V25.0109: General Chemistry I (Honors) **Professor M.E. Tuckerman**
Second Midterm Examination **November 16, 2007**

NAME and ID NUMBER:

There should be **18** pages to this exam, counting this cover sheet. Please check this exam NOW!

There are three pages of formulae/data and a periodic table (with molar masses) 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. (25 points)

2. (10 points)

3. (20 points)

4. (25 points)

5. (20 points)

TOTAL: 100 points

Extra Credit:

1. (**25 points**)
A positron is a particle that resembles an electron in all ways (same mass and spin) *except* for the fact that its charge is $+e$ rather than $-e$. Suppose an electron and a positron are at **fixed** positions in space in a uniform magnetic field $\mathbf{B} = (0, 0, B)$. The "classical" energy of the system is

$$E = -\gamma \mathbf{S}_1 \cdot \mathbf{B} - \gamma \mathbf{S}_2 \cdot \mathbf{B}$$

where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin vectors of the electron and positron, respectively, and γ is a constant known as the *spin-gyromagnetic ratio.* (The word "classical" is in quotes because there is no actual classical analog of spin!)

   a. (**5 points**)
   What are the quantum-mechanically allowed energies of this system?

b. (**5 points**)
What are the corresponding wave functions? (You may leave your wave functions in unnormalized form).

c. (**5 points**)
What is the degeneracy of each energy level?

d. (**5 points**)
Now suppose that the positron is replaced by another electron. What are the allowed energies and corresponding (unnormalized) wave functions?

e. (**5 points**)
Suppose we measure the spin of electron 1 and obtain a value of $\hbar/2$. What is the wave function of the system immediately after the measurement is made? Explain your answer.

2. (**10 points**)
In Chapter 3, we argued that the third-period atom sulfur (S) can form the molecule SF_6 by expanding its valence shell. Using quantum-mechanical concepts, we can now provide a better rationale for this phenomenon. Using the ideas of electron promotion and orbital hybridization, explain how the bonding pattern in SF_6 (which has an octahedral geometry) arises. It might help you to know that the lowest energy d orbitals are d_{z^2} and $d_{x^2-y^2}$. Describe qualitatively where you would expect the hybrid orbitals to have their maximum amplitudes. Note, you do not need to write down the explicit forms of the orbitals.

3. (**20 points**)
In problem set #6, we considered linear and square versions of the "molecule" H_4. Now, consider tetrahedral H_4. Each of the hydrogen atoms lies on the vertices of a regular triangular pyramid. By considering tetrahedral H_4 to be composed of two H_2 molecules (denoted A and B), we construct the four MOs from the bonding and antibonding σ orbitals of each H_2 according to

$$\psi_1 \propto \sigma_{g1s}(A) + \sigma_{g1s}(B)$$
$$\psi_2 \propto \sigma_{g1s}(A) - \sigma_{g1s}(B)$$
$$\psi_3 \propto \sigma^*_{u1s}(A) + \sigma^*_{u1s}(B)$$
$$\psi_4 \propto \sigma^*_{u1s}(A) - \sigma^*_{u1s}(B)$$

Describe the nodal structure of each of the MOs and determine their energetic ordering.

4. (**25 points**)
The electron in a hydrogen atom is in a particular energy state described by the following wave function

$$\psi(r,\theta,\phi) = \frac{4}{81}\left(\frac{1}{4\pi a_0^3}\right)^{1/2}\left(6\sigma - \sigma^2\right)e^{-\sigma/3}\sin\theta e^{i\phi}$$

where $\sigma = r/a_0$, and a_0 is the Bohr radius.

a. (**5 points**)
What are the quantum numbers of the electron?

b. (**10 points**)
What is the probability that a measurement of the electron's location will yield a value in a cone of infinite length, whose apex is at the origin and whose central axis is the positive z-axis, described by $0 \leq \theta \leq \pi/3$. You might find the mathematical identities at the back of the exam useful for this one. You must express your final answer as a numerical percentage, e.g. 15%.

c. (**5 points**)
The atom is now struck by a photon of frequency 2.9×10^{15} Hz. If a photosensitive detector is used to determine if the electron is ejected, will the detector register a hit? If so, with what velocity does the electron reach the detector?

5. (**20 points**)

a. (**4 points**)
Name the following molecule: $H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$

b. (**4 points**)
What is the hybridization state of the carbons in this molecule?

c. (**12 points**)
Based on your hybridization, would you expect π-type molecular orbitals in this molecule? If no, explain why not. If yes, provide explicit expressions (you can use whatever shorthand notation you like, but be clear about it) or an explicit sketch of these orbitals and determine their energetic ordering.

Extra Credit: (**20 points**)
Consider a one-dimensional version of the Born-Oppenheimer approximation involving just two particles with masses m and M, respectively, where $m \ll M$. Let x be the coordinate of the light (l) particle, whose mass is m and y be the coordinate of the heavy (h) particle, whose mass is M. The potential energy for this problem is $V(x,y) = V_l(x) + V_h(y) + V_{lh}(x,y)$. That is, each particle is in an external potential $V_l(x)$ or $V_h(y)$, and they interact through $V_{lh}(x,y)$. The Hamiltonian is

$$\hat{H} = \hat{H}_l(y) + \hat{K}_h + V_h(y)$$

where

$$\hat{H}_l(y) = \hat{K}_l + V_l(x) + V_{lh}(x,y)$$

Here, $\hat{K}_l$ and $\hat{K}_h$ are the kinetic energy operators for the light and heavy particles, respectively.

Suppose now we wish to treat the heavy particle classically within the Born-Oppenheimer approximation using the ground-state energy level from the Schrödinger equation for the light particle:

$$\hat{H}_l(y)\psi_{l,0}(x,y) = \varepsilon_0(y)\psi_{l,0}(x,y) \tag{1}$$

Here $\psi_{l,0}(x,y)$ is the ground-state wave function of the light particle and $\varepsilon_0(y)$ is the ground state energy when the heavy particle is at position y. In the Born-Oppenheimer approximation, the potential energy for the heavy particle is just $\varepsilon_0(y) + V_h(y)$. To treat the heavy particle classically, we need the force from this potential energy for use in Newton's second law. The force is:

$$F(y) = -\frac{d}{dy}\left[\varepsilon_0(y) + V_h(y)\right] = -\frac{d\varepsilon_0}{dy} - \frac{dV_h}{dy}$$

Now, $\varepsilon_0(y)$ is expressed in terms of the wave function $\psi_{l,0}(x,y)$ as

$$\varepsilon_0(y) = \int_{-\infty}^{\infty} \psi_{l,0}(x,y)\hat{H}_l(y)\psi_{l,0}(x,y)dx$$

so that the first term in the force is

$$\frac{d\varepsilon_0}{dy} = \frac{d}{dy}\int_{-\infty}^{\infty} \psi_{l,0}(x,y)\hat{H}_l(y)\psi_{l,0}(x,y)dx$$

By bringing the d/dy under the integral in the above expression, prove that

$$\frac{d\varepsilon_0}{dy} = \int_{-\infty}^{\infty} \psi_{l,0}(x,y)\frac{d\hat{H}_l}{dy}\psi_{l,0}(x,y)dx$$

Hint: Use eqn. (1), which can also be written as

$$\psi_{l,0}(x,y)\hat{H}_l = \psi_{l,0}(x,y)\varepsilon_0(y)$$

where $\hat{H}_l$ acts to the left. Also, do you obtain a useful result if you differentiate the normalization condition

$$\int_{-\infty}^{\infty} \psi_{l,0}^2(x,y)dx = 1$$

with respect to y? Use the next page for your work.

POSSIBLY USEFUL INFORMATION

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

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

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

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

$$c = 2.99769 \times 10^{8} \text{m/s} \qquad a_0 = 0.529177 \times 10^{-10} \text{m}$$

Some conversion factors

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

$1 \text{ D} = 3.336 \times 10^{-30} \text{ C} \cdot \text{m}$
$1 \text{ Ry} = 2.18 \times 10^{-18} \text{ J}$

Formulas

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

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

$$\text{SN} = (\text{\# atoms bonded to central atom}) + (\text{\# lone pairs on central atom})$$

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$V = V_{ee} + V_{en} + V_{nn} \qquad V_\mathrm{eff} = -\frac{Z_\mathrm{eff} e^2}{4\pi\epsilon_0 r}$$

$$\bar{K} = -\frac{1}{2}\bar{V} \qquad F(x) = -\frac{dV}{dx}$$

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

$$V(x) = \frac{1}{2}k\left(x - x_0\right)^2 \qquad F = -k\left(x - x_0\right) \qquad h\nu = -E_n + \frac{p^2}{2m_e} \qquad \lambda = \frac{h}{p}$$

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

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

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

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

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

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

$$E_n = \left(n + \frac{1}{2}\right)h\nu \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$dV = dxdydz = r^2 \sin\theta dr d\theta d\phi \qquad p(\mathbf{r})dV = |\psi(\mathbf{r})|^2 dV$$

$$\Psi(r,R) \approx \psi_{\text{elec}}(r,R)\psi_{\text{nucl}}(R) \qquad \psi_g(\mathbf{r}) = C_A\psi_{1s}(\mathbf{r} - \mathbf{r}_A) + C_B\psi_{1s}(\mathbf{r} - \mathbf{r}_B)$$

$$E_g = \frac{\int \psi_g(\mathbf{r})\hat{H}_{\text{elec}}\psi_g(\mathbf{r})dV}{\int \psi_g^2(\mathbf{r})dV}$$

$$\psi_{1/2}(S_z) = \psi_{\uparrow}(S_z) \qquad \psi_{-1/2}(S_z) = \psi_{\downarrow}(S_z)$$

$$\sum_{S_z=-\hbar/2}^{\hbar/2} |\psi_{\uparrow}(S_z)|^2 = \sum_{S_z=-\hbar/2}^{\hbar/2} |\psi_{\downarrow}(S_z)|^2 = 1$$

Hybrid orbitals

$$\chi(\mathbf{r}) = C_1\psi_{1s}(\mathbf{r}) + C_2\psi_{2p_x}(\mathbf{r}) + C_3\psi_{2p_y}(\mathbf{r}) + C_4\psi_{2p_z}(\mathbf{r})$$

$$\chi_1(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\psi_{2s}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})\right]$$
$$\chi_2(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\psi_{2s}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})\right]$$

$$\chi_1(\mathbf{r}) = \frac{1}{\sqrt{3}}\left[\psi_{2s}(\mathbf{r}) + \sqrt{2}\psi_{2p_x}(\mathbf{r})\right]$$
$$\chi_2(\mathbf{r}) = \frac{1}{\sqrt{6}}\left[\sqrt{2}\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) + \sqrt{3}\psi_{2p_y}(\mathbf{r})\right]$$
$$\chi_3(\mathbf{r}) = \frac{1}{\sqrt{6}}\left[\sqrt{2}\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) - \sqrt{3}\psi_{2p_y}(\mathbf{r})\right]$$

$$\chi_1(\mathbf{r}) = \frac{1}{2}\left[\psi_{2s}(\mathbf{r}) + \psi_{2p_x}(\mathbf{r}) + \psi_{2p_y}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})\right]$$
$$\chi_2(\mathbf{r}) = \frac{1}{2}\left[\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) - \psi_{2p_y}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})\right]$$
$$\chi_3(\mathbf{r}) = \frac{1}{2}\left[\psi_{2s}(\mathbf{r}) + \psi_{2p_x}(\mathbf{r}) - \psi_{2p_y}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})\right]$$
$$\chi_4(\mathbf{r}) = \frac{1}{2}\left[\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) + \psi_{2p_y}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})\right]$$

Mathematics

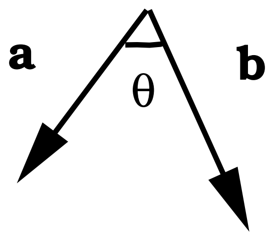

FIG. 1.

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

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

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

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

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

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

Trigonometry

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

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

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

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

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

Integrals

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

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

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

$$\int_0^\infty x^n e^{-x} dx = n!$$