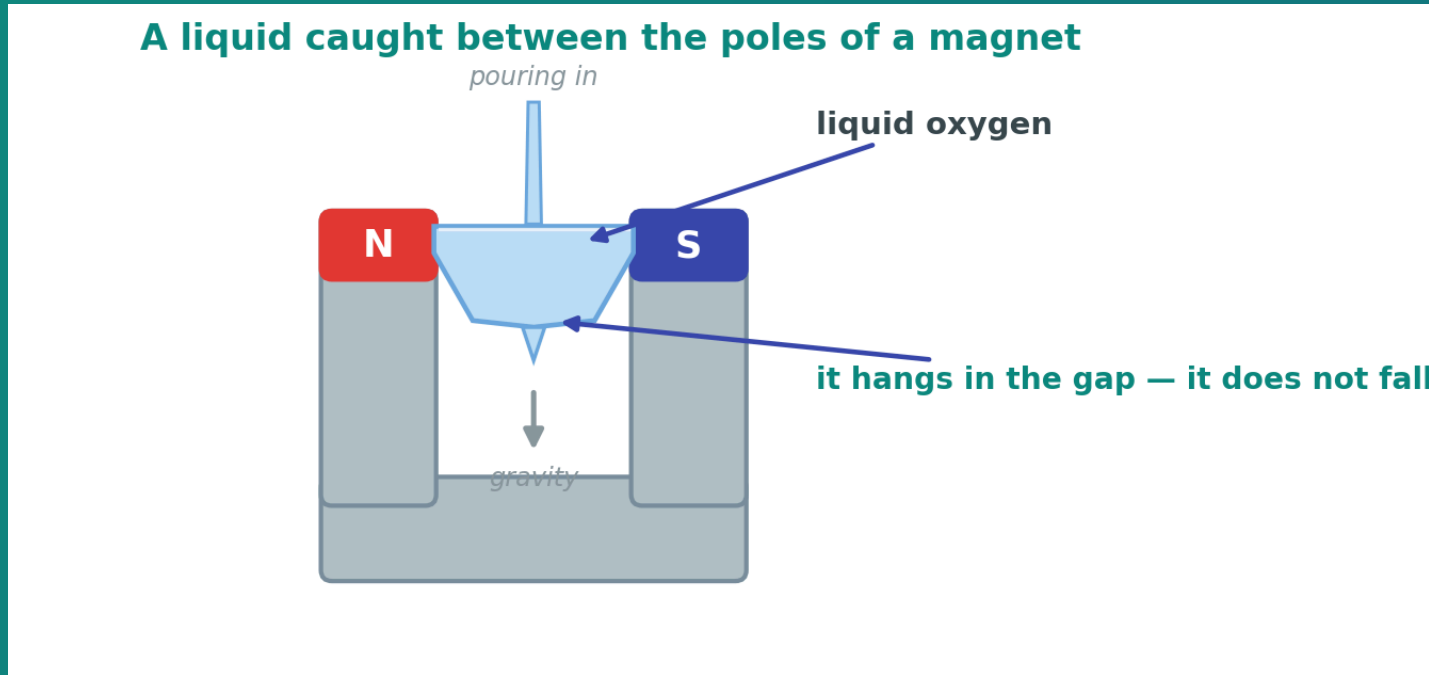
1.  $C_2$  has 8 valence electrons: 6 fill bonding orbitals and 2 fill antibonding. Find the bond order, and say whether  $C_2$  is held more or less tightly than  $N_2$ .
2. A molecule has equal numbers of bonding and antibonding electrons. What is its bond order, and can the molecule exist?

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

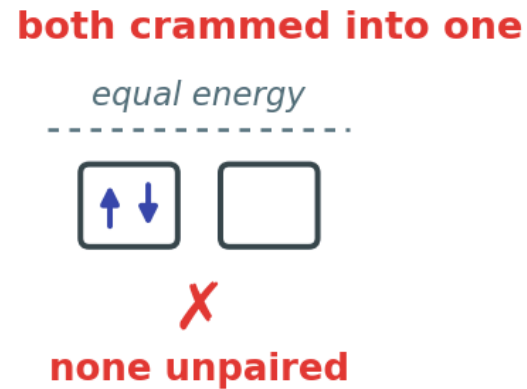
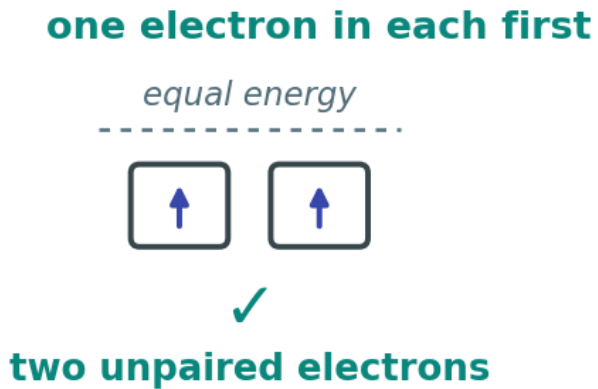
**O=O with two lone pairs on each O**

**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

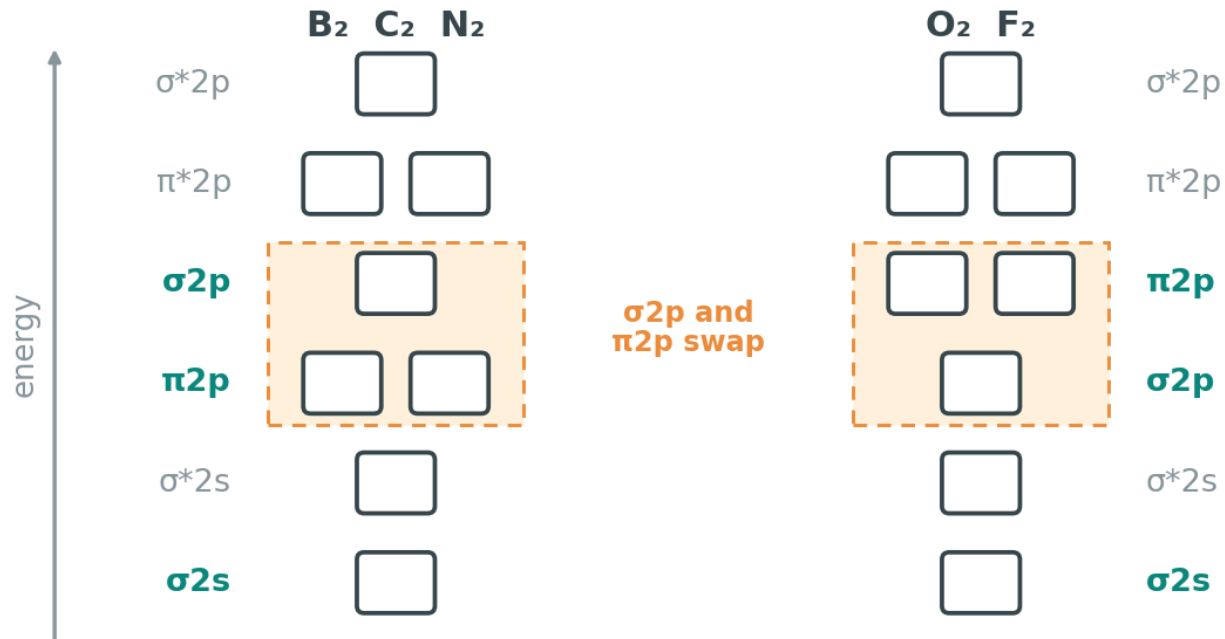
**Equal-energy orbitals take one electron each before any pairs**



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

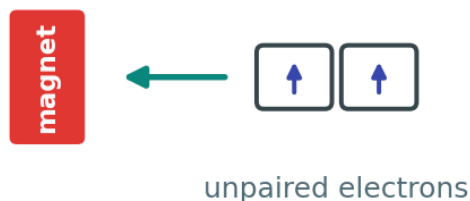


Each set pairs a lower bonding orbital with a higher antibonding one. The two  $\pi$  orbitals share one energy: a degenerate pair. Only the  $\sigma 2p$  and  $\pi 2p$  order changes.

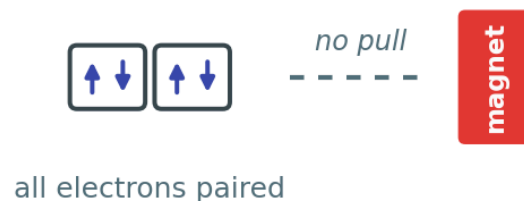
# Reading magnetism from the diagram

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, N<sub>2</sub>

### Step 1 • Count the valence electrons

**N<sub>2</sub>: 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.

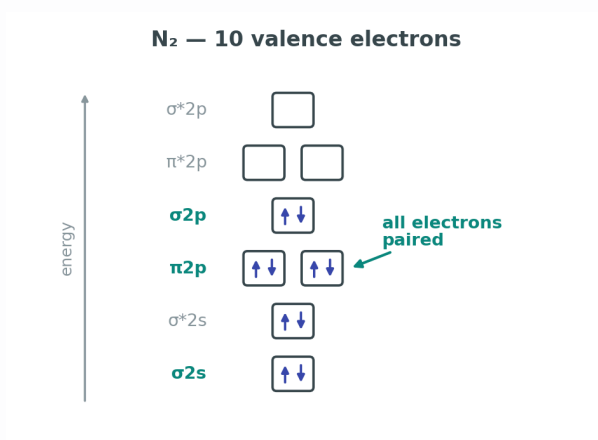
## ✓ Worked example 1: filling the diagram

$\text{N}_2$ : 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  $\text{N}_2$  diagram is ready to read for magnetism and bond order.

## ✓ Worked example 1: reading it

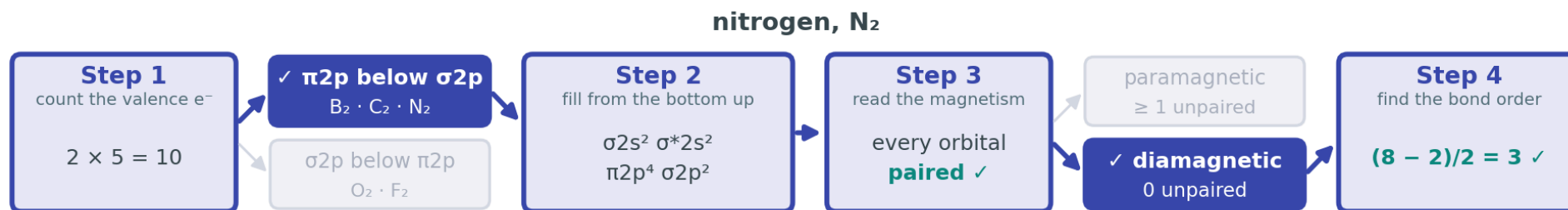
$\text{N}_2$ : 10 valence electrons, diagram filled  
 $\sigma 2s$ ,  $\sigma^* 2s$ , the  $\pi 2p$  pair, then  $\sigma 2p$  · every orbital paired

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:  $\text{N}_2$  carries a triple bond and no unpaired electrons, so it is diamagnetic.



## Worked example 2: oxygen, O<sub>2</sub>

### Step 1 • Count the valence electrons

O<sub>2</sub>: each O contributes 6 valence electrons

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

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

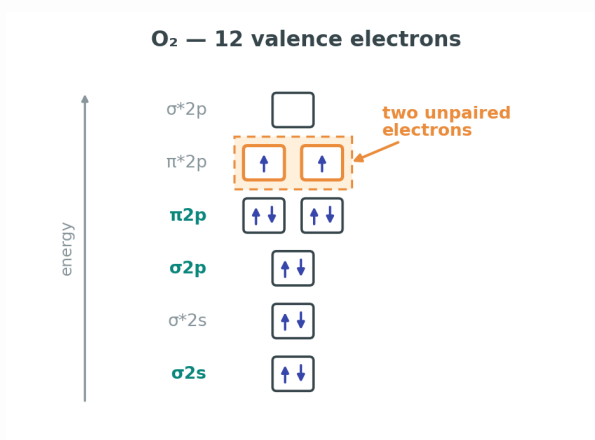
## ✓ Worked example 2: filling the diagram

$O_2$ : 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  $\pi^*2p$  orbital before either pairs.



 **Sense check:** Each  $\pi^*2p$  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

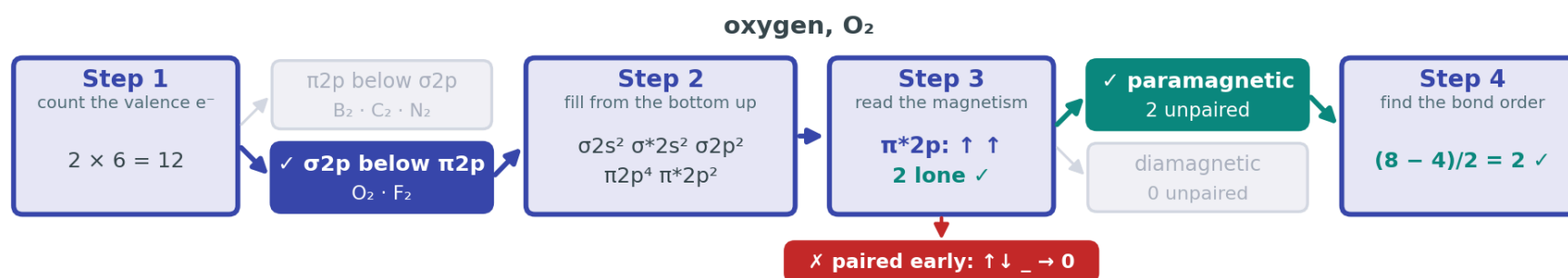
A common first attempt

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  $\pi^*2p$  orbital  
2 unpaired ·  $O_2$  is paramagnetic

✗ paired early: both crammed into one  $\pi^*2p$  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, B<sub>2</sub>

### Step 1 • Count the valence electrons

**B<sub>2</sub>: 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

**B<sub>2</sub>: 6 valence electrons**

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

### A common first attempt

✗ oxygen's order: σ2s<sup>2</sup> σ\*2s<sup>2</sup> σ2p<sup>2</sup> → 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**

σ2s<sup>2</sup> σ\*2s<sup>2</sup> n2p<sup>2</sup> → paramagnetic · bond order = (4 – 2)/2 = 1

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

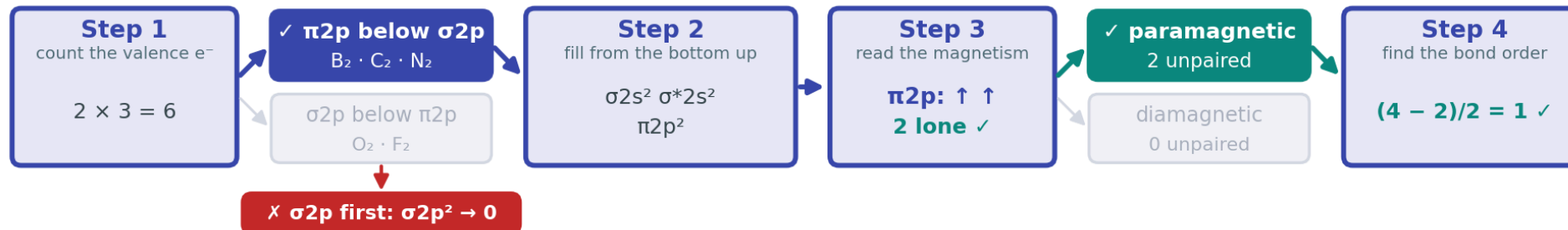
🧠 **Sense check:** B<sub>2</sub> is in fact paramagnetic: the magnet test shows n2p lies lowest for boron. ✓

## ✓ 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  $\pi^*2p$  pair. Fill the blanks, then name the magnetism.

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

$F_2 \rightarrow$  diamagnetic · bond order =  $(8 - 6)/2 = 1$   
 $\pi^*2p$  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  $\pi^*2p$  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  $\pi^*2p$  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,  $\text{O}_2^-$ : 13 valence electrons**

$\text{O}_2$  plus 1 more electron, into  $\pi^*2p$

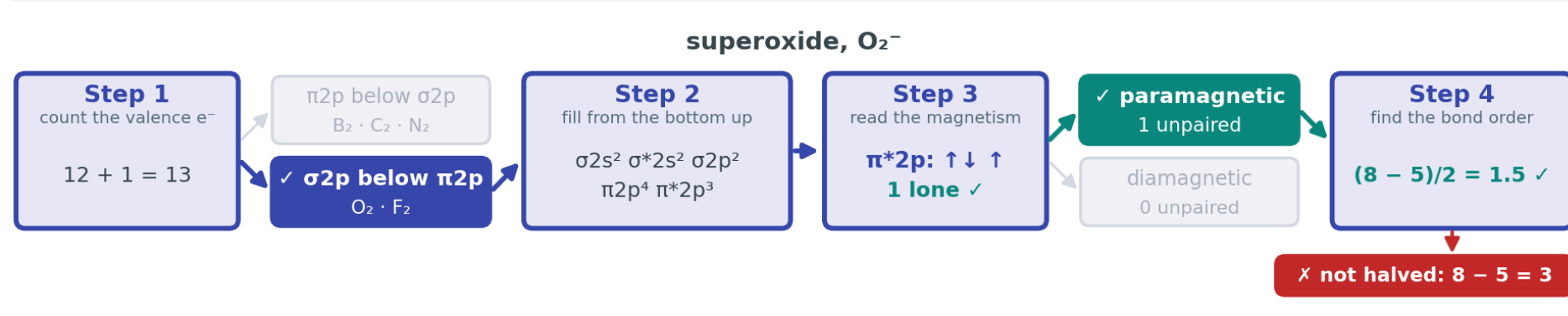
Give the bond order and the magnetic behavior of the superoxide ion.

- 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  
 $\pi^*2p$  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  $\text{O}_2$ 's 2.





## Worked example 3: the $\text{O}_2^+$ ion

### Step 1 • Count the valence electrons

$\text{O}_2^+$ :  $\text{O}_2$  with one electron removed

$12 - 1 = 11$  valence electrons to place

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

## ✓ Worked example 3: solution

$\text{O}_2^+$ : 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  $\text{O}_2$**

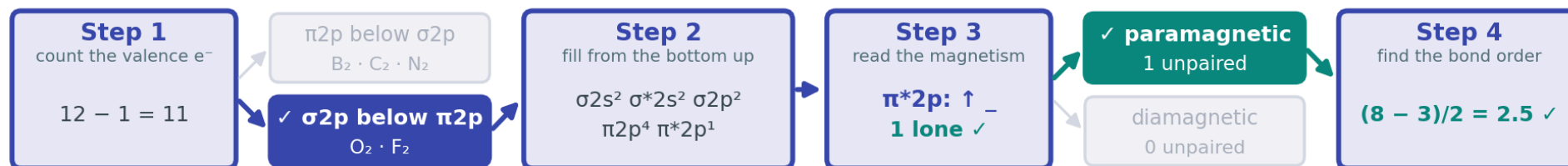
 **Sense check:** Pulling an electron from an antibonding orbital raises the bond order from 2 to 2.5. One electron stays unpaired, so  $\text{O}_2^+$  is paramagnetic.

## ✓ 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  $\text{Be}_2^-$  holds an unpaired electron?

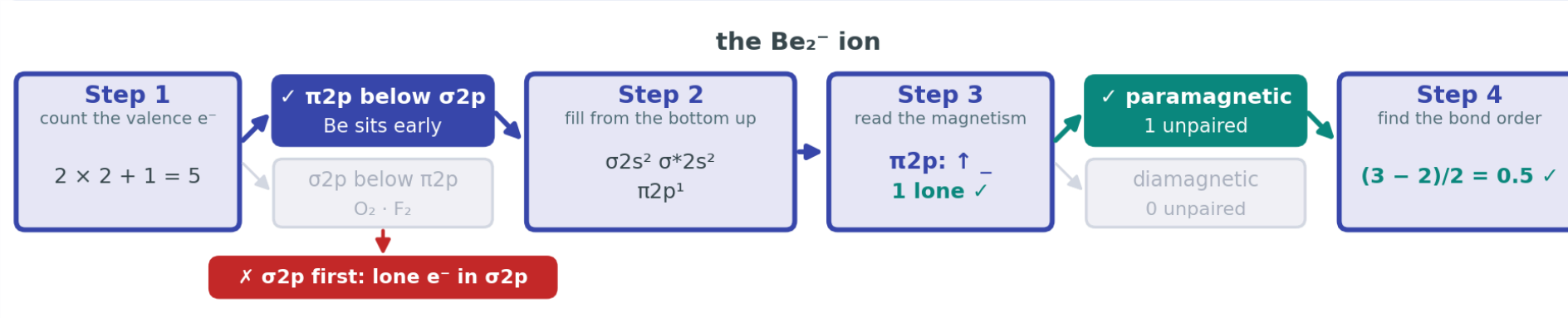
- A.  $\sigma^*2s$
- B.  $\pi 2p$
- C.  $\sigma 2p$
- D. None: every electron is paired

## ✓ 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  $\text{Be}_2$ 's 0. ✓





## Practice 3



wanted: the paramagnetic one · the higher bond order

Of  $\text{F}_2^-$  and the acetylide ion  $\text{C}_2^{2-}$ , which one is paramagnetic, and which one has the higher bond order?

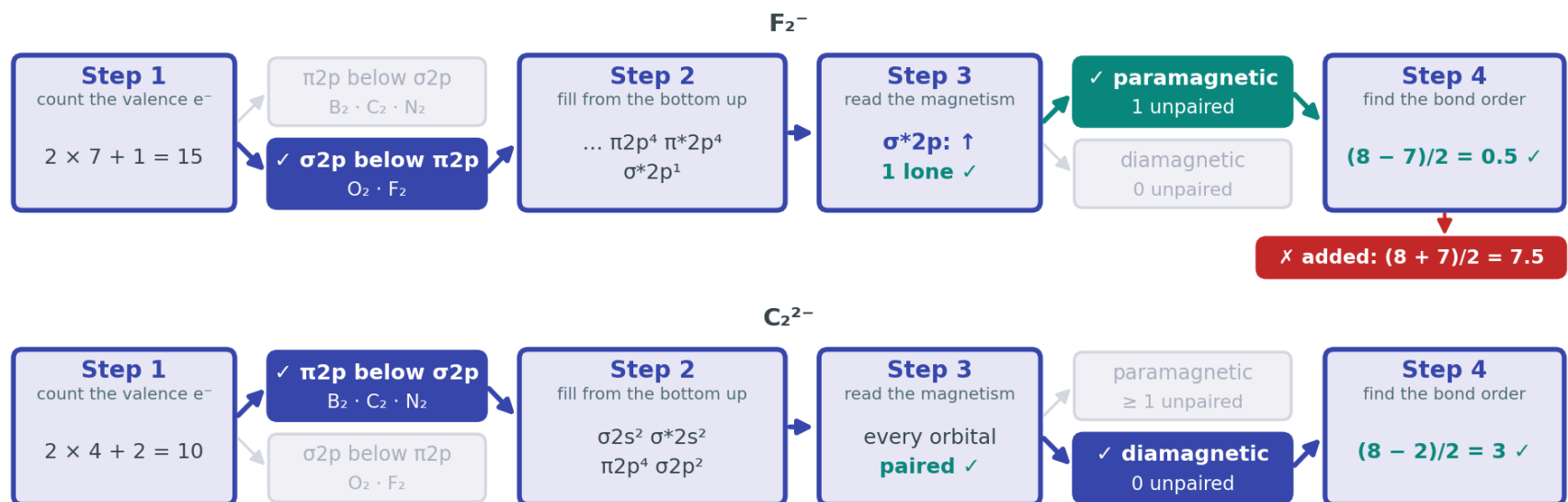
- A.  $\text{C}_2^{2-}$  is paramagnetic;  $\text{C}_2^{2-}$  has the higher bond order
- B.  $\text{F}_2^-$  is paramagnetic;  $\text{F}_2^-$  has the higher bond order
- C.  $\text{C}_2^{2-}$  is paramagnetic;  $\text{F}_2^-$  has the higher bond order
- D.  $\text{F}_2^-$  is paramagnetic;  $\text{C}_2^{2-}$  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

$F_2^-$ :  $2 \times 7 + 1 = 15$  ·  $\pi^*2p$  full, the 15th electron alone in  $\sigma^*2p$  ·  $(8 - 7)/2 = 0.5$  ·  $C_2^{2-}$ :  $2 \times 4 + 2 = 10$ , 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  $\pi^*2p$  into  $\sigma^*2p$ . An odd count always leaves an electron unpaired. ✓



## Check yourself

1.  $\text{N}_2^-$  has 11 valence electrons, one more than  $\text{N}_2$ , and the extra one enters  $\pi^*2p$ . How many electrons are unpaired, and what is the bond order?
2.  $\text{C}_2$  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. 🧪