Lecture #18: Non-Degenerate Perturbation Theory III

What is Perturbation Theory good for?

    1.   Computing the effects (pattern of energy levels, relative transition intensities in a spectrum, intramolecular dynamics) of a distortion of the potential energy function from an idealized form.
        * add a barrier to particle in a box or harmonic oscillator
        * include intra-mode vibrational anharmonicity (wave packet dynamics, effects on molecular constants ω_e, $\omega_e x_e$)
        * include inter-mode vibrational anharmonicity (IVR, spectroscopic perturbations, non-radiative decay)

    2.   Computing the mechanism for the flow of energy between different internal degrees of freedom is encoded in the energy level structure.

    3.   Computing how the internuclear distance dependence of a molecular property is manifest in the experimentally observable quantum number dependence of that quantity. One example, the subject of this lecture, is the rotational "constant" operator, B(R).

Centrifugal Distortion (D) and Vibration-Rotation Interaction (α) Constants

$$\mathrm{E}(v,J) = hc\left[\mathrm{B}_e - \alpha_e\,(v+1/2)\right]J(J+1) - hc\mathrm{D}_e\left[J(J+1)\right]^2$$

This lecture will illustrate two surprising tricks exploited by spectroscopists:

* It is possible, by observing the "pure *rotation*" spectrum (microwave spectroscopy) to measure a rotational quantity, the centrifugal distortion constant D_e, that provides an accurate measure of the harmonic *vibrational* frequency, ω_e.

* When the vibrational potential energy function, $V(\mathbf{Q})$, is expanded in a power series in the displacement coordinate, $\mathbf{Q}$, perturbation theory seems to tell us that we cannot determine the sign of the coefficients of odd powers of $\mathbf{Q}$. However, we can often obtain this sign from a cross term between rotation and vibration.

The *effective potential* is given by

$$V(\mathbf{Q}) = \frac{1}{2}k\mathbf{Q}^2 + \frac{1}{6}a\mathbf{Q}^3 + hcB(\mathbf{R})J(J+1)$$

First we must express B($\mathbf{R}$) as a power series in $\mathbf{Q}$. (This is an example of how we would determine the dependence of any $\mathbf{R}$-dependent quantity on the vibrational quantum number, v.)

$$B(\mathbf{R}) = \frac{\hbar}{2c\mu}\frac{1}{\mathbf{R}^2} \qquad \left[\text{cm}^{-1}\right]$$

$$\omega_e = \frac{1}{2\pi c}\left[\frac{k}{\mu}\right]^{1/2} \qquad \left[\text{cm}^{-1}\right]$$

$\mathbf{R} \equiv \mathbf{Q} + \text{R}_e$ do a power series expansion of $\dfrac{1}{\mathbf{R}^2} = \dfrac{1}{\text{R}_e^2\left(1 + \mathbf{Q}/\text{R}_e\right)^2}$

$$B(\mathbf{Q}) = B_e\left[1 - \frac{2\mathbf{Q}}{\text{R}_e} + \frac{3\mathbf{Q}^2}{\text{R}_e^2} + \cdots\right]$$

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

$$\left.\begin{array}{l}\dfrac{2\mathbf{Q}}{\text{R}_e} = \left[\dfrac{4h}{4\pi c\mu\omega_e\text{R}_e^2}\right]^{1/2}\left(\mathbf{a}+\mathbf{a}^\dagger\right) = \left(\dfrac{4B_e}{\omega_e}\right)^{1/2}\left(\mathbf{a}+\mathbf{a}^\dagger\right) \\[4mm] \dfrac{3\mathbf{Q}^2}{\text{R}_e^2} = \dfrac{3B_e}{\omega_e}\left(\mathbf{a}+\mathbf{a}^\dagger\right)^2 \end{array}\right\} \text{from } B(\mathbf{Q})$$

$$\frac{1}{6}a\mathbf{Q}^3 = \underbrace{\frac{a}{6}\left[\frac{h}{4\pi c\mu\omega_e}\right]^{3/2}}\left(\mathbf{a}+\mathbf{a}^\dagger\right)^3 = A(\mathbf{a}+\mathbf{a}^\dagger)^3 \qquad\qquad \text{from } V(\mathbf{Q})$$

absorb all of these constants temporarily into the fit parameter, A

A is a constant, the sign of which is the same as that of a in a$\mathbf{Q}^3$.

We are ready to begin to treat this problem by perturbation theory.

$$E_{vJ}^{(0)} = \langle vJ \mid \mathbf{H}^{(0)} \mid vJ \rangle = hc\omega_e(v+1/2) + hcB_eJ(J+1)$$

$$\mathbf{H}^{(1)} = hcB_eJ(J+1)\left[-\left(\frac{4B_e}{\omega_e}\right)^{1/2}(\mathbf{a}+\mathbf{a}^\dagger) + \frac{3B_e}{\omega_e}(\mathbf{a}+\mathbf{a}^\dagger)^2 \right] + A(\mathbf{a}+\mathbf{a}^\dagger)^3$$

$$\Delta v = \pm 1 \qquad \Delta v = 0, \pm 2 \qquad \Delta v = \pm 1, \pm 3$$

We begin by computing $E_{vj}^{(1)}$:

$$E_{vJ}^{(1)} = \langle vJ \mid \mathbf{H}^{(1)} \mid vJ \rangle = hcB_eJ(J+1)\left[\frac{3B_e}{\omega_e}(2\mathbf{N}_v+1) \right] \qquad \left(\text{from } \Delta v = 0\right)$$

$$E_{vJ}^{(1)} = hcB_eJ(J+1)\frac{6B_e}{\omega_e}(v+1/2)$$

$$\boxed{\alpha_e = -\frac{6B_e^2}{\omega_e}}.$$

This is the *harmonic* contribution to the vibration-rotation constant, α_e. Note that $\alpha_e < 0$, thus B_v increases as $(v + \frac{1}{2})$. We expect the vibrational excitation would on average lengthen R, thus cause B_v to decrease with v. But the harmonic contribution exhibits the opposite behavior. WHY?

Now we look at the effects of the $\Delta v \neq 0$ matrix elements on E_{vJ}.

$\underline{\Delta v = \pm 1 \text{ matrix elements}}$, from both $(\mathbf{a} + \mathbf{a}^\dagger)$ and $(\mathbf{a} + \mathbf{a}^\dagger)^3$ terms in $\mathbf{H}^{(1)}$:

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)|v+1\rangle = (v+1)^{1/2}$$

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)|v-1\rangle = v^{1/2}$$

$$(\mathbf{a}+\mathbf{a}^\dagger)^3 = \underbrace{\mathbf{a}^3}_{\Delta v=-3} + \underbrace{\mathbf{a}^{\dagger 3}}_{\Delta v=+3} + \underbrace{3(\mathbf{a}^2\mathbf{a}^\dagger - \mathbf{a})}_{\Delta v=-1} + \underbrace{3(\mathbf{a}^{\dagger 2}\mathbf{a} + \mathbf{a}^\dagger)}_{\Delta v=+1}$$

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)^3|v+1\rangle = \langle v|3(\mathbf{a}^{\dagger 2}\mathbf{a}+\mathbf{a}^\dagger)|v+1\rangle = 3(v+1)^{3/2}$$

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)^3|v-1\rangle = \langle v|3(\mathbf{a}^2\mathbf{a}^\dagger - \mathbf{a})|v-1\rangle = 3v^{3/2}$$

We are going to get a cross-term in $E_{vJ}^{(2)}$ between the $hcB_eJ(J+1)\left(\dfrac{4B_e}{\omega_e}\right)^{1/2}$ and $A(\mathbf{a}+\mathbf{a}^\dagger)^3$ terms.

$\underline{\Delta v = \pm 2}$

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)^2|v+2\rangle = \left[(v+2)(v+1)\right]^{1/2}$$

$$\langle v|(\mathbf{a}+\mathbf{a}^\dagger)^2|v-2\rangle = \left[v(v-1)\right]^{1/2}$$

<u>$\Delta v = \pm 3$</u>

$$\left\langle v \middle| (\mathbf{a} + \mathbf{a}^{\dagger})^3 \middle| v+3 \right\rangle = \left[(v+3)(v+2)(v+1) \right]^{1/2}$$

$$\left\langle v \middle| (\mathbf{a} + \mathbf{a}^{\dagger})^3 \middle| v-3 \right\rangle = \left[(v-2)(v-1)v \right]^{1/2}$$

Some algebra:

$$E_{vJ}^{(2)} = \left[hcB_e J(J+1) \right]^2 \left(\frac{4B_e}{\omega_e} \right) \left[\frac{v+1}{-hc\omega_e} + \frac{v}{hc\omega_e} \right]$$

$$-2 \left[hcB_e J(J+1) \right] \left(\frac{4B_e}{\omega_e} \right)^{1/2} A \left[\frac{3(v+1)^{3/2}(v+1)^{1/2}}{-hc\omega_e} + \frac{3(v)^{3/2}v^{1/2}}{hc\omega_e} \right]$$

$$+A^2 9 \left[\frac{(v+1)^3}{-hc\omega_e} + \frac{v^3}{hc\omega_e} \right]$$

$$+ \left[hcB_e J(J+1) \right]^2 \left(\frac{3B_e}{\omega_e} \right)^2 \left[\frac{(v+2)(v+1)}{-2hc\omega_e} + \frac{v(v-1)}{2hc\omega_e} \right]$$

$$+A^2 \left[\frac{(v+3)(v+2)(v+1)}{-3hc\omega_e} + \frac{(v-2)(v-1)v}{3hc\omega_e} \right]$$

$$E_{vJ}^{(2)} = -hc \frac{4B_e^3}{\omega_e^2} [J(J+1)]^2 + 24 \left(\frac{B_e}{\omega_e} \right)^{3/2} AJ(J+1)(v+1/2)$$

$$- \frac{9A^2}{hc\omega_e} \left[(v+1/2)^2 + \frac{1}{4} \right]$$

$$-hc \frac{B_e^4}{\omega_e^3} [J(J+1)]^2 9 \left[(v+1/2) + \frac{1}{2} \right]$$

$$- \frac{A^2}{hc\omega_e} \left[3(v+1/2)^2 + \frac{5}{4} \right].$$

Thus

$$D_e = \frac{4B_e^3}{\omega_e^2} \qquad \text{(Kratzer equation)}$$

> Note that A is not squared! So we sample its sign.

$$\alpha_e = -24\,A \left(\frac{B_e}{\omega_e} \right)^{3/2} - \frac{6B_e^2}{\omega_e} \quad \left(B_v \quad B_e - \alpha_e(v+1/2) \right) \; (A < 0)$$

$$\omega_e x_e = \frac{12\,A^2}{\omega_e}$$

$$\beta_e = -\frac{9B_e^4}{\omega_e^3} \quad \left(D_v = D_e + \beta_e(v+1/2) \right)$$

Note that, if $A < 0$, then $\alpha_e > 0$ and B_v decreases as v increases. For $A < 0$, the cubic term causes the potential energy curve to have the physically expected asymmetry. What is that?

Non-degenerate perturbation theory is a tool that no experimental spectroscopist can live without. It provides surprising and useful inter-relationships between observable quantities. It permits honing of intuition. It provides the observable consequences of every imaginable departure from ideality. It explains why experimentalists and theorists often "fail to communicate" because they use the same symbol to refer to physically different quantities.

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