Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 9 **Name:** ____________________

1. The variational principle is a very useful method for estimating the energy from an approximated wavefunction of a known hamiltonian. A trial function can be written as a linear combination of the true eigenfunctions of the hamiltonian that form a complete set,

$$\Psi_{trial} = \sum_n c_n \Psi_n \quad \text{where} \quad \hat{H}\Psi_n = E_n\Psi_n.$$

The eigenfunction Ψ_0 corresponds to the smallest eigenvalue E_0. Show that for any Ψ_{trial}, the value of the energy will be greater than E_0,

$$E_{trial} = \frac{\int \Psi^\star_{trial}\hat{H}\Psi_{trial}\mathrm{d}x}{\int \Psi^\star_{trial}\Psi_{trial}\mathrm{d}x} \geq E_0.$$

2. Consider the Hamiltonian $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$. The first order perturbation for the energy of this system is $\frac{\partial E}{\partial \lambda} = E'(\lambda) = \left\langle \Psi(\lambda) \middle| \hat{V} \middle| \Psi(\lambda) \right\rangle$. If the perturbation parameter can have two possible values, λ_1, and λ_2, then $\Psi(\lambda_1)$ yields the lowest energy $E(\lambda_1)$ for $\hat{H}(\lambda_1)$ and $\Psi(\lambda_2)$ yields the lowest energy $E(\lambda_2)$ for $\hat{H}(\lambda_2)$.

   (a) Use the variational principle to show that $\Psi(\lambda_2)$ gives a higher energy for $\hat{H}(\lambda_1)$.

   (b) Repeat this for $\Psi(\lambda_1)$ and $\hat{H}(\lambda_2)$.

   (c) Summing both inequalities, obtain the following expression:

   $$(\lambda_1 - \lambda_2)(E'(\lambda_1) - E'(\lambda_2)) < 0.$$

   (d) Based on this expression, explain what happens to the energy as λ increases.

   (e) If $E'(\lambda)$ is differentiable, what would be the behaviour of $E"(\lambda)$?

   (f) If the perturbation is stabilizing, so that $\left\langle \Psi(\lambda) \middle| \hat{V} \middle| \Psi(\lambda) \right\rangle = E'(\lambda) > 0$, what happens to the slope of the energy as the perturbation becomes stronger.

   (g) Make an illustrative graph of $E(\lambda)$ vs. λ.

3. Consider a mass m particle in a box of width, a, in the state, $\psi(x) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x))$, where ψ_1 and ψ_2 are the lowest two eigenstates.

   (a) Determine the expectation value of momentum for this state.

   (b) What are the possible outcomes of a measurement of energy of the particle?

   (c) What is the state of the system after time t?

   (d) Suppose that $\frac{h^2}{8ma^2} = 1.00eV$, at what time does the system state return to its orginal form $\psi(x)$?