

Lecture #27: Non-Degenerate Perturbation Theory III

Experiment ↔ Theory and In-Between

We have seen three methods for deriving or estimating $\{E_n\}$ and $\{\psi_n\}$. Hückel Theory and minimal basis set LCAO-MO Theory are based on estimates of the crucial parameters based on intuition and experience. They are “semi-empirical” because they are based on calibrated empirical estimates of fundamental-sounding quantities. They are not “fit models”, but they usually involve some sort of matrix-diagonalization or small basis-set variational calculation.

In contrast, Non-Degenerate Perturbation Theory is a fit model. It is based on a zero-order model (to define the $\{E_n\}$ and $\{\psi_n\}$ of a basis set) and some inconvenient terms in a realistic Hamiltonian, $\mathbf{H}^{(1)}$, which involve directly calculable diagonal and off-diagonal matrix elements that are used to compute $E_n^{(1)}$, $E_n^{(2)}$, and $\psi_n^{(1)}$. Perturbation Theory is, in principle, an infinite basis set method. We get from perturbation theory relationships between energy level formulas for observed levels and the structure-based formulas for $V_j(R)$. From this we get best possible fit models, relationships between fit parameters, ability to compute patterns in predicted energy levels, and *intramolecular dynamics*. Mechanism!

We are about to see *ab initio* computational methods that make no assumptions about empirical parameters. These calculations, when extended to a very large basis set, are capable of nearly exact representations of the properties of real molecules. In some sense these large basis calculations are identical to exact experimental measurements. Neither experiment nor calculation provide intuitive pictures of structure or dynamics. These intuitive pictures require reduction to toy models and special limiting cases. Insight and transferable prediction require finding an optional location along the continuum:

empirical — semi-empirical — *ab initio*.

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 $\omega_e, \omega_e x_e$)
 - * include inter-mode vibrational anharmonicity (IVR, spectroscopic perturbations, non-radiative decay)
2. The mechanism for the flow of energy between different internal degrees of freedom is encoded in the energy level structure. Rates and pathways for intramolecular energy transfer can be computed.

3. Computing how the internuclear distance dependence of a molecular property is manifest in the experimentally observable ν and J quantum number dependences of that quantity. One example, the subject of this lecture, is the rotational “constant” operator, $B(\mathbf{R})$.

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

Constants

$$E(\nu, J) = hc \left[B_e - \alpha_e \left(\nu + \frac{1}{2} \right) \right] J(J+1) - hc D_e [J(J+1)]^2$$

note
note
(expected sign)

↓
↓
↑
↑

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

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

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, ν .)

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

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

$$\mathbf{R} \equiv \mathbf{Q} + R_e \quad \text{do a power series expansion of } \frac{1}{\mathbf{R}^2} = \frac{1}{R_e^2 (1 + \mathbf{Q}/R_e)^2}$$

$$B(\mathbf{Q}) = B_e \left[1 - \frac{2\mathbf{Q}}{R_e} + \frac{3\mathbf{Q}^2}{R_e^2} + \dots \right]$$

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

$$\left. \begin{aligned} \frac{2\mathbf{Q}}{R_e} &= \left[\frac{4\hbar}{4\pi c\mu\omega_e R_e^2} \right]^{1/2} (\mathbf{a} + \mathbf{a}^\dagger) = \left(\frac{4B_e}{\omega_e} \right)^{1/2} (\mathbf{a} + \mathbf{a}^\dagger) \\ \frac{3\mathbf{Q}^2}{R_e^2} &= \frac{3B_e}{\omega_e} (\mathbf{a} + \mathbf{a}^\dagger)^2 \end{aligned} \right\} \text{from } B(\mathbf{Q})$$

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

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

A is a constant (in energy units) 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.

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

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

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

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

There is only one term with a $\Delta v = 0$ selection rule:

$$E_{vJ}^{(1)} = \langle vJ | \mathbf{H}^{(1)} | vJ \rangle = hcB_e J(J+1) \left[\frac{3B_e}{\omega_e} (2N_v + 1) \right] \quad (\text{from } \Delta v = 0)$$

$$E_{vJ}^{(1)} = hcB_e J(J+1) \frac{6B_e}{\omega_e} (v + 1/2) \quad [J(J+1)(v + 1/2) \text{ is the quantum number coefficient of } \alpha_e]$$

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

This is the *harmonic* contribution to the vibration-rotation constant, α_e . Note that $\alpha_e < 0$, thus B_v increases as $(v + 1/2)$. 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} .

$\Delta v = \pm 1$ 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 $hcB_e J(J+1) \left(\frac{4B_e}{\omega_e} \right)^{1/2}$ and $A(\mathbf{a} + \mathbf{a}^\dagger)^3$

terms.

$\Delta v = \pm 2$

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

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

$\Delta v = \pm 3$

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

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

Some algebra (the terms numbered 1 - 5 in the first equation are shown in simplified form in the second equation):

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

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

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

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

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

[1, 2, and 3 are $\Delta v = \pm 1$ terms from $[-B + A]^2 = B^2 - 2AB + A^2$]

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

$$- \frac{27A^2}{hc\omega_e} \left[(v+1/2)^2 + \frac{1}{4} \right]$$

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

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

combine $\Delta v = \pm 1$
and $\Delta v = \pm 3$ terms
from Q^3

Thus

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

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

$$\omega_e x_e = \frac{30A^2}{\omega_e} \quad 3 + 5 \quad \text{from } E^{(1)}$$

$$\beta_e = -\frac{9B_e^4}{\omega_e^3} (D_v = D_e + \beta_e (v+1/2)) \quad 4 \quad [\text{coefficient of } [J(J+1)]^2 (v+1/2)]$$

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

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. For example, if we have a molecular property, C , that is a function of internuclear distance, $C(R)$, then we can derive $C(R)$ from experimental observations of $C_{v,J}$. 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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