5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1982

Problem Set #1
Due February 17, 1982

1. See Problem Set # 1, 1977, Problem 1.

2. See Problem Set # 1, 1977, Problem 3.

3. See Problem Set # 1, 1977, Problem 4.

4. You are going to use the Van Vleck Transformation (a fancy name for second-order quasi-degenerate perturbation theory) to solve a coupled harmonic oscillator problem. Consider

$$\mathbf{H} = \mathbf{H}_x^\circ + \mathbf{H}_y^\circ + \zeta x^2 y^2$$

and let

$$\omega_x = \omega_y.$$

A. Given that

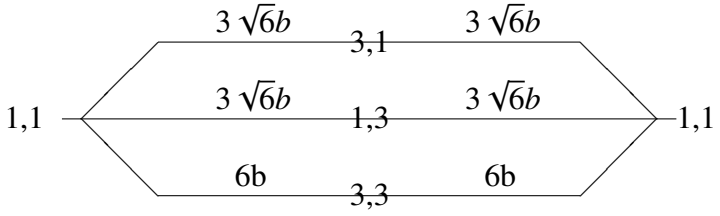
$$\left\langle n_x|\mathbf{x}^2|n_x\right\rangle = \frac{\hbar}{m\omega}(n_x + 1/2)$$
$$\left\langle n_x|\mathbf{x}^2|n_x \pm 2\right\rangle = \frac{\hbar}{m\omega}\left[n_x^2 + n_x + 1 \pm (2n_x + 1)\right]^{1/2}$$
$$\frac{\zeta\hbar}{4m^2\omega^3} \equiv b$$

Construct the **H** matrix through

$$n = n_x + n_y = 4.$$

Notice that the matrix factors nicely into an odd n and an even n block.

B. Apply the Van Vleck transformation to the $n = 0, 1$, and 2 blocks. Assume that $\hbar\omega \gg b$. Be sure to include corrections due to off-diagonal elements with $n > 4$ basis functions. Your bookkeeping will be simplified if you make use of "railroad" diagrams. For example,



The diagram places the initial and final basis functions at the left and at the right and in the middle are *all* basis functions that can simultaneously have non-zero matrix elements with both. Above each line is the actual value of the matrix element. All that remains is to look up the relevant energy denominators. The correction to the 1, 1; 1, 1 matrix element is (neglecting b terms in denominators)

$$-\frac{54b^2}{2\hbar\omega} - \frac{54b^2}{2\hbar\omega} - \frac{36b^2}{4\hbar\omega}.$$

C. Now that you have effectively uncoupled the $n = 0, 1, 2$ blocks from all other blocks, you can focus your attention individually on these 1×1, 2×2, and 3×3 isolated effective Hamiltonians. Construct the $(2, 0) \pm (0, 2)$ and $(1, 0) \pm (0, 1)$ basis functions. This is called a "Wang Transformation". Can you suggest any physical basis for this additional factorization? You should find that the $n = 0$ through 2 part of this Hamiltonian is now fully diagonal. Draw an energy level diagram for $n = 0$ through 2 which compares your eigenvalues against the unperturbed ($b = 0$) levels.