MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
Instructor: Prof. Robert Field

Normal ↔ Local Modes:
Classical, Morse, Minimal Model

Reading: Chapter 9.4.12, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

two level problem (A,B), (+,–)

$$|\Psi(0)\rangle = |A\rangle$$

$\boldsymbol{\rho}(t)$ in (A,B) and (+,–) representations

$$\mathbf{H} = \mathbf{H}^{\text{diag}} + \mathbf{H}^{\text{res}}$$

$$E_{\text{diag}}(t) = \left\langle \mathbf{H}^{\text{diag}} \right\rangle$$

$$E_{\text{res}}(t) = \left\langle \mathbf{H}^{\text{res}} \right\rangle = \sum_{\boldsymbol{\kappa}} \left\langle \boldsymbol{\Omega}_k + \boldsymbol{\Omega}_k^\dagger \right\rangle$$

$$\overline{E} = E_{\text{diag}}(t) + E_{\text{res}}(t)$$

$$\overline{E}_{\text{res},j} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt \left(\boldsymbol{\Omega}_j + \boldsymbol{\Omega}_j^\dagger \right)$$

$$f_j = \left| \frac{\overline{E}_{\text{res},j}}{\overline{E}_{\text{res}}} \right|$$

Today: Preparation for exam
Correction of misconceptions from Lecture #15
Overtone Spectroscopy
Classical treatment of 2 coupled harmonic oscillations

Consider excitation of a molecule, like H_2O, with two short pulses of radiation. The two pulses have different center frequencies and the second pulse can be delayed by τ relative to the first pulse, for $0 \leq \tau \leq 10ps$. After the two pulses have exited the sample, populations in the two-step excited eigenstates are measured by an unspecified method. The measured quantity is $\rho_{ff}(\tau)$ for each of the eigenstates in the two-step excited polyad (see figure) on page 16-3.

At $t = 0$ prepare $|\Psi(0)\rangle = |A\rangle$

** Only μ_{aA} and μ_{bB} (basis state to basis state) transition moments are non-zero.

The population in each of the two-step excited eigenstates, $\rho_{ff}(\tau)$, as a function of delay between the two pulses is

$$\rho_{ff}(\tau) = \langle f|\delta\boldsymbol{\mu}\overbrace{|\Psi(\tau)\rangle\langle\Psi(\tau)|}^{\rho(\tau)}\delta\boldsymbol{\mu}|f\rangle$$

transform from eigen-basis to zero-order basis state

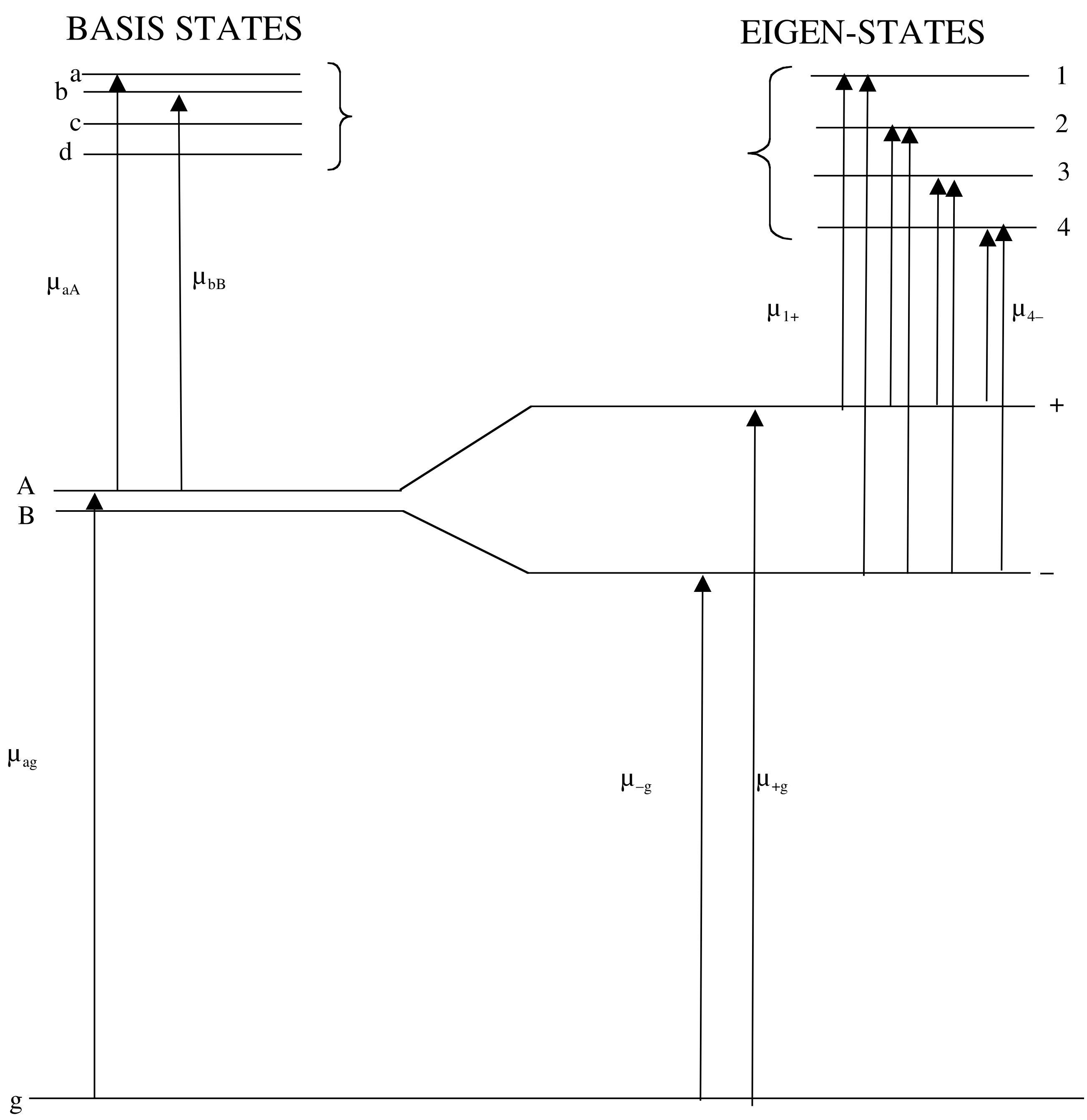
$$= \sum_{k,m} \langle f|k^{(0)}\rangle\langle k^{(0)}|\delta\boldsymbol{\mu}^{\dagger}\rho(\tau)\ \boldsymbol{\mu}|m^{(0)}\rangle\langle m^{(0)}|f\rangle$$

$|k^{(0)}\rangle$, $|m^{(0)}\rangle$ are zero-order basis states

$$= \sum_{k,m} \mathbf{T}_{fk}\left(\delta\boldsymbol{\mu}^{\dagger}\boldsymbol{\rho}(\tau)\ \boldsymbol{\mu}\right)_{km}\underbrace{\mathbf{T}^{\dagger}_{mf}}_{\langle m^{(0)}|f\rangle}$$

where **T** is the transformation that diagonalizes the (abcd) polyad.

$$\mathbf{T}^{\dagger}\mathbf{H}(abcd)\mathbf{T} = \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 \\ 0 & 0 & E_3 & 0 \\ 0 & 0 & 0 & E_4 \end{pmatrix}$$



At $t = 0$ prepare $|\psi(0)\rangle = |A\rangle$ with a short pulse.

After a delay, τ, a second pulse excites to a higher energy polyad.

Want $\rho(\tau)$ in the A,B basis set and $\delta\boldsymbol{\mu}$ in the {abcd}, {AB} basis set

There are 4 nonzero terms in the sum for $\rho_{ff}(\tau)$

$$\mathbf{T}_{fa}\delta\mu^{\dagger}_{aA}\rho_{AA}(\tau)\delta\mu_{aA}\mathbf{T}^{\dagger}_{af} \rightarrow \left|\mathbf{T}_{fa}\right|^2\left|\delta\mu_{aA}\right|^2\rho_{AA}(\tau)$$

$$+\mathbf{T}_{fb}\delta\mu^{\dagger}_{bB}\rho_{BB}(\tau)\delta\mu_{Bb}\mathbf{T}^{\dagger}_{bf} \rightarrow \left|\mathbf{T}_{fb}\right|^2\left|\delta\mu_{bB}\right|^2\rho_{BB}(\tau)$$

$$\left.\begin{array}{l}+\mathbf{T}_{fa}\delta\mu^{\dagger}_{aA}\rho_{AB}(\tau)\delta\mu_{Bb}\mathbf{T}^{\dagger}_{bf}\\+\mathbf{T}_{fb}\delta\mu^{\dagger}_{bB}\rho_{BA}(\tau)\delta\mu_{Aa}\mathbf{T}^{\dagger}_{af}\end{array}\right\} \rightarrow 2\,\mathrm{Re}\left(\rho_{AB}(\tau)\right)\left(\mathbf{T}_{fa}\mathbf{T}^{\dagger}_{bf}\right)\left(\delta\mu_{Aa}\delta\mu^{\dagger}_{bB}\right)$$

$$\text{Recall from 15 - 5 } \rho_{AA}(\tau) = 1 - \frac{V^2}{2\left(V^2+\delta E^2\right)}\left(1-\cos\omega_{+-}\tau\right)$$

$$\rho_{BB}(\tau) = \frac{V^2}{2\left(V^2+\delta E^2\right)}\left(1-\cos\omega_{+-}\tau\right) = 1-\rho_{AA}(\tau)$$

$$\mathrm{Re}\left(\rho_{AB}(\tau)\right) = \frac{V\delta E}{2\left(V^2+\delta E^2\right)}\left(1-\cos\omega_{+-}\tau\right)$$

(actually, there is an overall scale factor on $\boldsymbol{\rho}(\tau)$ for the A,B states that depends on the strength of the 1st laser pulse).

$$\begin{aligned}\rho_{ff}(\tau) = &\left[\left|\mathbf{T}_{fa}\right|^2\left|\delta\mu_{aA}\right|^2 - \left|\mathbf{T}_{fb}\right|^2\left|\delta\mu_{bB}\right|^2\right]\rho_{AA}(\tau)\\ &+\left|\mathbf{T}_{fb}\right|^2\left|\delta\mu_{bB}\right|^2\\ &+2\,\mathrm{Re}\left(\rho_{AB}(\tau)\right)\left(\mathbf{T}_{fa}\mathbf{T}^{\dagger}_{bf}\right)\left(\delta\mu_{aA}\delta\mu^{\dagger}_{Bb}\right)\end{aligned}$$

$$\begin{aligned}\rho_{ff}(\tau) = &\left|\mathbf{T}_{fa}\right|^2\left|\delta\mu_{aA}\right|^2\\ &-\frac{\left(1-\cos\omega_{+-}\tau\right)}{2\left(V^2+\delta E^2\right)}\left[V^2\left(\left|\mathbf{T}_{fa}\right|^2\left|\delta\mu_{aA}\right|^2 - \left|\mathbf{T}_{fb}\right|^2\left|\delta\mu_{Bb}\right|^2\right) - V\delta E\left(\mathbf{T}_{fa}\mathbf{T}^{\dagger}_{bf}\right)\left(\delta\mu_{aA}\delta\mu^{\dagger}_{Bb}\right)\right]\end{aligned}$$

(good idea to factor out $|\mathbf{T}_{fa}|^2\ |\delta\mu_{aA}|^2$ from entire equation).

$$\text{at } \tau = 0 \qquad \rho_{ff}(0) = |\mathbf{T}_{fa}|^2 |\delta\mu_{aA}|^2$$

Population is divided among the (1234) eigenstate components of the (bacd) polyad according to the fractional $|a\rangle$ character in each eigenstate. The intensity weighted average E is E_a

$$\langle E \rangle = \frac{\sum_f \rho_{ff} E_f}{\sum_f \rho_{ff}} = E_a$$

*populations oscillate at ω_{+-}, which is an eigenstate spacing in the (AB) polyad

* if we sum over the eigenstate populations in the (abcd) polyad, we get

$$\sum_f \rho_{ff}(\tau) = |\delta\mu_{aA}|^2 + \frac{(1-\cos\omega_{+-}\tau)}{2(V^2+\delta E^2)}\left[V^2\left(|\delta\mu_{aA}|^2 - |\delta\mu_{Bb}|^2\right)\right]$$

$$\text{because} \qquad \sum_f |\mathbf{T}_{fa}|^2 = 1$$

$$\sum_f \mathbf{T}_{fa}\mathbf{T}^\dagger_{bf} = \sum_f \mathbf{T}^\dagger_{bf}\mathbf{T}_{fa} = \mathbb{1}_{ba} = 0$$

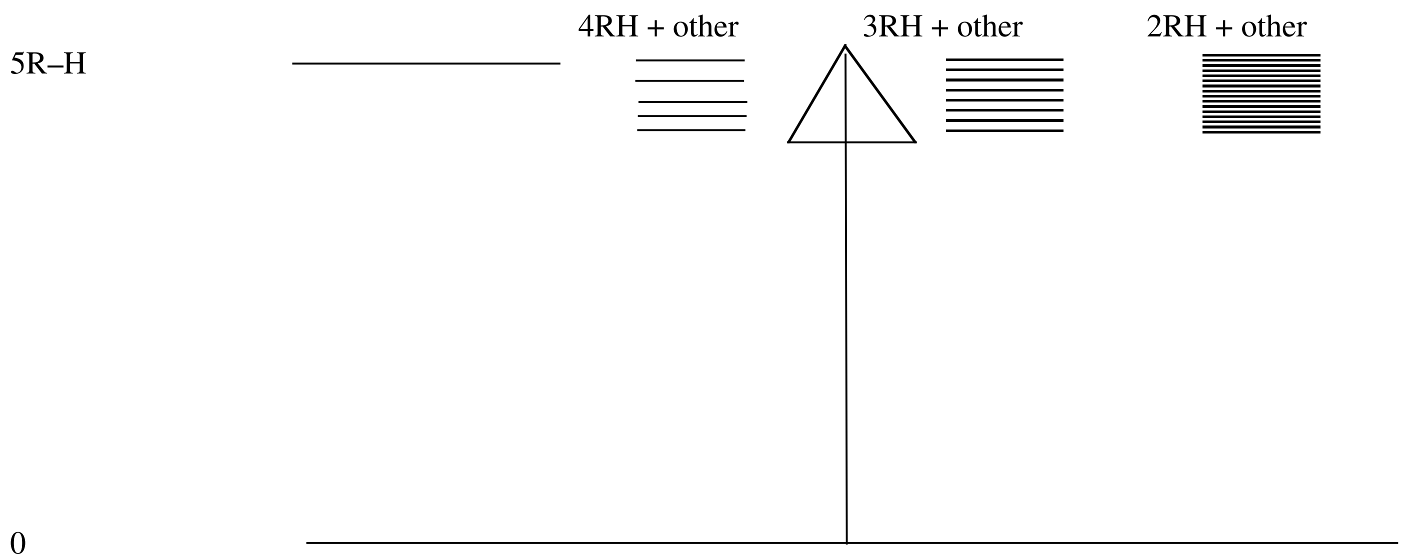
When $|V| >> \delta E$, get oscillation between $\sum_f \rho_{ff} = |\delta\mu_{aA}|^2$ and $2|\delta\mu_{aA}|^2 - |\delta\mu_{bB}|^2$.

Populations in (1234) are modulated by coherences in (A,B) polyad weighted by difference in *a–A* and *b–B* transition probabilities. These transition probabilities often have simple quantum number inter-relationships. In this simple (A,B) case, all populations are modulated at the same frequency, ω_{+-}, but with different amplitudes. More complicated when there are more than 2 states in the intermediate polyad.

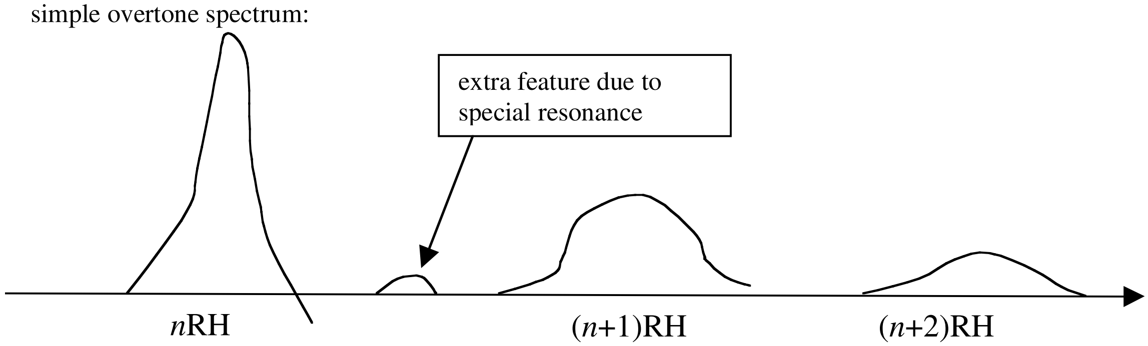
So we sample dynamics in (AB) polyad through τ-dependent populations in (abcd) polyad. We do not sample dynamics in (abcd) polyad.

Multi-step dynamics in frequency domain? See next example.

Overtone Spectroscopy in Larger Molecules



simple overtone spectrum:



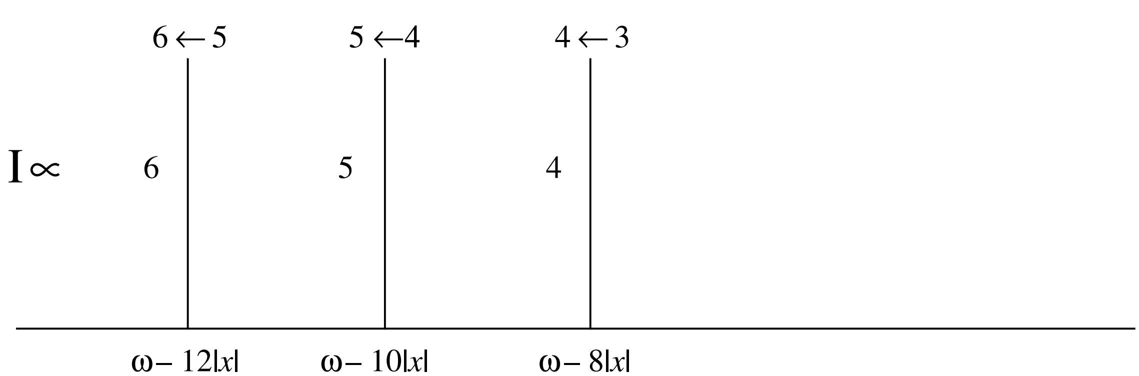
Expect increasing width as you go to higher overtone. Intensity decreases by factor of 10 to 100 per overtone. Spacings are ~ω. (See K. K. Lehmann, *J. Chem. Phys*. **93**, 6140 (1990).)

Double resonance
Based on change in anharmonicity of RH stretch

$$G(v) = \omega(v+1/2) + x(v+1/2)^2$$

$$\Delta G(v+1/2) = G(v+1) - G(v) = \omega + 2x(v+1) \qquad (x < 0)$$

5 R–H (first laser) + 1 R–H (second laser)



What do we see in the R–H fundamental region (actually 5R–H + 1R–H)?

* extent of mixing of 5 R–H into bath. For each quantum of R–H transferred into the bath, the density of dark states increases but the coupling matrix elements decrease (sequential vs. direct coupling mechanism?).

* intensity (area) of each anharmonically split out clump tells fractionation into lower # of quanta of RH and width tells rate of transfer $n \to n - 1$.

We see where the 5R–H pluck goes, and how fast. Early steps in the relaxation are typically dependent on a doorway state lying near the bright state. If this near degeneracy does not occur, there is a bottleneck in the energy flow.

What would you observe in an experiment with two short pulses (5ω) τ (1ω) with variable delay?

* in the absorption spectrum of the second pulse?
* in the populations produced?