Perturbation theory

Only a few physical systems can be solved precisely (and even those - only in some simplified cases)

Assume: $\hat{H}_0$ describes an unperturbed exactly solvable system

$$\hat{H}_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

$\{|n^{(0)}\rangle\}$ – known eigenvectors } of the unperturbed system
$E_n^{(0)}$ – known eigenenergies } of the unperturbed system

Now this known system is <u>slightly</u> modified

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

where sometimes $\lambda \ll 1$ or $\hat{V}$ is weak, and λ is just a marker to keep track of the perturbation terms

For now consider stationary (i.e non-time varying) perturbation $V \neq V(t)$ and <u>non-degenerate</u> set of $\{|n^{(0)}\rangle\}$

(i.e $E_n^{(0)} = E_m^{(0)}$ only for $n = m$)

Since the perturbation is weak, it changes the energy spectrum and the eigenstates only slightly $\longrightarrow$ can use a power series for the modified states

$$\hat{H} |n\rangle = E_n |n\rangle \qquad (1)$$

We are looking in the solution in the form

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \ldots$$

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

Plan: substitute to (1) and collect terms of the same order in λ

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$(\hat{H}_0 + \lambda\hat{V})\left[|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots\right\rangle =$$

$$(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots)$$

λ^0 : $\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$ no surprises

λ : $\hat{H}_0|n^{(1)}\rangle + \hat{V}|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle$

...

$\lambda^{(k)}$: $\hat{H}_0|n^{(k)}\rangle + \hat{V}|n^{(k-1)}\rangle = E_n^{(0)}|n^{(k)}\rangle + E_n^{(1)}|n^{(k-1)}\rangle + \ldots E_n^{(k)}|n^{(0)}\rangle$

Starting from the bottom $k = 1$

$$\cancel{\langle n^{(0)}|\hat{H}_0|n^{(1)}\rangle} + \langle n^{(0)}|\hat{V}|n^{(0)}\rangle = \cancel{E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle} + E_n^{(1)}$$

since $\langle n^{(0)}|\hat{H}_0|n^{(1)}\rangle = \langle n^{(0)}|E_n^{10}|n^{(1)}\rangle$

Thus, the first order energy correction is

$$E_n^{(1)} = \langle n^{(0)}|\hat{V}|n^{(0)}\rangle$$

Energy correction = average value of the perturbation in that state

$$(\hat{H}_0 - E_n^{(0)})|n^{(1)}\rangle = (E_n^{(1)} - \hat{V})|n^{(0)}\rangle$$

$$|n^{(1)}\rangle = \sum_{m\neq n} c_m |m^{(0)}\rangle$$

$$\sum_{m\neq n} c_m^{(n)}(E_m^{(0)} - E_n^{(0)})|m^{(0)}\rangle = (E_n^{(1)} - \hat{V})|n^{(0)}\rangle$$

Taking inner product $\langle s^{(0)}|$

$$c_s^{(n)}(E_s^{(0)} - E_n^{(0)}) = -\underbrace{\langle s^{(0)}|\hat{V}|n^{(0)}\rangle}_{V_{sn}}$$

$$c_s^{(n)} = \frac{V_{ns}}{E_n^{(0)} - E_s^{(0)}}$$

$$|n^{(1)}\rangle = \sum_{m\neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}|m^{(0)}\rangle$$

$$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{m\neq n} \frac{V_{mn}}{E_n^{(0)} - E_n^{(0)}}|m^{(0)}\rangle + \mathcal{O}(\lambda^2)$$

$$\hat H|n\rangle = E_n|n\rangle$$

$$(\hat H_0+\lambda\hat V)(|n^{(0)}\rangle+\lambda|n^{(1)}\rangle+\lambda^2|n^{(2)}\rangle+\dots) =$$

$$=(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\dots)(|n^{(0)}\rangle+\lambda|n^{(1)}\rangle+\lambda^2|n^{(2)}\rangle+\dots)$$

$\lambda^0: \quad \hat H_0|n^{(0)}\rangle = E_n^{(0)}$ no surprises

$\lambda^1: \quad \hat H_0|n^{(1)}\rangle+\hat V|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle+E_n^{(1)}|n^{(0)}\rangle$

$\dots$

$\lambda^k: \quad \hat H_0|n^{(k)}\rangle+\hat V|n^{(k-1)}\rangle = E_n^{(0)}|n^{(k)}\rangle+E_n^{(1)}|n^{(k-1)}\rangle+\dots+E_n^{(k)}|n^{(0)}\rangle$

At that point we need to agree on the normalization of the wave function

Choose

$$\langle n^{(0)}|n\rangle = 1 \quad \Rightarrow \quad |n\rangle = |n^{(0)}\rangle+\lambda|n^{(1)}\rangle+\dots$$

$$\lambda\langle n^{(0)}|n^{(1)}\rangle+\lambda^2\langle n^{(0)}|n^{(2)}\rangle+\dots = 0 \quad \text{for } \forall\lambda$$

$$\Rightarrow \langle n^{(0)}|n^{(k)}\rangle = 0 \quad \text{for } \forall k\neq n$$

Let's check back to the general expression

$$\hat H_0|n^{(k)}\rangle+V|n^{(k-1)}\rangle = E_n^{(0)}|n_k\rangle+E_n^{(0)}|n^{(k-1)}\rangle+\dots+E_n^{(k)}|n^{(0)}\rangle$$

Let's take the inner product with $\langle n^{(0)}|$

$$\langle n^{(0)}|\hat H_0|n^{(k)}\rangle+\langle n^{(0)}|\hat V|n^{(k-1)}\rangle = E_n^{(k)}$$

$\Downarrow$

$E_n^{(0)}\cancel{\langle n^{(0)}|n^{(k)}\rangle}$ $\quad\quad \underline{E_n^{(k)} = \langle n^{(0)}|V|n^{(k-1)}\rangle}$

for $k=1$ $\quad E_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$

Let's now figure out the corrections to the wave function

$$(\hat H_0-\hat E_n^{(0)})|n^{(k)}\rangle = (-\hat V+\hat E_n^{(1)})|n^{(k-1)}\rangle+E_n^{(2)}|n^{(k-2)}\rangle+\dots E_n^{(k)}|n^{(0)}\rangle$$

$m\neq n \quad \underbrace{\langle m^{(0)}|\hat H_0-E_n^{(0)}|n^{(k)}\rangle} = \langle m^{(0)}|(-\hat V+E_n^{(1)}|n^{(k-1)}\rangle+\dots+E_n^{(k-1)}\langle m^{(0)}|n^{(1)}\rangle$

$$(E_m^{(0)}-E_n^{(0)})\langle m^{(0)}|n^k\rangle = \langle m^{(0)}|\dots$$

$$\sum_{m\neq n}(E_m^{(0)}-E_n^{(0)})|m^{(0)}\rangle\langle m^{(0)}|n^{(k)}\rangle = \sum_{m\neq n}|m^{(0)}\rangle\langle m^{(0)}|\dots$$

$$|n^{(k)}\rangle = \frac{1}{E_m^{(0)}-E_m^{(0)}}\sum_{m\neq n}|m^{(0)}\rangle\langle m^{(0)}|\{(-\hat V+E_n^{(1)}|n^{(k-1)}\rangle-\dots-E_n^{(k-1)}|n^{(1)}\rangle\}$$

– orthogonality

For $k=1$

$$|n^{(1)}\rangle = \sum_{m\neq n}|m^{(0)}\rangle\frac{\langle m^{(0)}|\hat V-E_n^{(1)}|n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}} = \sum_{m\neq n}|m^{(0)}\rangle\frac{\overbrace{\langle m^{(0)}|\hat V|n^{(0)}\rangle}^{V_{mn}}}{E_n^{(0)}-E_m^{(0)}}$$

$$V_{nm} = V_{mn}^{*}$$

$$E_n^{(2)} = \langle n^{(0)}|\hat{V}|n^{(1)}\rangle = \langle n^{(0)}|\hat{V}| \sum_{m\neq n} |m^{(0)}\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

$$\boxed{E_n^{(2)} = \sum_{m\neq n} \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}}$$

Fun fact! the ground level always shifts down!

Two - level system

$|2\rangle$

$|1\rangle$

$$\hat{H}_0 = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix}$$

1. In order to affect the energy states in the first order, the perturbation matrix must have diagonal terms

$$\hat{V}_1 = \begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix}$$

trivial case, $\hat{V}|n\rangle = V_n|n\rangle$ no change in eigenstates

$$E_n = E_n^{(0)} + \lambda V_n$$

2. Suppose that $\hat{V}$ has off-diagonal terms

$$\hat{V} = V_{12}\,|1^{(0)}\rangle\langle 2^{(0)}| + V_{21}\,|2^{(0)}\rangle\langle 1^{(0)}| \qquad V_{21} = V_{12}^{*}$$

$$\hat{V} = \begin{pmatrix} 0 & V_{12} \\ V_{21} & 0 \end{pmatrix}$$

Such perturbation "induces" transitions between different states of an unperturbed basis

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

can solve for new eigenstates exactly

$$E_{1,2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{(E_1^{(0)} - E_2^{(0)})^2}{4} + \lambda^2 |V_{12}|^2}$$

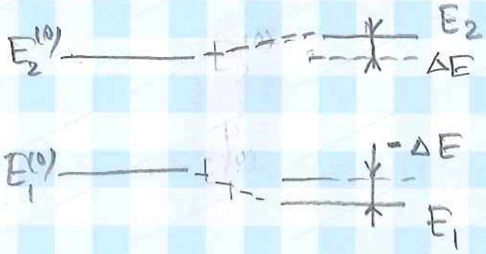
small compare to the energy splitting

$$\lambda |V_{12}|^2 \ll |E_1^{(0)} - E_2^{(0)}|$$

$$E_1 = E_1^{(0)} + \frac{\lambda^2 |V_{12}|^2}{E_1^{(0)} - E_2^{(0)}}$$

$$E_2 = E_2^{(0)} + \frac{\lambda^2 |V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$$

exactry as expected from second-order perturbation theory



$$\Delta E = \frac{\lambda^2 |V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$$

two levels "repel" each other!

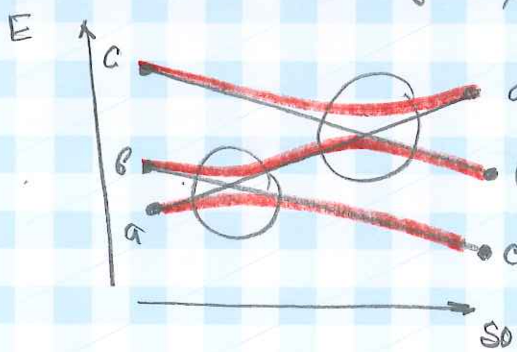
In fact, this is a very general behavior — levels repel when coupled.
Special term — avoided crossing!

If two levels $|n^{(0)}\rangle$ and $|m^{(0)}\rangle$ are closed, $E_n < E_m$)
$\mathcal{E} = E_m - E_n \ll$ all other energy splittings

If they are coupled

$$E_n^{(2)} = \sum_{s \neq n} \frac{|V_{ns}|^2}{E_n^{(0)} - E_s^{(0)}} \approx \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = -\frac{|V_{nm}|^2}{\mathcal{E}}$$

and analogously $E_m^{(2)} = \dfrac{|V_{mn}|^2}{\mathcal{E}}$

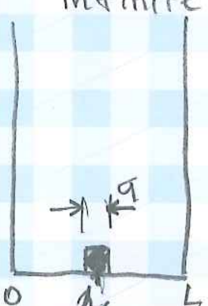


avoided crossings in the presence of coupling

some parameter of the system

Couple examples:

Infinite square well



$$\hat{H}_0 = \begin{cases} 0 & 0<x<L \\ \infty & \text{elsewhere} \end{cases}$$

$$\hat{V} = \begin{cases} V_0 & L/2 - a/2 < x < L/2 + a/2 \\ 0 & \text{elsewhere} \end{cases} \qquad a \ll L$$

$$|n\rangle = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L}$$

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

Physically: small bump can "slow down" a particle near the center
→ expect stronger effect for odd states (linear effect)

$$V_{nn} = V_0 \frac{2}{L} \int_{\frac{L-a}{2}}^{\frac{L+a}{2}} \sin^2 \frac{\pi n x}{L}\, dx \approx V_0 \frac{2a}{L} \sin^2 \frac{\pi n}{2} = \begin{cases} 0 & n=2,4 \\ \frac{2aV_0}{L} & n=1,3 \end{cases}$$

need "extra E_n" "kinetic" energy to compensate for the higher potential energy

Second order correction

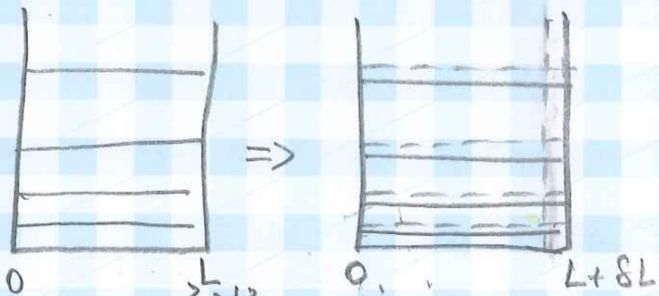
$$V_{nm} = V_0 \frac{2}{L} \int_{\frac{L-a}{2}}^{\frac{L+a}{2}} \sin\frac{\pi n x}{L} \sin\frac{\pi m x}{L}\, dx \approx \frac{2aV_0}{L} \sin\frac{\pi n}{2} \sin\frac{\pi m}{2} = \frac{2aV_0}{L}$$

for odd n, m

$$E_n^{(2)} = \sum_{\substack{m\neq n \\ \text{odd}}} \frac{4a^2V_0^2/\cancel{L^2}}{\frac{\pi^2\hbar^2}{2m\cancel{L^2}}(n^2-m^2)} = \frac{8ma^2V_0^2}{\pi^2\hbar^2} \sum_{\substack{n\neq m \\ \text{odd}}} \frac{1}{n^2-m^2}$$

Particle can reflect off the bump, giving rise to <u>interference</u>

More fun with the infinite potential
what if we stretch it a little?



$$E_n^{(0)} = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \qquad E_n = \frac{\pi^2 n^2\hbar^2}{2m(L+\delta L)^2} \approx \frac{\pi^2 n^2 \hbar^2}{2mL^2} - \frac{\pi^2 n^2\hbar^2}{mL^2}\frac{\delta L}{L}$$

Can we use the perturbation theory? Yes

$$x = x'\frac{L+\delta L}{L} \approx \left(1+\frac{\delta L}{L}\right)x'$$

$$\hat{H}_0 = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad \hat{H} = -\frac{\hbar^2}{2m}\left(1-\frac{2\delta L}{L}\right)\frac{d^2}{dx^2} =$$

$$= \frac{p^2}{2m} - \underbrace{\frac{2\delta L}{L}\frac{p^2}{2m}}_{\lambda\hat{V}}$$

$$E_n^{(1)} = \langle n|\lambda\hat{V}|n\rangle = \langle n| -\frac{2\delta L}{L}\frac{p^2}{2m}|n\rangle = -\frac{2\delta L}{L}\frac{\pi^2\hbar^2 n^2}{2mL^2}$$

A bit of a houskeeping...

Waveform renormalization

Remember we picked $\langle n | n^{(0)} \rangle = 1$?
Let's renormalize $|n\rangle$ to follow more conventional norm: ${}_N\langle n|n\rangle_N = 1$

$${}_N\langle n|n\rangle_N = Z_n^{1/2} |n\rangle \quad \Rightarrow \quad Z_n = \frac{1}{\langle n|n\rangle}$$

$$\frac{1}{Z_n} = \langle n|n\rangle = \left(\langle n^{(0)}| + \lambda^{+} \langle n^{(1)}| + \ldots \,|\, |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \ldots \right)$$

$$= \langle n^{(0)}|n^{(0)}\rangle + \lambda^2 \langle n^{(1)}|n^{(1)}\rangle + \ldots \lambda^4 \langle n^{(2)}|n^{(2)}\rangle + \ldots$$

$$= 1 + \lambda^2 \sum_{m, m' \neq n} \langle m| \frac{V_{nm}^*}{E_n^{(0)} - E_m^{(0)}} \cdot \frac{V_{nm'}}{E_n^{(0)} - E_{m'}^{(0)}} |m'\rangle + \ldots =$$

$$= 1 + \underbrace{\lambda^2 \sum_{m \neq n} |V_{nm}|^2 / (E_n^{(0)} - E_m^{(0)})^2}_{\text{always positive!}} + $$

$$Z_n \simeq 1 - \lambda^2 \sum_{m \neq n} \frac{|V_{nm}|^2}{(E_n^{(0)} - E_m^{(0)})^2} - O(\lambda^4)$$

$$Z_n^{1/2} \simeq 1 - \frac{\lambda^2}{2} \sum_{m \neq n} \frac{|V_{nm}|^2}{(E_n^{(0)} - E_m^{(0)})^2}$$

correction in the second order of λ thus it must be neglected when $|n^{(1)}\rangle$ are calculated

Convergence of the perturbation series

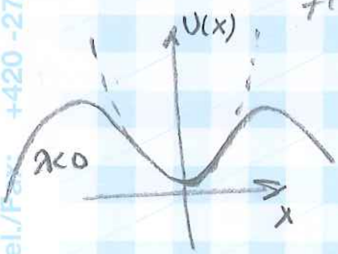
In general, perturbation series do not converge for most useful problems (anharmonic oscillator, QED, etc.)

but

For weak perturbations, a series usually converges near correct answer up to some order, then diverges

Simple mathematical example

$$f(\lambda) = \int_{-\infty}^{+\infty} dx\; e^{-\frac{1}{2}x^2 - \frac{\lambda}{4}x^4} \approx \int_{-\infty}^{+\infty} dx\, e^{-\frac{1}{2}x^2} \left[\sum_{k=0}^{\infty} (-1)^k \frac{\lambda^k x^{4k}}{4^k k!} \right]$$



$$= \sum_{k=0}^{\infty} \lambda^k f_k \quad \text{where} \quad f_k = \sqrt{2\pi}\, \frac{(-1)^k (4k)!}{16^k k! (2k)!}$$

$\lambda^k \rightarrow$ grows exponentially with k

$k! \sim \sqrt{2\pi}\; \underline{\underline{k^k}}\, e^{-k}$ faster than exponent

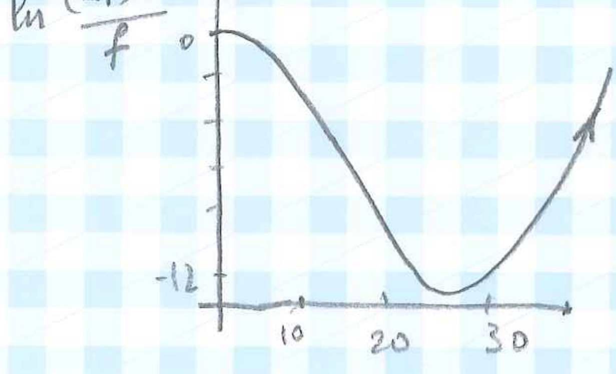
$\lambda^k f_k \sim \sqrt{2} \left(-\frac{4\lambda k}{e} \right)^k$ diverges badly for large k

but converges well for $k\lambda \ll 1$

For example, $\lambda = 0.01$

12 terms give accuracy of $\sim 10^{-10}$

25 terms give accuracy of $\sim 10^{-12}$



special technique to make the high oders converge are developed.

Potential energy as a small perturbation

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\hat{H}_0} + \underbrace{U(\bar{r})}_{weak}$$

$$\hat{H}_0 |\psi\rangle = E\psi\rangle$$

$$|\psi^{(0)}\rangle = \frac{1}{\sqrt{2\pi}} e^{\pm ikx} \qquad E = \frac{\hbar^2 k^2}{2m}$$

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle = |\psi^{(0)}\rangle + \underbrace{f(x)|\psi^{(0)}\rangle}_{\text{small perturbation}}$$

$$\frac{\hat{p}^2}{2m}(f|\psi^{(0)}\rangle) + U(\bar{r})|\psi^{(0)}\rangle = E^{(0)} f|\psi^{(0)}\rangle$$

$$+\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(f(x)e^{ikx}) + \frac{\hbar^2 k^2}{2m} f \cdot e^{ikx} = U(x)e^{ikx}$$

Let's assume that k is sufficiently large, thus e^{ikx} oscillates much „faster" than charges in potential $U(\bar{r})$)

Then $\frac{1}{f}\frac{df}{dx} \ll k$

$$\frac{d^2}{dx^2}(fe^{ikx}) \simeq -fk^2 e^{ikx} + ikf\frac{df}{dx}e^{ikx}$$

$$|\psi^{(1)}\rangle = -\frac{im}{\hbar^2 k} e^{ikx}\left(\int U dx\right)$$

For smallness

$$\frac{m}{\hbar^2 k} Ua \ll 1 \qquad U \ll \frac{\hbar^2 k}{ma}$$

Such perturbation method is equivalent to the "standard" one

$$|\psi\rangle = e^{ikx} + \sum_{k' \neq k} c_{kk'} e^{ik'x} \qquad (*)$$

indeed we can always decompose

$$f(x) = \int f_{\varkappa} e^{i\varkappa x} d\varkappa$$

and

$$|\psi^{(1)}\rangle = \int f_{\varkappa} e^{i(k+\varkappa)x} d\varkappa$$

same as (*) for $k' = k + \varkappa$