Lectures #14 & #15: <u>Non-Degenerate Perturbation Theory I</u>

Last time: finished with Harmonic Oscillator

Foundation for our picture of intra-molecular nuclear motions in all molecules.

Emphasis was on creating a non-stationary initial state ("wavepacket"), composed as a linear combination of Harmonic Oscillator eigenstates

$$\Psi(x, t = 0) = \sum_{v=0}^{\infty} c_v \psi_v(x),$$

and using the time-evolution of this wavepacket to illustrate some of the most fundamental dynamical processes:

 * dephasing and rephasing
 * Newton's laws for motion of "center" of wavepacket
 * tunneling through a barrier (to deal with this we had to wave our arms to describe the effect of the barrier on the *non*-Harmonic Oscillator pattern of energy eigenstates)

This is one of the things that perturbation theory will enable us to do.

Today: We have covered two exactly solved model systems:

   particle in box
   harmonic oscillator

and will soon cover two more:

   rigid rotor
   Hydrogen atom

These are much more than beads on a lovely necklace.

How do we use these exactly solved models to gain an understanding of molecular structure and dynamics? How are the quantities we want to know in order to form an intuitive physical picture of the molecule related to what we can measure in a do-able experiment.

Spectroscopy! Everything we might want to know about a molecule is *encoded* in the spectrum. For example, we never directly measure a bond length or a force constant.

<u>Perturbation Theory</u> tells us how the quantity we are interested in expresses itself in a do-able experiment.

Perturbation Theory:

ugly but useful
gives us *energy level formulas*
defines *molecular constants*
conversion of directly calculable R-dependent quantities into directly measureable
          quantum number dependent quantities
E(quantum numbers) = Σ(molecular constants)(quantum numbers)

One example:

$$E_{vib}(v_1, v_2) = hc\left[\omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2)\right.$$
$$\left. + x_{11}(v_1 + 1/2)^2 + x_{22}(v_2 + 1/2)^2 + x_{12}(v_1 + 1/2)(v_2 + 1/2)\right]$$

v_1, v_2 are quantum numbers

$\omega_1, \omega_2, x_{11}, x_{12}, x_{22}$ are molecular constants [How are these vibrational molecular constants related to the atomic masses and the potential energy function, $V(R_1, R_2, R_{12})$?]

Another example: the Stark Effect. How does an external electric field interact with the electric dipole moment of a molecule to *shift* and *split* the rotational energy levels of a diatomic molecule?

$$E(J, M_J; \varepsilon) = hc\left[B_v J(J+1) + (\mu\varepsilon)^2 f(J, M_J)\right]$$

where μ is the electric dipole moment (what we want to know), ε is the electric field, and $f(J, M_J)$ is a complicated algebraic function expressed in terms of B_v, J, M_J, which you will derive using perturbation theory.

Formal derivation of perturbation theory

$$\mathbf{H}\psi = E\psi$$

$$\mathbf{H} = \mathbf{H}^{(0)} + \lambda\mathbf{H}^{(1)} + \underbrace{\lambda^2\mathbf{H}^{(2)}}_{\substack{\text{usually we} \\ \text{ignore this}}}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}$$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \underbrace{\lambda^2\psi_n^{(2)}}_{\substack{\text{usually we} \\ \text{ignore this}}}$$

$\mathbf{H}^{(2)}$ is ignored because we decide to put all bad stuff into $\mathbf{H}^{(1)}$. This is a choice dictated by convenience.

$\psi_n^{(2)}$ is ignored because we observe energy levels, not wavefunctions, and it will be clear that energy terms calculated using $\psi_n^{(2)}$ will be very small.

λ is an "order-sorting" or "smallness" parameter that guides us through the derivation.

(MOSTLY) NON-LECTURE: Derivation of Perturbation Theory Formulas

$$\left[\mathbf{H}^{(0)} + \lambda\mathbf{H}^{(1)} + \lambda^2\mathbf{H}^{(2)}\right]\left[\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)}\right]$$
$$= \left[E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\right]\left[\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)}\right]$$

arrange the terms into three separate equations according to the power of λ. We want to find algebraic formulas, the form of which does not depend on λ.

$\underline{\lambda^0 \text{ equation}}$:

$$\mathbf{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

Evidently $\left\{\psi_i^{(0)}\right\}$ are eigenfunctions of $\mathbf{H}^{(0)}$ that belong to eigenvalues $\left\{E_i^{(0)}\right\}$.

The $\left\{\psi_i^{(0)}\right\}$ are *a "complete basis set"* that provides the algebraic and interpretive framework for everything. They are called "basis states" or "zero-order states." $\mathbf{H}^{(0)}$ is the Hamiltonian for one of four favorite exactly-solved problems.

$\underline{\lambda^1 \text{ equation}}$:

$$\boxed{\mathbf{H}^{(0)}\psi_n^{(1)} + \mathbf{H}^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}}$$

multiply on the left by $\psi_n^{(0)*}$ and integrate

$$\int\psi_n^{(0)*}\mathbf{H}^{(0)}\psi_n^{(1)}d\tau + \int\psi_n^{(0)*}\mathbf{H}^{(1)}\psi_n^{(0)}d\tau = E_n^{(0)}\int\psi_n^{(0)*}\psi_n^{(1)}d\tau + E_n^{(1)}\int\psi_n^{(0)*}\psi_n^{(0)}d\tau .$$

Simplifications result because $\psi_n^{(0)}$ is an eigenfunction of $\mathbf{H}^{(0)}$ that belongs to eigenvalue $E_n^{(0)}$ and the basis set, $\left\{\psi_i^{(0)}\right\}$, is both complete and orthonormal. Term by term we have

$$E_n^{(0)} \int \psi_n^{(0)*} \psi_n^{(1)} d\tau + H_{nn}^{(1)} = E_n^{(0)} \int \psi_n^{(0)*} \psi_n^{(1)} d\tau + E_n^{(1)}.$$

The $E_n^{(0)} \int \psi_n^{(0)} \psi_n^{(1)} d\tau$ term appears on both LHS and RHS. It is NOT assumed here to be zero. Cancel it. We are left with

$$H_{nn}^{(1)} = E_n^{(1)}.$$

This equation means that the *expectation value* of $\mathbf{H}^{(1)}$ with respect to $\psi_n^{(0)}$ is the first-order correction to the energy, $E_n^{(1)}$:

$$\boxed{E_n^{(1)} \equiv \int \psi_n^{(0)*} \mathbf{H}^{(1)} \psi_n^{(0)} d\tau = H_{nn}^{(1)}}.$$

Next, multiply the original equation on the left by $\psi_m^{(0)*}$ where m ≠ n and integrate.

$$\int \psi_m^{(0)*} \mathbf{H}^{(0)} \psi_n^{(1)} d\tau + \int \psi_m^{(0)*} \mathbf{H}^{(1)} \psi_n^{(0)} d\tau = E_n^{(0)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau + E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(0)} d\tau$$

$$E_m^{(0)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau + H_{mn}^{(1)} = E_n^{(0)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau + 0$$

$$\left(E_m^{(0)} - E_n^{(0)}\right) \int \psi_m^{(0)*} \psi_n^{(1)} d\tau = -H_{mn}^{(1)}$$

$$\boxed{\int \psi_m^{(0)*} \psi_n^{(1)} d\tau = \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}}}.$$

Exploit completeness of $\left\{\psi_i^{(0)}\right\}$ to expand unknown $\psi_n^{(1)}$ in terms of known $\left\{\psi_i^{(0)}\right\}$:

$$\psi_n^{(1)} = \sum_{m \neq n} a_m \psi_m^{(0)} \qquad$$ (m ≠ n because otherwise the RHS of the boxed equation above would blow up).

To evaluate the $\{a_m\}$ we multiply on the left by $\psi_m^{(0)*}$ and integrate, and then insert the result into the boxed equation above:

$$\int \psi_m^{(0)*} \sum_{m \neq n} a_m \psi_m^{(0)} d\tau = a_m = \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} .$$

This is a really useful result because now we have a simple expression for each of the $\psi_n^{(1)}$ in terms of the $\left\{\psi_i^{(0)}\right\}$ and the $\left\{E_i^{(0)}\right\}$:

$$\boxed{\psi_n^{(1)} = \sum_{m \neq n} \psi_m^{(0)} \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}}} .$$

It would be the ultimate in masochism for you to follow the derivation beyond this point!

$\underline{\lambda^2 \text{ equation}}$:

$$\mathbf{H}^{(0)}\psi_n^{(2)} + \mathbf{H}^{(1)}\psi_n^{(1)} + \mathbf{H}^{(2)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$$

Multiply on left by $\psi_n^{(0)}$ and integrate, then use what we already know about $\psi_n^{(1)}$ and $E_n^{(1)}$.

$$E_n^{(0)} \int \psi_n^{(0)*}\psi_n^{(2)}d\tau + \sum_{j \neq n} \frac{H_{nj}^{(1)}H_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}} + \int \psi_n^{(0)*}\mathbf{H}^{(2)}\psi_n^{(0)}d\tau$$

$$= E_n^{(0)} \int \psi_n^{(0)*}\psi_n^{(2)}d\tau + E_n^{(2)}$$

The $E_n^{(0)} \int \psi_n^{(0)*}\psi_n^{(2)}d\tau$ term is repeated on LHS and RHS, cancel it.

$$\boxed{E_n^{(2)} = \sum_{j \neq n} \frac{\mathbf{H}_{nj}^{(1)}\mathbf{H}_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}} + \mathbf{H}_{nn}^{(2)}}$$

Now multiply original equation on left by $\psi_m^{(0)*}$ $(m \neq n)$ and integrate:

$$\int \psi_m^{(0)*} \mathbf{H}^{(0)} \psi_n^{(2)} d\tau + \int \psi_m^{(0)*} \mathbf{H}^{(1)} \psi_n^{(1)} d\tau + \int \psi_m^{(0)*} \mathbf{H}^{(2)} \psi_n^{(0)} d\tau$$

$$= E_n^{(0)} \int \psi_m^{(0)*} \psi_n^{(2)} d\tau + E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau + E_n^{(2)} \int \psi_m^{(0)*} \psi_n^{(0)} d\tau$$

Evaluate the second term on the LHS

$$\int \psi_m^{(0)*} H^{(1)} \psi_n^{(1)} d\tau = \int \psi_m^{(0)*} H^{(1)} \left[\sum_{j \neq n} \psi_j^{(0)} \frac{H_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}} \right] d\tau = \sum_j \frac{H_{mj}^{(1)} H_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}}$$

Evaluate the second term on the RHS

$$E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau = E_n^{(1)} \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}}.$$

Combine the first term on the LHS with the first term on the RHS to get
$$\left(E_m^{(0)} - E_n^{(0)} \right) \int \psi_m^{(0)} \psi_n^{(2)} d\tau .$$

Putting it all together:

$$\left(E_m^{(0)} - E_n^{(0)} \right) \int \psi_m^{(0)} \psi_n^{(2)} d\tau + \sum_j \frac{H_{mj}^{(1)} H_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}} + H_{mn}^{(2)} - E_n^{(1)} \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} = 0$$

$$\int \psi_m^{(0)*} \psi_n^{(2)} d\tau = \frac{1}{\left(E_m^{(0)} - E_n^{(0)} \right)} \sum_j \frac{H_{mj}^{(1)} H_{jn}^{(1)}}{E_m^{(0)} - E_j^{(0)}} + \frac{H_{mn}^{(2)}}{E_m^{(0)} - E_n^{(0)}} + \frac{E_n^{(1)} H_{mn}^{(1)}}{\left(E_n^{(0)} - E_m^{(0)} \right)^2} = 0$$

Use completeness to evaluate $\psi_n^{(2)}$:

$$\psi_n^{(2)} = \sum_{m \neq n} \psi_m^{(0)} \left\{ -\frac{\mathbf{H}_{mn}^{(2)}}{E_n^{(0)} - E_m^{(0)}} + \frac{E_n^{(1)} \mathbf{H}_{mn}^{(1)}}{\left(E_n^{(0)} - E_m^{(0)} \right)^2} - \sum_{j \neq m} \frac{\mathbf{H}_{mj}^{(1)} \mathbf{H}_{jn}^{(1)}}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_m^{(0)} - E_j^{(0)} \right)} \right\} .$$

But we will NEVER use $\mathbf{H}^{(2)}$ or $\psi^{(2)}$ in standard problems. WHY?

END OF NON-LECTURE

Detailed worked example of Non-Degenerate Perturbation Theory

Suppose we have an anharmonic interaction between two vibrational normal modes. The two most important anharmonic interaction mechanisms are:

* Cubic

$$\frac{1}{2}k_{122}Q_1Q_2^2 \quad \text{and} \quad \frac{1}{2}k_{112}Q_1^2Q_2$$

* Quartic

$$\frac{1}{4}k_{1122}Q_1^2Q_2^2 .$$

These inter-mode anharmonic interactions contribute to terms in the vibrational energy level expression (*structure*) and to the flow of excitation from one normal mode to another (*dynamics*). This dynamical effect is called **Intramolecular Vibrational Redistribution (IVR)**.

The standard formulas of Perturbation Theory:

$$H = H^{(0)} + H^{(1)}$$

$$E_n = E_n^{(0)} + H_{nn}^{(1)} + \sum_{m \neq n} \frac{\left|H_{nm}\right|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \psi_m^{(0)} \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} .$$

For vibrations it is convenient to express everything in terms of creation and annihilation operators. We are using the *essential* tool for harmonic oscillators to describe anharmonic oscillators.

$$\mathbf{Q} = \left[\frac{\hbar}{2\pi c\mu\omega} \right]^{1/2} \widetilde{\mathbf{Q}} = \left[\frac{\hbar}{4\pi c\mu\omega} \right]^{1/2} \left(\mathbf{a} + \mathbf{a}^\dagger \right)$$

$$\mathbf{P} = \left[2\pi\hbar c\mu\omega \right]^{1/2} \widetilde{\mathbf{P}} = i\left[\pi\hbar c\mu\omega \right]^{1/2} \left(\mathbf{a}^\dagger - \mathbf{a} \right)$$

$$\omega = \frac{1}{2\pi c} \left[\frac{k}{\mu} \right]^{1/2}$$

following standard spectroscopic notation ω is now in cm^{-1} units rather than rad/sec

Recall

$$\mathbf{a}^\dagger \psi_v = (v+1)^{1/2} \psi_{v+1}$$

$$\mathbf{a}\psi_v = v^{1/2}\psi_{v-1}$$

$$\underbrace{\mathbf{a}^\dagger \mathbf{a}}\psi_v = \underbrace{\mathbf{N}}\psi_v = v\psi_v$$

number operator $\mathbf{aa}^\dagger = \mathbf{a}^\dagger\mathbf{a} + [\mathbf{a}, \mathbf{a}^\dagger] = \mathbf{a}^\dagger\mathbf{a} + 1$

$$\mathbf{H}^{(0)} = \frac{1}{2\mu}\mathbf{P}^2 + \frac{k}{2}\mathbf{Q}^2$$

$$= -\frac{1}{2\mu}\left[\pi\hbar c\mu\omega \right]\left(\mathbf{a}^{\dagger 2} + \mathbf{a}^2 - \mathbf{a}^\dagger\mathbf{a} - \mathbf{aa}^\dagger \right)$$

$$+ \frac{k}{2}\frac{\hbar}{4\pi c\mu\omega}\left(\mathbf{a}^{\dagger 2} + \mathbf{a}^2 + \mathbf{a}^\dagger\mathbf{a} + \mathbf{aa}^\dagger \right).$$

Simplify the coefficients in front of the $\widetilde{\mathbf{P}}^2$ and $\widetilde{\mathbf{Q}}^2$ terms

$$\frac{1}{2\mu}\left(\pi hc\mu\omega\right) = \frac{hc}{4}\omega \qquad\qquad (\hbar = h/2\pi)$$

$$\frac{k}{2}\frac{h}{4\pi c\mu\omega} = \underbrace{\left(\frac{1}{4\pi^2 c^2}\frac{k}{\mu}\right)}_{\omega^2}\frac{\pi}{2}\frac{hc}{\omega} = \frac{hc}{4}\omega$$

$$\mathbf{H}^{(0)} = \frac{hc\omega}{4}\left[-\mathbf{a}^{\dagger 2} - \mathbf{a}^2 + \mathbf{a}^{\dagger 2} + \mathbf{a}^2 + 2\mathbf{a}^\dagger\mathbf{a} + 2\mathbf{aa}^\dagger\right]$$

(note the cancelation of the $\mathbf{a}^2$ and $\mathbf{a}^{\dagger 2}$ terms)

$$= \frac{hc\omega}{2}[2\mathbf{N}+1]$$

$\mathbf{H}^{(0)}|v\rangle = hc\omega\,(v + \frac{1}{2})$ as expected.

Now we want to use this formalism to describe the energy levels and dynamics of two anharmonically coupled harmonic oscillators.

$$\mathrm{H}^{(0)} = \mathrm{H}_1^{(0)} + \mathrm{H}_2^{(0)}$$

$$|v_1 v_2\rangle^{(0)} = |v_1\rangle^0 |v_2\rangle^0 \qquad\qquad \text{two non-interacting harmonic oscillators}$$

$$\frac{E^{(0)}(v_1, v_2)}{hc} = \omega_1^{(0)}(v_1 + 1/2) + \omega_2^{(0)}(v_2 + 1/2) \quad \text{this is the "zero-order" energy level formula}$$

Introduce cubic and quartic coupling terms:

$$\mathbf{H}^{(1)} = \frac{1}{2}k_{112}\mathbf{Q}_1^2\mathbf{Q}_2 + \frac{1}{2}k_{122}\mathbf{Q}_1\mathbf{Q}_2^2 + \frac{1}{4}k_{1122}\mathbf{Q}_1^2\mathbf{Q}_2^2 .$$

The *empirical* spectroscopic fitting equation is

$$\frac{\mathrm{E}(v_1, v_2)}{hc} = \omega_1\left(v_1 + 1/2\right) + \omega_2\left(v_2 + 1/2\right) + \omega x_{11}\left(v_1 + 1/2\right)^2$$

$$+ \omega x_{22}\left(v_2 + 1/2\right)^2 + \omega x_{12}\left(v_1 + 1/2\right)\left(v_2 + 1/2\right).$$

Our goal is to express the experimentally measureable fit parameters

$$\{\omega_1, \omega_2, x_{11}, x_{22}, x_{12}\}$$

in terms of the computed microscopic parameters $\left\{\omega_1^{(0)}, \omega_2^{(0)}, k_{112}, k_{122}, k_{1122}\right\}$ [each of which is related to a derivative of the $V(\Delta R_1, \Delta R_2)$ potential energy function, computed at equilibrium geometry $(\Delta R_1 = 0, \Delta R_2 = 0)$].

To do this we have to write $\mathbf{H}^{(1)}$ in terms of $\mathbf{a}_1, \mathbf{a}_1^\dagger, \mathbf{N}_1, \mathbf{a}_2, \mathbf{a}_2^\dagger, \mathbf{N}_2$ and then apply non-degenerate perturbation theory. To minimize the ugliness, it is best to organize all of the ensuing algebra according to the selection rules of the various operators.

$$
\begin{aligned}
\mathbf{H}^{(1)} = {} & \frac{1}{2} k_{112} \mathbf{Q}_1^2 \mathbf{Q}_2 + \frac{1}{2} k_{122} \mathbf{Q}_1 \mathbf{Q}_2^2 + \frac{1}{4} k_{1122} \mathbf{Q}_1^2 \mathbf{Q}_2^2 \\
= {} & A\left[\mathbf{a}_1^{\dagger 2} \mathbf{a}_2^\dagger + \mathbf{a}_1^{\dagger 2} \mathbf{a}_2 + \mathbf{a}_1^2 \mathbf{a}_2^\dagger + \mathbf{a}_1^2 \mathbf{a}_2 + \left(2\mathbf{N}_1 + 1\right)\mathbf{a}_2 + \left(2\mathbf{N}_1 + 1\right)\mathbf{a}_2^\dagger \right] \\
& + B\left[\mathbf{a}_1^\dagger \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1^\dagger \mathbf{a}_2^2 + \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1 \mathbf{a}_2^2 + \left(2\mathbf{N}_2 + 1\right)\mathbf{a}_1 + \left(2\mathbf{N}_2 + 1\right)\mathbf{a}_1^\dagger \right] \\
& + C\Big[\mathbf{a}_1^{\dagger 2} \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1^{\dagger 2} \mathbf{a}_2^2 + \mathbf{a}_1^2 \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1^2 \mathbf{a}_2^2 \\
& \quad + \left(2\mathbf{N}_1 + 1\right)\left(2\mathbf{N}_2 + 1\right) + \left(2\mathbf{N}_1 + 1\right)\mathbf{a}_2^{\dagger 2} + \left(2\mathbf{N}_1 + 1\right)\mathbf{a}_2^2 \\
& \quad + \mathbf{a}_1^{\dagger 2}\left(2\mathbf{N}_2 + 1\right) + \mathbf{a}_1^2\left(2\mathbf{N}_2 + 1\right) \Big]
\end{aligned}
$$

A fair amount of simplifying algebra has been done, employing $[\mathbf{a}, \mathbf{a}^\dagger] = 1$ has been done, to combine terms

$$\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger \mathbf{a} = (2\mathbf{N} + 1).$$

All of the terms in $\mathbf{H}^{(1)}$ are sorted according to their $\Delta v_1, \Delta v_2$ Selection Rule. The constants $\{A, B, C\}$ are related, respectively, to $k_{112}, k_{122},$ and k_{1122}.

Following is an explicitly worked out, step-by-step example of the application of non-degenerate perturbation theory to a standard problem:

1. Express $\mathbf{H}$ in terms of $\mathbf{a}, \mathbf{a}^\dagger$, and $\mathbf{N}$.

    * $\mathbf{H}^{(0)}$ gives the zero-order energies that will appear in "energy denominators"
    * $\mathbf{H}^{(1)}$ contains all of the interaction terms. They contribute to both off-diagonal and diagonal terms in $\mathbf{H}$.

2. Organize all of the integrals of $\mathbf{H}^{(1)}$ and the energy denominators from $\mathbf{H}^{(0)}$ according to the selection rule.

3.   Algebraically combine all of the terms that involve the same family of selection rules. A "family" consists of all combinations with the same $|\Delta v_1|, |\Delta v_2|$.

4.   Simplify the algebraically horrible results into sums over integer powers of the quantum numbers, e.g. $(v_1 + ½)^n (v_2 + ½)^m$.

5.   Harvest the contributions to $\{\omega_i, x_{ij}\}$ from the coefficients of $(v_1 + ½)^n (v_2 + ½)^m$, e.g. $n = m = 1 \rightarrow x_{12}$.

6.   Spend the rest of your life checking the algebra.

<div align="center">NON-LECTURE</div>

$\underline{\Delta v_1 = 0, \Delta v_2 = 0}$
$(\Delta v_1, \Delta v_2)$

(0,0) $C(2\mathbf{N}_{v_1} + 1)(2\mathbf{N}_{v_2} + 1)$

$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 v_2 \rangle = 4C(v_1 + 1/2)(v_2 + 1/2)$

$\Delta E^{(0)} = 0$

$\underline{\Delta v_1 = 0, \Delta v_2 = \pm 1}$

(0,–1) $A(2\mathbf{N}_{v_1} + 1)(\mathbf{a}_2)$

$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 v_2 + 1 \rangle = 2A(v_1 + 1/2)(v_2 + 1)^{1/2}$

$\Delta E^{(0)}/hc = -\omega_2$

(0,+1) $A(2\mathbf{N}_{v_1} + 1)(\mathbf{a}_2^\dagger)$

$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 v_2 - 1 \rangle = 2A(v_1 + 1/2)(v_2)^{1/2}$

$\Delta E^{(0)}/hc = +\omega_2$

$\underline{\Delta v_1 = \pm 1, \Delta v_2 = 0}$

(–1,0) $B(\mathbf{a}_1)(2\mathbf{N}_{v_2} + 1)$

$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 + 1, v_2 \rangle = 2B(v_1 + 1)^{1/2}(v_2 + 1/2)$

$\Delta E^{(0)}/hc = -\omega_1$

(+1,0) $B(\mathbf{a}_1^\dagger)(2\mathbf{N}_{v_2} + 1)$

$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 1, v_2 \rangle = 2B(v_1)^{1/2}(v_2 + 1/2)$

$\Delta E^{(0)}/hc = +\omega_1$

$\underline{\Delta v_1 = \pm 2, \ \Delta v_2 = \pm 1}$

$(-2,-1)$ $A\left(\mathbf{a}_1^2\right)\left(\mathbf{a}_2\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 + 2, v_2 + 1 \rangle = A\left[(v_1 + 1)(v_1 + 2)(v_2 + 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -2\omega_1 - \omega_2$$

$(+2,-1)$ $A\left(\mathbf{a}_1^{\dagger 2}\right)\left(\mathbf{a}_2\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 2, v_2 + 1 \rangle = A\left[(v_1)(v_1 - 1)(v_2 + 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = 2\omega_1 - \omega_2$$

$(-2,+1)$ $A\left(\mathbf{a}_1^2\right)\left(\mathbf{a}_2^{\dagger}\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 + 2, v_2 - 1 \rangle = A\left[(v_1 + 2)(v_1 + 1)(v_2)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -2\omega_1 + \omega_2$$

$(+2,+1)$ $A\left(\mathbf{a}_1^{\dagger 2}\right)\left(\mathbf{a}_2^{\dagger}\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 2, v_2 - 1 \rangle = A\left[(v_1)(v_1 - 1)(v_2)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = 2\omega_1 + \omega_2$$

$\underline{\Delta v_1 = \pm 1, \ \Delta v_2 = \pm 2}$

$(-2,-1)$ $B\left(\mathbf{a}_1\right)\left(\mathbf{a}_2^2\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 + 1, v_2 + 2 \rangle = B\left[(v_1 + 1)(v_2 + 2)(v_2 + 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -\omega_1 - 2\omega_2$$

$(-1,+2)$ $B\left(\mathbf{a}_1\right)\left(\mathbf{a}_2^{\dagger 2}\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 + 1, v_2 - 2 \rangle = B\left[(v_1 + 1)(v_2)(v_2 - 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -\omega_1 + 2\omega_2$$

$(+1,-2)$ $B\left(\mathbf{a}_1^{\dagger}\right)\left(\mathbf{a}_2^2\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 1, v_2 + 2 \rangle = B\left[(v_1)(v_2 + 2)(v_2 + 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = \omega_1 - 2\omega_2$$

$(+1,+2)$ $B\left(\mathbf{a}_1^{\dagger}\right)\left(\mathbf{a}_2^{\dagger 2}\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 1, v_2 - 2 \rangle = B\left[(v_1)(v_2)(v_2 - 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = \omega_1 + 2\omega_2$$

<u>$\Delta v_1 = 0, \; \Delta v_2 = \pm 2$</u>

(0,+2) $C\left(2\mathbf{N}_{v_1}+1\right)\left(\mathbf{a}_2^{\dagger 2}\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1, v_2 - 2 \right\rangle = 2C\left(v_1 + 1/2\right)\left[\left(v_2\right)\left(v_2 - 1\right)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = 2\omega_2$$

(0,–2) $C\left(2\mathbf{N}_{v_1}+1\right)\left(\mathbf{a}_2^{2}\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1, v_2 + 2 \right\rangle = 2C\left(v_1 + 1/2\right)\left[\left(v_2 + 2\right)\left(v_2 + 1\right)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -2\omega_2$$

<u>$\Delta v_1 = \pm 2, \; \Delta v_2 = 0$</u>

(+2,0) $C\left(\mathbf{a}_1^{\dagger 2}\right)\left(2\mathbf{N}_{v_2}+1\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1 - 2, v_2 \right\rangle = 2C\left[\left(v_1\right)\left(v_1 - 1\right)\right]^{1/2}\left(v_2 + 1/2\right)$$
$$\Delta E^{(0)}/hc = 2\omega_1$$

(–2,0) $C\left(\mathbf{a}_1^{2}\right)\left(2\mathbf{N}_{v_2}+1\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1 + 2, v_2 \right\rangle = 2C\left[\left(v_1 + 2\right)\left(v_1 + 1\right)\right]^{1/2}\left(v_2 + 1/2\right)$$
$$\Delta E^{(0)}/hc = -2\omega_1$$

<u>$\Delta v_1 = \pm 2, \; \Delta v_2 = \pm 2$</u>

(–2,–2) $C\left(\mathbf{a}_1^{2}\right)\left(\mathbf{a}_2^{2}\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1 + 2, v_2 + 2 \right\rangle = C\left[\left(v_1 + 2\right)\left(v_1 + 1\right)\left(v_2 + 2\right)\left(v_2 + 1\right)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -2\omega_1 - 2\omega_2$$

(–2,+2) $C\left(\mathbf{a}_1^{2}\right)\left(\mathbf{a}_2^{\dagger 2}\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1 + 2, v_2 - 2 \right\rangle = C\left[\left(v_1 + 2\right)\left(v_1 + 1\right)\left(v_2\right)\left(v_2 - 1\right)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = -2\omega_1 + 2\omega_2$$

(+2,–2) $C\left(\mathbf{a}_1^{\dagger 2}\right)\left(\mathbf{a}_2^{2}\right)$

$$\left\langle v_1 v_2 \middle| \mathbf{H}^{(1)} \middle| v_1 - 2, v_2 + 2 \right\rangle = C\left[\left(v_1\right)\left(v_1 - 1\right)\left(v_2 + 2\right)\left(v_2 + 1\right)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = 2\omega_1 - 2\omega_2$$

(+2,+2) $C\left(\mathbf{a}_1^{\dagger 2}\right)\left(\mathbf{a}_2^{\dagger 2}\right)$

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 - 2, v_2 - 2 \rangle = C\left[(v_1)(v_1 - 1)(v_2)(v_2 - 1)\right]^{1/2}$$
$$\Delta E^{(0)}/hc = 2\omega_1 + 2\omega_2$$

These are *all* of the integrals and energy denominators that we will need. Now we need to input these results into the formulas of perturbation theory.

For $E_{v_1 v_2}^{(1)} = H_{v_1 v_2, v_1 v_2}^{(1)}$ we want diagonal integrals of $\mathbf{H}^{(1)}$. There is only one such non-zero term

$$\langle v_1 v_2 | \mathbf{H}^{(1)} | v_1 v_2 \rangle = 4C(v_1 + 1/2)(v_2 + 1/2)$$

For $E_{v_1 v_2}^{(2)}$ we need to evaluate many second-order perturbation summations

$$E_{v_1 v_2}^{(2)} = \sum_{v_1' v_2'}' \frac{H_{v_1 v_2, v_1' v_2'}^2}{E_{v_1 v_2}^{(0)} - E_{v_1' v_2'}^{(0)}}$$

It turns out to be algebraically most compact if we combine terms in the sum pairwise, where the energy denominators have the same magnitude but opposite sign.

$\underline{\Delta v_1 = 0, \Delta v_2 = \pm 1}$

$$E_{v_1 v_2}^{(2)} = \left[2A(v_1 + 1/2)\right]^2 \left[\frac{v_2}{\omega_2} - \frac{(v_2 + 1)}{\omega_2}\right] = \frac{\left[2A(v_1 + 1/2)\right]^2}{\omega_2}(-1)$$

$\underline{\Delta v_1 = \pm 1, \Delta v_2 = 0}$

$$E_{v_1 v_2}^{(2)} = \frac{\left[2B(v_2 + 1/2)\right]^2}{\omega_1}(-1)$$

$\underline{\Delta v_1 = \pm 2, \ \Delta v_2 = \pm 1}$

$$E_{v_1 v_2}^{(2)} = \frac{A^2}{2\omega_1 + \omega_2}\Big[v_1(v_1 - 1)v_2 - (v_1 + 1)(v_1 + 2)(v_2 + 1)\Big]$$

$$+ \frac{A^2}{2\omega_1 - \omega_2}\Big[v_1(v_1 - 1)(v_2 + 1) - (v_1 + 2)(v_1 + 1)(v_2)\Big]$$

$$E_{v_1 v_2}^{(2)} = \frac{-A^2}{2\omega_1 + \omega_2}\left[4(v_1 + 1/2)(v_2 + 1/2) + (v_1 + 1/2)^2 + \frac{3}{4}\right]$$

$$- \frac{A^2}{2\omega_1 - \omega_2}\left[-(v_1 + 1/2)^2 + 4(v_1 + 1/2)(v_2 + 1/2) - \frac{3}{4}\right]$$

$\underline{\Delta v_2 = \pm 2, \ \Delta v_1 = \pm 1}$

$$E_{v_1 v_2}^{(2)} = \frac{B^2}{\omega_1 + 2\omega_2}\Big[v_2(v_2 - 1)v_1 - (v_2 + 1)(v_2 + 2)(v_2 + 1)\Big]$$

$$+ \frac{B^2}{2\omega_2 - \omega_1}\Big[v_2(v_2 - 1)(v_1 + 1) - (v_2 + 2)(v_2 + 1)v_1\Big]$$

$$= -\frac{B^2}{\omega_1 + 2\omega_2}\Big[4(v_1 + 1/2)(v_2 + 1/2) + (v_2 + 1/2)^2 + 3/4\Big]$$

$$- \frac{B^2}{2\omega_2 - \omega_1}\Big[4(v_1 + 1/2)(v_2 + 1/2) - (v_2 + 1/2)^2 - 3/4\Big]$$

$\underline{\Delta v_1 = 0, \ \Delta v_2 = \pm 2}$

$$E_{v_1 v_2}^{(2)} = \frac{\big[2C(v_1 + 1/2)\big]^2}{2\omega_2}\Big[v_2(v_2 - 1) - (v_2 + 2)(v_2 + 1)\Big]$$

$$= -\frac{C^2}{2\omega_2}\Big[16(v_1 + 1/2)^2(v_2 + 1/2)\Big]$$

$\underline{\Delta v_1 = \pm 2, \ \Delta v_2 = 0}$

$$E_{v_1 v_2}^{(2)} = -\frac{C^2}{2\omega_1}\Big[16(v_2 + 1/2)^2(v_1 + 1/2)\Big]$$

$\underline{\Delta v_1 = \pm 2, \ \Delta v_2 = \pm 2}$

$$E^{(2)}_{v_1 v_2} = \frac{C^2}{(2\omega_1 + 2\omega_2)}\left[v_1(v_1-1)v_2(v_2-1) - (v_1+2)(v_1+1)(v_2+2)(v_2+1)\right]$$

$$+ \frac{C^2}{(2\omega_1 - 2\omega_2)}\left[v_1(v_1-1)(v_2+2)(v_2+1) - (v_1+2)(v_1+1)v_2(v_2-1)\right]$$

$$= \frac{-C^2}{(2\omega_1 + 2\omega_2)}\left[4(v_1+1/2)^2(v_2+1/2) + 4(v_1+1/2)(v_2+1/2)^2 + 3(v_1+1/2) + 3(v_2+1/2)\right]$$

$$+ \frac{C^2}{(2\omega_1 - 2\omega_2)}\left[4(v_1+1/2)^2(v_2+1/2) - 4(v_1+1/2)(v_2+1/2)^2 - 2(v_1+1/2)^2 + 2(v_2+1/2)^2 - (v_1+1/2) + (v_2+1/2)\right]$$

Now we have completed all of the algebra needed to write out the contributions to each of the fit parameters.

END of NON-LECTURE

v-dependent factor	contribution to molecular constant
$(v_i + \frac{1}{2})^1$	ω_i
$(v_i + \frac{1}{2})^2$	x_{ii}
$(v_i + \frac{1}{2})(v_j + \frac{1}{2})$	x_{ij}
$(v_i + \frac{1}{2})^3$	y_{iii}
$(v_i + \frac{1}{2})^2(v_j + \frac{1}{2})$	y_{iij}

$$\omega_1 = \omega_1^{(0)} - \frac{3C^2}{2\omega_1 + 2\omega_2} - \frac{C^2}{2\omega_1 - 2\omega_2}$$

$$\omega_2 = \omega_2^{(0)} - \frac{3C^2}{2\omega_1 + 2\omega_2} + \frac{C^2}{2\omega_1 - 2\omega_2}$$

$$x_{11} = -\frac{4A^2}{\omega_2} - \frac{A^2}{2\omega_1 + \omega_2} + \frac{A^2}{2\omega_1 - \omega_2} - \frac{2C^2}{2\omega_1 - 2\omega_2}$$

$$x_{22} = -\frac{4B^2}{\omega_1} - \frac{B^2}{\omega_1 + 2\omega_2} + \frac{B^2}{2\omega_2 - \omega_1} + \frac{2C^2}{2\omega_1 - 2\omega_2}$$

$$x_{12} = +\underbrace{4C}_{\substack{\text{from} \\ E^{(1)}}} - \frac{4A^2}{2\omega_1 + \omega_2} - \frac{4A^2}{2\omega_1 - \omega_2} - \frac{4B^2}{\omega_1 + 2\omega_2} - \frac{4B^2}{2\omega_2 - \omega_1}$$

$$y_{112} = -\frac{16C^2}{2\omega_2} - \frac{4C^2}{2\omega_1 + 2\omega_2} + \frac{4C^2}{2\omega_1 - 2\omega_2}$$

$$y_{122} = -\frac{16C^2}{2\omega_1} - \frac{4C^2}{2\omega_1 + 2\omega_2} - \frac{4C^2}{2\omega_1 - 2\omega_2}$$

Note that there are 7 fit parameters $(\omega_1, \omega_2, x_{11}, x_{12}, x_{22}, y_{112}, y_{122})$ but only 5 independent parameters $\left(\omega_1^{(0)}, \omega_2^{(0)}, A, B, C\right)$ in the effective Hamiltonian model.

<u>Inter-mode vibrational interactions: The "Small-Molecule" and "Large-Molecule" Limits</u>

You now know how to use perturbation theory to deal with anharmonic interactions between "zero-order" normal mode vibrational states.

There are 3N–6 normal modes in an N-atom molecule. There are anharmonic interactions between the zero-order states.

An example of **small molecule limit** behavior occurs in CO_2.

There is the famous 1:2 "Fermi Resonance" between one quantum of the symmetric stretch, ω_1, and two quanta of the bending mode, ω_2.

$$\omega_1 \approx 2\omega_2$$

This means that

$$\Delta E^{(0)} = E^{(0)}_{v_1, v_2, v_3} - E^{(0)}_{v_1-1, v_2+2, v_3} = hc(\omega_1 - 2\omega_2)$$

is so small that its magnitude is comparable to the cubic anharmonic interaction strength

$$\mathbf{H}^{(1)}_{v_1, v_2, v_3; v_1-1, v_2+2, v_3} \propto k_{122}\left[v_1(v_2+2)(v_2+1)\right]^{1/2} .$$

Thus we have "spectroscopic perturbations" where the level that is of predominant $|v_1, v_2, v_3\rangle$ character contains a significant admixture of $|v_1-1, v_2+2, v_3\rangle^{(0)}$

$$\left|v_1, v_2, v_3\right\rangle = \left|v_1, v_2, v_3\right\rangle^{(0)} + \frac{\mathbf{H}^{(1)}_{v_1, v_2, v_3; v_1-1, v_2+2, v_3}}{hc(\omega_1 - 2\omega_2)}\left|v_1-1, v_2+2, v_3\right\rangle^{(0)} .$$

Two things happen at a spectroscopic perturbation:

1. The vibrational level we expect to see in the spectrum (based on vibrational transition propensity rules) is *shifted* from its expected position by

$$\delta E = \frac{\left| \mathbf{H}^{(1)}_{v_1,v_2,v_3;v_1-1,v_2+2,v_3} \right|^2}{hc\left(\omega_1 - 2\omega_2\right)} \ .$$

2. There is an "extra line" in the spectrum, which is a transition into the level that was not expected to appear in the spectrum (because it violates the vibrational propensity rules). This extra line has *borrowed intensity*

$$I_{\text{extra}} = I_{\text{main}} \left[\frac{\mathbf{H}^{(1)}_{v_1,v_2,v_3;v_1-1,v_2+2,v_3}}{hc\left(\omega_1 - 2\omega_2\right)} \right]^2 \ .$$

A lot more can be said about such perturbations, and in fact I have devoted most of my research career to the study and exploitation of such perturbations.

In the **large molecule limit** there are many "dark states" near degenerate with the spectroscopically "bright state." Each dark state borrows a small amount of the character of the bright state. The result is that the bright state character is distributed over a quasi-continuous manifold of dark states. Instead of a **single sharp transition** one sees an unresolvable manifold of many transitions that appears as a **single broadened transition**.

The reciprocal of the width of this broadened transition is taken, via the time-energy uncertainty principle

$$\Delta E \Delta t > h$$
$$\Delta t \approx h/\Delta E$$

as the rate of intramolecular vibrational redistribution or the non-radiative lifetime of the zero-order bright state. Dynamics is encoded in the eigen-energy spectrum!

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