Quiz 6

Chemistry 3BB3; Winter 2004

1-4. Write a representative molecular orbital for each of the following states.

Orbital Symmetry Label	Molecular Orbital
σ_g^+	
π_g^+	
π_u^-	
σ_g^+	
δ_u^+	
δ_g^+	
δ_u^-	
δ_g^-	

5-7. Write the orbitals occupied by the valence electrons in each of the following molecules. Then, list the bond order and spin-multiplicity of the molecule.

Molecule	Slater Determinant	Multiplicity	Bond Order
Li_2			
Al_2			
O_2			

8. Write a "Valence Bond plus Ionic" wave function for the ground state of the Hydrogen molecule. Do not forget the "spin part" of the wave function. Weight the ionic terms with the number, κ. You do not need to worry about the normalization constant.

9. Write a "Molecular Orbital plus Configuration Interaction" wave function for the ground state of the Hydrogen molecule. Do not forget the "spin part" of the wave function. Weight the antibonding configuration with the number, δ. You do not need to worry about the normalization constant.

10. Write a valence-bond wave function (you can use the shorthand notation) for HF.

Key for Quiz 6

Chemistry 3BB3; Winter 2004

1-4. Write a representative molecular orbital for each of the following states.

Orbital Symmetry Label	Molecular Orbital
σ_g^+	$\psi_{2s}^{(l)}(\boldsymbol{r}) + \psi_{2s}^{(r)}(\boldsymbol{r})$
π_g^+	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) - \psi_{2p_x}^{(r)}(\boldsymbol{r})$
π_u^-	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) + \psi_{2p_y}^{(r)}(\boldsymbol{r})$
σ_g^+	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) - \psi_{2p_z}^{(r)}(\boldsymbol{r})$
δ_u^+	$\psi_{3d_{x^2-y^2}}^{(l)}(\boldsymbol{r}) - \psi_{3d_{x^2-y^2}}^{(r)}(\boldsymbol{r})$
δ_g^+	$\psi_{3d_{x^2-y^2}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{x^2-y^2}}^{(r)}(\boldsymbol{r})$
δ_u^-	$\psi_{3d_{xy}}^{(l)}(\boldsymbol{r}) - \psi_{3d_{xy}}^{(r)}(\boldsymbol{r})$
δ_g^-	$\psi_{3d_{xy}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{xy}}^{(r)}(\boldsymbol{r})$

5-7. Write a Slater determinant wave function, showing the occupied orbitals, for each of the following molecules. Then, list the bond order and spin-multiplicity of the molecule.

Molecule	Occupied Orbitals	Multiplicity	Bond Order
Li_2	$\sigma_g^+(2s)$ (doubly occupied)	1	1
Al_2	$\sigma_g^+(3s);\sigma_u^+(3s)$ (both doubly occupied) $\pi_u^+(3p),\pi_u^-(3p)$ (both singly occupied)	3	1
O_2	$\sigma_g^+(2s),\sigma_u^+(2s),\pi_u^+(2p),\pi_u^-(2p),\sigma_g^+(2s)$ (doubly occupied) $\pi_g^+(2p),\pi_g^-(2p)$ (both singly occupied)	3	2

8. Write a "Valence Bond plus Ionic" wave function for the ground state of the Hydrogen molecule. Do not forget the "spin part" of the wave function. Weight the ionic terms with the number, κ. You do not need to worry about the normalization constant.

$$\Psi_{VB+\kappa(Ionic)}(\boldsymbol{r}_1,\boldsymbol{r}_2) \propto \begin{pmatrix} \psi_{1s}^{(l)}(\boldsymbol{r}_1)\psi_{1s}^{(r)}(\boldsymbol{r}_2) + \psi_{1s}^{(l)}(\boldsymbol{r}_2)\psi_{1s}^{(r)}(\boldsymbol{r}_1) \\ +\kappa\left(\psi_{1s}^{(l)}(\boldsymbol{r}_1)\psi_{1s}^{(l)}(\boldsymbol{r}_2) + \psi_{1s}^{(r)}(\boldsymbol{r}_1)\psi_{1s}^{(r)}(\boldsymbol{r}_2)\right) \end{pmatrix} \left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

9. Write a "Molecular Orbital plus Configuration Interaction" wave function for the ground state of the Hydrogen molecule. Do not forget the "spin part" of the wave function. Weight the antibonding configuration with the number, δ. You do not need to worry about the normalization constant.

$$\Psi_{MO+\delta(CI)}(\boldsymbol{r}_1,\boldsymbol{r}_2) \propto \begin{pmatrix} \left(\psi_{1s}^{(l)}(\boldsymbol{r}_1) + \psi_{1s}^{(r)}(\boldsymbol{r}_1)\right)\left(\psi_{1s}^{(l)}(\boldsymbol{r}_2) + \psi_{1s}^{(r)}(\boldsymbol{r}_2)\right) \\ +\delta\left(\psi_{1s}^{(l)}(\boldsymbol{r}_1) - \psi_{1s}^{(r)}(\boldsymbol{r}_1)\right)\left(\psi_{1s}^{(l)}(\boldsymbol{r}_2) - \psi_{1s}^{(r)}(\boldsymbol{r}_2)\right) \end{pmatrix} \left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

10. Write a valence-bond wave function (you can use the shorthand notation) for HF.

$$\Psi_{HF}^{VB} \equiv c_{\text{cov}} \left| \psi_{1s}^F\alpha\ \psi_{1s}^F\beta\ \psi_{2s}^F\alpha\ \psi_{2s}^F\beta\ \psi_{2p_x}^F\alpha\ \psi_{2p_x}^F\beta\ \psi_{2p_y}^F\alpha\ \psi_{2p_y}^F\beta\ \widetilde{\psi_{2p_z}^F\alpha\ \psi_{1s}^H\beta} \right|$$
$$+c_{ionic} \left| \psi_{1s}^F\alpha\ \psi_{1s}^F\beta\ \psi_{2s}^F\alpha\ \psi_{2s}^F\beta\ \psi_{2p_x}^F\alpha\ \psi_{2p_x}^F\beta\ \psi_{2p_y}^F\alpha\ \psi_{2p_y}^F\beta\ \psi_{2p_z}^F\alpha\ \psi_{2p_z}^F\beta \right|$$