Lecture Fys4480, lecture November 2, 2023.

FCI and links with HF and MBPT

assume we can expand $|\Psi_0\rangle$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{PH} C_H^P |\Phi_H^P\rangle$$

$$\left(\langle \Phi_i | \Phi_j \rangle = \delta_{ij} \right)$$

$$= |\Phi_0\rangle + \sum_{ia} C_i^a a_a^\dagger a_i |\Phi_0\rangle$$

$$+ \sum_{\substack{ij \\ ab}} C_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$$

$$+ \cdots$$

$$= (1 + \hat{C}) |\Phi_0\rangle \qquad \underbrace{\langle \Phi_0 | \Psi_0 \rangle}_{=1}$$

$$\hat{H} c = \lambda c$$

$$\hat{H} = \begin{bmatrix} \langle \Phi_0 | H | \Phi_0 \rangle & \langle \Phi_0 | H | \Phi_i^a \rangle & \cdots \\ \langle \Phi_i^a | H | \Phi_0 \rangle & \langle \Phi_i^a | H | \Phi_j^b \rangle & \cdots \\ \vdots & \vdots & \end{bmatrix}$$

$$E_0^{ref} = \langle \Phi_0 | H | \Phi_0 \rangle =$$

$$\sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle_{AS}$$

$$\langle \Phi_0 | H | \Phi_i^a \rangle = \langle a | \hat{f} | i \rangle$$

$$\langle \Phi_0 | \hat{E}_0^{ref} + \hat{F}_N + \hat{V}_N | \Phi_i^a \rangle$$

$$\langle \Phi_0 | \sum_{pq} a_p^{+} a_q \langle p | f | q \rangle a_a^{+} a_i | \Phi_0 \rangle$$

$$= \langle i | f | a \rangle =$$

$$\langle i | h_0 | a \rangle + \sum_j \langle ij | v | aj \rangle_{AS}$$

with HF basis

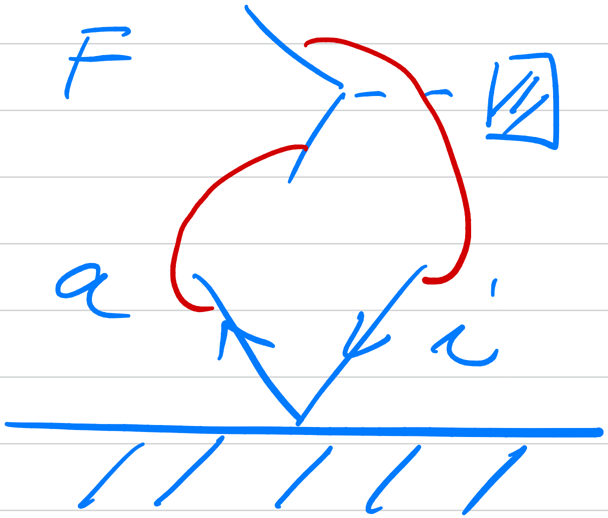
$$\langle i | f | a \rangle = 0$$

$$\langle \Phi_0 | \hat{V}_N | \Phi_i^a \rangle = 0$$

Diagrammatic representation

$\langle \Phi_0 |$ 

const $\langle \Phi_0 | \Phi_0 \rangle$



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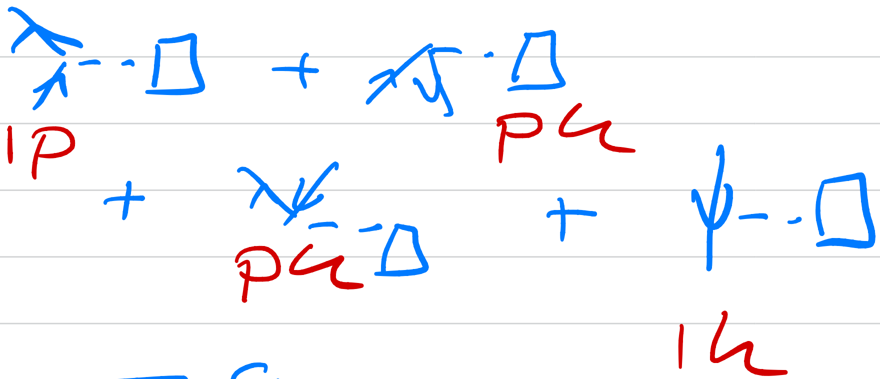


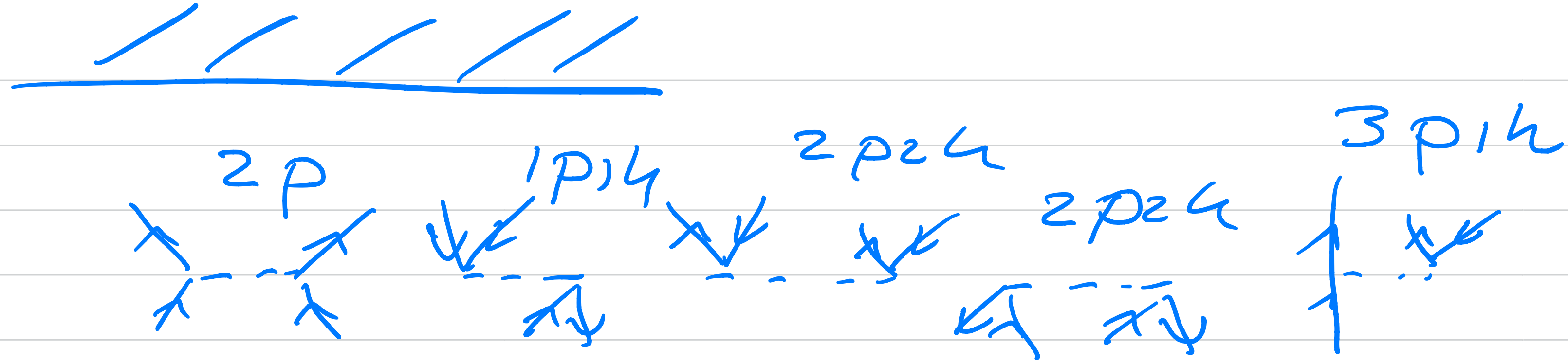
$|\Phi_i^a\rangle$

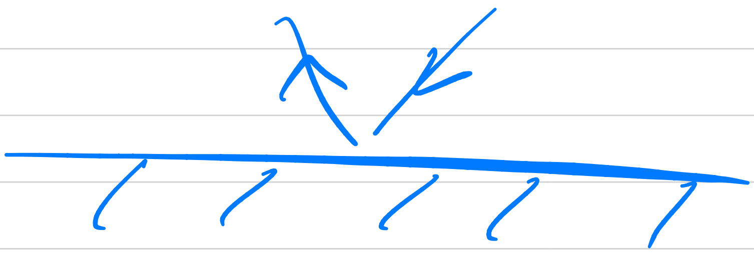
$$\sum_{pq} a_p^\dagger a_q \langle p | f | q \rangle$$

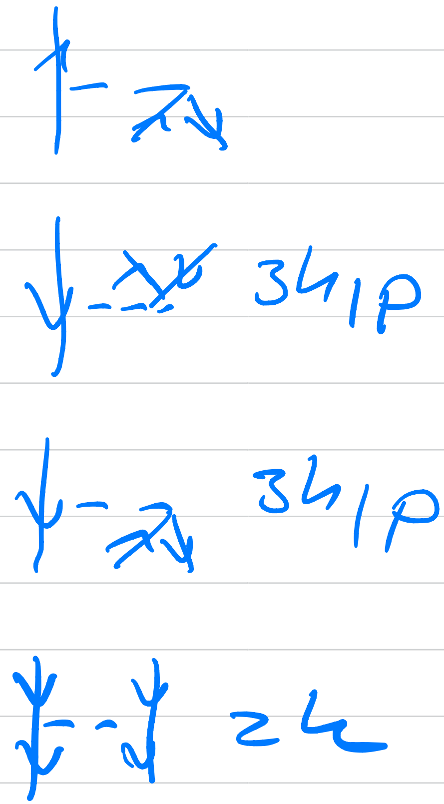
$$\sum_{ab} a_a^\dagger a_b \cdots + \sum_{ai} a_a^\dagger a_i \cdots$$

$$+ \sum_{ia} a_i^\dagger a_a \cdots + \sum_{ij} a_i^\dagger a_j \cdots$$

$\langle \Phi_c |$







0p0h ← 1p1h

Σ

P975

$$\langle \Phi_0 | \; a_p^\dagger a_q^\dagger a_s a_r \; a_a^\dagger a_i | \Phi_0 \rangle$$

want $\propto$ const $\langle \Phi_0 | \Phi_0 \rangle$

HF-basis

$$\langle \Phi_0 | H | \Phi_i^a \rangle = 0$$

$$\langle \Phi_i^a | H | \Phi_j^b \rangle = ?$$

Back to Hamiltonian matrix

$$
\begin{array}{c}
\langle \Phi_i | \\
\\
\\
\\
\end{array}
\begin{array}{cccc}
 & 1p1h & 2p2h & \\
\end{array}
$$

$$
\begin{bmatrix}
E_0^{Ref} & 0 & \sum_{\substack{ij \\ ab}} c_{ij}^{ab} \langle ij || ab \rangle & 0 \; \cdots \\
0 & \sum_{jb} c_j^b \langle \Phi_i^a | H | \Phi_j^b \rangle & \times & \times \\
\times & \times & & \times \\
0 & \times & & \\
0 & \vdots & & \\
\vdots & \vdots & & \\
0 & \vdots & & \\
\end{bmatrix}
$$

HF-basis

$$HC = \lambda C$$

$$\langle \Phi_0 | H | \Psi_0 \rangle = \overbrace{\langle \Phi_0 | H | \Phi_0 \rangle}^{E_0^{Ref}}$$

$$+ \sum_{ai} c_i^a \langle \Phi_0 | H | \Phi_i^a \rangle + \sum_{\substack{ij \\ ab}} c_{ij}^{ab} \langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle + 0$$

$$= \lambda = E_0$$

$$E_0 - E_0^{Ref} = \Delta E = \text{correlation energy}$$

$$\sum_{ai} c_i^a \langle \Phi_0 | H | \Phi_i^a \rangle + \sum_{\substack{ij \\ ab}} c_{ij}^{ab} \langle ij || ab \rangle$$

$$0 = \langle i | f | a \rangle$$

$$\Delta E = \sum_{\substack{ij\\ab}} c_{ij}^{ab} \underbrace{\langle ij || ab \rangle_{AS}}_{\langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle}$$

2nd row $\langle \Phi_i^a |$

$$\langle \Phi_i^a | H - \lambda | \Phi_0 \rangle \overset{HF}{=} 0 + \sum_{jb} c_j^b \langle \Phi_i^a | H - \lambda | \Phi_j^b \rangle$$

$$+ \sum_{\substack{jk\\bc}} c_{jk}^{bc} \underbrace{\langle \Phi_i^a | H - \lambda | \Phi_{jk}^{bc} \rangle}_{\langle j | f | b \rangle} = 0$$

$$+ \sum_{\substack{jkl\\bcd}} \underset{\substack{\shortparallel\\0}}{c_{jkl}^{bcd}} \langle \Phi_i^a | H - \lambda | \Phi_{jkl}^{bcd} \rangle = 0$$

$$\sum_{jb} c_j^b \langle \Phi_i^a | H - \lambda | \Phi_j^b \rangle = 0$$

$$\lambda \langle \Phi_i^a | \Phi_j^b \rangle c_j^b = \lambda \delta_{ij} \delta_{ab} c_i^a$$

$$\sum_{jb} c_j^b \langle \Phi_i^a | E_0^{ref} + \hat{F}_N + \hat{U}_A | \Phi_j^b \rangle$$

$$= \lambda c_i^a$$

$$c_i^a E_0^{ref} + \delta_{ij} \delta_{ab} \left(\varepsilon_a^{HF} - \varepsilon_i^{HF} \right) c_i^a$$

$$+ \sum_{jb} c_j^b \langle aj \| v \| ib \rangle_{AS} = \lambda c_i^a$$

$$ai = I \qquad bj = J$$

$$A_{IJ} = (\varepsilon_a - \varepsilon_i)\,\delta_{ij}\,\delta_{ab} \quad (\delta_{IJ})$$

$\Delta_{IJ} \cdot \delta_{IJ}$

$$+ \langle aj \| bi \rangle_{AS}$$

$$I = \{ai\} \quad J = \{bj\}$$

$$C_i^a \Rightarrow C_I \qquad C_j^b \Rightarrow C_J$$

$$(-E_c^{Ref})$$

$$\sum_J A_{IJ}\, C_J = \lambda\, C_I \Rightarrow$$

$$AC = \lambda C \quad (\mathrm{TDA})$$

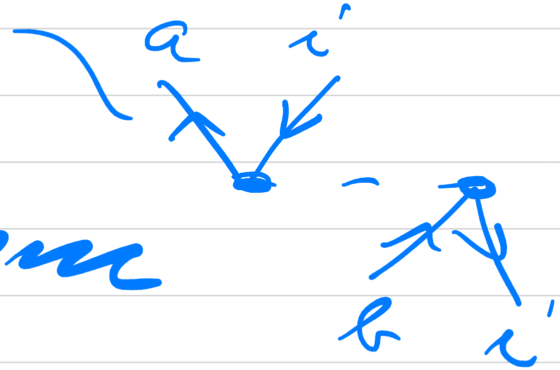
$$A_{IJ} = \Delta_{IJ} + v_{IJ}$$

$$\Delta_{IJ} = \varepsilon_I \delta_{IJ} \qquad \varepsilon_I = \varepsilon_a - \varepsilon_i$$

$$I = \{ai\}$$

$$v_{IJ} = \langle aj | v | ib \rangle_{AS}$$

$$v_{IJ} = -\gamma Q_I Q_J^*$$



eigenvalue problem

$$\gamma Q_I \sum_J Q_J^* C_J = (\varepsilon_I - \lambda) C_I$$

$$\left(\sum_J A_{IJ} C_J = \lambda C_I \right)$$

$$\langle aj|v|ik\rangle = \int d\vec{r} \int d\vec{r}\,' \; \psi_a^*(\vec{r})\, \psi_j^*(\vec{r}\,')\, v(\vec{r},\vec{r}\,')\, \psi_i(\vec{r})\, \psi_k(\vec{r}\,')$$

$$v(\vec{r},\vec{r}\,') = \varphi(\vec{r}) \cdot \varphi^*(\vec{r}\,')$$

$$= \int d\vec{r}\, \psi_a^* \varphi(\vec{r})\, \psi_i(\vec{r}) \int d\vec{r}\,' \,\psi_j^*(\vec{r}\,')\, \varphi^*(\vec{r}\,')\, \psi_k(\vec{r}\,')$$

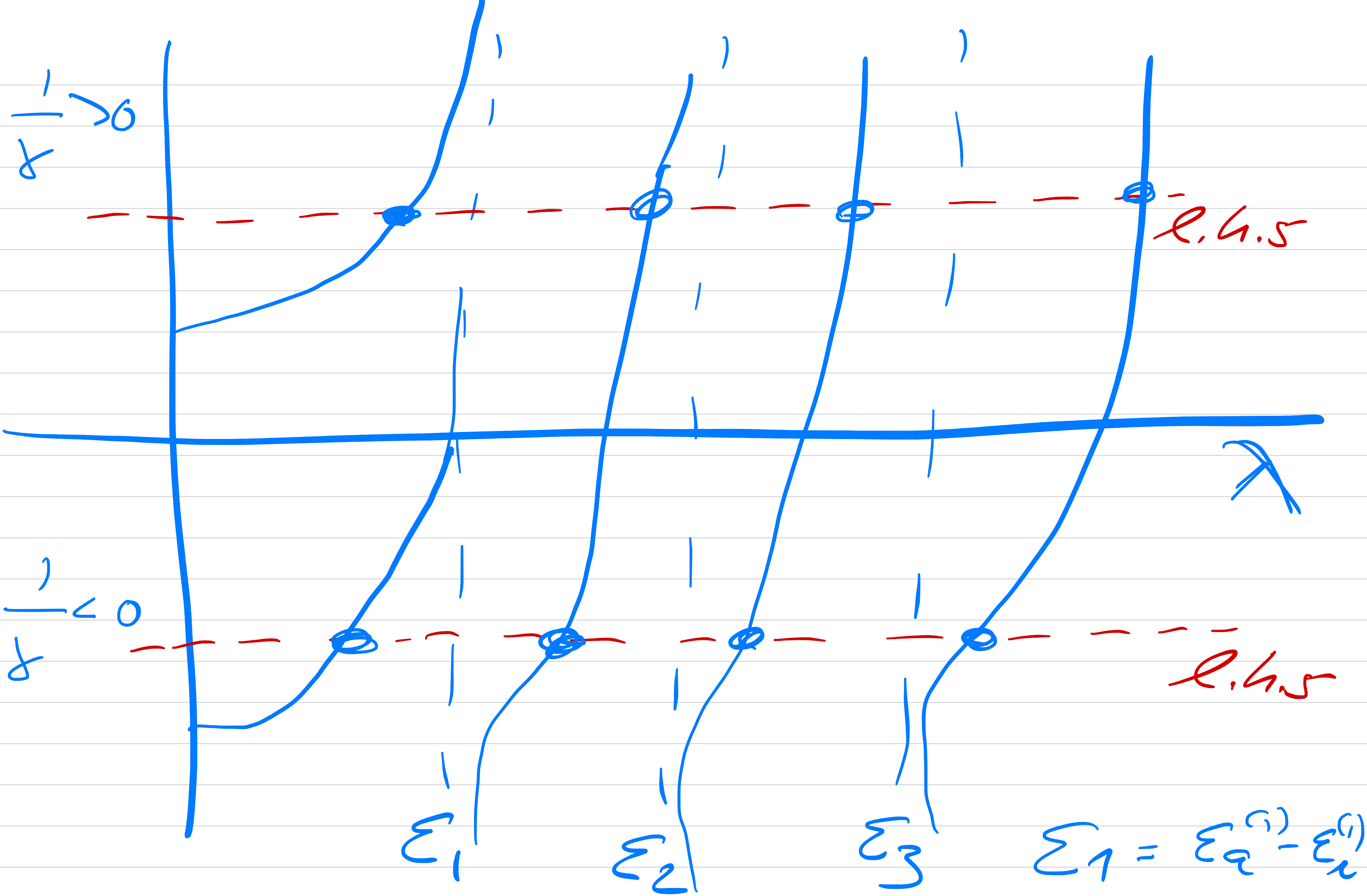
$$N = \gamma \sum_J \varphi_J^* c_J$$

$$c_I = \frac{N \varphi_I}{\varepsilon_I - \lambda}$$

multiply with $\gamma \varphi_I^*$ and sum over I $\Rightarrow$

$$\frac{1}{\gamma} = \sum_I \frac{|\varphi_I|^2}{\varepsilon_I - \lambda}$$

Dispersion Relation



$\frac{1}{\gamma} > 0$
e.h.s
λ
$\frac{1}{\gamma} < 0$
e.h.s
ε_1
ε_2
ε_3
$\varepsilon_1 = \varepsilon_a^{(1)} - \varepsilon_i^{(1)}$

Degenerate energies

$$E_I = E \quad \forall I$$

$$\lambda = \begin{cases} E - \gamma \sum_I |\underline{c_I}|^2 \\ E \quad \text{other states} \end{cases}$$

$$v_{IJ} = \langle aj|v|ib\rangle$$

$$v_{II} = \langle ai|v|ia\rangle_{AS}$$

Approximations ; MBPT

Definitions : Define our comp. basis as an eigenbasis of $\hat{H}_0$

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

$$\hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle$$

$$W_0 = \sum_{i \le F} \underbrace{\langle i | h_0 | i \rangle}_{\varepsilon_i}$$

$$\hat{H}_0 |\Phi_i^a\rangle = \left[(\varepsilon_a - \varepsilon_i) + \sum_{j \le F} \varepsilon_j \right] \times |\Phi_i^a\rangle$$

$$\langle \Phi_i^a | H_0 | \Phi_i^a \rangle =$$

$$\langle \Phi_i^a | \Big(\underbrace{\Big(\sum_{j \le r} \varepsilon_j\Big)}_{W_0} + \sum_{pq} \langle p | h_0 | q \rangle a_p^\dagger a_q \Big| \Phi_i^a \rangle$$

$$W_0 + \underbrace{\langle \Phi_0 | a_i^\dagger a_a a_p^\dagger a_q a_a^\dagger a_i | \Phi_0 \rangle}_{\varepsilon_a - \varepsilon_i}$$

$$\varepsilon_a - \varepsilon_i + W_0$$

$$H_0 | \Phi_{ij}^{ab} \rangle = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j + W_0$$

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0|$$

non-degenerate ground state

$$\sum_{m=1}^{\infty} c_m |\phi_m\rangle$$

$$\left(\sum_{PH} c_H^P |\phi_H^P\rangle \right)$$

$$\hat{Q} = \sum_{m=1}^{\infty} |\phi_m\rangle\langle\Phi_m|$$

$$\hat{P}^2 = \hat{P} \wedge \hat{Q}^2 = \hat{Q}, \quad [\hat{P}, \hat{Q}]$$

$$[\hat{P}, H_0] = [\hat{Q}, H_0] = 0$$