Fall 2011 CHEM 760: Introductory Quantum Chemistry

Homework 7 Due: Nov 15 in class

The material handed in must be original. You may not copy from other sources (including internet, books, and other's homework).

Choose 3 of the 4 problems.

- 1. (Will be discussed in lecture) Use the first-order perturbation theory to calculate the first-order correction to the ground-state energy of a quartic oscillator whose potential energy is $V(x) = cx^4$
 - a) Use a harmonic oscillator as the unperturbed system. What is the perturbing potential?
 - b) The normalized ground-state wave function for a harmonic oscillator is $\psi_0 = (\frac{\alpha}{\pi})^{1/4} e^{-\alpha x^2/2}$, where α is a constant. Calculate the first-order energy correction for this system.
- 2. The Morse potential $V(x) = D(1 e^{-\beta x})^2$ is a description of the internuclear potential energy of a diatomic molecule. Expand the Morse potential in a power series about x using the expansion

$$e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \cdots$$
, then the Hamiltonian operator can be written in the form
 $\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} \pi + ax^2 + bx^3 + dx^4 + \cdots$

- a) How are the constants a, b and c related to the constants D and β ?
- b) What part of the Hamiltonian operator would you associate with \hat{H}^0 ?
- c) What are the functions $\psi_0^{(0)}$ and $E_0^{(0)}$ for \hat{H}^0 ?
- d) Use perturbation theory to evaluate the first-order corrections to the energy of the ground state that arise from the cubic and the quartic terms.
- 3. The following Hamiltonian matrix has been constructed using an orthonormal basis set

 $H = H^{0} + H' = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & -2 \end{vmatrix} + \begin{vmatrix} 0 & c & 0 \\ c & 0 & 0 \\ 0 & 0 & c \end{vmatrix} = \begin{vmatrix} 1 & c & 0 \\ c & 3 & 0 \\ 0 & 0 & c - 2 \end{vmatrix}$ where *c* is a constant, $|c| \ll 1$.

- a) Find the exact eigenvalues of *H*.
- b) Use perturbation theory to determine the eigenvalues corrected to the second order, i.e. $E^{(0)}, E^{(1)}, and E^{(2)}$.
- 4. A particle of mass m moves in the x-dimension subject to the potential:

 $\begin{array}{ll} V(x) = \infty & \text{if} \quad x < 0 & \text{Region I} \\ V(x) = -V_0 \ x \ (L - x) & \text{if} \quad 0 \le x \le L & \text{Region II} \\ V(x) = \infty & \text{if} \quad x > L & \text{Region III} \\ \text{A sketch of this potential energy function is shown below:} \end{array}$



- a) What are the boundary conditions that must be satisfied by the wave function for this system?
- b) Using the variational method, we may write a trial wave function, ϕ , as a linear combination of basis functions, f_i , as:

$$\phi(x) = \sum_{n=1}^{N} C_n f_n(x)$$
$$f_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Is the basis set an acceptable set of basis functions for the solution of this problem?

c) Write down the equation that you would use to solve for the energy levels of this system, using the basis set given above. Make sure you define any symbols that appear in your expression.

An alternative approach to this problem is to break the Hamiltonian into two pieces:

$$\widehat{H} = \widehat{H}^0 + \widehat{H}$$

where $\hat{H}^0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V$, V=0 if $0 \le x \le L$; V = ∞ otherwise

and $\widehat{H}' = -V_0 x(L-x)$

Then perturbation theory may be used to approximate the energy levels for this system. In this approach, the zeroth order energy levels and wave functions are those of the particle in a box, given by $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$ for x < 0 or x > l, and $\psi_n = 0$ elsewhere; and $E_n = \frac{n^2 h^2}{8mL^2}$.

- d) Use the information above to set up the first-order perturbation theory correction to the energy of the ground state (n=1), E₁⁽¹⁾. Be as explicit as possible, including actual functions to be integrated, proper volume elements, and limits on the range of integration, limits on summations, etc. Do not need to evaluate any integrals that may appear in your expression.
- e) Write down an expression for the first-order perturbation correction to the wave function for the ground state of this system (n=1), given by $\psi_1^{(1)}$. Again, be as explicit as possible, including actual functions to be integrated, proper volume elements, limits on the range of integration, limits on summations, etc. Do not need to evaluate any integrals that may appear in your expression.
- f) Write down an expression for the second-order perturbation correction to the energy for the ground state of this system (n=1), denoted by $E_1^{(2)}$. Again, be as explicit as possible, including actual functions to be integrated, proper volume elements, limits on the range of integration, limits on summations, etc. Do not need to evaluate any integrals that may appear in your expression.