CHEMISTRY 3BB3 1999/2000

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ASSIGNMENT 1

DUE: January 25, 2000

1. A particle in a box is perturbed by a step in its potential. The box has length L, and so from 0 to L/2, the potential is zero, but from L/2 to L, the potential is equal to 1/10 of the energy of the lowest state. Using first-order perturbation theory, calculate the first order perturbation to the lowest energy level, and the contribution from ψ_2, ψ_3, and ψ_4 to the perturbed version of ψ_1, the lowest energy wavefunction.

2. A crude (but useful) picture of a π bond in a conjugated hydrocarbon is a particle-in-a-box. Calculate the first two energy levels (in cm^{-1}) which correspond to octatetraene. Use an average C-C bond length of 1.4 Å, and assume the box ends half a bond length beyond the terminal carbons.

3. Consider the matrix

$$U = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

   a. Show that U is unitary - *i.e.* that its determinant is equal to 1 and that U times its transpose, U^{tr} gives the unit matrix.

   b. Show that the product of the three matrices, U^{tr} A U, where A is given by

$$A = \begin{pmatrix} a & b \\ b & d \end{pmatrix}$$

   is diagonal, as long as $\tan(2\theta) = 2b/(a-d)$. (Look up the trig identities for double angles).

   c. Show that the two diagonal elements of the product are given by

$$\lambda_{1,2} = \frac{(a+d) +/- \sqrt{(a-d)^2 + 4b^2}}{2}$$