

# Mid-Term Examination

## Chemistry 3BB3

Winter, 2006

Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout this exam.

### Part 1. Multiple Choice/Short Answer (2 pts. each)

1. Write the electronic Hamiltonian for the hydrogen molecule ( $H_2$ ) in SI units, showing the dependence on  $\hbar$ ,  $e$ ,  $m_e$ , etc..
2. Write an expression for the lowest-energy molecular orbital in the Hydrogen molecule? What is the “symmetry label” for this orbital?
3. Write an expression for the second lowest-energy molecular orbital in the Hydrogen molecule? What is the “symmetry label” for this orbital?
4. Using the results from problems 3-5, what is the “molecular orbital plus configuration interaction correction” wave function for the ground state of  $H_2$ ? Write this out in all its glory; do not use Slater determinant notation.

5. What is the “valence bond plus ionic correction” wave function for the ground state of  $H_2$ ? Write this out in all its glory; do not use Slater determinant notation.
6. In order to successfully predict the bond length of the hydrogen molecule using valence-bond theory, the most important “generalization” to the simplest valence-bond wave function is
- Introducing an effective nuclear charge in the atomic  $1s$  orbital.
  - Including “polarization” by mixing the  $2p$  orbital with the  $1s$  orbital.
  - Including a small contribution from the ionic  $H^+ \cdots H^-$  electron configuration.
7. Consider the  $H_2$  and  $H_2^-$  molecules at their equilibrium geometries. The bond lengths in the two molecules will be different. Which molecule has the shortest bond?
- $H_2$
  - $H_2^-$
8. Continuing our discussion of  $H_2$  and  $H_2^-$ : the effective nuclear charges in the doubly-occupied molecular orbital in these molecules are denoted  $\zeta_{H_2}$  and  $\zeta_{H_2^-}$ . (The doubly occupied molecular orbital is the lowest-energy orbital; it is the molecular orbital you wrote in problems 2 and 3.) Assume both molecules are in their most stable geometry,
- The effective nuclear charge in  $H_2$  is greater than the effective nuclear charge in  $H_2^-$ ;  
 $\zeta_{H_2} > \zeta_{H_2^-}$ .
  - The effective nuclear charge in  $H_2$  is less than the effective nuclear charge in  $H_2^-$ ;  
 $\zeta_{H_2} < \zeta_{H_2^-}$ .
- 9,10. In general, the effective nuclear charges change as the bond length changes. In the separated atom limit, the effective nuclear charges are:

$$\zeta_{H_2}^{\text{sep. atoms}} =$$

$$\zeta_{H_2^-}^{\text{sep. atoms}} =$$

In the united atom limit, the effective nuclear charges are

$$\zeta_{H_2}^{\text{united atom}} =$$

$$\zeta_{H_2^-}^{\text{united atom}} =$$

11. Write a Slater determinant for the first excited state of the Carbon dimer,  $C_2$ . This is the lowest energy excited state. You can use the shorthand notation for Slater determinants.

12. Based on Hund's localization criterion, the wave function of sulfur hexafluoride ( $SF_6$ )

- (a) can be expressed in terms of localized molecular orbitals.
- (b) can not be expressed in terms of localized molecular orbitals.

13. Based on Hund's localization criterion, the wave function of the borane cation,  $BH_3^+$ ,

- (a) can be expressed in terms of localized molecular orbitals.
- (b) can not be expressed in terms of localized molecular orbitals.

14-19. Complete the following table by filling in the appropriate properties for the molecular ground states.

Molecule	Bond Order	Multiplicity
HHe		
LiBe		
NO		
CF		
OF		
OF <sup>+</sup>		

20. The bonding molecular orbital in Cesium Iodide has the form

$$\varphi(\mathbf{r}) = c_{Cs} \psi_{6s}^{Cs}(\mathbf{r}) + c_I \psi_{5p_z}^I(\mathbf{r})$$

This is an "ionic" bond with a significant covalent contribution, because the overlap of the large diffuse Cesium atom and the Iodine atom is nonnegligible,

$$S = \left| \int \psi_{6s}^{Cs}(\mathbf{r})^* \psi_{5p_z}^I(\mathbf{r}) d\mathbf{r} \right|$$

The magnitude of the dipole moment for this molecule can be approximated as the difference in the molecular charges divided by the bond length,

$$d = \frac{q_{Cs} - q_I}{R}$$

Using the Mulliken population analysis scheme, write an expression for the dipole moment.

21. Sketch a  $\pi_g^+$  molecular orbital and show how to form this orbital from a linear combination of atomic  $2p_x$  orbitals. Assume that the  $z$  axis is the internuclear axis.

22-25. The  $4f$  orbitals have the form

$$\phi_{0,\pm 1,\pm 2} \quad r, \theta, \phi \propto r^3 Y_3^{0,\pm 1,\pm 2} \quad \theta, \phi$$

As discussed in class, these “spherical harmonic” orbitals are appropriate for describing molecules in magnetic fields, but in the electric field from another atom, they are no longer appropriate. Instead, we should use “Cartesian” orbitals. A common choice of Cartesian orbitals is:

$$\begin{aligned} \psi_{z \ 5z^2-3r^2} \quad \mathbf{r} &\propto \phi_0 \quad \mathbf{r} & \psi_{x^2-y^2 \ z} \quad \mathbf{r} &\propto \frac{\phi_2 \mathbf{r} + \phi_{-2} \mathbf{r}}{2} \\ \psi_{x \ 5z^2-r^2} \quad \mathbf{r} &\propto \frac{\phi_1 \mathbf{r} + \phi_{-1} \mathbf{r}}{2} & \psi_{xyz} \quad \mathbf{r} &\propto \frac{\phi_2 \mathbf{r} - \phi_{-2} \mathbf{r}}{2i} \\ \psi_{y \ 5z^2-r^2} \quad \mathbf{r} &\propto \frac{\phi_1 \mathbf{r} - \phi_{-1} \mathbf{r}}{2i} & \psi_{x \ x^2-3y^2} \quad \mathbf{r} &\propto \frac{\phi_3 \mathbf{r} + \phi_{-3} \mathbf{r}}{2} \\ & & \psi_{y \ y^2-3x^2} \quad \mathbf{r} &\propto \frac{\phi_3 \mathbf{r} - \phi_{-3} \mathbf{r}}{2i} \end{aligned}$$

Label the following orbitals with the usual  $\sigma, \pi, \delta, \phi, u, g$ , and  $+, -$  symmetry labels. For the  $+, -$  symmetry, choose “+” to mean “symmetric with respect to reflection in the  $xz$  plane. (This is the same convention you used in problem #21.) Both the “left” and the “right” atom lie on the  $z$  axis.

Orbital	Symmetry Label
$\psi_{z \ 5z^2-3r^2}^{left} \quad \mathbf{r} + \psi_{z \ 5z^2-3r^2}^{right} \quad \mathbf{r}$	
$\psi_{z \ 5z^2-3r^2}^{left} \quad \mathbf{r} - \psi_{z \ 5z^2-3r^2}^{right} \quad \mathbf{r}$	
$\psi_{y \ 5z^2-r^2}^{left} \quad \mathbf{r} + \psi_{y \ 5z^2-r^2}^{right} \quad \mathbf{r}$	
$\psi_{x \ 5z^2-r^2}^{left} \quad \mathbf{r} - \psi_{x \ 5z^2-r^2}^{right} \quad \mathbf{r}$	
$\psi_{x^2-y^2 \ z}^{left} \quad \mathbf{r} - \psi_{x^2-y^2 \ z}^{right} \quad \mathbf{r}$	
$\psi_{xyz}^{left} \quad \mathbf{r} + \psi_{xyz}^{right} \quad \mathbf{r}$	
$\psi_{x \ x^2-3y^2}^{left} \quad \mathbf{r} + \psi_{x \ x^2-3y^2}^{right} \quad \mathbf{r}$	
$\psi_{x \ x^2-3y^2}^{left} \quad \mathbf{r} - \psi_{x \ x^2-3y^2}^{right} \quad \mathbf{r}$	

## Part 2. Closed-Book Problems (30 points)

1. The diagram on the next page is a sketch of the ground state and three excited states of the Hydrogen Molecule. I have included the symmetry labels; you do not need to understand what these mean (though it is obvious); you just need to be able to recognize whether states have “the same” or “different” symmetry.
  - a. Sketch in the  $3^1\Sigma_g^+$  state. (That is, draw in the third state with  $^1\Sigma_g^+$  symmetry) (4 pts.)

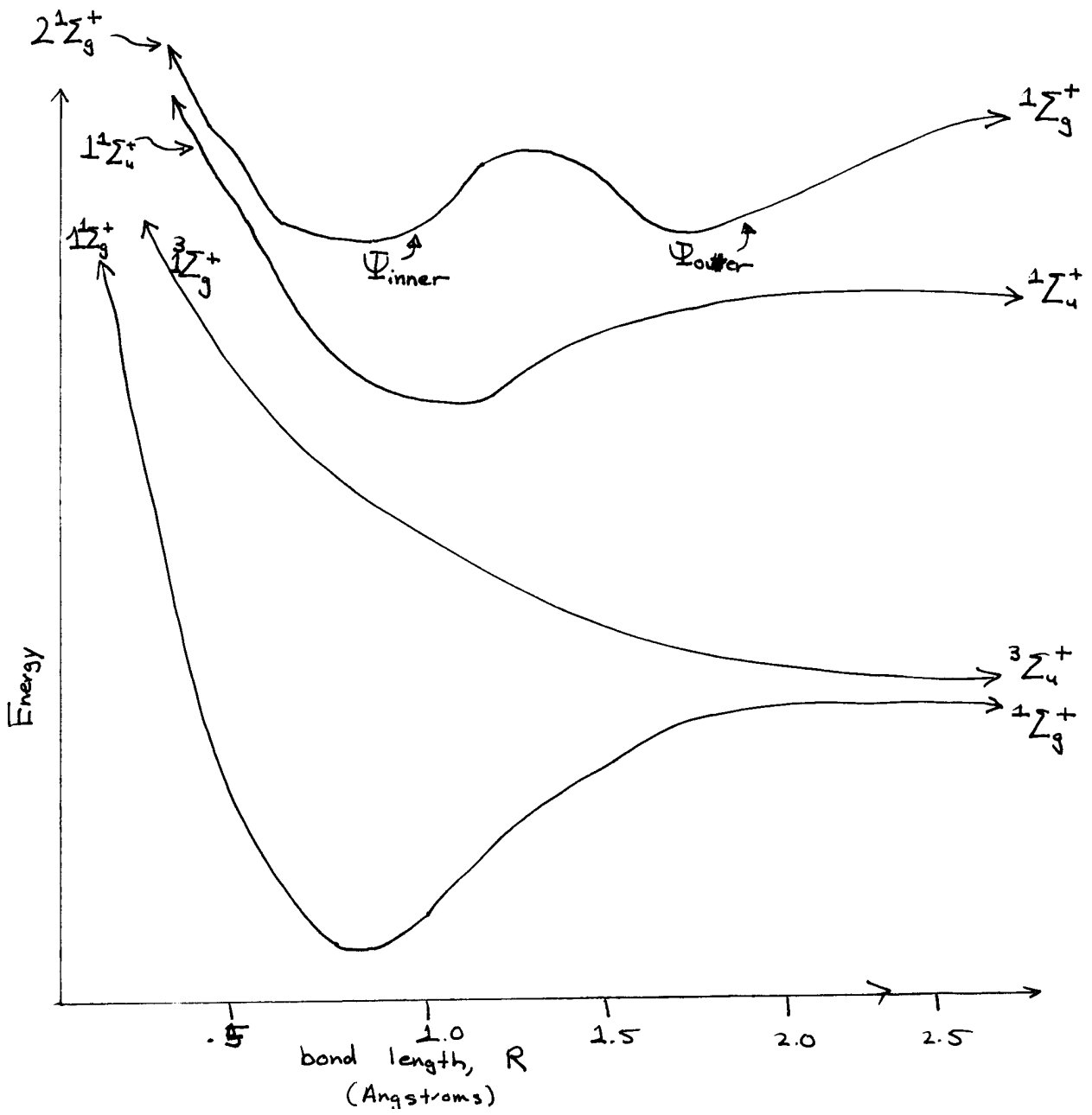
Near the first minimum, the wave function can be approximated by

$$\Psi_{\text{inner}} \propto \left| \begin{array}{cc} \phi_{1s}^l + \phi_{1s}^r & \alpha \\ \phi_{2s}^l + \phi_{2s}^r & \beta \end{array} \right| + \left| \begin{array}{cc} \phi_{1s}^l + \phi_{1s}^r & \beta \\ \phi_{2s}^l + \phi_{2s}^r & \alpha \end{array} \right|$$

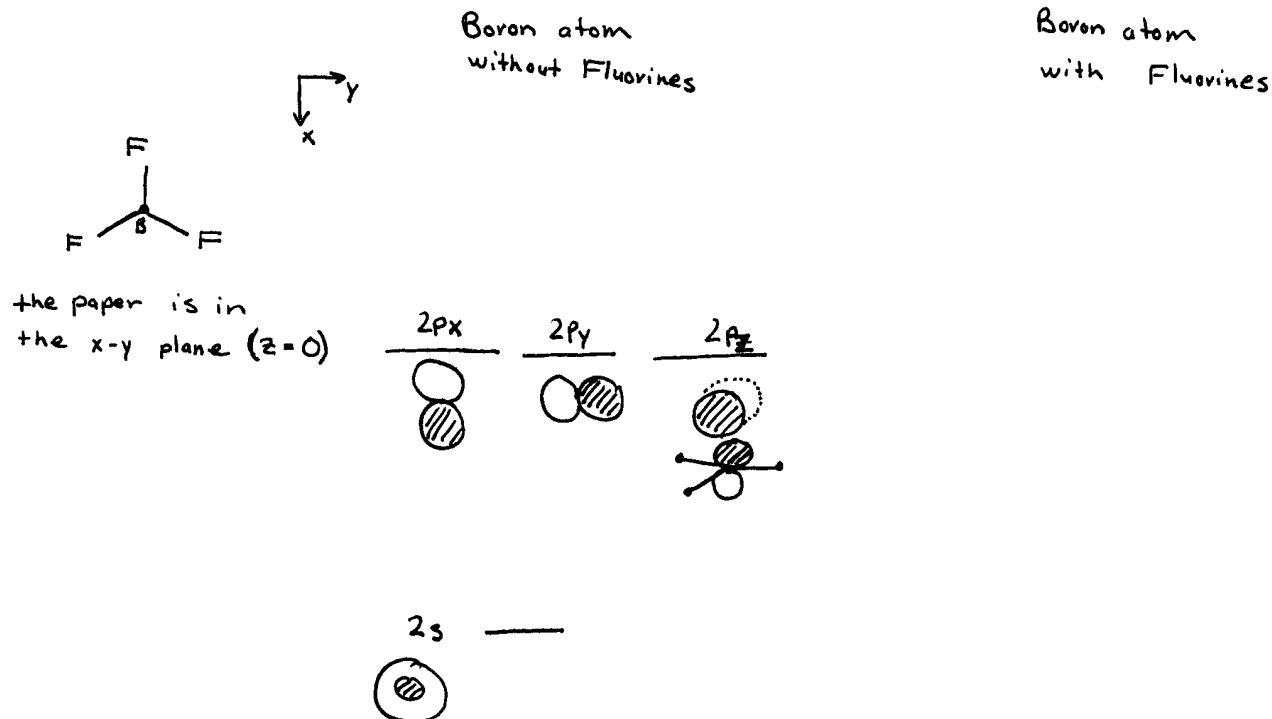
and near the outer minimum, the wave function can be approximated by

$$\Psi_{\text{outer}} \propto \left| \begin{array}{cc} \phi_{2p_z}^l + \phi_{2p_z}^r & \alpha \\ \phi_{2p_z}^l + \phi_{2p_z}^r & \beta \end{array} \right|.$$

- b. Why does the  $\Psi_{\text{inner}}$  have two Slater determinants but  $\Psi_{\text{outer}}$  have only one Slater determinant? (3 pts.)
  - c. What do you think the approximate wave function for the  $3^1\Sigma_g^+$  state looks like? Is it the same for all internuclear distances? (3 pts.)



2a. Show how the  $2s$  and  $2p$  orbitals in the Boron atom when it is surrounded by the three Fluorine atoms in  $\text{BF}_3$ . The  $\text{BF}_3$  molecule is planar; assume it lies in the “xy” plane (i.e., the plane  $z=0$ ). (5 points)



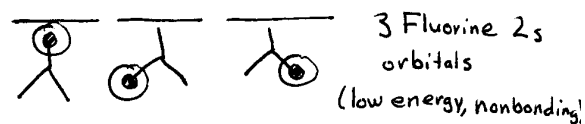
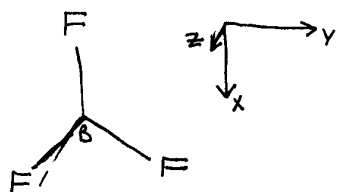
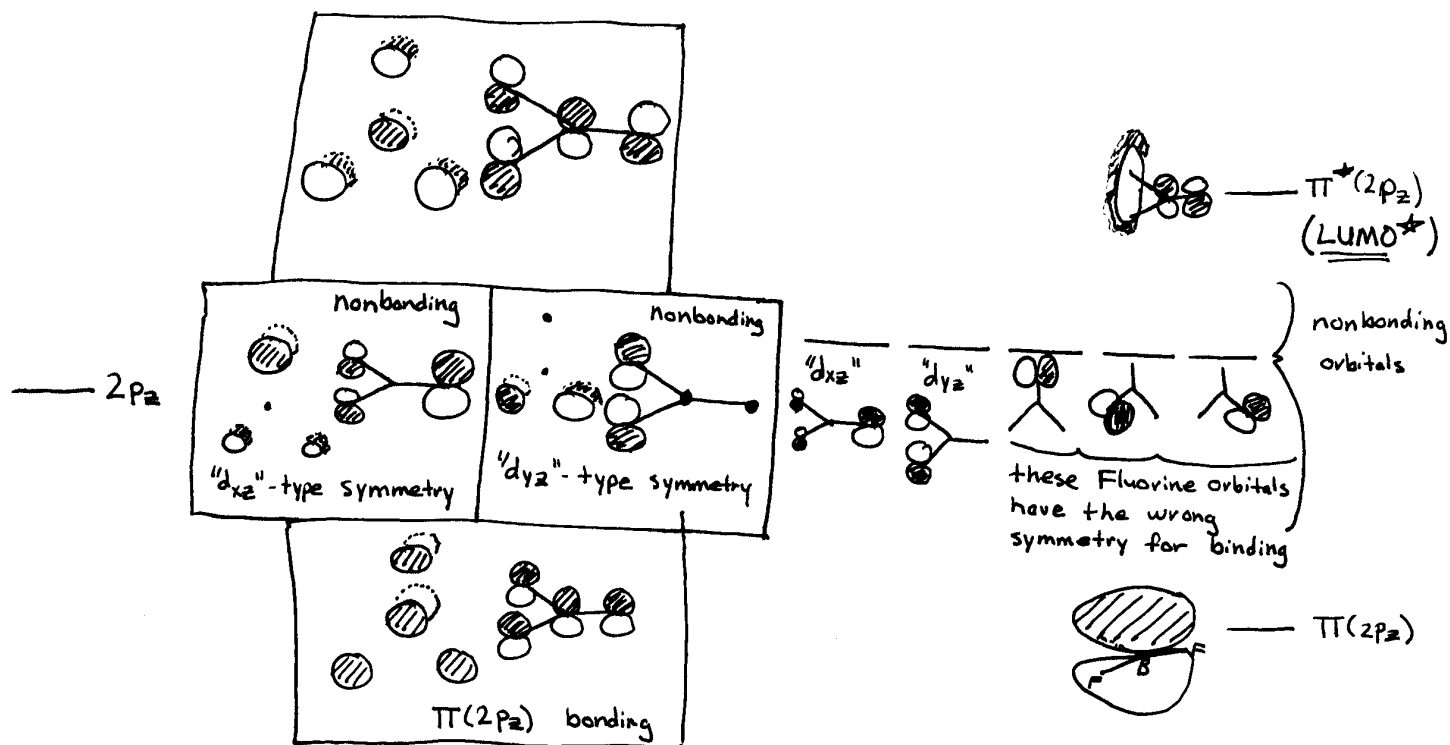
2b. Complete the Molecular Orbital Diagram for planar  $\text{BF}_3$  on the next page. (The structure is a triangle of Fluorine atoms, with a Boron in the middle.) **Include all the orbitals that can be formed between the  $2s$  and  $2p$  orbitals of the Fluorine atoms and the  $2s$ ,  $2p_x$ , and  $2p_y$  orbitals of the Boron atom.** The  $2s$  orbital of Fluorine is very low in energy compared to the  $2s$  orbital of Boron; thus, the  $2s$  orbitals of the Fluorine atoms are, to a first approximation, not involved in bonding.

You will notice that the MOs for the “pi” bonding are a little complicated; they can be generated because they have to have the same symmetry as a “d” orbital; (However, I didn’t expect you to know that.) I have filled in all the orbitals that form with the  $2p_z$  orbital of Boron, which should help get you started. The state labels in the MO diagram correspond (a) what type of bonding is involved and (b) which “Boron” orbital is used to generate this molecular orbital. There are two copies of the molecular orbital diagram; this way, if you mess one up, you can just use the second copy. (10 points)

Boron orbitals' energies in field of Fluorines

atomic orbital representation of molecular orbitals

Molecular Orbitals

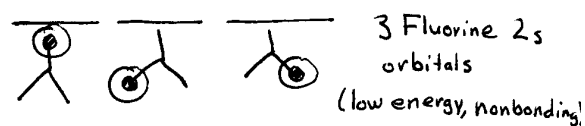
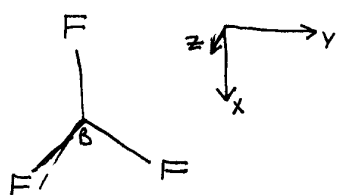
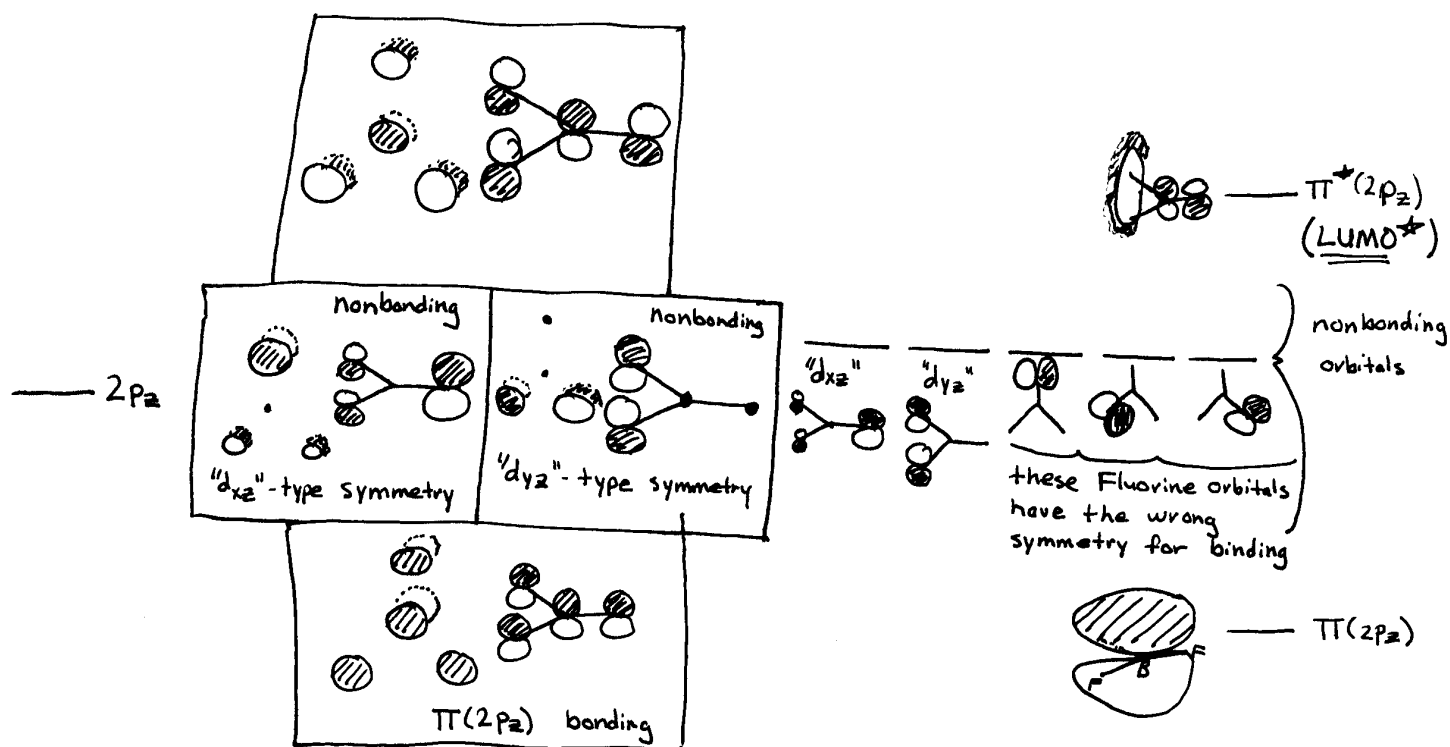




Boron orbitals' energies in field of Fluorines

atomic orbital representation of molecular orbitals

Molecular Orbitals



- 2c.  $\text{BF}_3$  is a very good Lewis acid. However, when you add an electron to  $\text{BF}_3$ , it is no longer planar. That is,  $\text{BF}_3^-$  is pyramidal: there is still a “triangle” of Fluorine atoms, but now the Boron atom is located above the center of the triangle, rather than in the center of the triangle. I have labeled the lowest unoccupied molecular orbital (LUMO) in  $\text{BF}_3$ . **Consider how this orbital would change if the Boron atom was “pulled” out of the plane. Redraw the orbital after the Boron atom has been pulled out of the plane. Using this result, explain why  $\text{BF}_3^-$  is not planar. (5 points)**

## Part 3. Thinking Problem (20 pts.)

- In the notes, we indicated that when one forms a single bond from two  $1s$  orbitals, charge accumulates between the atoms. Based on this, we can conclude that the difference in electron density between the ground state of the Hydrogen molecule and the sum of the two hydrogen atom densities is

$$\rho_{\sigma_g^2}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) \approx \frac{2\zeta^3}{\pi} e^{-\zeta R \xi} - S [\rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r})]$$

where

$$\xi = \frac{r_l + r_r}{R}$$

$$\rho_{1s}^l(\mathbf{r}) = \frac{\zeta^3}{\pi} e^{-2\zeta r_l}$$

$$S = \frac{\zeta^3}{\pi} \int e^{\zeta r_l} e^{-\zeta r_r} d\mathbf{r}$$

and  $r_l$  and  $r_r$  are the distances to the “left” and “right” nuclei and  $\zeta$  is the effective nuclear charge.

This is the prediction of how charge accumulates on the bond center in molecular orbital theory. In this problem, you will derive the corresponding result for valence-bond theory.

The simple “valence bond” function for  $H_2$  is

$$\Psi \propto \psi_{1s}^l(\mathbf{r}_1) \psi_{1s}^r(\mathbf{r}_2) + \psi_{1s}^l(\mathbf{r}_2) \psi_{1s}^r(\mathbf{r}_1) \quad \frac{\alpha^{1/2} \beta^{1/2} - \alpha^{1/2} \beta^{1/2}}{\sqrt{2}}$$

In this problem, you may find it useful to remember that the binomial series is

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$$

- What is the normalization constant for this wave function? (Write the normalization constant in terms of the overlap integral,  $S$ .) (5 pts.)



**B. The electron density for this valence-bond wave function can be computed from**

$$\rho_{VB}(\mathbf{r}_1) = 2 \int |\Psi_{VB}(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2$$

**Compute  $\rho_{VB}(\mathbf{r})$ . You do not need to worry about the spin part of the wave function, since that just gives a factor of “1.” (5 pts.)**



C. Compute the change in density due to bonding in the Valence bond model. (You will need to make some approximations, just as in the Molecular Orbital Theory analysis.) (7 pts.)

$$\rho_{VB}(\mathbf{r}) = \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r})$$





**D. Compare the result from part “C” with the result from molecular orbital theory. Does the result make sense based on what you know about chemical binding in simple VB theory versus simple MO theory? (3 pts.)**



# Mid-Term Examination

## Chemistry 3BB3

Winter, 2006

Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout this exam.

### Part 1. Multiple Choice/Short Answer (2 pts. each)

1. Write the electronic Hamiltonian for the hydrogen molecule ( $H_2$ ) in SI units, showing the dependence on  $\hbar$ ,  $e$ ,  $m_e$ , etc..

$$\hat{H}_{H_2} \equiv \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_{left}|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_{right}|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_{left}|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_{right}|} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

2. Write an expression for the lowest-energy molecular orbital in the Hydrogen molecule? What is the “symmetry label” for this orbital?

$$\varphi_{\sigma_g^+}(\mathbf{r}) \propto \phi_{1s}^{left}(\mathbf{r}) + \phi_{1s}^{right}(\mathbf{r})$$

symmetry label:  $\sigma_g^+$

3. Write an expression for the second lowest-energy molecular orbital in the Hydrogen molecule? What is the “symmetry label” for this orbital?

$$\varphi_{\sigma_u^+}(\mathbf{r}) \propto \phi_{1s}^{left}(\mathbf{r}) - \phi_{1s}^{right}(\mathbf{r})$$

symmetry label:  $\sigma_u^+$

4. Using the results from problems 3-5, what is the “molecular orbital plus configuration interaction correction” wave function for the ground state of  $H_2$ ? Write this out in all its glory; do not use Slater determinant notation.

$$\Psi_{H_2}^{MO+CI} \propto c_{g.s.} \psi_{\sigma_g^+}(\mathbf{r}_1) \psi_{\sigma_g^+}(\mathbf{r}_2) + c_{e.s.} \psi_{\sigma_u^+}(\mathbf{r}_1) \psi_{\sigma_u^+}(\mathbf{r}_2) \left( \frac{\alpha \ 1 \ \beta \ 2 \ -\alpha \ 2 \ \beta \ 1}{\sqrt{2}} \right)$$

5. What is the “valence bond plus ionic correction” wave function for the ground state of  $H_2$ ? Write this out in all its glory; do not use Slater determinant notation.

$$\Psi_{H_2}^{VB+ionic}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left( c_{\text{covalent}} \begin{vmatrix} \phi_{1s}^l & \mathbf{r}_1 & \phi_{1s}^r & \mathbf{r}_2 \\ \phi_{1s}^r & \mathbf{r}_1 & \phi_{1s}^l & \mathbf{r}_2 \end{vmatrix} + c_{\text{ionic}} \begin{vmatrix} \phi_{1s}^l & \mathbf{r}_1 & \phi_{1s}^l & \mathbf{r}_2 \\ \phi_{1s}^r & \mathbf{r}_1 & \phi_{1s}^r & \mathbf{r}_2 \end{vmatrix} \right) \left( \frac{\alpha \ 1 \ \beta \ 2 \ -\alpha \ 2 \ \beta \ 1}{\sqrt{2}} \right)$$

6. In order to successfully predict the bond length of the hydrogen molecule using valence-bond theory, the most important “generalization” to the simplest valence-bond wave function is

(a) Introducing an effective nuclear charge in the atomic  $1s$  orbital.

(b) Including “polarization” by mixing the  $2p$  orbital with the  $1s$  orbital.

(c) Including a small contribution from the ionic  $H^+ \cdots H^-$  electron configuration.

7. Consider the  $H_2$  and  $H_2^-$  molecules at their equilibrium geometries. The bond lengths in the two molecules will be different. Which molecule has the shortest bond?

(a)  $H_2$

(b)  $H_2^-$

8. Continuing our discussion of  $H_2$  and  $H_2^-$ : the effective nuclear charges in the doubly-occupied molecular orbital in these molecules are denoted  $\zeta_{H_2}$  and  $\zeta_{H_2^-}$ . (The doubly occupied molecular orbital is the lowest-energy orbital; it is the molecular orbital you wrote in problems 2 and 3.) Assume both molecules are in their most stable geometry,

(a) The effective nuclear charge in  $H_2$  is greater than the effective nuclear charge in  $H_2^-$ ;  $\zeta_{H_2} > \zeta_{H_2^-}$ .

(b) The effective nuclear charge in  $H_2$  is less than the effective nuclear charge in  $H_2^-$ ;  $\zeta_{H_2} < \zeta_{H_2^-}$ .

- 9,10. In general, the effective nuclear charges change as the bond length changes. In the separated atom limit, the effective nuclear charges are:

$$\zeta_{H_2}^{\text{sep. atoms}} = 1$$

$$\zeta_{H_2^-}^{\text{sep. atoms}} = 1$$

In the united atom limit, the effective nuclear charges are

$$\zeta_{H_2}^{\text{united atom}} = 2$$

$$\zeta_{H_2^-}^{\text{united atom}} = 2$$

11. Write a Slater determinant for the first excited state of the Carbon dimer,  $C_2$ . This is the lowest energy excited state. You can use the shorthand notation for Slater determinants.

$$\Phi_{C_2^{e.s.}} = \begin{vmatrix} \phi_{\sigma_g^+ 1s}^C \alpha & \phi_{\sigma_g^+ 1s}^C \beta & \phi_{\sigma_u^+ 1s}^C \alpha & \phi_{\sigma_u^+ 1s}^C \beta & \phi_{\sigma_g^+ 2s}^C \alpha & \phi_{\sigma_g^+ 2s}^C \beta & \phi_{\sigma_u^+ 2s}^C \alpha & \phi_{\sigma_u^+ 2s}^C \beta & \phi_{\pi_u^+ 2p_x}^C \alpha & \phi_{\pi_u^+ 2p_x}^C \beta & \phi_{\pi_u^- 2p_y}^C \alpha & \phi_{\sigma_g^+ 2p_z}^C \alpha \end{vmatrix}$$

(note that the lowest energy excited state will be a triplet.)

12. Based on Hund’s localization criterion, the wave function of sulfur hexafluoride ( $SF_6$ )

(a) can be expressed in terms of localized molecular orbitals.

(b) can not be expressed in terms of localized molecular orbitals.

13. Based on Hund’s localization criterion, the wave function of the borane cation,  $BH_3^+$ ,

(a) can be expressed in terms of localized molecular orbitals.

(b) can not be expressed in terms of localized molecular orbitals.

14-19. Complete the following table by filling in the appropriate properties for the molecular ground states.

Molecule	Bond Order	Multiplicity
HHe	$\frac{1}{2}$ (but really zero)	2
LiBe	1/2	2
NO	2.5	2
CF	2.5	2
OF	1.5	2
OF <sup>+</sup>	2	3

20. The bonding molecular orbital in Cesium Iodide has the form

$$\varphi(\mathbf{r}) = c_{Cs} \psi_{6s}^{Cs}(\mathbf{r}) + c_I \psi_{5p_z}^I(\mathbf{r})$$

This is an “ionic” bond with a significant covalent contribution, because the overlap of the large diffuse Cesium atom and the Iodine atom is nonnegligible,

$$S = \left| \int \psi_{6s}^{Cs}(\mathbf{r})^* \psi_{5p_z}^I(\mathbf{r}) d\mathbf{r} \right|$$

The magnitude of the dipole moment for this molecule can be approximated as the difference in the molecular charges divided by the bond length,

$$d = \frac{q_{Cs} - q_I}{R}$$

Using the Mulliken population analysis scheme, write an expression for the dipole moment.

The Cesium atom donates

$$1 - 2 |c_{Cs}|^2 + \text{Re}[c_{Cs}^* c_I] S$$

electrons, while the Iodine atom accepts

$$2 |c_I|^2 + \text{Re}[c_{Cs}^* c_I] S - 1$$

electrons. This means that the Cesium atom has charge

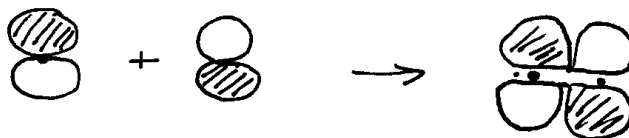
$$q_{Cs} = 1 - 2 |c_{Cs}|^2 + \text{Re}[c_{Cs}^* c_I] S$$

and the Iodine has minus this charge,  $q_I = -q_{Cs}$ . So

$$\begin{aligned} d &= \frac{q_{Cs} - (-q_{Cs})}{R} = \frac{2q_{Cs}}{R} \\ &= \frac{2 [1 - 2 |c_{Cs}|^2 + \text{Re}[c_{Cs}^* c_I] S]}{R} \end{aligned}$$

There are a number of alternative forms for this result.

21. Sketch a  $\pi_g^+$  molecular orbital and show how to form this orbital from a linear combination of atomic  $2p_x$  orbitals. Assume that the  $z$  axis is the internuclear axis.



$$\varphi_{\pi_g^+}(\mathbf{r}) \propto \phi_{2p_x}^{\text{left}}(\mathbf{r}) - \phi_{2p_x}^{\text{right}}(\mathbf{r})$$

22-25. The  $4f$  orbitals have the form

$$\phi_{0,\pm 1,\pm 2}(r, \theta, \phi) \propto r^3 Y_3^{0,\pm 1,\pm 2}(\theta, \phi)$$

As discussed in class, these “spherical harmonic” orbitals are appropriate for describing molecules in magnetic fields, but in the electric field from another atom, they are no longer appropriate. Instead, we should use “Cartesian” orbitals. A common choice of Cartesian orbitals is:

$$\psi_{z^2-3r^2}(\mathbf{r}) \propto \phi_0(\mathbf{r})$$

$$\psi_{xz^2-r^2}(\mathbf{r}) \propto \frac{\phi_1(\mathbf{r}) + \phi_{-1}(\mathbf{r})}{2}$$

$$\psi_{yz^2-r^2}(\mathbf{r}) \propto \frac{\phi_1(\mathbf{r}) - \phi_{-1}(\mathbf{r})}{2i}$$

$$\psi_{x^2-y^2z}(\mathbf{r}) \propto \frac{\phi_2(\mathbf{r}) + \phi_{-2}(\mathbf{r})}{2}$$

$$\psi_{xyz}(\mathbf{r}) \propto \frac{\phi_2(\mathbf{r}) - \phi_{-2}(\mathbf{r})}{2i}$$

$$\psi_{x^2-3y^2}(\mathbf{r}) \propto \frac{\phi_3(\mathbf{r}) + \phi_{-3}(\mathbf{r})}{2}$$

$$\psi_{y^2-3x^2}(\mathbf{r}) \propto \frac{\phi_3(\mathbf{r}) - \phi_{-3}(\mathbf{r})}{2i}$$

Label the following orbitals with the usual  $\sigma, \pi, \delta, \phi, u, g$ , and  $+, -$  symmetry labels. For the  $+, -$  symmetry, choose “+” to mean “symmetric with respect to reflection in the  $xz$  plane. (This is the same convention you used in problem #21.) Both the “left” and the “right” atom lie on the  $z$  axis.

Orbital	Symmetry Label
$\psi_{z^2-3r^2}^{\text{left}}(\mathbf{r}) + \psi_{z^2-3r^2}^{\text{right}}(\mathbf{r})$	$\sigma_u^+$
$\psi_{z^2-3r^2}^{\text{left}}(\mathbf{r}) - \psi_{z^2-3r^2}^{\text{right}}(\mathbf{r})$	$\sigma_g^+$
$\psi_{yz^2-r^2}^{\text{left}}(\mathbf{r}) + \psi_{yz^2-r^2}^{\text{right}}(\mathbf{r})$	$\pi_u^-$
$\psi_{xz^2-r^2}^{\text{left}}(\mathbf{r}) - \psi_{xz^2-r^2}^{\text{right}}(\mathbf{r})$	$\pi_g^+$
$\psi_{xyz}^{\text{left}}(\mathbf{r}) + \psi_{xyz}^{\text{right}}(\mathbf{r})$	$\delta_u^-$
$\psi_{x^2-y^2z}^{\text{left}}(\mathbf{r}) - \psi_{x^2-y^2z}^{\text{right}}(\mathbf{r})$	$\delta_g^+$
$\psi_{x^2-3y^2}^{\text{left}}(\mathbf{r}) + \psi_{x^2-3y^2}^{\text{right}}(\mathbf{r})$	$\phi_u^+$
$\psi_{y^2-3x^2}^{\text{left}}(\mathbf{r}) - \psi_{y^2-3x^2}^{\text{right}}(\mathbf{r})$	$\phi_g^-$

To do this problem, you first have to remember that the  $\sigma$  orbitals have 0 units of angular momentum around the bond,  $\pi$  orbitals have  $\pm 1$  unit of angular momentum around the bond,  $\delta$  orbitals have  $\pm 2$  units of angular momentum around the bond, and  $\phi$  orbitals have  $\pm 3$  units of angular momentum around the bond. Looking at the expressions for the orbitals, it is clear that the first "f" orbital is used to make  $\sigma$  bonds, the second two "f" orbitals are used to make  $\pi$  bonds, etc.. Alternatively, you can think about this starting with the last orbitals. Since  $\psi_{x^2-3y^2}$  has no "z" in its index, it has no component along the "z" axis, so it must be "entirely in the x-y directions." This means it has to be a  $\phi$  bond. (Compare the fact that the  $p_x$  and  $p_y$  orbitals are used to make  $\pi$  bonds and the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals are used to make  $\delta$  bonds.) An orbital like  $\psi_{x^2-y^2-z}$  has one component on the "z" axis and the projection on to the x-y plane should look like a  $d_{x^2-y^2}$  orbital. So this should be a  $\delta$  orbital and, in fact, it should be a  $\delta^+$  orbital since the  $d_{x^2-y^2}$  orbital is symmetric with respect to reflection in the xz plane.

To assign  $\pm$ , recall that the "y" axis is perpendicular to the x-z plane. This is why the  $\pi$  orbitals made with  $p_y$  orbitals are "-" while the  $\pi$  orbitals made with  $p_x$  orbitals are "+" This suggests that you replace all the y's in the orbital type with  $-y$ ; if you reflect (x,y,z) through the x-z plane, you get (x,-y,z). Now, if the orbital index changes, you have a "-" orbital. Otherwise it is a "+" orbital. You can figure this out from the fact that  $p_x, d_{x^2-y^2}$  give "+" MOs and  $p_y, d_{xy}$  give "-" MOs. Note that except for the last two entries in the table, the "x-y" part of the orbital looks exactly like a "p" or a "d" orbital. You should not be surprised that these orbitals behave the same way upon reflection through the x-z plane as those orbitals!

To assign "u" and "g", keep in mind that  $s$  orbitals and  $d$  orbitals are gerade, while p orbitals are ungerade. Thus, "f" orbitals are also ungerade, so the "p" orbitals are a good template. For the "p" orbitals, "g" molecular orbitals were formed via

$$\begin{aligned}\psi_{x,y}^{left} + \psi_{x,y}^{right} &\rightarrow \pi_u \\ \psi_{x,y}^{left} - \psi_{x,y}^{right} &\rightarrow \pi_g \\ \psi_z^{left} + \psi_z^{right} &\rightarrow \sigma_u \\ \psi_{x,y}^{left} - \psi_{x,y}^{right} &\rightarrow \sigma_g\end{aligned}$$

and so molecular orbitals formed from sums of atomic orbitals are "u" and differences of atomic orbitals are "g."



Part 2. Closed-Book Problems (30 points)

- The diagram on the next page is a sketch of the ground state and three excited states of the Hydrogen Molecule. I have included the symmetry labels; you do not need to understand what these mean (though it is obvious); you just need to be able to recognize whether states have “the same” or “different” symmetry.

a. Sketch in the  $3^1\Sigma_g^+$  state. (That is, draw in the third state with  $1^1\Sigma_g^+$  symmetry) (4 pts.)

(see figure) The actual situation is more complicated than this; cf. [E. R. Davidson, *J. Chem. Phys.* **33**, 1577 (1960); E. R. Davidson, *J. Chem. Phys.* **35**, 1189 (1961).] But the present “simplified” curve is all you could probably get based on the non-crossing rule alone. The following figure (from the second of these references) will give you some idea of what is involved

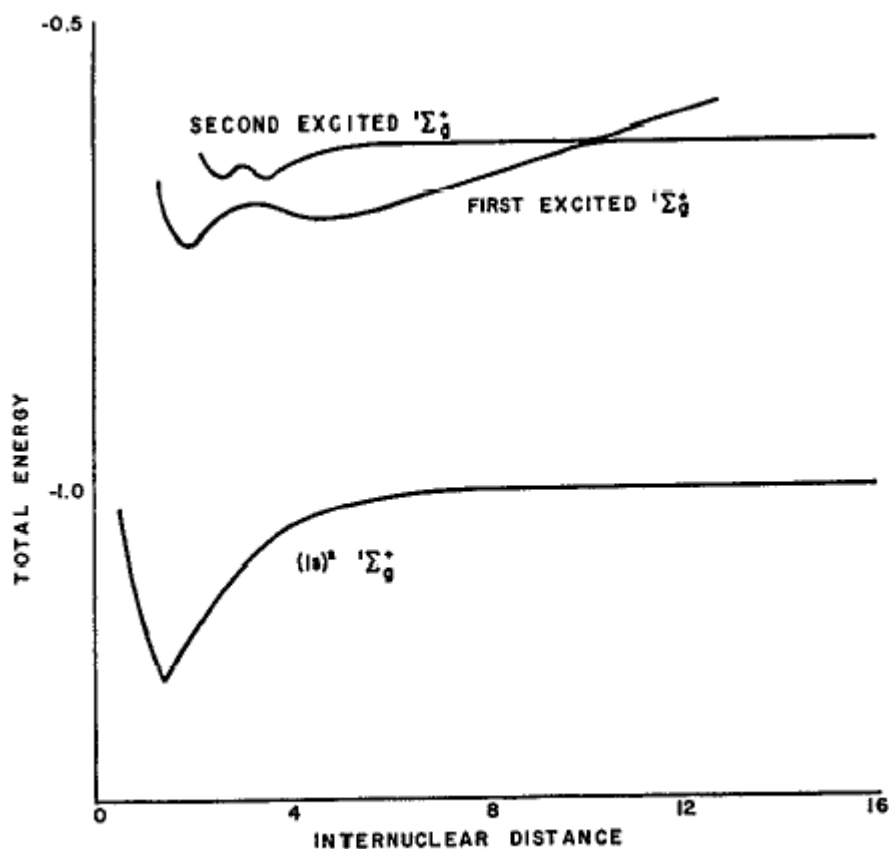


FIG. 2. A sketch of the potential curves for the first three  $1^1\Sigma_g^+$  states of  $H_2$ .

Note that the states actually try to cross *again*, a long way from the nuclei. That is, there is really a  $\Psi$  really, really far out that we're neglecting here.

Near the first minimum, the wave function can be approximated by

$$\Psi_{\text{inner}} \propto \left| \begin{array}{cc} \phi_{1s}^l + \phi_{1s}^r & \alpha \\ \phi_{2s}^l + \phi_{2s}^r & \beta \end{array} \right| + \left| \begin{array}{cc} \phi_{1s}^l + \phi_{1s}^r & \beta \\ \phi_{2s}^l + \phi_{2s}^r & \alpha \end{array} \right|$$

and near the outer minimum, the wave function can be approximated by

$$\Psi_{\text{outer}} \propto \left| \begin{array}{cc} \phi_{2p_z}^l + \phi_{2p_z}^r & \alpha \\ \phi_{2p_z}^l + \phi_{2p_z}^r & \beta \end{array} \right|.$$

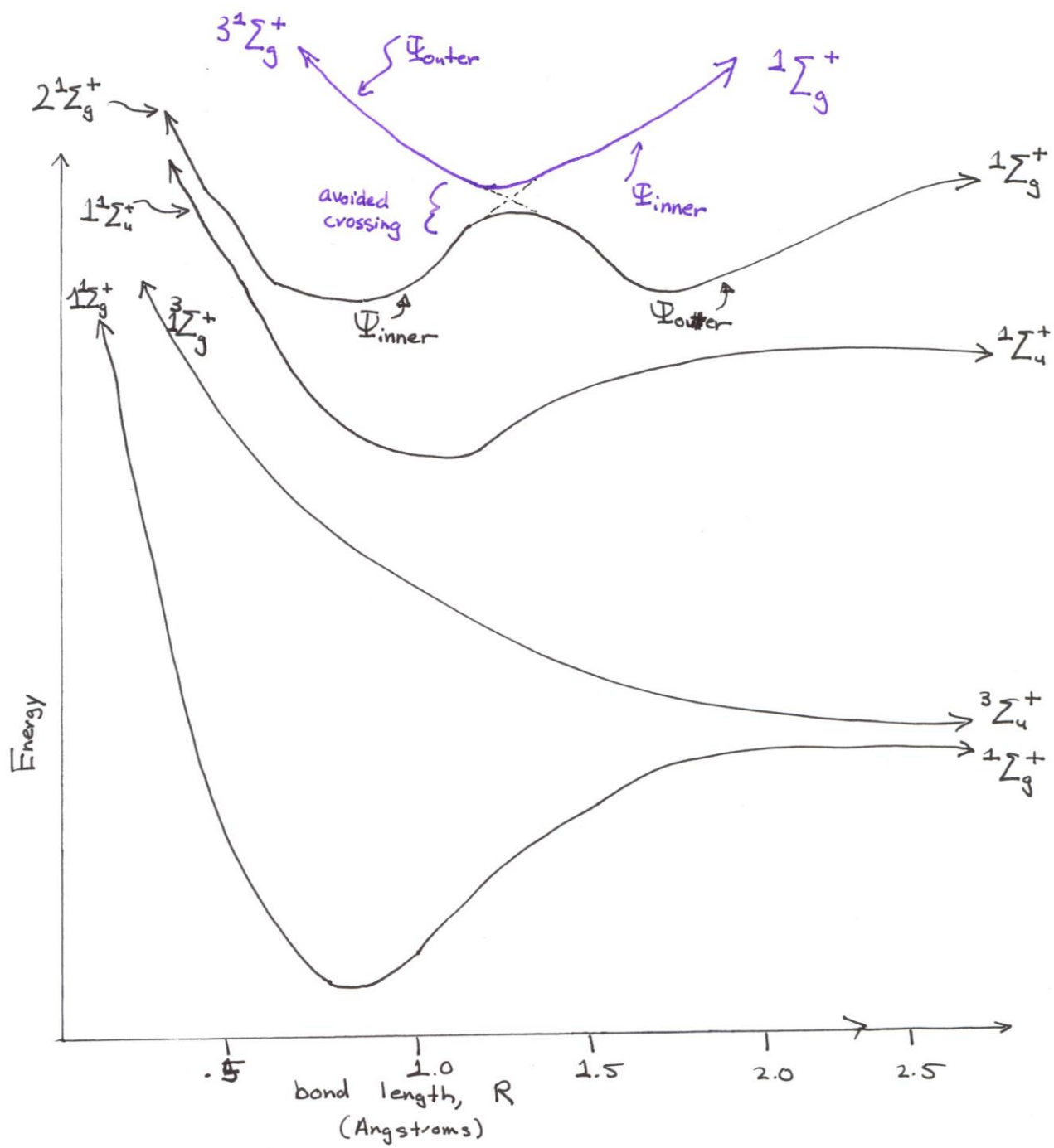
**b. Why does the  $\Psi_{\text{inner}}$  have two Slater determinants but  $\Psi_{\text{outer}}$  have only one Slater determinant? (3 pts.)**

If assumes that the “alpha spin” electron is in the  $\sigma_g 1s \sim \phi_{1s}^l + \phi_{1s}^r$  orbital while the “beta spin” electron is in the  $\sigma_g 2s \sim \phi_{2s}^l + \phi_{2s}^r$  then one would have a only the first term in  $\Psi_{\text{inner}}$ . However,

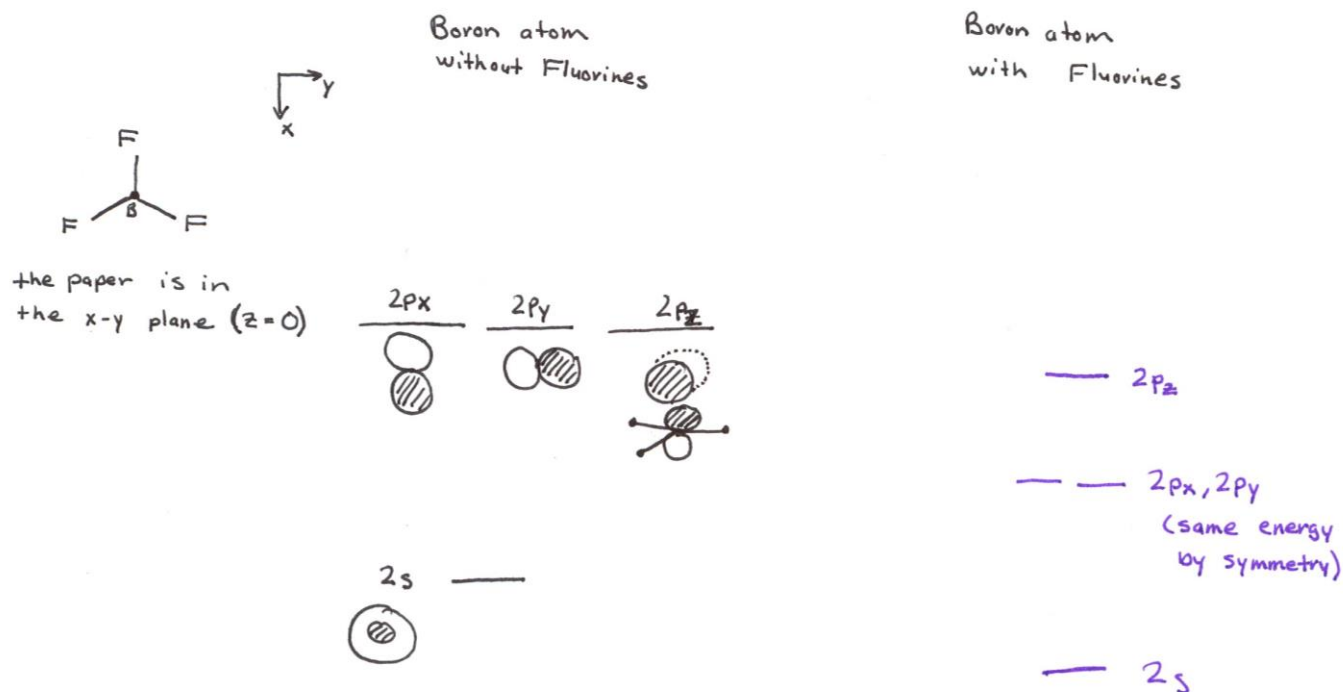
$\left| \begin{array}{cc} \phi_{1s}^l + \phi_{1s}^r & \alpha \\ \phi_{2s}^l + \phi_{2s}^r & \beta \end{array} \right|$  is not an eigenfunction of  $\hat{S}^2$ , and so it doesn't clearly correspond to a singlet state. As such, it isn't a legitimate wavefunction for the *singlet*  $^1\Sigma_g^+$  state!

**c. What do you think the approximate wave function for the  $3^1\Sigma_g^+$  state looks like? Is it the same for all internuclear distances? (3 pts.)**

The approximate wavefunction isn't the same for all internuclear distances; based on the non-crossing rule, we would expect that  $\Psi_{\text{inner}}^{3^1\Sigma_g^+}$  is similar to  $\Psi_{\text{outer}}^{2^1\Sigma_g^+}$  and  $\Psi_{\text{outer}}^{3^1\Sigma_g^+}$  is similar to  $\Psi_{\text{inner}}^{2^1\Sigma_g^+}$ .



- 2a. Show how the  $2s$  and  $2p$  orbitals in the Boron atom when it is surrounded by the three Fluorine atoms in  $\text{BF}_3$ . The  $\text{BF}_3$  molecule is planar; assume it lies in the “xy” plane (i.e., the plane  $z=0$ ). (5 points)



- 2b. Complete the Molecular Orbital Diagram for planar  $\text{BF}_3$  on the next page. (The structure is a triangle of Fluorine atoms, with a Boron in the middle.) **Include all the orbitals that can be formed between the  $2s$  and  $2p$  orbitals of the Fluorine atoms and the  $2s$ ,  $2p_x$ , and  $2p_y$  orbitals of the Boron atom.** The  $2s$  orbital of Fluorine is very low in energy compared to the  $2s$  orbital of Boron; thus, the  $2s$  orbitals of the Fluorine atoms are, to a first approximation, not involved in bonding.

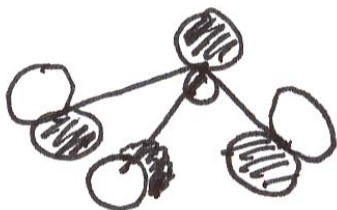
You will notice that the MOs for the “pi” bonding are a little complicated; they can be generated because they have to have the same symmetry as a “ $d$ ” orbital; (However, I didn’t expect you to know that.) I have filled in all the orbitals that form with the  $2p_z$  orbital of Boron, which should help get you started. The state labels in the MO diagram correspond (a) what type of bonding is involved and (b) which “Boron” orbital is used to generate this molecular orbital. There are two copies of the molecular orbital diagram; this way, if you mess one up, you can just use the second copy. I will also have a few spare copies. (10 points)

3 Fluorine  $2s$  orbitals  
(low energy, nonbonding)

- 2c.  $\text{BF}_3$  is a very good Lewis acid. However, when you add an electron to  $\text{BF}_3$ , it is no longer planar. That is,  $\text{BF}_3^-$  is pyramidal: there is still a “triangle” of Fluorine atoms, but now the Boron atom is located above the center of the triangle, rather than in the center of the triangle. I have labeled the lowest unoccupied molecular orbital (LUMO) in  $\text{BF}_3$ . **Consider how this orbital would change if the Boron atom was “pulled” out of the plane. Using this result, explain why  $\text{BF}_3^-$  is not planar. (5 points)**

Notice that when you “pull the Boron up”, the  $p_z$  orbitals of the Fluorine atoms start to point their “striped” phases towards each other to form a “bonding” interaction. This “bonding” interaction lowers the energy of the orbital. Consequently, if you occupy this orbital, the molecule will lower its energy by bending to “form a bond” between the Fluorine atoms.

See the below figure.



## Part 3. Thinking Problem (20 pts.)

- In the notes, we indicated that when one forms a single bond from two  $1s$  orbitals, charge accumulates between the atoms. Based on this, we can conclude that the difference in electron density between the ground state of the Hydrogen molecule and the sum of the two hydrogen atom densities is

$$\rho_{\sigma_g^2}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) \approx \frac{2\zeta^3}{\pi} e^{-\zeta R \xi} - S [\rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r})]$$

where

$$\begin{aligned}\xi &= \frac{r_l + r_r}{R} \\ \rho_{1s}^l(\mathbf{r}) &= \frac{\zeta^3}{\pi} e^{-2\zeta r_l} \\ S &= \frac{\zeta^3}{\pi} \int e^{\zeta r_l} e^{-\zeta r_r} d\mathbf{r}\end{aligned}$$

and  $r_l$  and  $r_r$  are the distances to the “left” and “right” nuclei and  $\zeta$  is the effective nuclear charge.

This is the prediction of how charge accumulates on the bond center in molecular orbital theory. In this problem, you will derive the corresponding result for valence-bond theory.

The simple “valence bond” function for  $H_2$  is

$$\Psi \propto \psi_{1s}^l(\mathbf{r}_1) \psi_{1s}^r(\mathbf{r}_2) + \psi_{1s}^l(\mathbf{r}_2) \psi_{1s}^r(\mathbf{r}_1) \quad \frac{\alpha 1 \beta 2 - \alpha 2 \beta 1}{\sqrt{2}}$$

**A. What is the normalization constant for this wave function? (Write the normalization constant in terms of the overlap integral,  $S$ .) (5 pts.)**

$$\begin{aligned}& \iint \left| \psi_{1s}^l(\mathbf{r}_1) \psi_{1s}^r(\mathbf{r}_2) + \psi_{1s}^l(\mathbf{r}_2) \psi_{1s}^r(\mathbf{r}_1) \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \left\langle \frac{\alpha 1 \beta 2 - \alpha 2 \beta 1}{\sqrt{2}} \middle| \frac{\alpha 1 \beta 2 - \alpha 2 \beta 1}{\sqrt{2}} \right\rangle \\&= \iint \left( \begin{aligned} & \left| \psi_{1s}^l(\mathbf{r}_1) \right|^2 \left| \psi_{1s}^r(\mathbf{r}_2) \right|^2 \\ & + \left[ \psi_{1s}^l(\mathbf{r}_1)^* \psi_{1s}^r(\mathbf{r}_1) \right] \left[ \psi_{1s}^r(\mathbf{r}_2)^* \psi_{1s}^l(\mathbf{r}_2) \right] \\ & + \left[ \psi_{1s}^r(\mathbf{r}_1)^* \psi_{1s}^l(\mathbf{r}_1) \right] \left[ \psi_{1s}^l(\mathbf{r}_2)^* \psi_{1s}^r(\mathbf{r}_2) \right] \\ & + \left| \psi_{1s}^l(\mathbf{r}_2) \right|^2 \left| \psi_{1s}^r(\mathbf{r}_1) \right|^2 \end{aligned} \right) d\mathbf{r}_1 d\mathbf{r}_2 \left( \frac{1}{2} \left( \begin{aligned} & \langle \alpha \uparrow \downarrow \uparrow \downarrow \rangle \langle \beta \uparrow \downarrow \uparrow \downarrow \rangle \\ & + \langle \alpha \uparrow \uparrow \downarrow \downarrow \rangle \langle \beta \uparrow \downarrow \uparrow \downarrow \rangle \\ & + \langle \beta \uparrow \downarrow \uparrow \downarrow \rangle \langle \alpha \uparrow \uparrow \downarrow \downarrow \rangle \\ & + \langle \alpha \uparrow \downarrow \uparrow \downarrow \rangle \langle \beta \uparrow \downarrow \uparrow \downarrow \rangle \end{aligned} \right) \right) \\&= \left( \langle \uparrow \downarrow | \uparrow \downarrow \rangle |S|^2 + |S|^2 + 1 \right) \langle \uparrow \downarrow | \uparrow \downarrow \rangle \langle \uparrow \downarrow | \uparrow \downarrow \rangle \\&= 2 + 2S^2\end{aligned}$$

The normalization constant is the number that makes the wave function normalized. Since

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2+2S^2}} \left( \psi_{1s}^l(\mathbf{r}_1) \psi_{1s}^r(\mathbf{r}_2) + \psi_{1s}^l(\mathbf{r}_2) \psi_{1s}^r(\mathbf{r}_1) \right) \frac{\alpha 1 \beta 2 - \alpha 2 \beta 1}{\sqrt{2}}$$

is normalized, the normalization constant is  $\frac{1}{\sqrt{2+2S^2}}$ .

**B. The electron density for this valence-bond wave function can be computed from**

$$\rho_{VB}(\mathbf{r}_1) = 2 \int |\Psi_{VB}(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2$$

Compute  $\rho_{VB}(\mathbf{r})$ . You do not need to worry about the spin part of the wave function, since that just gives a factor of “1.” (5 pts.)

We will rewrite the spatial integrand in part “A” in terms of the 1s orbitals. We do not need to worry about spin here. So

$$\begin{aligned} \rho(\mathbf{r}_1) &= 2 \left\{ \int \left( \frac{1}{\sqrt{2+2S^2}} \right)^2 \left[ \begin{aligned} &|\psi_{1s}^l(\mathbf{r}_1)|^2 |\psi_{1s}^r(\mathbf{r}_2)|^2 \\ &+ \left[ \psi_{1s}^l(\mathbf{r}_1)^* \psi_{1s}^r(\mathbf{r}_1) \right] \left[ \psi_{1s}^r(\mathbf{r}_2)^* \psi_{1s}^l(\mathbf{r}_2) \right] \\ &+ \left[ \psi_{1s}^r(\mathbf{r}_1)^* \psi_{1s}^l(\mathbf{r}_1) \right] \left[ \psi_{1s}^l(\mathbf{r}_2)^* \psi_{1s}^r(\mathbf{r}_2) \right] \\ &+ |\psi_{1s}^l(\mathbf{r}_2)|^2 |\psi_{1s}^r(\mathbf{r}_1)|^2 \end{aligned} \right] d\mathbf{r}_2 \right\} \\ &= \frac{2}{2+2S^2} \left\{ \int \left[ \begin{aligned} &\rho_{1s}^l(\mathbf{r}_1) \rho_{1s}^r(\mathbf{r}_2) \\ &+ \frac{\zeta^3}{\pi} e^{-\zeta(r_{l,1}+r_{r,1})} \left[ \psi_{1s}^l(\mathbf{r}_1)^* \psi_{1s}^r(\mathbf{r}_1) \right] \left[ \psi_{1s}^r(\mathbf{r}_2)^* \psi_{1s}^l(\mathbf{r}_2) \right] \\ &+ \frac{\zeta^3}{\pi} e^{-\zeta(r_{l,1}+r_{r,1})} \left[ \psi_{1s}^r(\mathbf{r}_1)^* \psi_{1s}^l(\mathbf{r}_1) \right] \left[ \psi_{1s}^l(\mathbf{r}_2)^* \psi_{1s}^r(\mathbf{r}_2) \right] \\ &+ \rho_{1s}^r(\mathbf{r}_1) \rho_{1s}^l(\mathbf{r}_2) \end{aligned} \right] d\mathbf{r}_2 \right\} \end{aligned}$$

Here we have substituted in the form of the 1s orbital, which is just

$$\psi_{1s}^l(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r_l}$$

Using the fact that the 1s orbital is normalized, and using the definition of the overlap integral, we have

$$\rho(\mathbf{r}_1) = \frac{1}{1+S^2} \left\{ \rho_{1s}^l(\mathbf{r}_1) + \rho_{1s}^r(\mathbf{r}_1) + \frac{2S\zeta^3}{\pi} e^{-\zeta(r_{l,1}+r_{r,1})} \right\}$$

It is helpful to state this in terms of ellipsoidal coordinates, with  $\xi_1 = \frac{r_{l,1} + r_{r,1}}{R}$ .

In those terms,

$$\rho(\mathbf{r}_1) = \frac{1}{1+S^2} \left\{ \rho_{1s}^l(\mathbf{r}_1) + \rho_{1s}^r(\mathbf{r}_1) + \frac{2S\zeta^3}{\pi} e^{-\zeta R \xi_1} \right\}$$



- C. Compute the change in density due to bonding in the Valence bond model. (You will need to make some approximations, just as in the Molecular Orbital Theory analysis.) (7 pts.)

$$\rho_{VB}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r})$$

Using the result from part B,

$$\rho_{VB}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) = \frac{1}{1+S^2} \left\{ \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r}) + \frac{2S\zeta^3}{\pi} e^{-\zeta R\xi} \right\} - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r})$$

It is helpful to now use the binomial series, which is

$$\frac{1}{1+S^2} = 1 - S^2 + S^4 - S^6 + \dots$$

Using this in the expression for the density difference, we have

$$\begin{aligned} \rho_{VB}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) &= 1 - S^2 + S^4 - \dots \left\{ \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r}) + \frac{2S\zeta^3}{\pi} e^{-\zeta R\xi} \right\} \\ &\quad - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) \\ &= \left( \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r}) + \frac{2S\zeta^3}{\pi} e^{-\zeta R\xi} - S^2 \rho_{1s}^l(\mathbf{r}) - S^2 \rho_{1s}^r(\mathbf{r}) \right. \\ &\quad \left. - S^3 \frac{2\zeta^3}{\pi} e^{-\zeta R\xi} + \dots \right) \\ &\quad - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r}) \\ &= \frac{2S\zeta^3}{\pi} e^{-\zeta R\xi} - S^2 \rho_{1s}^l(\mathbf{r}) - S^2 \rho_{1s}^r(\mathbf{r}) - S^3 \frac{2\zeta^3}{\pi} e^{-\zeta R\xi} + \dots \\ &\approx S \left( \frac{2\zeta^3}{\pi} e^{-\zeta R\xi} - S \left( \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r}) \right) \right) \end{aligned}$$

Because the overlap integral is rather small, terms that have factors of  $S^3$  or smaller were neglected in the last step.

D. Compare the result from part “C” with the result from molecular orbital theory. Does the result make sense based on what you know about chemical binding in simple VB theory versus simple MO theory? (3 pts.)

We can rewrite the result from “C” as

$$\rho_{VB}(\mathbf{r}) = \rho_{1s}^l(\mathbf{r}) + \rho_{1s}^r(\mathbf{r}) \approx S [\rho_{MO}(\mathbf{r}) - \rho_{1s}^l(\mathbf{r}) - \rho_{1s}^r(\mathbf{r})]$$

$$\Delta_{VB}(\mathbf{r}) \approx S \Delta_{MO}(\mathbf{r})$$

Some comments:

- The two results are exactly the same in the united atom limit, where  $S = 1$ .
- As the bond length increases,  $S$  falls off to zero exponentially. It follows that  $\Delta_{VB}(\mathbf{r})$  approaches zero very rapidly, then,  $\Delta_{MO}(\mathbf{r})$  doesn't fall off nearly as fast, because the first term doesn't depend on the overlap integral. Thus, when the bond length is large, valence bond theory predicts that the electron density of the molecule is very close to the sum of the electron densities of the separated atoms, while MO theory predicts the density of the molecule is pretty different from the density of the separated atoms. This partly explains why valence bond theory gives a better description of molecular dissociation than molecular orbital theory.
- In intermediate regions,  $0 < S < 1$ , so valence bond theory predicts a smaller amount of charge density accumulates in the bond than molecular orbital theory predicts. This might explain why this simple MO wave function predicts a slightly shorter bond than this simple VB wave function. At first, it doesn't seem to agree with the fact that the VB wave function gives a slightly stronger bond. However, it is also true that the MO wave function decreases the electric charge at the nuclei “too much” compared to the VB wave function, and electrons, of course, like to be near the nuclei.