Chem 452 – Exam II
October 13, 2010

Cover Sheet
Closed Book, Closed Notes

There are 4 problems. The point value of each problem is indicated.
At the end of the exam are tables with the spherical harmonics, the hydrogenic radial
wavefunctions, and the shapes of the familiar hydrogenic atomic orbitals.

Useful Equations:

Average value of operator $\langle A \rangle = \int \phi^* \hat{A} \phi \, dx$

$h = 6.626 \cdot 10^{-34}$ Js

$hbar = h/2\pi$

$E_n = -\hbar c R_n \frac{Z^2}{n^2} = -\frac{Z^2}{n^2} \frac{\hbar^2}{2\mu a_0^2}$

$R_n = 109677 \text{cm}^{-1}$

$\hbar c R_n = 13.6 eV$

$\rho = \left( \frac{2Z}{na_0} \right) r$

$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$

$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$

$\hat{L}_z = -i\hbar \frac{d}{d\phi}$

$|L_z| = m\hbar$

$L = \sqrt{l(l+1)} \hbar$

$E_m = \frac{m^2 \hbar^2}{2I}$

$E_l = \frac{l(l-1)\hbar^2}{2I}$

$E_v = (\nu + \frac{1}{2}) \hbar \omega$

$V = \frac{1}{2} kx^2$

$\omega = \sqrt{\frac{k}{m}}$

$\alpha = \left( \frac{\hbar^2}{km} \right)^{1/4}$

$x_{ct} = \sqrt{2\nu + 1} \alpha$

$y = x/\alpha$

$ax^2 + bx + c = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$l = 0, 1, 2, 3$

$s \quad p \quad d \quad f$

$\sin \phi = -\frac{1}{2} \left( e^{i\phi} - e^{-i\phi} \right)$

$\cos \phi = \frac{1}{2} \left( e^{i\phi} + e^{-i\phi} \right)$
<table>
<thead>
<tr>
<th>Problem</th>
<th>Possible Score</th>
<th>Your Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td></td>
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<tr>
<td>4</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
1. (30 points) Consider an electron with mass, \( m = 9.11 \cdot 10^{-31} \) kg, residing in a harmonic potential with spring constant, \( k = 150 \) N/m.

   a. (10 points) Calculate the total energy and the corresponding quantum number for the electron if its classical turning points occur at \( x = \pm 3.68 \cdot 10^{-10} \) m.

\[
X_{CT} = \sqrt{2n+1} \alpha = \sqrt{2n+1} \left( \frac{k}{\hbar m} \right)^{1/4}
\]

Solve for \( \sqrt{2n+1} \).

\[
\sqrt{2n+1} = X_{CT} \left( \frac{\hbar m}{k} \right)^{1/4}
\]

\[
V = \frac{1}{2} \left[ X_{CT}^2 \left( \frac{\hbar m}{k} \right)^{1/2} - 1 \right]
\]

\[
V = \frac{1}{2} \left[ (3.68 \cdot 10^{-10})^2 \sqrt{\left( \frac{150 \text{ N/m}}{9.11 \cdot 10^{-31} \text{ kg}} \right)} \left( \frac{1}{2n} \right) \left( 6.626 \cdot 10^{-34} \text{ Js} \right) - 1 \right]
\]

\[
V = 7.0
\]

\[
E_v = (V + \frac{1}{2}) \hbar \omega = (V + \frac{1}{2}) \hbar \sqrt{k/m}
\]

\[
E_{V=7} = \frac{15}{2} \left( \frac{1}{2n} \right) \left( 6.626 \cdot 10^{-34} \text{ Js} \right) \left( \frac{150 \text{ N/m}}{9.11 \cdot 10^{-31} \text{ kg}} \right)^{1/2}
\]

\[
E_{V=7} = 1.01 \cdot 10^{-17} \text{ J}
\]
b. (6 points) Based on what you know of the equations for the wavefunctions of the quantum mechanical harmonic oscillator, $\psi_n = N_n H_n(y) \exp\left(-y^2/2\right)$, identify the Hermite polynomials corresponding to the following two wavefunctions.

- 3 nodes $\Rightarrow$ 3rd order polynomial
  
  $H_3(y) = 8y^3 - 12y$

- 6 nodes $\Rightarrow$ 6th order polynomial
  
  $H_6(y) = 64y^6 - 480y^4 + 720y^2 - 120$

<table>
<thead>
<tr>
<th>$V$</th>
<th>$H_v(y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>$2y$</td>
</tr>
<tr>
<td>2</td>
<td>$4y^2 - 2$</td>
</tr>
<tr>
<td>3</td>
<td>$8y^3 - 12y$</td>
</tr>
<tr>
<td>4</td>
<td>$16y^4 - 48y^2 + 12$</td>
</tr>
<tr>
<td>5</td>
<td>$32y^5 - 160y^3 + 120y$</td>
</tr>
<tr>
<td>6</td>
<td>$64y^6 - 480y^4 + 720y^2 - 120$</td>
</tr>
</tbody>
</table>
c. Describe the change of the classical turning points of a quantum mechanical harmonic oscillator for the following changes… Justify your answers.

(4 points) the total energy is doubled
energy cannot be precisely doubled. Full credit for pointing this out.
approximating $E \approx V$, doubling $E$ causes $X_{CT}$ increase by $\sqrt{2}$.

(4 points) the mass is doubled
according to above formula,
doubling mass causes $X_{CT}$ to decrease by $(\frac{1}{2})^{1/4}$


d. (6 points) Explain why the quantum mechanical particle in a box cannot tunnel into the classically forbidden region but the quantum mechanical harmonic oscillator can.

In the P.B., the potential abruptly goes to infinity at the walls forcing $\Psi = 0$ at the walls => no tunneling.

In the H.O., the potential varies smoothly everywhere and is only equal to the total energy (not infinite) at the classical turning point. Thus, $\Psi = 0$ at the walls and the particle tunnels.
2. (16 points) A particle moves along the surface of a sphere with moment of inertia, $I$, and has the following wave function.

$$\psi = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{2i\phi}$$

a. (4 points) Use the tables at the end of the exam to identify the quantum number(s) associated with this state.

$$l = 3, \ m_l = 2$$

b. (4 points) Calculate the total angular momentum of this state?

$$L = \sqrt{l(l+1)} \hbar = \sqrt{12} \hbar$$

c. (4 points) What is the $z$-component of the total angular momentum?

$$L_z = m_e \hbar = 2 \hbar$$

d. (4 points) What is the total energy associated with this state?

$$E = \frac{l(l+1) \hbar^2}{2I} = \frac{6 \hbar^2}{I}$$
3. (32 points) The following questions are about hydrogenic atoms.

a. (6 points) Calculate the ionization energy of a C$^{5+}$ ion in the state with $n = 3$. Give your answer in electron-volts.

\[ \text{I. E. } = E_n - E_n = 0 - \left( -13.6 \text{ eV} \frac{Z^2}{n^2} \right) = 13.6 \left( \frac{6^2}{3^2} \right) = 54.4 \text{ eV} \]

b. (8 points) Below are plots of the 2s orbital of a H atom corresponding to the radial distribution function, $P_{2s}(r)$, and the wavefunction, $\Psi_{2s}(r)$. i) Write the expression used to calculate $P_{2s}(r)$ from the wavefunction. ii) Give a physical explanation of why the radius at which $P_{2s}(r)$ is maximum does not correspond to the radius at which the wavefunction is maximum.

\[ P_{2s}(r) = \int_0^\infty \int_0^{2\pi} |\Psi_{2s}|^2 r^2 \sin \theta \, d\theta \, d\phi \]

\[ = r^2 |R_{2s}(r)|^2 \]

where $\Psi_{2s} = R_{2s} \Psi_0$.

i) $P_{2s}$ is maximum at larger $r$ than $\Psi_{2s}$ because $P_{2s}$ includes an integration over a sphere of radius, $r$. The volume of the sphere of integration increases with $r$ which makes the second maximum around $r = 6$ the global maximum.

ii) Either answer is okay, but student must show relationship of $R_{2s}$ to $\Psi_{2s}$.
c. (10 points) i) Write the complete expression for the 3d\(_{xy}\) orbital of a hydrogenic atom. ii)
Identify the location(s) of any radial nodes in the wavefunction if any are present. Justify your answers. *Hint:* you may want to use the tables at the end of the exam and may also find it useful to take a linear combination of complex exponentials to answer this question.

\[ \psi_{3d_{xy}} = R_{3,2}(r) Y_{2,1} \]

*3d\(_{xy}\) orbital lies in xy plane, so look for Y\(_{2,1}\) with sin \( \Theta \) dependence \( \Rightarrow \) Y\(_{2,1}\)*

*3d\(_{xy}\) orbital has nodes on x and y axes \( (\phi=0) \quad (\phi=\frac{\pi}{2}) \)*

This behavior looks \( 2i\sin 2\phi \)

\[ 2i\sin 2\phi = e^{i2\phi} - e^{-i2\phi} \]

Angular distribution looks like \( \sin^2 \theta \sin 2\phi \Rightarrow Y_{2,2} - Y_{2,-2} \)

\[
\psi_{3d_{xy}} = \left[ \frac{1}{12430} \left( \frac{Z}{\alpha_0} \right)^{\frac{3}{2}} \rho^2 e^{-\rho/2} \right] \left( \frac{15}{32\pi} \right)^{\frac{1}{2}} \frac{2i}{\sqrt{2}} \sin^2 \theta \sin 2\phi
\]

\[ \rho = \frac{2Z}{3\alpha_0} r \]

ii) no radial nodes because polynomial is zeroth order.
d) (8 points) i) Calculate the number and locations of the radial nodes (if any) in the 3s hydrogenic orbital. ii) Arrange electrons in the following orbitals in order of increasing kinetic energy in the radial coordinate:

\[ 3s \quad 3p \quad 3d \]

It is essential to justify your answer to receive full credit on question ii. *Hint:* you may find it useful to consider the wave nature of matter and its relationship to momentum.

i) \( \psi_{3s} = R_{3s} Y_{0,0} \)

\[ R_{3s} = \frac{1}{\sqrt{24\pi^3}} \left( \frac{Z}{a_0} \right)^{3/2} (6 - 6\rho + \rho^2)e^{-\rho/2} \]

\[ \rho = \frac{2Z}{3a_0} r \]

Node where \( R_{3s} = 0 \) but not at \( r = 0 \)

occurs where \( 6 - 6\rho + \rho^2 = 0 \)

Solve for \( \rho = \frac{6 \pm \sqrt{6^2 - 4(1)(6)}}{2} = 3 \pm \frac{1}{2}\sqrt{12} \)

Two nodes at \( \rho = 3 - \sqrt{3} \) and \( 3 + \sqrt{3} \)

ii) recall that shorter wavelength corresponds to higher momentum \( p = \frac{\hbar}{\lambda} \) and thus higher k.E. = \( \frac{p^2}{2m} \).

\( \psi_{3s} \) has 2 radial nodes => highest k.E.
\( \psi_{3p} \) has 1 radial node => medium k.E.
\( \psi_{3d} \) has 0 radial nodes => lowest k.E.

Order of increasing k.E.: \( \psi_{3d} < \psi_{3p} < \psi_{3s} \)
4. (22 points) Many electrons atoms.

a. (6 points) The total angular momentum of the highest energy electrons of an element is $2.583 \cdot 10^{-34}$ kg m$^2$/s. To what block does this element belong in the Periodic Table (s, p, d, or f)?

\[ L = \sqrt{l(l+1)} \frac{\hbar}{\hbar} \text{ solve for } l \]
\[ \ell(\ell+1) = \left( \frac{1}{\ell} \right)^2 \left( \frac{2.583 \cdot 10^{-34} \text{ kg m}^2/\text{s}}{\frac{1}{2\pi} (6.626 \cdot 10^{-34} \text{ Kg m}^2/\text{s})} \right)^2 \]
\[ \ell(\ell+1) = 6.00 = 2(3) \]
\[ \ell = 2 \text{ d-block element} \]

b. (5 points) Write the exact Hamiltonian operator for He. Give the explicit functional forms for all operators but represent the Laplacian for electron $i$ as $\nabla_i^2$. Clearly indicate the physical meaning of each term.

\[ H_{He} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi \varepsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi \varepsilon_0 r_{12}} \]
\[ \text{K.E. of electrons 1 and 2} \]
\[ \text{P.E. of attraction of electrons to nucleus} \]
\[ \text{P.E. of repulsion of electrons from each other.} \]
c. (5 points) The orbital approximation always predicts energies of atoms that are too low (more negative than they should be). Give a physical reason why this is so and explain how adopting an effective nuclear charge partially corrects this error.

The orbital approximation predicts energies too low because it ignores the repulsion of electrons (which raises the energy of each electron and thus of the atom).

Adopting an effective nuclear charge artificially raises the energy of electrons (and thus the atom) by decreasing the calculated attraction of electrons to the nucleus.

d. (6 points) Give a complete space-spin wavefunction that satisfies the Pauli Principle for the excited (1s2s) triplet state of He.

Pauli Principle requires that \( \Psi_{(1,2)} = \Psi_{(2,1)} \)

\[ \Psi_{He} = \Psi_{\text{space}} \sigma_{\text{spin}} \]

\[ \Psi_{\text{space}} = \frac{1}{\sqrt{2}} (1s(1)2s(2) - 2s(1)1s(2)) \]

\[ \sigma_{\text{spin}} = \alpha(1) \alpha(2) \]

\[ \Psi_{He} = \frac{1}{\sqrt{2}} (1s(1)2s(2) - 2s(1)1s(2)) \alpha(1) \alpha(2) \]

also acceptable: \( \beta(1) \beta(2) \)

\[ \frac{1}{\sqrt{2}} (\alpha(1) \beta(2) + \beta(1) \alpha(2)) \]
Table 9.3 The spherical harmonics

<table>
<thead>
<tr>
<th>l</th>
<th>m_i</th>
<th>$Y_{lm_i}(\theta, \phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\left( \frac{1}{4\pi} \right)^{1/2}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\left( \frac{3}{4\pi} \right)^{1/2} \cos \theta$</td>
</tr>
<tr>
<td>±1</td>
<td>±1</td>
<td>$\pm \left( \frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left( \frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>±1</td>
<td>±1</td>
<td>$\pm \left( \frac{15}{8\pi} \right)^{1/2} \cos \theta \sin \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>±2</td>
<td>±2</td>
<td>$\left( \frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\left( \frac{7}{16\pi} \right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$</td>
</tr>
<tr>
<td>±1</td>
<td>±1</td>
<td>$\pm \left( \frac{21}{64\pi} \right)^{1/2} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>±2</td>
<td>±2</td>
<td>$\left( \frac{105}{32\pi} \right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>±3</td>
<td>±3</td>
<td>$\pm \left( \frac{35}{64\pi} \right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$</td>
</tr>
</tbody>
</table>
### Table 10.1 Hydrogenic radial wavefunctions

<table>
<thead>
<tr>
<th>Orbital</th>
<th>( n )</th>
<th>( l )</th>
<th>( R_{n,l} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\text{s}</td>
<td>1</td>
<td>0</td>
<td>( 2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2} )</td>
</tr>
<tr>
<td>2\text{s}</td>
<td>2</td>
<td>0</td>
<td>( \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2 - \rho) e^{-\rho/2} )</td>
</tr>
<tr>
<td>2\text{p}</td>
<td>2</td>
<td>1</td>
<td>( \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2} )</td>
</tr>
<tr>
<td>3\text{s}</td>
<td>3</td>
<td>0</td>
<td>( \frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/2} )</td>
</tr>
<tr>
<td>3\text{p}</td>
<td>3</td>
<td>1</td>
<td>( \frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4 - \rho) \rho e^{-\rho/2} )</td>
</tr>
<tr>
<td>3\text{d}</td>
<td>3</td>
<td>2</td>
<td>( \frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2} )</td>
</tr>
</tbody>
</table>

\( \rho = (2Z/na) r \) with \( a = 4\pi\varepsilon_0 \hbar^2/\mu e^2 \). For an infinitely heavy nucleus (or one that may be assumed to be so), \( \mu = m_e \) and \( a = a_0 \), the Bohr radius. The full wavefunction is obtained by multiplying \( R \) by the appropriate \( Y \) given in Table 9.3.