**Chemistry 410A** **Exam 3** **Fall 2008**

## 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) The Hamiltonian for atomic Li can be written

   $$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right) - \frac{3e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right).$$

   If we solved the Schrödinger equation for atomic Li using perturbation theory, **circle** the terms in the Hamiltonian that would correspond to the perturbation, and **underline** the terms that correspond to the zero-order Hamiltonian.

   (b) Referring to the Hartree-Fock orbital energies for ground state atomic lithium:

      i. what is the ionization energy of the $2s$ electron?

      ii. what is the energy required to *completely* ionize the atom to form $Li^{3+}$?

      iii. write the electron configuration for the lowest excited state of Li.

      iv. is the total Hartree-Fock energy **higher** (less negative) or **lower** (more negative) in the excited state than in the ground state (circle one)?

      v. is the $1s$ orbital energy **higher** or **lower** in the lowest excited state than in the ground state (circle one)?

   (c) For the $^4F$ ground state term of atomic iridium,

      i. what is the value of $L$?

      ii. what is the value of $S$?

   (d) Write the Hamiltonian for $H_3^+$.

2. The variational method is used to solve the Schrödinger equation for a particle of mass $m$ with potential energy $U(r) = kr$, starting with a normalized variational wavefunction $\psi(r) = (2a^{3/2})\, e^{-ar}$. The variational parameter is $a$. The expectation value of the energy obeys the equation

$$\langle E \rangle = \frac{\hbar^2 a^2}{2m} + \frac{3k}{2a}.$$

Find the optimized wavefunction and its energy.

3. Find all the term states, including $J$ values, resulting from the electron configuration [Kr]$5s4d$, and list the term symbols **in order of increasing energy**. Don't worry about the order of the $J$ values. (It is not necessary to work through the whole vector model to find the terms; there are 20 microstates if you do.)

4. What is the one term missing from the following symmetrized wavefunction for the $1s^2 2s3s$ excited state of Be?

$$\begin{aligned}\Psi = {} & 1s1s2s3s\alpha\beta\alpha\alpha \quad -1s1s3s2s\alpha\beta\alpha\alpha \quad -1s2s1s3s\alpha\alpha\beta\alpha \quad +1s2s3s1s\alpha\alpha\alpha\beta \\ & +1s3s1s2s\alpha\alpha\beta\alpha \quad -1s3s2s1s\alpha\alpha\alpha\beta \quad +1s1s2s3s\beta\alpha\alpha\alpha \quad -1s1s3s2s\beta\alpha\alpha\alpha \\ & -1s2s1s3s\beta\alpha\alpha\alpha \quad +1s2s3s1s\beta\alpha\alpha\alpha \quad +1s3s1s2s\beta\alpha\alpha\alpha \quad -1s3s2s1s\beta\alpha\alpha\alpha \\ & +2s1s1s3s\alpha\alpha\beta\alpha \quad -2s1s3s1s\alpha\alpha\alpha\beta \quad -2s1s1s3s\alpha\beta\alpha\alpha \quad +2s1s3s1s\alpha\beta\alpha\alpha \\ & +2s3s1s1s\alpha\alpha\alpha\beta \quad -3s1s1s2s\alpha\alpha\beta\alpha \quad +3s1s2s1s\alpha\alpha\alpha\beta \quad +3s1s1s2s\alpha\beta\alpha\alpha \\ & -3s1s2s1s\alpha\beta\alpha\alpha \quad -3s2s1s1s\alpha\alpha\alpha\beta \quad +3s2s1s1s\alpha\alpha\beta\alpha\end{aligned}$$

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:

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

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

| 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 | $1s$ |
| | −0.917 | −2.469 | −4.733 | −7.687 | −11.302 | −32.763 | −40.485 | $1s$ |
| | | −0.196 | −0.309 | −0.545 | −0.830 | −1.919 | −2.797 | $2s$ |
| | | | −0.309 | −0.446 | −0.584 | −1.919 | −2.797 | $2s$ |
| | | | | −0.318 | −0.439 | −0.840 | −1.520 | $2p$ |
| | | | | | −0.439 | −0.840 | −1.520 | $2p$ |
| | | | | | | −0.840 | −1.520 | $2p$ |
| | | | | | | −0.840 | −1.518 | $2p$ |
| | | | | | | −0.840 | −1.518 | $2p$ |
| | | | | | | −0.840 | −1.518 | $2p$ |
| | | | | | | | −0.182 | $3s$ |
| −0.500 | −2.862 | −7.433 | −14.573 | −24.533 | −37.694 | −128.547 | −161.859 | $E_{\mathrm{HF}}$ |

## 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 |