**Chemistry 410A** **Exam 2** **Fall 2011**

## NAME:

**Instructions:**

1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

**Other notes:**

- **The first page portion of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

   (a) What is the degeneracy of the lowest excited energy level for a particle in a box with dimensions $a = b = 4.0\,\text{nm}$, $c = 2.0\,\text{nm}$?

   (b) Write the wavefunction for an electron in the ground state of a cubical box, with each side of length $a$.

   (c) For the $6p$ subshell,

      i. what are the values of $n$ and $l$, and what are the possible values of $m_l$?

      ii. how many radial nodes does the wavefunction have?

      iii. how many angular nodes does the wavefunction have?

      iv. how many orbitals are there in the subshell?

      v. what is the probability density at $r = 0$?

2. A particle in a three-dimensional cubical box of volume $8.0\,\text{Å}^3$ is in the (2,2,2) state with a total kinetic energy of $6.0 \cdot 10^{-20}$ J. Give the following:

   (a) the zero-point energy (in J);

   (b) $\lambda_{\text{dB}}$ (in Å) of the particle along any axis;

   (c) the new energy in the (2,2,2) state if we double the length of each side of the box.

   (d) the mass (in kg) of the particle;

3. For the $7d$ state of $Li^{2+}$ with $m_l = -1$, calculate the following **in SI units**:

   (a) the energy;

   (b) the value of the orbital angular momentum;

   (c) the projection of the orbital angular momentum onto the $z$ axis.

4. To convert from the Cartesian coordinate $x$ to polar coordinates, we use the relation

$$x = r \sin\theta \cos\phi.$$

Write the expression we would need to solve in order to to find the **root mean square value of $x$, equal to $\sqrt{\langle x^2 \rangle}$,** of the electron in the $4f_{m_l=-3}$ state of atomic hydrogen. Factor your final answer into single-integral terms (meaning, one integral for each coordinate). Provide all the information needed for a computer to calculate the value.

Bohr atom:
$$r_n = \frac{n^2}{Z} a_0 \qquad v_n = \frac{Ze^2}{(4\pi\epsilon_0) n\hbar}$$
$$E_n = -\frac{Z^2}{2n^2} E_{\rm h} \qquad L_n = m_e r_n v_n = n\hbar$$

particle in a 3-D box:
$$\psi(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi x}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$
$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Laplacian:
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$
$$= \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

1-electron Hamiltonian:
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{2m_e r^2}\hat{L}^2(\theta,\phi) - \frac{Ze^2}{(4\pi\epsilon_0)r}$$

$$\hat{L}^2 Y_l^{m_l}(\theta,\phi) = \hbar^2\, l(l+1)\, Y_l^{m_l}(\theta,\phi)$$
$$\hat{L}_z Y_l^{m_l}(\theta,\phi) = \hbar\, m_l\, Y_l^{m_l}(\theta,\phi)$$

Angular and radial terms in the one-electron wavefunctions.

| $l$ | $m_l$ | $Y_l^{m_l}(\theta,\ \phi)$ | $n$ | $l$ | $R_{nl}(r)$ |
|---|---|---|---|---|---|
| 0 | 0 | $\sqrt{\frac{1}{4\pi}}$ | 1 | 0 | $2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$ |
| 1 | 0 | $\sqrt{\frac{3}{4\pi}}\ \cos\theta$ | 2 | 0 | $\frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/(2a_0)}$ |
| 1 | $\pm1$ | $\sqrt{\frac{3}{8\pi}}\ \sin\theta\ e^{\pm i\phi}$ | 2 | 1 | $\frac{1}{\sqrt{24}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) e^{-Zr/(2a_0)}$ |
| 2 | 0 | $\sqrt{\frac{5}{6\pi}}\ (3\cos^2\theta - 1)$ | 3 | 0 | $\frac{2}{\sqrt{27}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{2Zr}{3a_0}+\frac{2Z^2r^2}{27a_0^2}\right) e^{-Zr/(3a_0)}$ |
| 2 | $\pm1$ | $\sqrt{\frac{15}{8\pi}}\ \sin\theta\cos\theta\ e^{\pm i\phi}$ | 3 | 1 | $\frac{4\sqrt{2}}{27\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/(3a_0)}$ |
| 2 | $\pm2$ | $\sqrt{\frac{15}{32\pi}}\ \sin^2\theta\ e^{\pm 2i\phi}$ | 3 | 2 | $\frac{2\sqrt{2}}{81\sqrt{15}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/(3a_0)}$ |
| 3 | 0 | $\sqrt{\frac{7}{16\pi}}\ \cos\theta(5\cos^2\theta - 3)$ | 4 | 0 | $\frac{1}{4}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{3Zr}{4a_0}+\frac{Z^2r^2}{8a_0^2}-\frac{Z^3r^3}{192a_0^3}\right) e^{-Zr/(4a_0)}$ |
| 3 | $\pm1$ | $\sqrt{\frac{21}{64\pi}}\ \sin\theta(5\cos^2\theta - 1)\ e^{\pm i\phi}$ | 4 | 1 | $\frac{\sqrt{5}}{16\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{4a_0}+\frac{Z^2r^2}{80a_0^2}\right) e^{-Zr/(4a_0)}$ |
| 3 | $\pm2$ | $\sqrt{\frac{105}{32\pi}}\ \sin^2\theta\cos\theta\ e^{\pm 2i\phi}$ | 4 | 2 | $\frac{1}{64\sqrt{5}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2\left(1-\frac{Zr}{12a_0}\right) e^{-Zr/(4a_0)}$ |
| 3 | $\pm3$ | $\sqrt{\frac{35}{64\pi}}\ \sin^3\theta\ e^{\pm 3i\phi}$ | 4 | 3 | $\frac{1}{768\sqrt{35}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^3 e^{-Zr/(4a_0)}$ |

## Fundamental Constants

| | | |
|---|---|---|
| Avogadro's number | $\mathcal{N}_A$ | $6.0221367 \cdot 10^{23}$ mol$^{-1}$ |
| Bohr radius | $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ | $5.29177249 \cdot 10^{-11}$ m |
| Boltzmann constant | $k_B$ | $1.380658 \cdot 10^{-23}$ J K$^{-1}$ |
| electron rest mass | $m_e$ | $9.1093897 \cdot 10^{-31}$ kg |
| fundamental charge | $e$ | $1.6021773 \cdot 10^{-19}$ C |
| permittivity factor | $4\pi\epsilon_0$ | $1.113 \cdot 10^{-10}$ C$^2$ J$^{-1}$ m$^{-1}$ |
| gas constant | $R$ | 8.314510 J K$^{-1}$ mol$^{-1}$ |
| | $R$ | 0.08314510 L bar K$^{-1}$ mol$^{-1}$ |
| | $R$ | 0.08206 L atm K$^{-1}$ mol$^{-1}$ |
| hartree | $E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$ | $4.35980 \cdot 10^{-18}$ J |
| Planck's constant | $h$ | $6.6260755 \cdot 10^{-34}$ J s |
| | $\hbar$ | $1.05457266 \cdot 10^{-34}$ J s |
| proton rest mass | $m_p$ | $1.6726231 \cdot 10^{-27}$ kg |
| neutron rest mass | $m_n$ | $1.6749286 \cdot 10^{-27}$ kg |
| speed of light | $c$ | $2.99792458 \cdot 10^{8}$ m s$^{-1}$ |

## Unit Conversions

| | K | cm$^{-1}$ | kJ mol$^{-1}$ | kcal mol$^{-1}$ | erg | kJ |
|---|---|---|---|---|---|---|
| kHz = | $4.799 \cdot 10^{-8}$ | $3.336 \cdot 10^{-8}$ | $3.990 \cdot 10^{-10}$ | $9.537 \cdot 10^{-11}$ | $6.626 \cdot 10^{-24}$ | $6.626 \cdot 10^{-34}$ |
| MHz = | $4.799 \cdot 10^{-5}$ | $3.336 \cdot 10^{-5}$ | $3.990 \cdot 10^{-7}$ | $9.537 \cdot 10^{-8}$ | $6.626 \cdot 10^{-21}$ | $6.626 \cdot 10^{-31}$ |
| GHz = | $4.799 \cdot 10^{-2}$ | $3.336 \cdot 10^{-2}$ | $3.990 \cdot 10^{-4}$ | $9.537 \cdot 10^{-5}$ | $6.626 \cdot 10^{-18}$ | $6.626 \cdot 10^{-28}$ |
| K = | 1 | 0.6950 | $8.314 \cdot 10^{-3}$ | $1.987 \cdot 10^{-3}$ | $1.381 \cdot 10^{-16}$ | $1.381 \cdot 10^{-26}$ |
| cm$^{-1}$ = | 1.4388 | 1 | $1.196 \cdot 10^{-2}$ | $2.859 \cdot 10^{-3}$ | $1.986 \cdot 10^{-16}$ | $1.986 \cdot 10^{-26}$ |
| kJ mol$^{-1}$ = | $1.203 \cdot 10^{2}$ | 83.59 | 1 | 0.2390 | $1.661 \cdot 10^{-14}$ | $1.661 \cdot 10^{-24}$ |
| kcal mol$^{-1}$ = | $5.032 \cdot 10^{2}$ | $3.498 \cdot 10^{2}$ | 4.184 | 1 | $6.948 \cdot 10^{-14}$ | $6.948 \cdot 10^{-24}$ |
| eV = | $1.160 \cdot 10^{4}$ | $8.066 \cdot 10^{3}$ | 96.49 | 23.06 | $1.602 \cdot 10^{-12}$ | $1.602 \cdot 10^{-22}$ |
| hartree = | $3.158 \cdot 10^{5}$ | $2.195 \cdot 10^{5}$ | $2.625 \cdot 10^{3}$ | $6.275 \cdot 10^{2}$ | $4.360 \cdot 10^{-11}$ | $4.360 \cdot 10^{-21}$ |
| erg = | $7.243 \cdot 10^{15}$ | $5.034 \cdot 10^{15}$ | $6.022 \cdot 10^{13}$ | $1.439 \cdot 10^{13}$ | 1 | $10^{-10}$ |
| J = | $7.243 \cdot 10^{22}$ | $5.034 \cdot 10^{22}$ | $6.022 \cdot 10^{20}$ | $1.439 \cdot 10^{20}$ | $10^{7}$ | $10^{-3}$ |
| dm$^3$ bar = | $7.243 \cdot 10^{24}$ | $5.034 \cdot 10^{24}$ | $6.022 \cdot 10^{22}$ | $1.439 \cdot 10^{22}$ | $1.000 \cdot 10^{9}$ | 0.1000 |
| kJ = | $7.243 \cdot 10^{25}$ | $5.034 \cdot 10^{25}$ | $6.022 \cdot 10^{23}$ | $1.439 \cdot 10^{23}$ | $10^{10}$ | 1 |

| | | | |
|---|---|---|---|
| **distance** | 1 Å = | $10^{-10}$ m | |
| **mass** | 1 amu = | $1.66054 \cdot 10^{-27}$ kg | |
| **energy** | 1 J = | 1 kg m$^2$ s$^{-2}$ | = $10^7$ erg |
| **force** | 1 N = | 1 kg m s$^{-2}$ | = $10^5$ dyn |
| **electrostatic charge** | 1 C = | 1 A s | = $2.9979 \cdot 10^9$ esu |
| | 1 D = | $3.3357 \cdot 10^{-30}$ C m | = $1 \cdot 10^{-18}$ esu cm |
| **magnetic field strength** | 1 T = | 1 kg s$^{-2}$ A$^{-1}$ | = $10^4$ gauss |
| **pressure** | 1 Pa = | 1 N m$^{-2}$ | = 1 kg m$^{-1}$ s$^{-2}$ |
| | 1 bar = | $10^5$ Pa | = 0.98692 atm |