Chemistry 410A **Exam 2** **Spring 2008**

NAME:

Instructions:

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

Other notes:

- **Your 4 best scores of the 5 problems will constitute your total score.**
- Partial credit is available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points, but they are not intended to be equally easy.

1. Write the normalized wavefunction for any state of an electron in a cubical box with length a on each side and total energy $E = 14\pi^2\hbar^2/(8m_e a^2)$.

2. Let the atomic nucleus, instead of being a point charge, be a hollow sphere of radius r_0, such that the potential of the electron is

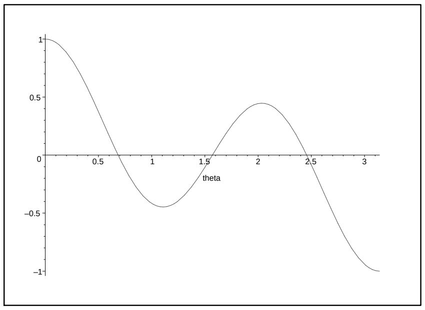
$$U(r) = -\frac{Ze^2}{4\pi\epsilon_0(r - r_0)}.$$

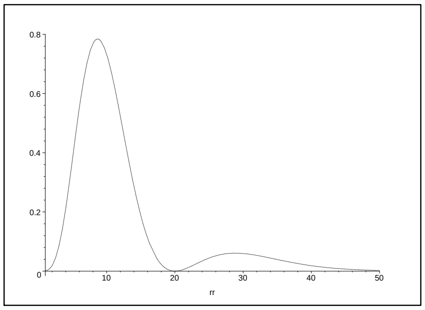
   (a) Do the wavefunctions for this new system have separable angular and radial coordinates?

   (b) Will the electron have any density at $r < r_0$?

   (c) Sketch below what you think a graph of the r-dependent part of the lowest energy wavefunction will look like.

3. Identify the $n,\ l,\ m_l$ quantum numbers of the orbital represented below. The angular wavefunction is shown, as a *linear* plot (rather than a polar plot) of $Y(\theta, \phi)$ vs. θ. The radial probability density, not the radial waverfunction, is given. The function does not depend on ϕ.





4. Write the expression necesary to calculate $\langle \phi^2 \rangle^{1/2}$, the root mean square ϕ value of the $2p_{m_l=1}$ state of Li^{2+}.

5. The table below lists several operators. If our wavefunctions for the one-electron atom are eigenfunctions of that operator, write "yes" and give the eigenvalue. If not, write "no."

operator	**is $\psi_{n,l,m_l}(r,\theta,\phi)$ an eigenfunction?**	**eigenvalue**
$\hat{K}$		
U		
$\hat{H}$		
$\hat{L}^2$		
$\hat{L}_z^2$		
r		

Bohr atom: $$r_n = \frac{n^2}{Z} a_0 \qquad v_n = \frac{Ze^2}{(4\pi\epsilon_0) n\hbar}$$

$$E_n = -\frac{Z^2}{2n^2}\, E_\mathrm{h} \qquad L_n = m_e r_n v_n = n\hbar$$

momentum operator: $$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

kinetic energy operator: $$\hat{K} = -\frac{\hbar^2}{2m}\nabla^2$$

particle in a 1-D box: $$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

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: $$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r}$$

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	±1	$\sqrt{\frac{3}{8\pi}}\ \sin\theta\ e^{\pm i\phi}$	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	±1	$\sqrt{\frac{15}{8\pi}}\ \sin\theta\cos\theta\ e^{\pm i\phi}$	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	±2	$\sqrt{\frac{15}{32\pi}}\ \sin^2\theta\ e^{\pm 2i\phi}$	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	±1	$\sqrt{\frac{21}{64\pi}}\ \sin\theta(5\cos^2\theta - 1)\ e^{\pm i\phi}$	4	1	$\frac{1}{16\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{4a_0}+\frac{Z^2r^2}{80a_0^2}\right) e^{-Zr/(4a_0)}$
3	±2	$\sqrt{\frac{105}{32\pi}}\ \sin^2\theta\cos\theta\ e^{\pm 2i\phi}$	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	±3	$\sqrt{\frac{35}{64\pi}}\ \sin^3\theta\ e^{\pm 3i\phi}$	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