CHEMISTRY 3BB3 1999/2000

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ASSIGNMENT 1

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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.

The unperturbed wavefunctions are

$$y_n = \sqrt{\frac{2}{L}}\sin\frac{np\,x}{L}$$

and the associated energies are

$$E_n = \frac{n^2h^2}{8mL^2}$$

The perturbation in this case is

$$\begin{aligned} H' &= 0 && 0 < x < \frac{L}{2} \\ &= \frac{n^2h^2}{10\times 8mL^2} && \frac{L}{2} < x < L \end{aligned}$$

The first order perturbation to the energy is given by

$$\begin{aligned} \langle y_1 | H' | y_1 \rangle &= \frac{2}{L}\int_0^L \sin\frac{p\,x}{L} H' \sin\frac{p\,x}{L} \quad dx \\ &= \frac{2}{L}\frac{h^2}{10\times 8mL^2}\int_{L/2}^{L}\sin^2\frac{p\,x}{L} \quad dx \\ &= \frac{2}{L}\frac{h^2}{10\times 8mL^2}\frac{L}{4} \\ &= \frac{1}{2}\frac{h^2}{10\times 8mL^2} \end{aligned}$$

The integral is just half the normalization constant (by symmetry). The perturbed energy is just half of the perturbation, as might be expected.

The perturbed wavefunction is given by

$$y_1' = y_1 + \sum_{i=2}^{\infty} c_{1i} y_i$$

where

$$c_{1i} = \frac{\langle y_1 | H' | y_i \rangle}{E_1 - E_i}$$

In particular,

$$c_{12} = \frac{\langle y_1 | H' | y_2 \rangle}{E_1 - E_2}$$

$$= \frac{\frac{2}{L}\frac{h^2}{10\times 8mL^2}\int_{L/2}^{L} \sin\frac{p x}{L}\sin\frac{2p x}{L}\,dx}{\frac{h^2}{8mL^2} - \frac{4h^2}{8mL^2}}$$

The integral is $-\frac{2L}{3p}$, so that

$$c_{12} = \frac{1}{10\times 3}\frac{4}{3p}$$

$$= 0.014147$$

By symmetry, $c_{13} = 0$, and by a similar calculation,

$$c_{14} = -\frac{1}{10\times 15}\frac{8}{15p}$$

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.

This is just a matter of substituting in values of the physical constants. The box length is 8x1.4 angstroms, which equals 1.12 nm.

$$\frac{h^2}{8mL^2} = \frac{\left(6.626\times 10^{-34}\right)^2}{8\times 9.109\times 10^{-31}\times\left(1.12\times 10^{-9}\right)^2}$$

$$= 4.803\times 10^{-20}\,\mathrm{J}$$

$$= 2418\ \mathrm{cm}^{-1}$$

The second, energy level is just 4 times this, 9675 cm^{-1}. A transition between these two would be in the near infra-red region of the spectrum.

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.

$$\det\begin{pmatrix} \cos q & -\sin q \\ \sin q & \cos q \end{pmatrix} = \begin{vmatrix} \cos q & -\sin q \\ \sin q & \cos q \end{vmatrix}$$
$$= \cos^2 q + \sin^2 q$$
$$= 1$$

Similarly,

$$\begin{pmatrix} \cos q & -\sin q \\ \sin q & \cos q \end{pmatrix}\begin{pmatrix} \cos q & \sin q \\ -\sin q & \cos q \end{pmatrix} = \begin{pmatrix} \cos^2 q + \sin^2 q & 0 \\ 0 & \cos^2 q + \sin^2 q \end{pmatrix}$$
$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

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(2θ) = 2b/(a-d). (Look up the trig identities for double angles).

$$\begin{pmatrix} \cos q & \sin q \\ -\sin q & \cos q \end{pmatrix}\begin{pmatrix} a & b \\ b & d \end{pmatrix}\begin{pmatrix} \cos q & -\sin q \\ \sin q & \cos q \end{pmatrix}$$
$$= \begin{pmatrix} a\cos^2 q + 2b\sin q\cos q + d\sin^2 q & (-a+d)\cos q\sin q + b(\cos^2 q - \sin^2 q) \\ (-a+d)\cos q\sin q + b(\cos^2 q - \sin^2 q) & a\cos^2 q - 2b\sin q\cos q + d\sin^2 q \end{pmatrix}$$

This is diagonal if the off-diagonal elements are zero. This means

$$(-a+d)\cos q\sin q + b(\cos^2 q - \sin^2 q) = 0$$
$$\frac{a-d}{2}\sin 2q = b\cos 2q$$
$$\tan 2q = \frac{2b}{a-d}$$

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

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

There are many ways of solving this. One is to use the formulae

$$\sin^2 q = \frac{1-\cos 2q}{2}$$

$$\cos^2 q = \frac{1+\cos 2q}{2}$$

In that case,

$$a\cos^2 q + 2b\sin q\cos q + d\sin^2 q = \frac{a+d}{2} + \frac{(a-d)\cos 2q + 2b\sin 2q}{2}$$

But

$$\cos 2q = \frac{a-d}{\sqrt{(a-d)^2 + 4b^2}}$$

$$\sin 2q = \frac{2b}{\sqrt{(a-d)^2 + 4b^2}}$$

Therefore,

$$a\cos^2 q + 2b\sin q\cos q + d\sin^2 q = \frac{a+d}{2} + \frac{(a-d)^2 + 4b^2}{2\sqrt{(a-d)^2 + 4b^2}}$$

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

Similarly, for the other expression.
As we have said in lectures, it is no coincidence that this is the quadratic formula.