V25.0109: General Chemistry I (Honors) **Professor M.E. Tuckerman**
First Midterm Examination **October 17, 2008**

NAME and ID NUMBER:

There should be **17** 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 hydrogen-atom wave functions at the back of this exam. Books, notes, etc. are not permitted, however calculators are. 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. (10 points)

2. (30 points)

3. (10 points)

4. (30 points)

5. (20 points)

TOTAL: 100 points

1. (**10 points**)
   Assume the following reaction

   $$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D}$$

   is balanced as written. In a certain experiment designed to produce this reaction, an amount m_{A} of A in grams is combined with an amount m_{B} of B in grams. After the reaction is complete, the reaction vessel is found to contain amounts of C, D, and A. Determine the amounts of C, D, and A in grams present in the vessel after the reaction in terms of the given initial amounts m_{A} and m_{B} of A and B, the molar masses M_{A}, M_{B}, M_{C} and M_{D} of A, B, C, and D, respectively and the stoichiometric coefficients.

2. (**30 points**)
The electron in a hydrogen atom is in the $2p_z$ orbital, for which the wave function is

$$\psi_{2p_z}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \left(\frac{r}{a_0} \right) e^{-r/2a_0} \cos\theta$$

where a_0 is the Bohr radius.

a. (**10 points**)
What is the probability that a measurement of the electron's position will yield a value in the cone defined by $0 \leq \theta \leq \pi/4$?

b. (**10 points**)
What is the probability that a measurement of the electron's position will yield a value in the cone defined by $\pi/4 \leq \theta \leq \pi/2$?

c. (**10 points**)
Explain any differences between the probabilities you obtained in parts (a) and (b) in terms of the general shape of this orbital.

3. (**10 points**)
Suppose you wanted to redefine relative masses such that all masses are calibrated to a scale in which oxygen has exactly one mass unit for each of its nucleons. Oxygen has $Z = 8$ and a mass number of $A = 16$. Using the fact that the mass of a proton is $1.6726216 \times 10^{-27}$ kg, the mass of a neutron is $1.6749272 \times 10^{-27}$ kg, and the mass of a carbon atom is $1.9264644 \times 10^{-26}$ kg, calculate the relative mass of carbon on the oxygen-based scale. Make any approximations you think are appropriate, but be sure to justify them.

4. (**30 points**)

a. (**10 points**)
A particle of mass m is in a one-dimensional box whose potential energy $V(x)$ is defined as follows: $V(x) = 0$ for $0 \leq x \leq L$ and $V(x) = \infty$ for $x < 0$ and $x > L$. Suppose the particle is in the $n = 3$ energy state. What is the probability that a measurement of the particle's position will yield a value between $x = 0.1L$ and $x = 0.2L$? The particle-in-a-box wave functions and energies are given by

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

b. (**10 points**)
What is the probability that a measurement of the particle's position will yield a value between $x = 0.3L$ and $x = 0.4L$ if the particle is in the $n = 3$ energy state?

c. (**5 points**)
In parts (a) and (b), the width of the interval for which you calculated the probability is the same, $0.1L$, in both cases. However, the *location* of the interval is clearly different in each case. Explain any similarity or difference between the probabilities you obtained in parts (a) and (b).

d. (**5 points**)

For a small interval Δx with endpoints at $x = a$ and $x = b$ with $\Delta x = b - a$, the probability that a measurement of the particle's position yields a value in this interval when the particle is an energy state with $n = 3$ can be *approximated* by the formula

$$P(a \leq x \leq b) \approx \psi_3^2(x_0)\Delta x$$

where x_0 is the midpoint of the interval: $x_0 = (b - a)/2$. Use this formula to approximate the probabilities in parts (a) and (b). How accurate is this approximation for each probability?

5. (**20 points**)

a. (**5 points**)
In classical mechanics, two potential energies $V(x)$ and $U(x)$ are considered the same if $U(x) = V(x) + C$, where C is a constant, because potential energies are always defined relative to some arbitrary energy value. In quantum mechanics, if two potential energies $U(x)$ and $V(x)$ differ only by a constant C, then the wave functions $\psi_n(x)$ associated with the two potential energies are the same, and only the energy levels E_n change. Starting with the Schrödinger equations for $U(x)$ and $V(x)$:

$$\left[\hat{K} + V(x)\right]\psi_n(x) = E_n\psi_n(x) \qquad\qquad \left[\hat{K} + U(x)\right]\psi_n(x) = E'_n\psi_n(x)$$

where $\hat{K}$ is the kinetic energy operator and E'_n are the energy levels for the potential energy $U(x)$, show that if $U(x) = V(x) + C$, then

$$E'_n = E_n + C$$

b. (**15 points**)
Now suppose that $U(x)$ and $V(x)$ are truly different, meaning that there is *no* constant C for which $U(x) = V(x) + C$. In this problem, you will attempt to prove that the ground-state wave functions for $V(x)$ and $U(x)$ *must* be different. Let $\psi_1(x)$ be the ground state wave function for $V(x)$ with energy E_1 and $\psi_1'(x)$ be the ground-state wave function for $U(x)$ with energy E_1'. These wave functions must satisfy the Schrödinger equations

$$\left[\hat{K} + V(x)\right] \psi_1(x) = E_1 \psi_1(x) \qquad\qquad \left[\hat{K} + U(x)\right] \psi_1'(x) = E_1' \psi_1'(x)$$

In order to prove that $\psi_1(x)$ and $\psi_1'(x)$ cannot be the same, you will use a proof by contradiction. That is, prove that the assumption $\psi_1(x) = \psi_1'(x)$ leads to a logical contradiction, from which it must follow that $\psi_1(x) \neq \psi_1'(x)$.

Hint: Try substituting $\psi_1(x)$ into both of the above Schrödinger equations and then subtracting one of the resulting Schrödinger equations from the other. What do you get?

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

$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$
$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$
$1 \text{ Ry} = 2.18 \times 10^{-18} \text{ J}$

Formulas

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

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

$$A(x,t) = A_0 \cos\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right) \qquad v = \lambda\nu \qquad c = \lambda\nu$$

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

$$h\nu = \Phi + \frac{p^2}{2m_e} \qquad \lambda = \frac{h}{p} \qquad A(y) = \cos\left(S(y)\right) + i\sin\left(S(y)\right) = e^{iS(y)} \qquad P(y) = \left|\sum_\text{paths} A_\text{path}(y)\right|^2$$

$$\Delta A \Delta B \geq \frac{1}{2}\hbar \qquad \Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2} \qquad \Delta x \Delta p \geq \frac{1}{2}\hbar$$

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

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

$$h\nu = E_{n_i} - E_{n_f} \quad \text{(emission)} \qquad h\nu = E_{n_f} - E_{n_i} \quad \text{(absorption)}$$

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

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

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

Mathematics

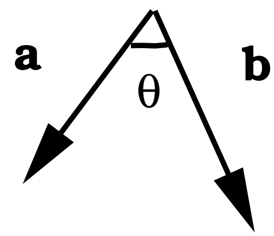

FIG. 1.

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

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

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

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

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

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

Trigonometry

$$\cos^2(x) + \sin^2(x) = 1$$

$$\cos^2(x) = \frac{1}{2} + \frac{1}{2}\cos(2x)$$

$$\sin^2(x) = \frac{1}{2} - \frac{1}{2}\cos(2x)$$

$$\sin(x)\cos(x) = \frac{1}{2}\sin(2x)$$

$$e^{ix} = \cos(x) + i\sin(x)$$

Indefinite integrals

$$\int x^4 e^{-x} dx = -e^{-x}\left[x^4 + 4x^3 + 12x^2 + 24x + 24\right]$$

$$\int \cos^2\theta \sin\theta d\theta = -\frac{\cos^3\theta}{3}$$

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

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

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