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
$\{\psi_n^{(0)}\},\{E_n^{(0)}\}$ are
basis functions and
zero-order energies

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

expectation value for $\psi_n^{(0)}$
of the perturbation operator

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

1st index

sum excludes k = n
matrix element vs. energy denominator

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

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

sum excludes k = n

Today:

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

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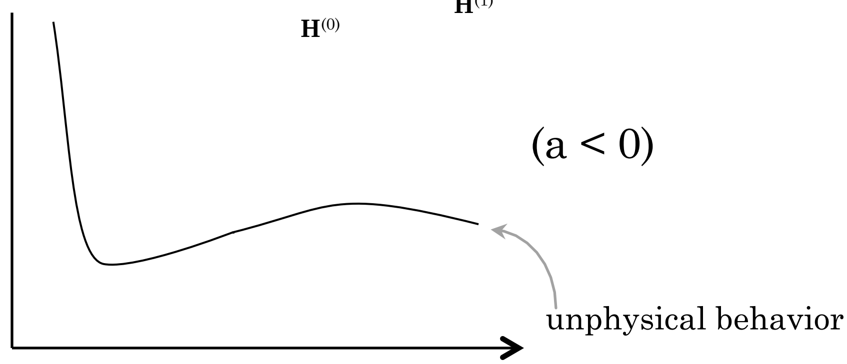
Example 1. $\mathbf{H} = \underbrace{\frac{\mathbf{p}^2}{2m} + \frac{1}{2}k\mathbf{x}^2}_{\mathbf{H}^{(0)}} \quad \underbrace{+a\mathbf{x}^3}_{\mathbf{H}^{(1)}}$



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

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

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

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

$\ell - i = 3 \qquad i \longrightarrow i+1,\ i+1 \longrightarrow i+2,\ i+2 \longrightarrow i+3$ $\quad$ one path for $\ell - i = 3$

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

$\ell - i = 1 \qquad i \longrightarrow i+1,\ i+1 \longrightarrow i+2,\ i+2 \longrightarrow i+1$ $\quad$ three paths for $\ell - i = 1$

$i \longrightarrow i-1,\ i-1 \longrightarrow i,\ i \longrightarrow i+1$

$i \longrightarrow i+1,\ i+1 \longrightarrow i,\ i \longrightarrow i+1$

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

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

algebraically complicated (but only apparently!)

an other (much shorter) alternative method: using $\mathbf{a}$, $\mathbf{a}^\dagger$, and $\mathbf{a}^\dagger\mathbf{a}$
[operator algebra rather than ordinary algebra]

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

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

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

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

$[\mathbf{a},\mathbf{a}^\dagger] = 1 \qquad \therefore \qquad \boxed{\mathbf{a}\mathbf{a}^\dagger = 1 + \mathbf{a}^\dagger\mathbf{a}}$ prescription for permuting $\mathbf{a}$ through $\mathbf{a}^\dagger$

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

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

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

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

$$\mathbf{a}^\dagger\mathbf{a}\mathbf{a} = \mathbf{a}\mathbf{a}^\dagger\mathbf{a} - \mathbf{a}$$

$\mathbf{a}^\dagger\mathbf{a}\mathbf{a} = \underbrace{[\mathbf{a}^\dagger,\mathbf{a}]}_{-1}\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger\mathbf{a}$

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

$$\underline{\mathbf{a}\mathbf{a}^\dagger\mathbf{a} = \mathbf{a}\mathbf{a}^\dagger\mathbf{a}}$$

$$3\mathbf{a}\mathbf{a}^\dagger\mathbf{a} + 0$$

3 operators combined into only one!

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

$\Delta n = +1 \quad [\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}]$ simplify as below

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

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

$$\underline{\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} = \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}}$$

$$3\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + 3\mathbf{a}^\dagger$$

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

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

Now do the perturbation theory:

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

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

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

Simplest path is to combine the pairs of $\Delta n = 3$ and -3, $\Delta n = 1$ and -1 terms

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

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

all levels are shifted down, regardless of sign of a. Can't measure the sign of the 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 $\omega_e x_e$.

NON-LECTURE

Relationship between Morse Oscillator and Perturbation Theory Treatment of Cubic Plus Quartic Anharmonic Oscillator

Morse oscillator

$$V_{\text{Morse}}(x) = D_e\left[1 - e^{-\alpha x}\right]^2 \qquad (D_e \text{ is the dissociation energy})$$

Cubic Plus Quartic Oscillator

$$V_{3,4}(x) = \frac{1}{2}kx^2 + ax^3 + bx^4$$

The exact energy levels of V_{Morse} (obtained via WKB or DVR) have the simple form

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

First we determine the relationship between D_e,α and ω, ωx for the Morse oscillator.

At the dissociation limit, $n \equiv n_D$

$$\frac{dE}{dn} = 0$$

$$\frac{dE}{dn} = 0 = \hbar\omega - \hbar\omega x\left(2n_D + 1\right)$$

$$\boxed{n_D = \frac{\omega}{2\omega x} - \frac{1}{2}}$$

$$E\left(n_D\right) = D_e$$

$$E(n_D) = \hbar\omega\left(\frac{\omega}{2\omega x}\right) - \hbar\omega x\left(\frac{\omega}{2\omega x}\right)^2$$

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

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

This is neat because we have related two easily measured molecular constants, ω and ωx, to one less easily measured molecular constant, D_e.

Now, in preparation for the perturbation theoretic comparison of V_{Morse} to $V_{3,4}$, we compute the derivatives of V_{Morse} at $x = 0$.

$$V(0) = 0$$

$$\frac{dV}{dx} = V'(x) = \frac{\hbar\omega^2}{4\omega x}\left[2\alpha e^{-\alpha x} - 2\alpha e^{-2\alpha x}\right]$$

As expected, $V(x)$ is a minimum at $x = 0$,

$$V'(0) = 0$$

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

$$V''(0) = \frac{\hbar\omega^2}{4\omega x}2\alpha^2 = k = m\omega^2 \quad \left(\omega^2 = k/m\right)$$

$$\boxed{\alpha = \left[\frac{2m\omega x}{\hbar}\right]^{1/2}}$$

Thus we know <u>both</u> D_e and α for V_{Morse} in terms of ω and ωx for an anharmonic oscillator.

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

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

$$V''''(x) = \frac{\hbar\omega^2}{4\omega x}\left[-2\alpha^4 e^{-\alpha x} + 16\alpha^4 e^{-2\alpha x}\right]$$

$$V''''(0) = \frac{\hbar\omega^2}{4\omega x}\left[14\alpha^4\right] = \frac{7}{2}\frac{\hbar\omega^2}{\omega x}\left[\frac{2m\omega x}{\hbar}\right]^2$$

$$= 14\frac{(\omega x)\omega^2}{\hbar}$$

Now we look at the same set of derivatives for $V_{3,4}$

$$V_{3,4}(x) = \frac{1}{2}kx^2 + ax^3 + bx^4$$
$$V''_{3,4}(0) = k$$
$$V'''_{3,4}(0) = 6a$$
$$V''''_{3,4}(0) = 24b$$
$$V'''_{\text{Morse}}(0) = V'''_{3,4}(0)$$
$$-3\left(\frac{2\omega x}{\hbar}\right)^{1/2} = 6a$$
$$\boxed{\omega x = \frac{2a^2\hbar}{\omega^4 m^3}}$$
$$V''''_{\text{Morse}}(0) = V''''_{3,4}(0)$$
$$\boxed{14\frac{(\omega x)\omega^2}{\hbar} = 24b}$$

Applying perturbation theory to $V_{3,4}$(x), we saw on page 15-4 that

$$\omega x = \frac{15}{4}\frac{a^2\hbar}{m^3\omega^4}$$

but the algebraic approach to V_{Morse} led to

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

This difference is due to neglect of the first order contribution from the $\mathbf{x}^4$ term in the power series expansion of $V_{\text{Morse}}(x)$.

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

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

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

It turns out that input of the algebraic relationships between k, a, b for the $V_{3,4}$ potential and D_e, α for V_{Morse} into perturbation theory gives correct results if the $a\mathbf{x}^3$ term is treated through second-order of perturbation theory but the $b\mathbf{x}^4$ term is treated only through first order of perturbation theory.

END OF NON-LECTURE

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 have been neglected from higher derivatives of the Morse potential 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.

To do this we need $\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$ in order to calculate matrix elements of the operator in question.

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

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

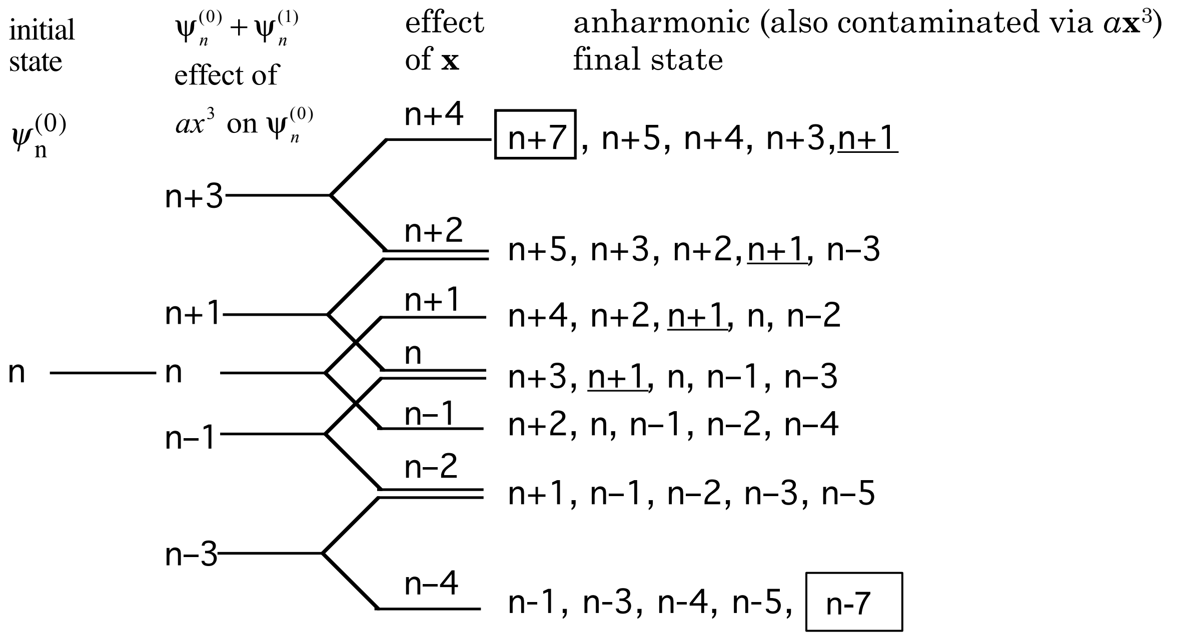
$$|\mathrm{x}_{nn+1}|^2 = \left(\frac{\hbar}{2m\omega}\right)(n+1)$$

Standard result. Now allow for both "mechanical" and "electronic" anharmonicity.

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 $|x_{nn'}|^2$

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

The transition strengths may be divided into 3 classes

1. direct: $n \rightarrow n \pm 1$
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

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

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

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

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

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

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

* 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 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 the sign of b!

It is very important to know whether perturbation theory can give us the sign of a perturbation parameter.

- an even power of $\mathbf{x}$ in $a\mathbf{x}^k$ gives contribution to $E_n^{(1)} = H_{nn}^{(1)}$, which depends on the sign of a.

- an odd power of $\mathbf{x}$ in ax^k gives a zero contribution to $E_n^{(1)}$ and a non-zero contribution proportional to a^2 to $E_n^{(2)}$, which *does not* depend on the sign of a.

- a cross term, as we will see in $B_v = B_e - \alpha(v + 1/2)$, can give the sign of the coefficient of an odd-k term in $\mathbf{H}^{(1)}$. A bit of a surprise!