Chemistry 410A **Exam 3** **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. In the table below, circle the orbital with the *lowest* energy in each row (i.e., the *most stable* orbital). (There is a small penalty for wrong answers.)

a.	He $1s$	U $1s$	Li $1s$
b.	Fe $3d$	Fe $4s$	Fe $4p$
c.	F $1s$	F^+ $1s$	F^- $1s$
d.	Li $2s$	Na $3s$	K $4s$
e.	O $2p$	F $2p$	Ne $2p$

2. The zero-order electronic energy of the Be atom is calculated assuming that each electron interacts with only the nucleus, as though in a one-electron atom.

   (a) Calculate the complete *zero-order* energy (in E_h) of ground state Be.

   (b) Based on the integrals given below, calculate the **total** *first-order* energy (in E_h) of ground state Be.

$$\int\int 1s(1)^2\,1s(2)^2\left(\frac{e^2}{4\pi\epsilon_0 r_{12}}\right)d\tau_1\,d\tau_2 = 2.494$$
$$\int\int 2s(1)^2\,2s(2)^2\left(\frac{e^2}{4\pi\epsilon_0 r_{12}}\right)d\tau_1\,d\tau_2 = 0.598$$
$$\int\int 1s(1)^2\,2s(2)^2\left(\frac{e^2}{4\pi\epsilon_0 r_{12}}\right)d\tau_1\,d\tau_2 = 0.839$$

3. Two atoms of ^{3}He occupy the ground state of a one-dimensional box of length a. The ^{3}He nucleus has a spin of 1/2 and the two electrons have canceling spins, so each atom can be treated as **a single particle with total spin of 1/2** and spin wavefunctions α and β (as for a single electron). Write the normalized and symmetrized two-atom wavefunction for this state.

4. Write the Hamiltonian for LiH^+.

5. A neutral atom from the second row of the periodic table (Li–Ne) has an excited electron configuration that leads to the term states ^2D, ^2P, 2^S, and ^4P. (No terms are left out.)

   (a) Write these term symbols, including J values, in order of **increasing** energy.

   (b) Identify the atom and the lowest energy electron configuration that leads to these terms.

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

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

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

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

2-electron Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$

He $1s2s$ energy:

$$E_1^{\rm PT} = E_0^{\rm PT} + \underbrace{\frac{1}{2}\int\int\left(\frac{e^2}{r_{12}}\right)1s(1)^2 2s(2)^2 d\tau_1 d\tau_2 + \frac{1}{2}\int\int\left(\frac{e^2}{r_{12}}\right)1s(2)^2 2s(1)^2 d\tau_1 d\tau_2}_{\text{Coulomb integral}}$$

$$\pm \underbrace{\int\int\left(\frac{e^2}{r_{12}}\right)1s(1)1s(2)2s(1)2s(2)d\tau_1 d\tau_2}_{\text{exchange integral}}$$

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