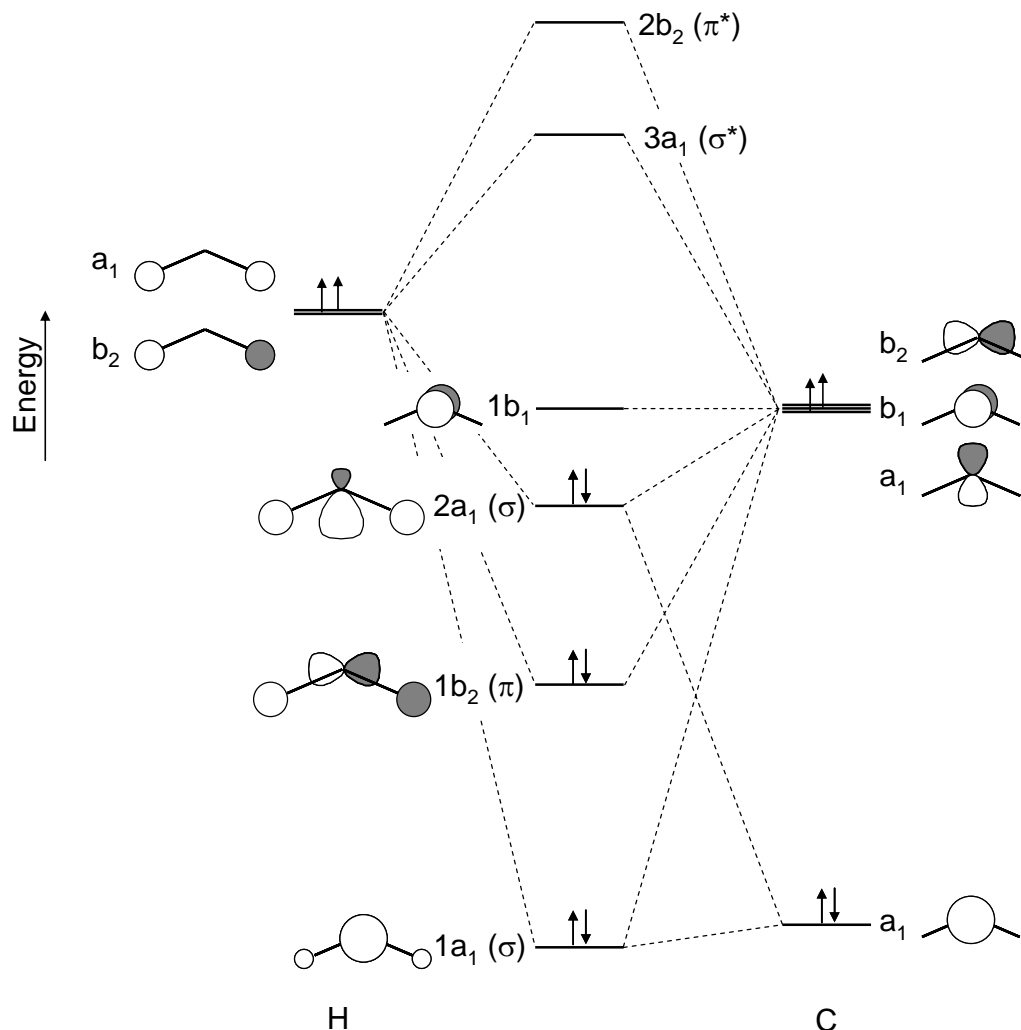


**Quiz 12**  
**CHEM 325**  
**Spring 2009**

Name: \_\_\_\_\_

1. The MO diagram for the  $C_{2v}$  carbene methylene,  $CH_2$ , is shown below (only the valence orbitals on the atoms shown).

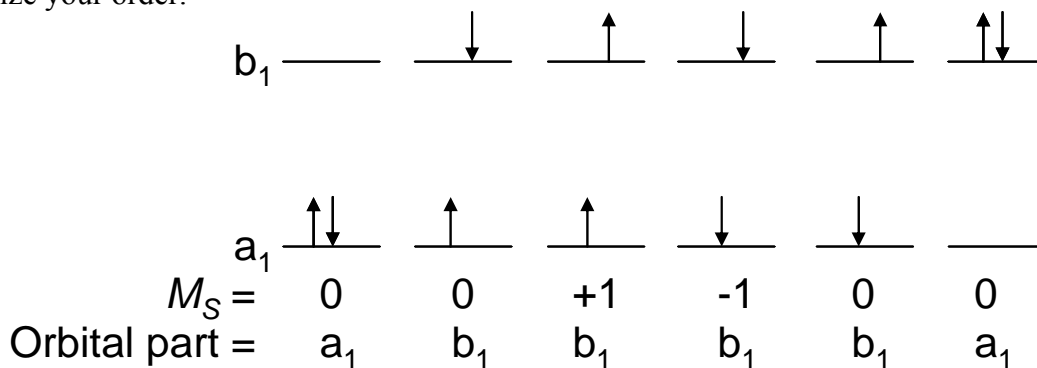


a. (2 Points) The electronic configuration of H is  $1s^1$  and that of C is  $[He] 2s^2 2p^2$ . Place the electrons in the diagram.

b. (3 Points) Normally we expect  $\sigma$  bonds to be lower in energy (i. e., stronger) than  $\pi$  bonds, but here the  $2a_1$   $\sigma$  bonding MO is higher in energy than the  $1b_2$   $\pi$  bonding MO. Why?

**There is a configurational interaction between the  $1a_1$  MO, which is predominantly the C  $2s$  orbital, and the  $2a_1$  MO formed by overlap of a C  $2p$  orbital with both H  $1s$  orbitals. This interaction destabilizes the  $2a_1$  and stabilizes the  $1a_1$ . Because the C  $2s$  and  $2p$  orbitals are relatively close in energy, this effect is large.**

c. (5 Points) Determine the electronic states arising from the distribution of electrons between the HOMO and the LUMO in CH<sub>2</sub>. Place the electronic states in order of increasing energy. Rationalize your order.



There is a  $^3B_1$  state ( $M_S = 0, \pm 1$  and the orbital part is  $b_1$ ).

There is a  $^1B_1$  state ( $M_S = 0$  and the orbital part is  $b_1$ ).

There are two  $^1A_1$  (both have  $M_S = 0$  and the orbital portion is  $a_1$ ), one of these (with the configuration  $(a_1)^2$ ) is expected to be the ground state and the other (the  $(b_1)^2$  state) is an excited state.

The  $^1A_1 (b_1)^2$  state is expected to be lowest in energy since it places both electrons in the lowest energy MO. The next highest state should be the  $^3B_1$  and then the  $^1B_1$ , based on Hund's rules. Finally, the  $^1A_1 (b_1)^2$  state which should be very high in energy because it has moved both electrons to the higher energy MO.

d. (4 Points) Methylene is known to have a triplet ground state. What does this result imply about the HOMO–LUMO energy difference and the spin pairing energy?

If the HOMO-LUMO energy difference is large compared to the energy to spin the electrons in an orbital, then the molecule will choose the lowest energy option. In this case, it would be to have both electrons in the  $2a_1$  MO, resulting in a  $^1A_1$  ground state. However, if the HOMO-LUMO gap is smaller than the spin pairing energy, it is energetically favorable for the electrons to not pair and to occupy different orbitals. This leads to one electron in the  $b_1$  MO and one electron in the  $a_1$  orbital and gives a  $^3B_1$  and a  $^1B_1$  state, of which the  $^3B_1$  is lower. Thus, the fact that methylene has a triplet ground state implies that the HOMO-LUMO energy difference is smaller than the spin pairing energy.

e. (4 Points) Valence bond theory considers the electrons in a triplet carbene to reside in a nonbonding  $sp^2$  hybrid orbital and an unhybridized p orbital on the carbon. Compare and contrast this with the MO model.

**In MO theory the electrons in triplet methylene occupy the non-bonding  $1b_1$  MO and the weakly bonding  $2a_1$  MO. The non-bonding  $1b_1$  MO is simply a C 2p atomic orbital, exactly as predicted by valence bond theory. However, the  $2a_1$  orbital is not a pure  $sp^2$  hybrid orbital. This MO is primarily a C 2p orbital with some degree of 2s character as a result of the mixing of the  $2a_1$  and  $1a_1$  MOs, but the amount of 2s character does not approach that predicted by valence bond theory. In addition, the  $2a_1$  MO has some H 1s character, which it would not in valence bond theory.**

2. (6 Points) The highest energy electronic transition that gaseous K can undergo occurs at  $35009.8140 \text{ cm}^{-1}$ . If we treat K as a one electron system, what is the effective nuclear charge,  $Z^*$ , of the 3s electron in K? Hint: assume that the 3s electron is in its lowest state.

**If we treat the 3s electron in K as a single electron orbiting a nucleus of charge  $Z^*$ , we can then write any change it can undergo in terms of a principle quantum number,  $n$ , as follows:**

$$\Delta E = E_{n_f} - E_{n_i} = -\frac{R_H Z^{*2}}{n_f^2} + \frac{R_H Z^{*2}}{n_i^2}$$

**Since the given energy is the highest energy transition that K can undergo, it must correspond to a transition from  $n = 1$  to  $n = \infty$ . Substituting these values in gives**

**$\Delta E = R_H Z^{*2}$ , which can be rearranged to  $Z^* = \sqrt{\frac{\Delta E}{R_H}}$  and after substitution of  $\Delta E$  and**

**$R_H$  gives the final answer of  $Z^* = 0.56$ . Note that although we could have up to six significant figures given the rather large approximation that we've made here, two significant figures is probably all we should quote.**

$$Z^* = \sqrt{\frac{\Delta E}{R_H}} = \sqrt{\frac{35009.8140 \text{ cm}^{-1}}{1.09737 \times 10^5 \text{ cm}^{-1}}} = 0.57$$