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 with $\mathbf{a}, \mathbf{a}^\dagger$

$\underbrace{a\mathbf{x}^3}\leftrightarrow \underbrace{\omega x \; \& \; Y_{00}}$

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

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

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

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

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

$$\left.\begin{aligned} \therefore \omega x &= 2\frac{a^2\hbar}{m^3\omega^4} \\ \text{from pert. theory (\#15 - 4)} \quad \omega x &= \frac{15}{4}\frac{a^2\hbar}{m^3\omega^4} \end{aligned}\right] \quad \text{same functional form}$$

Today:

1. Effect of cubic anharmonicity on transition probability orders of pert. theory, convergence [last class: #15-6,7,8].
2. Use of harmonic oscillator basis sets in wavepacket calculations.
3. What happens when $\mathbf{H}^{(0)}$ has 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 are neglected from higher derivatives of the Morse potential to the $(n + 1/2)^2$ term in the energy level expression. In particular

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

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

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

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

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

need $\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$

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

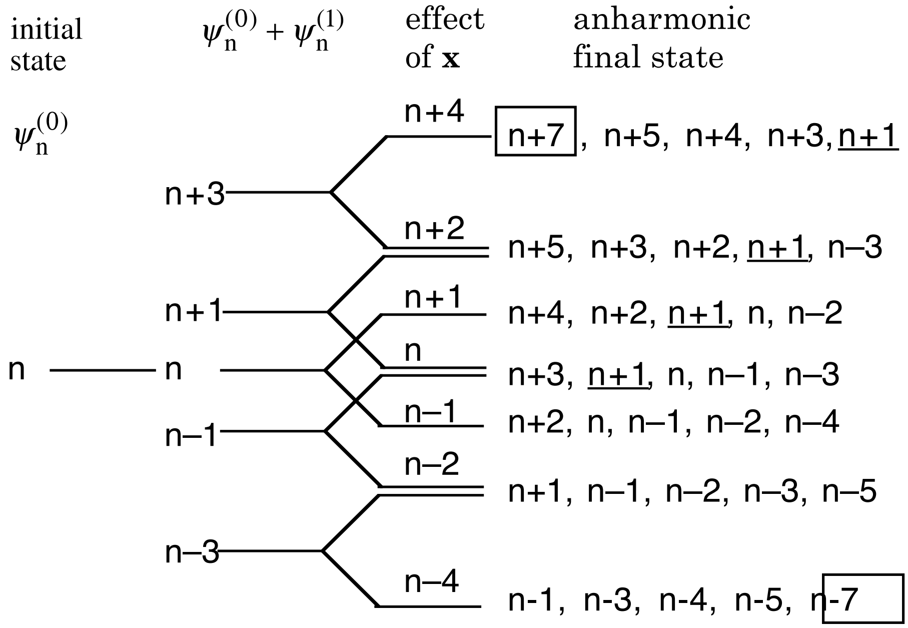
For H-O $n \to n \pm 1$ only

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

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

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

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



Many paths which interfere constructively and destructively in $|x_{nn'}|^2$

$$n' = n+7, n+5, n+4, n+3, n+2, \underbrace{\underline{n+1}, n, \underline{n-1}}_{\text{only paths for H-O!}}, n-2, n-3, n-4, n-5, n-7$$

The transition strengths may be divided into 3 classes

1. direct: $n \to n \pm 1$
2. one anharmonic step $n \to n+4, n+2, n, n-2, n-4$
3. 2 anharmonic steps $n \to n+7, n+5, n+3, n+1, n-1, n-3, n-5, n-7$

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

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

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

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

* 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

$$\left|x_{nn+1}\right|^2 \propto \frac{\hbar^1}{32 m^1 \omega^1}(n+1)$$

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 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!

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

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

$\Psi(x,0)$ expanded as superposition of $\psi_k^{(0)}$ terms (usually only one term, called the "bright state"). But we must also 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 state which is initially in a pure $\psi_n^{(0)}$ will dephase, then exhibit partial recurrences at

$$m2\pi \quad \approx \quad \omega t \qquad t = \frac{m2\pi}{\omega}$$

but * not perfect since

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

not quite integer multiples!

* time of 1st recurrence will depend on $\langle E \rangle$!

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

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

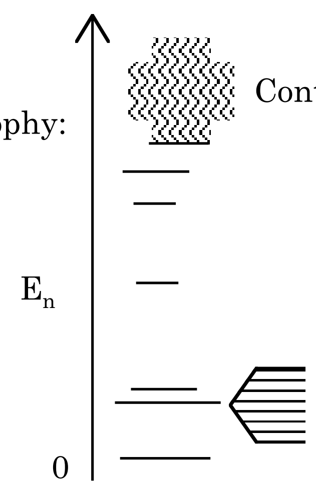
* Ordinary nondegenerate p.t. treats **H** as if it can be "diagonalized" by simple algebra.
* CTDL, pages 1104-1107 $\rightarrow$ find linear combination of degenerate $\psi_n^{(0)}$ for which $\mathbf{H}^{(1)}$ lifts degeneracy.
* This problem is usually treated in an abstract way by people who never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

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

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 — safe chunk of **H**
effects of remote states — Van Vleck Pert. Theroy - next time

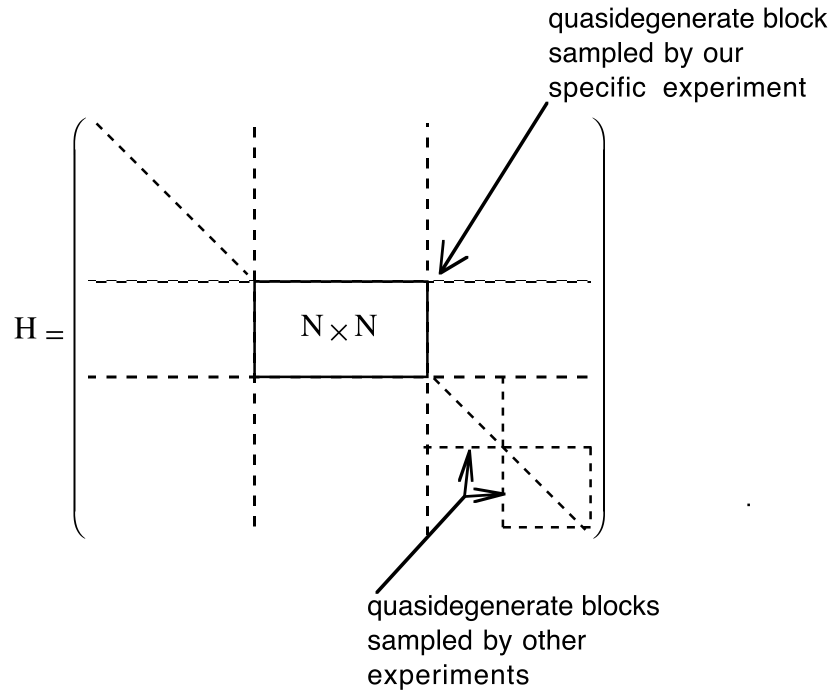
Philosophy:



particular class of experiments does not look at all 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 $N \times N$ block $\rightarrow$ 2 stripes of $\mathbf{H}$
* diagonalize augmented $N \times N$ 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]

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

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

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

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

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

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

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

systematic degeneracies

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

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

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

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

6 types of terms

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

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

List of <u>Pol y ads</u> by Membership		$E^{(0)}/\hbar\omega_2$		$P = 2n_1 + n_2$
		$[2(n_1+1/2)+(n_2+1/2)]$		
(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:

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

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

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

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

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

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

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

POLYAD

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

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

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.

$$\mathbf{H}^{(2)}_{\mathrm{P}_{nm}} = \sum_{\mathrm{P}'} \frac{H^{(1)}_{nk} H^{(1)}_{km}}{\dfrac{E^{(0)}_{n} + E^{(0)}_{m}}{2} - E^{(0)}_{k}}$$

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

* 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)

$$\underbrace{\frac{\hbar\omega_2 H^{(2)}_{6}}{\hbar^{3} m^{-3} \omega_1^{-1} \omega_2^{-2} k_{122}^{2} 2^{-3}}}_{\text{dimensionless}} = \begin{array}{c} 30 \\ 22 \\ 14 \\ 06 \end{array} \begin{pmatrix} \frac{3}{2} - \frac{4}{2} - \frac{8}{4} = -\frac{5}{2} & & & \\ & \frac{50}{2} - \frac{75}{3} + \frac{4}{4} - \frac{36}{4} = -8 & & \\ & & \frac{81}{2} - \frac{162}{2} + \frac{12}{4} - \frac{60}{4} = -\frac{105}{2} & \\ & & & -\frac{169}{2} - \frac{56}{4} = -\frac{197}{2} \end{pmatrix}$$

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)

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

	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

now what are **all** of the out of block elements of $\mathbf{x}_1\mathbf{x}_2^2$ that affect the P = 6 block?

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

$$\mathbf{H}_{P=6}^{\text{eff}} = \underbrace{\mathbf{H}_6^{(0)}}_{h\omega_2(6+3/2)} + \underbrace{\mathbf{H}_6^{(1)}}_{\begin{pmatrix} 0 & & 0 & 0 \\ & 0 & & 0 \\ 0 & & 0 & \\ 0 & 0 & & 0 \end{pmatrix}} + \underbrace{\mathbf{H}_6^{(2)}}_{\begin{pmatrix} & 0 & 0 & 0 \\ 0 & & 0 & 0 \\ 0 & 0 & & 0 \\ 0 & 0 & 0 & \end{pmatrix}}$$