V25.0109: General Chemistry I (Honors) **Professor M.E. Tuckerman**
Second Midterm Examination **November 14, 2008**

NAME and ID NUMBER:

There should be **21** pages to this exam, counting this cover sheet. Please check this exam NOW!

There are three pages of formulae/data, a periodic table (with molar masses), and a table of Mulliken electronegativities at the back of this exam. Books, notes, etc. are not permitted, however calculators are. Note that page 7 is intentionally left blank for you to use if you need additional space. Not all questions are equally difficult. Spending all your time on one question is generally a bad idea. Partial credit will be given but only if your answers can be deciphered. Therefore, make sure that your writing is neat and that your logic is clear, organized, and easy to follow. Unreadable answers will not be given the benefit of the doubt. Good luck.

GRADING

1. (32 points)

2. (34 points)

3. (10 points)

4. (14 points)

5. (10 points)

TOTAL: 100 points

Extra Credit:

1. (**32 points**)

   a. (**5 points**)
   Draw the Lewis structure of the molecule BF_2Cl.

b. (**12 points**)
If the BF and BCl bond lengths are 0.95 Å and 1.00 Å, respectively, and the FBF and BFCl angles are 129.4° and 115.3°, respectively, determine a set of coordinates for each atom in the molecule.

c. (**10 points**)
Suppose you wish to derive a set of partial charges for each atom in the molecule. You know from experiments that BF_2Cl has a small dipole moment whose magnitude is 0.08 D. Let χ_F and χ_{Cl} be the *Mulliken* electronegativities of fluorine and chlorine, respectively, and assume that the *magnitude* of the partial charge on fluorine is χ_F/χ_{Cl} larger than the *magnitude* of the partial charge on chlorine. Determine the partial charges on each atom in BF_2Cl. **WARNING**: You must assign these charges with their correct sign.

d. (**5 points**)
Determine the dipole moment vector in Debye and indicate this vector on a diagram of the molecule. Note, you must use the sign convention from class, not the one from the book!

2. (**34 points**)
A simple model of the helium atom consists of two electrons attached by harmonic springs to a nucleus of zero charge at the origin. If we label the two electrons as 1 and 2, and assign them coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, then the classical energy for this "helium" atom is

$$E = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}$$

where k is the spring constant, $p_1 = |\mathbf{p}_1|$, $p_2 = |\mathbf{p}_2|$, $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$, and ϵ_0 is the permittivity of free space.

a. (**10 points**)
The energy cannot be expressed as a sum $E_1 + E_2$ for electrons 1 and 2. However, consider making the following change of coordinates to the center-of-mass $\mathbf{R}$ and relative position $\mathbf{r}$ of the two electrons:

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

We also have to change the momentum variables to center of mass momentum $\mathbf{P}$ and relative momentum $\mathbf{p}$ according to

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 \qquad \mathbf{p} = \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2)$$

Show that if the classical energy is expressed in terms of the variables $\mathbf{r}$, $\mathbf{R}$, $\mathbf{p}$ and $\mathbf{P}$, the energy becomes a simple sum $E_{\text{COM}} + E_{\text{rel}}$ of only center-of-mass energy terms (kinetic and potential energies) and relative energy terms (kinetic and potential energies). Determine the expressions for E_{COM} and E_{rel}.

b. (**5 points**)
Let $F(\mathbf{R})$ be a function of $\mathbf{R}$ and $G(\mathbf{r})$ be a function of $\mathbf{r}$. In terms of $F(\mathbf{R})$ and $G(\mathbf{r})$, propose a general form for the spatial part of the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ of the two electrons and provide a justification for the form you propose.

c. (**4 points**)
How do the variables $\mathbf{R}$ and $\mathbf{r}$ change if an exchange of the electron coordinates, $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ and $\mathbf{r}_2 \rightarrow \mathbf{r}_1$, is performed?

d. (**5 points**)
Let $\mathbf{x}_1$ denote the position $\mathbf{r}_1$ and spin $s_{z,1}$ of electron one, and let $\mathbf{x}_2$ be the analogous variable for electron 2. The complete wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ for the two electrons must satisfy the Pauli exclusion principle. Suppose that the two electrons are in spin-up states. Based on your proposed wave function for part b, and considering your answer to part c, what conditions must be imposed on $F(\mathbf{R})$ and $G(\mathbf{r})$ in order to satisfy the Pauli exclusion principle? Write down the full wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ in terms of $F(\mathbf{R})$, $G(\mathbf{r})$ and the appropriate spin wave functions.

e. (**10 points**)
Suppose now that one of the electrons is a spin-up electron and the other is a spin-down electron. Based on your proposed wave function for part b, and considering your answer for part c, what conditions must be imposed on $F(\mathbf{R})$ and $G(\mathbf{r})$ in order to satisfy the Pauli exclusion principle? Write down the full wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ in terms of $F(\mathbf{R})$, $G(\mathbf{r})$ and the appropriate spin wave functions.

N.B.: There are two possible answers to this question! Give both of them.

3. (**10 points**)
An unknown molecule has the general form AB_n and is known to have a structure in which A is the central atom surrounded by B atoms. You are given the following information about the molecule:

   i. The molecule has 26 valence electrons.
   ii. In the Lewis structure, each atom has an octet.
   iii. The steric number of the molecule is 4.

Using just these facts and the rules for drawing Lewis structures (and without referring to the periodic table), derive the Lewis structure of the molecule and give at least one possible identity of the molecule.

N.B.: No credit will be given for guessing the answer. You must provide a coherent reasoning for your answer based on the given information and rules of Lewis structures. Be sure to show all of the steps in your derivation.

4. (**14 points**)

a. (**7 points**)
Benzene (C_6H_6) has a structure in which the 6 carbons lie on the vertices of a regular hexagon, and each carbon has one hydrogen attached to it, with the vectors $\mathbf{r}_{\mathrm{H}} - \mathbf{r}_{\mathrm{C}}$ pointing away from the center of the hexagon. Determine benzene's Lewis structure.

N.B.: Your answer must be the classical answer, not the quantum-mechanical one (which we will get to later).

b. (**7 points**)
Molecular beam experiments show that boron (B) is able to integrate into the ring structure of benzene to form a compound known as "benzoborirene", whose formula is C_6H_6B. The structure is that of a seven-membered ring in which each carbon has one hydrogen attached to it with the vectors $\mathbf{r}_H - \mathbf{r}_C$ pointint out. What is the Lewis structure of this compound?

5. (**10 points**)
In an ionic bond, the potential energy should include a term that prevents the oppositely charge ions from approaching each other so closely that their electronic charge distributions start to overlap. Suppose you are told that the potential energy is given by the expression

$$V(r) = \frac{A}{r^{10}} - \frac{e^2}{4\pi\epsilon_0 r} + \mathrm{IE}_1 - \mathrm{EA}$$

where r is the distance between the two ions, IE_1 is the first ionization energy of the electon donor, EA is the electron affinity of the electron acceptor, and A is a constant. Derive an expression for the equilibrium bond length in such an ionic bond, and explain the physical meaning of the energy that results when $r \to \infty$.

Extra Credit: (**10 points**)
Boranes are unusual compounds that, like ordinary alkanes, are composed of boron and hydrogen with the generic formula B_nH_m. An example is *diborane*, that has a chemical formula similar to the alkane ethylene, i.e. B_2H_6, however, unlike in ethylene (C_2H_6), no chemical bond exists between the two boron atoms. Based on this information, determine the Lewis structure of diborane.

POSSIBLY USEFUL INFORMATION

$$N_0 = 6.022 \times 10^{23}\ \text{mol}^{-1}$$

$$k_\text{B} = 1.38066 \times 10^{-23}\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.36262 \times 10^{-25}\ \text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$e = 1.60219 \times 10^{-19}\ \text{C} \qquad \epsilon_0 = 8.854 \times 10^{-12}\ \text{C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$$

$$h = 6.6208 \times 10^{-34}\ \text{J} \cdot \text{s} \qquad \hbar = \frac{h}{2\pi} = 1.105457 \times 10^{-34}\ \text{J} \cdot \text{s}$$

$$c = 2.99769 \times 10^{8} \text{m/s}$$

$$a_0 = 0.529177 \times 10^{-10}\ \text{m}$$

Some conversion factors

$$\begin{aligned} &1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m} \\ &1\ \text{J} = 1\ \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \\ &1\ \text{Ry} = 2.18 \times 10^{-18}\ \text{J} \\ &1\ \text{D} = 3.336 \times 10^{-30}\ \text{C} \cdot \text{m} \end{aligned} \qquad (1)$$

Formulas

$$E_\text{Coul} = \frac{q_1 q_2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} = \frac{q_1 q_2}{4\pi\epsilon_0 r} \qquad \mathbf{F} = \frac{q_1 q_2}{4\pi\epsilon_0 r^3}\mathbf{r}$$

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad A = \sum_{i=1}^{N} A_i p_i$$

SN = # atoms bonded to central atom + # lone pairs on central atom

$$\text{FC} = \text{Group \#} - \text{\# electrons in lone pairs} - \frac{1}{2}(\text{\# electrons in bonds})$$

$$V(x) = \frac{1}{2}k(x - x_0)^2 \qquad F = -k(x - x_0) \qquad I(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_\text{B}T} - 1}$$

$$\text{Electronegativity} \propto (\text{IE}_1 + \text{EA})$$

$$E = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} \qquad dV = r^2 \sin\theta dr d\theta d\phi$$

$$\boldsymbol{\mu} = \sum_{i=1}^{N} q_i \mathbf{r}_i \qquad \mu(\mathrm{D}) = \frac{\delta \times R(\text{Å})}{0.2082 \mathring{A} D^{-1}}$$

$$\chi_{\mathrm{A}} - \chi_{\mathrm{B}} = 0.102\Delta \qquad \Delta = \Delta E_{\mathrm{AB}} - \sqrt{\Delta E_{\mathrm{AA}} \Delta E_{\mathrm{BB}}}$$

$$E_n = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{Z^2}{n^2} \text{ (in Ry)} \qquad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e}$$

$$\hat{H}\psi(x) = E\psi(x) \qquad p(x)dx = |\psi(x)|^2 dx \qquad P(x \in [a,b]) = \int_a^b |\psi(x)|^2 dx$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \qquad \int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \qquad \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\mathrm{X} \longrightarrow \mathrm{X}^+ + \mathrm{e}^- \qquad \Delta E = \mathrm{IE}_1$$

$$\mathrm{X} + \mathrm{e}^- \longrightarrow \mathrm{X}^- \qquad \Delta E = -\mathrm{EA}$$

$$\psi_\uparrow(\hbar/2) = 1 \qquad \psi_\downarrow(\hbar/2) = 0$$

$$\psi_\uparrow(-\hbar/2) = 0 \qquad \psi_\downarrow(-\hbar/2) = 1$$

Mathematics

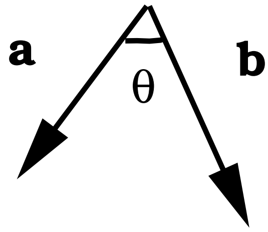

FIG. 1.

$$\mathbf{a} = (a_x, a_y, a_z)$$

$$|\mathbf{a}| = \sqrt{a_x^2 + a_y^2 + a_z^2}$$

$$\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$$

$$\mathbf{a} + \mathbf{b} = (a_x + b_x, a_y + b_y, a_z + b_z)$$

$$|\mathbf{a} + \mathbf{b}| = \sqrt{|\mathbf{a}|^2 + |\mathbf{b}|^2 + 2\mathbf{a} \cdot \mathbf{b}}$$

$$\theta = \cos^{-1}\left[\frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}|\,|\mathbf{b}|}\right]$$

Trigonometry

$$\begin{aligned}
\cos^2(x) + \sin^2(x) &= 1 \\
\cos^2(x) &= \frac{1}{2} + \frac{1}{2}\cos(2x) \\
\sin^2(x) &= \frac{1}{2} - \frac{1}{2}\cos(2x) \\
\sin(x)\cos(x) &= \frac{1}{2}\sin(2x) \\
e^{ix} &= \cos(x) + i\sin(x)
\end{aligned}$$

Indefinite integrals

$$\int x^2 e^{-x} dx = -e^{-x}\left[x^2 + 2x + 2\right]$$

$$\int \sin(ax)\sin(bx)dx = \frac{\sin[(a-b)x]}{2(a-b)} - \frac{\sin[(a+b)x]}{2(a+b)}$$

$$\int \sin^2(ax)dx = \frac{1}{2}x - \frac{1}{4a}\sin(2ax)$$

$$\int_a^b f(x)dx = F(b) - F(a) \qquad \frac{dF}{dx} = f(x)$$

General rules for drawing Lewis structures

1. Count up the total number of valence electrons. First add up the group numbers of all atoms in the molecule. If the molecule is an anion, add one electron for each unit of charge on the anion. If it is a cation, subtract one electron for each unit of charge on the cation.

2. Calculate the total number of electrons that would be needed for each atom to have an octet (or doublet for H).

3. Subtract the result of step 1 from the result of step 2. This is the total number of shared or bonding electrons.

4. Assign two bonding electrons to each bond.

5. If bonding electrons remain, assign them in pairs making some of the bonds double or triple bonds. (Usually, only C,N,O, and S can form double bonds, and only C and N can form triple bonds). There may be more than one way to do this. Keep all possible structures that result.

6. Assign remaining electrons as lone pairs, giving octets to all atoms except H.

7. Determine the formal charges and put them next to the appropriate atoms. (A formal charge of 0 need not be written explicitly). Check that the formal charges add up to the total charge on the molecule/ion. Do this for all structures obtained in step 5. The structure with the smallest formal charges should be considered as the preferred structure.