Non-degenerate Perturbation Theory

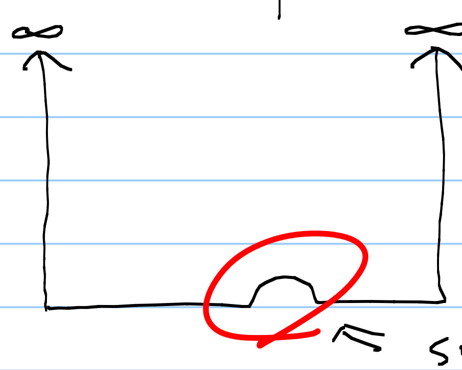
Note Title

In many cases, we run into a situation where the hamiltonian is a small change from an already solved hamiltonian.

Handling this kind of problem is called "Perturbation theory".

Here, we will discuss how to handle the perturbation theory if the unperturbed system is not degenerate.

A good example of a non-degenerate perturbation problem is



small bump in the infinite square well.

Let's assume that the unperturbed system is described by H^0, and its schrödinger equation is already solved such that its energy spectrum is $E_1^0, E_2^0, \cdots, E_n^0$ with the corresponding eigenfunctions $\psi_1^0, \psi_2^0, \cdots \psi_n^0$, such that $\boxed{H^0\psi_n^0 = E_n^0 \psi_n^0}$ with the standard orthonormality

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} .$$

Now the new perturbed Hamiltonian is given by

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

, where $\lambda H'$ is the small perturbation. Here, we assume that λ is a small number.

Now we write the new eigenfunctions and eigenenergies in terms of powers of λ such that

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

ψ_n^1 (E_n^1) is called the first-order correction and ψ_n^2 (E_n^2) is called the second-order correction, etc.

Now the new perturbed Schrödinger Eq. should be

$$H\psi_n = E_n\psi_n$$

$$\Rightarrow (H^0 + \lambda H')(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots)$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\psi_n^0 + \lambda\psi_n^1 + \cdots)$$

We equate terms with the same powers of λ on each side.

0th order gives

$H^0\psi_n^0 = E_n^0\psi_n^0$, which is simply the unperturbed Schröd. Eq.

1st order gives

$$\lambda(H^0\psi_n^1 + H'\psi_n^0) = \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0)$$

$$\Rightarrow E_n^1\psi_n^0 = H^0\psi_n^1 + H'\psi_n^0 - E_n^0\psi_n^1$$

$$\Rightarrow E_n^1\langle\psi_n^0|\psi_n^0\rangle = \langle\psi_n^0|H^0|\psi_n^1\rangle + \langle\psi_n^0|H'|\psi_n^0\rangle$$
$$- \langle\psi_n^0|E_n^0|\psi_n^1\rangle$$

Because $H^0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$

$$\Rightarrow \langle\psi_n^0|H^0 = E_n^0\langle\psi_n^0|$$

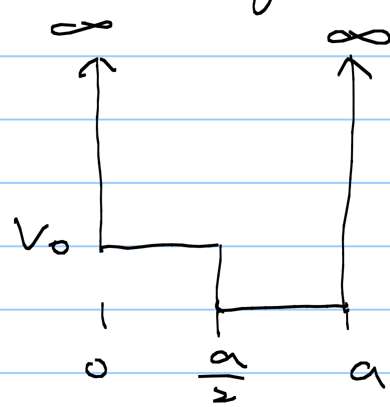
$$\Rightarrow \underline{E_n^1} = E_n^0\langle\psi_n^0|\psi_n^1\rangle + \langle\psi_n^0|H'|\psi_n^0\rangle$$
$$- E_n^0\langle\psi_n^0|\psi_n^1\rangle = \underline{\langle\psi_n^0|H'|\psi_n^0\rangle}$$

So $\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}$

This is the main result of the first-order perturbation theory.

It is also considered one of the MOST IMPORTANT equations in quantum mechanics.

$\boxed{\text{Ex. 1}}$



What are the new eigen energies up to the first order correction?

$$\text{With } H' = \begin{cases} V_0 & \text{for } 0 < x < \frac{a}{2} \\ 0 & \text{else} \end{cases}$$

$$\begin{aligned} E_n^1 &= \langle \psi_n^0 | H' | \psi_n^0 \rangle \\ &= \frac{2}{a} \left[\int_0^{\frac{a}{2}} \sin^2\left(\frac{n\pi}{a} x\right) V_0 \, dx \right] \\ &= \frac{2}{a} V_0 \cdot \frac{a}{4} = \frac{V_0}{2} \end{aligned}$$

So $E_n = E_n^0 + E_n^1 = \underline{\dfrac{\hbar^2}{2m}\dfrac{\pi^2}{a^2}n^2 + \dfrac{V_0}{2}}$

$\boxed{\text{Ex. 2}}$ In the center of the infinite square well, if $H' = \alpha\,\delta(x - a/2)$

Calculate the new energies up to the first order correction.

$$E_n^1 = \frac{2}{a}\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)\alpha\,\delta\left(x - \frac{a}{2}\right)dx$$

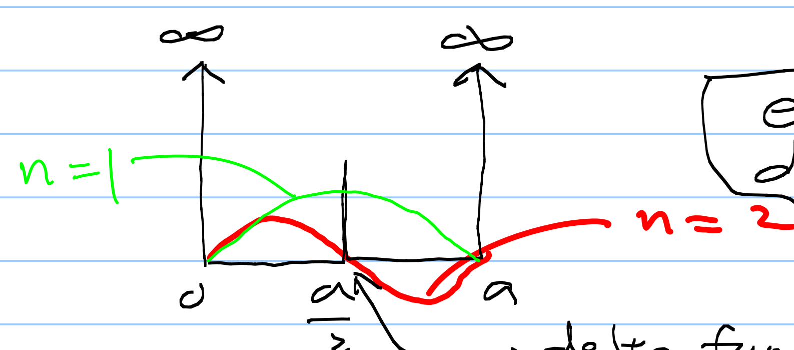
$$= \frac{2}{a}\cdot\sin^2\left(\frac{n\pi}{a}\cdot\frac{a}{2}\right)\alpha$$

$$= \alpha\frac{2}{a}\sin^2\left(\frac{n\pi}{2}\right)$$

$$= \begin{cases} 0 & n,\ \text{even } n \\ \dfrac{2}{a}\alpha & n,\ \text{odd} \end{cases}$$

So up to the first order,

$$E_n = \begin{cases} E_n^0 & \text{for } n \text{ even} \\ E_n^0 + \dfrac{2}{a}\alpha & \text{for } n \text{ odd.} \end{cases}$$



even eigen ftns do not feel the perturbation

delta function perturbation

Now let's consider the 1st order correction for the eigenfunction

From above for the 1st order

$$\lambda(H^\circ \psi_n^1 + H' \psi_n^\circ) = \lambda(E_n^\circ \psi_n^1 + E_n^1 \psi_n^\circ)$$

$$\Rightarrow (H^\circ - E_n^\circ)\psi_n^1 = (E_n^1 - H')\psi_n^\circ$$

Here we want to express ψ_n^1 by a linear combination of the unperturbed eigen functions such that

$$\psi_n^1 = \sum_{m \neq n} C_m^{(n)} \psi_m^\circ .$$

Then our job is to express $C_m^{(n)}$ by other known quantities.

$$(H^\circ - E_n^\circ) \sum_{m \neq n} C_m^{(n)} \psi_m^\circ = (E_n^1 - H')\psi_n^\circ$$

$\Rightarrow$ By applying $\langle \psi_\ell^\circ |$

$$\sum_{m \neq n} \langle \psi_\ell^\circ | (H^\circ - E_n^\circ) | \psi_m^\circ \rangle \cdot C_m^{(n)}$$

$$= E_n^1 \langle \psi_\ell^\circ | \psi_n^\circ \rangle - \langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle$$

$$\Rightarrow \sum_{m \neq n} (E_\ell^\circ - E_n^\circ)\, \delta_{\ell m}\, C_m^{(n)} = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle$$

since $\ell \neq n$

$$\Rightarrow \quad (E_l^0 - E_n^0)\, C_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle$$

$$\Rightarrow \quad C_l^{(n)} = \frac{\langle \psi_l^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_l^0}$$

$$\therefore \quad \psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}\, \psi_m^0$$

The total eigenfunction is thus

$$\psi_n = \psi_n^0 + \sum_{m \neq n} \frac{H'_{mn}}{E_n^0 - E_m^0}\, \psi_m^0$$

, with $H'_{mn} \equiv \langle \psi_m^0 | H' | \psi_n^0 \rangle$

up to the 1st order.

In practice, the perturbed wavefunction is not as useful as the perturbed energy obtained above.

* Now let's look into the 2nd order contribution.

$$\lambda^2 (H^0 \psi_n^2 + H' \psi_n^1) = \lambda^2 (E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0)$$

$$\Rightarrow \quad E_n^2 \psi_n^0 = (H^0 - E_n^0)\, \psi_n^2 + (H' - E_n^1)\, \psi_n^1$$

$$\Rightarrow \quad E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle = \langle \psi_n^0 | H^0 - E_n^0 | \psi_n^2 \rangle + \langle \psi_n^0 | H' - E_n^1 | \psi_n^1 \rangle$$

$$\Rightarrow E_n^2 = \langle \psi_n^0 | \cancel{E_n^0 - E_n^0}^{\,0} | \psi_n^2 \rangle + \langle \psi_n^0 | H' - E_n^1 | \psi_n^1 \rangle$$

$$= \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$$

Since $|\psi_n^1\rangle = \sum_{m \neq n} \frac{H'_{mn}}{E_n^0 - E_m^0} |\psi_m^0\rangle$,

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

→ Just a number

$$\Rightarrow = \sum_{m \neq n} \langle \psi_n^0 | H' \frac{H'_{mn}}{E_n^0 - E_m^0} | \psi_m^0 \rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_n^0 | H' | \psi_m^0 \rangle H'_{mn}}{E_n^0 - E_m^0}$$

$$= \sum_{m \neq n} \frac{H'_{nm} \cdot H'_{mn}}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^0 - E_m^0}$$

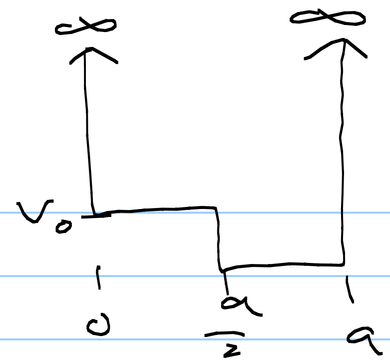
$$\therefore \boxed{E_n^2 = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^0 - E_m^0}}$$

with $H'_{nm} \equiv \langle \psi_n^0 | H' | \psi_m^0 \rangle$

Because the 2nd order eigenftn correction is not so useful as the energy correction, we will stop here.

In principle, we can continue like this for higher order corrections.

$\boxed{Ex.}$



Find the perturbed eigenenergies up to the 2nd order correction.

Above we have found the 1st order correction is

$$E_n^1 = H'_{nn} \left(\equiv \langle \psi_n^0 | H' | \psi_n^0 \rangle \right)$$
$$= \frac{V_0}{2}$$

$$E_n^2 = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^0 - E_m^0}$$

Since $\quad H'_{nm} = \langle \psi_n^0 | H' | \psi_m^0 \rangle$

$$= \frac{2}{a} \int_0^{\frac{a}{2}} \sin\left(\frac{n\pi}{a}x\right) V_0 \sin\left(\frac{m\pi}{a}x\right) dx$$

$$= \frac{2V_0}{a} \int_0^{\frac{a}{2}} \sin\left(\frac{n\pi}{a}x\right) \sin\left(\frac{m\pi}{a}x\right) dx$$

$$= \frac{2V_0}{\pi} \int_0^{\frac{\pi}{2}} \sin(ny) \sin(my)\, dy$$

$$\left[\frac{\pi}{a}x = y \Rightarrow dx = \frac{a}{\pi} dy \right]$$

$$= \frac{V_0}{\pi} \left[\int_0^{\frac{\pi}{2}} \left[\cos((n-m)y) - \cos((n+m)y) \right] dy \right]$$

$$= \frac{V_0}{\pi} \left[\frac{\sin((n-m)y)}{(n-m)} - \frac{\sin((n+m)y)}{n+m} \right]_0^{\frac{\pi}{2}}$$

$$= \frac{V_0}{\pi}\left[\frac{\sin\left(\frac{n-m}{2}\pi\right)}{n-m} - \frac{\sin\left(\frac{n+m}{2}\pi\right)}{n+m} \right.$$

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lengthy algebra, but basically we have found H'_{nm}.

Then $E_n^2 = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^0 - E_m^0}$ with this H'_{nm}, and the total eigenenergies should be, up to the 2nd order,

$$E_n = E_n^0 + E_n^1 + E_n^2$$
$$= \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} n^2 + \frac{V_0}{2} + E_n^2$$

, where E_n^2 is a rather length infinite series summation.