Perturbation Theory II

(See CTDL 1095-1104, 1110-1119)

Last time:

$$\mathbf{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$\mathbf{H}^{(0)}$ is diagonal
$\left\{\psi_n^{(0)}\right\},\left\{E_n^{(0)}\right\}$ are basis functions and zero - order energies

$$E_n^{(1)} = H_{nn}^{(1)}$$

expectation value of perturbation operator

$$E_n^{(2)} = \sum_k{}' \frac{\left|H_{nk}^{(1)}\right|^2}{\underbrace{E_n^{(0)}}_{\text{1st index}} - E_k^{(0)}}$$

sum excludes k = n
matrix element vs. energy denominator

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

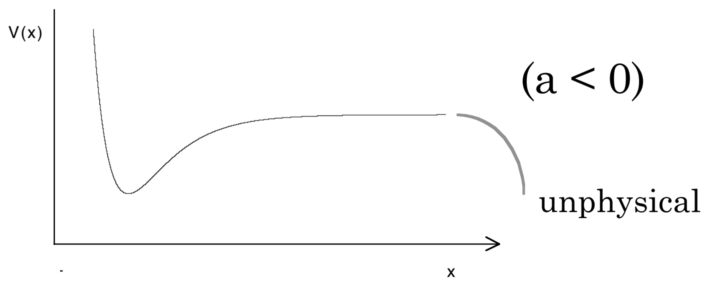
$$\psi_n^{(1)} = \sum_k{}' \underbrace{\frac{H_{nk}^{(1)}}{E_n^{(0)} - E_k^{(0)}}}_{\substack{\text{mixing coefficient, order}\\ \text{sorting parameter,}\\ \text{convergence criterion}}} \psi_k^{(0)}$$

sum excludes k = n

Today:

1. cubic anharmonic perturbation
   $\mathbf{x}^3$ vs. $\mathbf{a},\mathbf{a}^\dagger$
   $a\mathbf{x}^3$ ωx and Y_{00} contributions
2. nonlecture Morse oscillator $\leftrightarrow$ pert. theory for $a\mathbf{x}^3$
3. transition probabilities — orders and convergence of p.t.
   Mechanical and electronic anharmonicities.

Example 1. $\mathbf{H} = \underbrace{\frac{\mathbf{p}^2}{2m} + \frac{1}{2}k\mathbf{x}^2}_{\mathbf{H}^{(0)}} \qquad \underbrace{+a\mathbf{x}^3}_{\mathbf{H}^{(1)}}$



need matrix elements of $\mathbf{x}^3$

one (longer) way $\quad x^3_{i\ell} = \sum_{j,k} x_{ij}x_{jk}x_{k\ell}$

4 different selection rules: $\ell - i = 3, 1, -1, -3$ one path

$\ell - i = 3 \qquad i \to i+1,\ i+1 \to i+2,\ i+2 \to i+3$

$[(i+1)(i+2)(i+3)]^{1/2}$

$\ell - i = 1 \qquad i \to i+1,\ i+1 \to i+2,\ i+2 \to i+1$

$i \to i-1,\ i-1 \to i,\ i \to i+1$

$i \to i+1,\ i+1 \to i,\ i \to i+1$

There are three 3-step paths from i to $i+1$. Add them.

$$[(i+1)(i+2)(i+2)]^{1/2} + [(i)(i)(i+1)]^{1/2} + [(i+1)(i+1)(i+1)]^{1/2}$$

algebraically complicated

other (shorter) alternative: $\mathbf{a}$, $\mathbf{a}^\dagger$, and $\mathbf{a}^\dagger\mathbf{a}$

$$\mathbf{x}^3 = \left(\frac{\hbar}{m\omega}\right)^{3/2} \underset{\sim}{\mathbf{x}}^3 = \left(\frac{\hbar}{m\omega}\right)^{3/2} \left[2^{-1/2}\left(\mathbf{a}+\mathbf{a}^\dagger\right)\right]^3$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{3/2} \left(\mathbf{a}+\mathbf{a}^\dagger\right)^3$$

$$\left(\mathbf{a}+\mathbf{a}^\dagger\right)^3 = \mathbf{a}^3 + \left[\mathbf{a}^\dagger\mathbf{a}\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\mathbf{a}\mathbf{a}^\dagger\right] + \left[\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}\right] + \mathbf{a}^{\dagger 3}$$

four terms, four different selection rules.

Use simple $\mathbf{a},\mathbf{a}^\dagger$ algebra to work out all matrix elements and selection rules by inspection.

recall: $\mathbf{a}^\dagger|n\rangle = (n+1)^{1/2}|n+1\rangle, \quad \mathbf{a}|n\rangle = n^{1/2}|n-1\rangle, \quad \mathbf{a}^\dagger\mathbf{a}|n\rangle = n|n\rangle$

$\left[\mathbf{a},\mathbf{a}^\dagger\right] = 1 \qquad \therefore \quad \boxed{\mathbf{aa}^\dagger = 1 + \mathbf{a}^\dagger\mathbf{a}}$ prescription for permuting $\mathbf{a}$ thru $\mathbf{a}^\dagger$

$\Delta n = -3 \quad \mathbf{a}^3_{n-3,n} = \left[(n-2)(n-1)(n)\right]^{1/2}$

$\Delta n = +3 \quad \mathbf{a}^{\dagger 3}_{n+3,n} = \left[(n+3)(n+2)(n+1)\right]^{1/2}$

$\Delta n = -1 \quad \left[\mathbf{a}^\dagger\mathbf{aa} + \mathbf{aa}^\dagger\mathbf{a} + \mathbf{aaa}^\dagger\right]_{n-1,n}$

goal is to rearrange each product so that it has number operator at right

$$\begin{aligned}
\mathbf{a}^\dagger\mathbf{aa} &= \mathbf{aa}^\dagger\mathbf{a} - \mathbf{a}\\
\mathbf{aaa}^\dagger &= \mathbf{aa}^\dagger\mathbf{a} + \mathbf{a}\\
\mathbf{aa}^\dagger\mathbf{a} &= \mathbf{aa}^\dagger\mathbf{a}\\
\hline
&\ 3\mathbf{aa}^\dagger\mathbf{a} + 0
\end{aligned}$$

$\Delta n = -1 \quad [\quad]_{n-1,n} = 3\left(\mathbf{aa}^\dagger\mathbf{a}\right)_{n-1,n} = \langle n-1|3\mathbf{a}\left(\mathbf{a}^\dagger\mathbf{a}\right)|n\rangle = 3n^{3/2}$

$\Delta n = +1 \quad \left[\mathbf{aa}^\dagger\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{aa}^\dagger + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}\right]$

$$\begin{aligned}
\mathbf{aa}^\dagger\mathbf{a}^\dagger &= \mathbf{a}^\dagger\mathbf{aa}^\dagger + \mathbf{a}^\dagger = \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + 2\mathbf{a}^\dagger\\
\mathbf{a}^\dagger\mathbf{aa}^\dagger &= \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\\
\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} &= \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}\\
\hline
&\ 3\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + 3\mathbf{a}^\dagger
\end{aligned}$$

$$3\langle n+1|\left(\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}^\dagger\right)|n\rangle = 3\left(n(n+1)^{1/2} + (n+1)^{1/2}\right) = 3(n+1)^{3/2}$$

all done — not necessary to massage the algebra as it would have been for $\mathbf{x}^3$ by direct $\mathbf{x}$ multiplication!

Now do the perturbation theory:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \hbar\omega(n+1/2) + \underset{\boxed{x^3_{nn}=0}}{0} + \sum_k{}' \frac{\left|H_{nk}^{(1)}\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

	$\left\|H_{nk}^{(1)}\right\|^2$	$E_n^{(0)} - E_k^{(0)}$
$k = n-3$	$a^2\left(\frac{\hbar}{2m\omega}\right)^3 (n-2)(n-1)(n)$	$+3\hbar\omega$
$k = n-1$	$a^2\left(\frac{\hbar}{2m\omega}\right)^3 9n^3$	$+1\hbar\omega$
$k = n+3$	$a^2\left(\frac{\hbar}{2m\omega}\right)^3 9(n+1)^3$	$-1\hbar\omega$
$k = n+3$	$a^2\left(\frac{\hbar}{2m\omega}\right)^3 (n+3)(n+2)(n+1)$	$-3\hbar\omega$

$$E_n^{(2)} = \underbrace{\frac{a^2\left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega}}_{\text{all of the constants}} \left[\underbrace{\frac{(n-2)(n-1)(n)}{3} - \frac{(n+3)(n+2)(n+1)}{3}} + \underbrace{\frac{9n^3}{1} - \frac{9(n+1)^3}{1}} \right]$$

2 nearly cancelling pairs

$$E_n^{(2)} = \frac{a^2\hbar^2}{8m^3\omega^4}\left[-30(n+1/2)^2 - 3.5\right] \qquad \text{algebra}$$

$$E_n^{(2)} = -\frac{a^2\hbar^2}{m^3\omega^4}\left[\frac{15}{4}(n+1/2)^2 + \frac{7}{16}\right] \qquad (m^3\omega^4 = mk^2)$$

all levels shifted down regardless of sign of a — can't measure sign of cubic anharmonicity constant, a, from vibrational structure alone

$$E_n = \hbar\omega(n+1/2) - \underbrace{\hbar\frac{15}{4}\left(\frac{a^2\hbar}{m^3\omega^4}\right)}_{\hbar\omega_e x_e}(v+1/2)^2 - \underbrace{\hbar\frac{7}{16}\left(\frac{a^2\hbar}{m^3\omega^4}\right)}_{\hbar Y_{00}}$$

$$E_n = \hbar\left[Y_{00} + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 \ldots\right]$$

$a\mathbf{x}^3$ makes contributions exclusively to Y_{00} and $\omega_e x_e$

Nonlecture

Morse Oscillator via perturbation theory

by WKB or DVR

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

$$E_n = \hbar\left[(n+1/2)\omega - (n+1/2)^2\omega x\right]$$

known in advance — compare to pert. theory applied to Taylor series expansion of V(x)

Our initial goal is to re-express the Morse potential in terms of ω and ωx rather than D and α. Then we will expand V^{MORSE} in a Taylor series and look at the coefficient of the $\mathbf{x}^3$ term. First we must take derivatives of E_v with respect to $v \equiv n + 1/2$

at dissociation, $\frac{dE_v}{dv} = 0 = \hbar\left(\omega - 2(n+1/2)\omega x\right)$

$$\frac{\omega}{2\omega x} = n_D + 1/2$$

at dissociation asymptote

$$\therefore D = E_{n_D} = \hbar\left(\underbrace{\frac{\omega}{2\omega x}}_{n_D+1/2}\omega - \underbrace{\frac{\omega^2}{4\omega x^2}}_{(n_D+1/2)^2}\omega x\right)$$

$$\boxed{D = \hbar\frac{\omega^2}{4\omega x}}$$

now expand V(x)

$$V(0) = 0$$

$$V'(x) = \frac{\hbar\omega^2}{4\omega x}\left[+2\alpha e^{-\alpha x} - 2\alpha e^{-2\alpha x}\right] \quad , \quad V'(0) = 0$$

$$V''(x) = \frac{\hbar\omega^2}{4\omega x}\left[-2\alpha^2 e^{-\alpha x} + 4\alpha^2 e^{-2\alpha x}\right] \quad , \quad V''(0) = \frac{\hbar\omega^2}{4\omega x}2\alpha^2 = \frac{\hbar\alpha^2\omega^2}{2\omega x}$$

$$V'''(x) = \frac{\hbar\omega^2}{4\omega x}\left[+2\alpha^3 e^{-\alpha x} - 8\alpha^3 e^{-2\alpha x}\right] \quad , \quad V'''(0) = -\frac{3\hbar\omega^2\alpha^3}{2\omega x}$$

but

$$V''(0) \equiv k = m\omega^2 = \frac{\hbar\alpha^2\omega^2}{2\omega x} \rightarrow \alpha = \left(\frac{2m\omega x}{\hbar}\right)^{1/2}$$

$$V'''(0) = -\frac{3}{2}\frac{\hbar\omega^2}{\omega x}\left(\frac{2m\omega x}{\hbar}\right)^{3/2}$$

$$V(x) = \frac{1}{2}kx^2 + ax^3 \quad \text{thus} \quad V'''(x) = 6a$$

$$a = -\frac{1}{4}\frac{\hbar\omega^2}{\omega x}\left(\frac{2m\omega x}{\hbar}\right)^{3/2} \rightarrow a^2 = \frac{1}{2}\frac{\omega^4 m^3\omega x}{\hbar}$$

now we can eliminate α from higher derivatives (at x = 0). This is to be compared to V‴(0) for the cubic anharmonic potential.

$$\therefore\ \omega x = 2\frac{a^2\hbar}{m^3\omega^4}$$

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

same functional form but different numerical factor (2 vs. 3.75)

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

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

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

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 Use perturbation theory to compute some property other than Energy

need $\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$ to calculate matrix elements of the operator in question,

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

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

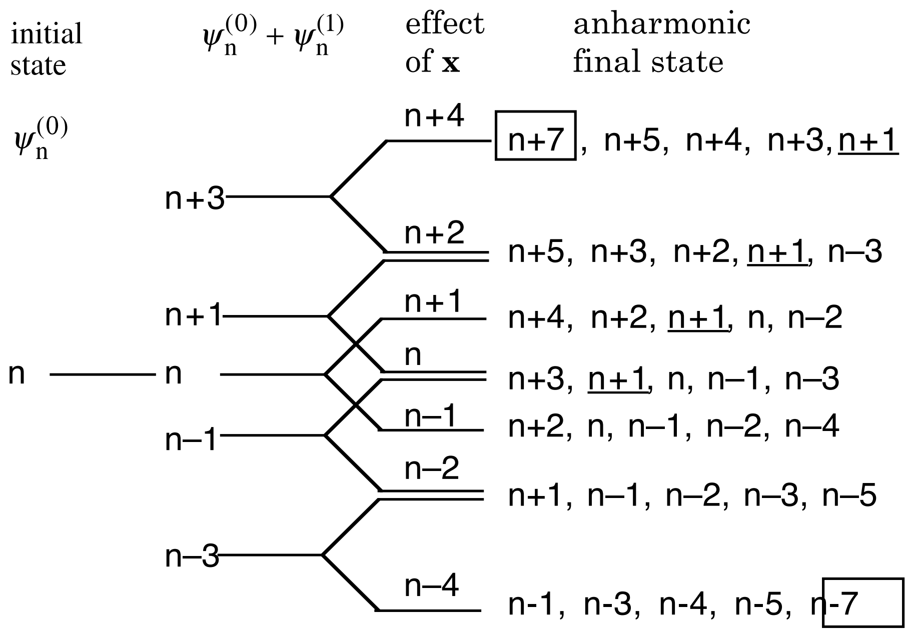
$$|x_{nn+1}|^2 = \left(\frac{\hbar}{2m\omega}\right)(n+1)$$

Standard result. Now allow for mechanical and electronic anharmonicity.

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!