# 2 Time-Independent Non-Degenerate Perturbation Theory

Problem: $\hat{H} = \underbrace{\hat{H}_0}_{\text{unperturbed Hamiltonian}} + \underbrace{\hat{V}}_{\text{perturbation}}$

$\Rightarrow$ determine eigenstates and eigenvalues of $\hat{H}$

## 2.1 Schrödinger Equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

Assumption: $\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$

orthonormal: $\langle\psi_n^{(0)}|\psi_m^{(0)}\rangle = \delta_{nm}$

basis: completeness: $\sum_n |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| = 1$

family of Hamilton operators: $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$

$\lambda = 0$: $\hat{H}(\lambda=0) = \hat{H}_0$, $\lambda = 1$: $\hat{H}(\lambda=1) = \hat{H}$

$\lambda$: "artificial smallness" $\Rightarrow$ $\hat{H}(\lambda)\,|\psi_n(\lambda)\rangle = E_n(\lambda)\,|\psi_n(\lambda)\rangle$ (1)

[example: $f(\lambda) = e^{-\frac{1}{\lambda}} = 0 + 0\cdot\lambda + 0\cdot\lambda^2 + \ldots$

$T_c^{BCS} \sim e^{-\frac{1}{N(E_F)g}}$ no Taylor series $\Rightarrow$ no perturbative

$\uparrow$ electron-phonon-coupling ]

Assumption: Taylor expansions

$$E_n(\lambda) = \sum_{r=0}^{\infty} E_n^{(r)}\lambda^r = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \ldots \quad (2)$$

$$|\psi_n(\lambda)\rangle = \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^\nu = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle \lambda + |\psi_n^{(2)}\rangle \lambda^2 + \dots \qquad (3)$$

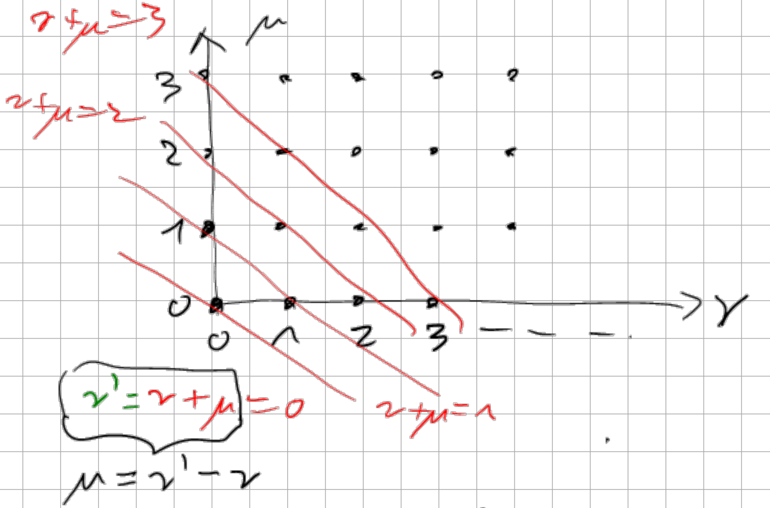
(2) and (3) into (1):

$$\hat H_0 \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^\nu + \hat V \underbrace{\sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^{\nu+1}}_{= \sum_{\nu'=1}^{\infty} |\psi_n^{(\nu-1)}\rangle \lambda^{\nu}} = \underbrace{\sum_{\nu=0}^{\infty} E_n^{(\nu)} \lambda^\nu \sum_{\mu=0}^{\infty} |\psi_n^{(\mu)}\rangle \lambda^\mu}_{\sum_{\nu=0}^{\infty} \sum_{\mu=0}^{\infty} E_n^{(\nu)} |\psi_n^{(\mu)}\rangle \lambda^{\nu+\mu}} \qquad (4)$$

$\nu' = \nu + 1$

Cauchy product

$$= \sum_{\nu'=0}^{\infty} \left( \sum_{\mu=0}^{\nu'} E_n^{(\nu'-\mu)} |\psi_n^{(\mu)}\rangle \right) \lambda^{\nu'}$$




(4) for $\nu = 0$: $\hat H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$

(4) for $\nu = 1, 2, 3, \dots$

$$\hat H_0 |\psi_n^{(\nu)}\rangle + \hat V |\psi_n^{(\nu-1)}\rangle = \sum_{\mu=0}^{\nu} E_n^{(\nu-\mu)} |\psi_n^{(\mu)}\rangle$$

$\nu = 1$: $\hat H_0 |\psi_n^{(1)}\rangle + \hat V |\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle$ (A)

$\nu = 2$: $\hat H_0 |\psi_n^{(2)}\rangle + \hat V |\psi_n^{(1)}\rangle = E_n^{(2)} |\psi_n^{(0)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(0)} |\psi_n^{(2)}\rangle$

## 2.2 Normalisation:

The above equations can not uniquely solved, as we will see. Some other condition is needed:

$$\langle \psi_n(\lambda) | \psi_m(\lambda) \rangle = \delta_{nm} \qquad (5)$$

(3) in (5): $$\sum_{\nu=0}^{\infty} \sum_{\mu=0}^{\infty} \langle \psi_n^{(\nu)} | \psi_m^{(\mu)} \rangle \lambda^{\nu+\mu} = \delta_{nm} \qquad (6)$$

Cauchy product $$= \sum_{\nu'=0}^{\infty} \left( \sum_{\mu=0}^{\nu'} \langle \psi_n^{(\nu'-\mu)} | \psi_m^{(\mu)} \rangle \right) \lambda^{\nu'}$$

$\nu' = \nu + \mu$

$\nu = \nu' - \mu$

$\nu = 0$ in (6): $\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}$ ✓

$\nu = 1, 2, 3, \ldots$ in (6): $\sum_{\mu=0}^{\nu'} \langle \psi_n^{(\nu'-\mu)} | \psi_m^{(\mu)} \rangle = 0$ for all $n, m$

$\nu = 1$: $\langle \psi_n^{(0)} | \psi_m^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_m^{(0)} \rangle = 0 \qquad$ (C)

$\nu = 2$: $\langle \psi_n^{(0)} | \psi_m^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_m^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_m^{(0)} \rangle = 0$

solution ansatz: $$|\psi_n^{(1)}\rangle = \sum_l c_{nl}^{(1)} |\psi_l^{(0)}\rangle \qquad (B)$$

$$|\psi_n^{(2)}\rangle = \sum_l c_{nl}^{(2)} |\psi_l^{(0)}\rangle$$

## 2.3 First Order:

(B) in (A): $$\sum_l c_{nl}^{(1)} \hat{H}_0 |\psi_l^{(0)}\rangle + \hat{V} |\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + \sum_l c_{nl}^{(1)} E_n^{(0)} |\psi_l^{(0)}\rangle \quad \Big| \, \langle \psi_m^{(0)} |$$

$$\sum_l c_{nl}^{(1)} \underbrace{\langle \psi_m^{(0)} | \underbrace{\hat{H}_0 |\psi_l^{(0)}\rangle}_{= E_l^{(0)} |\psi_l^{(0)}\rangle}}_{= E_l^{(0)} \delta_{ml}} + \underbrace{\langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}_{= V_{mn}} = E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle}_{= \delta_{mn}} + \sum_l c_{nl}^{(1)} E_n^{(0)} \underbrace{\langle \psi_m^{(0)} | \psi_l^{(0)} \rangle}_{= \delta_{ml}}$$

$$\underbrace{\qquad}_{c_{nm}^{(1)} E_m^{(0)}} \qquad\qquad \underbrace{\qquad}_{c_{nm}^{(1)} E_n^{(0)}}$$

$$V_{mn} = E_n^{(1)} \delta_{mn} + c_{nm}^{(1)} \left[ E_n^{(0)} - E_m^{(0)} \right]$$

$m = n$: $\quad E_n^{(1)} = V_{nn} = \langle \psi_n^{(0)} | \hat{V} | \psi_n^{(0)} \rangle$

$m \neq n$: $\quad c_{nm}^{(1)} = \dfrac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \qquad (D)$

$$| \psi_n^{(1)} \rangle = \sum_l c_{nl}^{(1)} | \psi_l^{(0)} \rangle = c_{nn}^{(1)} | \psi_n^{(0)} \rangle + \sum_{l \neq n} \frac{V_{ln}}{E_n^{(0)} - E_l^{(0)}} | \psi_l^{(0)} \rangle \qquad (E)$$

intermediate result from Schrödinger equation

still undetermined

(C) in (B): $\quad \sum_l \left\{ \langle \psi_n^{(0)} | \underline{c_{nl}^{(1)}} | \psi_l^{(0)} \rangle + \langle \underline{c_{nl}^{(1)}} \psi_l^{(0)} | \psi_n^{(0)} \rangle \right\} = 0$

scalar product $\hat{=}$ sequilinear

$c \in \mathbb{C}$: $\quad \langle \psi_1 | c \psi_2 \rangle = c \langle \psi_1, \psi_2 \rangle, \quad \langle c \psi_1 | \psi_2 \rangle = c^* \langle \psi_1 | \psi_2 \rangle$

$\Rightarrow \quad \sum_l \left( c_{nl}^{(1)} + c_{nl}^{(1)*} \right) \delta_{nl} = 0 \quad \Rightarrow \boxed{c_{nn}^{(1)} + c_{nn}^{(1)*} = 0}$

$c_{nn}^{(1)}$ purely imaginary: $\boxed{c_{nn}^{(1)} = i\, \gamma_n^{(1)};} \quad \gamma_n^{(1)} \in \mathbb{R}$

hermiticity

$$\boxed{V_{mn}} = \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle = \langle \psi_m^{(0)} | \hat{V} \psi_n^{(0)} \rangle = \langle \underbrace{\hat{V}^+}_{= \hat{V}} \psi_m^{(0)} | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle^* = \boxed{V_{nm}^*}$$

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \lambda \underbrace{i\gamma_n^{(1)}}_{=c_{nn}^{(1)}} |\psi_n^{(0)}\rangle + \lambda \sum_{l\neq n} \frac{V_{ln}}{E_n^{(0)}-E_l^{(0)}} |\psi_l^{(0)}\rangle + \cdots$$

$$\overbrace{\left(1+i\gamma_{nn}^{(1)}\lambda\right)|\psi_n^{(0)}\rangle} = e^{i\gamma_n^{(1)}\lambda}|\psi_n^{(0)}\rangle$$

$$= \underbrace{e^{i\gamma_n^{(1)}\lambda}}_{\text{phase factor}} \left\{ |\psi_n^{(0)}\rangle + \lambda \sum_{l\neq n} \frac{V_{ln}}{E_n^{(0)}-E_l^{(0)}} |\psi_l^{(0)}\rangle + \cdots \right\}$$

As such a phase factor is physically unimportant, we can put it to zero: $c_{nn}^{(1)} = 0 = \gamma_n^{(1)}$

## 2.4 Second Order:

$\langle\psi_m^{(0)}|$

$$\sum_l c_{nl}^{(2)} \hat{H}_0 |\psi_l^{(0)}\rangle + \sum_l c_{nl}^{(1)} \hat{V} |\psi_l^{(0)}\rangle = E_n^{(2)}|\psi_n^{(0)}\rangle + \sum_l E_n^{(1)} c_{nl}^{(1)} |\psi_l^{(0)}\rangle + \sum_l E_n^{(0)} c_{nl}^{(2)} |\psi_l^{(0)}\rangle$$

$$\sum_l c_{nl}^{(2)} E_l^{(0)} \delta_{ml} + \sum_l c_{nl}^{(1)} V_{ml} = E_n^{(2)}\delta_{nm} + \sum_l E_n^{(1)} c_{nl}^{(1)} \delta_{ml} + \sum_l E_n^{(0)} c_{nl}^{(2)} \delta_{ml}$$

$$\underline{c_{nm}^{(2)} E_m^{(0)}} + \sum_l c_{nl}^{(1)} V_{ml} = \underline{E_n^{(2)}\delta_{nm}} + E_n^{(1)} c_{nm}^{(1)} + \underline{E_n^{(0)} c_{nm}^{(2)}}$$

m is at our disposal!

$\underline{n=m:}$ $$E_n^{(2)} = \sum_{l\neq n} c_{nl}^{(1)} V_{nl} - E_n^{(1)} \underbrace{c_{nn}^{(1)}}_{=0} = \sum_{l\neq n} \frac{V_{nl}V_{ln}}{E_n^{(0)}-E_l^{(0)}}$$

$V_{nl}\cdot V_{nl}^* = |V_{nl}|^2$

$n_0 \hat{=}$ ground state $\qquad E_{n_0}^{(2)} - E_l^{(0)} < 0 \quad \Rightarrow$ second-order lowers ground-state energy

$n \neq m$: $\cancel{\left[E_n^{(0)} - E_m^{(0)}\right]} c_{nm}^{(2)} = \sum_{l \neq n} c_{nl}^{(1)} V_{ml} - E_n^{(1)} c_{nm}^{(1)}$

$$= \sum_{l \neq n} \frac{V_{ln}}{(E_n^{(0)} - E_l^{(0)})(E_m^{(0)} - E_m^{(0)})} V_{ml} - \underbrace{E_n^{(1)}}_{V_{nn}} \sum_{m \neq n} \frac{V_{nm}}{(E_n^{(0)} - E_m^{(0)})^2}$$

$$|\psi_n(\lambda)\rangle = (1 + c_{nn}^{(2)} \lambda^2) |\psi_n^{(0)}\rangle + \sum_{m \neq n} \lambda \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

$$+ \lambda^2 \sum_{m \neq n} \left[ \sum_{l \neq n} \frac{V_{ml} V_{ln}}{(E_n^{(0)} - E_l^{(0)})(E_m^{(0)} - E_l^{(0)})} - V_{nn} \frac{V_{nm}}{(E_n^{(0)} - E_m^{(0)})^2} \right] |\psi_m^{(0)}\rangle + \dots$$

go back to normalization:

$$\underline{c_{nm}^{(2)}} + \sum_l c_{nl}^{(1)} c_{ml}^{(1)} + \underline{c_{nm}^{(2)*}} = 0$$

$m \neq n$: all coefficients known, can be inserted

$$\frac{1}{\cancel{x-y}} \frac{1}{x-z} + \frac{1}{y-x} \frac{1}{y-z} + \frac{1}{z-x} \frac{1}{z-y} = 0 \qquad x \neq y \neq z \neq x$$

$\Rightarrow$ no new information

$m = n$: $c_{nn}^{(2)} + c_{nn}^{(2)*} = - \sum_{l \neq n} c_{nl}^{(1)} c_{nl}^{(1)}$

$$c_{nn}^{(2)} = i \underbrace{\gamma_n^{(2)}}_{\text{unknown}} - \underbrace{\frac{1}{2} \sum_{l \neq n} \frac{|V_{nl}|^2}{(E_n^{(0)} - E_l^{(0)})^2}}_{\text{will affect } E_n^{(3)}}$$

without loss of generality 0