(1) $V(x) = \frac{1}{2} k_2 x^2 + \frac{1}{3!} k_3 x^3$

(a) $H^{(0)} = \frac{1}{2} k_2 x^2 \quad , \quad E_v^{(0)} = \hbar\omega(v + 1/2) \, , \; \psi_v^{(0)} = \cancel{\ } = |v\rangle$

$$H^{(1)} = \frac{1}{6} k_3 x^3$$

$$E_v^{(1)} = \langle v | \tfrac{1}{6} k_3 x^3 | v \rangle = \tfrac{1}{6} k_3 \langle v | x^3 | v \rangle$$

$$= 0 \quad \text{by symmetry}$$

$$E_v^{(2)} = \sum_{v' \neq v} \frac{|\langle v' | \frac{1}{6} k_3 x^3 | v \rangle|^2}{E_v^{(0)} - E_{v'}^{(0)}}$$

from HW #3 , $x^3 = \left(\frac{\hbar}{2\mu\omega}\right)^{3/2} (a + a^+)(a + a^+)(a + a^+)$

$$\langle v' | x^3 | v \rangle = \left(\frac{\hbar}{2\mu\omega}\right)^{3/2} \Big\{ \sqrt{v(v-1)(v-2)} \, \delta_{v',v-3}$$

$$+ 3v\sqrt{v} \, \delta_{v',v-1} + 3(v+1)\sqrt{v+1} \, \delta_{v',v+1}$$

$$+ \sqrt{(v+1)(v+2)(v+3)} \, \delta_{v',v+3} \Big\}$$

so $$E_v^{(2)} = \frac{1}{36} k_3^2 \left(\frac{\hbar}{2\mu\omega}\right)^3 \left\{ \frac{v(v-1)(v-2)}{E_v^{(0)} - E_{v-3}^{(0)}} + \frac{9v^2 \cdot v}{E_v^{(0)} - E_{v-1}^{(0)}} + \frac{9(v+1)^2(v+1)}{E_v^{(0)} - E_{v+1}^{(0)}} + \frac{(v+1)(v+2)(v+3)}{E_v^{(0)} - E_{v+3}^{(0)}} \right\}$$

$$E_v^{(0)} = \hbar\omega(v + 1/2)$$

$$E_v^{(0)} - E_{v-3}^{(0)} = \hbar\omega\left(v + 1/2 - (v-3) - 1/2\right) = 3\hbar\omega$$

$$E_v^{(0)} - E_{v-1}^{(0)} = \hbar\omega$$

$$E_v^{(0)} - E_{v+1}^{(0)} = -\hbar\omega$$

$$\cancel{E_{v+3}} \; E_v^{(0)} - E_{v+3}^{(0)} = -3\hbar\omega$$

$$E_v^{(2)} = \frac{k_3^2}{36\hbar\omega} \left(\frac{\hbar}{2\mu\omega}\right)^3 \left[\frac{v(v-1)(v-2)}{3} + 9v^3 - 9(v+1)^3 - \frac{(v+1)(v+2)(v+3)}{3} \right]$$

(b) **see next page**

(1b) for $v=0$

$$E_0^{(2)} = \frac{k_3^2}{36\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3\left[-9(1)^3 - \frac{6}{3}\right]$$

$$= \frac{-k_3^2}{3\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3$$

$$E_0 = E_0^{(0)} + E_0^{(2)} = \frac{\hbar\omega}{2} - \frac{k_3^2}{3\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3$$

$$E_1^{(2)} = \frac{k_3^2}{36\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3\left[9(1)^3 - 9(2)^3 - \frac{24}{3}\right]$$

$$= \frac{k_3^2}{36\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3(-71)$$

$$E_1 = \frac{3\hbar\omega}{2} - 71\frac{k_3^2}{36\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3$$

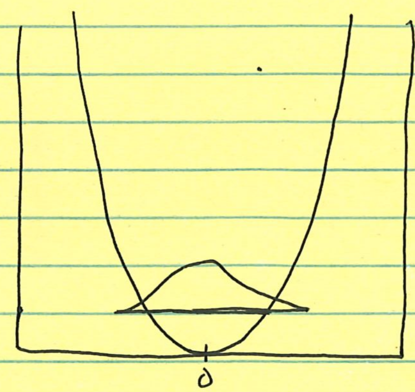
(c) harmonic $v=0-1$: $E_1^{(0)} - E_0^{(0)} = \frac{3}{2}\hbar\omega - \frac{1}{2}\hbar\omega = \hbar\omega$

anharmonic $v=0-1$: $\hbar\omega - 70\frac{k_3^2}{36\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3$

(2)

Example – 1-dim. harmonic oscillator

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$



guess $\phi = \cos\alpha x$

where $\frac{-\pi}{2\alpha} \leq x \leq \frac{\pi}{2\alpha}$

$\alpha \equiv$ variational parameter

$$E_{trial} = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$ ← variational integral

$$\langle\phi|H|\phi\rangle = \int_{-\pi/2\alpha}^{\pi/2\alpha} \cos\alpha x \left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\cos\alpha x \, dx$$

$$= \frac{\pi\hbar^2}{4\mu}\alpha + \left(\frac{\pi^3}{48} - \frac{\pi}{8}\right)\frac{k}{\alpha^3}$$

$$\langle\phi|\phi\rangle = \int_{-\pi/2\alpha}^{\pi/2\alpha} \cos^2\alpha x \, dx = \frac{\pi}{2\alpha}$$

hence
$$E_{trial} = \frac{\hbar^2 \alpha^2}{2\mu} + \left(\frac{\pi^2}{24} - \frac{1}{4}\right)\frac{k}{\alpha^2}$$

$\Rightarrow$ minimize E_{trial} with respect to α

$$\frac{\partial E_{trial}}{\partial \alpha} = 0 = \frac{\hbar^2 \alpha}{\mu} - 2\left(\frac{\pi^2}{24} - \frac{1}{4}\right)\frac{k}{\alpha^3}$$

$$\text{so} \quad \alpha^2_{opt} = \sqrt{\frac{2\mu k}{\hbar^2}\left(\frac{\pi^2}{24} - \frac{1}{4}\right)}$$

plug back into our expression for E_{trial}:

$$E_{min} = 2\hbar\sqrt{\frac{k}{2\mu}\left(\frac{\pi^2}{24} - \frac{1}{4}\right)}$$
$$= (1.14)\,\frac{1}{2}\hbar\,(k/\mu)^{1/2}$$
$$= (1.14)\,\frac{1}{2}\hbar\omega \qquad \text{14\% too large}$$

<u>Note:</u> the variation method can lead to accurate energies but does not insure an accurate wavefunction. the latter generally requires careful choices about the functional form.

(3) Apply the linear variation function

$$\phi = c_1 x^2 (L-x) + c_2 x (L-x)^2$$

to the 1-dim. particle in a box. Calculate the percent errors for the $n=1$ and $n=2$ energies. Determine the coefficients c_1 and c_2 for $n=1$.

basis:

$$\phi_1 = x^2(L-x)$$

$$\phi_2 = x(L-x)^2$$

Secular determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$H_{11} = \langle \phi_1 | H | \phi_1 \rangle \qquad H_{22} = \langle \phi_2 | H | \phi_2 \rangle$

$H_{12} = \langle \phi_1 | H | \phi_2 \rangle \qquad H_{21} = \langle \phi_2 | H | \phi_1 \rangle$

$S_{11} = \langle \phi_1 | \phi_1 \rangle$, $S_{22} = \langle \phi_2 | \phi_2 \rangle$,

$S_{12} = S_{21} = \langle \phi_1 | \phi_2 \rangle$

$$H = -\frac{1}{2} \frac{d^2}{dx^2} \qquad \text{(a.u.)}$$

$$H\phi_1 = -\frac{1}{2}\frac{d^2}{dx^2}\left[x^2(L-x)\right] = -\frac{1}{2}\frac{d}{dx}\left[-x^2 + 2xL - 2x^2\right]$$

$$= 3x - L$$

$$H\phi_2 = -\frac{1}{2}\frac{d^2}{dx^2}\left[x(L-x)^2\right] = -\frac{1}{2}\frac{d}{dx}\left[-2x(L-x) + (L-x)^2\right]$$

$$= 2L - 3x$$

$$\langle\phi_1|H|\phi_1\rangle = \int_0^L x^2(L-x)(3x-L)\,dx$$

$$= \int_0^L \left(3Lx^3 - L^2x^2 - 3x^4 + Lx^3\right)dx$$

$$= \left[\frac{3Lx^4}{4} - \frac{L^2x^3}{3} - \frac{3x^5}{5} + \frac{Lx^4}{4}\right]_0^L$$

$$= \frac{L^5}{15}$$

$$\langle\phi_2|H|\phi_2\rangle = \int_0^L x(L-x)^2(2L-3x)\,dx$$

$$= \int_0^L \left(-3x^4 + 8Lx^3 - 7L^2x^2 + 2L^3x\right)dx$$

$$= \left[\frac{-3x^5}{5} + \frac{8Lx^4}{4} - \frac{7L^2x^3}{3} + \frac{2L^3x^2}{2}\right]_0^L$$

$$= \frac{L^5}{15}$$

$$\langle \phi_1 | H | \phi_2 \rangle = \int_0^L x^2 (L-x)(2L-3x)\, dx$$

$$= \int_0^L (3x^4 - 5Lx^3 + 2L^2x^2)\, dx$$

$$= \left[\frac{3x^5}{5} - \frac{5Lx^4}{4} + \frac{2L^2x^3}{3} \right]_0^L$$

$$= \frac{L^5}{60}$$

$$\langle \phi_2 | H | \phi_1 \rangle = \int_0^L x(L-x^2)(3x-L)\, dx$$

$$= \int_0^L (3x^4 - 7Lx^3 + 5L^2x^2 - L^3x)\, dx$$

$$= \left[\frac{3x^5}{5} - \frac{7Lx^4}{4} + \frac{5L^2x^3}{3} - \frac{L^3x^2}{2} \right]_0^L$$

$$= \frac{L^5}{60}$$

H is hermitian and basis functions are real, so should have known this was the same as H12

$$\langle \phi_1 | \phi_1 \rangle = \int_0^L x^4 (L-x)^2\, dx = \int_0^L (x^6 - 2Lx^5 + L^2x^4)\, dx$$

$$= \left[\frac{x^7}{7} - \frac{2Lx^6}{6} + \frac{L^2x^5}{5} \right]_0^L = \frac{L^7}{105}$$

$$\langle \phi_2 | \phi_2 \rangle = \int_0^L x^2 (L-x)^4 \, dx = -\left[\frac{(L-x)^7}{7} - \frac{2L(L-x)^6}{6} + \frac{L^2(L-x)^5}{5} \right]_0^L$$

$$= \frac{L^7}{105}$$

$$\langle \phi_1 | \phi_2 \rangle = \int_0^L x^3 (L-x)^3 \, dx = \int_0^L \left(-x^6 + 3Lx^5 - 3L^2x^4 + L^3x^3 \right) dx$$

$$= \left[\frac{-x^7}{7} + \frac{3Lx^6}{6} - \frac{3L^2x^5}{5} + \frac{L^3x^4}{4} \right]_0^L$$

$$= \frac{L^7}{140}$$

$$\begin{vmatrix} \frac{L^5}{15} - \frac{L^7}{105} E & \frac{L^5}{60} - \frac{L^7}{140} E \\ \frac{L^5}{60} - \frac{L^7}{140} E & \frac{L^5}{15} - \frac{L^7}{105} E \end{vmatrix} = 0$$

expands to:

$$\frac{L^{10}}{240} - \frac{13 L^{12}}{12600} E + \frac{L^{14}}{25200} E^2 = 0$$

roots: $\frac{5}{L^2}$, $\frac{21}{L^2}$

exact results: $$E_n = \frac{n^2\pi^2}{2L^2} \quad \text{(in a.u.)}$$

$$E_1 = 4.935\ L^{-2}$$

$$E_2 = 19.739\ L^{-2}$$

% errors: 1.3 % and 6.4 %

For the coefficients, insert our approx. E_1 into the 1st secular eqn:

$$\left[\frac{L^5}{15} - \frac{L^7}{105}\left(\frac{5}{L^2}\right)\right]c_1 + \left[\frac{L^5}{60} - \frac{L^7}{140}\left(\frac{5}{L^2}\right)\right]c_2 = 0$$

$$\left(\frac{1}{15} - \frac{L^2}{105}\cdot\frac{5}{L^2}\right)c_1 + \left(\frac{1}{60} - \frac{L^2}{140}\cdot\frac{5}{L^2}\right)c_2 = 0$$

$$0.01905\ c_1 - 0.01905\ c_2 = 0$$

$$c_1 = c_2$$

the values of c_1 & c_2 are obtaining by normalization

$$\langle \phi | \phi \rangle = 1 = \langle c_1 \phi_1 + c_2 \phi_2 \,|\, c_1 \phi_1 + c_2 \phi_2 \rangle$$

$$1 = c_1^2 \langle \phi_1 | \phi_1 \rangle + 2 c_1 c_2 \langle \phi_1 | \phi_2 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle$$

$$= c_1^2 \langle \phi_1 | \phi_1 \rangle + 2 c_1^2 \langle \phi_1 | \phi_2 \rangle + c_1^2 \langle \phi_2 | \phi_2 \rangle$$

since $c_1 = c_2$

$$1 = c_1^2 \left[\frac{L^7}{105} + \frac{2L^7}{140} + \frac{L^7}{105} \right]$$

$$= c_1^2 \left[\frac{140}{14700} L^7 + \frac{210}{14700} L^7 + \frac{140}{14700} L^7 \right]$$

$$= L^7 c_1^2 \left(\frac{1}{30} \right)$$

$$\boxed{c_1 = c_2 = \sqrt{\frac{30}{L^7}}}$$ taking + sign