Lecture #16: Nondegenerate Perturbation Theory II: Harmonic Oscillators using \( a, a^\dagger \)

Trick is always to find easy way to evaluate \( H^{(1)}_{\nu'} \) integrals.

Non-degenerate Perturbation Theory: standard equations

Convergence criterion:

\[
\left| \frac{H^{(1)}_{12}}{E_1^{(0)} - E_2^{(0)}} \right| \ll 1
\]

Today: Example of anharmonic oscillator

\( Q \rightarrow \tilde{Q} \rightarrow a, a^\dagger \)

operator algebra for \((a + a^\dagger)\)

selection rules and quantum number scaling

sensitivity to sign of term in \( V(Q) \) like \( bQ^3 + cQ^4 \)

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

\[
\begin{bmatrix}
E_2 \\
E_1
\end{bmatrix}
\]

\[
\begin{bmatrix}
E_1^{(0)} \\
E_2^{(0)}
\end{bmatrix}
\]

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Anharmonic Oscillator

\[ V(Q) = \frac{1}{2} k Q^2 + b Q^3 + c Q^4 \]

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 \(|Q|\).

\[ V(\alpha) \]

works at intermediate range of \(|Q|\)

Standard approach: use \(a,a^\dagger\) operator algebra

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

\[ \langle v' | a aaa a^\dagger | v \rangle \quad \Delta v = v' - v \text{ selection rule} \]
\[ \#(a^\dagger) - \#(a) = -4 + 1 = -3 \quad \Delta v = 3 \]

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

usual conversion to universal forms

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

\(\bar{\omega}\) in cm\(^{-1}\) units

\[ \bar{\omega} = \frac{1}{2 \pi \hbar c} \left[ \frac{k}{\mu} \right]^{1/2} \quad \text{(previous units of } \omega \text{ in radians } \omega = [k/\mu]^{1/2}) \]

This enables us to factor out the molecule-specific part of problem, leaving behind the universal part.
1. \[ \hat{Q}^n = \left[ \frac{\hbar}{4\pi\mu c\omega} \right]^{n/2} (a + a')^n \]

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

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

\[ (a + a')^2 = a^2 + a'^2 + aa' + a'a \]

\[ \Delta v = -2 \quad \Delta v = 0 \quad \Delta v = +2 \]

Tricks with \([a,a^\dagger] = 1\) commutation rule

\[ aa' = [a,a'] + a'a = 1 + N \]

\[ (aa' + a'a) = 2N + 1 \]

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

\[ (a + a')^3 = a^3 + (aaa' + aa'a + a'a) \]

\[ \Delta v = -3 \quad -1 \]

\[ + (a'a'a + a'a' + aa'a + a'a^2) + a^3 \]

\[ \Delta v = +1 \quad +3 \]

\[ \Delta v = -1 \text{ terms: Want to collect all } \Delta v = -1 \text{ terms as } aN \text{ terms} \]

\[ aaa' = a[a,a^\dagger] + aa'a = a + aN \]

\[ aa'a = aN \]

\[ a'a'a = [a',a]a + aa'a = -a + aN \]

sum of \( \Delta v = -1 \) terms: \( 3aN \)

\[ \Delta v = +1 \text{ terms: Want all } a'^N \text{ terms} \]
\[ a^a a^a + a^a a^a = a^a N \]
\[ a^a a^a = a^a [a^a a^a] + a^a a^a = a^a + a^a N \]
\[ a^a a^a = [a^a a^a] a^a + a^a a^a = a^a + a^a N \]

Sum of \( \Delta v = \pm 1 \) terms:

\[ 3a^a N + 3a^a = 3a^a (N + 1) \]

\[ Q^3 = \left( \frac{\hbar}{4 \pi c \mu \bar{\omega}} \right)^{3/2} \left[ a^3 + 3a^a N + 3a^a (N + 1) + a^{13} \right] \]

\[ \Delta v = \begin{array}{cccc}
-3 & -1 & +1 & +3 \\
\end{array} \]

Now for NDPT:

\[ H^{(1)} = b Q^3 \]

\[ E_v^{(1)} = \langle v | H^{(1)} | v \rangle = 0 \quad \Delta v = 0 \]

\[ E_v^{(2)} = \sum_{v'v} \frac{\langle v' | H^{(1)} | v \rangle}{E_v^{(0)} - E_{v'}^{(0)}} \]

For numerator:

\[ \left[ \frac{\hbar}{4 \pi c \mu \bar{\omega}} \right]^{3/2} \]

For denominator

\[ h c \bar{\omega} (v - v') \]

check sign: if \( E_{v'} > E_v \), then \( v \) level is pushed down, denominator must be negative

\[ E_v^{(2)} = \frac{b^2}{h c \bar{\omega}} \left[ \frac{\hbar}{4 \pi c \mu \bar{\omega}} \right]^{3/2} \sum_{v'v} \left( \frac{\langle v' | a^3 + 3a^a N + 3a^a (N + 1) + a^{13} | v \rangle}{v - v'} \right)^2 \]

\[ \begin{array}{ccc}
\nu' = v + 3 & \mathbf{a}^{13} \\
\nu' = v + 1 & 3a^a (N + 1) \\
\nu' = v - 1 & 3aN \\
\nu' = v - 3 & \mathbf{a}^3 \\
\end{array} \]

get simple squares of each matrix element.

Why? Because we have reduced the expression to one operator for each value of \( \Delta v \).

\[ \nu' = v + 3 \]

\[ \langle v' | a^{13} | v \rangle = [(v + 1)(v + 2)(v + 3)]^{1/2} \]

\[ \nu' = v + 1 \]

\[ \langle v' | 3a^a (N + 1) | v \rangle = [(v + 1)^{(1/2)} (v + 1)] = (v + 1)^{3/2} \]

\[ \nu' = v - 1 \]

\[ \langle v' | 3aN | v \rangle = 3v^{3/2} \]
\[ \nu' = \nu - 3 \quad \langle \nu' | a^3 | \nu \rangle = [(\nu)(\nu-1)(\nu-2)]^{1/2} \]

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

Highest power of \( \nu \) terms cancel pairwise — minimize algebra at the end.

\[ E_v^{(2)} = \frac{b^2}{\hbar c \tilde{\omega}} \left[ \left( \frac{\hbar}{4 \pi c \mu \tilde{\omega}} \right)^3 \left( \frac{\nu^3 + 6 \nu^2 + 11 \nu + 6}{\nu-3} + \frac{\nu^3 - 3 \nu^2 + 2 \nu + 2}{\nu+1} + \frac{9 \nu^3}{\nu+1} + \frac{9(\nu+1)^3}{\nu-1} \right) \right] \]

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

\[ E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} \]

\[ = \hbar c \tilde{\omega} (\nu + 1/2) + 0 - C \left( (\nu + 1/2)^2 \ldots \right) \]

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

so we get

\[ \frac{E_v}{\hbar c} = \tilde{\omega}_x (\nu + 1/2) - \tilde{\omega}_x x (\nu + 1/2)^2 \]

\[ \tilde{\omega}_x x = 6 \frac{b^2}{(\hbar c)^2 \tilde{\omega}} \left[ \frac{\hbar}{4 \pi c \mu \tilde{\omega}} \right]^3 \]

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

\[ \frac{E_v}{\hbar c} = \tilde{\omega}_x (\nu + 1/2) - \tilde{\omega}_x x (\nu + 1/2)^2 + \tilde{\omega}_x (\nu + 1/2)^3 \]

\[ V(Q) = \frac{1}{2} k Q^2 + b Q^3 + c Q^4 \]
\[ \{ \tilde{\omega}_e, \tilde{\omega}_e x_e, \tilde{\omega}_e y_e \} \quad \leftrightarrow \quad \{ k, b, c \} \]

molecular constants \hspace{1cm} 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.