Chem. 562
Fall 2009

Name ___________________________

Please put your name on all pages.

Exam 2

1. This exam contains 6 pages of questions and instructions, two pages of equations, a page of wavefunctions, a periodic table, and a page of constants and conversion factors.

2. Show your work and make your reasoning clear.

3. You have 1.5 hours to work on the exam.

1.__________/25

2.__________/25

3.__________/20

4.__________/30

Total_______/100

Chem. 562 Name ___________________________

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1a. (10 pts.) Draw the Radial wavefunctions of He+ in $\underline{n=2,\ l=0}$ and $\underline{n=2,\ l=1}$.

1b. (5 pts) What is the probability of finding the electron at the He^+ nucleus in $n=2$, $l=0$? Explain.

1c. (10 pts) Using the equation for $R_{nl}(r)$ given at the back of the exam, find the distance r in which the radial probability distribution of the 1s orbital of He^+ is maximum.

2a. (5 pts.) Write down the Hamiltonian for He.

2b. (5 pts.) What terms do we neglect in the Hamiltonian of He when we make the orbital approximation?

2b. (5 pts.) Since electrons are fermions, what property must the wavefunction have?

2b. (10 pts.) The $1s^1 2s^1$ excited state of Helium has 4 possible wavefunctions. There are two possible spatial wavefunctions:

$$\Psi_{\pm} = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) \pm 2s(1)1s(2)\right]$$

Write the 4 wavefunctions including both the spatial and spin functions, and label each as a singlet or a triplet state.

Wavefunction 1 ____________________ ________________________ _____

spatial wavefunction spin wavefunction S or T

Wavefunction 2 ____________________ ________________________ _____

Wavefunction 3 ____________________ ________________________ _____

Wavefunction 4 ____________________ ________________________ _____

Name ________________________

3. (5 pts.) For a homonuclear diatomic, what approximation must we make so that the Hamiltonian can be solved with a separable electronic and nuclear wavefunction?

3b. (10 pts) Derive an equation for the energies of the molecular orbitals $\langle E_{\pm} \rangle$ for a homonuclear diatomic composed of the atoms A and B. Write your answer in terms of the normalization constant N, the Coulomb integral α and the resonance integral β.

3c. (5 pts) Are the normalization terms the same for $\langle E_{+} \rangle$ and $\langle E_{-} \rangle$? Explain.

Name ________________________

4. The potential energy curves drawn below are for CO in its lowest singlet state (S_0), its first singlet state (S_1), and its first triplet state (T_1).

4b. (pts) Draw the molecular orbital diagrams for each of the three states. Fill them in with electrons. Label the molecular orbitals. The molecular orbitals of CO have the same ordering as N_2.

Name ________________________

4b. (5 pts) For the S_0 and S_1 electronic states, draw the spatial distribution of the electronic wavefunction for the highest energy molecular orbital that contains an electron.

4c. (5 pts) What is the most likely vibrational state to be accessed in the S_1 state if the molecule is excited with light from the ground state? Draw the transition on the diagram from the last page. Be precise.

4d. (5 pts) If the molecule is in a gas or solvent so that it can vibrationally relax, what is the most likely vibrational state on S_0 to be accessed when the molecule fluoresces? Draw the transition on the previous page.

4d. (5 pts) Which will be more intense, fluorescence from the S_1 state or phosphorescence from the T_1 state? Explain.

4e. (pts) The ionization energy of CO is higher than for either C or O, but the ionization energy of O_2 is less than that of O. Explain.