MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
Fall, 2018

Professor Robert W. Field

Problem Set #6

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

Problems #1 and #2 are based on material not covered in the Lecture Notes #17R on the Stellar site. The background for these problems is on pages 17-5, 17-6, and 17-7 of Lecture Notes #17, also found on the Stellar site. I have renumbered the pages in Lecture 17(R) to 17(R)-# to avoid confusion.

Problems:

1. You are going to derive the "x–k" relationships given on pages 17-5 and 17-6 in Lecture #17 [not 17(R)]. 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 the "molecular constants" 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 2nd-order perturbation theory summations over several combinations of oscillators. In all of your derivations ignore the $\left(\frac{\hbar}{m\omega}\right)^{1/2}$ factor that makes **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 17-6 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 17-6 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: $(\Delta n_i, \Delta n_j, \Delta n_t) = (1,1,1), (-1,1,1), \ldots (-1,-1,-1)$ 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, $\alpha_i^{[A,\ B,\ \text{or}\ C]}$ to the coefficients of the q_i^3 cubic anharmonicity term in the potential, e.g.

$$B_{n_1, n_2, \ldots n_{3N-6}} = B_e - \sum_{i=1}^{3N-6} \alpha_i (n_i + 1/2).$$

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 $B_n = B_e - \alpha_e(n + 1/2)$ for a diatomic molecule. The rotational "constant" operator is proportional to R^{-2},

$$\mathbf{x} = R - R_e$$

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

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

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

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

$$B_e = \frac{h}{8\pi^2 c\mu R_e^2}$$

$$\mathbf{H}^{(1)}/hc = \left(a/hc\right)\mathbf{x}^3 - 2B_e\left(\mathbf{x}/R_e\right)J(J+1)$$

and the second-order corrections to $E_{n,J}$ will contain three terms

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

$$-\frac{2aB_e}{hcR_e}J(J+1)\sum_{n'} \frac{\langle n|\mathbf{x}|n'\rangle\langle n'|\mathbf{x}^3|n\rangle}{\left(E_{n,J}^{(0)} - E_{n',J}^{(0)}\right)/hc}$$

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 $(n+1/2)J(J+1)$ dependence of the α_e term. Note that there is also a first order correction to the energy $E_{n,J}^{(1)}/hc = \frac{3B_e}{R_e^2}J(J+1)\langle n,J|x^2|n,J\rangle$. 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.