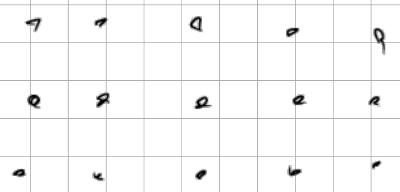
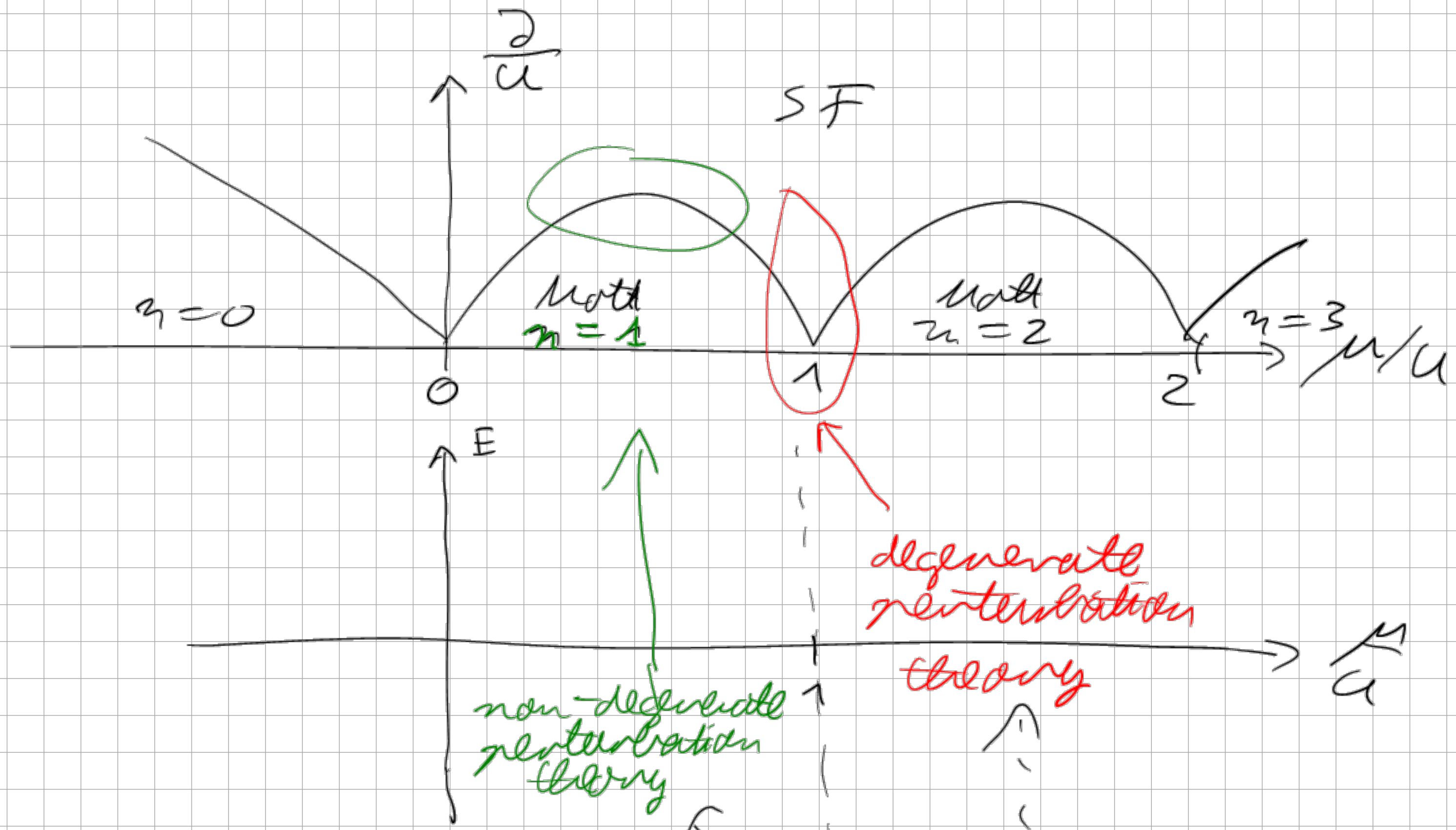
Chapter 4: Brillouin-Wigner Perturbation Theorie

Motivation:



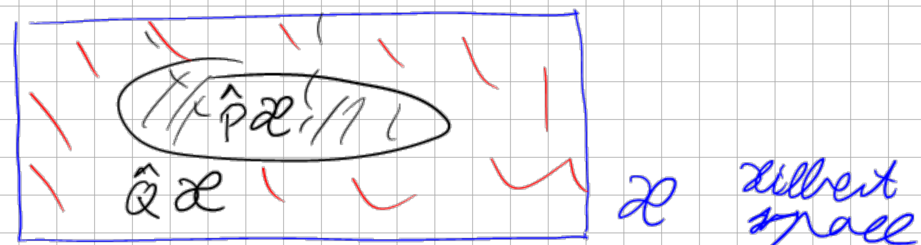


Unite non-degenerate and degenerate perturbation

4.1 General Formalism:

projection operator $\hat{P}$

idempotent property: $\hat{P}^2 = \hat{P}$



complementary projection operator: $\hat{Q} = 1 - \hat{P}$

$$\hat{Q}^2 = (1-\hat{P})(1-\hat{P}) = 1 - 2\hat{P} + \underbrace{\hat{P}^2}_{\hat{P}} = 1 - \hat{P} = \hat{Q} \quad ✓$$

$\hat{P}$ and $\hat{Q}$ project onto disjunct subspaces $\hat{P}\mathcal{H}$ and $\hat{Q}\mathcal{H}$:

$$\hat{P}\hat{Q} = \hat{P}(1-\hat{P}) = \hat{P} - \underbrace{\hat{P}^2}_{=\hat{P}} = 0 = \hat{Q}\hat{P} \quad \Rightarrow [\hat{P},\hat{Q}]_- = 0$$

eigenvalue problem: $\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$

$$\hat{1} = \hat{P} + \hat{Q} \qquad 1 = \hat{P} + \hat{Q}$$

$$\hat{H}\hat{P}|\Psi_n\rangle + \hat{H}\hat{Q}|\Psi_n\rangle = E_n\hat{P}|\Psi_n\rangle + E_n\hat{Q}|\Psi_n\rangle \quad \Big|\,\hat{P}\cdot \quad \Big|\,\hat{Q}\cdot$$

$$\hat{P}\hat{H}\hat{P}|\Psi_n\rangle + \hat{P}\hat{H}\hat{Q}|\Psi_n\rangle = \underbrace{E_n\underbrace{\hat{P}^2}_{=\hat{P}}|\Psi_n\rangle + E_n\underbrace{\hat{P}\hat{Q}}_{=0}|\Psi_n\rangle}$$

$$= E_n\hat{P}|\Psi_n\rangle \qquad (1)$$

$$\hat{Q}\hat{H}\hat{P}|\Psi_n\rangle + \hat{Q}\hat{H}\underbrace{\hat{Q}}_{=\hat{Q}^2}|\Psi_n\rangle = E_n\hat{Q}|\Psi_n\rangle \qquad (2)$$

Two intertwined equations connecting $\hat{P}|\Psi_n\rangle$ and $\hat{Q}|\Psi_n\rangle$

Aim: Find single equation for $\hat{P}|\Psi_n\rangle$ by eliminating $\hat{Q}|\Psi_n\rangle$

(2): $\quad \hat{Q}\hat{H}\hat{P}|\Psi_n\rangle = (E_n - \hat{Q}\hat{H}\hat{Q})\hat{Q}|\Psi_n\rangle$

$$\Rightarrow \hat{Q}|\Psi_n\rangle = \hat{Q}(E_n - \hat{Q}\hat{H}\hat{Q})^{-1}\hat{Q}\hat{H}\hat{P}|\Psi_n\rangle \quad \Big| \; \hat{Q}\cdot \qquad (2')$$

$(2')$ in (1): $\left\{\hat{P}\hat{H}\hat{P} + \hat{P}\boxed{\hat{H}}\hat{Q}\underbrace{(E_n - \hat{Q}\hat{H}\hat{Q})^{-1}}_{\text{resolvent}}\hat{Q}\boxed{\hat{H}}\hat{P}\right\}|\Psi_n\rangle = E_n\hat{P}|\Psi_n\rangle$

$\cancel{\hat{H}_0} + \lambda\hat{V}$ $\qquad \cancel{\hat{H}_0} + \lambda\hat{V}$

One equation for $\hat{P}|\Psi_n\rangle$.

Implement now perturbation theory: $\hat{H} = \hat{H}_0 + \lambda\hat{V}$

4.2 Specialization:

So far: $\hat{P}$ was considered to be independent of $\hat{H}_0$

Now: $[\hat{P}, \hat{H}_0]_- = 0$; $\hat{H}_0|\Psi_n^{(0)}\rangle = E_n^{(0)}|\Psi_n^{(0)}\rangle$, $\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle = \delta_{nm}$

$$\hat{P} = \sum_{n \in \underbrace{N}_{\text{subset of quantum numbers } n}} \underbrace{|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|}_{\text{dyadic product}}$$

$\hat{P}_n = |\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|$, $\quad \hat{P}_n^2 = \hat{P}_n$, $\quad \hat{P}_n\hat{P}_{n'} = \delta_{nn'}\hat{P}_n$

$\Rightarrow \;\_\_\_\; \Rightarrow \hat{P}^2 = \hat{P}$

$$\hat{\rho}(x) = \sum_n \rho_n(\vec{x})\,|n\rangle\langle n|$$

density operator

$$\hat{Q} = \sum_{n \in \underbrace{\bar{N}}_{\text{complement of } N}} |\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|$$

$$\hat{O} = \hat{1}\cdot\hat{O}\,\hat{1} = \sum_n |n\rangle\langle n|\,\hat{O}\sum_{n'}|n'\rangle\langle n'| = \sum_n\sum_{n'} \underbrace{O_{nn'}}_{=\langle n|\hat{O}|n'\rangle} |n\rangle\langle n'|$$

$$\underbrace{\hat{Q}\,\hat{H}_0\,\hat{P}}_{} = \sum_{n\in N} E_n^{(0)}\,\underbrace{\hat{Q}\,|\psi_n^{(0)}\rangle}\langle\psi_n^{(0)}| = 0$$

$$= \sum_{n\in N}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| = 1-\hat{P}$$

$$\hat{P}\,\hat{H}_0\,\hat{Q} = 0$$

$$\Longrightarrow \quad \underbrace{\hat{P}\left\{\hat{H} + \lambda^2\,\hat{V}\hat{Q}\left(E_n - \hat{Q}\hat{H}\hat{Q}\right)^{-1}\hat{Q}\hat{V}\right\}}_{=\hat{H}_{\text{eff}}}\hat{P}\,|\psi_n\rangle = E_n\,\hat{P}\,|\psi_n\rangle \Longleftarrow$$

$\hat{P}$-subspace

$\hat{Q}$-subspace

4.3 Resolvent:

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \lambda\hat{V} + \lambda^2\,\hat{V}\,\hat{Q}\,R(E_n)\,\hat{Q}\,\hat{V}$$

$$(\hat{A}\,\hat{B})^{-1} = \hat{B}^{-1}\hat{A}^{-1}$$

$$\hat{R}(E_n) = \left[E_n - \hat{Q}(\hat{H}_0 + \lambda\hat{V})\,\hat{Q}\right]^{-1}$$

Idea: Taylor expansion in λ where λ appears explicitly

$$\hat{R}(E_n) = \left(E_n - \hat{Q}\,\hat{H}_0\,\hat{Q}\right)^{-1}\underbrace{\left\{1 - \lambda\,\hat{Q}\,\hat{V}\,\hat{Q}\left(E_n - \hat{Q}\,\hat{H}_0\,\hat{Q}\right)^{-1}\right\}^{-1}}$$

geometric series $= \sum_{s=0}^{\infty} \Big[\lambda \hat{Q} \hat{V} \underbrace{\hat{Q} (E_n - \hat{Q} \hat{H}_0 \hat{Q})^{-1}}_{= \hat{R}^{(0)}(E_n)} \Big]^s$

$$\hat{H}_{eff} = \hat{H}_0 + \lambda \hat{V} + \lambda^2 \hat{V} \hat{Q} \hat{R}^{(0)}(E_n) \hat{Q} \hat{V}$$

$$+ \lambda^3 \hat{V} \hat{Q} \hat{R}^{(0)}(E_n) \hat{Q} \hat{V} \hat{Q} \hat{R}^{(0)}(E_n) \hat{Q} \hat{V} + \lambda^4 * \cdots$$

$$\langle \psi_e^{(0)} | \underbrace{\hat{R}^{(0)}(E_n)}_{(E_n - \hat{Q}\hat{H}_0\hat{Q})^{-1}} | \psi_e^{(0)} \rangle = \frac{1}{E_n - E_e^{(0)}} \qquad n \in N, \quad e \in \bar{N}$$

$$(E_n - \hat{Q}\hat{H}_0\hat{Q})^{-1} = E_n \Big(1 + \frac{1}{E_n} \hat{Q} \hat{H}_0 \hat{Q} + \cdots \Big)$$

geometric series

$$\hat{Q} | \psi_e^{(0)} \rangle = \sum_{e' \in \bar{N}} | \psi_{e'}^{(0)} \rangle \underbrace{\langle \psi_{e'}^{(0)} | \underbrace{\psi_e^{(0)}}_{\in \bar{N}} \rangle}_{= \delta_{ee'}} = | \psi_e^{(0)} \rangle$$

$$\hat{H}_{eff} = \hat{H}_0 + \lambda \hat{V} + \lambda^2 \sum_{e \in \bar{N}} \frac{\hat{V} | \psi_e^{(0)} \rangle \langle \psi_e^{(0)} | \hat{V}}{E_n - E_e^{(0)}}$$

$$+ \lambda^3 \sum_{e, e' \in \bar{N}} \frac{\hat{V} | \psi_e^{(0)} \rangle \langle \psi_e^{(0)} | \hat{V} | \psi_{e'}^{(0)} \rangle \langle \psi_{e'}^{(0)} | \hat{V}}{(E_n - E_e^{(0)}) \, (E_n - E_{e'}^{(0)})} + \cdots$$

$$\hat{P}\,\hat{H}_{eff}\,\hat{P}|\psi_m\rangle = E_m\,\hat{P}|\psi_m\rangle \qquad \Big|\,\langle\psi^{(0)}_{n''}|$$

$$\sum_{n\in N}\sum_{n'\in N} |\psi^{(0)}_n\rangle\langle\psi^{(0)}_n|\hat{H}_{eff}|\psi^{(0)}_{n'}\rangle\langle\psi^{(0)}_{n'}|\psi_m\rangle = E_m \sum_{n'\in N}|\psi^{(0)}_{n'}\rangle\langle\psi^{(0)}_{n'}|\psi_n\rangle$$

$$\sum_{n'\in N}\left(\langle\psi^{(0)}_{n''}|\hat{H}_{eff}|\psi^{(0)}_{n'}\rangle - E_m\,\delta_{n'n''}\right)\langle\psi^{(0)}_{n'}|\psi_m\rangle = 0$$

$\Rightarrow$ nontrivial solution $\quad \det\left(\langle\psi^{(0)}_n|\hat{H}_{eff}|\psi^{(0)}_{n'}\rangle - \underbrace{E_m}\,\delta_{nn'}\right) = 0$

$\Rightarrow$ equation for E_m

4.4 Specific Cases:

4.4.1 One-State Approach:

$$\hat{P} = \hat{P}_n = |\psi^{(0)}_n\rangle\langle\psi^{(0)}_n|$$

$$\Rightarrow \quad E_n = \langle\psi^{(0)}_n|\hat{H}_{eff}|\psi^{(0)}_n\rangle$$

$$E_n = E^{(0)}_n + \lambda V_{nn} + \lambda^2 \sum_{l\neq n}\frac{V_{nl}V_{ln}}{E_n - E^{(0)}_l}$$

$$+\lambda^3 \sum_{l,l'\neq n}\frac{V_{nl}V_{ll'}V_{l'n}}{(E_n-E^{(0)}_l)(E_n-E^{(0)}_{l'})} + \cdots$$