Chem. 562
Spring 2012

Name ______________________

Please put your name on all pages.

Exam Key

Exam 2

1. This exam contains 7 pages of questions and instructions, two pages of equations and integrals, and a page of tables.

2. Show your work and make your reasoning clear.

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

1.________/20

2.________/20

3.________/15

4.________/20

5.________/25

Total ______/100

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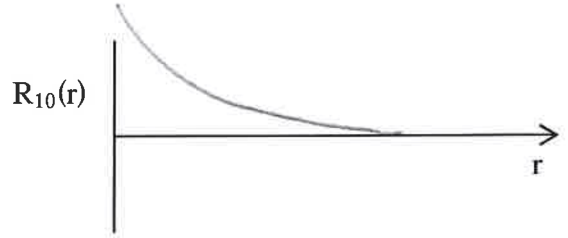
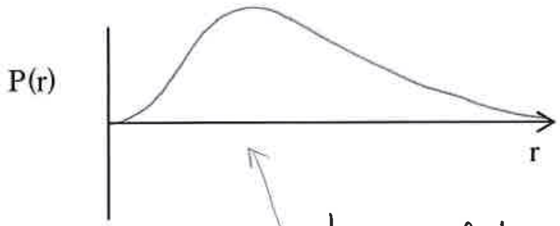
1. Answer the following questions about atomic orbitals.

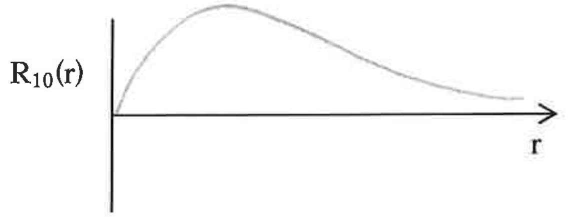
1a. (5 pts.) Draw the 1s radial wavefunction, $R_{10}(r)$, and its radial distribution function, $P(r)$.

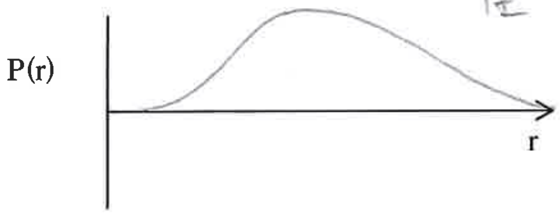




larger distance for Pz

1b. (5 pts) Draw the same two plots for the $2p_z$ orbital.





y contract x

1c. (5 pts) For the $2p_z$ orbital, calculate the most likely distance from the nucleus that one would find an electron.

from Tabl 10.1 $2p_z = \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta \qquad \rho = \frac{Zr}{a_0}$

$= c\, r\, e^{-Zr/2a_0}$

calc $\frac{d}{dr}|\psi|^2 r^2 = \frac{d}{dx} r^4 e^{-Zr/a_0}$

$= 4r^3 \cancel{e^{-Zr/a_0}} - \frac{Z}{a_0} r^4 \cancel{e^{-Zr/a_0}} = 0$

expand

$4\cancel{r^3} = \frac{Z}{a_0} \cancel{r^4} \qquad r = \frac{4a_0}{Z}$

1d. (5 pts) List all the wavefunctions $\Psi_{n,\ell}(r,\theta,\varphi)$ that have two nodes (list using n and ℓ)? For each, specify the number of radial and angular nodes.

all n=3 wavefxns

		radial	ang
$n=3$	$\ell=0$	2	0
$n=3$	$\ell=1$	1	1
$n=3$	$\ell=2$	0	2

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2. Answer the following questions. No need to convert to c.o.m.

2a (10 pts). Write down the full Hamiltonian for H_2. How many terms are there? 4 k.E + 6 P.E = 10

$$\hat{H} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_{e1}}\nabla_1^2 - \frac{\hbar^2}{2m_{e2}}\nabla_2^2$$

$$+\frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R} + \frac{1}{|r_1 - r_2|}\right)$$

expand

5 modify

2b (5 pts). In your answer from 2a, which term do we ~~neglect and which term do we hold constant~~ when we make the Born Oppenheimer Approximation?

neglect k.E. terms $-\frac{\hbar^2}{2m_A}\nabla_A^2$ and $-\frac{\hbar^2}{2m_B}\nabla_B^2$

hold $\frac{1}{R}$ constant.

2c (5 pts). Which term do we neglect when we make the orbital approximation?

neglect $\frac{1}{|r_1 - r_2|}$

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3. Answer the following questions about spins.

3a. (5 pts). Consider two electrons that are both in a 1s orbital (e.g. 1s(1) and 1s(2)). Each electron can be either spin up (a) or spin down (b).

Write 4 wavefunctions that obey the criteria of indistinguishability.

Label each wavefunction as "good for fermions",✓ or "good for bosons", ~~or "neither~~."

$1s(1)\,1s(2)\,\alpha(1)\,\alpha(2)$ good for bosons

$1s(1)\,1s(2)\,\beta(1)\,\beta(2)$ good for bosons

$1s(1)\,1s(2)\overbrace{\left[\dfrac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{2^{1/2}}\right]}^{\sigma_+}$ good for bosons

$1s(1)\,1s(2)\underbrace{\left[\dfrac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{2^{1/2}}\right]}_{\equiv\sigma_-}$ good for fermions

3b. (5 pts). Consider two electrons, one of which is in a 1s orbital and the other in a 2s orbital. Write down a valid wavefunction for a triplet state and another for a singlet.

need linear combinations of spatial

Singlet $\dfrac{1}{\sqrt{2}}\left[1s(1)\,2s(2)+2s(1)\,1s(2)\right]\sigma_-$

any of these 3 for triplet

$\dfrac{1}{\sqrt{2}}\left[1s(1)\,2s(2)-2s(1)\,1s(2)\right]\times\begin{bmatrix}\alpha(1)\,\alpha(2)\\ \beta(1)\,\beta(2)\\ \sigma_+\end{bmatrix}$

3c. (5 pts). Using your wavefunctions from 2b, calculate the spin selection rule (ΔS) for transitioning from a singlet state to a triplet state. Since the space part and spin part of atomic wavefunctions are separable, the only integral you need to do is over the spin coordinates:

$$\Delta S=\int\psi_{s1}\psi_{s2}\,d\tau_{s1}\,d\tau_{s2}$$

example of 1 integral $\Delta S=\int\sigma_-\,\alpha(1)\,\alpha(2)$

$$=\frac{1}{\sqrt{2}}\int\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\alpha(1)\,\alpha(2)\,d\tau_1\,d\tau_2$$

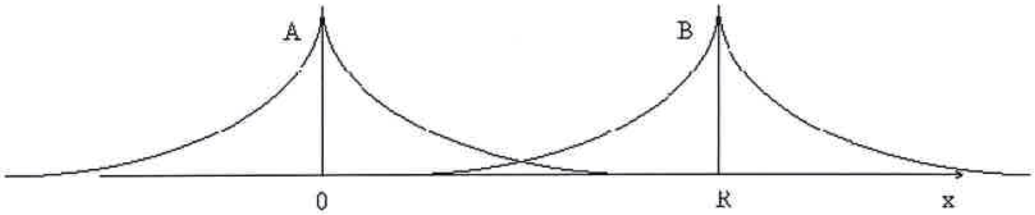
$$=\frac{1}{\sqrt{2}}\int\alpha(1)\beta(2)\,\alpha(1)\,\alpha(2)\,d\tau_1\,d\tau_2-\frac{1}{\sqrt{2}}\int\beta(1)\,\alpha(2)\,\alpha(1)\,\alpha(2)\,d\tau_1\,d\tau_2$$

$$=\frac{1}{\sqrt{2}}\left[\overset{1}{\int\alpha(1)\cancel{\alpha(1)}\,d\tau_1}\,\overset{0}{\int\beta(2)\cancel{\alpha(2)}\,d\tau_2}-\overset{0}{\int\beta(1)\cancel{\alpha(1)}\,d\tau_1}\,\overset{1}{\int\alpha(2)\cancel{\alpha(2)}\,d\tau_2}\right]$$

$=0.\quad\therefore\ \Delta S=0$

4. Answer the questions below about a homonuclear diatomic molecule AB.

Consider the 1s atomic orbitals of A and B as shown below, which are plotted on a common x-axis. Atom A is centered at x=0 and atom B is center at x=R.



4a. (5 pts.) Write the equation for the $1s_A$ wavefunction between 0<x<R as a function of x (not r!).

$$R_A(x) = \frac{2}{a_0^{3/2}} e^{-2x/a_0} \qquad \left(2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zx/a_0} \right)$$

4b. (5 pts.) Write the equation for the $1s_B$ wavefunction between 0<x<R as a function of x.

$$R_B(x) = \frac{2}{a_0^{3/2}} e^{+\frac{2}{a_0}(x-R)} \qquad \left(2\left(\frac{Z}{a_0}\right)^{3/2} e^{+\frac{Z}{a_0}(x-R)} \right)$$

4c. (5 pts) Calculate the spatial overlap integral S as a function of R. (Only consider the integral over the range of 0<x<R.)

$$S = \int_0^R R_A(x) R_B(x)\, dx = \frac{4}{a_0^3} \int_0^R e^{-2x/a_0} e^{+\frac{2}{a_0}(x-R)} dx$$

$$= \frac{4}{a_0^3} e^{-\frac{2R}{a_0}} \int_0^R dx = \frac{4R}{a_0^3} e^{-2R/a_0}$$

4d. (5 pts) The integral $\beta = \int A\hat{H}_e B d\tau$ is related to an overlap integral. In one sentence, explain why $\beta \neq E_B \int AB d\tau = E_B S$

Because $\hat{H}_e B \neq E_B B$ because full $\hat{H}_e$ was not used to obtain B. So not an eigenfunction.

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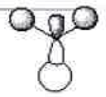
5. Answer the following questions about the molecular orbitals of ammonia. In ammonia, the nitrogen orbitals $2S_N$, $2P_{xN}$, $2P_{yN}$, and $2P_{zN}$ mix with the three hydrogen orbitals $1S_A$, $1S_B$, and $1S_C$.

5a. (5 pts.) Shown below are the molecular orbital wavefunctions of ammonia, numbered 1 through 7. Label each energy level in the diagram on the right with the number corresponding to its molecular orbital. Some of the energy levels are degenerate.

1

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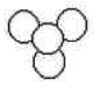
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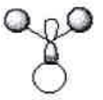
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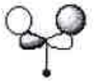
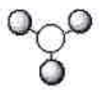
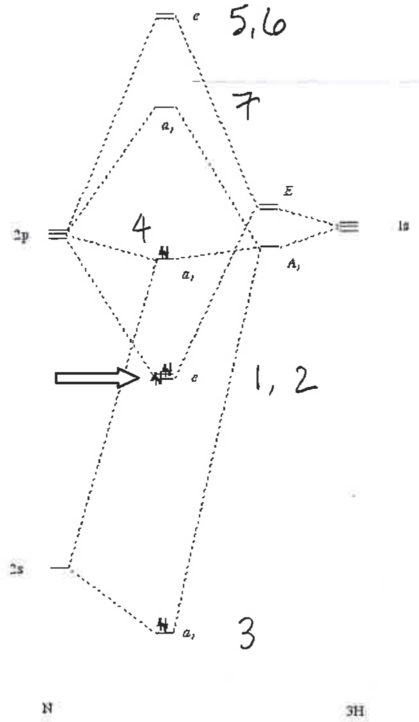

7




5b. (5 pts). The E and A_1 labels refer to the symmetries of linear combinations of hydrogen atoms (similar to how we mixed the H orbitals in class when discussing H_2O). Write the wavefunctions for these mixed states. Call them Ψ_{E1} Ψ_{E2} & Ψ_{A1}

$$\Psi_{A1} = \frac{1}{\sqrt{3}}(1s_A + 1s_B + 1s_C)$$

$$\Psi_{E2} = \frac{1}{\sqrt{2}}(1s_A - 1s_B)$$

$$\Psi_{E1} = \frac{1}{\sqrt{3}}(1s_A + 1s_B - 1s_C)$$

5c. (5 pts). The molecular orbital labeled "4" above is a lone pair formed by a single 2P orbital. That 2P orbital has A1 symmetry just like one of the hydrogen wavefunctions. Why does this 2P orbital form a lone pair rather than mixing with the other atomic orbitals?

Poor spatial overlap.

Using your answer from 5b

for one ~~of the~~ bonding + antibonding e molecular orbitals

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5d (5 pts). Write a 2x2 secular matrix ~~that includes α, β, and S~~ from which one could calculate the energies of the e molecular orbitals. ~~Use one E and one 2P wavefunction (No need to specify which E and 2P that you use.)~~ Define each integral.

$$\begin{vmatrix} \alpha_{E2} - E & \beta - ES \\ \beta - ES & \alpha_{2P_x} - E \end{vmatrix} = 0$$

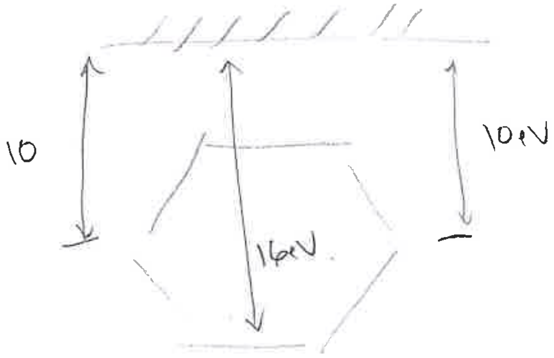
$$\alpha_{E2} = \int \Psi^*_{E2} \hat{H}_e \Psi_{E2} \, d\tau$$

$$\alpha_{2P_x} = \int \psi^*_{2P_x} \hat{H}_e \psi_{2P_x} \, d\tau$$

$$S = \int \psi^*_{2P_x} \Psi_{E2} \, d\tau$$

$$\beta = \int \psi^*_{2P_x} \hat{H}_e \Psi_{E2} \, d\tau$$

5e. (5 pts). The 2P and E atomic orbitals have about the same ionization energy of 10 eV. The ionization energy of the orbital pointed at by the arrow is about 16 eV. Estimate the value of β. You can neglect S.



$$(\alpha_{E2} - E)(\alpha_{2P_x} - E) = \beta^2$$

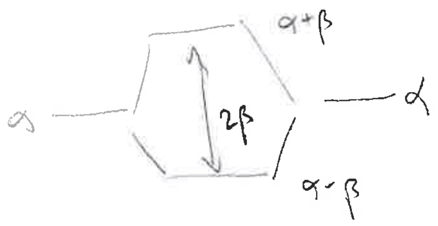
$$(10 - 16)^2 = \beta^2$$

$$(-6)^2 = \beta$$

$$36 = \beta^2 \qquad \beta = 6\text{eV}$$

Since degenerate, $\alpha_{E2} \approx \alpha_{2P_x}$ + $S = 0$, so its like a homonuclear diatomic.

$$\langle E_\pm \rangle = \alpha \pm \beta$$



$$\Delta E = 2\beta$$

$$\beta = 6\text{eV}.$$