Name:

Quiz 5

Chemistry 3BB3; Winter 2003

When we started talking about molecules, we discussed the hydrogen molecule ion, which was the "prototype" for molecules in the same sense that the Hydrogen atom is the "prototype" for atoms. The next six questions pertain to this system and, in particular, the "correlation diagram."

1. **In the $R = 0$ limit, the system becomes the Helium atom cation. This is called the**
   (a) united-atom limit
   (b) separated atom limit
   (c) electron-coalescence limit
   (d) separated-electron approximation

2. **In the limit as $R \to \infty$, the system becomes a two protons, infinitely separated, "sharing" an electron. This is called the**
   (a) united-atom limit
   (b) separated atom limit
   (c) electron-coalescence limit
   (d) separated-electron approximation

3. **When "connecting" the $R = 0$ and $R \to \infty$ limits, we discussed the non-crossing rule. This rule states that**
   (a) electronic states whose wave functions have different symmetry never cross.
   (b) electronic states whose wave functions have the same symmetry never cross.
   (c) electronic states with the same energy in the $R = 0$ limit never have the same energy in the $R \to \infty$ limit.
   (d) electronic states with the same energy in the $R \to \infty$ limit never have the same energy in the $R = 0$ limit.

4. **Label the following approximate (unnormalized) molecular orbitals using the σ, π, δ, u, g, and $+, -$ designations. Here, we denote the $1s$ orbital on the "left-hand" atom as $\psi_{1s}^{(l)}(\boldsymbol{r})$, with the obvious generalization of notation to the other orbitals and the "right-hand" atom. (Worth 20 points.)**

Orbital Symmetry Label	Molecular Orbital
	$\psi_{2s}^{(l)}(\boldsymbol{r}) + \psi_{2s}^{(r)}(\boldsymbol{r})$
	$\psi_{2s}^{(l)}(\boldsymbol{r}) - \psi_{2s}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) + \psi_{2p_x}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) - \psi_{2p_x}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) + \psi_{2p_y}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) - \psi_{2p_y}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) + \psi_{2p_z}^{(r)}(\boldsymbol{r})$
	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) - \psi_{2p_z}^{(r)}(\boldsymbol{r})$

Name:

5. We can approximate the wave function for a homonuclear diatomic by filling the "molecular orbitals" using the aufbau principle, just as we approximated the wave function for an atom by filling the orbitals of the hydrogen atom using the aufbau principle. For a first-row homonuclear diatomic molecule (e.g., $Li_2, Be_2, B_2, C_2, N_2, O_2, F_2$, the orbitals from question 5 fill in which order?

6. Which of the following orbital types are "bonding" orbitals (as opposed to antibonding).
(a) σ_u (c) π_u^+ (e) π_g^+
(b) σ_g (d) π_u^- (f) π_g^-

We wrote two different approximate wave functions for the ground state of the Hydrogen molecule, H_2. The first was the molecular-orbital theory wave function,

where $\psi_{1s}(r - R_A)$ is a Hydrogenic $1s$ orbital centered on atom **A**, and $\psi_{1s}(r - R_B)$ is a Hydrogenic $1s$ orbital centered on atom **B**. The other approximant wave function we considered was the Valence-Bond, or Heitler-London wave function.

7. Write the Heitler-London Wave function for the hydrogen atom. You can neglect the normalization constant.

8. We said that the simple molecular-orbital wave function was very poor as $R \to \infty$, and that we could improve it with:
(a) resonance structures.
(b) ionic terms.
(c) configuration interaction.
(d) both (a) and (b).
(e) both (a) and (c).

9. We said that the most important correction(s) to the valence-bond wave function were
(a) ionic terms.
(b) polarization effects.
(c) configuration interaction.
(d) both (a) and (b).
(e) both (a) and (c).

Key for Quiz 5

Chemistry 3BB3; Winter 2003

When we started talking about molecules, we discussed the hydrogen molecule ion, which was the "prototype" for molecules in the same sense that the Hydrogen atom is the "prototype" for atoms. The next six questions pertain to this system and, in particular, the "correlation diagram."

1. **In the $R = 0$ limit, the system becomes the Helium atom cation. This is called the**
    (a) united-atom limit
    (b) separated atom limit
    (c) electron-coalescence limit
    (d) separated-electron approximation

2. **In the limit as $R \to \infty$, the system becomes a two protons, infinitely separated, "sharing" an electron. This is called the**
    (a) united-atom limit
    (b) separated atom limit
    (c) electron-coalescence limit
    (d) separated-electron approximation

3. **When "connecting" the $R = 0$ and $R \to \infty$ limits, we discussed the non-crossing rule. This rule states that**
    (a) electronic states whose wave functions have different symmetry never cross.
    (b) electronic states whose wave functions have the same symmetry never cross.
    (c) electronic states with the same energy in the $R = 0$ limit never have the same energy in the $R \to \infty$ limit.
    (d) electronic states with the same energy in the $R \to \infty$ limit never have the same energy in the $R = 0$ limit.

4. **Label the following approximate (unnormalized) molecular orbitals using the σ, π, δ, u, g, and $+, -$ designations. Here, we denote the $1s$ orbital on the "left-hand" atom as $\psi_{1s}^{(l)}(\boldsymbol{r})$, with the obvious generalization of notation to the other orbitals and the "right-hand" atom. (Worth 20 points.)**

Orbital Symmetry Label	Molecular Orbital
σ_g^+ *plus designation is optional for σ-states.*	$\psi_{2s}^{(l)}(\boldsymbol{r}) + \psi_{2s}^{(r)}(\boldsymbol{r})$
σ_u^+	$\psi_{2s}^{(l)}(\boldsymbol{r}) - \psi_{2s}^{(r)}(\boldsymbol{r})$
π_u^+	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) + \psi_{2p_x}^{(r)}(\boldsymbol{r})$
π_g^+	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) - \psi_{2p_x}^{(r)}(\boldsymbol{r})$
π_u^-	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) + \psi_{2p_y}^{(r)}(\boldsymbol{r})$
π_g^-	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) - \psi_{2p_y}^{(r)}(\boldsymbol{r})$
σ_u^+	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) + \psi_{2p_z}^{(r)}(\boldsymbol{r})$
σ_g^+	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) - \psi_{2p_z}^{(r)}(\boldsymbol{r})$

Name:

5. We can approximate the wave function for a homonuclear diatomic by filling the "molecular orbitals" using the aufbau principle, just as we approximated the wave function for an atom by filling the orbitals of the hydrogen atom using the aufbau principle. For a first-row homonuclear diatomic molecule (e.g., $Li_2, Be_2, B_2, C_2, N_2, O_2, F_2$, the orbitals from question 5 fill in which order?

$$\sigma_g\left(2s\right)\sigma_u\left(2s\right),\pi_u^{\pm}\left(2p\right),\sigma_g\left(2p\right),\pi_g^{\pm}\left(2p\right),\sigma_u\left(2p\right)$$

6. Which of the following orbital types are "bonding" orbitals (as opposed to antibonding).

(a) σ_u (c) π_u^+ (e) π_g^+

(b) σ_g (d) π_u^- (f) π_g^-

We wrote several different approximate wave functions for the ground state of the Hydrogen molecule, H_2. The first was the molecular-orbital theory wave function,

$$\psi_{H_2}^{MO}\left(r_1, r_2\right) \propto \left(\psi_{1s}^{(l)}\left(r_1\right) + \psi_{1s}^{(r)}\left(r_1\right)\right)\left(\psi_{1s}^{(l)}\left(r_2\right) + \psi_{1s}^{(r)}\left(r_2\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \beta\left(2\right)\alpha\left(1\right)\right)$$

Another approximate wave function we considered was the Valence-Bond, or Heitler-London wave function.

7. Write the Heitler-London wave function for the hydrogen atom. You can neglect the normalization constant.

$$\psi_{H_2}^{VB}\left(r_1, r_2\right) \propto \left(\psi_{1s}^{(l)}\left(r_1\right)\psi_{1s}^{(r)}\left(r_2\right) + \psi_{1s}^{(r)}\left(r_1\right)\psi_{1s}^{(l)}\left(r_2\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \beta\left(2\right)\alpha\left(1\right)\right)$$

8. We said that the simple molecular-orbital wave function was very poor as $R \to \infty$, and that we could improve it with:

(a) resonance structures.
(b) ionic terms.
(c) configuration interaction.
(d) both (a) and (b).
(e) both (a) and (c).

9. We said that the most important correction(s) to the valence-bond wave function were

(a) ionic terms.
(b) polarization effects.
(c) configuration interaction.
(d) both (a) and (b).
(e) both (a) and (c).

Name: