Quantum Chemistry
Exercises 7A

1. Identify $\hat{H}^{(0)}, \hat{H}^{(1)}, \psi^{(0)}$ and $E^{(0)}$ for the following problems

a. An oscillator governed by the potential

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4$$

b. A particle in a box with the potential

$$\begin{aligned} U(x) &= \infty && x < 0, x > a \\ &= 0 && 0 \le x \le \frac{a}{2} \\ &= b && \frac{a}{2} \le x \le a \end{aligned}$$

c. A helium atom

d. A hydrogen atom in an electric field of strength E. The Hamiltonian operator for this system is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} + eEr\cos\theta$$

e. A rigid rotor with a dipole moment μ in an electric field of strength E. The Hamiltonian operator for this system is:

$$\hat{H} = -\frac{\hbar^2}{2I}\nabla^2 + \mu E\cos\theta$$

2. Using a harmonic oscillator as the unperturbed problem, calculate the first order correction to the energy of the n=1 level for the system described in problem 1a. To evaluate the integrals, you can use where appropriate the raising and lowering operators that were introduced in chapter 3.

3a. Using a particle-in-a-box as the perturbed problem, calculate the first-order correction to the ground state energy for the system described in problem 1b.

b. Modify the Matlab code of Exercise 2b to find the numerical result for a=5.78 Å and values of b ranging from 0 to 20 eV.

c. Compare the result from perturbation theory to the numerical result.

4. Using the result of problem 1d, calculate the first-order correction to the ground state energy of a hydrogen atom in an external electric field of strength E.

5. Use first-order perturbation theory to calculate the first-order correction to the ground state energy of a quartic oscillator whose potential energy is

$$U(x) = cx^4$$

In this case, use a harmonic oscillator as the unperturbed system. What is the perturbing potential?