

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) _____

Problem 2 (30 pts) _____

Problem 3 (30 pts) _____

TOTAL: (100 pts) _____

Name : _____

TA: _____

Short Answer (40 points)

1) (7 Points) For a particular hydrogen orbital, ψ_{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 He^+ ?

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

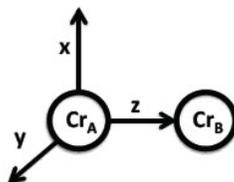
3p_x3p_y4d_{xy}4d_{z²}

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.

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

- 6) (10 points) Consider the MO picture of bonding in 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	$d_{x^2-y^2}^A$	$d_{x^2-y^2}^B$
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$d_{z^2}^A$	(
$d_{z^2}^B$									
d_{xz}^A									
d_{xz}^B									
d_{yz}^A									
d_{yz}^B									
d_{xy}^A									
d_{xy}^B									
$d_{x^2-y^2}^A$									
$d_{x^2-y^2}^B$									

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

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 [$1s^2 2s^1$]?
- B) Compute the IP of Li in the $1s^2 3s^1$ excited state. Is the ionization potential larger or smaller?
- C) Compute the IP of Li in the $1s^2 4s^1$ excited state. Is the ionization potential larger or smaller?

- 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_{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_{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_{eff} values for the 2s, 3s and 4s orbitals in Li. How do you rationalize your results?

PROBLEM 3 (30 points)— Molecular Orbital Theory

Consider the σ 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 ,

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

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

- 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.]

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

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.

ϵ_{Li}	increase	Decrease	No Change
ϵ_H	increase	Decrease	No Change
V	increase	Decrease	No Change
q_{Li}	increase	Decrease	No Change

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.

ϵ_{Li}	increase	Decrease	No Change
ϵ_H	increase	Decrease	No Change
V	increase	Decrease	No Change
q_{Li}	increase	Decrease	No Change

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