Lecture #16: Nondegenerate Perturbation Theory II: Harmonic Oscillators using a,a†

Trick is always to find easy way to evaluate $H^{(1)}_{v',v}$ integrals.

Non-degenerate Perturbation Theory: standard equations

Convergence criterion:

$$\left|\frac{H^{(1)}_{12}}{E^{(0)}_1 - E^{(0)}_2}\right| \ll 1$$

Today: Example of anharmonic oscillator

$Q \rightarrow \tilde{Q} \rightarrow \mathbf{a},\mathbf{a}^\dagger$

operator algebra for ($\mathbf{a} + \mathbf{a}^\dagger$)

selection rules and quantum number scaling

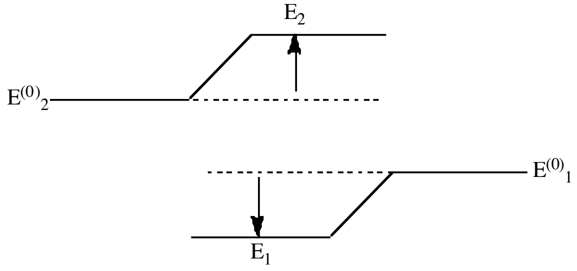
sensitivity to sign of term in V(Q) like $b\text{Q}^3 + c\text{Q}^4$

Effect of anharmonicity on parameters other than those in the energy level expression $E(v)$

Inter-mode interactions - mode specific chemistry is impossible

Long-Range interactions between neutral, non-polar molecules.

Metaphors



- off-diagonal matrix elements $\langle 2|H^{(1)}|1\rangle = H^{(1)}_{21}$
- level repulsion
- equal and opposite level shifts
- mixing
  - coefficients
  - angle
  - fraction

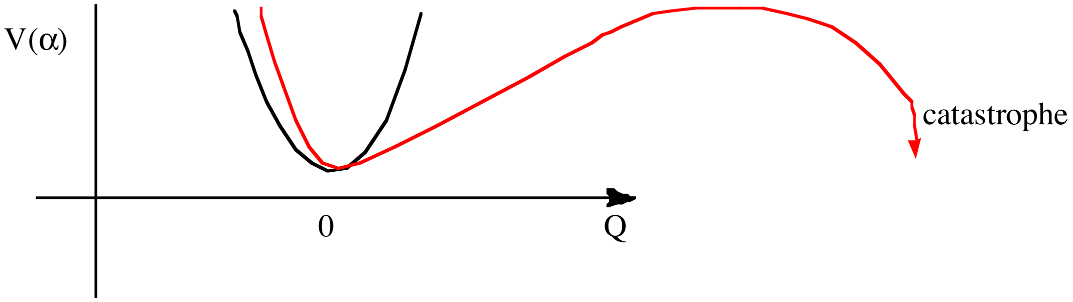
Anharmonic Oscillator

$$V(Q)=\underbrace{\frac{1}{2}kQ^2}_{V^{(0)}}+bQ^3+cQ^4$$

b < 0 creates correct asymmetry of V(Q)

$c > 0$ makes potential *steeper* at bottom
$c < 0$ makes potential *flatter* at bottom

both bQ^3 and cQ^4 have non-physical effect at large $|Q|$.



works at intermediate range of $|Q|$

Standard approach: use $\mathbf{a},\mathbf{a}^\dagger$ operator algebra

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

	$\langle v'\vert\mathbf{aaaa}^\dagger\mathbf{a}\vert v\rangle$	$\Delta v = v' - v$ selection rule
$\#(\mathbf{a}^\dagger) - \#(\mathbf{a})$	$-4 + 1 = -3$	$\Delta v = 3$

$\langle v + n|\mathbf{aaaa}^\dagger\mathbf{a}|v' + n\rangle$ quantum number scaling for $n = 0, 1, 2, \ldots$

usual conversion to universal forms

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

$\tilde{\omega}$ in cm^{-1} units

$$\tilde{\omega}=\frac{1}{2\pi hc}[k/\mu]^{1/2}$$ (previous units of ω in radians $\omega = [k/\mu]^{1/2}$)

This enables us to factor out the molecule-specific part of problem, leaving behind the universal part.

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

Need to do some operator algebra at the beginning to be able to most efficiently deal with any polynomial in Q for $V(Q)$.

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

$$(\mathbf{a}+\mathbf{a}^\dagger)^2 = \underset{\substack{\uparrow \\ \Delta \mathrm{v} = -2}}{\mathbf{a}^2} + \underset{\substack{\uparrow \\ \Delta \mathrm{v} = +2}}{\mathbf{a}^{\dagger 2}} + \underbrace{\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}}_{\substack{\text{combine these 2 terms} \\ \uparrow \\ \Delta \mathrm{v} = 0}}$$

Tricks with $[\mathbf{a},\mathbf{a}^\dagger] = 1$ commutation rule

$$\mathbf{a}\mathbf{a}^\dagger = [\mathbf{a},\mathbf{a}^\dagger] + \mathbf{a}^\dagger\mathbf{a} = 1 + \mathbf{N}$$

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

2. $$\mathbf{Q}^3 = \left[\frac{\hbar}{4\pi\mu c\omega}\right]^{3/2}(\mathbf{a}+\mathbf{a}^\dagger)^3$$

$$(\mathbf{a}+\mathbf{a}^\dagger)^3 = \underset{\Delta \mathrm{v} = -3}{\mathbf{a}^3} + \underset{-1}{(\mathbf{a}\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\mathbf{a}\mathbf{a})}$$

$$+ \underset{\Delta \mathrm{v} = +1}{(\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger)} + \underset{+3}{\mathbf{a}^{\dagger 3}}$$

Δv = –1 terms: <u>Want to collect all Δv = –1 terms as **aN** terms</u>

$$\mathbf{a}\mathbf{a}\mathbf{a}^\dagger = \mathbf{a}[\mathbf{a},\mathbf{a}^\dagger] + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} = \mathbf{a} + \mathbf{a}\mathbf{N}$$

$$\mathbf{a}\mathbf{a}^\dagger\mathbf{a} = \mathbf{a}\mathrm{N}$$

$$\mathbf{a}^\dagger\mathbf{a}\mathbf{a} = [\mathbf{a}^\dagger,\mathrm{a}]\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} = -\mathbf{a} + \mathbf{a}\mathbf{N}$$

<u>sum of $\Delta v = -1$ terms</u>: $3\mathbf{a}\mathbf{N}$

$\Delta v = +1$ terms: <u>Want all $\mathbf{a}^\dagger\mathbf{N}$ terms</u>

$\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger \quad \mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger$

$\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} = \mathbf{a}^\dagger \mathrm{N}$
$\mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger = \mathbf{a}^\dagger[\mathbf{a},\mathbf{a}^\dagger] + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} = \mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{N}$
$\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger = [\mathbf{a},\mathbf{a}^\dagger]\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger = \mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{N}$

<u>Sum of Δv = ±1 terms</u>: $3\mathbf{a}^\dagger\mathbf{N} + 3\mathbf{a}^\dagger = 3\mathbf{a}^\dagger(\mathbf{N} + 1)$

$$\mathbf{Q}^3 = \left[\frac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^{3/2}\left[\mathbf{a}^3 + 3\mathbf{a}\mathbf{N} + 3\mathbf{a}^\dagger(\mathbf{N}+1) + \mathbf{a}^{\dagger 3}\right]$$

$\Delta v =$ $\quad -3 \quad -1 \quad +1 \quad +3$

Now for NDPT: $\mathbf{H}^{(1)} = \mathrm{b}\mathbf{Q}^3$

$$E_v^{(1)} = \langle v|H^{(1)}|v\rangle = 0 \qquad \Delta v = 0$$

$$E_v^{(2)} = \sum_{v'\neq v}\frac{\left|\langle v'|H^{(1)}|v\rangle\right|}{E_v^{(0)} - E_{v'}^{(0)}}$$

For numerator: $\left[\frac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^{3} \leftarrow \frac{3}{2}\times 2$

for denominator $hc\,\tilde{\omega}\,(v - v')$ $\quad \begin{cases}\text{check sign: if } E_{v'} > E_v\text{, then v level is} \\ \text{pushed down, denominator must be negative}\end{cases}$

$$E_v^{(2)} = \frac{b^2\left[\frac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^3}{hc\tilde{\omega}}\sum_{v'\neq v}\frac{\left|\langle v'|\mathbf{a}^3 + 3\mathbf{a}\mathbf{N} + 3\mathbf{a}^\dagger(\mathbf{N}+1) + \mathbf{a}^{\dagger 3}|v\rangle\right|^2}{v - v'}$$

for
$$\left.\begin{array}{ll} v' = v+3 & \mathbf{a}^{\dagger 3} \\ v' = v+1 & 3\mathbf{a}^\dagger(\mathbf{N}+1) \\ v' = v-1 & 3\mathbf{a}\mathbf{N} \\ v' = v-3 & \mathbf{a}^3 \end{array}\right\}$$

get simple squares of each matrix element.
Why? Because we have reduced the expression to one operator for each value of Δv.

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

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

$v' = v - 1$ $\quad \langle v'|3\mathbf{a}\mathbf{N}|v\rangle = 3v^{3/2}$

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

$$E_v^{(2)} = \frac{b^2\left[\dfrac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^3}{hc\tilde{\omega}}\left[\frac{(v+1)(v+2)(v+3)}{-3} + \frac{(v)(v-1)(v-2)}{+3} + \frac{3^2(v^{3/2})^2}{+1} + \frac{3^2\left[(v+1)^{3/2}\right]^2}{-1}\right]$$

Highest power of v terms cancel pairwise — minimize algebra at the end.

$$\begin{aligned} E_v^{(2)} &= \frac{b^2\left[\dfrac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^3}{hc\tilde{\omega}}\left[\underbrace{\frac{v^3+6v^2+11v+6}{-3} + \frac{v^3-3v^2+2v+2}{+3}}_{} + \underbrace{\frac{9v^3}{+1} + \frac{9(v+1)^3}{-1}}_{}\right] \\ &= \frac{b^2\left[\dfrac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^3}{hc\tilde{\omega}}\left[\underbrace{-3v^2-3v-4/3}_{\text{from first 2 terms}} - 3v^2 - 3v - 1\right] \end{aligned}$$

Total $-6v^2 - 6v - 7/3 \approx 6(v + 1/2)^2$

$$\begin{aligned} E_v &= E_v^{(0)} + E_v^{(1)} + E_v^{(2)} \\ &= hc\tilde{\omega}(v+1/2) + 0 - C\left((v+1/2)^2 \ldots\right) \end{aligned}$$

$$C = \frac{6b^2\left[\dfrac{\hbar}{4\pi c\mu\tilde{\omega}}\right]^3}{hc\tilde{\omega}}$$

so we get

$$\begin{aligned} E_v/hc &= \tilde{\omega}_e(v+1/2) - \tilde{\omega}_e x_e(v+1/2)^2 \\ \tilde{\omega}_e x_e &= 6\frac{b^2\left[\dfrac{\hbar}{4\pi c\mu\tilde{\omega}_e}\right]^3}{(hc)^2\tilde{\omega}_e} \end{aligned}$$

Anything sensible we do to a V(Q) can be expressed by NDPT

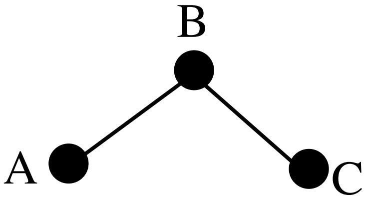
$$\frac{E_v}{hc} = \tilde{\omega}_e(v+1/2) - \widetilde{\omega_e x_e}(v+1/2)^2 + \widetilde{\omega_e y_e}(v+1/2)^3$$

$$V(Q) = \frac{1}{2}kQ^2 + bQ^3 + cQ^4$$

$\left\{\tilde{\omega}_e, \widetilde{\omega_e x_e}, \widetilde{\omega_e y_e}\right\}$ ↔ $\{k, b, c\}$

molecular constants potential energy terms

Polyatomic Molecules



AB stretch affects BC Stretch and ABC bend

Inter-mode anharmonicity

see Lecture 15 non-lecture pages at end for background information for this lecture.

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