EXAM 3
PRACTICE SOLUTIONS

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CHEMISTRY 161A // FALL 2019

Which photon has a greater energy?

<div style="text-align:center">Photon A with ν = 2.45 GHz   Photon B with λ = 965 nm</div>

— answer —

There are three ways you can solve this problem since we can relate energy (*E*), wavelength (λ), and frequency (ν) via:

$$E = \frac{hc}{\lambda} = h\nu \quad ; \quad \text{where } c = \lambda\nu$$

Comparing Energies (*E*)	Comparing Wavelengths (λ)	Comparing Frequencies (ν)
$E_A = h\nu_A$ $\quad = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.45 \times 10^9 \text{ s}^{-1})$ $E_A = 1.62 \times 10^{-24} \text{ J}$	$c = \lambda_A \nu_A$ $3.00 \times 10^8 \frac{\text{m}}{\text{s}} = \lambda_A \times (2.45 \times 10^9 \text{ s}^{-1})$ $\lambda_A = 0.122 \text{ m}$	$\nu_A = 2.45 \times 10^9 \text{ s}^{-1}$
$E_B = \frac{hc}{\lambda_B}$ $\quad = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})\left(3.00 \times 10^8 \frac{\text{m}}{\text{s}}\right)}{965 \times 10^{-9} \text{ m}}$ $E_B = 2.06 \times 10^{-19} \text{ J}$	$\lambda_B = 965 \times 10^{-9} \text{ m}$	$c = \lambda_B \nu_B$ $3.00 \times 10^8 \frac{\text{m}}{\text{s}} = (965 \times 10^{-9} \text{ m}) \times \nu_B$ $\nu_B = 3.11 \times 10^{14} \text{ s}^{-1}$
Photon B has greater energy.	Photon B has a shorter wavelength; thus, photon B has greater energy.	Photon B has a larger frequency and a shorter wavelength; thus, photon B has greater energy.

PRACTICE PROBLEM 2.1

Calculate the frequencies (in Hz or s^{-1}) associated with the following four electron transitions in the hydrogen atom.

— answer —

For electron transitions in the hydrogen atom, we can apply the Rydberg equation to calculate the wavelengths.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad ; \quad R_H = 1.10 \times 10^7 \, \frac{1}{m}$$

	Electron Transition	Wavelengths	Frequencies
(a)	$n = 5 \rightarrow n = 4$	$\frac{1}{\lambda_{5 \rightarrow 4}} = \left[1.10 \times 10^7 \frac{1}{m} \right] \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = 2.47_6 \times 10^6 \frac{1}{m}$ $\lambda_{5 \rightarrow 4} = 4.04_0 \times 10^{-6} \, m$	$c = \lambda_{5 \rightarrow 4} \nu_{5 \rightarrow 4}$ $3.00 \times 10^8 \frac{m}{s} = (4.04_0 \times 10^{-6} \, m)(\nu_{5 \rightarrow 4})$ $\nu_{5 \rightarrow 4} = 7.43 \times 10^{13} \, Hz$
(b)	$n = 4 \rightarrow n = 3$	$\frac{1}{\lambda_{4 \rightarrow 3}} = \left[1.10 \times 10^7 \frac{1}{m} \right] \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = 5.34_7 \times 10^6 \frac{1}{m}$ $\lambda_{4 \rightarrow 3} = 1.87_0 \times 10^{-6} \, m$	$c = \lambda_{4 \rightarrow 3} \nu_{4 \rightarrow 3}$ $3.00 \times 10^8 \frac{m}{s} = (1.87_0 \times 10^{-6} \, m)(\nu_{4 \rightarrow 3})$ $\nu_{4 \rightarrow 3} = 1.60 \times 10^{14} \, Hz$
(c)	$n = 3 \rightarrow n = 2$	$\frac{1}{\lambda_{3 \rightarrow 2}} = \left[1.10 \times 10^7 \frac{1}{m} \right] \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1.52_8 \times 10^6 \frac{1}{m}$ $\lambda_{3 \rightarrow 2} = 6.54_5 \times 10^{-7} \, m$	$c = \lambda_{3 \rightarrow 2} \nu_{3 \rightarrow 2}$ $3.00 \times 10^8 \frac{m}{s} = (6.54_5 \times 10^{-7} \, m)(\nu_{3 \rightarrow 2})$ $\nu_{3 \rightarrow 2} = 4.58 \times 10^{14} \, Hz$
(d)	$n = 2 \rightarrow n = 1$	$\frac{1}{\lambda_{2 \rightarrow 1}} = \left[1.10 \times 10^7 \frac{1}{m} \right] \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 8.25_0 \times 10^6 \frac{1}{m}$ $\lambda_{2 \rightarrow 1} = 1.21_2 \times 10^{-7} \, m$	$c = \lambda_{2 \rightarrow 1} \nu_{2 \rightarrow 1}$ $3.00 \times 10^8 \frac{m}{s} = (1.21_2 \times 10^{-7} \, m)(\nu_{2 \rightarrow 1})$ $\nu_{2 \rightarrow 1} = 2.48 \times 10^{15} \, Hz$

Energy of transitions (the spacings) get smaller as higher transitions occur.
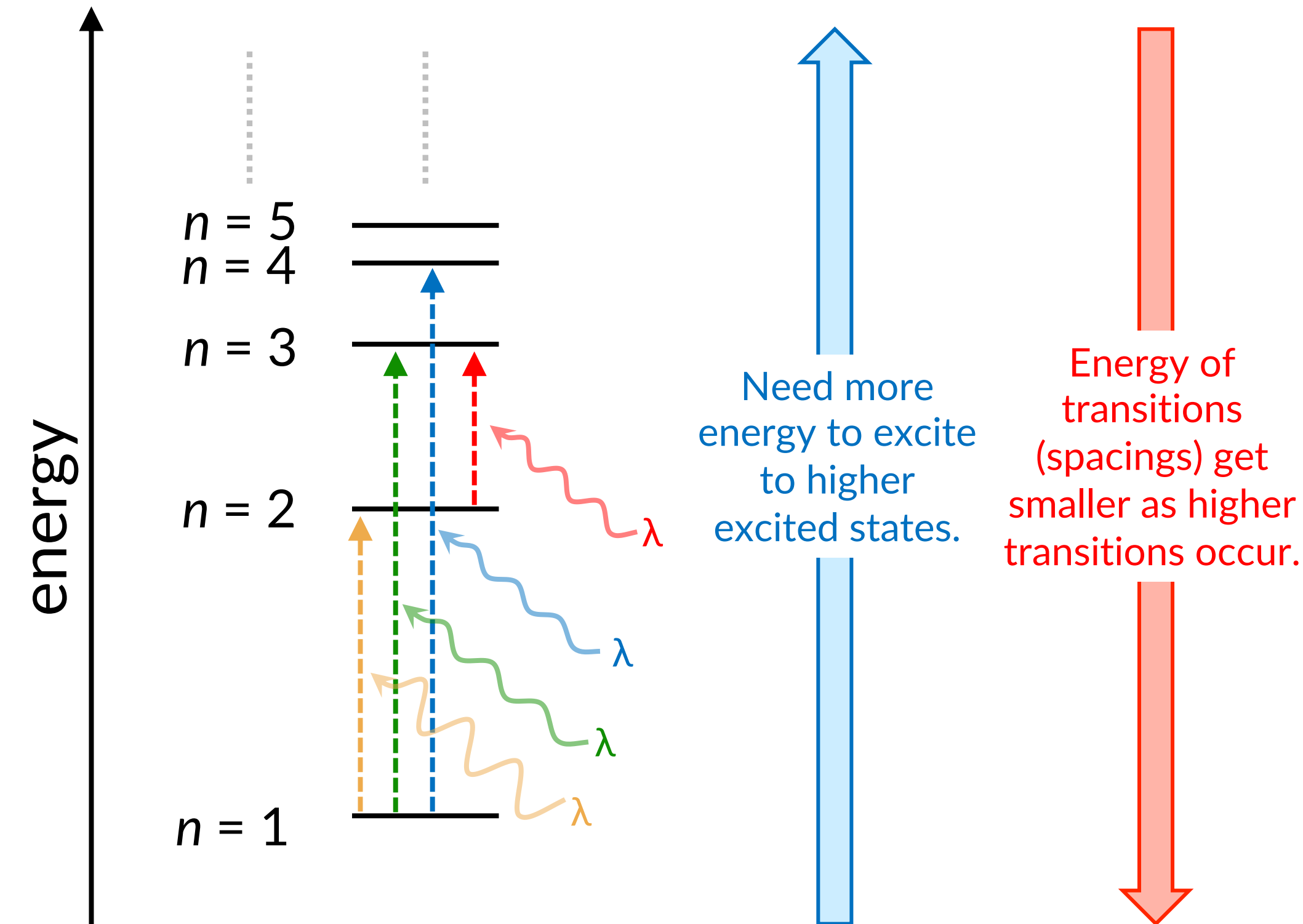
PRACTICE PROBLEM 2.2

Calculate the wavelength of radiation required for the following four <u>absorptions</u> in the hydrogen atom.

– answer –

We can still apply the Rydberg equation to calculate the wavelengths, but this corresponds to *absorptions* now, not emissions.

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad ; \quad R_{\mathrm{H}} = 1.10 \times 10^7 \, \frac{1}{\mathrm{m}}$$

	Electron Transition	Wavelengths
(a)	$n = 1 \rightarrow n = 2$	$\frac{1}{\lambda_{2\rightarrow1}} = \left[1.10 \times 10^7 \, \frac{1}{\mathrm{m}} \right] \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 8.25_0 \times 10^6 \, \frac{1}{\mathrm{m}}$ $\lambda_{2\rightarrow1} = 1.21 \times 10^{-7} \, \mathbf{m}$
(b)	$n = 1 \rightarrow n = 3$	$\frac{1}{\lambda_{3\rightarrow1}} = \left[1.10 \times 10^7 \, \frac{1}{\mathrm{m}} \right] \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = 9.77_8 \times 10^6 \, \frac{1}{\mathrm{m}}$ $\lambda_{3\rightarrow1} = 1.02 \times 10^{-7} \, \mathbf{m}$
(c)	$n = 1 \rightarrow n = 4$	$\frac{1}{\lambda_{4\rightarrow1}} = \left[1.10 \times 10^7 \, \frac{1}{\mathrm{m}} \right] \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = 1.03_1 \times 10^7 \, \frac{1}{\mathrm{m}}$ $\lambda_{4\rightarrow1} = 9.70 \times 10^{-8} \, \mathbf{m}$
(d)	$n = 2 \rightarrow n = 3$	$\frac{1}{\lambda_{3\rightarrow2}} = \left[1.10 \times 10^7 \, \frac{1}{\mathrm{m}} \right] \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1.52_8 \times 10^6 \, \frac{1}{\mathrm{m}}$ $\lambda_{3\rightarrow2} = 6.55 \times 10^{-7} \, \mathbf{m}$

energy

n = 5
n = 4
n = 3
n = 2
n = 1

Need more energy to excite to higher excited states.

Energy of transitions (spacings) get smaller as higher transitions occur.

PRACTICE PROBLEM 2.3

Which of the following electron transitions in the hydrogen atom results in the emission of light with the longest wavelength?

(a) $n = 4 \rightarrow n = 3$ (b) $n = 1 \rightarrow n = 2$ (c) $n = 1 \rightarrow n = 6$ (d) $n = 3 \rightarrow n = 2$

– answer –

This problem should not require any calculations—even though you will get the right answer, it will take you longer to do.
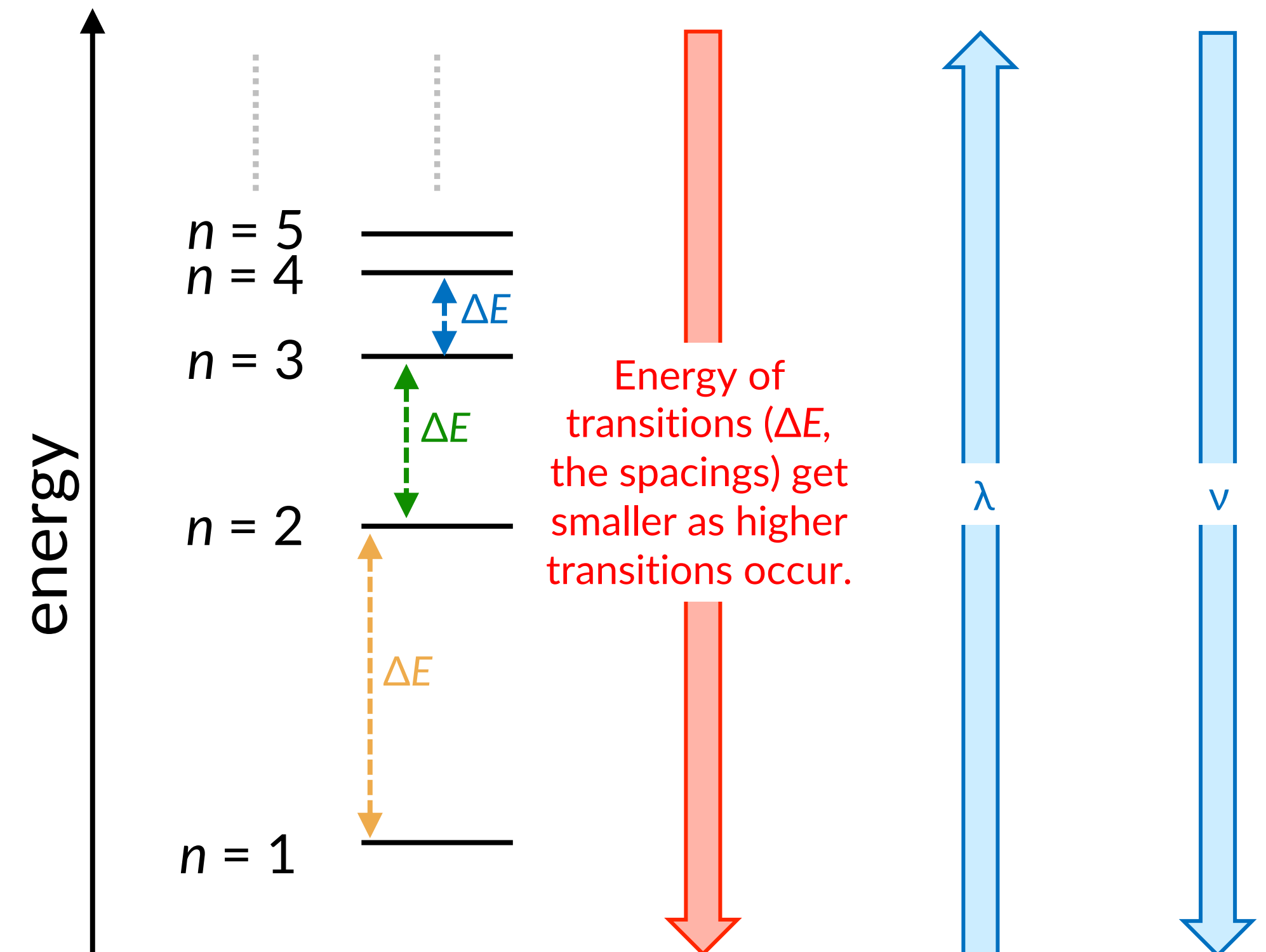
First, eliminate choices B and C since these are both transitions from lower to higher excited states, which require the *absorption* of light.

Second, you need to understand that the spacing (ΔE) between adjacent states gets smaller and smaller as the values of n increase (i.e. higher excited states).

The *largest* energy spacing will occur for the $n = 2 \rightarrow n = 1$ transition, which results in the shortest wavelength and highest frequency of light. Every successive emission has a smaller ΔE, longer λ, and higher v.

$$|\Delta E| = \frac{hc}{\lambda} = h\nu$$

So, the answer is (a).

Energy of transitions (ΔE, the spacings) get smaller as higher transitions occur.

n = 5
n = 4
ΔE
n = 3
ΔE
n = 2
ΔE
n = 1

energy

λ ν

What are the possible values of m_ℓ if n = 4?

— answer —

Remember the general, ordered scheme for assigning/generating quantum numbers:

1. Start with n, the principal quantum number.

2. Then assign ℓ, the angular momentum quantum number.
   The values of ℓ range from 0 to (n – 1) in integers.
   The value of ℓ determines the orbital shape (s, p, d, or f).

3. Next assign m_ℓ, which is the magnetic quantum number.
   m_ℓ can take on integer values ranging from –ℓ to + ℓ.
   The number of possible m_ℓ values determines how many orbitals exist.

4. Finally, assign m_s, the spin quantum number.
   m_s can only take on two values: +½ and –½.
   This tells us that only two electrons can occupy an orbital.

n	ℓ	m_ℓ	m_s
4	0 (s)	0 ⎫ 1	+½ or –½
	1 (p)	–1 ⎫	+½ or –½
		0 ⎬ 3	+½ or –½
		+1 ⎭	+½ or –½
	2 (d)	–2 ⎫	+½ or –½
		–1	+½ or –½
		0 ⎬ 5	+½ or –½
		+1	+½ or –½
		+2 ⎭	+½ or –½
	3 (f)	–3 ⎫	+½ or –½
		–2	+½ or –½
		–1	+½ or –½
		0 ⎬ 7	+½ or –½
		+1	+½ or –½
		+2	+½ or –½
		+3 ⎭	+½ or –½

Which of the following sets of quantum numbers is(are) <u>not</u> allowed?

— *answer* —

Set I	Set II	Set III	Set IV
$n = 1$	$n = 3$	$n = 1$	$n = 2$
⟹ $\ell = 2$	$\ell = 0$	$\ell = 0$	$\ell = 1$
$m_\ell = 0$	$m_\ell = 0$	⟹ $m_\ell = 1$	⟹ $m_\ell = 2$
$m_s = +\frac{1}{2}$	$m_s = -\frac{1}{2}$	$m_s = -\frac{1}{2}$	$m_s = +\frac{1}{2}$

⇧

For $n = 1$, the only possible value of ℓ is 0.

Therefore, Set I is not allowed.

⇧

For $n = 1$, the only possible value of ℓ is 0.

But, for $\ell = 0$, the only possible value of m_ℓ is 0.

Therefore, Set III is not allowed.

⇧

For $n = 2$, the possible values of ℓ are 0 and 1.

But, for $\ell = 1$, the only possible values of m_ℓ are −1, 0, +1.

Therefore, Set IV is not allowed.

General scheme for generating quantum numbers:

1. Start with n, the principal quantum number.

2. Then assign ℓ, the angular momentum quantum number. The values of ℓ range from 0 to $(n - 1)$ in integers.

3. Next assign m_ℓ, which is the magnetic quantum number. m_ℓ can take on integer values ranging from $-\ell$ to $+\ell$.

4. Finally, assign m_s, the spin quantum number. m_s can only take on two values: $+\frac{1}{2}$ and $-\frac{1}{2}$.

PRACTICE PROBLEM 4.1

Arrange the following sets of atoms in order of <u>increasing atomic radii/size</u>.

— answer —

	Atoms	Ordered Set
(a)	Sn, Xe, Rb, Sr	Xe < Sn < Sr < Rb
(b)	Rn, He, Xe, Kr	He < Kr < Xe < Rn
(c)	Pb, Ba, Cs, At	At < Pb < Ba < Cs
(d)	Ga, N, Cs, P	N < P < Ga < Cs
(e)	O^{2-}, F^-, Na^+, Mg^{2+}	Mg^{2+} < Na^+ < F^- < O^{2-}

Size <u>increases</u> down a column:
- Adding electrons to larger and larger energy levels (n).
- Electrons are farther and farther from the nucleus.
- Less attraction from the positively charged nucleus.

Size <u>decreases</u> across a row:
- Adding electrons to the same energy level (n).
- But also adding more and more protons (positive charge) to nucleus.
- Electrons are pulled more tightly by the increased number of protons (i.e. greater positive charge of nucleus).

For the <u>ions</u>, consider that each ion has 10 electrons, but a different number of protons. As the number of protons increases, the size decreases.

PRACTICE PROBLEM 4.2

Arrange the following sets of atoms in order of <u>increasing first ionization energies</u>.

– answer –

Atoms	Ordered Atoms
(a) B, N, Rb	Rb < B < N
(b) Li, C, Si	Li < Si < C
(c) Mg, O, P, Na	Na < Mg < P < O
(d) Te, Cs, F, Sn, Se	Cs < Sn < Te < Se < F

IE <u>decreases</u> down a column:
- Adding electrons to larger and larger energy levels (n).
- Electrons are farther and farther from the nucleus.
- Less attraction (more screening) from the positively charged nucleus.
→ <u>easier to remove electron!</u>

IE <u>increases</u> across a row:
- Adding electrons to the same energy level (n).
- But also adding more and more protons (positive charge).
- Electrons are pulled more tightly by the increased number of protons (i.e. greater positive charge of nucleus).
→ <u>harder to remove electron!</u>

PRACTICE PROBLEM 4.3

For each of the following sets of atom/ions, determine which of the set has the _____.

— answer —

	Set	Property	Answer
(a)	H, He$^+$, Li^{2+}, Be^{3+}	Largest ionization energy?	Be^{3+}
(b)	S^{2-}, Ca^{2+}, K$^+$, Cl$^-$	Largest size?	S^{2-}
(c)	K$^+$, Ca$^+$, Ar$^+$, Cl$^+$, S$^+$	Smallest ionization energy?	Ca$^+$
(d)	V, Mn^{2+}, Ti^{2+}, Cu^{2+}	Smallest size?	Cu^{2+}
(e)	Se^{2-}, Br$^-$, Sr^{2+}, Zr^{4+}, Rb$^+$	Smallest ionization energy?	Se^{2-}
(f)	S^{2-}, S, S^{2+}, Cs$^+$, Sr^{2+}	Smallest size?	S^{2+}
(g)	S^{2-}, S, S^{2+}, Cs$^+$, Sr^{2+}	Largest ionization energy?	S^{2+}

PRACTICE PROBLEM 5.1

Write the electronic configuration for the following atoms/ions.

— answer —

	Atom/Ion	Full Configuration	Noble-Gas Configuration
(a)	Cl^+	$1s^22s^22p^63s^23p^4$	$[Ne]3s^23p^4$
(b)	V	$1s^22s^22p^63s^23p^64s^23d^3$	$[Ar]4s^23d^3$
(c)	Mn	$1s^22s^22p^63s^23p^64s^23d^5$	$[Ar]4s^23d^5$
(d)	Mn^{2+}	$1s^22s^22p^63s^23p^63d^5$	$[Ar]3d^5$
(e)	Ti^{2+}	$1s^22s^22p^63s^23p^63d^2$	$[Ar]3d^2$
(f)	Cu	$1s^22s^22p^63s^23p^64s^13d^{10}$	$[Ar]4s^13d^{10}$
(g)	Cu^{2+}	$1s^22s^22p^63s^23p^63d^9$	$[Ar]3d^9$
(h)	Cu^+	$1s^22s^22p^63s^23p^63d^{10}$	$[Ar]3d^{10}$
(i)	Te^{2-}	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$	$[Kr]5s^24d^{10}5p^6$

Special Notes:
1. Cu is an exception: fills half an s orbital and all d orbitals.
2. For transition metal cations, remove electrons from s orbital first.

PRACTICE PROBLEM 5.2

Determine the number of unpaired electrons for the following atoms/ions.

– answer –

	Atom/Ion	Noble-Gas Configuration	Unpaired Electrons
(a)	Cl^+	$[Ne]3s^23p^4$	2
(b)	V	$[Ar]4s^23d^3$	3
(c)	Mn	$[Ar]4s^23d^5$	5
(d)	Mn^{2+}	$[Ar]3d^5$	5
(e)	Ti^{2+}	$[Ar]3d^2$	2
(f)	Cu	$[Ar]4s^13d^{10}$	1
(g)	Cu^{2+}	$[Ar]3d^9$	1
(h)	Cu^+	$[Ar]3d^{10}$	0
(i)	Te^{2-}	$[Kr]5s^24d^{10}5p^6$	0

For most of these, the orbital diagram is as shown on the right for Mn with 25 electrons.

General principles are:

(1) determine total number of electrons in atom/ion,
(2) fill from the lowest to highest energy orbitals, and
(3) fill across orbitals before pairing electrons to maximize unpaired electrons.
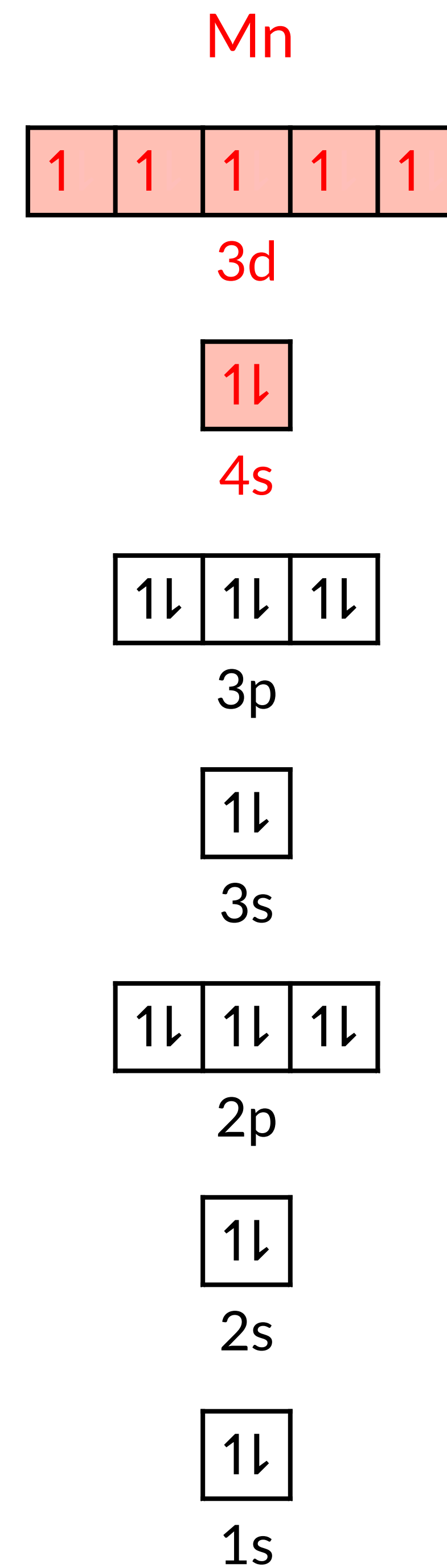
Cl⁺
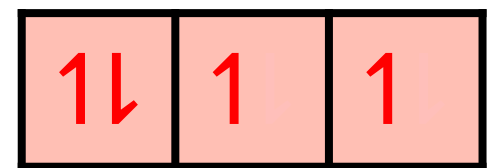
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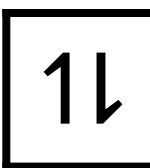
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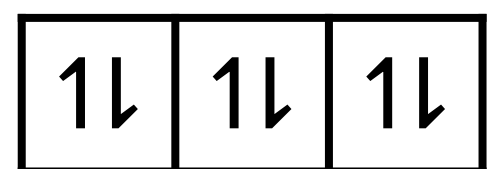
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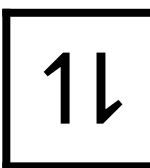
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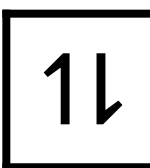
1s: ↑↓

V
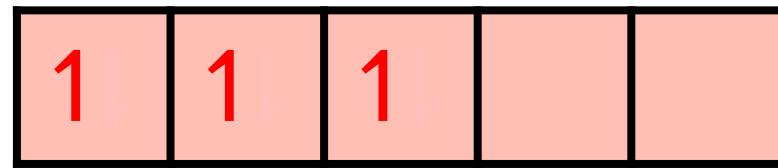
3d: ↑ | ↑ | ↑ | |
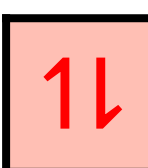
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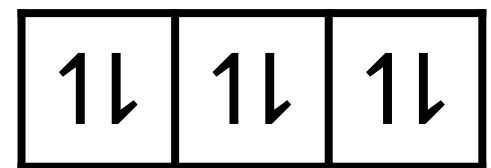
3p: ↑↓ | ↑↓ | ↑↓

3s: ↑↓

2p: ↑↓ | ↑↓ | ↑↓

2s: ↑↓

1s: ↑↓

Mn²⁺

3d: ↑ | ↑ | ↑ | ↑ | ↑

4s: (empty)
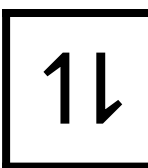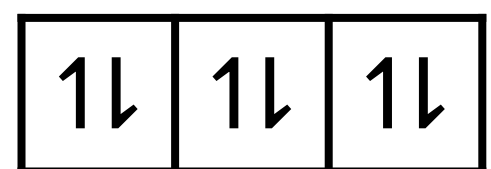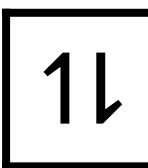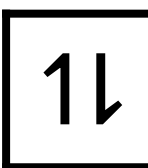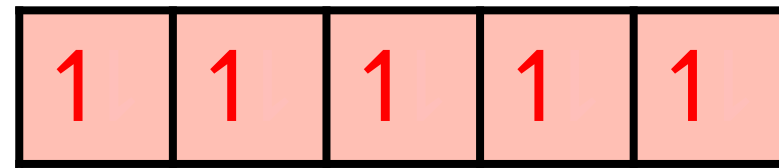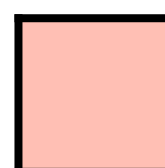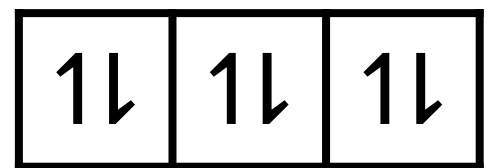
3p: ↑↓ | ↑↓ | ↑↓

3s: ↑↓

2p: ↑↓ | ↑↓ | ↑↓

2s: ↑↓

1s: ↑↓

Cu

3d: ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓

4s: (empty)
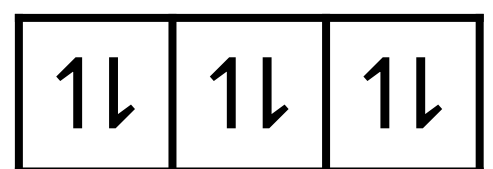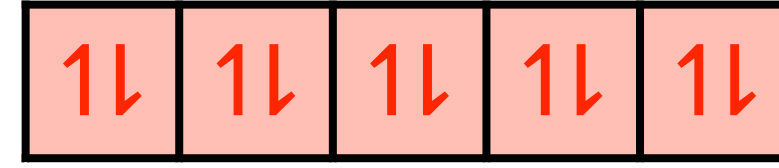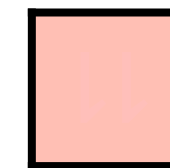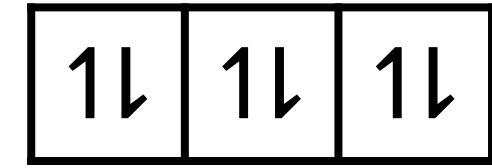
3p: ↑↓ | ↑↓ | ↑↓

3s: ↑↓

2p: ↑↓ | ↑↓ | ↑↓

2s: ↑↓

1s: ↑↓

Cu²⁺

3d: ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑

4s: (empty)
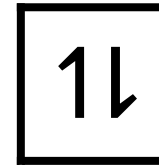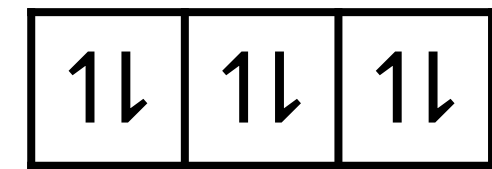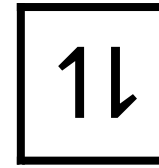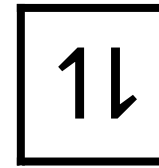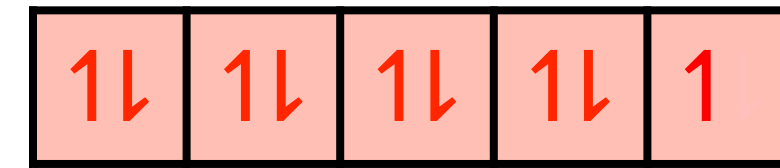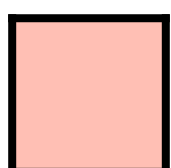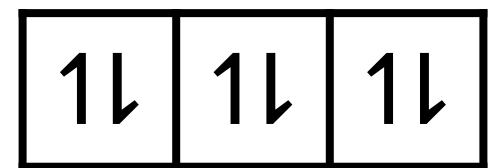
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3s: ↑↓
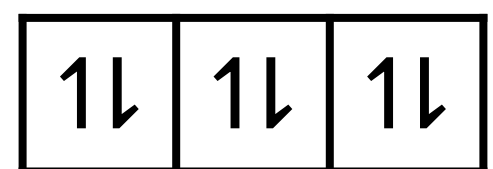
2p: ↑↓ | ↑↓ | ↑↓

2s: ↑↓

1s: ↑↓

PRACTICE PROBLEM 6

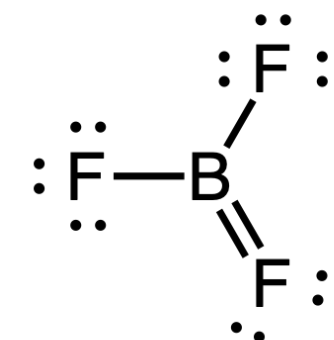Consider the following seven Lewis structures. Assume the total number of electrons in each structure is correct.
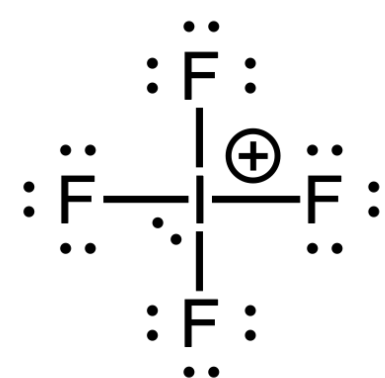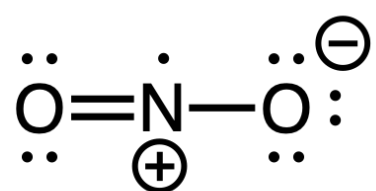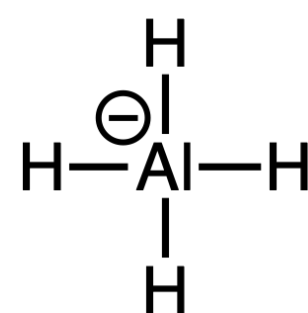
— answer —

H   H
 \   /
 :N—N:
 /   \
H   H

I

:N≡C—O: (⊕ on C, ⊖ on O)

II

:F:
  \
:F—B
  ‖
  F:

III

:F:
  |
:F—I⊕—F:
  |
:F:

IV

O=N—O: (⊕ on N, ⊖ on O)

V

H
|
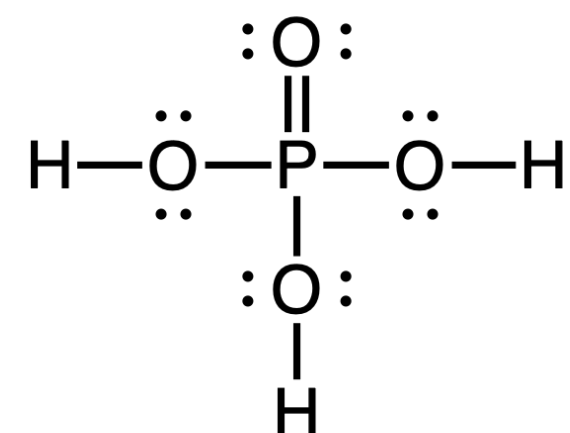H—Al⊖—H
|
H

VI

:O:
‖
H—O—P—O—H
|
:O:
|
H

VII

(A)   Which structures have an atom that breaks the octet rule?

Structure IV   →   Iodine has 10 electrons

Structure V   →   Nitrogen has 5 electrons

Structure VII   →   Phosphorus has 10 electrons

(B)   Which structures have an incorrect formal charge assignment?

Structure II   →   Carbon should be 0

Structure III   →   Boron should be +1 and F (in B=F bond) should be –1

(C)   Which structures could have a reasonable resonance structure that obeys the octet rule?

Structures II and III

(D)   If the electronegativities of H and B are equal, which structure has the most polar bond?
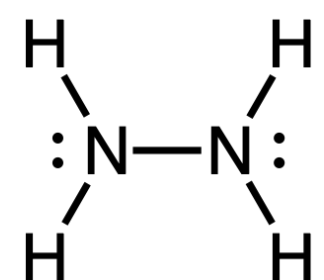
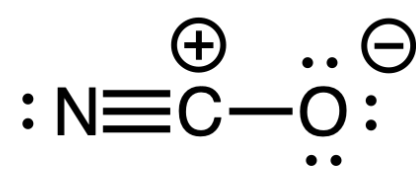Structure III   Structure VI   Structure VII

PRACTICE PROBLEM 7

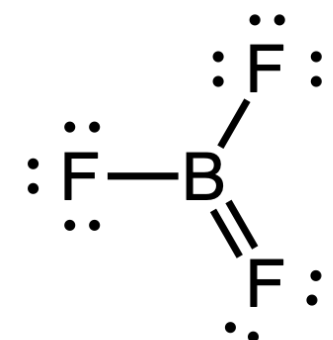Consider the following seven Lewis structures. Assume the total number of electrons in each structure is correct.
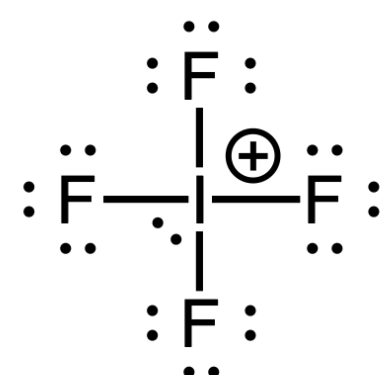
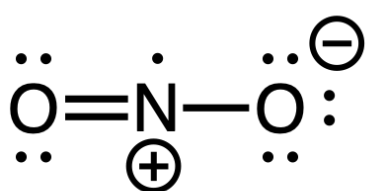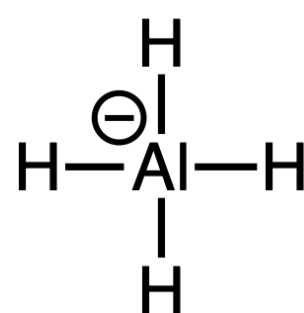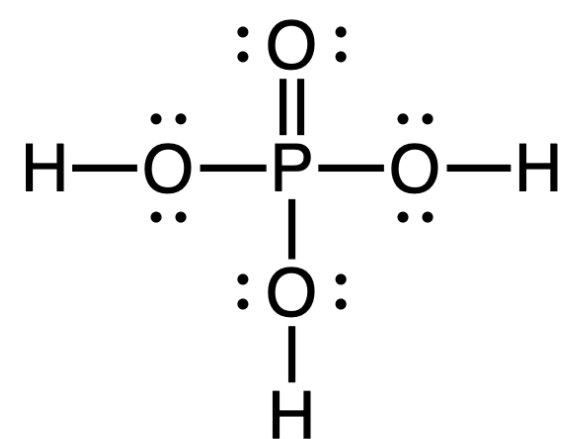*− answer −*

I

II

III

IV

V

VI

VII

(A) Which structures contain only <u>one</u> π bond?

Structures III and VII

(B) Which structures would be paramagnetic based only on the Lewis structures?

Structure V　　→　　Nitrogen has one unpaired electron

(C) Which structures contain an sp-hybridized atom?

Structure II　　→　　Both C and N are sp-hybridized

(D) Which structures contain an sp²-hybridized atom?

Structure III　　→　　B and F (in B=F bond) are sp²-hybridized

Structure V　　→　　N and O (in N=O bond) are sp²-hybridized

Structure VI　　→　　O atom (in P=O bond) is sp²-hybridized

(E) Which structures have a bond angle that is 180°?

Structure II　　→　　Linear geometry

Structure IV　　→　　See-saw geometry; one F–I–F bond angles is 180°

PRACTICE PROBLEM 8.1

Consider the molecular ion $[GeCl_3]^-$.

   (a) Draw the Lewis structure, including any lone pairs and formal charges.

   (b) Give the molecular geometry at the central atom.

   (c) State the hybridization at the central atom.

   (d) Determine if the molecule is polar or nonpolar.

– answer –
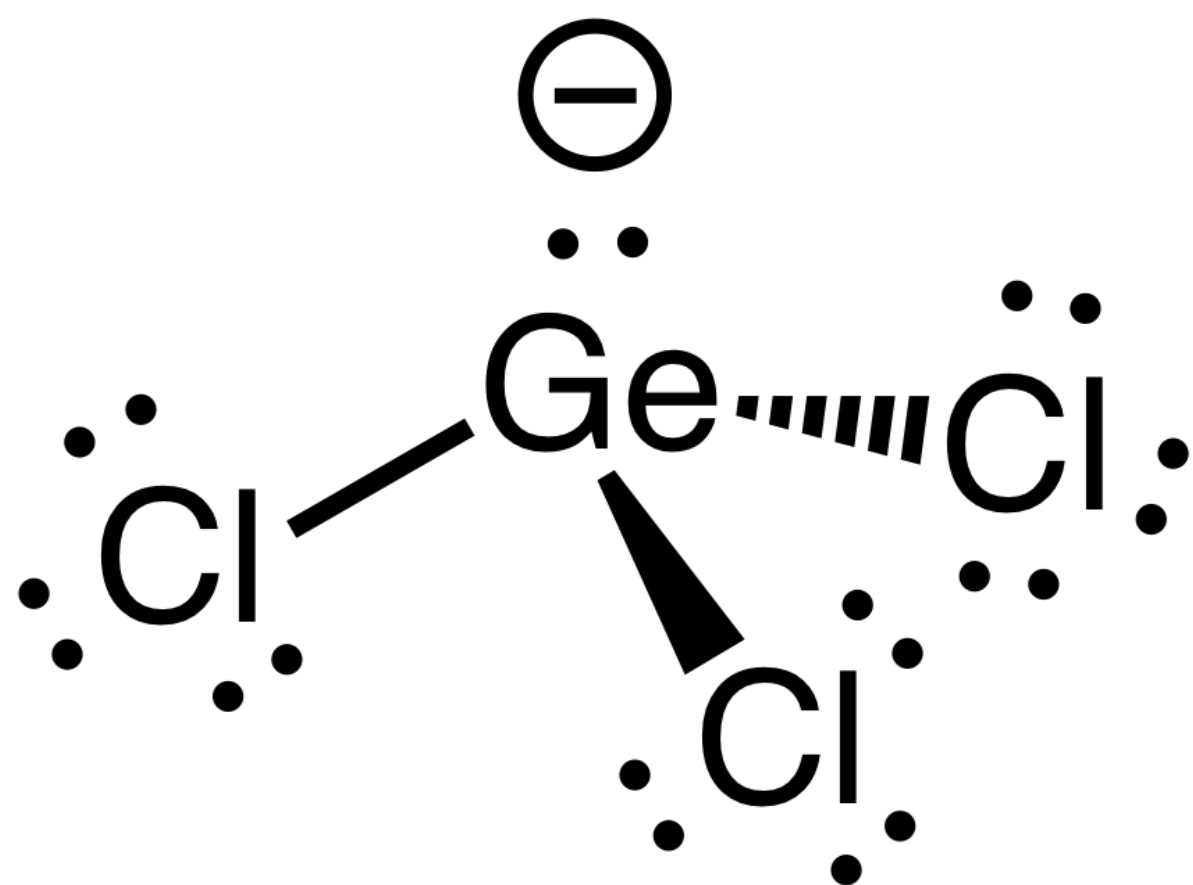
Steric Number at Ge   = 4 (3 atoms + 1 lone pair)
Molecular Geometry at Ge   = Trigonal Pyramid
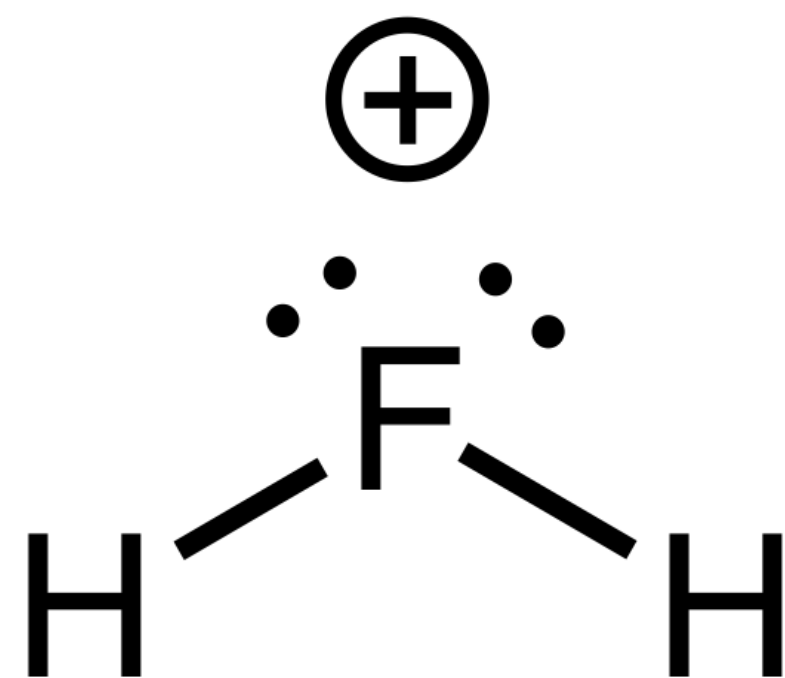Hybridization at Ge   = sp^3
Polar/Nonpolar?   = Polar

PRACTICE PROBLEM 8.2

Consider the molecular ion $[FH_2]^+$.

   (a) Draw the Lewis structure, including any lone pairs and formal charges.

   (b) Give the molecular geometry at the central atom.

   (c) State the hybridization at the central atom.

   (d) Determine if the molecule is polar or nonpolar.

– answer –

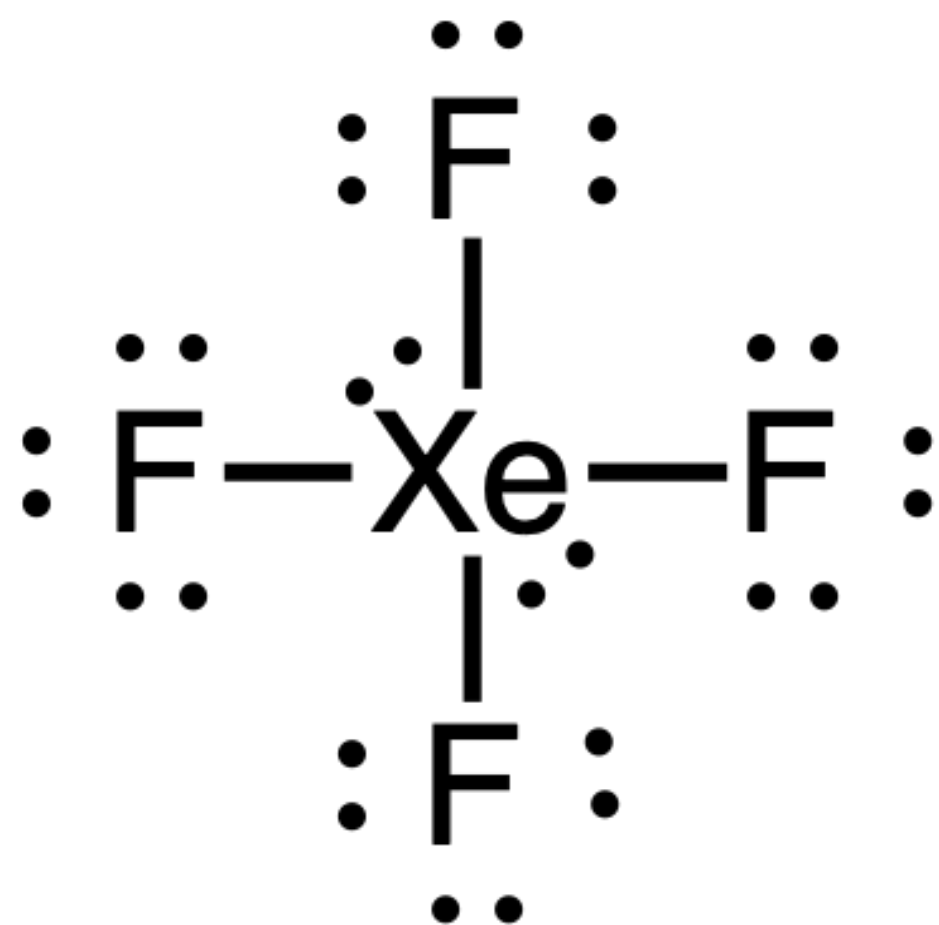|	
Steric Number at F	= 4 (2 atoms + 2 lone pair)
Molecular Geometry at F	= Bent (or angular)
Hybridization at F	= sp^3
Polar/Nonpolar?	= Polar

PRACTICE PROBLEM 8.3

Consider the molecule XeF_4.

   (a) Draw the Lewis structure, including any lone pairs and formal charges.

   (b) Give the molecular geometry at the central atom.

   (c) State the hybridization at the central atom.

   (d) Determine if the molecule is polar or nonpolar.

– answer –

Steric Number at Xe   = 6 (4 atoms + 2 lone pair)
Molecular Geometry at Xe   = Square Planar
Hybridization at Xe   = sp^3d^2
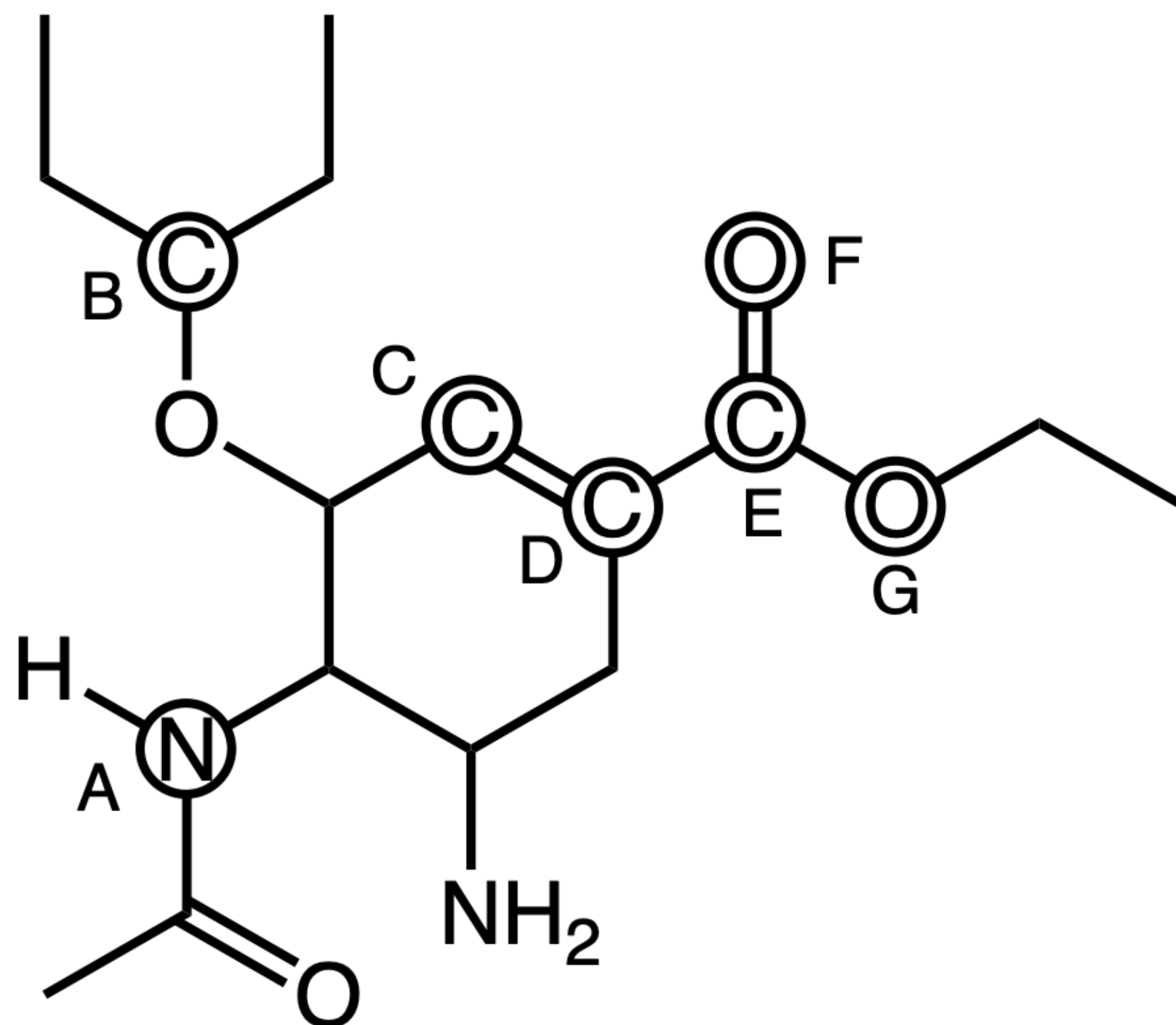Polar/Nonpolar?   = Nonpolar

PRACTICE PROBLEM 9

Consider the molecule Tamiflu shown below. For each circled atom (labeled A-G), give the ...

    (a) Molecular geometry

    (b) Hybridization

− answer −

Atom Label	Geometry	Hybridization
A	Trigonal pyramid	sp^3
B	Tetrahedral	sp^3
C	Trigonal planar	sp^2
D	Trigonal planar	sp^2
E	Trigonal planar	sp^2
F	N/A	sp^2
G	Bent (or angular)	sp^3

PRACTICE PROBLEM 10

Consider carbon monoxide (CO) and its molecular orbital diagram below.

— answer —

2p

2p

σ^*_{2p}

π^*_{2p}

σ_{2p}

π_{2p}

σ^*_{2s}

2s

2s

σ_{2s}

C   CO   O

Molecular Orbitals
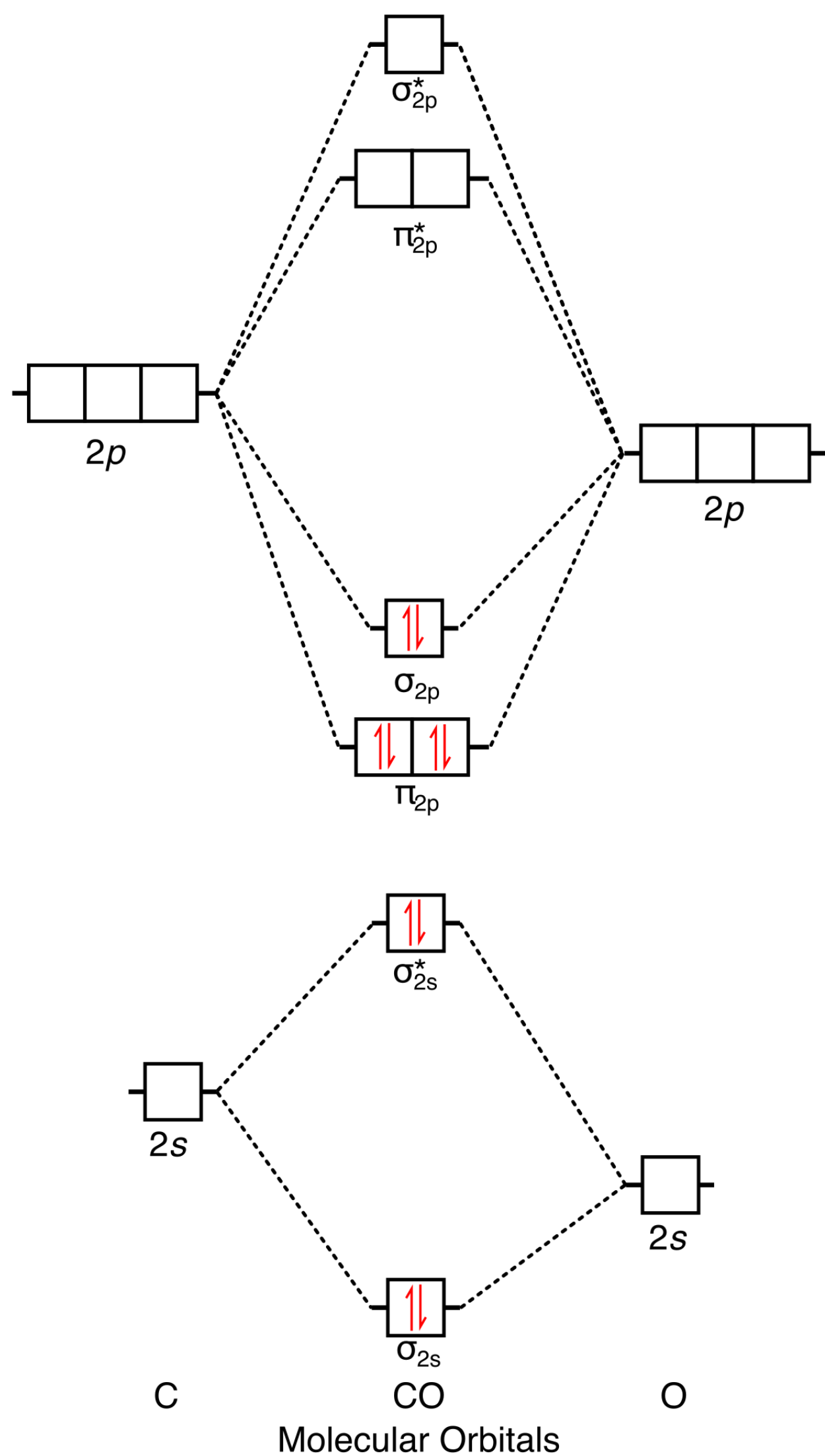
(A) Using the diagram on the left, fill in the electrons for the molecular orbitals of CO.

See diagram (not necessary to fill atomic orbitals)

(B) Determine the bond order for CO based on your diagram.

BO = ½ [bonding e⁻ – antibonding e⁻] = ½ [8 – 2] = 3   → triple bond

(C) Do you expect CO to be paramagnetic or diamagnetic?

Diamagnetic (all electrons are paired)

(D) Do you expect CO⁴⁺ to be paramagnetic or diamagnetic?

Paramagnetic (2 unpaired electrons; 1 in each π_{2p} orbital)

(E) Do you expect CO²⁻ to be paramagnetic or diamagnetic?

Paramagnetic (2 unpaired electrons; 1 in each π^*_{2p} orbital)