Perturbation Theory III

Last time
1. $V(x) = \frac{1}{2} kx^2 + ax^3$ cubic anharmonic oscillator

   algebra with $x^3$ vs. operator with $a, a^\dagger$

   $ax^3 \leftrightarrow \omega x & Y_{(\omega)}$

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

2. Morse Oscillator

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

   * $D, \alpha \leftrightarrow \omega, \omega x, m$
   * $\frac{d^3V}{dx^3} = 6a = \frac{3h}{2} \omega^2 \alpha^3 = \left. \frac{d^3V_{\text{morse}}}{dx^3} \right|_{x=0}$
   * $\omega x = 2 \frac{a^2h}{m^3 \omega^4}$ direct from Morse vs. $\frac{15}{4} \frac{a^2h}{m^3 \omega^4}$ from pert. theory on $\frac{1}{2}kx^2 + ax^3$

   $\therefore \omega x = 2 \frac{a^2h}{m^3 \omega^4}$ same functional form

   from pert. theory (#15 - 4) $\omega x = \frac{15}{4} \frac{a^2h}{m^3 \omega^4}$

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 $H^{(0)}$ 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 \( V(x) = kx^2/2 + ax^3 \) 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

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

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

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

transition probability: for electric dipole transitions \( P_{n' \rightarrow n} \propto |x_{nn'}|^2 \)

For \( H - O \) \( n \rightarrow n \pm 1 \) only

\[
|x_{nn+1}|^2 = \left( \frac{h}{2m\omega} \right)(n+1)
\]

for perturbed \( H - O \) \( H^{(1)} = ax^3 \)

\[
\psi_n = \psi_n^{(0)} + \sum_{k} \frac{H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)}
\]

\[
\psi_n = \psi_n^{(0)} + \frac{H_{nn+3}^{(1)}}{-3h\omega} \psi_{n+3}^{(0)} + \frac{H_{nn+1}^{(1)}}{-h\omega} \psi_{n+1}^{(0)} + \frac{H_{nn-1}^{(1)}}{h\omega} \psi_{n-1}^{(0)} + \frac{H_{nn-3}^{(1)}}{3h\omega} \psi_{n-3}^{(0)}
\]
Many paths which interfere constructively and destructively in $|x_{nn}|^2$

\[ n' = n + 7, n + 5, n + 4, n + 3, n + 2, n + 1, n, n - 1, n - 2, n - 3, n - 4, n - 5, n - 7 \]

only paths for H-O!

The transition strengths may be divided into 3 classes

1. direct: \( n \rightarrow n \pm 1 \)
2. one anharmonic step \( n \rightarrow n + 4, n + 2, n, n - 2, n - 4 \)
3. 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

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

\[
|x_{nn+7}|^2 \approx \frac{\hbar^3 a^4 n^7}{3^{2/7} 2^{1/7} m^1 \omega^{11}}
\]
* you show that the single-step anharmonic terms go as

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

\[ |x_{nn+4}|^2 \propto \frac{\hbar^2a^2n^4}{3^22^4m^4\omega^6} \]

* Direct term

\[ |x_{nn+1}|^2 \propto \frac{\hbar^1}{32m^1\omega^1} (n+1) \]

each higher order term gets smaller by a factor \( \frac{\hbar^3a^2}{3^22^3m^3\omega^5} \)
which is a very small dimensionless factor.

RAPID CONVERGENCE OF PERTURBATION THEORY!

What about Quartic perturbing term \( bx^4 \)?

Note that \( E^{(1)} = \langle n | bx^4 | n \rangle \neq 0 \)
and is directly sensitive to sign of \( b \)!
2. What about wave packet calculations?

\( \Psi_n \) 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, \( \psi_k \), terms.

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

\[ E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \]

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

\[ m2\pi \approx \omega t \quad t = \frac{m2\pi}{\omega} \]

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 \( \frac{E_{n+1} - E_{n-1}}{2} \) decreases as \( n \) increases.
### 5.73 Lecture #16

**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 $H^{(1)}$ lifts degeneracy.
* This problem is usually treated in an abstract way by people who never actually use perturbation theory!

\[
\text{Whenever } \frac{H_{nk}^{(1)}}{E_n^{(0)} - E_k^{(0)}} \approx 1 \text{ must diagonalize the n,k } 2 \times 2 \text{ block of } H = H^{(0)} + H^{(1)}
\]

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:**

<table>
<thead>
<tr>
<th>E_n</th>
<th>Continuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

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 $\infty$ dimension $H$ by simpler finite one that does really well for the class of states sampled by particular experiment.

<table>
<thead>
<tr>
<th>NMR</th>
<th>nuclear spins (hyperfine)</th>
<th>don't care about excited vib. or electronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>vibr. and rotation</td>
<td>don't care about Zeeman</td>
</tr>
<tr>
<td>UV</td>
<td>electronic</td>
<td>don't care about Zeeman</td>
</tr>
</tbody>
</table>
each finite block along the diagonal is an $H$ 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 $H$
* diagonalize augmented $N \times N$ block - refine parameters that define the block against observed energy levels.

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

$$H = \begin{pmatrix} p_1^2 + \frac{1}{2} k_1 \vec{x}_1^2 & \frac{1}{2} k_{12} \vec{x}_1 \vec{x}_2 & \cdots \\ \frac{1}{2} k_{12} \vec{x}_1 \vec{x}_2 & \ddots & \ddots \\ \cdots & \ddots & \ddots \end{pmatrix}$$

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

$H_1^{(0)}$ $H_2^{(0)}$

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

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

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

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

systematic degeneracies
\[ H^{(1)} = k_{122} x_1^2 x_2^2 = k_{122} \left( \frac{\hbar}{2m} \right)^{3/2} \left( \frac{1}{\omega_1 \omega_2} \right)^{1/2} \left[ (a_1 + a_1^\dagger) (a_2^2 + a_2^\dagger^2 + a_2 a_2^\dagger + a_2^\dagger a_2) \right] \]

\[ a^\dagger a + a^\dagger a = 2a^\dagger a + 1 \]

\[ H_{nm; k\ell}^{(1)} \]

<table>
<thead>
<tr>
<th>( n-k )</th>
<th>( m-\ell )</th>
<th>( H^{(1)} )</th>
</tr>
</thead>
</table>
| -1 | -2 | \([(n+1)(m+2)(m+1)]^{1/2} \]
| -1 | +2 | \([(n+1)(m)(m-1)]^{1/2} \]
| -1 | 0 | \([(n+1)(2m+1)]^{1/2} \]
| +1 | -2 | \([(n)(m+2)(m+1)]^{1/2} \]
| +1 | +2 | \([(n)(m)(m-1)]^{1/2} \]
| +1 | 0 | \([(n)(2m+1)]^{1/2} \]

Seems complicated – but all we need to do is look for systematic near degeneracies

Recall \( \omega_1 = 2\omega_2 \)

List of Pol yads by Membership

<table>
<thead>
<tr>
<th>( (n_1, n_2) )</th>
<th>degeneracy</th>
<th>( E^{(0)}/\hbar \omega_2 )</th>
<th>( P = 2n_1 + n_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0)</td>
<td>1</td>
<td>( 1+1/2 = 3/2 )</td>
<td>0</td>
</tr>
<tr>
<td>(0,1)</td>
<td>1</td>
<td>( 1+3/2 = 5/2 )</td>
<td>1</td>
</tr>
<tr>
<td>(1,0), (0,2)</td>
<td>2</td>
<td>( 3+1/2 = 7/2 )</td>
<td>2</td>
</tr>
<tr>
<td>(1,2), (0,3)</td>
<td>2</td>
<td>( 3+3/2 = 9/2; \ 1+7/2 = 9/2 )</td>
<td>3</td>
</tr>
<tr>
<td>(2,0), (1,2), (0,4)</td>
<td>3</td>
<td>11/2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>13/3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>15/2</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>17/2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>etc.</td>
<td>19/2</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
5.73 Lecture #16

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

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

- \( P + \frac{1}{2} \) states, odd P
  \[ \left( n_1 = \frac{P-1}{2}, n_2 = 0 \right), \left( n_1 = \frac{P-3}{2}, n_2 = 1 \right), \ldots (0, P) \]

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

\[ H^{(1)}_P (\hbar \omega_2^{-3/2} m^{-3/2} \omega_1^{1/2} \omega_2^{-1/2} k_{1222}^{-3/2}) = a_1 a_2^\dagger + a_1^\dagger a_2^2 + a_1 a_2^2 + a_1^\dagger a_2^2 + a_1 \left( 2a_2 a_2 + 1 \right) + a_1^\dagger \left( 2a_2^\dagger a_2 + 1 \right) \]

\[ \Delta P = \begin{array}{cccc} 0 & 0 & -4 & +4 \\ 0 & 0 & +2 & -2 \end{array} \]

inside polyad

between polyad blocks

POLYAD

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

\[ \frac{H^{(i)}_P}{\text{stuff}} = \begin{pmatrix} \frac{P}{2} - 1,2 & \frac{P}{2} - 1,2 & \frac{P}{2} - 2,4 & \ldots & \ldots & 0, P \\ \frac{P}{2} - 1,2 & \frac{P}{2} - 1,2 & \frac{P}{2} - 2,4 & \ldots & \ldots & 0, P \\ \frac{P}{2} - 1,2 & \frac{P}{2} - 1,2 & \frac{P}{2} - 2,4 & \ldots & \ldots & 0, P \\ \frac{P}{2} - 1,2 & \frac{P}{2} - 1,2 & \frac{P}{2} - 2,4 & \ldots & \ldots & 0, P \\ \frac{P}{2} - 1,2 & \frac{P}{2} - 1,2 & \frac{P}{2} - 2,4 & \ldots & \ldots & 0, P \end{pmatrix} \]

(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.

$$H_{nm}^{(2)} = \sum_{P'} \frac{H_{nk}^{(1)}H_{km}^{(1)}}{E_n^{(0)} + E_m^{(0)} - E_k^{(0)}}$$

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)

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.

\[
\frac{\hbar \omega_2 H_6^{(2)}}{\hbar^2 \frac{m^{-3}}{\omega_1^{-1} \omega_2^{-1}} k_{122}^{-2}} = \left( \begin{array}{c}
30 \\
22 \\
14 \\
06
\end{array} \right)
\left( \begin{array}{c}
\frac{3}{2} \\
\frac{4}{2} \\
\frac{8}{4} \\
\frac{5}{2}
\end{array} \right) = \left( \begin{array}{c}
\frac{50}{2} \\
\frac{75}{3} \\
\frac{4}{4} \\
\frac{36}{4}
\end{array} \right) = -8
\]

\[
\left( \begin{array}{c}
\frac{81}{2} \\
\frac{162}{2} \\
\frac{12}{4} \\
\frac{60}{4} \\
\frac{105}{2}
\end{array} \right) = \left( \begin{array}{c}
\frac{-169}{2} \\
\frac{-56}{4} \\
\frac{-197}{2}
\end{array} \right)
\]
For concreteness, look at $P = 6$ polyad 
$(3,0), (2,2), (1,4), (0,6)$

<table>
<thead>
<tr>
<th>$\mathbf{H}_{6}^{(1)}$ stuff</th>
<th>30</th>
<th>22</th>
<th>14</th>
<th>06</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0</td>
<td>$(3 \cdot 2 \cdot 1)^{1/2}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>sym</td>
<td>0</td>
<td>$(2 \cdot 4 \cdot 3)^{1/2}$</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>sym</td>
<td>$(1 \cdot 5 \cdot 6)^{1/2}$</td>
<td>0</td>
</tr>
<tr>
<td>06</td>
<td>0</td>
<td>0</td>
<td>sym</td>
<td>0</td>
</tr>
</tbody>
</table>

now what are all of the out of block elements of $x_{1}x_{2}^{2}$ that affect the $P = 6$ block?

$\Delta P = -2$

$P = 6 \rightarrow P = 4$

$a_{1} \left( 2a_{2}^{\dagger}a_{2} + 1 \right)$

<table>
<thead>
<tr>
<th>$H^{(1)}$/stuff</th>
<th>$E_{P}^{(0)} - E_{P-2}^{(0)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3,0 \rightarrow 2,0$</td>
<td>$3^{1/2}$</td>
</tr>
<tr>
<td>$2,2 \rightarrow 1,2$</td>
<td>$2^{1/2} \cdot 2.5$</td>
</tr>
<tr>
<td>$1,4 \rightarrow 0,4$</td>
<td>$1^{1/2} \cdot 9$</td>
</tr>
<tr>
<td>$0,6 \rightarrow -$</td>
<td>-$</td>
</tr>
</tbody>
</table>

$\Delta P = +2$

$a_{1}^{\dagger} \left( 2a_{2}^{\dagger}a_{2} + 1 \right)$

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>$3,0 \rightarrow 4,0$</td>
<td>$4^{1/2}$</td>
</tr>
<tr>
<td>$2,2 \rightarrow 3,2$</td>
<td>$3^{1/2} \cdot 5$</td>
</tr>
<tr>
<td>$1,4 \rightarrow 2,4$</td>
<td>$2^{1/2} \cdot 9$</td>
</tr>
<tr>
<td>$0,6 \rightarrow 1,6$</td>
<td>$1^{1/2} \cdot 13$</td>
</tr>
</tbody>
</table>

$\Delta P = -4$

$a_{1}a_{2}^{2}$

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>$3,0 \rightarrow -$</td>
<td>-$</td>
</tr>
<tr>
<td>$2,2 \rightarrow 1,0$</td>
<td>$2^{1/2} (2 \cdot 1)^{1/2}$</td>
</tr>
<tr>
<td>$1,4 \rightarrow 0,2$</td>
<td>$1^{1/2} (4 \cdot 3)^{1/2}$</td>
</tr>
<tr>
<td>$0,6 \rightarrow -$</td>
<td>-$</td>
</tr>
</tbody>
</table>

$\Delta P = +4$

$a_{1}^{\dagger}a_{2}^{\dagger 2}$

<table>
<thead>
<tr>
<th>$H^{(1)}$/stuff</th>
<th>$E_{P}^{(0)} - E_{P-2}^{(0)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3,0 \rightarrow 4,2$</td>
<td>$[4 \cdot 2 \cdot 1]^{1/2}$</td>
</tr>
<tr>
<td>$2,2 \rightarrow 3,4$</td>
<td>$[3 \cdot 4 \cdot 3]^{1/2}$</td>
</tr>
<tr>
<td>$1,4 \rightarrow 2,6$</td>
<td>$[2 \cdot 6 \cdot 5]^{1/2}$</td>
</tr>
<tr>
<td>$0,6 \rightarrow 1,8$</td>
<td>$[1 \cdot 8 \cdot 7]^{1/2}$</td>
</tr>
</tbody>
</table>

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

$$
\hbar\omega_{2}(6 + 3 / 2)
$$