Time-independent nondegenerate perturbation theory

Goal: given H, find its eigenvalues & eigenstates

$$H|E_n\rangle = E_n|E_n\rangle$$

Suppose H is "close" to another Hamiltonian H^0 whose eigenvalues & eigenstates are known exactly

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

$$H = H^0 + \lambda H^1$$

H^0 = unperturbed Hamiltonian

H^1 = perturbation

λ = small parameter

Assumptions:
- $|E_n^0\rangle$ are nondegenerate eigenstates (i.e. uniquely labelled by E_n^0)
- H^0 and H^1 are independent of t
- All eigenstates are normalized

$$\langle E_n^0|E_m^0\rangle = \delta_{nm}$$

$$\langle E_n|E_m\rangle = \delta_{nm}$$

We will find E_n and $|E_n\rangle$ in a perturbation series in λ

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

$$|E_n\rangle = |E_n^0\rangle + \underbrace{\lambda|E_n^1\rangle}_{\text{1st order correction}} + \underbrace{\lambda^2|E_n^2\rangle}_{\text{2nd order correction}} + \ldots$$

$$H|E_n\rangle = E_n|E_n\rangle$$

$$(H^0 + \lambda H^1)(|E_n^0\rangle + \lambda|E_n^1\rangle + \lambda^2|E_n^2\rangle + \ldots)$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots)(|E_n^0\rangle + \lambda|E_n^1\rangle + \lambda^2|E_n^2\rangle + \ldots)$$

Eqn is true for arbitrary λ, so match coefficients of λ^l on each side

$O(\lambda^0) \Rightarrow \quad H^0|E_n^0\rangle = E_n^0|E_n^0\rangle$ ✓

$O(\lambda^1) \Rightarrow \quad H^1|E_n^0\rangle + H^0|E_n^1\rangle = E_n^1|E_n^0\rangle + E_n^0|E_n^1\rangle$

$O(\lambda^2) \Rightarrow \quad H^1|E_n^1\rangle + H^0|E_n^2\rangle = E_n^2|E_n^0\rangle + E_n^1|E_n^1\rangle + E_n^0|E_n^2\rangle$

$O(\lambda^1)$: take inner product w/ $\langle E_l^0|$

$$\Rightarrow \langle E_l^0|H^1|E_n^0\rangle + \underbrace{\langle E_l^0|H^0}_{E_l^0\langle E_l^0|}|E_n^1\rangle = E_n^1\underbrace{\langle E_l^0|E_n^0\rangle}_{\delta_{ln}} + E_n^0\langle E_l^0|E_n^1\rangle$$

Let $l = n$: 2 terms cancel

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

$$E_n = E_n^0 + \lambda E_n^1 + \ldots = E_n^0 + \lambda\langle E_n^0|H^1|E_n^0\rangle + O(\lambda^2)$$

Let $l \neq n$:

$$\langle E_l^0|H^1|E_n^0\rangle = (E_n^0 - E_l^0)\langle E_l^0|E_n^1\rangle$$

$$\langle E_l^0|E_n^1\rangle = \frac{\langle E_l^0|H^1|E_n^0\rangle}{E_n^0 - E_l^0} \qquad l \neq n$$

$$|E_n\rangle = |E_n^0\rangle + \lambda |E_n^1\rangle + \ldots = |E_n^0\rangle + \lambda \sum_l |E_l^0\rangle\langle E_l^0|E_n^1\rangle$$

$$= |E_n^0\rangle + \lambda |E_n^0\rangle\langle E_n^0|E_n^1\rangle + \lambda \sum_{l\neq n} \frac{|E_l^0\rangle\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0}$$

$$= \Big(1 + \lambda \underbrace{\langle E_n^0|E_n^1\rangle}\Big) |E_n^0\rangle + \lambda \sum_{l\neq n} \frac{|E_l^0\rangle\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0}$$

this is imaginary; call it $i\theta$
(it will not affect the result)

Proof: $|E_n\rangle$ and $|E_n^0\rangle$ are both normalized

$$\underbrace{\langle E_n|E_n\rangle}_{1} = \underbrace{\langle E_n^0|E_n^0\rangle}_{1} + \lambda\langle E_n^0|E_n^1\rangle + \lambda\langle E_n^1|E_n^0\rangle + O(\lambda^2)$$

so $\langle E_n^0|E_n^1\rangle + \langle E_n^0|E_n^1\rangle^* = 0$

$\Rightarrow \langle E_n|E_n^1\rangle$ is imag.

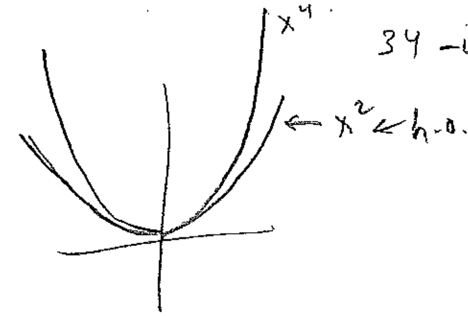
$$|E_n\rangle = \underbrace{(1 + i\lambda\theta)}_{e^{i\lambda\theta} + O(\lambda^2)} |E_n^0\rangle + \underbrace{\lambda}_{\lambda e^{i\lambda\theta} + O(\lambda^2)} \sum_{l\neq n} \cdots$$

$$= e^{i\lambda\theta}\left[|E_n^0\rangle + \lambda \sum_{l\neq n} |E_l^0\rangle \frac{\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0} + O(\lambda^2)\right]$$

just an overall phase change; can ignore it $\Rightarrow |E_n\rangle = e^{i\lambda\theta}|E_n\rangle'$

$$\boxed{|E_n\rangle = |E_n^0\rangle + \lambda \sum_{l\neq n} \frac{|E_l^0\rangle\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0} + O(\lambda^2)}$$

As long as nondegenerate, denominators are nonzero, otherwise degenerate p.t.



Example: anharmonic oscillator

$$H^0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 X^2$$

$$\lambda H^1 = \lambda X^4 = \lambda \left(\frac{\hbar}{2m\omega}\right)^2 (a + a^\dagger)^4$$

$$\Rightarrow E_n^1 = \langle E_n^0 | H^1 | E_n^0 \rangle = \left(\frac{\hbar}{2m\omega}\right)^2 \langle n | \underbrace{(a+a^\dagger)^4}_{\downarrow} | n \rangle$$

$$\underbrace{\langle n | \underbrace{aaa^\dagger a^\dagger}_{(n+1)(n+2)} + \underbrace{aa^\dagger aa^\dagger}_{(n+1)^2} + \underbrace{a^\dagger aaa^\dagger}_{n(n+1)} + \underbrace{aa^\dagger a^\dagger a}_{n(n+1)} + \underbrace{a^\dagger aa^\dagger a}_{n^2} + \underbrace{a^\dagger a^\dagger aa}_{(n-1)n}}_{6n^2 + 6n + 3}$$

Let $\beta = \frac{3\hbar\lambda}{2m^2\omega^3}$

$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) + \lambda \frac{3}{2}\left(\frac{\hbar}{m\omega}\right)^2 \left(n^2 + n + \tfrac{1}{2}\right)$$

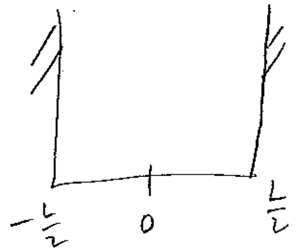
$$= \hbar\omega\Big[\underbrace{\tfrac{1}{2}(1+\beta)}_{\text{gnd state } (n=0) \text{ shifts up}} + \underbrace{n(1+\beta)}_{\text{spacing increases}} + \underbrace{\beta n^2}_{\text{spacing gets bigger w/ n}}\Big]$$

$\downarrow$

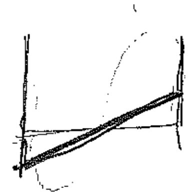
pert. th breaks down for large n because x gets large

example: charged particle in a box and external const. electric field

center box at $x=0$. $H^0 = \frac{p^2}{2m} + V_{box}(x)$



$\lambda H' = V_{ext} = \lambda x$

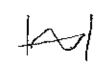


$E_n^1 = \langle E_n^0 | H' | E_n^0 \rangle$ evaluate in position space

$$= \int dx \underbrace{\langle E_n^0 | x \rangle}_{u_n^*(x)} \underbrace{\langle x | H' | x \rangle}_{\lambda x} \underbrace{\langle x | E_n^0 \rangle}_{u_n(x)}$$

$$= \int_{-\frac{L}{2}}^{\frac{L}{2}} dx \; |u_n(x)|^2 \; \lambda x$$

Since for a symmetric (wrt $x \to -x$) potential eigenfunctions are either even $u_n(x) = u_n(-x)$ or odd $u_n(x) = -u_n(-x)$, $|u_n(x)|^2$ is even.



Since qEx is odd, $E_n^1 = 0$. (Need go to 2nd order)

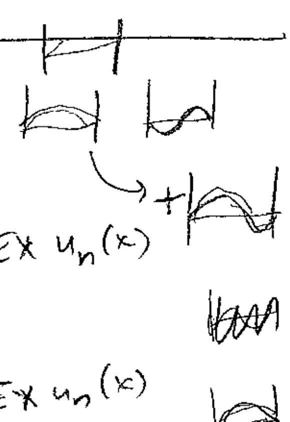
$$|E_n\rangle = |E_n^0\rangle + \lambda \sum_l \frac{|E_l^0\rangle \langle E_l^0 | H' | E_n^0 \rangle}{E_n^0 - E_l^0}$$

Even though correction to energy vanishing the wavefunction is altered

position space

$$\langle x | E_n \rangle = \langle x | E_n^0 \rangle + \lambda \sum_l \frac{\langle x | E_l^0 \rangle}{E_n^0 - E_l^0} \int_{-\frac{L}{2}}^{\frac{L}{2}} dy \; u_l^*(y) \, qEx \, u_n(x)$$

$$u_n(x) = u_n^0(x) + \lambda \sum_l \frac{u_l^0(x)}{E_n^0 - E_l^0} \int_{-\frac{L}{2}}^{\frac{L}{2}} dy \; u_l^*(y) \, qEx \, u_n(x)$$



↑ only contribute if $u_l(x)$ & $u_n(x)$ have opposite parity (even vs odd)

2nd order pert. th (use if 1st order vanishes)

$O(\lambda^2)$: take inner product w/ $\langle E_n^0|$

$$\langle E_n^0|H'|E_n^1\rangle + \underbrace{\langle E_n^0|H^0}_{E_n^0\langle E_n^0|}|E_n^2\rangle = E_n^2 + E_n^1\langle E_n^0|E_n^1\rangle + E_n^0\langle E_n^0|E_n^2\rangle$$

cancels

$$E_n^2 = \langle E_n^0|H'|E_n^1\rangle - E_n^1\langle E_n^0|E_n^1\rangle$$

Plug in $|E_n^1\rangle = \sum_{l\neq n} \dfrac{|E_l^0\rangle\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0}$

$$E_n^2 = \sum_{l\neq n} \frac{\langle E_n^0|H'|E_l^0\rangle\langle E_l^0|H'|E_n^0\rangle}{E_n^0 - E_l^0} + 0 \quad (\text{because } \langle E_n^0|E_l^0\rangle = 0 \text{ if } n\neq l)$$

$$= \sum_{l\neq n} \frac{|\langle E_n^0|H'|E_l^0\rangle|^2}{E_n^0 - E_l^0}$$

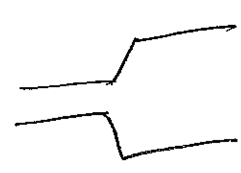
$$\Rightarrow \boxed{E_n = E_n^0 + \lambda\langle E_n^0|H'|E_n^0\rangle + \lambda^2 \sum_{l\neq n}\frac{|\langle E_n^0|H'|E_l^0\rangle|^2}{E_n^0 - E_l^0} + O(\lambda^3)}$$

E_l^0 {☰} these states push down because $E_n^0 - E_l^0 < 0$

E_n^0 ——

E_l^0 {☰} these states push up because $E_n^0 - E_l^0 > 0$

- Near states have a bigger effect because denominator is small.
- Consider two nearby sts:



"eigenvalue repulsion"

- gnd st always goes down in 2nd order pert. th