Chemistry 881 **Examination 3**

October 22, 2001

Student Name______________________________

1. (10 points) Show that $Y_1^1(\theta,\phi)$ is an eigenfunction of $\hat{L}^2$

$$Y_1^1(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

2. (20 points) Show that the hydrogenic atomic wave function ψ_{210} given below is normalized and that it is orthogonal to ψ_{200}.

$$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos(\theta)$$

$$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2} \quad \text{where } \sigma = r/a_0$$

Note: $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$

3. (10 points) Show that the most probable value of r in a 1s state is a_0

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\sigma} \text{ where } \sigma = r / a_0$$

4. (10 points) Determine the degeneracy of each of the hydrogen atom energy levels.

Recall that $E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0 n^2}$

5. (10 points) State the variation method.

6. (20 points) Given the trial function for the He atom as $\tilde{\psi}(1)\tilde{\psi}(2)$ where

$\tilde{\psi}(i) = \sqrt{\frac{z^3}{\pi}} e^{-zr_i}$ where z is a variation parameter, one can show that

$E(z) = z^2 - \frac{27}{8} z$.

a. Determine E_{opt}

b. Interpret the meaning of z_{opt}

7. (20 points) Consider a linear variation function of the form

$$\tilde{\psi} = c_1 f_1 + c_2 f_2 + c_3 f_3$$

where $\left\langle f_i \middle| f_j \right\rangle = S_{ij}$ and $\left\langle f_i \middle| \hat{H} \middle| f_j \right\rangle = H_{ij}$

Write out the secular determinant and describe how you would determine the coefficients c_i.