Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 10 **Name:** _____

1. Write the Hamiltonian for a P-atom N-electron molecule in SI units, keeping track of physical constants like the charge and mass of the electron.

2. Write the Hamiltonian for a P-atom N-electron molecule in atomic units.

3. Write the electronic Schrödinger equation for the P-atom N-electron molecule in atomic units, assuming the Born-Oppenheimer approximation.

4. Write the nuclear Schrödinger equation for the P-atom molecule, assuming that the Born-Oppenheimer approximation holds.

5. For which of the following systems is the Born-Oppenheimer approximation less justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation to be the most important? For which of the following systems do you expect corrections due to relativistic effects to be the most important? Explain your selection.

   (a) KBr (b) Si_{60} (c) UF_6 (d) $XeCl_2$

6. The energy eigenvalues and two eigenfunctions of a one-electron atom are:

$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2}$$

$$\Psi_{2,1,0}(r,\theta,\phi) = -\sqrt{\frac{Z^3}{\pi}} e^{-Zr}.$$

$$\Psi_{2,1,0}(r,\theta,\phi) = -\sqrt{\frac{Z^3}{2^5\pi}} (Zr) e^{-Zr/2} \cos\theta.$$

   (a) Use the Hellmann-Feynman theorem to obtain the expectation value of the Laplacian for the one-electron atom.

   (b) What is the expectation value of the distance of the electron from the nucleus for each of the wavefunctions?

   (c) What is the expectation value of r for a hydrogen atom in its ground state? What is the most probable radius?

   (d) What is the expectation value of the Coulomb potential energy for the $1s$ state of He^+?

   (e) What is the expectation value of the kinetic energy for the $1s$ state of He^+?