- Wick-tétel

$$\hat{A}\hat{B}\hat{C}\hat{D}\ldots = \{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\} + \sum_{\substack{1\times\text{-es}\\ \text{kont}}} \{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\} + \sum_{\substack{2\times\text{-es}\\ \text{kont}}} \underbrace{\{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\}}_{\text{normálrendezett op.}} + \ldots$$

$$+ \sum_{\substack{3\times\text{-es}\\ \text{kontr}}} \{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\} + \ldots + \sum_{\substack{\text{teljesen}\\ \text{kontrahált}}} \underbrace{\{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\}}_{\text{szám!}}$$

példa: $i^+ j^+ k^- e^- = -i^+ k^- j^+ e^- + i^+ e^- \delta_{jk} = k^- i^+ j^+ e^- - \delta_{ik} j^+ e^-$

$+ i^+ e^- \delta_{jk} = -k^- i^+ e^- j^+ + \delta_{je} k^- i^+ - \delta_{ik} j^+ e^- + i^+ e^- \delta_{jk}$

$= k^- e^- i^+ j^+ - \delta_{ie} k^- j^+ + \delta_{je} k^- i^+ - \delta_{ik} j^+ e^- + i^+ e^- \delta_{jk}$

$= k^- e^- i^+ j^+ - \delta_{ie} k^- j^+ + \delta_{je} k^- i^+ + \delta_{ik} e^- j^+ - \delta_{ik}\delta_{je} - e^- i^+ \delta_{jk} + \delta_{jk}\delta_{ie}$

$= \{i^+ j^+ k^- e^-\} + \{i^+ j^+ k^- e^-\} + \{i^+ j^+ k^- e^-\} + \{i^+ j^+ k^- e^-\} + \{i^+ j^+ k^- e^-\} + \{i^+ j^+ k^- e^-\}$

$+ \{i^+ j^+ k^- e^-\}$

~ $\langle \Phi_0 | \{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\} | \Phi_0 \rangle = 0 \Rightarrow \langle \Phi_0 | \hat{A}\hat{B}\hat{C}\hat{D}\ldots | \Phi_0 \rangle =$

$= \langle \Phi_0 | \sum_{\substack{\text{teljesen}\\ \text{kontr.}}} \{\hat{A}\hat{B}\hat{C}\hat{D}\ldots\} | \Phi_0 \rangle$

~ általánosított Wick-tétel

Shavitt-Bartlett

Szalay P. előadása

$\{\hat{A}\hat{B}\hat{C}\}\{\hat{D}\hat{E}\}\{\hat{F}\hat{G}\}\ldots =$

$\{\hat{A}\hat{B}\hat{C}\hat{D}\hat{E}\hat{F}\hat{G}\ldots\} + \sum_{1\times\text{es}} \{\{\hat{A}\hat{B}\hat{C}\}\{\hat{D}\hat{E}\}\{\hat{F}\hat{G}\}\} +$

$\sum_{2\times\text{es}} \{\{\hat{A}\hat{B}\hat{C}\}\{\hat{D}\hat{E}\}\{\hat{F}\hat{G}\}\} + \ldots + \underbrace{\sum_{\substack{\text{teljesen}\\ \text{kontrahált}}} \{\{\hat{A}\hat{B}\hat{C}\}\{\hat{D}\hat{E}\}\{\hat{F}\hat{G}\}\ldots\}}$

$= \langle \Phi_0 | \{ABC\}\{DE\}\{FG\}\ldots | \Phi_0 \rangle$

- A normálrendezett Hamilton op.

$$\hat{H} = \hat{H}_N + \langle 0|\hat{H}|0\rangle$$

$$\hat{H}_N = \sum_{p,q} f_{pq} \{p^+ q^-\} + \frac{1}{4} \sum_{pqrs} \langle pq||sr\rangle \{p^+ q^+ r^- s^-\}$$

$f_{pq}$: Fock-mátrix

igazolás:

Wick-tétel

$$\hat{H} = \sum_{pq} h_{pq}\, p^+ q^- + \frac{1}{4}\sum_{pqrs} \langle pq||sr\rangle\, p^+ q^+ r^- s^- =$$

$$\sum_{pq} h_{pq} \{p^+ q^-\} + \sum_{pq} h_{pq} \{p^+ q^-\} + \frac{1}{4}\sum_{pqrs}\langle pq||sr\rangle \Big[\{p^+ q^+ r^- s^-\}$$

$\delta_{qr},\ q \in occ.$

$$+ \{p^+ q^+ r^- s^-\} + \{p^+ q^+ r^- s^-\} + \{p^+ q^+ r^- s^-\} + \{p^+ q^+ r^- s^-\}$$

$$+ \{p^+ q^+ r^- s^-\} + \{p^+ q^+ r^- s^-\}\Big] =$$

$$\sum_{pq} h_{pq} \{p^+ q^-\} + \sum_{i \in occ.} h_{ii} + \frac{1}{4}\sum_{pqrs} \langle pq||sr\rangle \{p^+ q^+ r^- s^-\} +$$

$$\sum_{\substack{pq \\ i \in occ.}} \langle pi||qi\rangle \{p^+ q^-\} + \frac{1}{2}\sum_{ij \in occ.} \langle ij||ij\rangle ,$$

mivel $f_{pq} = h_{pq} + \sum_{i \in occ} \langle pi||qi\rangle$ és

$$\langle 0|\hat{H}|0\rangle = \sum_{i \in occ} h_{ii} + \frac{1}{2}\sum_{ij \in occ} \langle ij||ij\rangle$$

$$\hat{H} = \underbrace{\sum_{pq} f_{pq} \{p^+ q^-\} + \frac{1}{4}\sum_{pqrs} \langle pq||sr\rangle \{p^+ q^+ r^- s^-\}}_{\hat{H}_N} + \langle 0|\hat{H}|0\rangle$$

# Az ē korreláció (variációs módszerek)

- Átlagtér közelítés: egydeterminánsos kép
- Az egzakt hullámfv.: $\Psi_{norm.} = C_{HF}\Phi^{HF} + \sum_{ai} c_i^a \Phi_i^a + \sum_{\substack{ab\\ij}} c_{ij}^{ab} \Phi_{ij}^{ab} + \dots$

  ~ CI (Configuration-Interaction) sorfejtés

  $\|\Psi_{norm.}\| = 1$

- Átmeneti normálás: $\Psi = \Phi^{HF} + \sum_{ai} d_i^a \Phi_i^a + \sum_{\substack{ab\\ij}} d_{ij}^{ab} \Phi_{ij}^{ab} + \dots$

  $\langle \Phi^{HF} | \Psi \rangle = 1$

- Korrelációs energia: $\hat{H}\Psi = E\Psi$

$$(\hat{H}_N + \underbrace{\langle \Phi^{HF} | \hat{H} | \Phi^{HF} \rangle}_{E_{HF}})\Psi = E\Psi \Rightarrow \hat{H}_N \Psi = \underbrace{(E - E_{HF})}_{\Delta E \text{ korr. energia}}\Psi$$

$$\boxed{\hat{H}_N \Psi = \Delta E \Psi}$$

$\langle \Phi^{HF} | /$

$$\sum_{\substack{ab\\ij}} \langle \Phi^{HF} | \hat{H}_N | \Phi_{ij}^{ab} \rangle d_{ij}^{ab} \overset{\text{átmeneti norm. + Brillouin-tétel}}{=} \Delta E$$

- csak a 2x-es gerj.-re van szükség?
- a CI koeff. meghatározása kor megjelennek az 1x-es, 3x-os, ... gerjesztések is!

- Full-CI: a teljes CI-sort figyelembe vesszük.
  - az adott bázisban egzakt
  - a det. száma: $\binom{m}{N_\alpha}\binom{m}{N_\beta}$ ⟹ DRÁGA!!!

  $N_\alpha, N_\beta$: $\alpha/\beta$ ē-ok száma

  $m$: bázisfv.-ek száma

- Csonkolhatjuk a sort egy adott gerjesztési szintnél:

  CIS, CISD, CISDT, ... módszerek ~ méretkonzisztencia probléma!

$$\psi^{CISD} = C_{HF}\Phi^{HF} + \sum_{ai} c_i^a \Phi_i^a + \sum_{\substack{ab\\ij}} c_{ij}^{ab}\Phi_{ij}^{ab}$$

az együtthatók meghatározása a variációs elvből:

$$E(\underline{c}) = \frac{\langle \psi^{CISD} | \hat{H} | \psi^{CISD} \rangle}{\langle \psi^{CISD} | \psi^{CISD} \rangle}$$

$$\frac{\partial E}{\partial \underline{c}} = 0 \quad \Rightarrow \quad \underline{\underline{H}}\,\underline{c} = E_{CISD}\,\underline{c}$$

- méretkonzisztencia
  - nem-kölcsönható alrendszerekre: az MO-k vagy az A v. a B alrendszerre lokalizálódnak

$$\left.\begin{aligned} E_{AB}^{UHF} &= E_A^{UHF} + E_B^{UHF} \\ \Phi_{AB}^{UHF} &= \Phi_A^{UHF}\,\Phi_B^{UHF} \end{aligned}\right\} \text{ teljesül a méretkonzisztencia}$$

  - a CID hullámfv.: $\psi^{CID} = \Phi^{HF} + \sum_{\substack{ab\\ij}} d_{ij}^{ab}\Phi_{ij}^{ab} \overset{\text{röviden}}{=} \Phi^{HF} + \eta$

$$\psi_{AB}^{CID} \neq \psi_A^{CID}\,\psi_B^{CID} = \Phi_A^{HF}\Phi_B^{HF} + \eta_A\Phi_B^{HF} + \Phi_A^{HF}\eta_B + \eta_A\eta_B$$

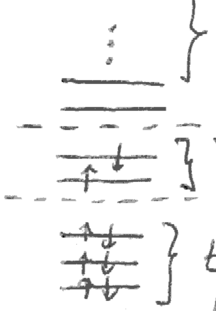
$$\eta_A\eta_B = \sum d_{A\,ij}^{ab}\, d_{B\,kl}^{cd}\, \Phi_{A\,ij}^{ab}\,\Phi_{kl}^{cd} \sim \Phi_{ijkl}^{abcd}$$

4x-es gerjesztés!

$\Rightarrow$ a csonkolt CI módszerek nem méretkonzisztensek!

---

- Complete active space (CAS)
  - kiválasztunk egy aktív alteret:
  - az aktív térben „egzakt" megoldást v. megoldásokat keresünk
  - A CI sorban az „aktív" det.-ok jelennek meg
  - az aktív pályákat is variációsan optimáljuk $\Rightarrow$ MCSCF módszer (multi-configurational self-consistent field)
  - MÉRETKONZISZTENS!



# Perturbáció számítás (Rayleigh–Schrödinger)

$$\hat H = \hat H_0 + \lambda \underbrace{\hat V}_{\text{perturbáció}}, \qquad \hat H_0 \Phi_0 = E_0 \Phi_0$$

Tfh. a $\hat H_0 \Phi_k = E_k \Phi_k$ relációban $E_k$ és $\Phi_k$ $\forall k$-ra adott!

$$\hat H \Psi = E \Psi \qquad \Phi_0 = \Psi^{(0)}$$

$$\Psi = \Phi_0 + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots$$

$$E = E_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$\langle \Phi_0 | \Psi \rangle = 1$, $\boxed{\langle \Phi_0 | \Psi^{(n)} \rangle = 0}$ $n \neq 0$

közbenső normálás

$$(\hat H_0 + \lambda \hat V)(\Phi_0 + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots) = (E_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots)(\Phi_0 + \lambda \Psi^{(1)} + \dots$$

Tfh. $\forall \lambda$-ra teljesül!

0. rend: $\hat H_0 \Phi_0 = E_0 \Phi_0$

1. rend: $\hat H_0 \lambda \Psi^{(1)} + \lambda \hat V \Phi_0 = E_0 \lambda \Psi^{(1)} + \lambda E^{(1)} \Phi_0$

⋮

n. rend: $\hat H_0 \Psi^{(n)} + \hat V \Psi^{(n-1)} = E_0 \Psi^{(n)} + \sum_{k=0}^{n-1} E^{(n-k)} \Psi^{(k)}$

$\langle \Phi_0 |$ $\qquad (E_0 - \hat H_0) \Psi^{(n)} = \hat V \Psi^{(n-1)} - \sum_{k=0}^{n-1} E^{(n-k)} \Psi^{(k)}$

– az energia:

$$\underbrace{\langle \Phi_0 | E_0 - \hat H_0 | \Psi^{(n)} \rangle}_{0} = \langle \Phi_0 | \hat V | \Psi^{(n-1)} \rangle - E^{(n)}$$

$$\Downarrow \quad \boxed{E^{(n)} = \langle \Phi_0 | \hat V | \Psi^{(n-1)} \rangle} \Rightarrow E^{(1)} = \langle \Phi_0 | \hat V | \Phi_0 \rangle$$

– hullámfv.:

1. rend $\quad (E_0 - \hat H_0) \Psi^{(1)} = (\hat V - E^{(1)}) \Phi_0$

$$\hat I = \hat P + \hat Q = |\Phi_0\rangle\langle\Phi_0| + \hat Q$$

rezolvens operátor

$$\hat R = \frac{\hat Q}{E_0 - \hat H_0}$$

( ha $\hat H_0 \Phi_k = E_k \Phi_k$ $\quad k = 0, 1, \dots$

$\hat R \Phi_k = \dfrac{1}{E_0 - E_k}$, ha $k \neq 0$

$\hat R \Phi_0 = 0$ )

$\hat R$ az $(\hat H_0 - E_0)$ op. inverze a $\Phi_0$-ra merőleges altéren!

( $\hat H_0 |\Phi_k\rangle = E_k |\Phi_k\rangle \Rightarrow \hat R = \sum_{k \neq 0} \dfrac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k}$ )

$$\hat{R}\,(E_0-\hat{H}_0)\,\Psi^{(1)} = \hat{R}\,\hat{V}\,\Phi_0 \,,$$

mivel $\langle \Psi^{(1)} | \Phi_0 \rangle = 0$ $\quad \Psi^{(1)} = \hat{R}\,\hat{V}\,\Phi_0$

$$E^{(2)} = \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle = \langle \Phi_0 | \hat{V}\,\hat{R}\,\hat{V} | \Phi_0 \rangle$$

$$\hat{Q} = \sum_{k \neq 0} | \Phi_k \rangle \langle \Phi_k |$$

$$\hat{R} = \sum_{k \neq 0} \frac{| \Phi_k \rangle \langle \Phi_k |}{E_0 - E_k}$$

$$E^{(2)} = \sum_{k \neq 0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{E_0 - E_k}$$

2. rend $\quad (E_0-\hat{H}_0)\,\Psi^{(2)} = \hat{V}\,\Psi^{(1)} - E^{(2)}\Phi_0 - E^{(1)}\Psi^{(1)}$

$\hat{R}\ / \quad \Psi^{(2)} = \hat{R}\,\hat{V}\,\Psi^{(1)} - E^{(1)}\hat{R}\,\Psi^{(1)}$ $\qquad \hat{R}\Phi_0 = 0$

$$\Psi^{(2)} = \hat{R}\,\hat{V}\,R\,\hat{V}\,\Phi_0 - E^{(1)}\,\hat{R}\,\hat{R}\,\hat{V}\,\Phi_0$$

$$E^{(3)} = \sum_{\substack{k \neq 0 \\ l \neq 0}} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_l \rangle \langle \Phi_l | \hat{V} | \Phi_0 \rangle}{(E_0-E_k)(E_0-E_l)}$$

$$- E^{(1)} \sum_{k \neq 0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{(E_0-E_k)^2} \quad \hat{R}^2$$

3. rend

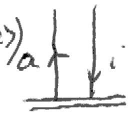
$$\Psi^{(3)} = \hat{R}\hat{V}\hat{R}\hat{V}\hat{R}\hat{V}\Phi_0 - E^{(1)}\hat{R}\hat{V}RR\hat{V}\Phi_0 - E^{(1)^2}\hat{R}\hat{R}\hat{R}\,V\Phi_0$$

$$- E^{(1)}\hat{R}\hat{R}\hat{V}\hat{R}V\Phi_0 - \hat{E}^{(2)}\hat{R}\hat{R}\hat{V}\,\Phi_0$$

$$E^{(4)} = \langle \Phi_0 | \hat{V}\hat{R}\hat{V}\hat{R}\hat{V}\hat{R}\hat{V} | \Phi_0 \rangle - E^{(1)} \langle \Phi_0 | \hat{V}\hat{R}\hat{V}\hat{R}\hat{R}\hat{V} | \Phi_0 \rangle$$

$$- E^{(1)} \langle \Phi_0 | \hat{V}\hat{R}\hat{R}\hat{V}\hat{R}V | \Phi_0 \rangle - E^{(1)^2} \langle \Phi_0 | \hat{V}\hat{R}\hat{R}\hat{R}V | \Phi_0 \rangle - E^{(2)} \langle \Phi_0 | \hat{V}\hat{R}\hat{R}\hat{V} | \Phi_0 \rangle$$

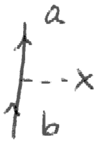
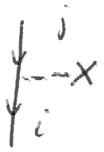
- Diagramok
  - lyukak és részecskék

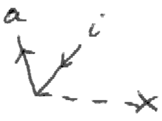
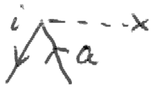
$|\Phi_i^a\rangle = \{a^+ i^-\}|0\rangle \; (= a^+ i^- |0\rangle)$  $\{a^+ i^-\}|0\rangle$ ~ részecske–lyuk pár

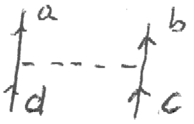
↑ : virtuális $\qquad |0\rangle$ ~ Fermi-vákuum

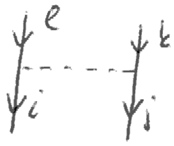
↓ : betöltött

  - a $\hat{H}_N$ diagramok (antiszimmetrikus Goldstone-diagramok)

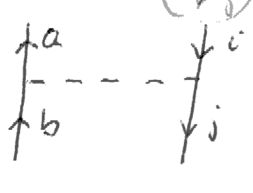
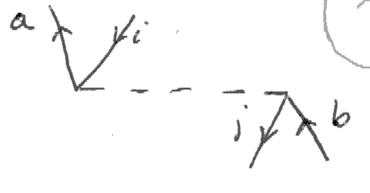
$f_{ab}\{a^+ b^-\}$  $\quad f_{ij}\{i^+ j^-\}$  ~ a keltő op.-ok kifelé, az eltüntető op.-ok befelé futnak!

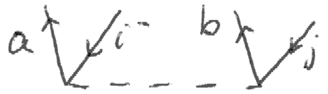
$f_{ai}\{a^+ i^-\}$  $\quad f_{ia}\{i^+ a^-\}$ 

$\langle ab||dc\rangle\{a^+ b^+ c^- d^-\}$  ~ szabály: ⟨leftout rightout || leftin rightin⟩

$\langle ij||ek\rangle\{i^+ j^+ k^- e^-\}$ 

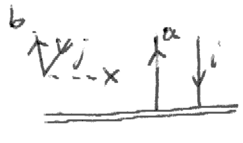
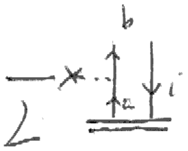
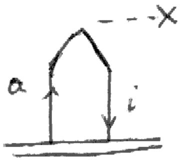
$\langle aj||bi\rangle\{a^+ j^+ i^- b^-\} = \langle aj||ib\rangle\{a^+ j^+ b^- i^-\}$

 =  (~ vertex)

$\langle ab||ij\rangle\{a^+ b^+ j^- i^-\}$ 

stb....

  - példa: $\hat{F}_N|\Phi_i^a\rangle = \sum_{p,q} f_{pq}\{p^+ q\}\{a^+ i\}|0\rangle =$

$\sum_{b,j}$  $+ \sum_b$  $+ \sum_j$  $+$  $=$

$$\left\{\sum_{b,j} f_{bj}\{b^+ a^+ i^- j^-\} + \sum_b f_{ba}\{b^+ i^-\} + \sum_j f_{ij}\{a^+ j^-\} + f_{ai}\right\}|0\rangle$$