MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
Fall, 2002

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Problem Set #6

DUE: At the start of Lecture on Friday, October 25.

Reading: CTDL pp. 290-307, 1148-1155. [optional, 1169-1199]

Problems:

1. You are going to derive the "x–k" relationships given on pages 17-4 and 17-5. You have worked out the relationships between *m, k, a*, and *b* in

$$\mathbf{H} = \mathbf{p}^2/2m + \frac{1}{2}k\mathbf{x}^2 + a\mathbf{x}^3 + b\mathbf{x}^4$$

and Y_{00}, ω_e, $\omega_e x_e$ in

$$E_n / hc = Y_{00} + \omega_e(n+1/2) - \omega_e x_e (n+1/2)^2,$$

for a single-oscillator (diatomic) molecule. Now you are going to consider 3N–6 anharmonically coupled, anharmonic oscillators in an N-atom polyatomic molecule. The only thing that is different is that there are many more terms in $\mathbf{H}^{(1)}$ and the $E_n^{(2)}$ terms involve short summations over several combinations of oscillators. In all of your derivations ignore the $\left(\frac{\hbar}{m\omega}\right)^{1/2}$ factor that makes $\mathbf{q}$ dimensionless.

A. x_{ii} appears in the energy level expression as

$$E_{n_1 n_2 \ldots n_{3N-6}} = \cdots x_{ii}(n_i + 1/2)^2.$$

The first term in the equation for x_{ii} on page 17-4 comes from one of the two strictly diagonal matrix elements of $\mathbf{H}^{(1)}$. These are the $\Delta n_i = 0$ matrix elements of q_i^4. Derive this term.

B. The second term in x_{ii} comes from matrix elements of terms like $q_i q_s^2$. There are several classes of such matrix elements: $(\Delta n_i, \Delta n_s) = (1,0)$, $(-1,0)$, $(1,2)$, $(1,-2)$, $(-1,2)$, and $(-1,-2)$. The first two have only $\pm\,\omega_i$ in the denominator, while the other four have energy denominators of the form $\pm\omega_i \pm 2\omega_s$. Sum these terms and derive the second term in the x_{ii} equation.

C. The first term in x_{ij} on page 17-5 comes from another strictly diagonal matrix element of $\mathbf{H}^{(1)}$

$$E_{n_1 n_2 \ldots n_{3N-6}} = \cdots x_{ij}(n_i + 1/2)(n_j + 1/2)$$

which comes from diagonal ($\Delta n_i = 0$, $\Delta n_j = 0$) matrix elements of $q_i^2 q_j^2$. Derive this contribution to x_{ij}.

D. The second term in x_{ij} on page 17-5 comes from $\Delta n_i = 0$, $\Delta n_j = 0$ matrix elements of terms like $q_i^2 q_t$ and $q_j^2 q_t$. The selection rules for q_t is $\Delta n_t = \pm 1$ and the energy denominator will be $\pm\omega_t$. Derive this term.

E. [OPTIONAL] The final term in x_{ij} comes from matrix elements of terms like $q_i q_j q_t$. There are eight such terms: $(\Delta n_i, \Delta n_j, \Delta n_t) = (1,1,1)$, $(-1,1,1)$, … $(-1,-1,-1)$ with corresponding energy denominators. Derive this term.

2. In addition to the x-k relationships by which the vibrational anharmonicity constants, x_{ij}, are related to the cubic and quartic anharmonicity constants of the potential surface, perturbation theory can be used to derive the relationships of the rotational anharmonicity constants, $\alpha_i^{[\mathrm{A,\ B,\ or\ C}]}$ to the coefficients of the q_i^3 cubic anharmonicity term in the potential, e.g.

$$B_{v_1, v_2, \ldots v_{3N-6}} = B_e - \sum_{i=1}^{3N-6} \alpha_i (v_i + 1/2).$$

For a polyatomic molecule, you need to know the partial derivatives of the reciprocal moments of inertia with respect to each of the normal coordinate displacements, and that information comes from a normal coordinate analysis (**F** and **G** matrices) that is beyond the scope of this class. Here, you will solve the simpler problem of $B_v = B_e - \alpha_e(v + 1/2)$ for a diatomic molecule. The rotational "constant" operator is proportional to R^{-2},

$$x = R - R_e$$
$$R^{-2} = R_e^{-2}\left[1 - 2\left(\frac{x}{R_e}\right) + 3\left(\frac{x}{R_e}\right)^2 + \ldots\right]$$
$$B_v = B_e\left[1 - 2\left(\frac{x}{R_e}\right) + 3\left(\frac{x}{R_e}\right)^2 + \ldots\right].$$

So, by writing **H** as $\mathbf{H}^{(0)} + \mathbf{H}^{(1)}$

$$\mathbf{H}^{(0)}/hc = \frac{1}{2}\left(\mathbf{a}\mathbf{a}^{\dagger} + \mathbf{a}^{\dagger}\mathbf{a}\right)\frac{1}{2\pi c}(k/\mu)^{1/2} + B_e J(J+1)$$
$$B_e = \frac{h}{8\pi^2 c\mu R_e^2}$$
$$\mathbf{H}^{(1)}/hc = (a/hc)\mathbf{x}^3 - 2B_e(\mathbf{x}/R_e)J(J+1)$$

and the second-order corrections to E_{vJ} will contain three terms

$$\frac{E_{vJ}^{(2)}}{hc} = \left(\frac{a}{hc}\right)^2 \sum_{v'} \frac{\left|\langle vJ|\mathbf{x}^3|v'J\rangle\right|^2}{\left(E_{vJ}^{(0)} - E_{v'J}^{(0)}\right)/hc} + \frac{4B_e^2}{R_e^2} J^2(J+1)^2 \sum_{v'} \frac{\left|\langle v|\mathbf{x}|v'\rangle\right|^2}{\left(E_{vJ}^{(0)} - E_{v'J}^{(0)}\right)/hc}$$
$$- \frac{2aB_e}{hcR_e} J(J+1) \sum_{v'} \frac{\langle v|\mathbf{x}|v'\rangle\langle v'|\mathbf{x}^3|v\rangle}{\left(E_{vJ}^{(0)} - E_{v'J}^{(0)}\right)/hc}$$

where the first term is a contribution to $\omega_e x_e$, the second term gives the centrifugal distortion $\left(D_e \approx 4B_e^3/\omega_e^2\right)$, and the third term is the one that will contain the desired $(v+1/2)J(J+1)$ dependence of the α_e term. Note that there is also a first order correction to the energy $E_{vJ}^{(1)}/hc = \frac{3B_e}{R_e^2} J(J+1)\langle vJ|\mathbf{x}^2|vJ\rangle$. This gives the harmonic contribution to α_e, which is usually smaller and of opposite sign to the cubic term (when $a < 0$). Derive the two contributions to α_e and express them in terms of B_e, ω_e, μ, and fundamental constants (h, c, etc.).

3. CTDL, page 205, #9.