Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 13 **Name:** ____________________

1. The water molecule has three vibrational modes, corresponding to the symmetric stretch, the asymmetric stretch, and the bending motion. Its Hamiltonian can be written as:

$$\hat{H}_{vibration\, H_2O} = -\frac{1}{2}\frac{d^2}{dx_{sym}^2} - \frac{1}{2}\frac{d^2}{dx_{asym}^2} - \frac{1}{2}\frac{d^2}{dx_{bend}^2} + \frac{1}{2}\alpha_{sym}^2 x_{sym}^2 + \frac{1}{2}\alpha_{asym}^2 x_{asym}^2 + \frac{1}{2}\alpha_{bend}^2 x_{bend}^2.$$

   (a) What is the ground-state energy of the vibrational Hamiltonian of the water molecule? Write the answer in terms of ω_{sym}, ω_{asym}, and ω_{bend}.

   (b) What is the ground-state wavefunction of the vibrational Hamiltonian of the water molecule? Write the answer in terms of α_{sym}, α_{asym}, and α_{bend}.

2. Make a rough sketch of the first 3 energy levels for the particle in a one-dimensional, two-dimensional box, on a ring, harmonic oscillator, and hydrogen atom. Remember to include the degenerate states. the gap between the energies increase or decrease as the quantum number increases?

3. What is the ground state energy of Be^{2+} using for each of these cases?

   (a) No electron-electron interaction.

   (b) First order perturbation, where the electron-electron repulsion term in the Hamiltonian is treated as the perturbation.

   (c) Variational method, using trial wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\sqrt{\frac{\zeta^3}{\pi}} \cdot e^{-\zeta r_1}\right)\left(\sqrt{\frac{\zeta^3}{\pi}} \cdot e^{-\zeta r_2}\right)\left(\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}\right)$$

4. Consider the ground state of a harmonic oscillator. As a trial function, try

$$\phi(x) = \cos\lambda x \qquad -\frac{\pi}{2\lambda} < x < \frac{\pi}{2\lambda},$$

   where λ is a variational parameter. Use this trial function to calculate the ground-state energy of a harmonic oscillator. First, you must obtain the expression of the energy and then minimize with respect to λ. The Hamiltonian operator for this system is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k}{2}x^2.$$

   What is the error of using this trial function? Is the energy higher or lower than the exact value? Do your results agree with the variational principle?