Lecture #3: Building an Effective Hamiltonian

Last time: diatomic molecule as anharmonic non-rigid rotor

\[ Q = R - R_e \]
\[ V(Q) = \frac{1}{2}kQ^2 + \frac{1}{6}aQ^3 + \frac{1}{24}bQ^4 + \ldots \]
\[ \text{B(R)} = \frac{\hbar^2}{\hbar c} \frac{1}{2\mu R^2} \]
\[ \text{B(Q)} = B_e \left[ 1 - \frac{1}{2} \left( \frac{Q}{R_e} \right) + \frac{1}{3} \left( \frac{Q}{R_e} \right)^3 + \ldots \right] \]
\[ \omega_e = \frac{1}{2\pi c} \sqrt{\left[ k/\mu \right]/2} \]
\[ E_{vJ}/\hbar c = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 \ldots \]
\[ + J(J + 1) \left[ B_e - \alpha_e (v + 1/2) + \gamma_e (v + 1/2)^2 \ldots \right] \]
\[ - J(J + 1)^2 \left[ D_e + \beta_e (v + 1/2) + \ldots \right] \]

Problem: find \( \tilde{\omega}_e, \omega_e x_e, \omega_e y_e, \alpha_e, D_e \) in terms of \( k, a, b, R_e, \mu \) using non-degenerate perturbation theory (over-tilde implies additional corrections).

\[ H^{(0)} \psi^{(0)}_v = E^{(0)}_v \psi^{(0)}_v \] defines basis states
\[ \frac{H^{(0)}}{\hbar c} = \frac{1}{2}kQ^2 + \frac{p^2}{2\mu} + B_e J(J + 1) \Rightarrow E^{(0)}_{vJ}/\hbar c = \omega_e (v + 1/2) + B_e J(J + 1) \]
\[ \Rightarrow |v,J\rangle^0 = |v^{\text{HO}}\rangle |J M J\rangle \]

\( H' \) is everything not in \( H^{(0)}. \)

Some tools:
\[ Q = \left[ \frac{\hbar}{2\pi c \mu \omega_e} \right]^{1/2} \hat{Q} \]
\[ P = \left[ \hbar^2 2\pi c \mu \omega_e \right]^{1/2} \hat{P} \]
\[ \hat{Q} = 2^{-1/2} (a + a^\dagger) \]
\[ \hat{P} = 2^{-1/2} i(a^\dagger - a) \]
\[ \langle v | a^\dagger | v - 1 \rangle = v^{1/2} \]
\[ \langle v - 1 | a | v \rangle = v^{1/2} \]
\[ N = a^{\dagger}a \quad N|\psi\rangle = \psi|\psi\rangle \]

\[ [a^{\dagger}, a] = a^{\dagger}a - aa^{\dagger} \]

\[ [a^{\dagger}, a]|\psi\rangle = (v - (v + 1)|\psi\rangle = -v|\psi\rangle \]

\[ [a^{\dagger}, a] = -1 \quad \text{OR} \quad [a, a^{\dagger}] = +1 \]

\[ [N, a^{\dagger}] = [a^{\dagger}aa^{\dagger} - a^{\dagger}a'a] = a^{\dagger}(aa^{\dagger} - a^{\dagger}a) = a^{\dagger} \]

\[ [N, a] = [a^{\dagger}aa - aa^{\dagger}a] = (a^{\dagger}a - aa^{\dagger})a = -a \]

\[ \hat{Q}^2 = \frac{1}{2}(a + a^{\dagger})^2 = \frac{1}{2}(a^2 + a^{\dagger 2} + aa^{\dagger} + a^{\dagger}a) \]

\[ = \frac{1}{2}[a^2 + a^{\dagger 2} + (2N + 1)] \]

\[ \hat{P}^2 = -\frac{1}{2}(a^{\dagger} - a)^2 = -\frac{1}{2}[a^2 + a^{\dagger 2} - (2N + 1)] \]

\[ \hat{Q}^2 + \hat{P}^2 = (2N + 1) \quad \text{(off-diagonal elements cancel)} \]

\[ \hat{Q}^3 = 2^{-3/2}(a^3 + a^{\dagger 3} + a^{\dagger}a^{\dagger}a + aa^{\dagger}a^{\dagger} + aa^{\dagger}a + a^{\dagger}aa) \]

\[ = 2^{-3/2}[a^3 + a^{\dagger 3} + 3a^{\dagger}(N + 1) + 3aN] \]

\[ \hat{Q}^4 = \frac{1}{4}[a^4 + a^{\dagger 2} + a^{\dagger 2}(4N + 6) + a^2(4N - 6) + 6N^2 + 9N + 4] \quad \{\text{check this}\} \]

OK. We are ready to begin some polyatomic molecule problems.

Suppose we have a bent ABA triatomic molecule where

\[ \omega_1 \approx 2\omega_2, \quad \omega_3 \approx 1.20\omega_1, \quad \omega_1, \omega_2 \text{ totally sym. } \omega_3 \text{ not tot. sym.} \]

\[ H' = k_{122}Q_1Q_2^2 + \frac{1}{4} k_{1133}Q_1^2Q_3^2 + \frac{1}{12} k_{2223}Q_2^2Q_3^2 \]

Fermi Darling-Dennison high order

\[ E(V) = \sum_i \omega_i(v_i + 1/2) + \sum_{i \geq j} x_{ji}(v_i + 1/2)(v_j + 1/2) + \ldots \]

Why do we have only these leading terms in the inter-mode coupling in \( H' \)?

- symmetry
- resonance

why not higher order terms?

when you put in the \( Q \rightarrow \hat{Q} \) scale factor and reasonable estimates of higher derivatives of \( V(Q_1, Q_2, Q_3) \) get factor of 10 decrease per order in \( Q \).
How do we begin to solve a problem like this?

1. **Perturbation Theory** (non-degenerate)

   \[
   E^{(0)}_{(v_1, v_2, v_3)} = \omega_1 (v_1 + 1/2) + \omega_2 (v_2 + 1/2) + \omega_3 (v_3 + 1/2)
   \]

   \[
   E^{(1)}_{(v_1, v_2, v_3)} = H^{(1)}_{v_1, v_2, v_3, v_1, v_2, v_3} \quad \text{there is a } \Delta v_1 = \Delta v_3 = 0 \text{ term!}
   \]

   \[
   E^{(2)}_{(v_1, v_2, v_3)} = \sum' \left( \frac{H^{(1)}_{v_1, v_2, v_3; v_1', v_2', v_3'}}{E^{(0)}_{(v_1, v_2, v_3)} - E^{(0)}_{(v_1', v_2', v_3')}} \right)^2
   \]

2. **Off-diagonal matrix element selection rules**

   \[
   Q_1 Q_2^2 \Delta v_1 = \pm 1, \Delta v_2 = 0, \pm 2: \quad (\Delta v_1, \Delta v_2) = (1,0), (-1,0), (1,2), (1,-2), (-1,2), (-1,-2)
   \]

   \[
   Q_1^2 Q_3^2 \Delta v_1 = 0, \pm 2, \Delta v_3 = 0, \pm 2 \quad (\Delta v_1, \Delta v_3) = (0,0), (0,2), (0,-2), (2,0), (-2,0), (2,-2), (-2,2)
   \]

   \[
   Q_2^3 Q_3^2 \Delta v_2 = \pm 1, \pm 3, \Delta v_3 = 0, \pm 2 \quad (1,0), (-1,0), (3,0), (-3,0), (1,2), (1,-2), (-1,2), (-1,-2), (3,2), (3,2), (3,2), (-3,2), (-3,-2)
   \]

   Each selection rule gives a specific combination of \( a_i^+, a_i \). Try it!

3. Look for “accidental” resonances \( \omega_1 \approx 2\omega_2 \) (\( \omega_1 \neq \omega_3 \))

   denominator \( \rightarrow 0 \)

   quasi-degenerate perturbation theory \( \rightarrow \) set up

   polyad \( H^{\text{eff}} \)

   \[ P = 2v_1 + v_2 \]

4. Correct for effects of remote perturbers (and look out for accidents).

5. **Algebraic reduction** (or use computer algebra) (combine terms \( (\Delta v_1, \Delta v_2) = (1,-2) \) AND \( (-1,2) \) because both have small energy denominator.

So where does this leave us?

The \( Q_1 Q_3^2 \) matrix element appears in 1\(^{\text{st}}\) order, but it is not resonant.

Consider only one term in \( H' \):
We have related $x_{13}$ to $k_{1133}$!

Could get lots of second-order corrections to $E(V)$, but we need to do something more important first.

NOW we worry about resonances: $\omega_i \approx 2\omega_2$. We need $\frac{1}{2}k_{122}Q_1Q_2^2$. Why?

Relevant term in $H'$ is

$$H' = \frac{1}{2}k_{122} \left[ \frac{\hbar^{1/2}}{(k_1\mu_1)^{1/4}} \frac{\hbar}{(k_2\mu_2)^{1/4}} \right] k_{1133} \left[ 2^{-3/2} (a_1 + a_1^\dagger)(a_2 + a_2^\dagger)^2 \right]$$

Resonant combination is $a_1^\dagger a_2^\dagger + a_1^\dagger a_2^\dagger$

Hermitian (good!)

Matrix element

$$\left\langle v_1v_2 | a_1^\dagger a_2^\dagger | v_1 + 1, v_2 - 2 \right\rangle = \left[ (v_1 + 1)v_2(v_2 - 1) \right]^{1/2}$$

Scaling

$$\left\langle v_1v_2 | a_1^\dagger a_2^\dagger | v_1 - 1, v_2 + 2 \right\rangle = \left[ v_1(v_2 + 2)(v_2 + 1) \right]^{1/2}$$

Polyad

<table>
<thead>
<tr>
<th>$P$</th>
<th>$v_1, v_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(0,1)</td>
</tr>
<tr>
<td>2</td>
<td>(0,2), (1,0)</td>
</tr>
<tr>
<td>3</td>
<td>(1,1), (0,3)</td>
</tr>
<tr>
<td>4</td>
<td>(2,0), (1,2), (0,4)</td>
</tr>
<tr>
<td>5</td>
<td>(2,1), (1,3), (0,5)</td>
</tr>
</tbody>
</table>

Each polyad has $P/2 + 1$ or $P/2 + 1/2$ members

$P$ (even $P$) $P/2 + 1$ members

$P$ (odd $P$) $P/2 + 1/2$ members
Look at $P = 6$ polyad

$\begin{array}{cccc}
(3,0) & (2,2) & (1,4) & (0,6) \\
G(3,0) & G(2,2) & G(1,4) & G(0,6) \\
K^{3\cdot2\cdot1} & K^{2\cdot4\cdot3} & K^{1\cdot6\cdot5} & 0 \\
1/2 & 0 & 0 & 0 \\
\end{array}$

$G(v_1,v_2) = \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2)$

$\quad + [x_{11}(v_1 + 1/2)^2 + x_{22}(v_2 + 1/2)^2 + x_{12}(v_1 + 1/2)(v_2 + 1/2)]$

called diagonal anharmonicity

Most of $x_{11}$ comes from $\frac{1}{6}k_{111}Q_1^3$ in 2nd order, $\frac{1}{24}k_{1111}Q_1^4$ in 1st order.

Most of $x_{22}$ comes from $\frac{1}{6}k_{222}Q_2^3$ in 2nd order, $\frac{1}{24}k_{2222}Q_2^4$ in 1st order.

Most of $x_{12}$ comes from $\frac{1}{6}k_{1122}Q_1^2Q_2^2$ in first order?

\[ \text{can we use this? yes! Why?} \]
\[ \text{k}_{122} \text{ in 2nd order?} \]
\[ \text{can we use this? NO! Why?} \]

Find the eigenvalues and eigenvectors of this block? Not yet. But if we did, would not fit simple polynomial in $(v_1 + 1/2)^n(v_2 + 1/2)^m$.

Why not?

Next we need to make out-of-block corrections to each element of polyad block.

“Van Vleck” transformation.

\[
\left( H^0 + \tilde{H}' \right)_{ij} = H'_{ij} + \sum_k \frac{H'_{ik}H'_{kj}}{E_i^{(0)} + E_j^{(0)}} - \frac{E_k^{(0)}}{2} \]

looks like 2nd order perturbation theory
This example is for out-of-block corrections on diagonal. There are also out-of-block corrections off-diagonal within block, e.g.

\[(3, 0, v_3) \quad \text{— intermediate states —} \quad (2, 2, v_3)\]

This gives you a glimpse of the machinery needed to set up \(E(v)\) for one anharmonic oscillator and for anharmonic interactions between several (an)harmonic oscillators. “Anharmonically coupled harmonic oscillators”: The standard tool for coupled normal modes.
Atoms — ideas to represent “electric structure” beyond Bernath

Tinkham Group Theory and Quantum Mechanics pages 154-188
Weissbluth Atoms and Molecules pages 413-454

My goal is a survey of the key ideas — whet your appetite.

3-Lecture Outline

1. 1e⁻ atoms 
   \[ |nℓmJ⟩ \]
   \[ |nℓsjm⟩ \]
   all properties of all states → \( f(n, ℓ, j; Z, μ) \)
   SCALING

2. alkali 1e⁻ outside closed shell 
   \[ Z \rightarrow Z_{eff}(r) \rightarrow Z_{nℓ}^{eff} \]
   \[ n \rightarrow n^* = n - δ_ℓ \]
   ← quantum defect \( δ_ℓ \pi \) is a phase shift 
   1 : 1 corresponding \( nℓ \) orbital ↔ electronic state 
   modified scaling

3. many - e⁻ atoms 
   configurations → L,S terms (several) 
   \( ε_{nℓ}, F^k(nℓ, n′ℓ′), G^k(nℓ, n′ℓ′), ζ_{nℓ} \)
   limiting coupling cases [characteristic patterns of levels] 
   \( H_{eff} \) models 
   scaling in \( ε, F, G, ζ \)

Many of these ideas will be used (and developed) for molecules.

See Lectures #5 - #8.