Chemistry 410A **Exam 3** **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) Write the Hamiltonian for the electrons in the C^{3+} ion.

   (b) In the circles below, fill in the correct signs (+ or −) that make the overall wavefunction antisymmetric with respect to exchange of the labels on electrons 1 and 2.

   $$\Psi(1,2) = \exp(-r_1/a_0)\exp(-2r_2/a_0)\alpha(1)\beta(2) \bigcirc \exp(-2r_1/a_0)\exp(-r_2/a_0)\beta(1)\alpha(2)$$

   $$\bigcirc \exp(-r_1/a_0)\exp(-2r_2/a_0)\beta(1)\alpha(2) \bigcirc \exp(-2r_1/a_0)\exp(-r_2/a_0)\alpha(1)\beta(2)$$

   (c) Rank the following in order of increasing orbital energy (less negative = higher energy) of the **valence** electrons: He, Ar, K

   (d) Rank the following in order of increasing orbital energy (less negative = higher energy) of the $1s$ **core** electrons: He, Ar, K

2. We want to use perturbation theory to estimate the energy of a box with a slope. The zero-order system is the ordinary particle of mass m in a one-dimensional box that runs from $x = 0$ to a. The perturbation is an added potential energy term,

$$U_a(x) = E_1(1 - \frac{x}{a}),$$

where E_1 is the zero-order ground state energy, and is equal to $0.100\,E_\mathrm{h}$. The following integral may be useful:

$$\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\left(1 - \frac{x}{a}\right)\,dx = \frac{a}{4}$$

(a) Make a graph of the potential energy function below.

(b) On your graph, draw a line for the zero order energy.

(c) Calculate the ground state energy to first order.

(d) On your graph, draw a line for the first order energy.

(e) Finally, on your line for the first order energy, sketch (approximately) what you think the first order wavefunction will look like.

3. We change the particle in a one-dimensional box to add a well in the middle. Our variational wavefunction is

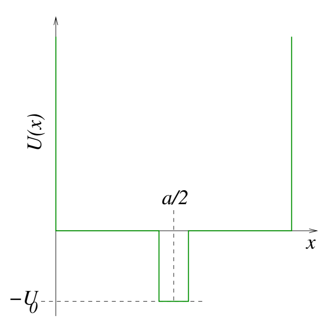
$$\psi(x)^{\text{var}} = \sum_{n=1}^{3} c_n \sin\left(\frac{n\pi x}{a}\right),$$

where we vary the three parameters c_1, c_2, and c_3. After the variational problem is solved:

(a) Which of the three parameters will have the greatest magnitude?

(b) Which of the three parameters will be equal to zero?

(c) Sketch what you think the wavefunction will look like.



4. The hydride ion, H^-, has the same number of electrons as atomic helium, He. In the table below, the values for certain parameters are given for He. In the next column, write the value of the same parameter for H^- if you can calculate it using algebra or arithmetic. If you cannot solve for the value exactly, then write "$>$" if the value for H^- is *greater* than the value for He, "$<$" if the value for H^- is *less than* the value for He.

	He	$\mathbf{H^-}$
Z	2	
Z_{eff}	1.69	
ϵ_1 (E_{h})	-0.917	
E_{HF} (E_{h})	-2.862	
zero-order energy (E_{h})	-4.00	
first-order correction (E_{h})	$+1.25$	

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:	$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{1}{4\pi\epsilon_0}\left[-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}\right]$

H	He	Li	Be	B	C	Ne	Na	orbital
−0.500	−0.917	−2.487	−4.733	−7.702	−11.348	−32.763	−40.488	1*s*
	−0.917	−2.469	−4.733	−7.687	−11.302	−32.763	−40.485	1*s*
		−0.196	−0.309	−0.545	−0.830	−1.919	−2.797	2*s*
			−0.309	−0.446	−0.584	−1.919	−2.797	2*s*
				−0.318	−0.439	−0.840	−1.520	2*p*
					−0.439	−0.840	−1.520	2*p*
						−0.840	−1.520	2*p*
						−0.840	−1.518	2*p*
						−0.840	−1.518	2*p*
						−0.840	−1.518	2*p*
							−0.182	3*s*
−0.500	−2.862	−7.433	−14.573	−24.533	−37.694	−128.547	−161.859	E_{HF}

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