Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 6 **Name:** _____

1. State if the following statements are true of false. If it is false, explain the reason.

   (a) Every pair of observables in quantum mechanics is subject to an uncerainty principle such that if one observable has well-defined value, the other is completely uncertain.

   (b) Energy eigenstates are unaltered by time evolution in accord with the time dependent Scchrödinger equation.

   (c) The harmonic oscillator energy levels increase with quantum number at a slower rate than those of the particle in a box.

2. The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. Calculate the force constant of BrF.

3. Follow the steps taken in class and obtain the expression for the second order perturbation energy.

4. The energy eigenvalues and the Hamiltonian for a one-electron atom are

$$E_n = \frac{m_e Z^2 e^4}{8\varepsilon_0^2 h^2 n^2}$$

$$\hat{H}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

   Using the Hellmann-Feynman theorem, what is the expectation value of the Laplacian for the one-electron atom, $< \nabla^2 >$?

5. Consider a particle in a one dimensional box from $x = 0$ to $x = a$ subject to a perturbation $\varepsilon > 0$,

$$V(x) = \begin{cases} \varepsilon & 0 \leq x \leq a/2 \\ 0 & \text{otherwise} \end{cases}$$

   (a) Determine the energy levels of this particle, at the level of first order perturbation theory. Is the first order correction positive or negative? Does this make sense?

   (b) What is the transition frequency for the $n = 1$ to $n = 2$ transition?

   (c) Determine the first order correction to the wavefunction.