Perturbation Theory IV

Last time: Transition probabilities in the presence of cubic anharmonicity

direct	$\psi_n^{(0)} \rightarrow \psi_{n\pm1}^{(0)}$	$\Delta n = \pm 1$
singly forbidden	$\psi_n^{(0)} \rightarrow \psi_{n'}^{(0)} + \underline{\psi_{n'}^{(1)}}$	$\Delta n = \pm 4, \pm 2, 0$
doubly forbidden	$\psi_n^{(0)} + \underline{\psi_{n'}^{(1)}} \rightarrow \psi_{n'}^{(0)} + \underline{\psi_{n'}^{(1)}}$	$\Delta n = \pm 7, \pm 5, \pm 3, \pm 1$

Extra basis states mixed in by a$\mathbf{x}^3$ anharmonicity denoted by underline.

Today

** brief remarks about $\Psi(x,0) = \psi_n^{(0)}$ in the presence of anharmonic mixing:
  * partial recurrences depend on $\overline{\omega}$
  * rate of dephasing of recurrences depends on $\frac{d\overline{\omega}}{dn}\Big/\overline{\omega}$, the fractional change in the average frequency.

** "x-k" relationships

** Quasi degeneracy

$$\text{when } \left|\frac{H_{nk}^{(1)}}{E_n^{(0)} - E_k^{(0)}}\right| \approx 1 \text{ must diagonalize}$$

** coupled oscillator example: POLYADS, IVR

Possibility:

Intramolecular Vibrational Redistribution in Acetylene

What about Quartic perturbing term bx^4?

special hint

Note that $E_n^{(1)} = \left\langle n \middle| bx^4 \middle| n \right\rangle \neq 0$ and is directly sensitive to sign of b!

What about wave packet calculations?

ψ_n expressed as superposition of $\psi_k^{(0)}$ basis state terms (perturbed eigenstates)

$\Psi(x,0)$ expanded as superposition of $\psi_k^{(0)}$ terms (state prepared at t = 0)

$\Psi(x,t)$ oscillates at $e^{-iE_n t/\hbar}$ (evolving prepared state)

$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$

A state which is initially in a pure $\psi_n^{(0)}$ will dephase, then exhibit partial recurrences at

$m2\pi \approx \bar{\omega}_n t \quad \therefore t_{recurrence} = \frac{m2\pi}{\omega}$ where m is an integer

not quite integer multiples

but recurrence is not perfect since

$$E_n - E_m \neq \hbar\omega(n-m)$$

because $\frac{E_n + E_{n+1}}{2}$ decreases as n increases

* time of 1st recurrence will depend on $\langle E \rangle$!
* successive recurrences will occur with larger phase error for $\omega_{n,n-1}$ vs. $\omega_{n+1,n}$

1st recurrence phase discrepancy is δ

2nd recurrence phase discrepancy is 2δ

etc.

On pages 16-5 through 16-11 I worked out how a block of $\mathbf{H}^{eff}$ is corrected so that "out-of-block" off-diagonal matrix elements can be safely ignored. These corrections come in two forms:

(i) Second-order perturbation theory corrections to diagonal matrix elements. One example is the "x–k" relationships by which the x_{ij} vibrational anharmonicity constants are evaluated in terms of third and fourth derivatives of V(**Q**).

(ii) Van Vleck transformation of "quasi-degenerate" or "resonant" blocks of $\mathbf{H}^{eff}$. Something analogous to second-order perturbation theory is used to fold out-of-block off-diagonal matrix elements into polyad blocks along the diagonal of **H**. These corrections occur both on and off the diagonal within these quasi-degenerate polyad blocks. "Resonance" is not accidental. Once it appears it affects larger and larger groups of near-degenerate basis states.

Consider the following 3×3 example of a Van Vleck transformed $\mathbf{H}^{eff}$:

$$\mathbf{H} = \begin{pmatrix} 0 & 5 & 2 \\ 5 & 2 & 0.5 \\ 2 & 0.5 & 20 \end{pmatrix}$$

This **H** has a $2 \leftrightarrow 2$ quasidegenerate block and both members of this block interact weakly with a non-quasidegenerate remote state.

$$\mathbf{H}^{(0)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 20 \end{pmatrix}$$

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & 5 & 2 \\ 5 & 0 & 0.5 \\ 2 & 0.5 & 0 \end{pmatrix}$$

$$\mathbf{H}^{(2)} = \begin{pmatrix} \dfrac{2^2}{-20} & \dfrac{(2)(0.5)}{\dfrac{0+2}{2} - 20} & 0 \\ -\dfrac{1}{19} & \dfrac{0.5^2}{-18} & 0 \\ 0 & 0 & \left(\dfrac{2^2}{20} + \dfrac{0.5^2}{18}\right) \end{pmatrix}$$

$$\mathbf{H}^{(2)}_{nn'} = \sum_{\substack{k \\ \text{out-of-block}}}{}_{\text{in-block}} \frac{\mathrm{H}^{(1)}_{nk}\mathrm{H}^{(1)}_{kn'}}{\dfrac{\mathrm{E}^{(0)}_{n} + \mathrm{E}^{(0)}_{n'}}{2} - \mathrm{E}^{(0)}_{k}}$$

See Ian M. Mills "Vibration-Rotation Structure in Asymmetric- and Symmetric-Top Molecules", pages 115-140 in Molecular Spectroscopy: Modern Research, Volume I, K. Narahari Rao, and C. Weldon Mathews, Academic, 1972.

Second-order perturbation theory is used to derive the famous "x-k" relationships, namely the relationship between the second, third, and fourth derivatives of V(**Q**) and the normal mode ω_i and x_{ij} molecular constants.

$$G(\mathbf{V}) = \sum_i \omega_i (v_i + 1/2) + \sum_{\substack{i,j \\ i \geq j}} x_{ij} (v_i + 1/2)(v_j + 1/2)$$

$$V(\mathbf{Q}) = \frac{1}{2} \sum_r \frac{\partial^2 V}{\partial q_r^2} q_r^2 + \frac{1}{6} \sum_{rst} \frac{\partial^3 V}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t + \frac{1}{24} \sum_{rstu} \frac{\partial^4 V}{\partial q_r \partial q_s \partial q_t \partial q_u} q_r q_s q_t q_u$$

[unrestricted sums: get several identical partial derivatives.] Lengthy derivations:

$$x_{ii} = \frac{1}{16} \frac{\partial^4 V}{\partial q_i^4} - \frac{1}{16} \sum_s \left(\frac{\partial^3 V}{\partial q_i^2 \partial q_s} \right)^2 \left[\frac{\left(8\omega_i^2 - 3\omega_s^2\right)}{\omega_s \left(4\omega_i^2 - \omega_s^2\right)} \right]$$

direct first-order contribution from quartic force constant

second-order summation over cubic force constants

$$x_{ij} = \frac{1}{4}\frac{\partial^4 V}{\partial q_i^2 \partial q_j^2} - \frac{1}{4}\sum_t \left(\frac{\partial^3 V}{\partial q_i^2 \partial q_t} \frac{\partial^3 V}{\partial q_j^2 \partial q_t} \Big/ \omega_t \right) -$$

first-order from quartic force constant

second-order sum over $\Delta v_i = \Delta v_j = 0$ terms for cubic force constants

$$\frac{1}{2}\sum_t \left[\left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_t} \right)^2 \omega_t \left(\omega_t^2 - \omega_i^2 - \omega_j^2 \right) \Big/ \Delta_{ijt} \right]$$

second-order sum over all $\Delta v_i = \pm 1$, $\Delta v_j = \pm 1$ terms for cubic force constants

$$\Delta_{ijt} = \left(\omega_i + \omega_j + \omega_t\right)\left(\omega_i - \omega_j - \omega_t\right)\left(-\omega_i + \omega_j - \omega_t\right)\left(-\omega_i - \omega_j + \omega_t\right)$$

Δ_{ijt} is "Resonance denominator". When

$$\omega_i = \omega_j + \omega_t$$

or $$\omega_j = \omega_i + \omega_t$$

or $$\omega_t = \omega_i + \omega_j$$

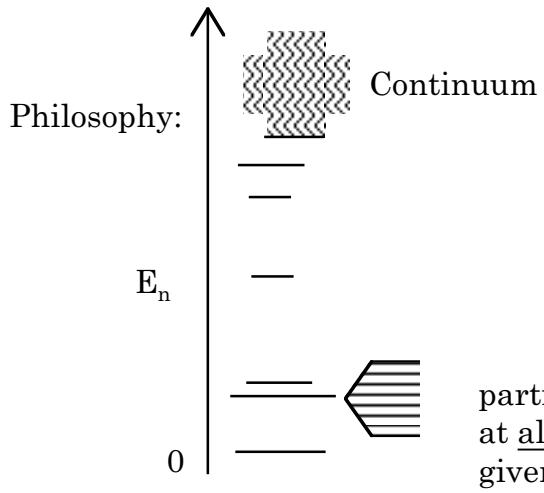
perturbation theory blows up. Must go to $\mathbf{H}^{eff}$ polyads and diagonalize.

Degenerate and Near Degenerate $E_n^{(0)}$

* Ordinary nondegenerate p.t. treats **H** as if it can be "diagonalized" by simple algebra.
* CTDL, pages 1104-1107 → find linear combination of degenerate $\psi_n^{(0)}$ for which $\mathbf{H}^{(1)}$ lifts degeneracy.
* This problem is usually treated in an abstract way by people who never actually use perturbation theory!

Whenever $\left|\frac{H_{nk}^{(1)}}{E_n^{(0)} - E_k^{(0)}}\right| \approx 1$ must diagonalize the n,k 2×2 block of $\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$

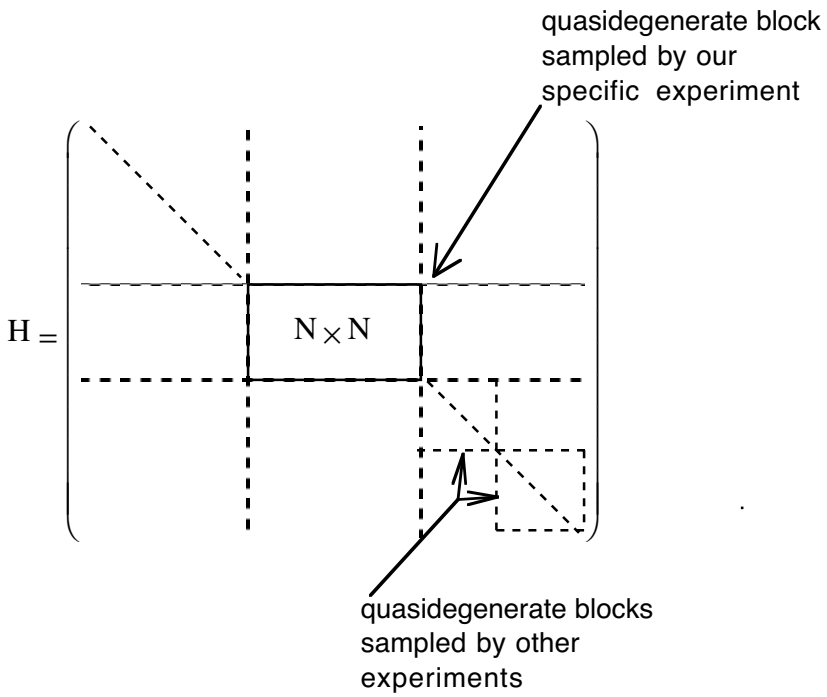
accidental degeneracy — spectroscopic perturbations
systematic degeneracy — 2-D isotropic H-O, "polyads"
quasi-degeneracy — safe chunk of **H**
effects of remote states — Van Vleck Pert. Theroy - next time



particular class of experiments does not look at <u>all</u> E_n's - only a given E range and only a given E resolution!

Want a model that replaces ∞ dimension **H** by simpler finite one that does really well for the class of states sampled by particular experiment.

NMR	nuclear spins (hyperfine)	don't care about excited vib. or electronic
IR	vibr. and rotation	don't care about Zeeman
UV	electronic	don't care about Zeeman



each finite block along the diagonal is an $\mathbf{H}^{\text{effective}}$ fit model. We want these fit models to be as accurate and physically realistic as possible.

* fold important out-of-block effects into N × N block → 2 stripes of **H**
* diagonalize augmented N × N block - refine parameters that define the block against observed energy levels.

next time review V-V transformation

4. Best to illustrate with an example — 2 coupled harmonic oscillators: "Fermi Resonance" [approx. integer ratios between characteristic frequencies of subsystems]

$$\mathbf{H} = \left[\frac{\mathbf{p}_1^2}{2m} + \frac{1}{2}k_1\mathbf{x}_1^2\right] + \left[\frac{\mathbf{p}_2^2}{2m} + \frac{1}{2}k_2\mathbf{x}_2^2\right] + k_{122}\mathbf{x}_1\mathbf{x}_2^2 \qquad \text{why not } k_{12}\mathbf{x}_1\mathbf{x}_2?$$

$$\psi^{(0)}_{n_1n_2} = \psi^{(1)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2)$$

$$\mathbf{H}_1^{(0)} \qquad\qquad \mathbf{H}_2^{(0)}$$

$$E^{(0)}_{n_1} = \hbar\omega_1(n_1 + 1/2)$$

$$E^{(0)}_{n_2} = \hbar\omega_2(n_2 + 1/2)$$

$$\Big\rangle\ E^{(0)}_{nm} = \hbar\left[\omega_1(n + 1/2) + \omega_2(n + 1/2)\right]$$

let $\omega_1 = 2\omega_2 \quad (m_1 = m_2, k_1 = 4k_2)$

systematic degeneracies

$$\mathbf{H}^{(1)} = k_{122}\mathbf{x}_1\mathbf{x}_2^2 = k_{122}\left(\frac{\hbar}{2m}\right)^{3/2}\left(\frac{1}{\omega_1\omega_2^2}\right)^{1/2}\left[\left(\mathbf{a}_1+\mathbf{a}_1^\dagger\right)\left(\mathbf{a}_2^2+\mathbf{a}_2^{\dagger 2}+\mathbf{a}\mathbf{a}^\dagger+\mathbf{a}^\dagger\mathbf{a}\right)\right]$$

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

$\mathbf{H}^{(1)}$ = (constants)

6 types of terms

	$H^{(1)}_{nm;k\ell}$		
	$n-k$	$m-\ell$	$\mathbf{H}^{(1)}$
$\mathbf{a}_1\mathbf{a}_2^2$	–1	–2	$\left[(n+1)(m+2)(m+1)\right]^{1/2}$
$\mathbf{a}_1\mathbf{a}_2^{\dagger 2}$	–1	+2	$\left[(n+1)(m)(m-1)\right]^{1/2}$
$\mathbf{a}_1\left(2\mathbf{a}_2^\dagger\mathbf{a}_2+1\right)$	–1	0	$\left[(n+1)(2m+1)\right]^{1/2}$
$\mathbf{a}_1^\dagger\mathbf{a}_2^2$	+1	–2	$\left[(n)(m+2)(m+1)\right]^{1/2}$
$\mathbf{a}_1^\dagger\mathbf{a}_2^{\dagger 2}$	+1	+2	$\left[(n)(m)(m-1)\right]^{1/2}$
$\mathbf{a}_1^\dagger\left(2\mathbf{a}_2^\dagger\mathbf{a}_2+1\right)$	+1	0	$\left[(n)(2m+1)\right]^{1/2}$

Seems complicated – but all we need to do is look for systematic near degeneracies Recall $\omega_1 = 2\omega_2$

List of Polyads by Membership			$E^{(0)}/\hbar\omega_2$		$P = 2n_1 + n_2$
(n_1, n_2)	degeneracy				
(0,0)	1	1+1/2 =	3/2		0
(0,1)	1	1+3/2 =	5/2		1
(1,0), (0,2)	2	3+1/2 =	7/2		2
(1,2), (0,3)	2	3+3/2 =	9/2;	1+7/2=9/2	3
(2,0), (1,2), (0,4)	3		11/2		4
	3		13/3		5
	4		15/2		6
	4		17/2		7
	etc.		19/2		8

General P block:

$$E_p^{(0)} \Big/ \hbar\omega_2 = \frac{3}{2} + (2n_1 + n_2) = P + 3/2$$

# of terms in P block depends on whether P is even or odd

$\frac{P+2}{2}$ states even P $\left(n_1 = \frac{P}{2}, n_2 = 0\right), \left(n_1 = \frac{P_2}{2} - 1, 2\right), \ldots (0, 2P)$

$\frac{P+1}{2}$ states odd P $\left(n_1 = \frac{P-1}{2}, n_2 = 1\right), \ldots (0, 2P-1)$

$$\left(\frac{\mathbf{H}^{(1)}}{\hbar^{3/2} m^{-3/2} \omega_1^{-1/2} \omega_2^{-1} k_{122} 2^{-3/2}}\right) = \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1^\dagger \mathbf{a}_2^2 + \mathbf{a}_1 \mathbf{a}_2^2 + \mathbf{a}_1^\dagger \mathbf{a}_2^{\dagger 2} + \mathbf{a}_1 \left(2\mathbf{a}_2^\dagger \mathbf{a}_2 + 1\right) + \mathbf{a}_1^\dagger \left(2\mathbf{a}_2^\dagger \mathbf{a}_2 + 1\right)$$

$\Delta P =$ 0 (inside polyad) 0 | −4 +4 −2 +2 (between polyad blocks)

POLYAD

$$\frac{\mathbf{H}_P^{(0)}}{\hbar\omega_2} = \begin{pmatrix} P+3/2 & 0 & 0 & 0 \\ 0 & P+3/2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & P+3/2 \end{pmatrix}$$

$$\frac{\mathbf{H}_P^{(1)}}{stuff} = \begin{array}{c} n\ m \\ \frac{P}{2}, 0 \\ \frac{P}{2} - 1, 2 \\ \vdots \\ 0, P \end{array} \begin{array}{c} \begin{array}{ccccc} \frac{P}{2}, 0 & & \frac{P}{2} - 1, 2 & & \frac{P}{2} - 2, 4 \end{array} \\ \begin{pmatrix} 0 & \left[\left(\frac{P}{2}\right)(2 \cdot 1)\right]^{1/2} & 0 & 0 & 0 \\ sym & 0 & \left[\left(\frac{P}{2} - 1\right)(3 \cdot 4)\right]^{1/2} & 0 & 0 \\ 0 & sym & 0 & \cdots & 0 \\ 0 & 0 & sym & 0 & [(1)(2P)(2P-1)]^{1/2} \end{pmatrix} \end{array}$$

Note that all matrix elements may be written in terms of a general formula — computer decides membership in polyad and sets up matrix

So now we have listed ALL of the connections of P = 6 to all other blocks!
So we use these results to add some correction terms to the P = 6 block according to the formula suggested by Van Vleck.

$$\mathbf{H}^{(2)}_{P_{nm}} = \sum_{P'} \frac{H^{(1)}_{nk} H^{(1)}_{km}}{\frac{E^{(0)}_n + E^{(0)}_m}{2} - E^{(0)}_k}$$

for our case*, the denominator is $\hbar\omega_2[P - P']$

* For this particular example there are no cases where there are nonzero elements for $n \neq m$ (many other problems exist where there are nonzero $n \neq m$ terms)

$$\underbrace{\frac{\hbar\omega_2 H^{(2)}_6}{\hbar^3 m^{-3}\omega_1^{-1}\omega_2^{-2}k_{122}^2 2^{-3}}}_{\text{dimensionless}} = \begin{matrix}30\\22\\14\\06\end{matrix}\begin{pmatrix} \frac{3}{2}-\frac{4}{2}-\frac{8}{4}=-\frac{5}{2} & \frac{50}{2}-\frac{75}{3}+\frac{4}{4}-\frac{36}{4}=-8 & \frac{81}{2}-\frac{162}{2}+\frac{12}{4}-\frac{60}{4}=-\frac{105}{2} & -\frac{169}{2}-\frac{56}{4}=-\frac{197}{2} \end{pmatrix}$$

Computers can easily set these things up.
Could add additional perturbation terms such as diagonal anharmonicities that cause $\omega_1 : \omega_2$ 2 : 1 resonance to detune.

For concreteness, look at P = 6 polyad
(3,0), (2,2), (1,4), (0,6)

$\mathbf{H}_6^{(1)}$ / stuff

	30	22	14	06
30	0	$(3\cdot 2\cdot 1)^{1/2}$	0	0
22	sym	0	$(2\cdot 4\cdot 3)^{1/2}$	0
14	0	sym	0	$(1\cdot 5\cdot 6)^{1/2}$
06	0	0	sym	0

now what are **all** of the out of block elements that affect the P = 6 block?

			$\mathbf{H}^{(1)}$/stuff	$E_P^{(0)} - E_{P-2}^{(0)}$
$\Delta P = -2$	$\mathbf{a}_1\left(2\mathbf{a}_2^\dagger\mathbf{a}_2 + 1\right)$	3,0 ~ 2,0	$3^{1/2}$	$+2\hbar\omega_2$
$P = 6 \sim P = 4$				
		2,2 ~ 1,2	$2^{1/2}\cdot 5$	$+2\hbar\omega_2$
		1,4 ~ 0,4	$1^{1/2}\cdot 9$	$+2\hbar\omega_2$
		0,6 ~ —	—	—
$\Delta P = +2$	$\mathbf{a}_1^\dagger\left(2\mathbf{a}_2^\dagger\mathbf{a}_2 + 1\right)$	3,0 ~ 4,0	$4^{1/2}$	$-2\hbar\omega_2$
		2,2 ~ 3,2	$3^{1/2}\cdot 5$	$-2\hbar\omega_2$
		1,4 ~ 2,4	$2^{1/2}\cdot 9$	$-2\hbar\omega_2$
		0,6 ~ 1,6	$1^{1/2}\cdot 13$	$-2\hbar\omega_2$
$\Delta P = -4$	$\mathbf{a}_1\mathbf{a}_2^2$	3,0 ~ —	—	—
		2,2 ~ 1,0	$2^{1/2}(2\cdot 1)^{1/2}$	$+4\hbar\omega_2$
		1,4 ~ 0,2	$1^{1/2}(4\cdot 3)^{1/2}$	$+4\hbar\omega_2$
		0,6 ~ —	—	—
$\Delta P = +4$	$\mathbf{a}_1^\dagger\mathbf{a}_2^{\dagger 2}$	3,0 ~ 4,2	$[4\cdot 2\cdot 1]^{1/2}$	$-4\hbar\omega_2$
		2,2 ~ 3,4	$[3\cdot 4\cdot 3]^{1/2}$	$-4\hbar\omega_2$
		1,4 ~ 2,6	$[2\cdot 6\cdot 5]^{1/2}$	$-4\hbar\omega_2$
		0,6 ~ 1,8	$[1\cdot 8\cdot 7]^{1/2}$	$-4\hbar\omega_2$

$$\mathbf{H}_{P=6}^{\text{eff}} = \mathbf{H}_6^{(0)} + \mathbf{H}_6^{(1)} + \mathbf{H}_6^{(2)}$$

$\mathbf{H}_6^{(0)}$: $\hbar\omega_2(6 + 3/2)$

$\mathbf{H}_6^{(1)}$:
$$\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \\ 0 & 0 & & \\ 0 & 0 & & \end{pmatrix}$$

$\mathbf{H}_6^{(2)}$:
$$\begin{pmatrix} 0 & 0 & 0 & \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & \end{pmatrix}$$