Chemistry 410A **Exam 2** **Spring 2016**

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) put your name on your exam;
   (b) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (c) specify the correct units, if any, for your final answers;
   (d) use an appropriate number of significant digits for final numerical answers;
   (e) **stop writing and close your exam immediately when time is called.**

Other notes:

- **Problem 1 (covering all of page 3) 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) Write the complex conjugate ψ^* of the wavefunction for the $m_l = +2$ orbital of the $3d$ subshell of C^{5+}.

   (b) Circle the number for each **allowed** transition of a one-electron atom in the following list (regardless of whether absorption or emission takes place).

      i. $2s \rightarrow 1s$
      ii. $2s \rightarrow 3s$
      iii. $2s \rightarrow 3p$
      iv. $2s \rightarrow 3d$
      v. $2s \rightarrow 4s$
      vi. $2s \rightarrow 4p$
      vii. $5s \rightarrow 4p$
      viii. $4f \rightarrow 3d$

   (c) Write the Hamiltonian for B^{2+}. Use ∇^2 to represent the Laplacian operator.

   (d) Write the ground state electron configuration for the S^{2-} anion.

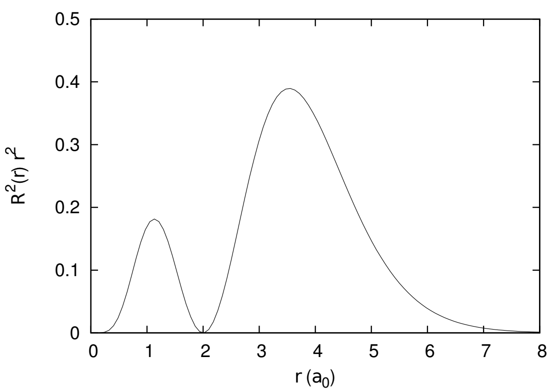
2. A the single electron in an atomic ion has orbital wavefunction $\psi_{n,l,m_l}(r,\theta,\phi)$. The unnormalized imaginary part of the angular wavefunction of $\psi_{n,l,m_l}(r,\theta,\phi)$ is equal to $-i\sin\theta\,\cos\theta\,\sin\phi$. The radial probability density is graphed below. Give the following values, and show or briefly explain how you determined each:

   (a) n

   (b) l

   (c) m_l

   (d) Z



3. The Bohr model of the atom predicts that $r_n = \frac{n^2}{Z} a_0$.

   (a) Find the value of $1/r$ for a $4f$ electron, according to the Bohr model of the hydrogen atom. Leave the answer in terms of a_0.

   (b) Now find the quantum mechanical expectation value $\langle 1/r \rangle$ for the same $4f$ electron.

4. In class, Mr. Mattocks pointed out an inconsistency in requiring the photon to have angular momentum equal to $\hbar$ while also setting the angular momentum L of the electron equal to $\hbar\sqrt{l(l+1)}$. Let's look into that more carefully (but of course please don't hold Mr. Mattocks responsible). Leave the angular momenta values in units of $\hbar$.

   (a) Find L for an electron in the $2p$ subshell.

   (b) Find L for an electron in the $3d$ subshell.

   (c) Find $\Delta L - \hbar$ for the $2p \to 3d$ subshell (write this as a decimal value times $\hbar$). This is the error in assuming that the photon angular momentum is equal to $\hbar$.

   (d) Explain the origin of this error. If you remember the explanation I offered in class, you can use that. Otherwise, a better explanation is available if you know: (i) the photon has a linear momentum $p = h/\lambda$, and (ii) like p and x, there is an uncertainty principle for p and L.

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	$E_h = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ 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

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

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

binding force: $$F_\mathrm{binding} = \frac{Z_\mathrm{A}e^2}{4\pi\epsilon_0 r_\mathrm{A}^2}\cos\theta_\mathrm{A} - \frac{Z_\mathrm{B}e^2}{4\pi\epsilon_0 r_\mathrm{B}^2}\cos\theta_\mathrm{B} - \frac{Z_\mathrm{A}Z_\mathrm{B}e^2}{4\pi\epsilon_0 R^2}$$

NMR transition energy: $$\Delta E_{\mathrm{mag},I} = |g_I\mu_N B_0(1-\sigma)|$$

chemical shift: $$\delta = \frac{\sigma_0-\sigma}{1-\sigma_0}$$

harmonic osc. $$\eta_v(R) = A_v H_v(y)e^{-(R-R_e)^2/(2c^2)}, \qquad c = \left(\frac{\hbar^2}{k\mu}\right)^{1/4}$$
$$E_v = \omega_e\left(v+\tfrac{1}{2}\right)$$

vibration $$E_\mathrm{vib} = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(v+\tfrac{1}{2}\right)^3 + \ldots$$

$$\omega_e = \hbar\sqrt{\frac{k}{\mu}} \qquad \omega_e\,(\mathrm{cm}^{-1}) = 130.28\sqrt{\frac{k\,(\mathrm{N\,m^{-1}})}{\mu\,(\mathrm{amu})}}$$

Morse potential $$U_\mathrm{M}(R) = D_e\left\{\left[1 - e^{-\beta(R-R_e)}\right]^2 - 1\right\}, \qquad \beta \approx \sqrt{\frac{k}{2D_e}}$$
$$E_{\mathrm{M},v} = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2$$

rotation $$E_\mathrm{rot} = B_v J(J+1) - D_v[J(J+1)]^2 + \ldots$$
$$B(\mathrm{cm}^{-1}) = \frac{\hbar^2}{2I(\mathrm{amu\,\AA}^2)} = \frac{16.858}{\mu(\mathrm{amu})\left[R(\mathrm{\AA})\right]^2} \quad \text{for diatomics}$$

monopole-dipole: $$u_{1-2}(R) = -\frac{\mu_\mathrm{A}q_\mathrm{B}}{R^2}$$

dipole-dipole: $$u_{2-2}(R) = -\frac{2\mu_\mathrm{A}\mu_\mathrm{B}}{(4\pi\epsilon_0)R^3}$$

dipole-dipole: $$\langle u_{2-2}\rangle_{N,\theta,\phi} = -\frac{2\mu_\mathrm{A}^2\mu_\mathrm{B}^2}{(4\pi\epsilon_0)^2 3k_\mathrm{B}TR^6},$$

dipole-induced dipole: $$u_{2-2^*}(R) = -\frac{4\mu_\mathrm{A}^2\alpha}{(4\pi\epsilon_0)R^6}$$

dispersion: $$u_\mathrm{disp}(R) \approx -\frac{\alpha^2\Delta E}{(4\pi\epsilon_0)^2\,2R^6}$$

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	$\frac{1}{768\sqrt{35}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^3 e^{-Zr/(4a_0)}$