

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY**  
Department of Chemistry  
*Chemistry - 5.61*  
*Physical Chemistry*

**Exam III**

**(1) PRINT** your name on the cover page.

**(2)** It is suggested that you **READ THE ENTIRE EXAM** before beginning work, since you may be better prepared for some questions than others.

**(3) ANSWER ALL QUESTIONS** as completely as possible.

*GOOD LUCK !!!!*

Short Answer (40 pts) \_\_\_\_\_ *40* \_\_\_\_\_

Problem 2 (30 pts) \_\_\_\_\_ *30* \_\_\_\_\_

Problem 3 (30 pts) \_\_\_\_\_ *30* \_\_\_\_\_

TOTAL: (100 pts) \_\_\_\_\_ *100* \_\_\_\_\_

Name : \_\_\_\_\_ *Key* \_\_\_\_\_

TA: \_\_\_\_\_

### Short Answer (40 points)

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- 1) (7 Points) For a particular hydrogen orbital,  $\psi_{nlm}$ , the average potential energy turns out to be  $\langle V(r) \rangle = -0.0625$  a.u. What is  $\langle V(r) \rangle$  for the analogous orbital in  $\text{He}^+$ ?

*The potential energy scales as  $Z^2$ .  $\text{He}^+$  has  $Z=2$ , so the average potential will be  $-0.0625 \times 2^2 = \underline{0.25 \text{ a.u.}}$*

- 2) (5 points) In performing spectroscopy of the Hydrogen atom, which pairs of orbitals below would have **allowed** transitions? [Note: the Solid harmonics are related to the spherical harmonics by:  $p_x \propto Y_1^1 + Y_1^{-1}$ ;  $p_y \propto Y_1^1 - Y_1^{-1}$ ;  $d_{xz} \propto Y_2^1 + Y_2^{-1}$ ;  $d_{yz} \propto Y_2^1 - Y_2^{-1}$ ;  $d_{xy} \propto Y_2^2 + Y_2^{-2}$ ;  $d_{x^2-y^2} \propto Y_2^2 - Y_2^{-2}$ ]

5s                      3p<sub>x</sub>                      3p<sub>y</sub>                      4d<sub>xy</sub>                      4d<sub>z<sup>2</sup></sub>

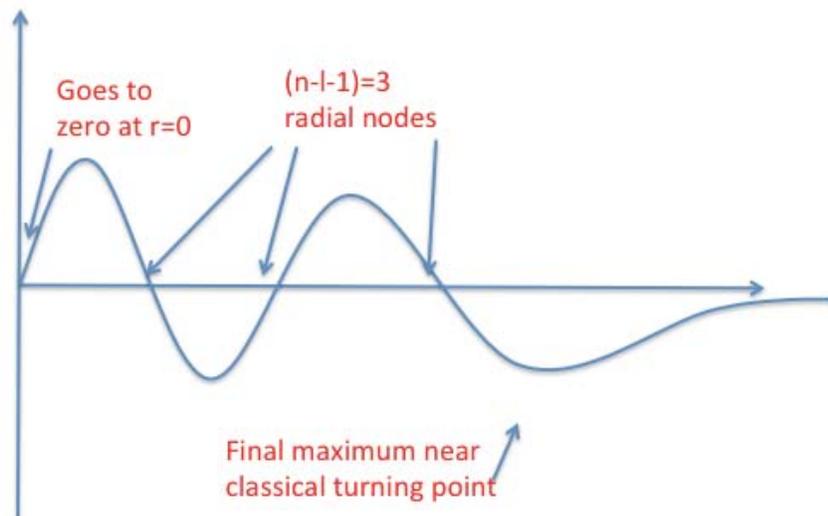
*For polarized light, the selection rule will be  $\Delta l = \pm 1$   $\Delta m = 0$ . There is no selection rule on  $n$ . Thus, none of the above would be allowed.*

*Alternatively, if the light is not polarized, the selection rule will be  $\Delta l = \pm 1$ ,  $\Delta m = \pm 1, 0$ . In this case the allowed transitions will be*

*5s  $\rightarrow$  3p<sub>x</sub>      5s  $\rightarrow$  3p<sub>y</sub>      3p<sub>x</sub>  $\rightarrow$  4d<sub>xy</sub>      3p<sub>x</sub>  $\rightarrow$  4d<sub>z<sup>2</sup></sub>      3p<sub>y</sub>  $\rightarrow$  4d<sub>xy</sub>      3p<sub>y</sub>  $\rightarrow$  4d<sub>z<sup>2</sup></sub>*

*plus the reverse transitions. Full credit was given for either answer.*

- 3) (6 points) Sketch a picture of the 5p radial function for a hydrogen atom,  $R_{nl}(r)$ . Note any important features.



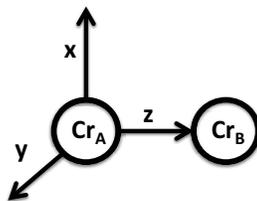
- 4) (4 points) For a particular atom, the spin part of the wavefunction is  $(\alpha(1)\beta(2)+\alpha(2)\beta(1))/\sqrt{2}$ . Write down one possible form for the spatial wavefunction in this case.

*Spin part is symmetric, so space part must be antisymmetric. Thus, one possibility would be  $[1s(1)2s(2)-1s(2)2s(1)]/\sqrt{2}$ .*

- 5) (4 points) What is a Slater Determinant and what is it used for?

*A Slater determinant is an **antisymmetric** wavefunction built out of **orbitals**. It corresponds to a **unique stick diagram**. It is used to create physically appropriate electronic wavefunctions for atoms and molecules with many electrons. [Note: A perfect answer would include the boldface terms in some reasonable fashion together with a bit about what the slater determinant is used for. Partial credit for imperfect answers, of course.]*

- 6) (10 points) Consider the MO picture of bonding in  $\text{Cr}_2$ . Ignore all the orbitals except for the outermost d shell, so that there are 10 atomic orbitals available for making molecular orbitals ( $d_{z^2}^A, d_{z^2}^B, d_{xz}^A, d_{xz}^B, d_{yz}^A, d_{yz}^B, d_{xy}^A, d_{xy}^B, d_{x^2-y^2}^A, d_{x^2-y^2}^B$ ). Assume the molecule is oriented along the z axis:



When you build the Hamiltonian matrix,  $\mathbf{H}$ , for this molecule, it will be a 10x10 matrix. However, as was the case for first row diatomics treated in class, the matrix will be block diagonal - many of the matrix elements will be zero and only a few will be non-zero. In the matrix below, shade in the blocks of the matrix you expect to be non-zero.

	$d_{z^2}^A$	$d_{z^2}^B$	$d_{xz}^A$	$d_{xz}^B$	$d_{yz}^A$	$d_{yz}^B$	$d_{xy}^A$	$d_{xy}^B$	$d_{x^2-y^2}^A$	$d_{x^2-y^2}^B$
$d_{z^2}^A$										
$d_{z^2}^B$										
$d_{xz}^A$										
$d_{xz}^B$										
$d_{yz}^A$										
$d_{yz}^B$										
$d_{xy}^A$										
$d_{xy}^B$										
$d_{x^2-y^2}^A$										
$d_{x^2-y^2}^B$										

*Note: these blocks correspond to  $\sigma$ ,  $\pi$  and  $\delta$  bonding orbitals respectively, moving from the upper left to the lower right. There are also a few elements ( $d_{xz}^A-d_{yz}^A$ ,  $d_{xz}^B-d_{yz}^B$ ,  $d_{xy}^A-d_{x^2-y^2}^A$ ,  $d_{xy}^B-d_{x^2-y^2}^B$ ) within these blocks that are zero, but no points were associated with these terms, as the question specifically asks us to identify the blocks.*

7) (4 Points) What is the Born Oppenheimer Approximation?

*The Born Oppenheimer approximation is the physical observation that, because the nuclei are much heavier than the electrons, they move more slowly. As a result, we can think of the electrons as moving in the field arising from the fixed nuclei. We can therefore separate the electronic and nuclear parts of the wavefunction and retain a semi-classical picture of the atomic positions.*

**PROBLEM 2 (30 points)– Effective Nuclear Charge**

Consider the Lithium atom within the independent particle model (IPM). You may find the following two electron integrals useful (energies in eV; atomic unit of energy=27.2 eV):

$$\begin{array}{llll}
 J_{1s1s} = 10.0 Z & J_{1s2s} = 4.4 Z & J_{1s3s} = 2.0 Z & J_{1s4s} = 1.13 Z \\
 K_{1s2s} = 0.5 Z & & K_{1s3s} = 0.1 Z & K_{1s4s} \approx 0.0 Z
 \end{array}$$

A) What is the ionization potential (IP) of Li in its ground state [ $1s^2 2s^1$ ]?

*(7 points)  $IP = E(1s^2) - E(1s^2 2s) = -E_{2s} - 2J_{1s2s} + K_{1s2s} = 30.6 - 2*(13.2) + 1.5 = 5.7 \text{ eV}$*

B) Compute the IP of Li in the  $1s^2 3s^1$  excited state. Is the ionization potential larger or smaller?

*(5 points)  $IP = E(1s^2) - E(1s^2 3s) = -E_{3s} - 2J_{1s3s} + K_{1s3s} = 13.6 - 2*(6) + 0.3 = 1.9 \text{ eV}$*

*The IP is lower, as the excited electron is easier to remove.*

C) Compute the IP of Li in the  $1s^2 4s^1$  excited state. Is the ionization potential larger or smaller?

*(5 points)  $IP = E(1s^2) - E(1s^2 4s) = -E_{4s} - 2J_{1s4s} + K_{1s4s} = 7.65 - 2*(3.39) + 0.0 = 0.87 \text{ eV}$*

*The IP is even lower, as the highly excited electron is even easier to remove.*

- D) You may have been taught in earlier chemistry courses that the valence electrons in an atom like Li see an effective nuclear charge,  $Z_{\text{eff}}$ , that is lower than the actual nuclear charge. Use your results from parts A)-C) to make this connection quantitative. Assume that the ionization potentials you computed arose *exactly* from a Hydrogenic atom with nuclear charge  $Z_{\text{eff}}$

$$IP = E(\text{cation}) - E(\text{neutral}) = \frac{me^4 Z_{\text{eff}}^2}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

Compute the correct  $Z_{\text{eff}}$  values for the 2s, 3s and 4s orbitals in Li. How do you rationalize your results?

*(13 points) For 2s:  $IP = 5.7 \text{ eV} = Z_{\text{eff}}^2 / (2 n^2) \text{ a.u.} = Z_{\text{eff}}^2 / (2 \cdot 2^2) \text{ a.u.} = Z_{\text{eff}}^2 / 8 \text{ a.u.} = 3.4 * Z_{\text{eff}}^2 \text{ eV.}$*

$$\rightarrow Z_{\text{eff}} = 1.38$$

*For 3s:  $IP = 1.9 \text{ eV} = Z_{\text{eff}}^2 / (2 n^2) \text{ a.u.} = Z_{\text{eff}}^2 / (2 \cdot 3^2) \text{ a.u.} = Z_{\text{eff}}^2 / 18 \text{ a.u.} = 1.51 * Z_{\text{eff}}^2 \text{ eV.}$*

$$\rightarrow Z_{\text{eff}} = 1.12$$

*For 4s:  $IP = 0.87 \text{ eV} = Z_{\text{eff}}^2 / (2 n^2) \text{ a.u.} = Z_{\text{eff}}^2 / (2 \cdot 4^2) \text{ a.u.} = Z_{\text{eff}}^2 / 32 \text{ a.u.} = 0.85 * Z_{\text{eff}}^2 \text{ eV.}$*

$$\rightarrow Z_{\text{eff}} = 1.01$$

*As we go up in  $n$ ,  $Z_{\text{eff}}$  goes down progressively, as the electron spends more and more of its time outside the 1s shell, where the effective charge approaches  $Z_{\text{eff}}=1$ . Clearly, the effective charge is asymptotically approaching  $Z_{\text{eff}}=1$  as  $n$  increases. This agrees with my chemical intuition that Li should have an effective charge much closer to 1 than 3. However, it is also clear that this is only qualitatively correct.*

**PROBLEM 3 (30 points)— Molecular Orbital Theory**

Consider the  $\sigma$  bond in LiH in the valence approximation, so that the molecular orbitals can be written

$$\psi_{el} = c_1 2s_{Li} + c_2 1s_H$$

At a particular bond length,  $R$ ,

$$\varepsilon_{Li} = \int 2s_{Li} \hat{H} 2s_{Li} d\tau = -7.0 \text{ eV} \quad \varepsilon_H = \int 1s_H \hat{H} 1s_H d\tau = -10.0 \text{ eV}$$

$$V = \int 2s_{Li} \hat{H} 1s_H d\tau = -2.0 \text{ eV} \quad S = \int 2s_{Li} 1s_H d\tau \approx 0$$

- A) Show that  $\psi = \frac{1}{\sqrt{5}} 2s_{Li} + \frac{2}{\sqrt{5}} 1s_H$  and  $\psi = \frac{2}{\sqrt{5}} 2s_{Li} - \frac{1}{\sqrt{5}} 1s_H$  are energy eigenstates for LiH.

What are the corresponding eigenvalues? [Note: You do not need to solve for the eigenvectors. Just show that the given eigenvectors are correct.]

*(12 points) The Hamiltonian is*

$$\mathbf{H} = \begin{pmatrix} \varepsilon_{Li} & V \\ V & \varepsilon_H \end{pmatrix}$$

*Plugging in the two eigenvectors, we find*

$$\mathbf{H}\mathbf{c} = \begin{pmatrix} \varepsilon_{Li} & V \\ V & \varepsilon_H \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{5}} \\ \frac{2}{\sqrt{5}} \end{pmatrix} = \begin{pmatrix} -7 & -2 \\ -2 & -10 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{5}} \\ \frac{2}{\sqrt{5}} \end{pmatrix} = \begin{pmatrix} \frac{-7}{\sqrt{5}} - \frac{4}{\sqrt{5}} \\ \frac{-2}{\sqrt{5}} - \frac{20}{\sqrt{5}} \end{pmatrix} = -11 \begin{pmatrix} \frac{1}{\sqrt{5}} \\ \frac{2}{\sqrt{5}} \end{pmatrix}$$

$$E = -11 \text{ eV}$$

$$\mathbf{H}\mathbf{c} = \begin{pmatrix} \varepsilon_{Li} & V \\ V & \varepsilon_H \end{pmatrix} \begin{pmatrix} \frac{2}{\sqrt{5}} \\ \frac{-1}{\sqrt{5}} \end{pmatrix} = \begin{pmatrix} -7 & -2 \\ -2 & -10 \end{pmatrix} \begin{pmatrix} \frac{2}{\sqrt{5}} \\ \frac{-1}{\sqrt{5}} \end{pmatrix} = \begin{pmatrix} \frac{-14}{\sqrt{5}} + \frac{2}{\sqrt{5}} \\ \frac{-4}{\sqrt{5}} + \frac{10}{\sqrt{5}} \end{pmatrix} = -6 \begin{pmatrix} \frac{2}{\sqrt{5}} \\ \frac{-1}{\sqrt{5}} \end{pmatrix}$$

$$E = -6 \text{ eV}$$

B) Using the orbitals above, what is the partial charge on Li,  $q_{Li}$ , when LiH is in its electronic ground state?

*(6 points) The first vector is the ground state, which will have two valence electrons. The number probability that each of those electrons ends up on Li is just  $|c_1|^2$ . Thus, the number of electrons on Li is  $2 |c_1|^2$  and the charge is going to be  $1 - 2 |c_1|^2$ . Plugging in:*

$$q_{Li} = 1 - 2 |c_1|^2 = 1 - 2 * (1/\sqrt{5})^2 = 3/5 = +0.6.$$

*This seems about right: The Hydrogen is more electronegative and so it should grab more of the bonding electrons.*

C) If the nuclear charge on Li were increased (say to +3.1 e), how would each of the MO quantities below change? You may briefly justify your answers. Recall that a negative number becoming more positive corresponds to an increase, even though the absolute value decreases.

$\epsilon_{Li}$	<b>Increase</b>	<u><b>Decrease</b></u>	<b>No Change</b>
$\epsilon_H$	<b>Increase</b>	<b>Decrease</b>	<u><b>No Change</b></u>
$V$	<b>Increase</b>	<b>Decrease</b>	<u><b>No Change</b></u>
$q_{Li}$	<u><b>Increase</b></u>	<b>Decrease</b>	<b>No Change</b>

*(6 points) Intended Answer: Increased charge will lower energy on Li. Charge on Li will increase because the nuclear charge has increased (more electrons will flow to it, but less than the change in nuclear charge). All other quantities do not change. A case could be made for the following variations:*

*$\epsilon_H$  decreases slightly because of attraction of H 1s to Li nucleus.*

*$V$  decreases slightly because Li 2s orbital contracts.*

*$q_{Li}$  decreases because you forgot that the nuclear charge went up.*

*Points given for variant answers if they were justified.*

D) If we increased the bond length,  $R$ , how would each of the MO quantities below change? You may briefly justify your answers. Recall that a negative number becoming more positive corresponds to an increase, even though the absolute value decreases.

$\epsilon_{Li}$	<b>Increase</b>	<b>Decrease</b>	<u><b>No Change</b></u>
$\epsilon_H$	<b>Increase</b>	<b>Decrease</b>	<u><b>No Change</b></u>
$V$	<u><b>Increase</b></u>	<b>Decrease</b>	<b>No Change</b>
$q_{Li}$	<u><b>Increase</b></u>	<b>Decrease</b>	<b>No Change</b>

*(6 points) Intended Answer: Increased bond distance reduces the magnitude of the resonance integral (increases in absolute value), which means less equal electron sharing (less covalency) and thus more ionic character, which will increase the charge on Li. All other quantities do not change. A case could be made that the energies will both go up slightly due to lower electron-nuclear attraction, and points were given for this answer if a justification was given.*

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