SOLUTIONS

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1) An electron in a hydrogen atom undergoes a transition from an unknown initial state n_i to a final state n_f=3, emitting a photon with wavelength = 1290 nm.
Identify the initial state and the region of the electromagnetic spectrum in which the emitted light is observed.

● n_i=5, infrared
○ n_i=4, infrared
○ n_i=6, infrared
○ n_i=4, radio
○ n_i=5, radio
○ n_i=6, radio

$$\frac{91\text{ nm}}{1290\text{ nm}} = \frac{1}{3^2} - \frac{1}{n_i^2}$$

2) For a hydrogen atom or one-electron ion, how many atomic orbitals share the same principle quantum number n?

○ $n - 1$
○ $n + 1$
○ $2n$
● n^2

How many radial and angular nodes does a 4d orbital possess?

○ radial = 0, angular = 3
● radial = 1, angular = 2
○ radial = 2, angular = 1
○ radial = 3, angular = 0

'l' angular, '$n-l-1$' radial

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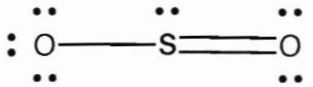
3) Select the best Lewis structure for sulfur dioxide, SO_2.

all octets full, least amount of formal charge

●



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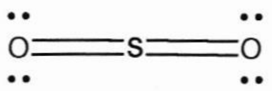

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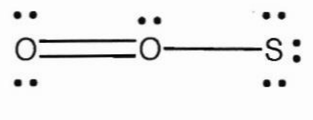

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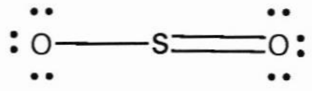


Does the structure you selected have a **non-zero** dipole moment?

● Yes

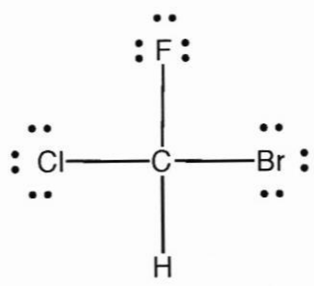
○ No

bent geometry

4) Lewis structures are shown below for four different molecules. Which of these molecules is chiral? Mark all that apply.

●

tetrahedral + four different groups



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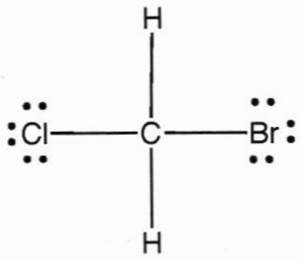

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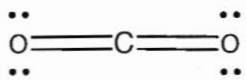

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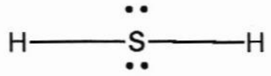

5) Ionization is the process of removing an electron from an atom. For an atom X, the first and second ionizations are given by the following equations.

First ionization: $X (g) \rightarrow X^{+} (g) + e^{-}$

Second ionization: $X^{+} (g) \rightarrow X^{2+} (g) + e^{-}$

Which element in the second period has the **highest second ionization energy**?

● Li
○ Be
○ B
○ C
○ N
○ O
○ F
○ Ne

(Li^{+}) $1s^{2} 2s^{0}$ configuration
→ difficult to lose another electron

Which element in the second period has the **lowest second ionization energy**?

○ Li
● Be
○ B
○ C
○ N
○ O
○ F
○ Ne

(Be^{+}) $1s^{2} 2s^{1}$ configuration
→ easy to lose an electron & go to closed shell

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6) This question concerns elements in the fourth row of the periodic table, such as vanadium (V) and chromium (Cr).

i. What is the full electronic configuration for vanadium? (Do not worry about possible exceptions to the standard Aufbau rules.)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ \overset{3}{\cancel{4}}d^3$

ii. How many valence electrons does a vanadium atom have? Consider all electrons in the 4s, 3d, and 4p orbitals to be part of the valence shell.

[2 in 4S + 3 in 3d]

$\cdot\ddot{V}:$

Final Answer

5 electrons

iii. Now consider a diatomic molecule V_2 composed of two covalently bonded vanadium atoms. Draw a Lewis structure for this molecule, assuming that the octet rule applies to its valence electrons. What bond order is suggested by your structure?

5 valence electrons ⇒ similar to nitrogen

$:V\equiv V:$

→ triple bond

3 Bond Order

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Some of the molecular orbitals for bonding in V_2 involve d orbitals.

The picture below shows a d orbital centered on one vanadium atom, together with a d orbital centered on the other vanadium atom. The two V nuclei are located on the *z* axis, as indicated by the black spheres (or dashed outlines where they are obscured by other surfaces).

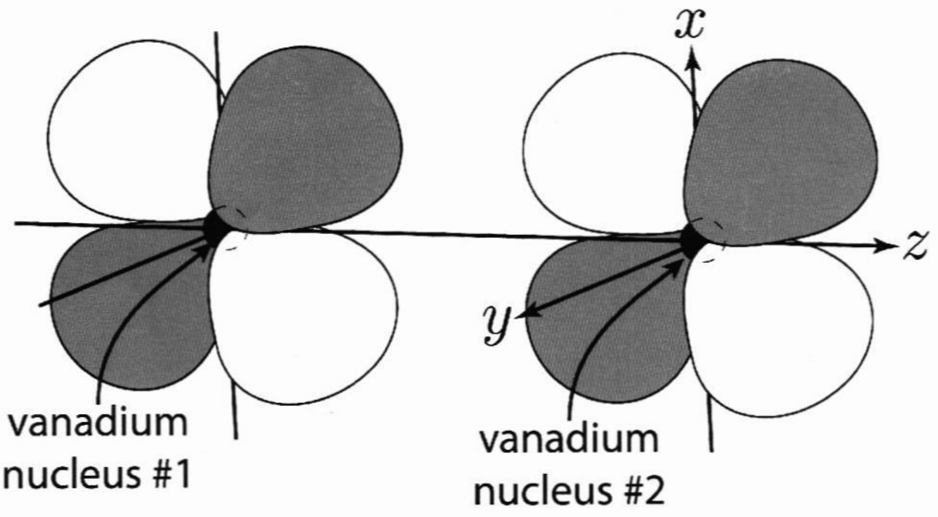


Figure 1

Gray and white lobes in this picture depict isosurfaces of the two d-orbital wavefunctions. White lobes indicate a positive value of the atomic wavefunction, and gray lobes indicate a negative value of the atomic wavefunction. Each of these orbitals therefore has two nodal planes: One is perpendicular to the *z* axis. The other is the *yz*-plane, which runs through both nuclei.

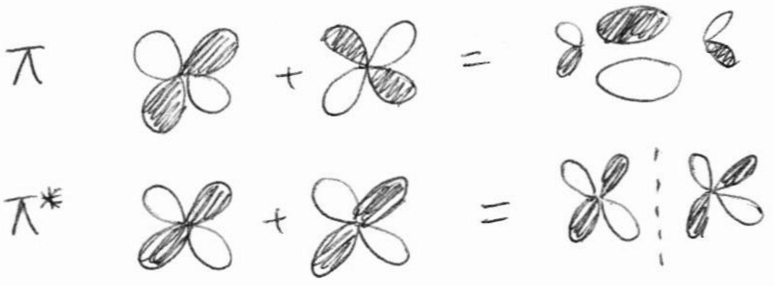
iv. When the two nuclei are brought together along the *z* axis, hybridizing the d orbitals in Figure 1 produces one or more molecular orbitals. Which of the following molecular orbitals can be formed by **adding or subtracting** the atomic orbitals shown in Figure 1? (Check all that apply.) **Note**: the nuclei cannot move off the *z* axis.

○ σ bonding orbital

○ σ^* antibonding orbital

● π bonding orbital

● π^* antibonding orbital



The picture below shows a different pair of d orbitals, one centered on each nucleus. In this case the nuclei are completely obscured by the wavefunction's isosurfaces, so they are shown as dashed outlines. The nodal surfaces for these two orbitals do not include the *z* axis.

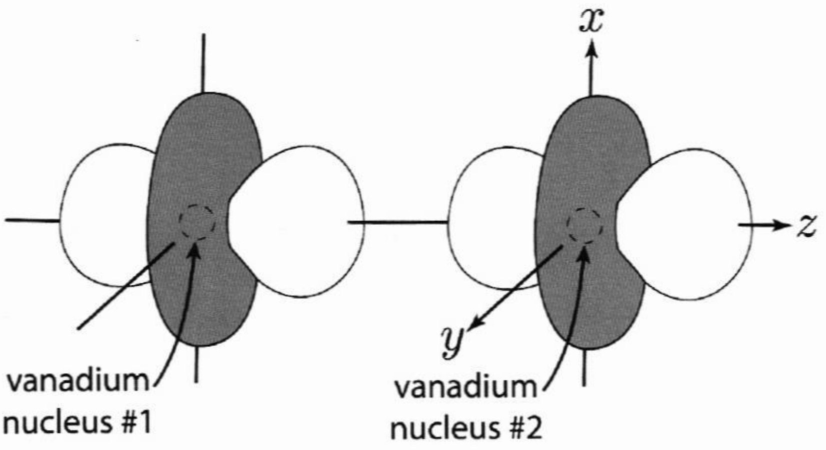


Figure 2

v. When the two nuclei are brought together along the *z* axis, hybridizing the d orbitals in Figure 2 produces one or more molecular orbitals. Which of the following molecular orbitals can be formed by **adding or subtracting** the atomic orbitals shown in Figure 2? (Check all that apply.) **Note**: the nuclei cannot move off the *z* axis.

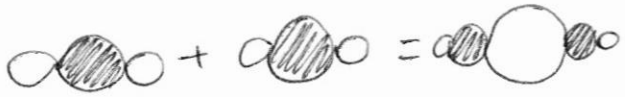
● σ bonding orbital

● σ^* antibonding orbital

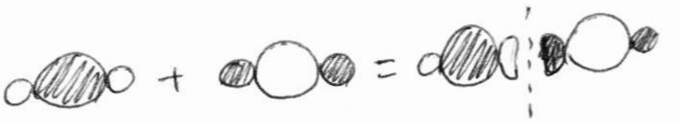
○ π bonding orbital

○ π^* antibonding orbital

σ



σ^*



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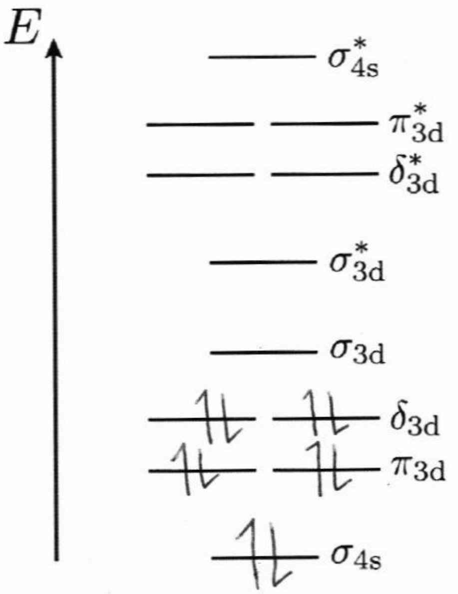
The diagram below shows all the molecular orbitals available to valence electrons in our analysis of V_2. Orbitals marked with a $*$ are antibonding orbitals; all others are bonding orbitals. (Note: Orbitals labeled δ have two nodal planes passing through the bonded nuclei, but this detail is not important for the exam.)

vi. Complete this molecular orbital diagram for the ground state of V_2. Specifically, populate the orbitals with valence electrons. (Consider all electrons from the 4s, 3d, and 4p atomic orbitals to be part of the valence shell.) Indicate the spin of each electron.

10 electrons in total as for each V, we have 5 electrons.



vii. Based on your molecular orbital diagram in part (vi), what is the bond order of V_2? Do you expect the molecule to be magnetic?

BO = 5 bonding pairs − 0 anti-bonding pairs = 5

No unpaired electrons ⇒ diamagnetic

NO Magnetic (yes or no)

5 Bond Order

viii. Assume that the diatomic Cr_2 molecule involves the same set of molecular orbitals, whose energies are ordered in the same way. Do you expect the dissociation energy of Cr_2 to be larger or smaller than the dissociation energy of V_2? Explain your reasoning.

Cr_2 has two more electrons that fill up the σ_{3d} bonding orbital.

$\Rightarrow$ BO = 6 & bond is stronger.

$\Rightarrow$ Cr_2 has larger dissociation energy.

ix. Which do you expect to have the larger electron affinity, Cr_2 or Cr_2^-? Give a clear reason for your expectation.

Cr_2 has larger electron affinity because

i] Cr_2^- already has a negative charge and adding more electrons is difficult.

ii] the second electron for Cr_2^- goes into an orbital that is already half-full & anti-bonding, reducing the bond order.

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7) In class, we used the hydrogen atom as a model to describe the electron configuration of many-electron atoms. For this question, you will do the same with a modified version of the hydrogen atom, where the orbital energies have been shifted by an external force on the electron. (In the laboratory, this force could be achieved by applying an electric field to the atom.)

The 1s ground state of our modified hydrogen atom is unchanged by the external force,

$$E_{1s} = -Ry\,,$$

where Ry is the Rydberg energy.

The $2p_x$ and $2p_y$ orbitals are also unaffected by the external force,

$$E_{2p_x} = E_{2p_y} = -\frac{Ry}{4}.$$

Due to the external force, the $2s$ and $2p_z$ orbitals become mixed, and the hybridized orbitals are no longer degenerate with the rest of the second shell. These hybrids (labeled "$2s - 2p_z$" and "$2s + 2p_z$") have energies:

$$E_{2s-2p_z} = -\frac{Ry}{4} + 2\delta$$

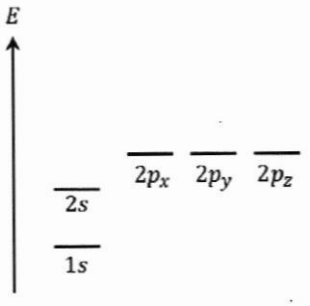
$$E_{2s+2p_z} = -\frac{Ry}{4} - 2\delta$$

$$\boxed{E_{2s+2p_z} < E_{2p_x} = E_{2p_y} < E_{2s-2p_z}}$$

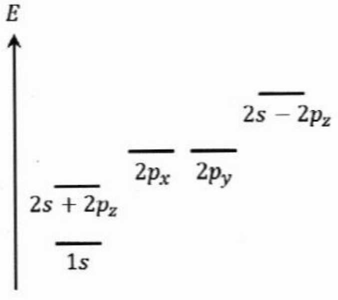
In the above expressions, δ is a *positive* constant indicating the strength of the external force.

i. Which of the following energy level diagrams describes this force-modified hydrogen atom?

○



●



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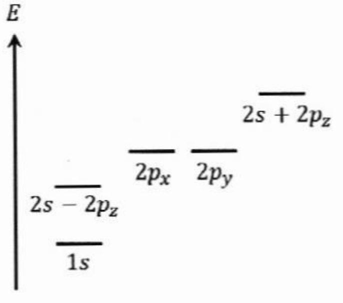

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ii. Using Aufbau and Pauli principles, Hund's rule, and the orbital labels and energies given above, determine the electron configuration of an **oxygen atom** in the presence of the external force. Be specific about which orbitals are occupied (for example, if the $2p_x$ and $2p_y$ orbitals are the only ones occupied, you should write $2p_x^2 2p_y^2$ instead of $2p^4$).

oxygen = 8 electrons

$1s^2(2s+2p_z)^2 2p_x^2 2p_y^2$ Configuration

iii. Using the same rules as in part (b), determine the electron configuration of a **carbon atom** in the presence of the external force.

carbon = 6 electrons

$1s^2(2s+2p_z)^2 2p_x^1 2p_y^1$ Configuration

iv. Suppose that the ordering of orbital energies described above was called into question for multi-electron atoms. Specifically, someone suggests that screening causes the degenerate $2p_x$ and $2p_y$ orbitals of force-modified atoms to have an energy that is higher than all of the other $n = 2$ orbitals. Could this issue of orbital energy ordering be resolved by measuring the magnetism of **carbon** and/or **oxygen atoms** in the presence of the external force? Check all that apply and explain your reasoning in 1-2 sentences.

○ No.

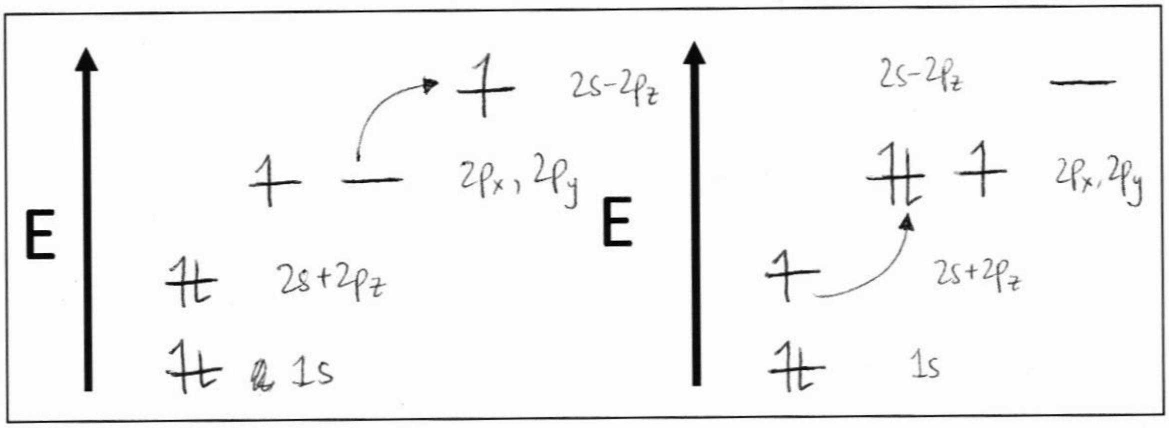
● Yes, measuring the magnetism of carbon alone would be sufficient.] both options work

● Yes, measuring the magnetism of oxygen alone would be sufficient.

○ Yes, but the magnetism of both carbon and oxygen would need to be measured.

Explanation: With current ordering, if carbon is magnetic, then we know suggestion is wrong. With suggested ordering, if oxygen is magnetic, then we know suggestion is correct.
⇒ measuring either atom confirms the correct ordering.

v. Consider *excited* states of a **carbon** atom in the presence of the external force. Starting with the ground state, these excited states are produced by promoting an electron to a higher energy orbital. During the transition the spin of this electron does not change, and Pauli's exclusion principle must be obeyed.
Draw energy level diagrams below for the excited states of force-modified carbon with the two *lowest* energies. Indicate the occupation of each orbital, and the spin(s) of electron(s) that populate them.



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vi. As the strength δ of the external force increases, do you expect **fluorine's** ionization energy to increase or decrease, or should it stay the same? What about its electron affinity? Explain your reasoning in 1-2 sentences.
Hint: it might be helpful to consider the electronic configurations of F^+, F and F^-.

○ Ionization energy and electron affinity should both increase.

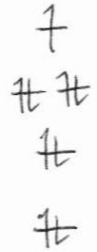
● Ionization energy and electron affinity should both decrease.

○ Ionization energy should increase, and electron affinity should decrease.

○ Ionization energy should decrease, and electron affinity should increase.

○ Neither ionization energy nor electron affinity should change.

Explanation: Fluorine has 9 electrons ⇒ $(1s)^2(2s+2p_z)^2 2p_x^2 2p_y^2 (2s-2p_z)^1$



→ removing an electron is easy (lower energy)
→ adding an electron is hard (goes to high energy orbital)