One Dimensional Examples 3

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Previous Problems

Particle in a box

$$H = T + V = \frac{p_x^2}{2m} + V(x) \qquad V(x) = 0 \quad for \;\; 0 < x < L$$

$$V(x) = \infty \quad for \;\; x \le 0, x \ge L$$

$$\psi_n(x) = C \sin \frac{n\pi}{L} x$$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

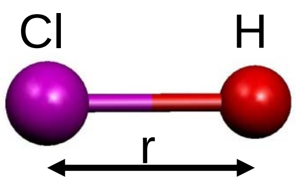
Harmonic Oscillator

$$\left[-\frac{\eta^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right] \psi(x) = E \psi(x)$$

$$\psi_n(y) = C_n H_n(y) \exp\left(-\frac{y^2}{2} \right) \qquad y = \sqrt{\frac{m\omega}{\eta}} x$$

$$E_n = \left(n + \frac{1}{2} \right) \eta \omega$$

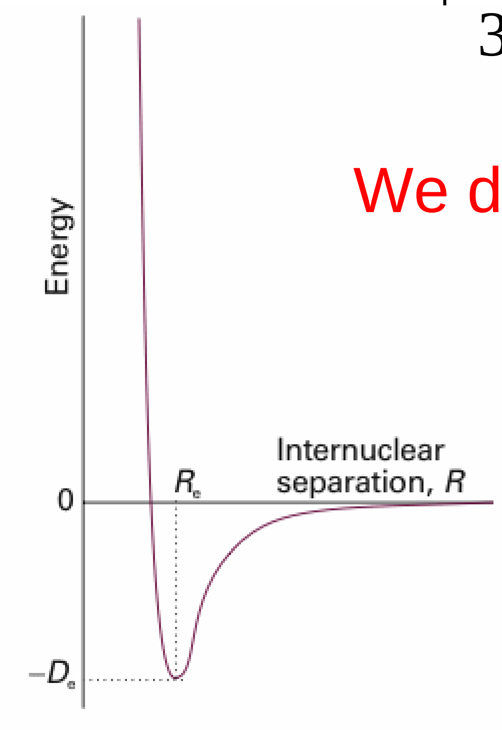
Real Systems

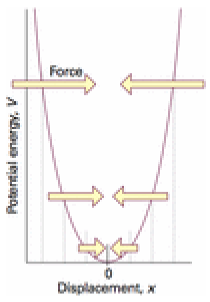


$$V(r) = V(r_{eq}) + \left.\frac{dV}{dr}\right|_{r_{eq}} (r - r_{eq}) + \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r_{eq}} (r - r_{eq})^2$$

$$+ \frac{1}{3!}\left.\frac{d^3V}{dr^3}\right|_{r_{eq}} (r - r_{eq})^3 + \frac{1}{4!}\left.\frac{d^4V}{dr^4}\right|_{r_{eq}} (r - r_{eq})^4 + \ldots..$$

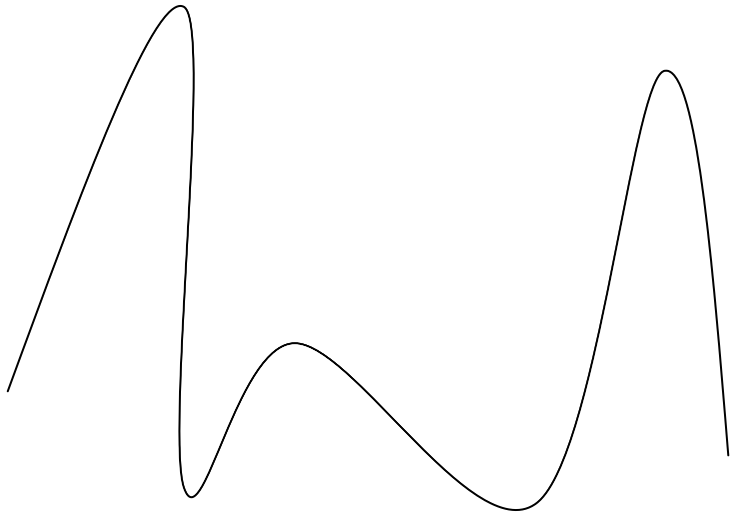
We do not have analytical solutions!





Linear Combination

Expansion of a function :



$$
\begin{aligned}
f(x) &= C_0 + C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + \ldots \\
&= D_1 \cos(kx) + D_2 \cos(2kx) + D_3 \cos(3kx) + D_4 \cos(4kx) + D_5 \cos(5kx) + \ldots \\
&= E_1 \sin(kx) + E_2 \sin(2kx) + E_3 \sin(3kx) + E_4 \sin(4kx) + E_5 \sin(5kx) + \ldots \\
&= \sum_n C_n g_n(x)
\end{aligned}
$$

Perturbation Theory

$$\hat{H} = \hat{H}^0 + \hat{H}'$$

$$\hat{H}^0 = \text{zeroth order Hamiltonian}$$

$$\hat{H}' = \text{perturbation Hamiltonian}$$

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

We know the solution for the zeroth order Hamiltonian

Obtain the full solution

$$\hat{H} \psi_n = E_n \psi_n$$

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}'$$

Expand solution in terms of λ then make it equal to 1 at the end

Expand the Solution

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots.$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots.$$

Bra-Ket Notation

$$|n\rangle = \psi_n(x)$$

$$\langle m| = \psi_m{}^*(x)$$

$$\langle n|\hat{x}|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x)\, x\, \psi_m(x)\, dx$$

$$\langle n|\hat{1}|m\rangle = \langle n|m\rangle = \langle n\|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x) \psi_m(x)\, dx$$

Perturbation Theory 1

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \qquad H|n\rangle = E_n|n\rangle \qquad H^0|n^0\rangle = E_n^{(0)}|n^0\rangle$$

$$|n\rangle = |n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle \ldots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..$$

$$\langle n|n\rangle = \left(\langle n^0| + \lambda\langle n^1| + \lambda^2\langle n^2| + \lambda^3\langle n^3|\ldots\right)\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle\ldots\right)$$

$$= \langle n^0|n^0\rangle + \lambda\left(\langle n^1|n^0\rangle + \langle n^0|n^1\rangle\right) + \lambda^2\left(\langle n^2|n^0\rangle + \langle n^0|n^2\rangle + 2\langle n^1|n^1\rangle\right) = 1$$

$$\langle n^0|n^0\rangle = 1$$

$$\lambda\left(\langle n^1|n^0\rangle + \langle n^0|n^1\rangle\right) = 0$$

$$\lambda^2\left(\langle n^2|n^0\rangle + \langle n^0|n^2\rangle + 2\langle n^1|n^1\rangle\right) = 0$$

Perturbation Theory 2

$$\hat{H}|n\rangle = \hat{H}^0 + \lambda \hat{H}'\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle ...\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..\right)\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle ...\right)$$

Collect equal orders of λ

$$\hat{H}^0\left(|n^0\rangle\right) = \left(E_n^{(0)}\right)\left(|n^0\rangle\right)$$

$$\lambda\left(\hat{H}'|n^0\rangle + \hat{H}^0|n^1\rangle\right) = \lambda\left(E_n^{(1)}|n^0\rangle + E_n^{(0)}|n^1\rangle\right)$$

$$\lambda^2\left(\hat{H}'|n^1\rangle + \hat{H}^0|n^2\rangle\right) = \lambda^2\left(E_n^{(2)}|n^0\rangle + E_n^{(1)}|n^1\rangle + E_n^{(0)}|n^2\rangle\right)$$

Mutiply from the left with $\langle n^0|$

First Order Perturbation Theory 1

$$\hat{H}'\left|n^0\right\rangle + \hat{H}^0\left|n^1\right\rangle = E_n^{(1)}\left|n^0\right\rangle + E_n^{(0)}\left|n^1\right\rangle$$

$$\left\langle n^0\middle|\hat{H}'\middle|n^0\right\rangle + \left\langle n^0\middle|\hat{H}^0\middle|n^1\right\rangle = \left\langle n^0 \middle| n^0\right\rangle E_n^{(1)} + \left\langle n^0 \middle| n^1\right\rangle E_n^{(0)}$$

$$\left\langle n^0\middle|\hat{H}'\middle|n^0\right\rangle + E_n^{(0)}\left\langle n^0 \middle| n^1\right\rangle = E_n^{(1)} + \left\langle n^0 \middle| n^1\right\rangle E_n^{(0)}$$

$$E_n^{(1)} = \left\langle n^0\middle|\hat{H}'\middle|n^0\right\rangle$$

$$\left|n^1\right\rangle = \sum_j C_{nj}\left|j^0\right\rangle$$

Expand the first order perturbed wavefunction

$$\hat{H}'\left|n^0\right\rangle + \hat{H}^0\left|n^1\right\rangle = E_n^{(1)}\left|n^0\right\rangle + E_n^{(0)}\left|n^1\right\rangle$$

$$\hat{H}^0\left|n^1\right\rangle - E_n^{(0)}\left|n^1\right\rangle = E_n^{(1)}\left|n^0\right\rangle - \hat{H}'\left|n^0\right\rangle$$

$$\left(\hat{H}^0 - E_n^{(0)}\right)\left|n^1\right\rangle = \left(E_n^{(1)} - \hat{H}'\right)\left|n^0\right\rangle$$

First Order Perturbation Theory 2

$$\sum_j C_{nj}\left(\hat{H}^0 - E_n^{(0)}\right)\left| j^0 \right\rangle = \left(E_n^1 - \hat{H}'\right)\left| n^0 \right\rangle$$

Multiply both sides by $\left\langle k^0 \right|$

$$\sum_j C_{nj}\left\langle k^0 \left| \left(\hat{H}^0 - E_n^0\right) \right| j^0 \right\rangle = \left\langle k^0 \left| \left(E_n^1 - \hat{H}'\right) \right| n^0 \right\rangle$$

$$\sum_j C_{nj}\left\langle k^0 \left| \left(\hat{H}^0 - E_n^0\right) \right| j^0 \right\rangle = E_n^1 \left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

$$\text{if } k = n \quad \sum_j C_{nj}\left(E_n^{(0)} - E_n^{(0)}\right)\left\langle n^0 \| j^0 \right\rangle = E_n^{(1)} \left\langle n^0 \| n^0 \right\rangle - \left\langle n^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

$$0 = E_n^{(1)} - \left\langle n^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

First Order Perturbation Theory 3

$$\sum_j C_{nj}\left(\hat{H}^0 - E_n^{(0)}\right)\left| j^0 \right\rangle = \left(E_n^{(1)} - \hat{H}'\right)\left| n^0 \right\rangle$$

Multiply both sides by $\left\langle k^0 \right|$

$$\sum_j C_{nj}\left\langle k^0 \right|\left(\hat{H}^0 - E_n^0\right)\left| j^0 \right\rangle = E_n^1 \left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$$

$$\text{if } k \neq n \quad \sum_j C_{nj}\left(E_k^0 - E_n^0\right)\left\langle k^0 \| j^0 \right\rangle = E_n^1 \left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$$

$$C_{nk}\left(E_k^{(0)} - E_n^{(0)}\right) = -\left\langle k^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$$

$$C_{nk} = \frac{\left\langle k^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)} \qquad \left| n^1 \right\rangle = \sum_{k \neq n} C_{nk}\left| k^0 \right\rangle$$

Second Order Perturbation 1

$$\left(\hat{H}'\left|n^1\right\rangle + \hat{H}^0\left|n^2\right\rangle\right) = \left(E_n^{(2)}\left|n^0\right\rangle + E_n^{(1)}\left|n^1\right\rangle + E_n^{(0)}\left|n^2\right\rangle\right)$$

Mutiply from the left with $\left\langle n^0\right|$

$$\left\langle n^0\right|\hat{H}'\left|n^1\right\rangle + \left\langle n^0\right|\hat{H}^0\left|n^2\right\rangle = E_n^{(2)}\left\langle n^0 \| n^0\right\rangle + E_n^{(1)}\left\langle n^0 \| n^1\right\rangle + E_n^{(0)}\left\langle n^0 \| n^2\right\rangle$$

$$\left\langle n^0\right|\hat{H}'\left|n^1\right\rangle + E_n^{(0)}\left\langle n^0 \| n^2\right\rangle = E_n^{(2)} + E_n^{(0)}\left\langle n^0 \| n^2\right\rangle$$

$$E_n^{(2)} = \left\langle n^0\right|\hat{H}'\left|n^1\right\rangle$$

$$\left|n^1\right\rangle = \sum_{k \neq n} C_{nk}\left|k^0\right\rangle \qquad C_{nk} = \frac{\left\langle k^0\right|\left(\hat{H}'\right)\left|n^0\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)}$$

$$E_n^2 = \left\langle n^0\right|\hat{H}'\left|n^1\right\rangle = \sum_{k \neq n} C_{nk}\left\langle n^0\right|\hat{H}'\left|k^0\right\rangle = \sum_{k \neq n}\frac{\left\langle k^0\right|\hat{H}'\left|n^0\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)}\left\langle n^0\right|\hat{H}'\left|k^0\right\rangle$$

Perturbation Theory Summary

$$E_n^1 = \left\langle n^0 \middle| \hat{H}' \middle| n^0 \right\rangle$$

First order perturbation to energy is expectation value of the perturbation

$$\left| n^1 \right\rangle = \sum_{k \neq n} \frac{\left\langle k^0 \middle| \left(\hat{H}'\right) \middle| n^0 \right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)} \left| k^0 \right\rangle$$

First order perturbation to wave function usually mixes the states that are close in energy

$$E_n^2 = \sum_{k \neq n} \frac{\left| \left\langle k^0 \middle| \hat{H}' \middle| n^0 \right\rangle \right|^2}{\left(E_n^{(0)} - E_k^{(0)}\right)}$$

Second order perturbation to energy is obtained from the first order perturbed wave function

Atomic Units

For quantum systems such as electrons and molecules it is easier to use units that fit them=ATOMIC UNIT

Use mass of electron (not kg)
Use charge of electron (not coulomb)
Use hbar for angular momentum (not kg m^2 s^{-1})
Use $4\pi\varepsilon_0$ for permittivity (not C^2 s^2 kg^{-1} m^{-3})

TABLE 9.1
Atomic Units and Their SI Equivalents

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\frac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} $C^2 \cdot J^{-1} \cdot m^{-1}$

Examples 1

$$H^0 = T + V = \frac{p_x^2}{2m} + V(x)$$

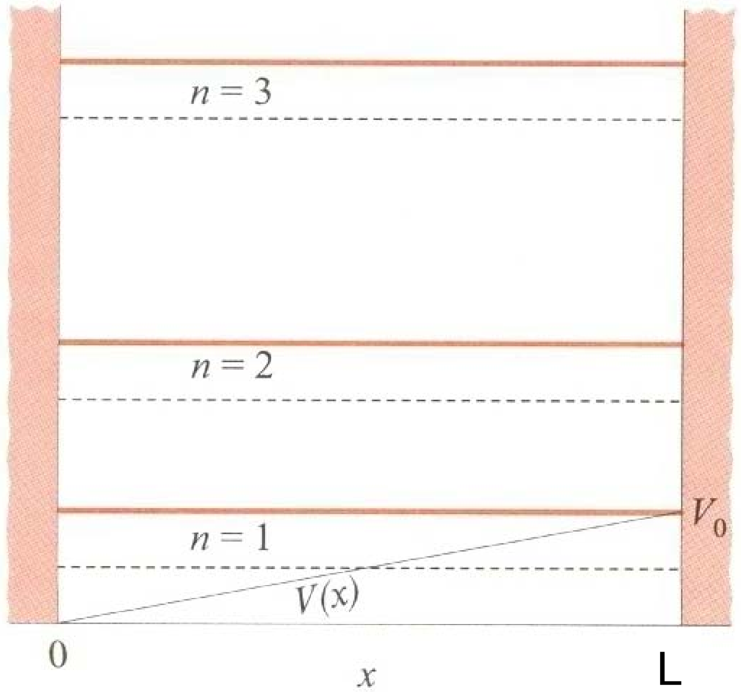
$$V(x) = 0 \quad \mathit{for} \;\; 0 < x < L$$

$$V(x) = \infty \quad \mathit{for} \;\; x \le 0, x \ge L$$

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

$$E_n^{(0)} = \frac{n^2 h^2}{8mL^2}$$

$$H' = \frac{V_0 x}{L} \quad \mathit{for} \;\; 0 < x < L$$

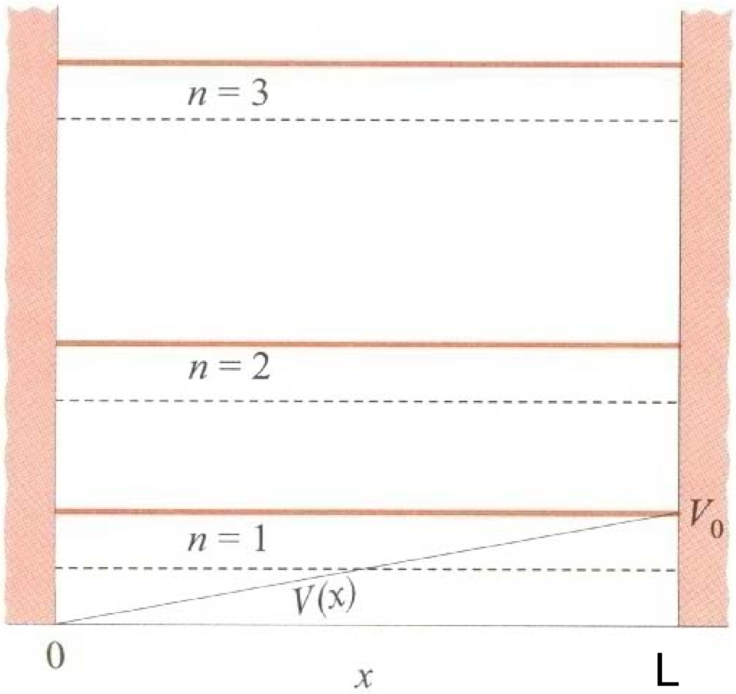


First Order Correction to Energy

$$E_n^1 = \left\langle n^0 \middle| \hat{H}' \middle| n^0 \right\rangle$$

$$\int_{-\infty}^{\infty} \psi_n^0 * (x) H' \psi_n^0 (x) dx = \frac{2}{L} \frac{V_0}{L} \int_{-\infty}^{\infty} \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L} \frac{V_0}{L} \frac{L^2}{4} = \frac{V_0}{2}$$

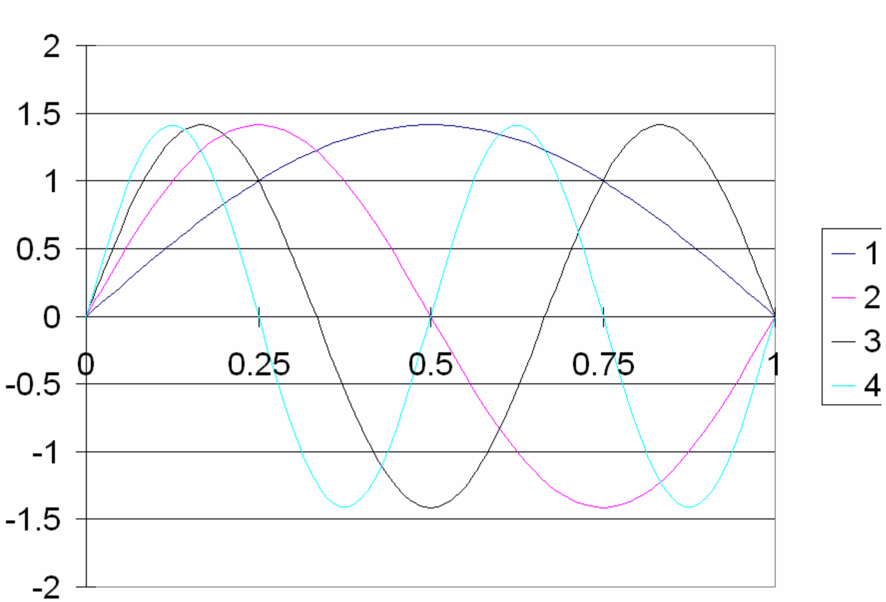


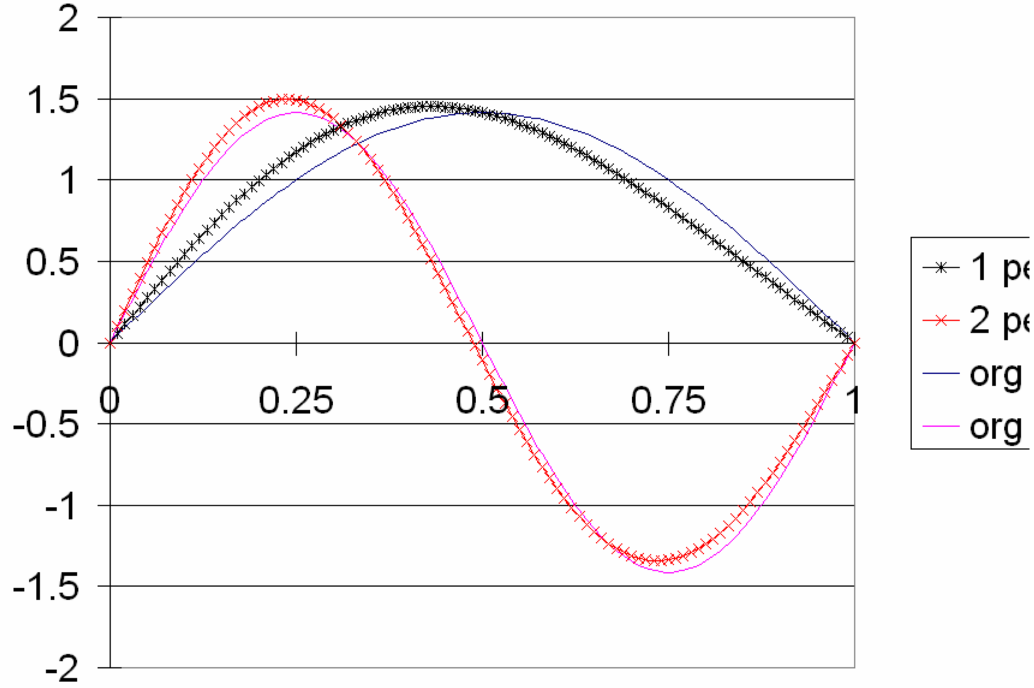
$$E_n \approx \frac{n^2 h^2}{8mL^2} + \frac{V_0}{2}$$

First Order Correction To Wavefunction

$$\left|n^1\right\rangle = \sum_{k \neq n} \frac{\left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle}{\left(E_n^0 - E_k^0\right)} \left|k^0\right\rangle$$

$$\left|n\right\rangle = \left|n^0\right\rangle + \left|n^1\right\rangle$$





Examples 2

$$\left[-\frac{\eta^2}{2m}\frac{d^2}{dx^2}+\frac{kx^2}{2}\right]\psi(x)=E\psi(x)$$

$$\psi_n^0(y)=\left[\frac{1}{2^n n!}\left(\frac{m\omega}{\eta\pi}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}H_n(y)\exp\left(-\frac{y^2}{2}\right) \qquad y=\sqrt{\frac{m\omega}{\eta}}x$$

$$E_n^0=\left(n+\frac{1}{2}\right)\eta\omega$$

$$H'=C_3x^3+C_4x^4$$

First Order Correction to Energy

$$E_n^1 = \langle n^0 | \hat{H}' | n^0 \rangle$$

$$\int_{-\infty}^{\infty} \psi_n^0 *(x) H' \psi_n^0(x) dx = \int_{-\infty}^{\infty} \psi_n^0 *(x)\left(C_3 x^3 + C_4 x^4\right)\psi_n^0(x) dx$$

$$\langle n | x^3 | n+3 \rangle = \left[\frac{(n+1)(n+2)(n+3)}{8(\omega m/\hbar)^3}\right]^{\frac{1}{2}}$$

$$\langle n | x^3 | n+1 \rangle = 3\left[\frac{(n+1)^3}{8(\omega m/\hbar)^3}\right]^{\frac{1}{2}}$$

$$\langle n-1 | x^3 | n \rangle = 3\left[\frac{(n)^3}{8(\omega m/\hbar)^3}\right]^{\frac{1}{2}}$$

$$\langle n-3 | x^3 | n \rangle = \left[\frac{(n)(n-1)(n-2)}{8(\omega m/\hbar)^3}\right]^{\frac{1}{2}}$$

$$\text{else } \langle n | x^3 | m \rangle = 0$$

$$\langle n | x^4 | n+4 \rangle = \frac{1}{4(\omega m/\hbar)^2}[(n+1)(n+2)(n+3)(n+4)]^{\frac{1}{2}}$$

$$\langle n | x^4 | n+2 \rangle = \frac{1}{2(\omega m/\hbar)^2}(2n+3)[(n+1)(n+2)]^{\frac{1}{2}}$$

$$\langle n | x^4 | n \rangle = \frac{3}{4(\omega m/\hbar)^2}\left(2n^2+2n+1\right)$$

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

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

$$\text{else } \langle n | x^4 | m \rangle = 0$$