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

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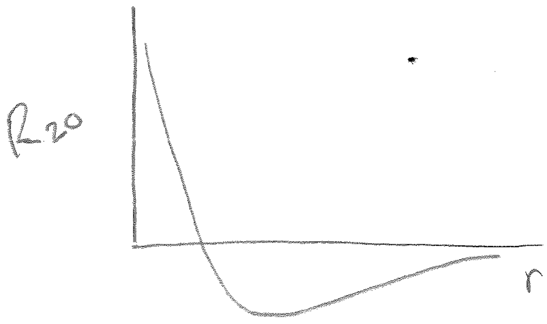
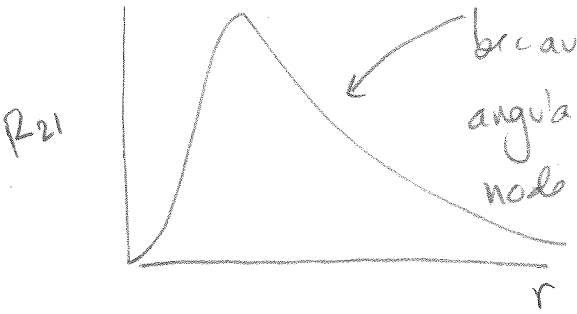
1a. (10 pts.) Draw the Radial wavefunctions of He+ in <u>n=2, l=0</u> and <u>n=2, l=1</u>.





no radial node because angular node instead

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

Radial Prob. $\propto |\psi|^2 r^2$ ← because of volume element r^2, <u>zero</u> probability

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.

$$P_{10}(r) = R_{10}^2(r)\cdot r^2$$

$$= \left[2\left(\frac{Z}{a_0^3}\right)^{1/2} e^{-Zr/a_0}\right]^2 r^2$$

$$\frac{dP_{10}(r)}{dr} = 0 = \frac{d}{dr}\left[4\left(\frac{Z}{a_0^3}\right)e^{-2Zr/a_0}\, r^2\right]$$

$$= \frac{4Z}{a_0^3}\left[r^2\left(-\frac{2Z}{a_0}\right)e^{-2Zr/a_0} + 2re^{-2Zr/a_0}\right]$$

$\frac{rZ}{a_0} = 1 \qquad r = \frac{a_0}{Z} \qquad Z = 2$ for He$^+$ $\qquad \therefore r = \frac{a_0}{2}$

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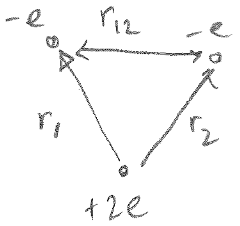
2a. (5 pts.) Write down the Hamiltonian for He.



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

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

neglect electron-electron repulsion

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

wavefxn must be anti-sym. upon exchange of electrons

$\psi(1,2) = -\psi(2,1)$

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.

symmetric

asymmetric

	spatial wavefunction	spin wavefunction	S or T
Wavefunction 1	$\frac{1}{\sqrt{2}}[1s(1)\,2s(2) + 2s(1)\,1s(2)]$	$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$	S
Wavefunction 2	asym → [−]	$\alpha(1)\alpha(2)$	T
Wavefunction 3	[−]	$\beta(1)\beta(2)$	T
Wavefunction 4	[−]	$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$	T

only one that is asym

Possible spin wavefxns: $\alpha(1)\alpha(2)$; $\beta(1)\beta(2)$; $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$; $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

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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?

Born-Oppenheimer Approx. Nuclei move much slower than electrons: So fix R and solve for $\psi_e(r;R)$

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.

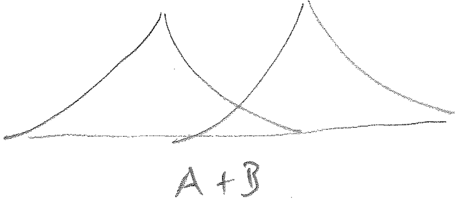
$$\langle E_\pm \rangle = N_\pm^2 \int (A \pm B)\,\hat{H}_e\,(A \pm B)\,d\tau \qquad A^* = A$$

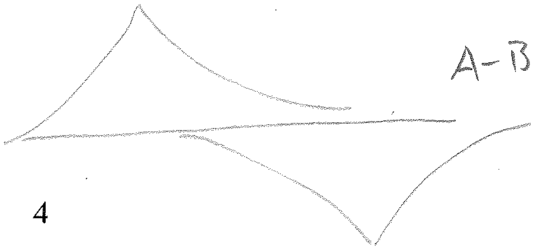
$$= N_\pm^2 \left[\underbrace{\int A \hat{H}_e A\,d\tau}_{\equiv \alpha} + \underbrace{\int A \hat{H}_e B\,d\tau}_{\equiv \beta} + \underbrace{\int B \hat{H}_e A\,d\tau}_{\equiv \beta} + \underbrace{\int B \hat{H}_e B\,d\tau}_{\equiv \alpha} \right]$$

$$= 2 N_\pm^2 (\alpha \pm \beta)$$

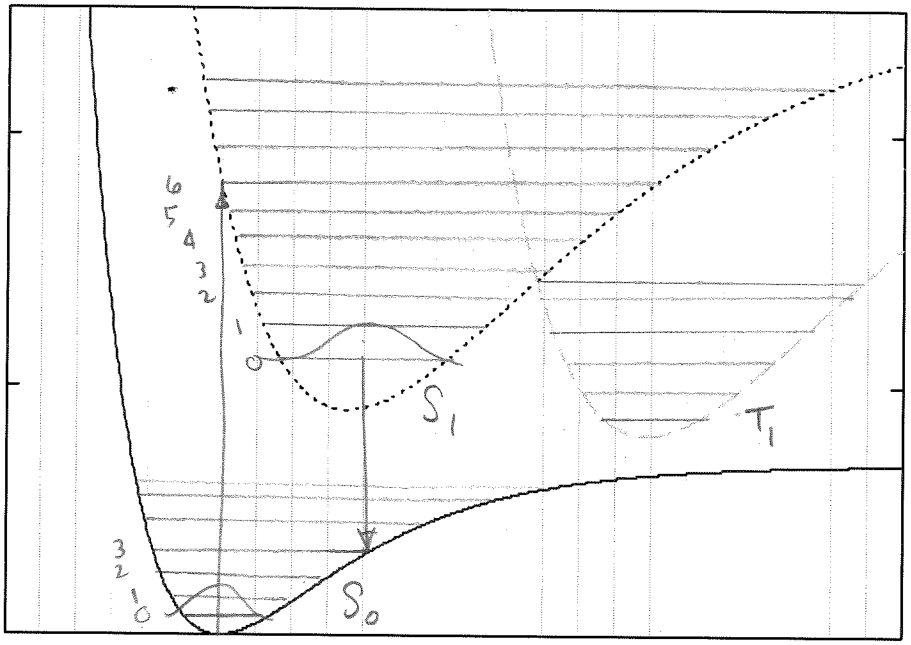
3c. (5 pts) Are the normalization terms the same for $\langle E_+ \rangle$ and $\langle E_- \rangle$? Explain.

No, because the overlap of A+B and A−B differs.



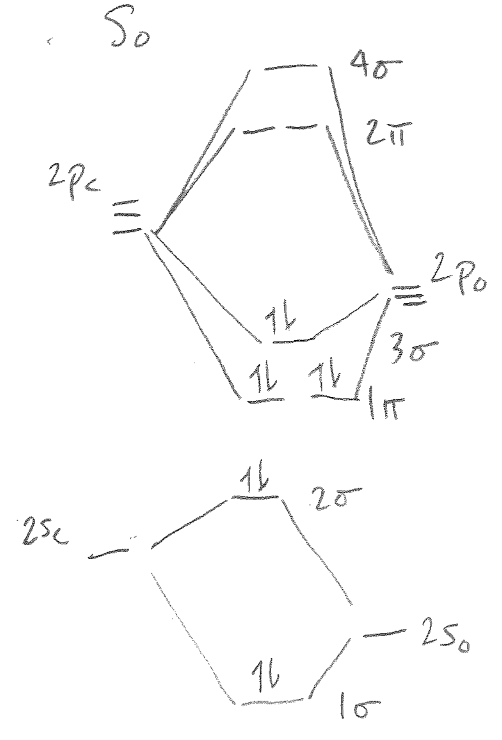


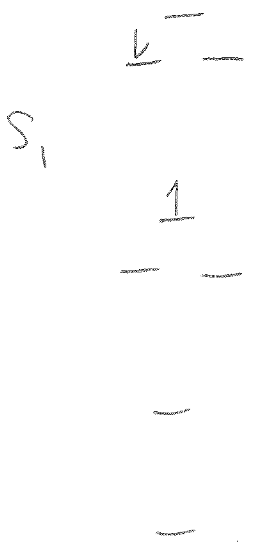
4. The potential energy curves drawn below are for CO in its lowest singlet state (S_0), its first singlet state (S_1), and its first triplet state (T_1).



4 b. (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.

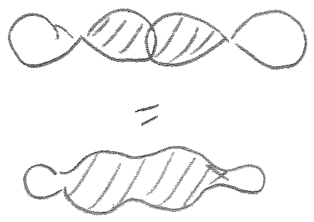
$CO = 4 + 6 = 10e^-$



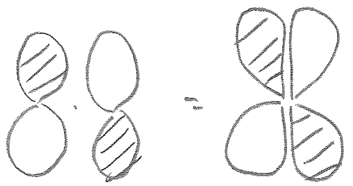


4b. (5 pts) For the S_0 and S_1 electronic states, draw the spatial distribution of the electronic wavefunction for the highest energy molecular orbital that contains an electron.

S_0 : 3σ



S_1 : $2\pi^*$



4c. (5 pts) <u>What</u> 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? <u>Draw</u> the transition on the diagram from the last page. Be precise.

$v = 6$

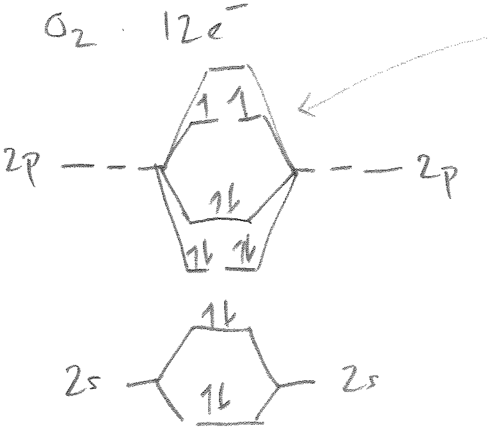
4d. (5 pts) If the molecule is in a gas or solvent so that it can vibrationally relax, <u>what</u> is the most likely vibrational state on S_0 to be accessed when the molecule fluoresces? <u>Draw</u> the transition on the previous page.

$v = 3$

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

fluorescence because phosphorescence is spin forbidden

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.



electrons are ionized out of antibond orbital.

for CO, comes out of bonding orbital