Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 8 **Name:** _____

1. Write the Hamiltonian for H_2 and identify each interaction. Can the terms be split in terms that only depend on nuclei positions and those that only depend on electrons? If positions of nuclei is fixed, which terms would be constant?

2. Consider a particle on a ring on the xy-plane. The Hamiltonian in two dimensions in polar coordinates is

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

   (a) The motion is fixed on a ring, so r is constant, show that $\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi}$ is an eigenfunction of the Hamiltonian.

   (b) What is the expression for the energy of the particle? Notice that m is not quantized.

   (c) The particle's motion on the ring is cyclic, meaning that $\Phi(\phi + 2\pi) = \Phi(\phi)$. From this boundary condition, show that the values of m are now limited to $m = 0, \pm 1, \pm 2, ...$

   (d) Is there degeneracy in this system? If so, when?

   (e) What is the zero-point energy of the particle on a ring?

3. The probability that an electron absorbs the energy of a photon of light is given by $P_{n_i \to n_f} = |\int_0^a \phi_{n_f}(x)\hat{\nu_e}\phi_{n_i}(x)dx|^2$, where $\hat{\nu_e} = -ex$ and e is the charge of the electron. Calculate the probability of a transition from $n = 1$ to $n = 2$ and from $n = 1$ to $n = 3$ for the particle in a one-dimensional box.