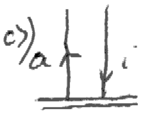
- Diagramok

  - lyukak és részecskék

$|\Phi_i^a\rangle = \{a^+ i^-\}|0\rangle (= a^+ i^- |0\rangle)$



$\{a^+ i^-\}|0\rangle$ ~ részecske–lyuk pár

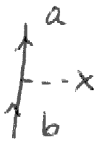
↑ : virtuális

$|0\rangle$ ~ Fermi-vákuum

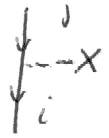
↓ : betöltött

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

$f_{ab}\{a^+ b^-\}$

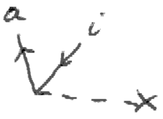


$f_{ij}\{i^+ j^-\}$

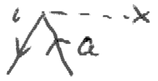


~ a keltő op.-ok kifelé, az eltüntető op.-ok befelé futnak!

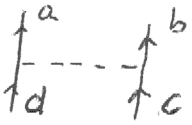
$f_{ai}\{a^+ i^-\}$



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

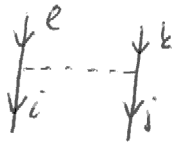


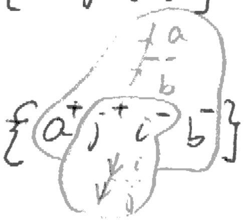
$\langle ab||dc\rangle\{a^+ b^+ c^- d^-\}$



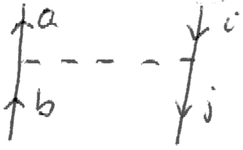
~ szabály:
⟨leftout rightout|| leftin rightin⟩

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

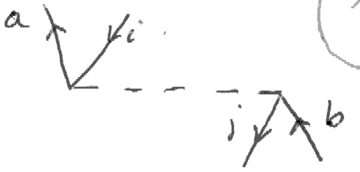


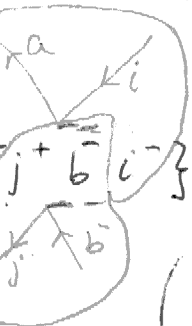


$\langle aj||bi\rangle\{a^+ j^+ i^- b^-\} = \langle aj||ib\rangle\{a^+ j^+ b^- i^-\}$



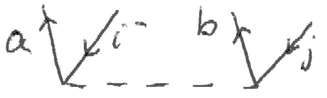
=





(---- / ---x } ~ vertex)

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

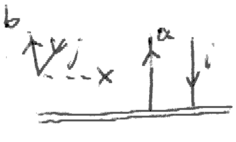


stb. ...

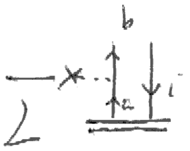
  - példa: $\hat{F}_N|\Phi_i^a\rangle = \sum_{p,q} f_{pq}\{p^+ q^-\}\{a^+ i^-\}|0\rangle =$

2.
3.
4.

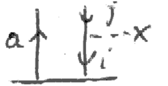
$\sum_{b,j}$



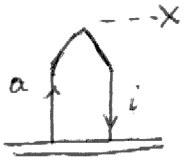
$+ \sum_b$



$+ \sum_j$



+



=

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

- Many-Body PT (MBPT)

$$\hat{H} = \underbrace{\langle\Phi_0|\hat{H}|\Phi_0\rangle + \sum_p f_{pp}\{p^+p^-\}}_{\hat{H}_0} + \underbrace{\frac{1}{4}\sum_{pqrs}\langle pq||sr\rangle\{p^+q^+r^-s^-\}}_{\hat{V}=\hat{V}_N}$$

$\varepsilon_i = f_{ii}$, $i \in occ$

$\varepsilon_a = f_{aa}$, $a \in virt$

$\hat{V} = \hat{V}_N \rightarrow f_{ai} = 0$ (HF kanonikus bázis)

$$\hat{H}_0|\Phi_0\rangle = E_{HF}|\Phi_0\rangle$$

$$\hat{H}_0|\Phi_i^a\rangle = (E_{HF} + \varepsilon_a - \varepsilon_i)|\Phi_i^a\rangle \qquad \left(= (\langle 0|H|0\rangle + f_{aa}a^+a^- - f_{ii}i^-i^+)|\Phi_i^a\rangle\right)$$

$$\hat{H}_0|\Phi_{ij}^{ab}\rangle = (E_{HF} + \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)|\Phi_{ij}^{ab}\rangle$$

$$\vdots$$

$$''(H_0 - E_0)^{-1}'' = \hat{R} = \sum_{I\neq 0}\frac{|\Phi_I\rangle\langle\Phi_I|}{E_0 - E_I},$$

$\hat{H}_0|\Phi_0\rangle = E_0|\Phi_0\rangle$,

$\hat{H}_0|\Phi_I\rangle = E_I|\Phi_I\rangle$

$$\hat{R} = \sum_{i,a}\frac{|\Phi_i^a\rangle\langle\Phi_i^a|}{\varepsilon_i - \varepsilon_a} + \sum_{\substack{ab\\ij}}\frac{|\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}|}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \ldots$$

$$\hat{R} = \hat{R}_N = \sum_{ai}\frac{\{a^+i^-\}|\Phi_0\rangle\langle\Phi_0|\{i^+a^-\}}{\varepsilon_i - \varepsilon_a} + \sum_{\substack{ab\\ij}}\frac{\{a^+b^+j^-i^-\}|\Phi_0\rangle\langle\Phi_0|\{i^+j^+b^-a^-\}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \ldots$$

automatikusan normálrendezett!

$$E^{(1)} = \langle\Phi_0|\hat{V}_N|\Phi_0\rangle = 0$$

ált. Wick-tétel

$$E^{(2)} = \langle\Phi_0|\hat{V}_N\hat{R}_N\hat{V}_N|\Phi_0\rangle = \sum_{ai}\frac{\langle\Phi_0|\hat{V}_N\{a^+i^-\}|\Phi_0\rangle\langle\Phi_0|\{i^+a^-\}\hat{V}_N|\Phi_0\rangle}{\varepsilon_i - \varepsilon_a} + \boxed{\sum_{\substack{ab\\ij}}}\frac{\langle\Phi_0|\hat{V}_N\{a^+b^+j^-i^-\}|\Phi_0\rangle\langle\Phi_0|\{i^+j^+b^-a^-\}\hat{V}_N|\Phi_0\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

ha nincs 1e⁻ tag a $\hat{V}$-ban, akkor kiesik.

- az „i" és az „a" a két oldalon kontrahált a $\hat{V}_N$-el!
- az „i" és az „a" indexek definiálják a nevezőt!
- az „a" és az „i" indexeken keresztül a $\hat{V}_N$-op.-ok indexei is egybe esnek, kontrahálódnak

$$= \langle\Phi_0|\hat{V}_N\hat{R}_N\hat{V}_N|\Phi_0\rangle$$

- az $\hat{R}_N$ közvetíti a kontrakciót a V_N-ek között
- az R_N nevezőit a fölötte elhúzott kontrakciók adják

- csak a teljesen kontrahált tagok adnak járulékot!
- $\hat{R}$ „szimmetrikus" az indexekre

- Møller-Plesset PT (MP PT)

$\hat{H} = \underbrace{\hat{F}_{N_{e^-}}}_{\hat{H}_{0_{MP}}} + \hat{V}_{MP}$, ahol $\hat{F}_{N_{e^-}}$ az N-elektronos Fock-op.: $\hat{F}_{N_{e^-}} = \sum_{i=1}^{N_{e^-}} \hat{f}(x_i) =$

$$\overline{\sum_{pq}} f_{pq}\; p^+ q^-$$

- ez a particionálás független a betöltött pályák megválasztásától! (az $\hat{f}$ op. invariáns a betöltött pályák forgatására)

$$\hat{F} \underset{\uparrow}{=} \overline{\sum_{p}} f_{pp}\; p^+ p^- = \overline{\sum_{p}} f_{pp}\; \overline{p^+ p^-} + \overline{\sum_{p}} f_{pp} \{p^+ p^-\}$$

HF kanonikus bázisban

$$= \overline{\sum_{i \in occ}} \varepsilon_i + \overline{\sum_{p}} f_{pp} \{p^+ p^-\}$$

$$\left.\begin{aligned} H_{0_{MP}} - \overline{\sum_i} \varepsilon_i &= H_{0_{MBPT}} - \langle 0|\hat{H}|0\rangle \\ V_{MP} + \overline{\sum_i} \varepsilon_i &= V_{MBPT} + \langle 0|\hat{H}|0\rangle \end{aligned}\right\} \oplus \; = \hat{H}$$

$$\hat{V}_{MP} = \hat{V}_{MBPT} + \langle 0|\hat{H}|0\rangle - \overline{\sum_i} \varepsilon_i$$

$E^{(0)}_{MP} = \langle 0|\hat{F}|0\rangle = \overline{\sum_i} \varepsilon_i$; $\quad E^{(0)}_{MBPT} = \langle 0|\hat{H}|0\rangle$

$E^{(1)}_{MBPT} = \langle 0|\hat{V}_{MP}|0\rangle = \langle 0|\hat{H}|0\rangle - \overline{\sum_i} \varepsilon_i$; $\quad E^{(1)}_{MBPT} = 0$

$$E^{(0)}_{MP} + E^{(1)}_{MP} = E^{(0)}_{MBPT} + E^{(1)}_{MBPT}$$

$$E^{(2)}_{MP} = E^{(2)}_{MBPT}$$

$$E^{(3)}_{MP} = E^{(3)}_{MBPT}$$

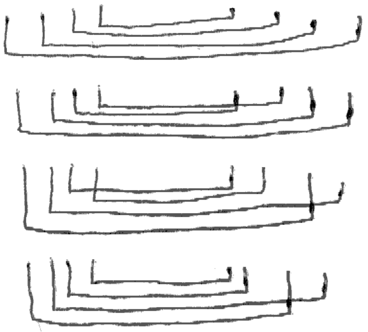
$$\vdots$$

stb.

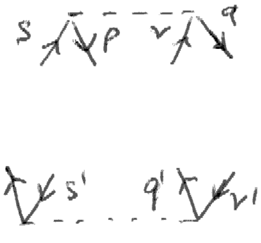
- kanonikus bázisban az MP és MBPT formalizmus gyakorlatilag ua.

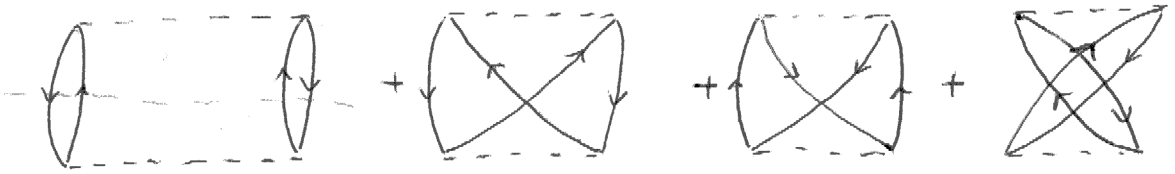
$\langle\Phi_0|\hat{V}\hat{R}\hat{V}|\Phi_0\rangle$

$$E^{(2)} = \frac{1}{16}\overline{\sum_{pqrs}}\ \overline{\sum_{p'q'r's'}} \langle pq||sr\rangle\langle p'q'||s'r'\rangle\langle\Phi_0|\{p^{+}q^{+}\bar{r}\bar{s}\}\hat{R}\{p'^{+}q'^{+}r'^{-}s'^{-}\}|\Phi_0\rangle$$



Csak azok a kontrakciók nem nullák, amelyeknél r', s', p és $q \in$ occ. és q', p', r és $s \in$ virt.



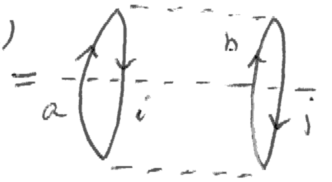


- 4 azonos értékű kontrakciós séma elég 1-et megtartani és a „kiértékelésnél" egy szorzóval figyelembe venni a többit.
  → maximáljuk a hurkok számát!

⇓

- Diagram szabályok

$$E^{(2)} =$$



$$= \frac{1}{4}\overline{\sum_{abij}} \frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

1, ↑ virt. ↓ occ.

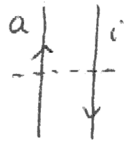
2, $\langle LO\ RO || LI\ RI\rangle$

3, összegzés a (nem nyílt) vonalakra

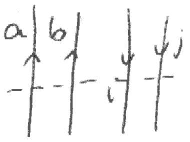
4, előjel: $(-1)^{h+l}$ h: betöltött vonalak száma
l: hurkok száma

5, $\left(\frac{1}{2}\right)^n$ szorzó, ahol n az ekvivalens vonalak száma
(azonos vertexből induló és azonos vertexbe érkező virt-virt v. occ-occ párok)

6, nevező:



$\rightarrow \frac{1}{\varepsilon_i-\varepsilon_a}$



$\rightarrow \frac{1}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$

7, ekvivalens vertexek: $\frac{1}{2}$-es szorzó

8, az ekvivalens nyílt vonalak permutációját is figyelembe kell venni!

– A diagram szabályok „igazolása"

– szorzófaktor:

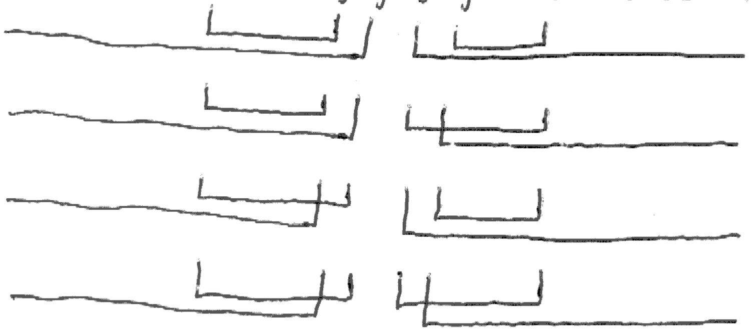
$$\ldots \underset{i.}{\frac{1}{4}} \ldots \underset{j.}{\frac{1}{4}} \underset{k.}{\frac{1}{4}} \ldots \langle p_i q_i || s_i r_i \rangle \ldots \langle p_j q_j || s_j r_j \rangle \langle p_k q_k || s_k r_k \rangle \ldots \{ p_i^+ q_i^+ r_i s_i \} \ldots \{ p_j^+ q_j^+ r_j s_j \} \{ p_k^+ q_k^+ r_k s_k \} \ldots$$

Figyeljük a j-edik integrálhoz tartozó kontrakciókat!

– ha a kiemelt integrálon nincs ekvivalens kontrakciópár 4 db azonos értékű kontrakciós sémát találunk:

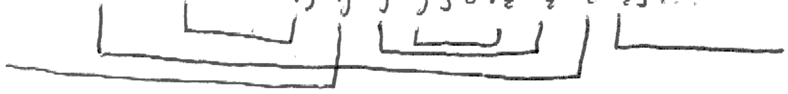
a négy db kontr. sémát 1 db diagram reprezentálja ⟹ a 4-es szorzó „kiöltja" a j-edik $\frac{1}{4}$-es faktort

$$\ldots \{ p_i^+ q_i^+ r_i s_i \} \ldots \{ p_j^+ q_j^+ r_j s_j \} \{ p_k^+ q_k^+ r_k s_k \} \ldots$$



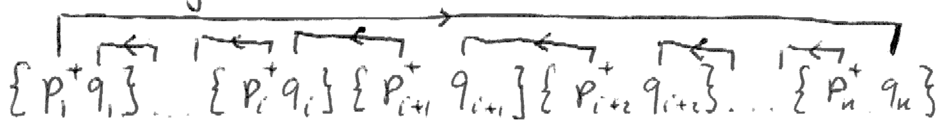
– ha a j-edik és k-adik integrált ekvivalens kontrakciópár köti össze:

$$\ldots \{ p_i^+ q_i^+ r_i s_i \} \ldots \{ p_j^+ q_j^+ r_j s_j \} \{ p_k^+ q_k^+ r_k s_k \} \ldots$$

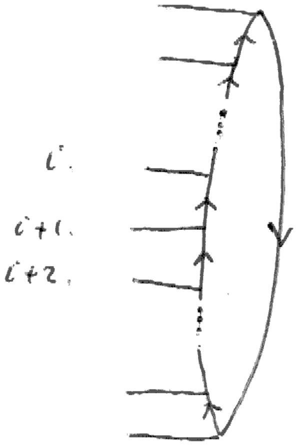


a j-edik és k-adik integrálokhoz tartozó kontrakciók „lábait" felcserélgetve csak 8 db kontrakciós sémát kapunk, mert az $r_j \longleftrightarrow s_j$, $p_k \longleftrightarrow q_k$ szimultán csere nem ad új tagot. ⟹ az $\underset{j.}{\frac{1}{4}} \underset{k.}{\frac{1}{4}}$ faktort is figyelembe véve egy $\frac{1}{2}$-es szorzót kapunk. ⟹ Ha n db ekvivalens kontrakció van, $\left(\frac{1}{2}\right)^n$ szorzót kapunk.

– az előjel:

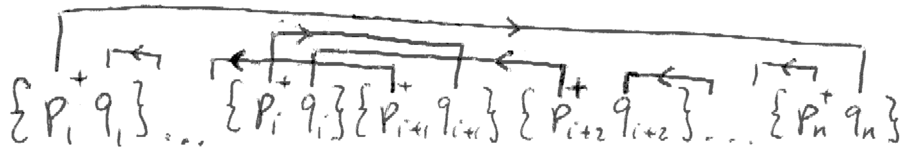


$\{p_1^+ q_1\} \dots \{p_i^+ q_i\}\{p_{i+1}^+ q_{i+1}\}\{p_{i+2}^+ q_{i+2}\} \dots \{p_n^+ q_n\}$

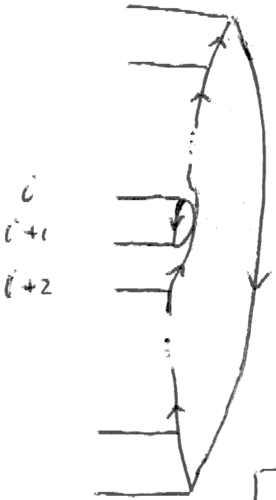


1 hurok, 1 occ. $(\ell=1, h=1)$

pozitiv előjel

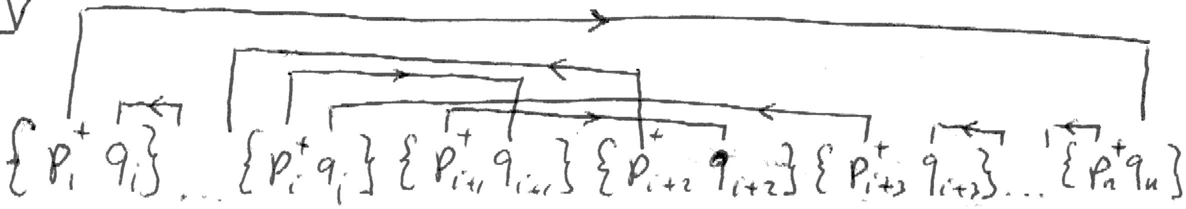


$\{p_1^+ q_1\} \dots \{p_i^+ q_i\}\{p_{i+1}^+ q_{i+1}\}\{p_{i+2}^+ q_{i+2}\} \dots \{p_n^+ q_n\}$

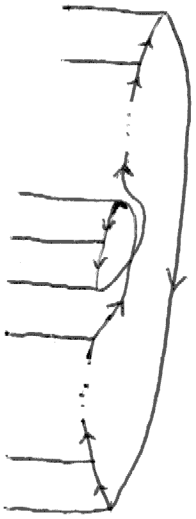


1 hurok, 2 occ. $(\ell=1, h=2)$

negativ előjel



$\{p_1^+ q_1\} \dots \{p_i^+ q_i\}\{p_{i+1}^+ q_{i+1}\}\{p_{i+2}^+ q_{i+2}\}\{p_{i+3}^+ q_{i+3}\} \dots \{p_n^+ q_n\}$

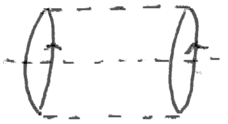


1 hurok, 3 occ $(\ell=1, h=3)$

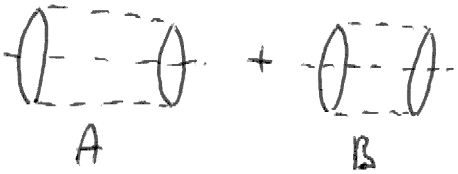
pozitiv előjel

stb... $\Rightarrow (-1)^{h+\ell}$

– MBPT(2)

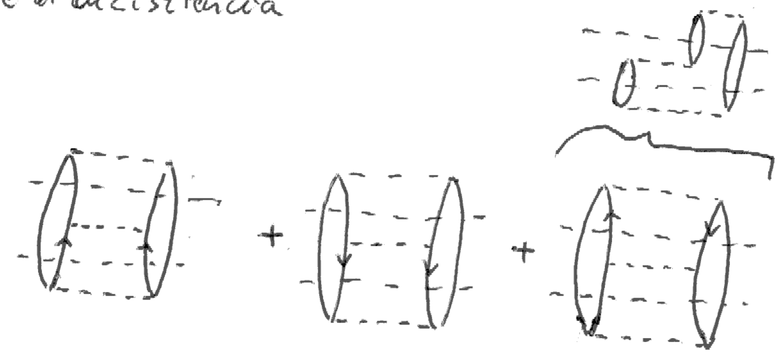
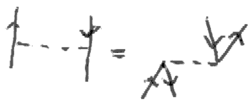
$E^{(2)} =$  $\sim n_{occ}^2 n_{virt}^2$ $\sim n^4$

– az MBPT(2) méretkonzisztens, mert az egymástól elszeparált A és B alrendszereken lokalizált integrálokra

$E^{(2)} =$ 

Az MBPT(2) energia összefüggő diagramból számolható (connected)
=> méretkonzisztencia

– MBPT(3)

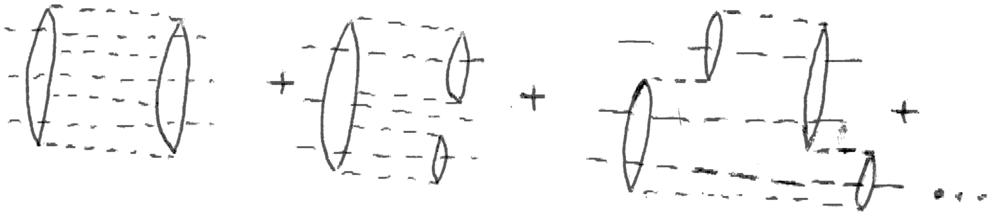
$E^{(3)} =$  , mert 

$(E^{(1)}=0\ !)$

az első a legdrágább $\sim n_{occ}^2 n_{virt}^4$ $\sim n^6$

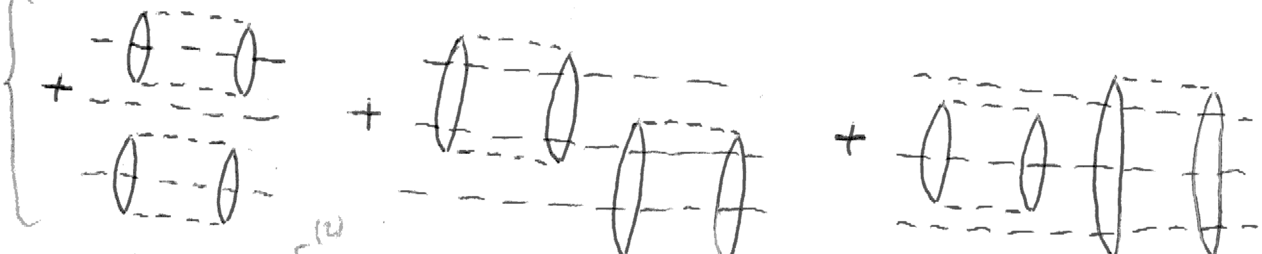
az MBPT(3) energia is connected => szintén méretkonzisztens

– MBPT(4)

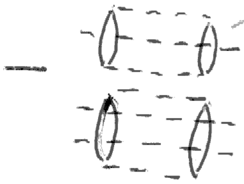
$E^{(4)} =$ 

connected tagok

ez a tag nulla!



disconnected tagok

–  $\rightarrow E^{(2)}$ ← renormálási tag

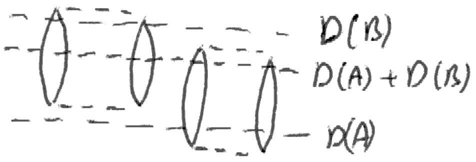
$= \langle \Phi_0 | \hat{V}_N \hat{R} \hat{V}_N \hat{R} \hat{V}_N R \hat{V}_N | \Phi_0 \rangle - E^{(2)} \langle \Phi_0 | \hat{V}_N \hat{R} \hat{R} \hat{V} | \Phi_0 \rangle$

- Az első tag disconnected járulékainak összege kiejti a renormálási tagot!

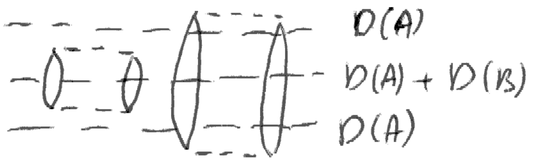
Koncentráljunk a nevezőkre!

pl. $D(A) = \varepsilon_a - \varepsilon_i$,

$D(B) = \varepsilon_b + \varepsilon_c - \varepsilon_j - \varepsilon_k$

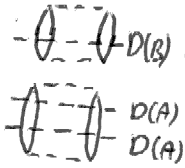


+



$$\sim \frac{1}{D(A)\,D(B)\,(D(A)+D(B))} + \frac{1}{D(A)\,D(A)\,(D(A)+D(B))} = \frac{1}{D^2(A)\,D(B)}$$

ez épp kiejti a –



renormálási tagot!

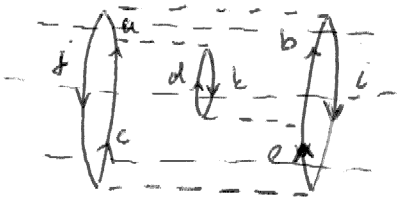
$$E^{(4)} = \langle \Phi_0 | \hat{V}_N \hat{R} \hat{V}_N \hat{R} \hat{V}_N \hat{R} \hat{V}_N | \Phi_0 \rangle_c \Rightarrow$$ az MBPT(4) is méretkonzisztens

linked cluster tétel: az MBPT minden rendben connected

$$E^{(n)} = \langle \Phi_0 | \hat{V}_N \hat{R} \hat{V}_N \hat{R} \ldots \hat{R} \hat{V}_N | \Phi_0 \rangle_c \quad (n \text{ db } \hat{V}_N)$$

- intermedierek segítségével az $E^{(4)}$ n^7-el számolható

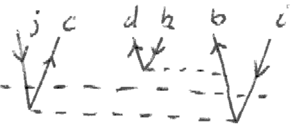
pl.:



$\sim n_{occ}^3 n_{virt}^5$

$$= \frac{1}{2} \sum_{ijk} \sum_{cdb} \frac{U^{cbd}_{jik}\, U^{bcd}_{ijk}}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_b - \varepsilon_c - \varepsilon_d}$$, ahol

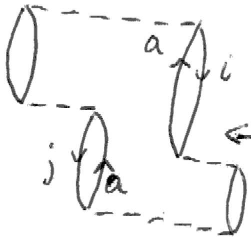
$U^{bcd}_{ijk} =$



$$U^{bcd}_{ijk} = \sum_{e \in virt} \frac{\langle db||ke \rangle \langle ce||ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$\sim n_{occ}^3 n_{virt}^4$

- az MBPT(4) diagramjaiban megjelennek nem fizikai járulékok: exclusion principle violating terms (EPV)



$\leftarrow \Phi^{aa}_{ij}$

- be lehet látni, hogy ezek kiejtik egymást. Ezt a tagot a

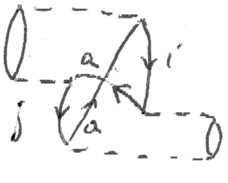


diagram ejti ki.