Perturbation Theory III

Last time

1. $V(\mathbf{x}) = \frac{1}{2}k\mathbf{x}^2 + a\mathbf{x}^3$ cubic anharmonic oscillator

   algebra with $\mathbf{x}^3$ vs. operator algebra with $\mathbf{a}, \mathbf{a}^\dagger$
   $a\mathbf{x}^3 \leftrightarrow \omega x$ and Y_{00}

   can' t know sign of a from vibrational information alone. [Can know it if rotation-vibration interaction is included.]

2. Morse Oscillator $V(\mathbf{x}) = D_e\left[\mathbf{1} - e^{-\alpha\mathbf{x}}\right]^{\mathbf{2}}$

   * $D_e, \alpha \leftrightarrow \omega, \omega x, m$

   * $\frac{d^3V}{dx^3} = 6a = -\frac{3\hbar}{2}\frac{\omega^2\alpha^3}{\omega x} = \left.\frac{d^3V_{morse}}{dx^3}\right|_{x=0}$

   * $\omega x = 2\frac{\alpha^2\hbar}{m^3\omega^4}$ direct from Morse vs. $\frac{15}{4}\frac{a^2\hbar}{m^3\omega^4}$ from pert. theory on $\frac{1}{2}k\mathbf{x}^2 + a\mathbf{x}^3$

$$\left.\begin{array}{l} \therefore \omega x = 2\frac{\alpha^2\hbar}{m^3\omega^4} \\ \omega x = \frac{15}{4}\frac{a^2\hbar}{m^3\omega^4} \end{array}\right] \text{same functional form}$$

from pert. theory on power series expansion of Morse potential (page #15-4) $\omega x = \frac{15}{4}\frac{a^2\hbar}{m^3\omega^4}$

Today:

1. Effect of cubic anharmonicity on transition probability orders of pert. theory, convergence [previous lecture: #15-6,7,8].
2. Use of harmonic oscillator basis sets in wavepacket calculations.
3. What happens when $\mathbf{H}^{(0)}$ has (near) degenerate $E_n^{(0)}$'s? Diagonalize block which contains (near) degeneracies. "Perturbations" — accidental and systematic.
4. 2 coupled non-identical harmonic oscillators: "polyads".

One reason that the result from second-order perturbation theory applied directly to V(x) = k$\mathbf{x}^2/2$ + a$\mathbf{x}^3$ and the term-by-term comparison of the power series expansion of the Morse oscillator are not identical is that contributions to the $(n + 1/2)^2$ term are neglected from higher derivatives of the Morse potential. In particular

$$E_n^{(1)} = V''''(0)\mathbf{x}^4/4! = \left[7/2\frac{\hbar\omega^2\alpha^4}{\omega\mathbf{x}}\right]\mathbf{x}^4/24$$

$$\left\langle n\middle|\mathbf{x}^4\middle|n\right\rangle = \left(\frac{\hbar}{2m\omega}\right)^2\left[4(n+1/2)^2+2\right]$$

contributes in first-order of perturbation theory to the $(n + 1/2)^2$ term in E_n.

$$E_n^{(1)} = \frac{7}{12}\omega x(n+1/2)^2 + \frac{7}{24}\omega x$$

Example 2 Compute some property other than Energy (repeat of pages 15-6, 7, 8)

need $\psi_\mathrm{n} = \psi_\mathrm{n}^{(0)} + \psi_\mathrm{n}^{(1)}$

transition probability: for electric dipole transitions $P_{n'\leftarrow n} \propto |x_{nn'}|^2$

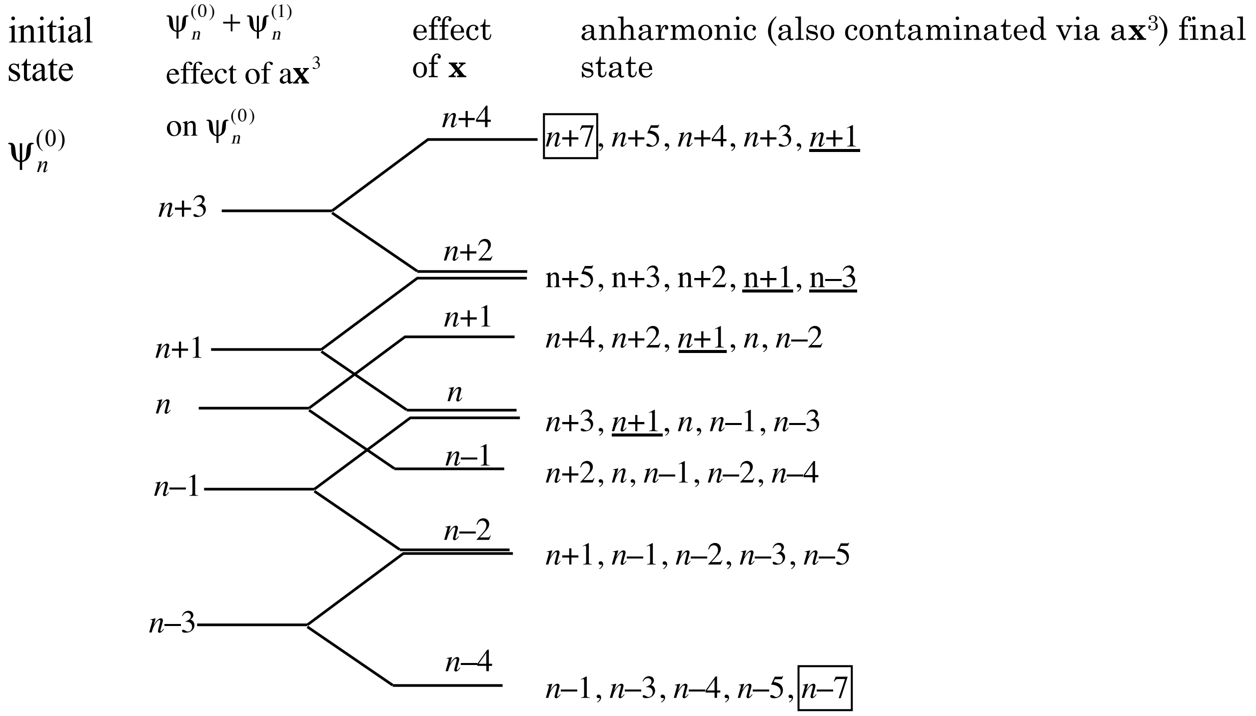
For H-O $n \rightarrow n \pm 1$ only

$$|\mathrm{x}_{\mathrm{nn+1}}|^2 = \left(\frac{\hbar}{2m\omega}\right)(n+1)$$

for perturbed H-O $\mathbf{H}^{(1)} = \mathrm{a}\mathbf{x}^3$

$$\psi_n = \psi_n^{(0)} + \sum_k{}' \frac{H_{nk}^{(1)}}{E_n^{(0)} - E_k^{(0)}}\psi_k^{(0)}$$

$$\psi_n = \psi_n^{(0)} + \frac{H_{nn+3}^{(1)}}{-3\hbar\omega}\psi_{n+3}^{(0)} + \frac{H_{nn+1}^{(1)}}{-\hbar\omega}\psi_{n+1}^{(0)} + + \frac{H_{nn-1}^{(1)}}{\hbar\omega}\psi_{n-1}^{(0)} + \frac{H_{nn-3}^{(1)}}{3\hbar\omega}\psi_{n-3}^{(0)}$$



Many paths from initial to final state, which interfere constructively and destructively in $\left|x_{nn'}\right|^2$

$n¢$ = n + 7, n+5, n+4, n+3, n+2, $\underline{n+1}$, n, $\underline{n-1}$, $n-2$, $n-3$, $n-4$, $n-5$, $n-7$

only paths for H-O!

The transition strengths may be divided into 3 classes

1. direct via $\mathbf{x}$: $n \rightarrow n \pm 1$
2. direct plus one anharmonic step $n \rightarrow n+4,\ n+2,\ n,\ n-2,\ n-4$
3. direct plus 2 anharmonic steps $n \rightarrow n+7,\ n+5,\ n+3,\ n+1,\ n-1,\ n-3,\ n-5,\ n-7$

Work thru the $\Delta n = -7$ path

$$\langle n|x|n+7\rangle = \left(\frac{h}{2m\omega}\right)^{3/2+3/2+1/2}\left[\frac{a^2}{(-3h\omega)^2}\right]\left[\underbrace{(n+1)(n+2)(n+3)}_{x_{n,n+3}}\underbrace{(n+4)}_{x_{n+3,n+4}}\underbrace{(n+5)(n+6)(n+7)}_{x_{n+4,n+7}}\right]^{1/2}$$

$\boxed{x^3_{n,n+3}}$ $\boxed{x^3_{n+4,n+7}}$ $\boxed{x_{n+3,n+4}}$

$$\left|x_{nn+7}\right|^2 \propto \frac{\hbar^3 a^4 n^7}{3^4 2^7 m^7 \omega^{11}}$$

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* you show that the single-step anharmonic terms go as

$$\left|x_{nn+4}\right| \propto \left(\frac{\hbar}{2m\omega}\right)^{3/2+1/2} \frac{a}{(-3\hbar\omega)}\left[(n+1)(n+2)(n+3)(n+4)\right]^{1/2}$$

$$\left|x_{nn+4}\right|^{2} \propto \frac{\hbar^{2}a^{2}n^{4}}{3^{2}2^{4}m^{4}\omega^{6}}$$

* Direct term

$$\left|x_{nn+1}\right|^{2} \propto \frac{\hbar^{1}}{2m^{1}\omega^{1}}(n+1)$$

each higher order term gets smaller by a factor $\left(\frac{\hbar n^{3}a^{2}}{3^{2}2^{3}m^{3}\omega^{5}}\right)$,
which is a very small dimensionless factor.
RAPID CONVERGENCE OF PERTURBATION THEORY!

What about the Quartic perturbing term b$\mathbf{x}^4$?

Note that $E^{(1)} = \left\langle n\middle|b\mathbf{x}^{4}\middle|n\right\rangle \neq 0$

and is directly sensitive to sign of b!

We get scaling with respect to powers of a, n, ω, and m.
We get magnitudes.
Sometimes we get signs.

2. <u>What about wave-packet calculations</u>?

ψ_n expressed as superposition of $\psi_k^{(0)}$ terms

$\Psi(\mathrm{x},0)$ expanded as superposition of $\psi_k^{(0)}$ terms (usually only one term, called the "bright state"). But we must instead expand $\psi_k^{(0)}$ as a superposition of eigenbasis, ψ_k, terms.

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

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

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

$$\text{any integer} \longrightarrow m\mathbf{2}\pi \quad \approx \omega\mathrm{t} \qquad \mathrm{t} = \frac{m\mathbf{2}\pi}{\omega}$$

but * the rephasing is not perfect since, due to anharmonicity:

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

These are not-quite-integer multiples of a common factor ($\hbar\omega$)!

* t*ime* of 1st recurrence will depend on $\langle \mathrm{E} \rangle$!

because $\dfrac{E_{n+1} - E_{n-1}}{2}$ decreases as n increases.

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

* Ordinary nondegenerate perturbation theory 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.

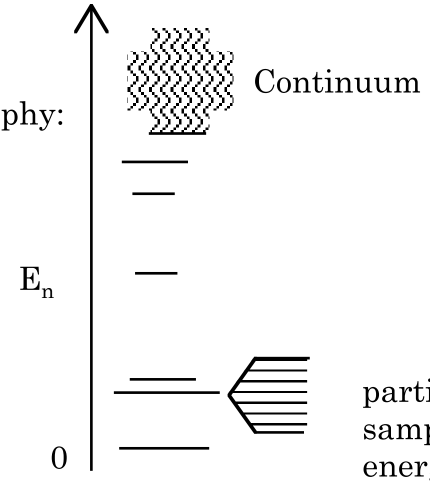
* This problem is usually treated in an abstract way by people who have never actually used perturbation theory!

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

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 — special chunk of **H**
effects of remote states — Van Vleck Perturbation Theory - next lecture

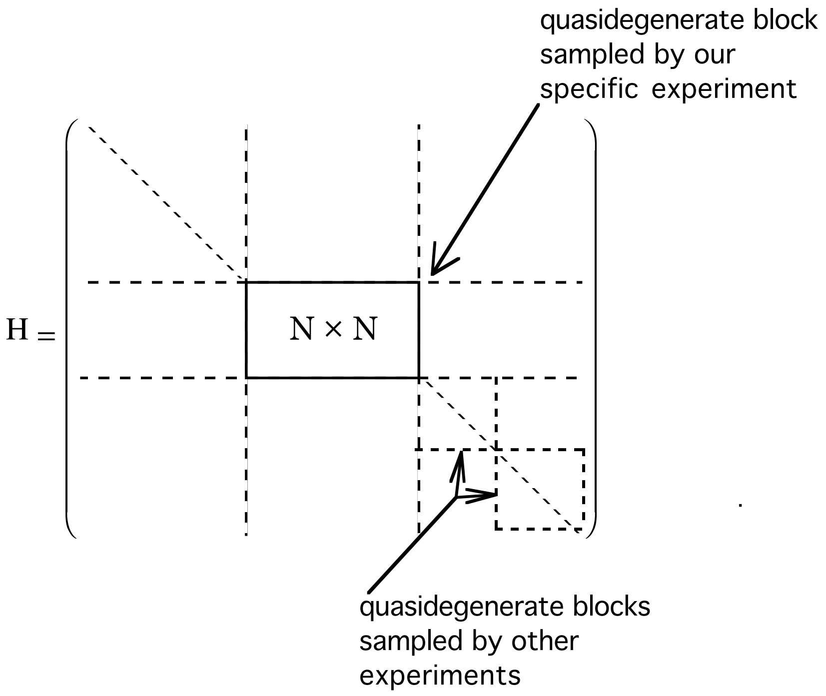
Philosophy:



particular class of experiment does not sample <u>all</u> E_n' s - only samples over a given energy range and only at a given energy resolution!

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

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



quasidegenerate block sampled by our specific experiment

quasidegenerate blocks sampled by other experiments

Each finite block along the diagonal of **H** is described by 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 → involves 2 strips 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 vibrational subsystems]

$$\mathbf{H} = \left[\frac{\mathbf{p}_1^2}{2m_1} + \frac{1}{2}k_1\mathbf{x}_1^2\right] + \left[\frac{\mathbf{p}_2^2}{2m_2} + \frac{1}{2}k_2\mathbf{x}_2^2\right] + k_{122}\mathbf{x}_1\mathbf{x}_2^2 \qquad \text{why not } k_{12}\mathbf{x}_1\mathbf{x}_2?$$

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

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

$$\left.\begin{array}{l} E^{(0)}_{n_1} = \hbar\omega_1\left(n_1 + 1/2\right) \\ E^{(0)}_{n_2} = \hbar\omega_2\left(n_2 + 1/2\right) \end{array}\right\rangle \; E^{(0)}_{nm} = \hbar\left[\omega_1\left(n + 1/2\right) + \omega_2\left(m + 1/2\right)\right]$$

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

There are systematic degeneracies.

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

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

$\mathbf{H}^{(1)}_{nm;k\ell}$

		n – k	m – ℓ	$\mathbf{H}^{(1)}$
$\mathbf{H}^{(1)}$ = (constants)	$a_1a_2^2$	–1	–2	$[(n+1)(m+2)(m+1)]^{1/2}$
	$a_1a_2^{\dagger 2}$	–1	+2	$[(n+1)(m)(m-1)]^{1/2}$
6 types of terms	$a_1\left(2a_2^\dagger a_2+1\right)$	–1	0	$[(n+1)(2m+1)^2]^{1/2}$
	$a_1^\dagger a_2^2$	+1	–2	$[(n)(m+2)(m+1)]^{1/2}$
	$a_1^\dagger a_2^{\dagger 2}$	+1	+2	$[(n)(m)(m-1)]^{1/2}$
	$a_1^\dagger\left(2a_2^\dagger a_2+1\right)$	+1	0	$[(n)(2m+1)^2]^{1/2}$

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 (n_1, n_2)	degeneracy	$E^{(0)}/\hbar\omega_2$ $[2(n_1+1/2)+(n_2+1/2)]$			"Polyad Number" $P = 2n_1 + n_2$
(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
(2,1),(1,3),(0,5)	3		13/3		5
?	4		15/2		6
?	4		17/2		7
	etc.		19/2		8

General P block:

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

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

$$\frac{P+2}{2}\text{states} \qquad \text{even P} \left(\mathrm{n}_1 = \frac{P}{2}, n_2 = 0\right), \left(n_1 = \frac{P}{2} - 1, 2\right), \ldots (0, P)$$

$$\frac{P+1}{2}\text{states} \qquad \text{odd P} \qquad \left(\mathrm{n}_1 = \frac{P-1}{2}, n_2 = 1\right), \ldots (1, P)$$

not 0 because $P = 2n_1 + n_2$ is odd

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

$$\Delta\text{P}=\underbrace{0 \qquad 0}_{\text{inside polyad}} \quad \underbrace{-4 \qquad +4 \qquad -2 \qquad +2}_{\text{between polyad blocks}}$$

POLYAD

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

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

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

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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 example*, the denominator is $\hbar\omega_2 \left[P - P' \right]$

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

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

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

For concreteness, look at $P = 6$ polyad, which includes the (n_1, n_2) states for $2n_1 + n_2 = 6$: (3,0), (2,2), (1,4), (0,6)

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

	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

We need to identify what are **all** of the out-of-block elements of the $\mathbf{x}_1\mathbf{x}_2^2$ term that affect the $P = 6$ block?

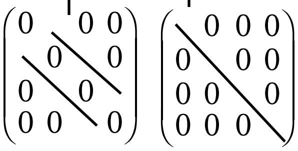
		$P = 6, P'$	$\mathbf{H}^{(1)}$/stuff	$E_P^{(0)} - E_{P-2}^{(0)}$
$P = 6$, $\Delta P = -2$ $P' = P-2 = 4$	$\mathbf{a}_1\left(2\mathbf{a}_2^\dagger\mathbf{a}_2+1\right)$	3,0 ~ 2,0	$3^{1/2}$	$+2\hbar\omega_2$
		2,2 ~ 1,2	$2^{1/2}\cdot 5$	$+2\hbar\omega_2$
		1,4 ~ 0,4	$1^{1/2}\cdot 9$	$+2\hbar\omega_2$
		0,6 ~ —	—	—
$\Delta P = +2$ $P' = P+2 = 8$	$\mathbf{a}_1^\dagger\left(2\mathbf{a}_2^\dagger\mathbf{a}_2+1\right)$	3,0 ~ 4,0	$4^{1/2}$	$-2\hbar\omega_2$
		2,3 ~ 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	$1^{1/2}\cdot 13$	$-2\hbar\omega_2$
$\Delta P = -4$ $P' = P-4 = 2$	$\mathbf{a}_1\mathbf{a}_2^2$	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 ~ —	—	—
$\Delta P = +4$ $P' = P+4 = 10$	$\mathbf{a}_1^\dagger\mathbf{a}_2^{\dagger 2}$	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	$[1\cdot 8\cdot 7]^{1/2}$	$-4\hbar\omega_2$

Within $P = 6$ block elements of $\mathbf{H}^{(1)}$

$P' \neq P = 6$: out-of-$P = 6$ block interactions folded into the $P = 6$ block on-diagonal

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

$\hbar\omega_2(6+3/2)$



5.73 Quantum Mechanics I
Fall 2018