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

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^3 + bx^4$$

and $Y_{00}, \omega_e, \omega_ex_e$ in

$$E_n / \hbar c = Y_{00} + \omega_e(n + 1/2) - \omega_ex_e(n + 1/2)^2,$$

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 $H^{(1)}$ 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 $q$ dimensionless.
A. \( x_{ii} \) appears in the energy level expression as
\[
E_{n_1, n_2 \ldots n_{3N-6}} = \ldots x_i (n_i + 1/2)^2.
\]
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 \( q_i q_i^2 \). There are several classes of such matrix elements: \((\Delta n_i, \Delta n_j) = (1,0), (\Delta n_i, \Delta n_j) = (-1,0), (1,2), (1,-2), (\Delta n_i, \Delta n_j) = (-1,2), \text{ and } (-1,-2)\). The first two have only \( \pm \omega_i \) in the denominator, while the other four have energy denominators of the form \( \pm \omega_i \pm 2 \omega_j \). 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 \( \mathbf{H}^{(1)} \)
\[
E_{n_1, n_2 \ldots n_{3N-6}} = \ldots x_{ij} (n_i + 1/2)(n_j + 1/2)
\]
which comes from diagonal \((\Delta n_i = 0, \Delta n_j = 0)\) matrix elements of \( q_i q_j^2 \). 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 \( q_i^2 q_j \) and \( q_j^2 q_i \). The selection rules for \( q_i \) is \( \Delta n_i = \pm 1 \) and the energy denominator will be \( \pm \omega_i \). Derive this term.

E. [OPTIONAL] The final term in \( x_{ij} \) comes from matrix elements of terms like \( q_i q_j q_k \). There are eight such terms: \((\Delta n_i, \Delta n_j, \Delta n_k) = (1,1,1), (1,-1,1), \ldots (-1,-1,-1)\) 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.
\[
B_{v_1, v_2 \ldots v_{3N-6}} = B_k - \sum_{i=1}^{3N-6} \alpha_i (v_i + 1/2).
\]
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.
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 $H^{(0)} + H^{(1)}$

$$H^{(0)}/\hbar c = \frac{1}{2} (aa^\dagger + a^\dagger a) \frac{1}{2\pi \epsilon} (k/\mu)^{1/2} + B_e (J + 1)$$

$$B_e = \frac{\hbar}{8\pi^2 \epsilon \mu R_e^2}$$

$$H^{(1)}/\hbar c = (a/\hbar c) x^3 - 2B_e (x/R_e) J(J + 1)$$

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

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

$$- \frac{2aB_e}{\hbar c R_e} J(J + 1) \sum_v \frac{\langle v| x^3 \rangle^2}{\langle E_v^{(0)} - E_v^{(0)} \rangle / \hbar c} \sum_{v'v} \langle v| x^3 \rangle \langle v'| x^3 \rangle \frac{\langle v'| x^3 | v \rangle}{\langle E_v^{(0)} - E_v^{(0)} \rangle / \hbar c}$$

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

3. CTDL, page 205, #9.