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① Rayleigh-Schrödinger perturbation theory (RSPT)

$$\hat{H}\psi_0 = E_0\psi_0 \qquad \lambda = 1$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}$$

$$\psi_0 = \psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots$$

perturbation order

state (0 = GS, 1 = ES, ...)

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots$$

$$\hat{H}_0\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}$$

$$(\hat{H}_0 + \lambda\hat{V})(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots) = (E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots)(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots)$$

$$\lambda^0 : \hat{H}_0\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)} \quad \text{Ⓐ}$$

$$\lambda^1 : \hat{H}_0\psi_0^{(1)} + \hat{V}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(1)} + E_0^{(1)}\psi_0^{(0)} \quad \text{Ⓑ} \quad ☆$$

$$\lambda^2 : \hat{H}_0\psi_0^{(2)} + \hat{V}\psi_0^{(1)} = E_0^{(0)}\psi_0^{(2)} + E_0^{(1)}\psi_0^{(1)} + E_0^{(2)}\psi_0^{(0)} \quad \text{Ⓒ}$$

$$\lambda^3 : \hat{H}_0\psi_0^{(3)} + V\psi_0^{(2)} = E_0^{(0)}\psi_0^{(3)} + E_0^{(1)}\psi_0^{(2)} + E_0^{(2)}\psi_0^{(1)} + E_0^{(3)}\psi_0^{(0)} \quad \text{Ⓓ}$$

Ⓑ $\psi_0^{(1)} = \sum_{k\neq 0} C_k^{(1)}\psi_k^{(0)}$

$$\sum_{k\neq 0} C_k^{(1)}E_k^{(0)}\psi_k^{(0)} + \hat{V}\psi_0^{(0)} = E_0^{(0)}\sum_{k\neq 0} C_k^{(1)}\psi_k^{(0)} + E_0^{(1)}\psi_0^{(0)}$$

$\downarrow \int \psi_0^{(0)*}d\tau$

$$E_0^{(1)} = \int \psi_0^{(0)*}\hat{V}\psi_0^{(0)}\,d\tau$$

$\int \psi_k^{(0)*}d\tau$ ↓

$$C_k^{(1)} = \frac{\int \psi_k^{(0)*}\hat{V}\psi_0^{(0)}d\tau}{E_0^{(0)} - E_k^{(0)}}$$

Ⓒ $\psi_0^{(2)} = \sum_{k\neq 0} C_k^{(2)}\psi_k^{(0)}$ ☆

$$\sum_{k\neq 0} C_k^{(2)}E_k^{(0)}\psi_k^{(0)} + \hat{V}\sum_{k\neq 0} C_k^{(1)}\psi_k^{(0)} = E_0^{(0)}\sum_{k\neq 0} C_k^{(2)}\psi_k^{(0)} + E_0^{(1)}\sum_{k\neq 0} C_k^{(1)}\psi_k^{(0)} + E_0^{(2)}\psi_0^{(0)}$$

$\downarrow \int \psi_k^{(0)*}d\tau$

$$E_0^{(2)} = \sum_{k\neq 0} C_k^{(1)}\int \psi_0^{(0)*}\hat{V}\psi_k^{(0)}d\tau = \sum_{k\neq 0}\frac{\langle\psi_0^{(0)}|\hat{V}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{E_0^{(0)} - E_k^{(0)}} \quad \int\psi_0^{(0)*}d\tau$$

$$C_k^{(2)}E_k^{(0)} + \sum_{k'\neq 0} C_{k'}^{(1)}\int \psi_k^{(0)*}\hat{V}\psi_{k'}^{(0)}d\tau = C_k^{(2)}E_0^{(0)} + C_k^{(1)}E_0^{(1)}$$

$$C_k^{(2)} = \sum_{k'\neq 0}\frac{\langle\psi_k^{(0)}|\hat{V}|\psi_{k'}^{(0)}\rangle\langle\psi_{k'}^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{(E_0^{(0)} - E_k^{(0)})(E_0^{(0)} - E_{k'}^{(0)})} - E_0^{(1)}\frac{\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{(E_0^{(0)} - E_k^{(0)})^2} \quad ☆$$

Ⓓ

$$E_0^{(3)} = \langle\psi_0^{(0)}|\hat{V}|\psi_0^{(2)}\rangle = \sum_{k,k'\neq 0}\frac{\langle\psi_0^{(0)}|\hat{V}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{V}|\psi_{k'}^{(0)}\rangle\langle\psi_{k'}^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{(E_0^{(0)} - E_k^{(0)})(E_0^{(0)} - E_{k'}^{(0)})} - E_0^{(1)}\sum_{k\neq 0}\frac{\langle\psi_0^{(0)}|\hat{V}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle}{(E_0^{(0)} - E_k^{(0)})^2}$$

② Møller-Plesset (MP) partitioning

$$\hat H = E_{HF} + \left(\sum_{p,q}\langle p|\hat f|q\rangle\{\hat p^\dagger \hat q\} + \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{\hat p^\dagger \hat q^\dagger \hat s \hat r\}\right)$$

$$E_{HF} = \sum_i \langle i|\hat f|i\rangle - \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle$$

$\hat H_0$ (rest is $\hat V$)

$$E^{(0)}_{MP} = \langle \Psi_0^{(0)}|\hat H_0|\Psi_0^{(0)}\rangle = \sum_i \langle i|\hat f|i\rangle + \sum_{p,q}\langle p|\hat f|q\rangle\underbrace{\langle\Psi_0^{(0)}|\{\hat p^\dagger \hat q\}|\Psi_0^{(0)}\rangle}_{0}$$

$$= \sum_i \langle i|\hat f|i\rangle$$

$$E^{(1)}_{MP} = \langle \Psi_0^{(0)}|\hat V|\Psi_0^{(0)}\rangle = -\frac{1}{2}\sum_{i,j}\langle ij||ij\rangle + \cdots \underbrace{\langle\Psi_0^{(0)}|\{\hat p^\dagger \hat q^\dagger \hat s \hat r\}|\Psi_0^{(0)}\rangle}_{0}$$

$$E^{(0)}_{MP} + E^{(1)}_{MP} = \langle \Psi_0^{(0)}|\hat H|\Psi_0^{(0)}\rangle = E_{HF}$$

$$E^{(2)}_{MP} = \sum_{k\neq 0}\frac{\langle\Psi_0^{(0)}|\hat V|\Psi_k^{(0)}\rangle\langle\Psi_k^{(0)}|\hat V|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_k^{(0)}}$$

$$E_0^{(0)} = \sum_i \langle i|\hat f|i\rangle$$

$$E_k^{(0)} = \sum_i \langle i|\hat f|i\rangle + \sum_{p,q}\langle p|\hat f|q\rangle \langle\Phi_0|\{\hat i^\dagger \hat j^\dagger \hat b \hat a\}\{\hat p^\dagger \hat q\}\{\hat a^\dagger \hat b^\dagger \hat j \hat i\}|\Phi_0\rangle \quad \text{etc}$$

$$= \sum_i \langle i|\hat f|i\rangle + \underbrace{\langle a|\hat f|a\rangle}_{\epsilon_a} + \underbrace{\langle b|\hat f|b\rangle}_{\epsilon_b} - \underbrace{\langle i|\hat f|i\rangle}_{\epsilon_i} - \underbrace{\langle j|\hat f|j\rangle}_{\epsilon_j}$$

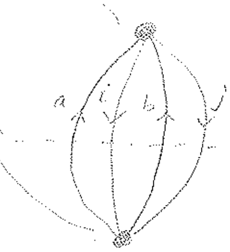
$$\frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\langle\Phi_0|\{\hat p^\dagger \hat q^\dagger \hat s \hat r\}\{\hat a^\dagger \hat b^\dagger \hat j \hat i\}|\Phi_0\rangle \quad \times 4$$

$= \langle ij||ab\rangle$ (const. part contributes nothing)

$$\Rightarrow\ = \frac{1}{4}\sum_{i,j,a,b}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

two equivalent pairs

$(-1)^{2+2}$



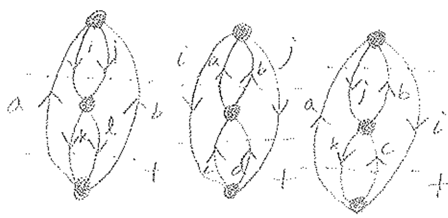
$$E_{MP}^{(3)} = \sum_{k,k'\neq 0} \frac{\langle \Psi_0^{(0)}|\hat V|\Psi_k^{(0)}\rangle\langle \Psi_k^{(0)}|\hat V|\Psi_{k'}^{(0)}\rangle\langle \Psi_{k'}^{(0)}|\hat V|\Psi_0^{(0)}\rangle}{(E_0^{(0)}-E_k^{(0)})(E_0^{(0)}-E_{k'}^{(0)})} - E_0^{(1)}\sum_{k\neq 0}\frac{\langle \Psi_0^{(0)}|\hat V|\Psi_k^{(0)}\rangle\langle \Psi_k^{(0)}|\hat V|\Psi_0^{(0)}\rangle}{(E_0^{(0)}-E_k^{(0)})^2}$$

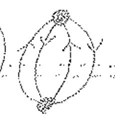
$-\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$

+

$-\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$

$\left(-\frac{1}{2}\sum_{ij}\langle ij||ij\rangle\right)\cdot$  : disconnected



$+\left(-\frac{1}{2}\sum_{ij}\langle ij||ij\rangle\right)\cdot$  : disconnected

connected!

cancel

$E_{MP}^{(3)} =$

$$= (-1)^{2+4}\left(\frac{1}{2}\right)^3 \sum_{\substack{i,j\\k,l\\a,b}} \frac{\langle ij||ab\rangle\langle ab||kl\rangle\langle kl||ij\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)(\epsilon_k+\epsilon_l-\epsilon_c-\epsilon_d)}$$

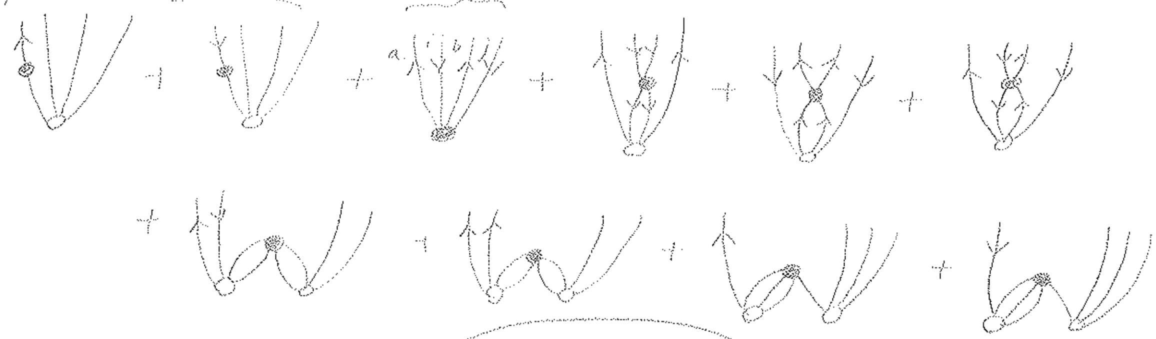
$$+ (-1)^{2+2}\left(\frac{1}{2}\right)^3 \sum_{\substack{i,j\\a,b\\c,d}} \frac{\langle ij||ab\rangle\langle ab||cd\rangle\langle cd||ij\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)(\epsilon_i+\epsilon_j-\epsilon_c-\epsilon_d)}$$

$$+ (-1)^{2+3} \sum_{\substack{i,j,k\\a,b,c}} \frac{\langle ji||ab\rangle\langle kb||jc\rangle\langle ac||ki\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)(\epsilon_i+\epsilon_k-\epsilon_a-\epsilon_c)}$$

(3) CCD redux

$$E_{corr.}^{CCD} = $$  $$= \frac{1}{4} \sum_{\substack{i,j\\a,b}} \langle ij||ab\rangle t_{ij}^{ab} \quad \text{—— (A)}$$

$(\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j)t_{ij}^{ab}$ $\langle ab||ij\rangle$

$$0 = $$  —— (B)

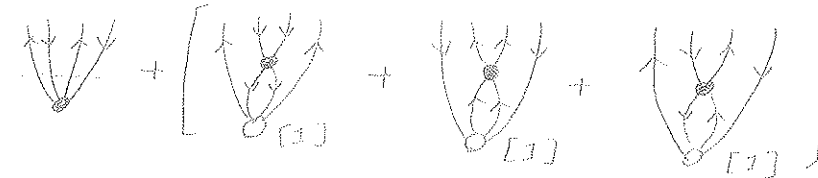
connected!

all connected

Consider solving (B) iteratively starting w/ $t_{ij}^{ab}=0$ except the first two terms

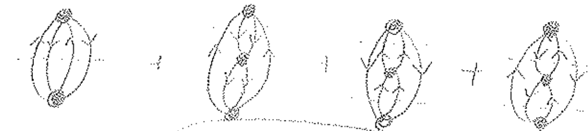
$$t_{ij}^{ab[1]} = \frac{\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} = $$ 

$$E_{corr.}^{CCD[1]} = \frac{1}{4}\sum_{\substack{i,j\\a,b}} \langle ij||ab\rangle t_{ij}^{ab[1]} = \frac{1}{4}\sum_{\substack{i,j\\a,b}} \frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} = $$  $$= E_{MP}^{(2)}$$

$$t_{ij}^{ab[2]} = $$  $$/(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)$$

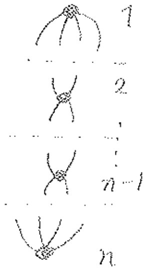
[1] [1] [1]

$$= $$ 

$$E_{corr.}^{CCD[2]} = $$  $$= E_{MP}^{(2)} + E_{MP}^{(3)}$$

connected!

(4) Goldstone's linked-diagram theorem

$$E_{MP}^{(n)} = $$  } connected

1, 2, ⋮, n-1, n

March et al. time-dependent derivation

Shavitt & Bartlett time-independent derivation