Chemical Physics Cumulative Examination ***September 21, 2011***

Very few problems in Quantum Mechanics may be solved exactly and accordingly one makes extensive use of approximations. Two approximations in general use are Perturbation Theory and the Variation Principle and this exam will explore your understanding of both. The first part of the exam focuses on the derivation of the formal equations characterizing these approximations while in the second part you are asked to use the two approximations to solve a model problem.

Part 1

1. (10 points) State the Variation Principle

2. (20 points) Prove the Variation Principle

3. (30 points) The equation determining the first order correction to a non-degenerate state ϕ_μ^0 is $\left(\hat{H}^0 - E_\mu^0\right)\phi_\mu^{(1)} = -\left(\hat{V} - E_\mu^{(1)}\right)\phi_\mu^0$ where the unperturbed system is characterized by $\hat{H}^0\phi_\mu^0 = E_\mu^0\phi_\mu^0$, $\hat{V}$ is the perturbation and $\phi_\mu^{(1)}$ & $E_\mu^{(1)}$ are the first order correction to the wavefunction and energy.

a. Derive the equation $\left(\hat{H}^0 - E_\mu^0\right)\phi_\mu^{(1)} = -\left(\hat{V} - E_\mu^{(1)}\right)\phi_\mu^0$

b. Show that $E_\mu^{(1)} = \left\langle \phi_\mu^0 \middle| \hat{V} \middle| \phi_\mu^0 \right\rangle$

c. Show that $\phi_\mu^{(1)} = \sum_{\nu \neq \mu} \frac{\left\langle \phi_\mu^0 \middle| \hat{V} \middle| \phi_\nu^0 \right\rangle \phi_\nu^0}{E_\mu^0 - E_\nu^0}$

Part 2

The Hamiltonian for a particle of charge *q* and mass *m* constrained to move along the x axis, $0 \le x \le a$, in the presence of a constant electric field *F* is $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - qFx$.

a. (20 points) Derive an expression for the energy of the system using the Variation Principle.

b. (20 points) Derive an expression for the energy of the system using perturbation theory.