Chemistry 410A **Exam 3** **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 perturbation term $\hat{H}'$ in the Hamiltonian for the lithium atom.

(b) Calculate the zero order energy in E_h for the ground state lithium atom.

(c) The *binding region* is the region between two nuclei in which the binding force (as we've defined it) is positive, and forces pulling the two nuclei together exceed the forces pulling them apart. Indicate whether each of the following changes, if we could make them, would increase (write "+") or decrease (write "–") the volume of the binding region:

i. making the electron charge more negative

ii. making the nuclear charge more positive

iii. increasing the separation between the nuclei.

(d) Write the Hamiltonian for the molecule HeH^-. Use ∇^2 to represent the Laplacian operator.

2. Fill in the electron configurations in table below for the ground state of F and the lowest excited state of F^-. In the other rows of the table, Hartree-Fock energy values for F atom are given. For F^-, write $\uparrow$ if the value is greater than for F atom, $\downarrow$ if it is less than for F atom, and "0" if it is the same. (As always, when comparing negative numbers, "greater" means "less negative.")

	ground state F	**lowest excited state F^-**
electron configuration		
total energy	$-99.402\,E_\mathrm{h}$	
average energy per electron	$-11.045\,E_\mathrm{h}$	
$1s$ orbital energy	$-26.368\,E_\mathrm{h}$	
total kinetic energy	$99.300\,E_\mathrm{h}$	
average kinetic energy per electron	$11.033\,E_\mathrm{h}$	
total electron-electron repulsion	$39.796\,E_\mathrm{h}$	

3. For the $1s^2 2s^2 2p^4 3p^4$ excited electron configuration of atomic calcium:

   (a) **Begin** to apply the vector model to this system by drawing out **any four** distinct, valid microstates (called *basis states* in the text) for this electron configuration, and give the M_L and M_S values for each.

   (b) In the complete vector model, how many microstates have *all* the electrons paired?

   (c) There were 15 microstates for the ground state oxygen atom. What is the total number of microstates in this case?

   (d) For the $1s^2 2s^2 2p^4 3p^2$ configuration, what is the greatest possible value of S?

   (e) What is the greatest possible value of L?

   (f) What is the greatest possible value of J?

4. Consider a set of three ^{16}O atoms. The nuclear spin of the ^{16}O nucleus is zero.

   (a) What is the total spin quantum number S of each oxygen atom in its ground electronic term state?

   (b) Is each oxygen atom (counting all the particles in the atom) a boson or a fermion?

   (c) We place the three atoms in a one-dimensional box with quantum states identified by the quantum number n, where for example the spatial wavefunction of the $n = 1$ state of oxygen atom 2 may be written $\psi_1(2)$. Write the **three-particle** spatial wavefunction for the lowest energy state of the three atoms in this box.

   (d) Let the total spin quantum number of all three atoms be equal to S_T, with projection onto the z axis given by the magnetic quantum number M_{ST}. What is the maximum value of S_T?

   (e) For that maximum value of S_T, give all the possible values of M_{ST}.

   (f) Finally, use α to label the spin wavefunction for the maximum value of M_{ST}, use β for the next lowest M_{ST}, and γ for the next, and so on. Write one valid spin wavefunction to go with your spatial wavefunction such that $M_{ST} = 0$.

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

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

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

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

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

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

He $1s2s$ energy:
$$E_1^{\rm PT} = E_0^{\rm PT} + \underbrace{\frac{1}{2}\int\int\left(\frac{e^2}{r_{12}}\right)1s(1)^2 2s(2)^2 d\tau_1 d\tau_2 + \frac{1}{2}\int\int\left(\frac{e^2}{r_{12}}\right)1s(2)^2 2s(1)^2 d\tau_1 d\tau_2}_{\text{Coulomb integral}}$$
$$\pm \underbrace{\int\int\left(\frac{e^2}{r_{12}}\right)1s(1)1s(2)2s(1)2s(2)d\tau_1 d\tau_2}_{\text{exchange integral}}$$

2-electron diatomic:
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla(1)^2 - \frac{\hbar^2}{2m_e}\nabla(2)^2 + \frac{e^2}{4\pi\epsilon_0}\left[-\frac{Z_{\rm A}}{r_{\rm A1}} - \frac{Z_{\rm B}}{r_{\rm B1}} - \frac{Z_{\rm A}}{r_{\rm A2}} - \frac{Z_{\rm B}}{r_{\rm B2}}\right.$$
$$\left. + \frac{1}{r_{12}} + \frac{Z_{\rm A}Z_{\rm B}}{R_{\rm AB}}\right] - \frac{\hbar^2}{2m_{\rm A}}\nabla(A)^2 - \frac{\hbar^2}{2m_{\rm B}}\nabla(B)^2.$$

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