5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #3: Building an Effective Hamiltonian

Last time: diatomic molecule as anharmonic non-rigid rotor

$$Q = R - R_e$$

$$V(Q) = \frac{1}{2}kQ^2 + \frac{1}{6}aQ^3 + \frac{1}{24}bQ^4 + \ldots \underbrace{B(Q)J(J+1)}_{\text{really KE}}$$

$$B(R) = \frac{\hbar^2}{hc}\frac{1}{2\mu R^2}$$

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

$$\omega_e = \frac{1}{2\pi c}[k/\mu]^{1/2}$$

$$E_{vJ}/hc = \widetilde{\omega}_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 \ldots$$

$$+ J(J+1)\left[B_e - \alpha_e(v+1/2) + \gamma_e(v+1/2)^2 \ldots\right]$$

$$- J(J+1)^2\left[D_e + \beta_e(v+1/2) + \ldots\right]$$

<u>Problem</u>: find $\widetilde{\omega}_e$, $\omega_e x_e$, $\omega_e y_e$, α_e, D_e in terms of k, a, b, R_e, μ using non-degenerate perturbation theory (over-tilde implies additional corrections).

$$\mathbf{H}^{(0)}\psi_v^{(0)} = E_v^{(0)}\psi_v^{(0)} \quad \text{defines basis states}$$

$$\frac{\mathbf{H}^{(0)}}{hc} = \frac{1}{2}kQ^2 + \frac{p^2}{2\mu} + B_e J(J+1) \Rightarrow E_{vJ}^{(0)}/hc = \omega_e(v+1/2) + B_e J(J+1)$$

$$\Rightarrow |v,J\rangle^0 = \left|v^{HO}\right\rangle|JM_J\rangle$$

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

Some tools:

$$Q = \left[\frac{\hbar}{2\pi c\mu\omega_e}\right]^{1/2}\widehat{Q}$$

$$P = [\hbar 2\pi c\mu\omega_e]^{1/2}\widehat{P}$$

$$\widehat{Q} = 2^{-1/2}(\mathbf{a} + \mathbf{a}^\dagger)$$

$$\widehat{P} = 2^{-1/2}i(\mathbf{a}^\dagger - \mathbf{a})$$

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

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

$\mathbf{N} = \mathbf{a}^\dagger\mathbf{a}$ $\mathbf{N}|v\rangle = v|v\rangle$

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

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

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

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

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

$$\widehat{Q}^2 = \frac{1}{2}(\mathbf{a} + \mathbf{a}^\dagger)^2 = \frac{1}{2}(\mathbf{a}^2 + \mathbf{a}^{\dagger 2} + \mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a})$$

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

$$\widehat{P}^2 = -\frac{1}{2}(\mathbf{a}^\dagger - \mathbf{a})^2 = -\frac{1}{2}\left[\mathbf{a}^2 + \mathbf{a}^{\dagger 2} - (2\mathbf{N}+1)\right]$$

$$\widehat{Q}^2 + \widehat{P}^2 = (2\mathbf{N}+1) \qquad \text{(off-diagonal elements cancel)}$$

$$\widehat{Q}^3 = 2^{-3/2}(\mathbf{a}^3 + \mathbf{a}^{\dagger 3} + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger + \mathbf{a}\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\mathbf{a}\mathbf{a})$$

$$= 2^{-3/2}\left[\mathbf{a}^3 + \mathbf{a}^{\dagger 3} + 3\mathbf{a}^\dagger(\mathbf{N}+1) + 3\mathbf{a}\mathbf{N}\right]$$

$$\widehat{Q}^4 = \frac{1}{4}\left[\mathbf{a}^4 + \mathbf{a}^{\dagger 2} + \mathbf{a}^{\dagger 2}(4\mathbf{N}+6) + \mathbf{a}^2(4\mathbf{N}-6) + 6\mathbf{N}^2 + 9\mathbf{N} + 4\right] \qquad \text{\{check this\}}$$

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

$$\boxed{C_{2v} : A_1, A_2, B_1, B_2}$$
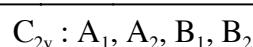
Suppose we have a bent ABA triatomic molecule where

$$\underbrace{\omega_1 \approx 2\omega_2}_{\text{resonant}} \quad , \quad \underbrace{\omega_3 \approx 1.20\omega_1}_{\text{not resonant}} \quad , \quad \omega_1, \omega_2 \text{ totally sym. } \omega_3 \text{ not tot. sym.}$$

$$\mathbf{H}' = \frac{1}{2}k_{122}Q_1Q_2^2 + \frac{1}{4}k_{1133}Q_1^2Q_3^2 + \frac{1}{12}k_{22233}Q_2^3Q_3^2$$

     Fermi   Darling-Dennison   high order

$$E(\mathbf{V}) = \sum_i \omega_i\left(v_i + 1/2\right) + \sum_{i \geq j} x_{ij}(v_i + 1/2)(v_j + 1/2) + \dots$$

Why do we have only these leading terms in the inter-mode coupling in $\mathbf{H}'$?

symmetry
resonance

why not higher order terms?

when you put in the $Q \to \widehat{Q}$ scale factor and reasonable estimates of higher derivatives of $V(Q_1, Q_2, Q_3)$ get factor of 10 decrease per order in $\mathbf{Q}$.

How do we begin to solve a problem like this?

1.   <u>Perturbation Theory</u>   (non-degenerate)

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

$$E^{(1)}_{(v_1,v_2,v_3)} = \mathbf{H}^{(1)}_{v_1,v_2,v_3;v_1,v_2,v_3} \qquad \text{there is a } \Delta v_1 = \Delta v_3 = 0 \text{ term!}$$

$$E^{(2)}_{(v_1,v_2,v_3)} = \sum_{v_1',v_2',v_3'}{}' \frac{\left(\mathbf{H}^{(1)}_{v_1,v_2,v_3;v_1',v_2',v_3'}\right)^2}{E^{(0)}_{(v_1,v_2,v_3)} - E^{(0)}_{(v_1',v_2',v_3')}}$$

2.   <u>Off-diagonal matrix element selection rules</u>
$Q_1Q_2^2$ $\Delta v_1 = \pm 1, \Delta v_2 = 0, \pm 2$: $(\Delta v_1, \Delta v_2) = (1,0), (-1,0), (1,2), (1,-2), (-1,2), (-1,-2)$

$Q_1^2 Q_3^2$ $\Delta v_1 = 0, \pm 2, \Delta v_3 = 0, \pm 2$ $(\Delta v_1, \Delta v_3) = (0,0), (0,2), (0,-2), (2,0), (-2,0), (2,-2),$
                   $(-2,2)$

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

    Each selection rule gives a specific combination of $\mathbf{a}_i^\dagger, \mathbf{a}_i$. Try it!

3.   <u>Look for "accidental" resonances</u> $\omega_1 \approx 2\omega_2$ $(\omega_1 \not\approx \omega_3)$

denominator $\to 0$

quasi-degenerate perturbation theory $\to$ set up
  polyad $\mathbf{H}^{\text{eff}}$ $P = 2v_1 + v_2$

4.   <u>Correct for effects of remote perturbers</u> (and look out for accidents).

5.   <u>Algebraic reduction</u>   (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 $Q_1^2 Q_3^2$ matrix element appears in <u>1st order</u>, but it is <u>not resonant</u>.

Consider only one term in $\mathbf{H}'$:

$$\underline{\frac{1}{4}k_{1133}Q_1^2 Q_3^2} = \frac{1}{4}k_{1133}\left[\frac{\hbar}{2\pi c \mu_1 \omega_1}\right]\left[\frac{\hbar}{2\pi c \mu_3 \omega_3}\right]\frac{1}{4}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)^2\left(\mathbf{a}_3 + \mathbf{a}_3^\dagger\right)^2$$

$$= \frac{1}{16}\left[\frac{\hbar}{[k_1 \mu_1]^{1/2}}\frac{\hbar}{[k_3 \mu_3]^{1/2}}\right]k_{1133}\left(\mathbf{a}_1^2 + \mathbf{a}_1^{\dagger 2} + 2\mathbf{N}_1 + 1\right)\left(\mathbf{a}_3^2 + \mathbf{a}_3^{\dagger 2} + 2\mathbf{N}_3 + 1\right)$$

$$\langle v_1 v_3 | \mathbf{H}' | v_1 v_3 \rangle = \boxed{\frac{1}{4}\left(\frac{\hbar}{\left(k_1 \mu_1\right)^{1/2}\left(k_3 \mu_3\right)^{1/2}}\right)k_{1133}}\underbrace{(v_1 + 1/2)(v_3 + 1/2)}_{\text{coefficient of } x_{13}}$$

$$\underbrace{}_{\text{constant}}$$

We have related x_{13} to k_{1133}!

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

NOW we worry about resonances: $\omega_1 \approx 2\omega_2$ We need $\frac{1}{2}k_{122}Q_1 Q_2^2$. Why?

Relevant term in $\mathbf{H}'$ is

$$\mathbf{H}' = \frac{1}{2}k_{122}\underbrace{\left[\frac{\hbar^{1/2}}{(k_1 \mu_1)^{1/4}}\frac{\hbar}{(k_2 \mu_2)^{1/2}}\right]2^{-3/2}}_{K}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)\left(\mathbf{a}_2 + \mathbf{a}_2^\dagger\right)^2$$

resonant combination is $\underbrace{\mathbf{a}_1 \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1^\dagger \mathbf{a}_2^2}_{\text{Hermitian (good!)}}$

matrix element
scaling
$$\begin{cases}\left\langle v_1, v_2 \left| \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} \right| v_1 + 1, v_2 - 2 \right\rangle = \left[(v_1 + 1)v_2(v_2 - 1)\right]^{1/2}\\[2mm]\left\langle v_1, v_2 \left| \mathbf{a}_1^\dagger \mathbf{a}_2^2 \right| v_1 - 1, v_2 + 2 \right\rangle = \left[v_1(v_2 + 2)(v_2 + 1)\right]^{1/2}\end{cases}$$

Polyad QN

$$\begin{array}{ll}P = 1 & (v_1, v_2) = (0,1) \\ \quad\ \ 2 & (0,2), (1,0) \\ \quad\ \ 3 & (1,1), (0,3) \\ \quad\ \ 4 & (2,0), (1,2), (0,4) \\ \quad\ \ 5 & (2,1), (1,3), (0,5)\end{array} \Bigg\} \text{ membership scaling}$$

Each polyad has
        $P/2 + 1$ or $P/2 + 1/2$ members
        (even P)   (odd P)

Look at P = 6 polyad

	3,0	2,2	1,4	0,6
(3,0)	G(3,0)	$K[3 \cdot 2 \cdot 1]^{1/2}$	0	0
(2,2)	sym	G(2,2)	$K[2 \cdot 4 \cdot 3]^{1/2}$	0
(1,4)	0	sym	G(1,4)	$K[1 \cdot 6 \cdot 5]^{1/2}$
(0,6)	0	0	sym	G(0,6)

$$G(v_1, v_2) = \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2)$$
$$+ [x_{11}(v_1 + 1/2)^2 + x_{22}(v_2 + 1/2)^2 + x_{12}(v_1 + 1/2)(v_2 + 1/2)]$$

called diagonal anharmonicity

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

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

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

can we use this? yes! Why?
k_{122} in 2nd order?
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 <u>out-of-block</u> corrections to each element of polyad block.

"Van Vleck" transformation.

$$\left(\mathbf{H}^0 + \widetilde{\mathbf{H}}'\right)_{ij} = \mathbf{H}'_{ij} + \sum_k \frac{\mathbf{H}'_{ik}\mathbf{H}'_{kj}}{\dfrac{E_i^{(0)} + E_j^{(0)}}{2} - E_k^{(0)}}$$

looks like 2nd order
perturbation theory

initial   intermediate states   final

$(3, 0, v_3)$ $(1, 0, v_3 + 2)$
                 $(5, 0, v_3 - 2)$ $\left.\right\} \quad \left(Q_1^2 Q_3^2 \right)$ $(3, 0, v_3)$

                 $(4, 2, v_3)$ $\left(Q_1 Q_2^2 \right)$

                 $(3, 3, v_3 + 2)$
                 $(3, 3, v_3\ )$ $\left(Q_2^3 Q_3^2 \right)$
                 $(3, 3, v_3 - 2)$
                 $(3, 1, v_3 + 2)$
                        etc.
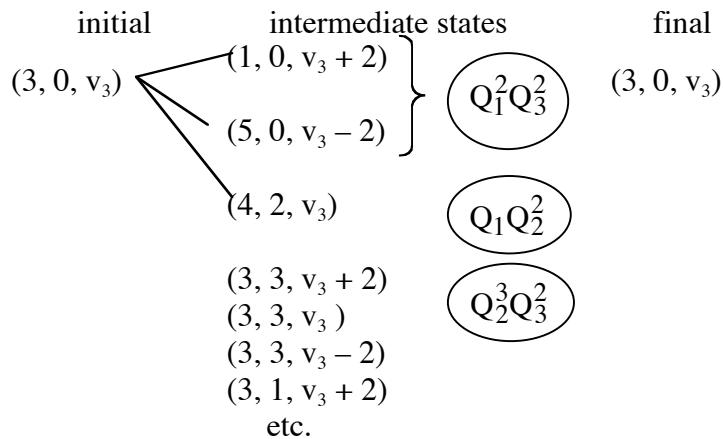
This example is for out-of-block corrections on diagonal. There are also out-of-block corrections off-diagonal within block, e.g.

$(3, 0, v_3)$ — intermediate states — $(2, 2, v_3)$

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 $|n\ell m_\ell s m_s\rangle$

                        $|n\ell sjm\rangle$

        <u>all</u> properties of all states $\rightarrow$ f(n, ℓ, j; Z, μ)

                SCALING

2.   alkali $1e^-$ outside closed shell

                $Z \rightarrow Z^{eff}(r) \rightarrow Z^{eff}_{n\ell}$

                $n \rightarrow n^* = n - \delta_\ell$ $\leftarrow$ quantum defect $\delta_\ell \pi$ is a phase shift

        1 : 1 corresponding $n\ell$ orbital $\leftrightarrow$ electronic state

                                modified scaling

3.   many - e^- atoms

                configurations $\rightarrow$ L,S terms (several)

                $\varepsilon_{n\ell}$, $F^k(n\ell, n'\ell')$, $G^k(n\ell, n'\ell')$, $\zeta_{n\ell}$

        limiting coupling cases [characteristic patterns of levels]

                $\mathbf{H}^{eff}$ models

                scaling in ε, F, G, ζ

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