Techniques of Approximation.

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The semiclassical approximation (WKB)

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Consider the 1D time-ind Sch. Equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

We may rewrite it as

$$\hbar^2 \frac{d^2\psi}{dx^2} - 2mV(x)\psi = -2mE\psi$$

or

$$\hbar^2 \frac{d^2\psi}{dx^2} + 2m\left[E - V(x)\right]\psi = 0$$

From classical mechanics, we know

$$\begin{cases} E = T + V \\ E = \dfrac{p^2}{2m} + V(x) \end{cases} \longrightarrow \quad p^2 = 2m(E - V(x))$$

So we define now

$$p^2(x) \equiv 2m\left[E - V(x)\right]$$

and write SE as

$$\boxed{\hbar^2 \frac{d^2\psi}{dx^2} + p^2(x)\,\psi = 0}$$

We know that when the pot. energy is uniform

$$V(x) \equiv V_0$$

$p(x) = p$ is constant and we have the free particle solutions

$$\psi_p(x) = c_+ e^{ip\frac{x}{\hbar}} + c_- e^{-ip\frac{x}{\hbar}}$$

with energy $\frac{p^2}{2m} + V_0$. If the potential is not constant anymore, but rather varies slowly, we replace the product px by a more general function $S(x)$.

$$+px \longrightarrow S_+(x)$$
$$-px \longrightarrow S_-(x)$$

We write a temptative solution as

$$\psi(x) = C_+ \psi_+(x) + C_- \psi_-(x)$$

with

$$\psi_\pm(x) = \exp\left(\pm i \frac{S_\pm(x)}{\hbar} \right)$$

From

$$\hbar^2 \frac{d^2\psi}{dx^2} + p^2\psi = 0$$

we get

$$\hbar^2 \frac{d}{dx}\left[\frac{i}{\hbar} S_+' \, e^{i\frac{S_+}{\hbar}} \right] + p^2 e^{i\frac{S_+}{\hbar}} = 0$$

$$i\hbar \left[S_+'' e^{i\frac{S_+}{\hbar}} + \frac{i}{\hbar} S_+'^2 e^{i\frac{S_+}{\hbar}} \right] + p^2 e^{i\frac{S_+}{\hbar}} = 0$$

$$i\hbar S_+'' - S_+'^2 + p^2 = 0$$

$$\boxed{-S_+'^2 + i\hbar S_+'' + p^2 = 0}$$

and

$$\hbar^2 \frac{d}{dx}\left[-i\frac{S_-'}{\hbar} \, e^{-i\frac{S_-}{\hbar}} \right] + p^2 e^{-i\frac{S_-}{\hbar}} = 0$$

$$-i\hbar \left[S_-'' \cancel{e^{-i\frac{S_-}{\hbar}}} - \frac{i}{\hbar} S_-'^2 \cancel{e^{-i\frac{S_-}{\hbar}}} \right] + p^2 \cancel{e^{-i\frac{S_-}{\hbar}}} = 0$$

$$-i\hbar S_-'' - S_-'^2 + p^2 = 0 \quad \therefore \quad \boxed{-S_-'^2 - i\hbar S_-'' + p^2 = 0}$$

So we have

$$\begin{cases} -S_+'^2 + i\hbar S_+'' + p^2 = 0 \\ -S_-'^2 - i\hbar S_-'' + p^2 = 0 \end{cases}$$

Now we consider the expansion

$$S_\pm = S_\pm^{(0)} + S_\pm^{(1)}\hbar + S_\pm^{(2)}\hbar^2 + \dots$$

$$S_\pm' = S_\pm^{(0)'} + S_\pm^{(1)'}\hbar + S_\pm^{(2)'}\hbar^2 + \dots$$

$$S_\pm'' = S_\pm^{(0)''} + S_\pm^{(1)''}\hbar + S_\pm^{(2)''}\hbar^2 + \dots$$

$$-\left(S_\pm^{(0)'} + S_\pm^{(1)'}\hbar + \dots\right)^2 \pm i\hbar\left(S_\pm^{(0)} + S_\pm^{(1)}\hbar + \dots\right)'' + p^2 = 0$$

zero order: $\boxed{-S_\pm^{(0)'2} + p^2 = 0}$

First order: $\boxed{-2S_\pm^{(0)'}S_\pm^{(1)'} \pm i S_\pm''^{(0)} = 0}$

second order: $\boxed{-2S_\pm^{(0)'}S_\pm^{(2)'} - S_\pm^{(1)'2} \pm i\, S_\pm^{(1)''} = 0}$

For zero order we have

$$-S_{\pm}^{(0)'2} + p^2 = 0$$

$$S_{\pm}^{(0)'} = \pm p.$$

$$\boxed{S_{\pm}^{(0)}(x) = S_{\pm}^{(0)}(0) \pm \int_0^x p(x)\,dx}$$

For first order

$$2 S_{\pm}^{(0)'} S_{\pm}^{(1)'} = \pm\, i\, S_{\pm}^{(0)''}$$

$$2 S_{\pm}^{(1)'} = \pm\, i\, \frac{S_{\pm}^{(0)''}}{S_{\pm}^{(0)'}}$$

$$2 S_{\pm}^{(1)'} = \pm\, i\, \frac{d}{dx} \ln S_{\pm}^{(0)'}$$

$$d\left(S_{\pm}^{(1)}\right) = \pm \frac{i}{2}\, d\left(\ln S_{\pm}^{(0)'}\right)$$

$$S_{\pm}^{(1)}(x) - S_{\pm}^{(1)}(0) = \pm \frac{i}{2} \ln \frac{S_{\pm}^{(0)'}(x)}{S_{\pm}^{(0)'}(0)}$$

$$S^{(1)}_{\pm}(x) = S^{(1)}_{\pm}(0) \pm \frac{i}{2} \ln \frac{p(x)}{p(0)}$$

To first order we approximate

$$\psi(x) = c_+ \psi_+(x) + c_- \psi_-(x)$$

$$\psi_+(x) = \exp\left[i \frac{S_+(x)}{\hbar} \right]$$

$$\simeq \exp\left[\frac{i}{\hbar} S^{(0)}_+(x) + i S^{(1)}_+(x) \right]$$

$$= \exp\left[\frac{i}{\hbar} \cancel{p} + i S^{(1)}_+(0) - \frac{1}{2} \ln \frac{p(x)}{p(0)} \right]$$

$$= \exp\left[\frac{i}{\hbar} p(x) \right] \cdot \frac{p^{1/2}(0)}{p^{1/2}(x)} \quad C_+$$

$$\psi_-(x) = \exp\left[-i \frac{S_-(x)}{\hbar} \right]$$

$$= \exp\left[-\frac{i}{\hbar} \left(S^{(0)}_- + \hbar S^{(1)}_- \right) \right]$$

$$= \exp\Big[$$

Perturbation of a Two-Level System

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Consider a physical system, defined by a Hamiltonian $H^{(0)}$ sitting inside a two dimensional Hilbert space $\mathcal{H}$. That is

$$H^{(0)} \in L(\mathcal{H})$$

Since $H^{(0)}$ is Hermitian, it is diagonalizable and we may choose $\mathcal{B} = \{|1\rangle, |2\rangle\}$ as an orthonormal basis for $\mathcal{H}$ composed of eigenvectors of $H^{(0)}$:

$$H^{(0)}|1\rangle = E_1^{(0)}|1\rangle$$

$$H^{(0)}|2\rangle = E_2^{(0)}|2\rangle$$

Now, considering the same Hilbert space $\mathcal{H}$, we define the Hermitian operator

$$H = H^{(0)} + H^{(1)} \in L(\mathcal{H})$$

The Hermitian operator H can be viewed as another Hamiltonian, for a different problem defined on the same Hilbert space.

We want to solve the eigenvalue problem for the new Hamiltonian

$$H |\psi\rangle = E |\psi\rangle$$

wich can be written

$$(H - E)|\psi\rangle = 0$$

Expanding

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$$

we have

$$c_1 (H - E)|1\rangle + c_2 (H - E) \cdot |2\rangle = 0$$

Projecting into $|1\rangle$ and $|2\rangle$ we get

$$c_1 \langle 1|(H-E)|1\rangle + c_2 \langle 1|(H-E)|2\rangle = 0$$

$$c_1 (H_{11} - E) + c_2 H_{12} = 0$$

$$c_1 \langle 2|(H-E)|1\rangle + c_2 \langle 2|(H-E)|2\rangle = 0$$

$$c_1 H_{21} + c_2 (H_{22} - E) = 0$$

Thus we have the linear system

$$\begin{cases} c_1 (H_{11} - E) + c_2 H_{12} = 0 \\ c_1 H_{21} + c_2 (H_{22} - E) = 0 \end{cases}$$

Since we are interested in non trivial solutions for the coeffs c_1, c_2, the determinant must vanish:

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

$$(H_{11} - E)(H_{22} - E) - H_{12} H_{21} = 0$$

$$E^2 - E (H_{11} + H_{22}) + H_{11} H_{22} - H_{12} H_{21} = 0$$

$$E_\pm = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\sqrt{(H_{11} + H_{22})^2 - 4 (H_{11} H_{22} - H_{12} H_{21})}$$

$$\boxed{E_\pm = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4 H_{12} H_{21}}}$$

Consider now the special case where the perturbation is off-diagonal

$$H = H^{(0)} + H^{(1)}$$

$$H = H^{(0)} + \begin{pmatrix} 0 & H_{12} \\ H_{21} & 0 \end{pmatrix}$$

$$H = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix} + \begin{pmatrix} 0 & H_{12} \\ H_{21} & 0 \end{pmatrix}$$

$$H = \begin{pmatrix} E_1^{(0)} & H_{12} \\ H_{21} & E_2^{(0)} \end{pmatrix}$$

$$E_\pm = \frac{1}{2}\left(H_{11} + H_{22}\right) \pm \frac{1}{2}\sqrt{\left(H_{22} - H_{11}\right)^2 + 4 H_{12} H_{21}}$$

$$E_\pm = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\sqrt{\left(E_1^{(0)} - E_2^{(0)}\right)^2 + 4\epsilon^2}$$

where we defined

$$\epsilon^2 = H_{12} H_{21}$$

$$E_{\pm} = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\sqrt{\Delta E^2 + 4\epsilon^2}$$

$$= \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\Delta E\sqrt{1 + \frac{4\epsilon^2}{(\Delta E)^2}}$$

Using $\sqrt{1+x} \cong 1 + \frac{1}{2}x$

$$E_{\pm} \cong \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm \frac{1}{2}\Delta E\left(1 + \frac{1}{2}\cdot\frac{4\epsilon^2}{\Delta E^2}\right)$$

$$E_{+} \cong E_1^{(0)} + \frac{\epsilon^2}{\Delta E^{(0)}}$$

$$E_{-} = E_2^{(0)} - \frac{\epsilon^2}{\Delta E^{(0)}}$$

Perturbation Theory For Many-Level Systems

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To begin with we shall consider time-independent non degenerate perturbation theory. Our aim is to solve the time independent Schrödinger equation

$$\hat{H}\,\psi_m = E_m\,\psi_m$$

Assume though, that we know the solution to

$$H^0\,\psi_m^{(0)} = E_m^{(0)}\,\psi_m^{(0)}$$

where the time-independent Hamiltonian H^0 is defined in the same Hilbert space as $\hat{H}$. We shall call H^0 the <u>unperturbed Hamiltonian</u> and $\hat{H}$ the <u>target Hamiltonian</u>. From $\hat{H}$ and H^0, we define

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

as the <u>perturbation</u> or <u>perturbing Hamiltonian</u>. Finally we define

$$H = H^0 + \lambda H'$$

as the <u>perturbed Hamiltonian</u> with λ a real parameter between 0 and 1. In the following, we aim to solve the eigenvalue problem for the perturbed Hamiltonian H which will coincide with $\hat{H}$ when $\lambda = 1$.

The posed problem to be solved is then

$$H\psi_m = (H^0 + \lambda H^1)\psi_m = E_m \psi_m$$

Since H depends on the parameter λ, so do ψ_m and E_m

$$\psi_m = \psi_m(q, \lambda)$$

$$E_m = E_m(\lambda)$$

Expand ψ_m and E_m as a Taylor series in powers of λ

$$\begin{cases} \psi_m = \overbrace{\psi_m\Big|_{\lambda=0}}^{\psi_m^{(0)}} + \overbrace{\dfrac{\partial \psi_m}{\partial \lambda}\Big|_{\lambda=0}}^{\psi_m^{(1)}} \lambda + \overbrace{\dfrac{1}{2!}\dfrac{\partial^2 \psi_m}{\partial \lambda^2}\Big|_{\lambda=0}}^{\psi_m^{(2)}} \lambda^2 + \cdots \\ E_m = \overbrace{E_m\Big|_{\lambda=0}}^{E_m^{(0)}} + \overbrace{\dfrac{dE_m}{d\lambda}\Big|_{\lambda=0}}^{E_m^{(1)}} \lambda + \overbrace{\dfrac{1}{2}\dfrac{d^2 E_m}{d\lambda^2}}^{E_m^{(2)}} \lambda^2 + \dfrac{1}{3!}\dfrac{d^2 E_m}{d\lambda^3}\lambda^3 + \cdots \end{cases}$$

$$\begin{cases} \psi_m = \psi_m^{(0)} + \psi_m^{(1)}\lambda + \psi_m^{(2)}\lambda^2 + \cdots \\ E_m = E_m^{(0)} + E_m^{(1)}\lambda + E_m^{(2)}\lambda^2 + E_m^{(3)}\lambda^3 + \cdots \end{cases}$$

Now substitute the λ expansions into the posed problem to get

$$(H^0 + \lambda H^1)(\psi_m^{(0)} + \psi_m^{(1)}\lambda + \psi_m^{(2)}\lambda^2 + \cdots) =$$

$$= (E_m^{(0)} + E_m^{(1)}\lambda + E_m^{(2)}\lambda^2 + \cdots)(\psi_m^{(0)} + \psi_m^{(1)}\lambda + \psi_m^{(2)}\lambda^2 + \cdots)$$

$$\left(H^{0}+\lambda H^{1}\right)\left(\psi_m^{(0)}+\psi_m^{(1)}\lambda+\psi_m^{(2)}\lambda^2+\cdots\right)=$$

$$=\left(E_m^{(0)}+E_m^{(1)}\lambda+E_m^{(2)}\lambda^2+E_m^{(3)}\lambda^3+\cdots\right)\left(\psi_m^{(0)}+\psi_m^{(1)}\lambda+\psi_m^{(2)}\lambda^2+\cdots\right)$$

collecting terms order by order in lambda we get

$$H^{(0)}\psi_m^{(0)}=E_m^{(0)}\psi_m^{(0)}$$

$$H^{(0)}\psi_m^{(1)}+H^{1}\psi_m^{(0)}=E_m^{(0)}\psi_m^{(1)}+E_m^{(1)}\psi_m^{(0)}$$

$$H^{0}\psi_m^{(2)}+H^{1}\psi_m^{(1)}=E_m^{(0)}\psi_m^{(2)}+E_m^{(1)}\psi_m^{(1)}+E_m^{(2)}\psi_m^{(0)}$$

$$H^{0}\psi_m^{(3)}+H^{1}\psi_m^{(2)}=E_m^{(0)}\psi_m^{(3)}+E_m^{(1)}\psi_m^{(2)}+E_m^{(2)}\psi_m^{(1)}+E_m^{(3)}\psi_m^{(0)}$$

$$\vdots$$

The solution to the first equation is known. From the second we can obtain the first order corrections both in the energies $E_m^{(1)}$ and eigenfunctions ψ_m^{1}.

<u>First Order Correction in the Energy</u>

Consider now the second equation

$$H^{(0)}\psi_m^{(1)}+H^{1}\psi_m^{(0)}=E_m^{(0)}\psi_m^{(1)}+E_m^{1}\psi_m^{(0)}$$

and expand $\psi_m^{(1)}$ in the basis of eigenvectors of $H^{(0)}$

$$\psi_m^{(1)}=\sum_k c_{mk}\psi_k^{(0)}$$

Substituting

$$\psi_0^{(1)} = \sum_k c_{mk} \psi_k^{(0)}$$

we get

$$\left(H^{(0)} - E_m^{(0)} \right) \sum_k c_{mk} \psi_k^{(0)} = \left(E_m^{(1)} - H' \right) \psi_m^{(0)}$$

Using ket notation and performing the sandwhich with $|\psi_m^{(0)}\rangle$ we get

$$\sum_k c_{mk} \langle \psi_m^{(0)} | \left(H^{(0)} - E_m^{(0)} \right) | \psi_k^{(0)} \rangle = \langle \psi_m^{(0)} | \left(E_m^{(1)} - H' \right) | \psi_m^{(0)} \rangle$$

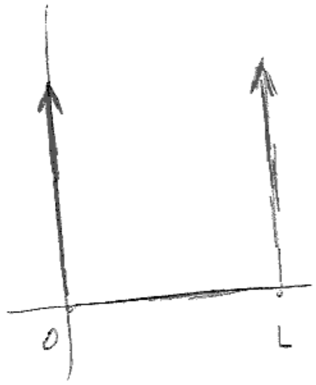
$$\sum_k c_{mk} \left(E_k^{(0)} - E_m^{(0)} \right) \underbrace{\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{mk}} = E_m^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_m^{(0)} \rangle}_{1} - \langle \psi_m^{(0)} | H' | \psi_m^{(0)} \rangle$$

$$c_{mm} \left(E_m^{(0)} - E_m^{(0)} \right) = E_m^{(1)} - \langle \psi_m^{(0)} | H' | \psi_m^{(0)} \rangle$$

$$\therefore \boxed{E_m^{(1)} = \langle \psi_m^{(0)} | H' | \psi_m^{(0)} \rangle}$$

Example: As a first example, let us consider a small perturbation to the infinite square well potential

initial problem ($H^{(0)}$):



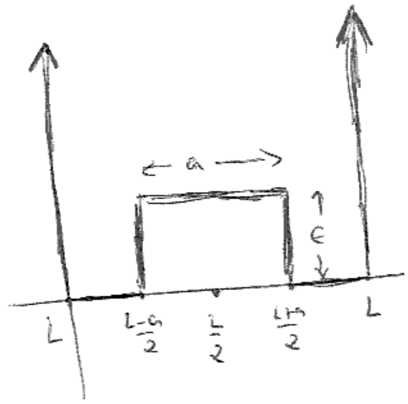
Energies

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

Eigenfunctions

$$\psi_n^{(0)}(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

perturbed problem ($H^{(0)} + H'$)



$$H' = \begin{cases} \epsilon, & \text{if } \frac{L-a}{2} \le x \le \frac{L+a}{2} \\ 0, & \text{otherwise} \end{cases}$$

The first order correction in the energies are

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

For the first level, we have

$$E_1^{(1)} = \int_0^L \left[\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)\right]^* H' \left[\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)\right] dx$$

$$E_1^{(1)} = \frac{2}{L}\int_{\frac{L-a}{2}}^{\frac{L+a}{2}} \epsilon \sin^2\left(\frac{\pi x}{L}\right) dx$$

$$= \frac{2\epsilon}{L}\left[\frac{x}{2} - \frac{\sin\left(\frac{2\pi x}{L}\right)}{4\pi} L\right]_{\frac{L\pm a}{2}}^{\frac{L+a}{2}}$$

$$= \frac{\epsilon}{L}\left[a - \frac{L}{2\pi}\left(\sin\left(\frac{2\pi}{L}\left(\frac{L+a}{2}\right)\right) - \sin\left(\frac{2\pi}{L}\left(\frac{L-a}{2}\right)\right)\right)\right]$$

$$= \epsilon\left[\frac{a}{L} - \frac{1}{2\pi}\left[\sin\left(\pi + \pi\frac{a}{L}\right) - \sin\left(\pi - \frac{\pi a}{L}\right)\right]\right]$$

$$= \epsilon\left[\frac{a}{L} - \frac{1}{2\pi}\left[\sin\pi\cos\frac{\pi a}{L} + \sin\frac{\pi a}{L}\cos\pi - \sin\pi\cos\frac{\pi a}{L} + \sin\frac{\pi a}{L}\cos\pi\right]\right]$$

$$= \epsilon\left\{\frac{a}{L} - \frac{1}{2\pi}\left(-\sin\frac{\pi a}{L} - \sin\frac{\pi a}{L}\right)\right]$$

$$= \epsilon\left[\frac{a}{L} + \frac{1}{\pi}\sin\left(\frac{\pi a}{L}\right)\right]$$

considering now the m-th level first order correction, we have

$$E_m^{(1)} = \int_0^L \left[\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{m\pi x}{L}\right)\right]^* H^{(1)} \left[\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{m\pi x}{L}\right)\right] dx$$

$$= \int_{\frac{L-a}{2}}^{\frac{L+a}{2}} \left(\frac{2}{L}\right)\sin^2\left(\frac{m\pi x}{L}\right)\epsilon \, dx$$

$$= \frac{2\epsilon}{L}\left[\frac{x}{2} - \frac{\sin\left(\frac{2m\pi x}{L}\right)L}{4m\pi}\right]_{x=\frac{L-a}{2}}^{x=\frac{L+a}{2}}$$

$$= \frac{\epsilon}{L}\left\{a - \frac{L}{2m\pi}\left[\sin\left(m\pi + \frac{m\pi a}{L}\right) - \sin\left(m\pi - \frac{m\pi a}{L}\right)\right]\right\}$$

$$= \frac{\epsilon}{L}\left\{a - \frac{L}{2m\pi}\left[+\sin\left(\frac{m\pi a}{L}\right)(-1)^m + \sin\left(\frac{m\pi a}{L}\right)(-1)^m\right]\right\}$$

$$= \epsilon\left\{\frac{a}{L} - \frac{(-1)^m}{m\pi}\sin\left(\frac{m\pi a}{L}\right)\right\}$$

Example: The anharmonic oscillator. Consider the following correction for the quadratic potential

$$V(x) = \frac{kx^2}{2} + cx^3 + dx^4$$

leading to the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2} + cx^3 + dx^4$$

where c and d are real parameters. The perturbation in this case is thus

$$\hat{H}' = cx^3 + dx^4$$

Let us determine the first order energy correction for the ground state.

Recall

$$\psi_0^{(0)}(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

with $\alpha = \frac{2\pi\nu m}{\hbar} = \frac{1}{\hbar}\sqrt{mk}$ $\left(\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}\right)$

The first-order energy correction then reads

$$E_0^{(1)} = \langle \psi_0^{(0)} | (c x^3 + d x^4) | \psi_0^{(0)} \rangle$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2} (c x^3 + d x^4)\, dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha x^2} d x^4\, dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} d \underbrace{\int_{-\infty}^{+\infty} e^{-\alpha x^2} x^4\, dx}_{\frac{3\sqrt{\pi}}{4 \alpha^{5/2}}}$$

$$= \frac{3d}{4\alpha^2} = \frac{3d}{4} \cdot \frac{\hbar^2}{mk}$$

In order to proceed to the first-order correction in the wave function, we shall adopte the <u>intermediate normalization</u>. We assume $\psi_m^{(0)}$ normalized

$$\langle \psi_m^{(0)} | \psi_m^{(0)} \rangle = 1$$

and require ψ_m to satisfy

$$\langle \psi_m^{(0)} | \psi_m \rangle = 1$$

Given an arbitrary ψ_m', multiply by $\dfrac{1}{\langle \psi_m^{(0)} | \psi_m' \rangle}$ to get

$$\psi_m = \frac{\psi_m'}{\langle \psi_m^{(0)} | \psi_m' \rangle}$$

and then

$$\langle \psi_m^{(0)} | \psi_m \rangle = \frac{\langle \psi_m^{(0)} | \psi_m' \rangle}{\langle \psi_0^{(0)} | \psi_m' \rangle} = 1$$

From the intermediate normalization condition we have

$$1 = \langle \psi_m^{(0)} | \psi_m \rangle$$

$$= \langle \psi_m^{(0)} | \left\{ |\psi_m^{(0)}\rangle + \lambda |\psi_m^{(1)}\rangle + \lambda^2 |\psi_m^{(2)}\rangle + \dots \right\}$$

$$= \underbrace{\langle \psi_m^{(0)} | \psi_m^{(0)} \rangle}_{1} + \lambda \langle \psi_m^{(0)} | \psi_m^{(1)} \rangle + \lambda^2 \langle \psi_0^{(0)} | \psi_m^{(2)} \rangle + \dots$$

thus $\langle \psi_m^{(0)} | \psi_m^{(k)} \rangle = \delta^{ok}$

First-Order Wave Function Correction

Now we come back to the 2nd equation

$$\left(H^{(0)} - E_n^{(0)}\right) \sum_k c_{nk} \psi_k^{(0)} = \left(E_n^{(1)} - H'\right) \psi_n^{(0)}$$

Using ket notation we perform the sandwich with

$|\psi_m^{(0)}\rangle$ with $m \neq n$

$$\sum_k c_{nk} \langle \psi_m^{(0)} | \left(H^{(0)} - E_n^{(0)}\right) | \psi_k^{(0)} \rangle = \langle \psi_m^{(0)} | \left(E_n^{(1)} - H'\right) | \psi_n^{(0)} \rangle$$

$$\sum_k c_{nk} \left(E_k^{(0)} - E_n^{(0)}\right) \underbrace{\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{mk}} = E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle}_{\delta_{mn}} - \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle$$

$$c_{nm} \left(E_m^{(0)} - E_n^{(0)}\right) = - \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle \qquad (m \neq n)$$

$$c_{nm} = \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \qquad (m \neq n)$$

Recall that the first order wave function correction $\psi_n^{(1)}$ is written as a linear combination of the basis $\psi_m^{(0)}$

$$\psi_n^{(1)} = \sum_m c_{nm} \psi_m^{(0)}$$

The previous equation gives all coefficients c_{mn} for $m \neq n$. For the case $m = n$ we have

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \sum_m c_{mn} \underbrace{\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle}_{\delta_{n,m}}$$

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = c_{nn}$$

and from the intermediate normalization condition we get

$$c_{nn} = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$$

Thus the first order wave function correction reads

$$\boxed{\psi_n^{(1)} = \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)}}$$

The Secon-Order Correction to the Energy

Recall the equation coming from terms in λ^2:

$$H^0 \psi_m^{(2)} + H^1 \psi_m^{(1)} = E_m^{(0)} \psi_m^{(2)} + E_m^{(1)} \psi_m^{(1)} + E_m^{(2)} \psi_m^{(0)}$$

and rewrite it as

$$\left(H^0 - E_m^{(0)}\right) \psi_m^{(2)} = \left(E_m^{(1)} - H^1\right) \psi_m^{(1)} + E_m^{(2)} \psi_m^{(0)}$$

Now expand $\psi_m^{(2)}$ and $\psi_m^{(1)}$ as

$$\psi_m^{(2)} = \sum_k \ell_{mk} \psi_k^{(0)} \quad \text{and} \quad \psi_m^{(1)} = \sum_k c_{mk} \psi_k^{(1)} ,$$

multiply all terms by $\psi_m^{(0)*}$ and integrate. In bracket notation this leads to

$$\sum_k \ell_{mk} \langle \psi_m^{(0)} | (H^0 - E_m^{(0)}) | \psi_k^{(0)} \rangle =$$

$$= \sum_k c_{mk} \langle \psi_m^{(0)} | (E_m^{(1)} - H^1) | \psi_k^{(0)} \rangle + E_m^{(2)} \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle$$

$$\sum_k \ell_{mk} \left(E_k^{(0)} - E_m^{(0)}\right) \underbrace{\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{m,k}} = \sum_k c_{mk} E_m^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{mk}} - \sum_k c_{mk} \langle \psi_m^{(0)} | H^1 | \psi_k^{(0)} \rangle + E_m^{(2)}$$

$$0 = c_{mm} E_m^{(1)} - \sum_k c_{mk} \langle \psi_m^{(0)} | H' | \psi_k^{(0)} \rangle + E_m^{(2)}$$

Recall from intermediate normalization

$$c_{mm} = \langle \psi_m^{(0)} | \psi_m^{(1)} \rangle = 0$$

and then

$$E_m^{(2)} = \sum_k c_{mk} \langle \psi_m^{(0)} | H' | \psi_k^{(0)} \rangle$$

Now recall we had already calculated c_k

$$c_{mk} = \frac{\langle \psi_k^{(0)} | H' | \psi_m^{(0)} \rangle}{E_m^{(0)} - E_k^{(0)}} \qquad (k \neq m)$$

$$E_m^{(2)} = \sum_{k \neq m} \frac{\langle \psi_k^{(0)} | H' | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | H' | \psi_k^{(0)} \rangle}{E_m^{(0)} - E_k^{(0)}}$$

$$\boxed{E_m^{(2)} = \sum_{k \neq m} \frac{| \langle \psi_k^{(0)} | H' | \psi_m^{(0)} \rangle |^2}{E_m^{(0)} - E_k^{(0)}}}$$