(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, $\psi_{nlm}$, 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 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: $p_x \propto Y_1^1 + Y_1^{-1}$; $p_y \propto Y_1^1 - Y_1^{-1}$; $d_{xz} \propto Y_2^1 + Y_2^{-1}$; $d_{yz} \propto Y_2^1 - Y_2^{-1}$; $d_{xy} \propto Y_2^2 + Y_2^{-2}$; $d_{x^2-y^2} \propto Y_2^2 - Y_2^{-2}$]

<table>
<thead>
<tr>
<th>5s</th>
<th>3px</th>
<th>3py</th>
<th>4dxy</th>
<th>4dz$^2$</th>
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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 Cr₂. Ignore all the orbitals except for the outermost d shell, so that there are 10 atomic orbitals available for making molecular orbitals (d₂", d₁", dₓz", dᵧz", dₓy", dₓ₂₋ᵧ²", dᵧ₂₋ₓ²"). Assume the molecule is oriented along the z axis:

![Diagram of Cr₂ molecule]

When you build the Hamiltonian matrix, \( H \), 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.

\[
\begin{bmatrix}
  dᵧz^A & dᵧz^B & dₓy^A & dₓy^B & dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & \\
  dᵧz^A & dᵧz^B & dₓy^A & dₓy^B & dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & \\
  dₓy^A & dₓy^B & dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & & & \\
  dₓy^A & dₓy^B & dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & & & \\
  dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & & & & & \\
  dₓ₂₋ᵧ²^A & dₓ₂₋ᵧ²^B & & & & & & & & \\
\end{bmatrix}
\]
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{align*}
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{align*}

A) What is the ionization potential (IP) of Li in its ground state [1s²2s¹]?

B) Compute the IP of Li in the 1s²3s¹ excited state. Is the ionization potential larger or smaller?

C) Compute the IP of Li in the 1s²4s¹ 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, \( Z_{\text{eff}} \), 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 \( Z_{\text{eff}} \)

\[
IP = E(\text{cation}) - E(\text{neutral}) = \frac{m e^4 Z_{\text{eff}}^2}{32 \pi^2 \varepsilon_0^2 \hbar^2 n^2}
\]

Compute the correct \( Z_{\text{eff}} \) values for the 2s, 3s and 4s orbitals in Li. How do you rationalize your results?
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
$$\psi_{\sigma} = c_1 2s_{Li} + c_2 1s_{H}$$

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.]
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.

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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.

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5.61 Physical Chemistry
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