Time-Independent Perturbation Theory

$$H = H_0 + V$$

small

independent of time

Time-Dependent Perturbation Theory

– next quarter

$$H = H_0 + V(t)$$

depends on time

independent of time

Systems Without Analytic Solutions

Schrodinger equation has only a few analytic solutions

- free particle
- particle in a box
- harmonic oscillator
- hydrogen atom
- 2-state system

Many important modifications to a system with an analytic solution

e.g. Harmonic oscillator $\longrightarrow$ Anharmonic oscillator

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2}_{H_0} + \underbrace{a x^4}_{V}$$

e.g. Hydrogen atom

$$H = \underbrace{\frac{\vec{p}^{\,2}}{2m} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}}_{H_0} + V_{\substack{\text{fine}\\\text{structure}}} + V_{\text{hyperfine}} + V_{QED}$$

small   smaller   even smaller

$$V_{\substack{\text{fine}\\\text{structure}}} = \underbrace{-\frac{\vec{p}^{\,4}}{8m^3c^2}}_{\substack{\text{relativistic}\\\text{"mass shift"}}} + \underbrace{\frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\frac{\vec{L}\cdot\vec{S}}{r^3}}_{\text{spin-orbit}}$$

$$V_B = \frac{e}{2m}(\vec{L} + 2\vec{S})\cdot\vec{B} \qquad \text{Zeeman}$$

$$V_E = e\vec{r}\cdot\vec{E} \qquad \text{Stark}$$

Unknown solution from known solution

$$\underline{\text{Known:}} \quad H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

$$\underline{\text{Solve:}} \quad (\underbrace{H_0 + V}_{\text{new } H = H_0 + V}) |n\rangle = E_n |n\rangle$$

E_n, $|n\rangle$ ← unknown

Exact matrix eigenvalue equation → solve numerically typically

$$\langle m^{(0)} | H_0 + V | n\rangle = \langle m^{(0)} | E_n | n\rangle$$

$$\sum_{m'} \Big[\underbrace{\langle m^{(0)} | H_0 | m'^{(0)}\rangle}_{E_m^{(0)} \delta_{m'm}} + \underbrace{\langle m^{(0)} | V | m'^{(0)}\rangle}_{V_{mm'}}\Big] \langle m'^{(0)} | n\rangle = E_n \langle m^{(0)} | n\rangle$$

exact

$$\sum_{m'} \underbrace{\left[E_m^{(0)} \delta_{m'm} + V_{mm'}\right]}_{H_{mm'} = E_m^{(0)} \delta_{mm'} + V_{mm'}} \langle m'^{(0)} | n\rangle = E_n \langle m^{(0)} | n\rangle$$

exact

$$\begin{pmatrix} E_m^{(0)} \delta_{mm'} + V_{mm'} \end{pmatrix} \begin{pmatrix} \langle m'^{(0)} | n\rangle \end{pmatrix} = E_n \begin{pmatrix} \langle m^{(0)} | n\rangle \end{pmatrix}$$

"Small" perturbation to $E_k^{(0)}$ and $|k^{(0)}\rangle$

<u>Exact:</u> $$\underbrace{\sum_n \left[E_m^{(0)}\delta_{mn}\right.}_{E_m^{(0)}\langle m^{(0)}|k\rangle} \left. + V_{mn}\right]\langle n^{(0)}|k\rangle = E_k\langle m^{(0)}|k\rangle$$

<u>Also exact:</u> $$\boxed{0 = \sum_n V_{mn}\langle n^{(0)}|k\rangle + (E_m^{(0)} - E_k)\langle m^{(0)}|k\rangle}$$

<u>What does "small" mean?</u>

① <u>Case I:</u> <u>Non-degenerate case</u> ← not a great label

i.e. level $|k\rangle$ is not degenerate with any other

<u>Better description:</u> Energy shift of level k is small compared to energy spacing of level k and any other

$$|V_{mn}| << |E_m^{(0)} - \underbrace{E_k| \approx |E_m^{(0)} - E_k^{(0)}}_{\text{small difference}}|$$

for all m,n

$\Longrightarrow$ sets a size scale $\lambda \sim \dfrac{|V_{mn}|}{|E_m^{(0)} - E_k^{(0)}|}$

$$\boxed{0 = \underbrace{\sum_n \lambda V_{mn}\langle n^{(0)}|k\rangle}_{\text{smaller}} + \underbrace{(E_m^{(0)} - E_k)\langle m^{(0)}|k\rangle}_{\text{bigger}}}$$

to keep track of rel. size

expand: $|k\rangle = |k^{(0)}\rangle + \lambda|k^{(1)}\rangle + \ldots$

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \ldots$$

③ Case II: Degenerate case ← not a good label

i.e. one or more levels are nearly degenerate with $E_k^{(0)}$

$$E_{k'}^{(0)} \approx E_k^{(0)}$$

Better description: Energy shifts of level k are not greatly smaller than the energy spacing of level k and one or more others

$$\lambda V_{mn} \sim \lambda (E_{k'}^{(0)} - E_k)$$

① No states nearly degenerate with $|k^{(0)}\rangle$ (case I)

$$0 = \sum_n \lambda V_{mn} \langle n^{(0)}|k\rangle + (E_m^{(0)} - E_k)\langle m^{(0)}|k\rangle$$

$$= \sum_n \lambda V_{mn} \left[\langle n^{(0)}|k^{(0)}\rangle + \lambda \langle n^{(0)}|k^{(1)}\rangle + \dots\right]$$

$$+ \left[E_m^{(0)} - E_k^{(0)} - \lambda E_k^{(1)} - \lambda^2 E_k^{(2)} - \dots\right]\left[\underbrace{\langle m^{(0)}|k^{(0)}\rangle}_{\delta_{mk}} + \lambda \langle m^{(0)}|k^{(1)}\rangle + \dots\right]$$

$$= \lambda^0 \left\{\cancel{(E_m^{(0)} - E_k^{(0)})\delta_{mk}}\right\}$$

$$+ \lambda^1 \left\{V_{mk} + (E_m^{(0)} - E_k^{(0)})\langle m^{(0)}|k^{(1)}\rangle - E_k^{(1)}\delta_{mk}\right\}$$

$$+ \lambda^2 \left\{\sum_n V_{mn}\langle n^{(0)}|k^{(1)}\rangle + (E_m^{(0)} - E_k^{(0)})\langle m^{(0)}|k^{(2)}\rangle - E_k^{(1)}\langle m^{(0)}|k^{(1)}\rangle - E_k^{(2)}\delta_{mk}\right\}$$

$$+ \dots$$

$\boxed{\lambda}$ $$0 = V_{mk} + (E_m^{(0)} - E_k^{(0)})\langle m^{(0)}|k^{(1)}\rangle - E_k^{(1)}\delta_{mk}$$ ✓

<u>m=k:</u> $$0 = V_{kk} - E_k^{(1)} \longrightarrow \boxed{E_k^{(1)} = V_{kk}}$$

<u>m≠k:</u> $$0 = V_{mk} + (E_m^{(0)} - E_k^{(0)})\langle m^{(0)}|k^{(1)}\rangle$$

$$\boxed{\langle m^{(0)}|k^{(1)}\rangle = \frac{-V_{mk}}{E_m^{(0)} - E_k^{(0)}}}$$ ← $m \neq k$

$$|k\rangle = |k^{(0)}\rangle + \lambda |k^{(0)}\rangle \underbrace{\langle k^{(0)}|k^{(1)}\rangle}_{\text{missing}} + \lambda \sum_{m\neq k} |m^{(0)}\rangle\langle m^{(0)}|k^{(1)}\rangle$$

normalization ?

Normalize to get $\langle k^{(0)}|k^{(1)}\rangle$

$$1 = \langle k|k\rangle = \left[\langle k^{(0)}| + \lambda\langle k^{(1)}|\right]\left[|k^{(0)}\rangle + \lambda|k^{(1)}\rangle\right]$$

$$= \underbrace{\langle k^{(0)}|k^{(0)}\rangle}_{1} + \lambda\underbrace{\left\{\langle k^{(0)}|k^{(1)}\rangle + \langle k^{(1)}|k^{(0)}\rangle\right\}}_{\substack{=0 \text{ to normalize} \\ \text{through } O(\lambda)}} + \cdots$$

$$0 = \langle k^{(0)}|k^{(1)}\rangle + \langle k^{(0)}|k^{(1)}\rangle^*$$

$$= 2\,\mathrm{Re}\underbrace{\langle k^{(0)}|k^{(1)}\rangle}$$

$$\therefore \langle k^{(0)}|k^{(1)}\rangle = i\alpha \quad \text{pure imag.}$$

small $|\alpha| < 1$ $\leftarrow$ since $O(\lambda)$

Back to $|k\rangle$ $= \underbrace{|k^{(0)}\rangle + \lambda|k^{(0)}\rangle\langle k^{(0)}|k^{(1)}\rangle}_{|k^{(0)}\rangle(1+i\alpha)} + \lambda\sum_{m\neq k}|m^{(0)}\rangle\langle m^{(0)}|k^{(1)}\rangle$

$$|k^{(0)}\rangle\underbrace{(1+i\alpha)}$$

$e^{i\alpha} \approx 1 + i\alpha$ for small α

$$|k\rangle = e^{i\alpha}|k^{(0)}\rangle + \lambda\sum_{m\neq k}\frac{-V_{mk}}{E_m^{(0)} - E_k^{(0)}}$$

$$\underbrace{e^{-i\alpha}|k\rangle}_{\substack{\text{redefine} \\ |k\rangle}} = |k^{(0)}\rangle + \lambda\underbrace{e^{-i\alpha}}_{1 - i\alpha}\sum_{m\neq k}\frac{-V_{mk}}{E_m^{(0)} - E_k^{(0)}}$$

2nd order

$$\boxed{|k\rangle = |k^{(0)}\rangle + \sum_{m\neq k}\frac{-V_{mk}}{E_m^{(0)} - E_k^{(0)}}}$$

$$\boxed{\lambda^2} \quad 0 = \sum_n V_{mn}\langle n^{(0)}|k^{(1)}\rangle + (E_m^{(0)} - E_k^{(0)})\langle m^{(0)}|k^{(2)}\rangle - E_k^{(1)}\langle m^{(0)}|k^{(1)}\rangle - E_k^{(2)}\delta_{mk}$$

<u>m=k:</u>

$$0 = \sum_n V_{kn}\langle n^{(0)}|k^{(1)}\rangle - E_k^{(1)}\langle k^{(0)}|k^{(1)}\rangle - E_k^{(2)}$$

$$E_k^{(2)} = \sum_{n\neq k} V_{kn}\langle n^{(0)}|k^{(1)}\rangle + \cancel{V_{kk}\langle k^{(0)}|k^{(1)}\rangle} - \cancel{E_k^{(1)}\langle k^{(0)}|k^{(1)}\rangle}$$

equal

$$= \sum_{n\neq k} V_{kn}\frac{-V_{nk}}{E_n^{(0)} - E_k^{(0)}}$$

$$\boxed{E_k^{(2)} = \sum_{n\neq k}\frac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}}$$

✓