diagrams pt. 2

Coefficient Graphs

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recall that $G = (O, L, h, \tau)$

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$O \downarrow$ m-electron operators

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what about $\langle \Phi_{ij}^{ab} | H_c \Omega | \Phi \rangle$?

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$\tilde{a}_{ab}^{ij}$

Coefficient Graphs

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what about $\langle \Phi_{ij}^{ab} | H_c \Omega | \Phi \rangle$?

$\downarrow$

$\tilde{a}_{ab}^{ij}$

(bare excitation operator)

Coefficient Graphs

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a neat trick:

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$$\tilde{a}^{i}_{a}$$

Coefficient Graphs

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$$\tilde{a}_a^{\,i} = \bar{\delta}_{i'}^{\,a'} \, \tilde{a}_{a'}^{\,i'}$$

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Coefficient Graphs

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$$\tilde{a}^{ij}_{ab} = \left(\frac{1}{2!}\right)^{2} \bar{\delta}^{a'b'}_{i'j'} \tilde{a}^{i'j'}_{a'b'}$$

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interaction tensor

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interaction tensor

Try it out!

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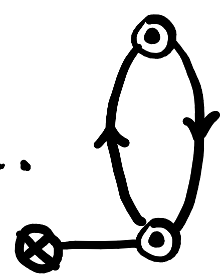
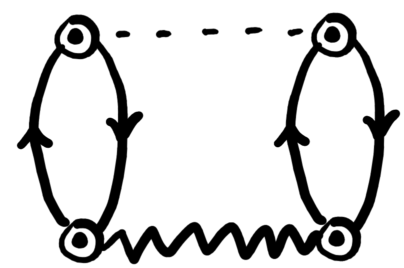
interaction tensor

Try it out!

1. 

2. 

Coefficient Graphs

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notation

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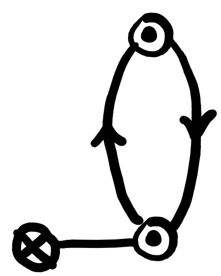

Coefficient Graphs

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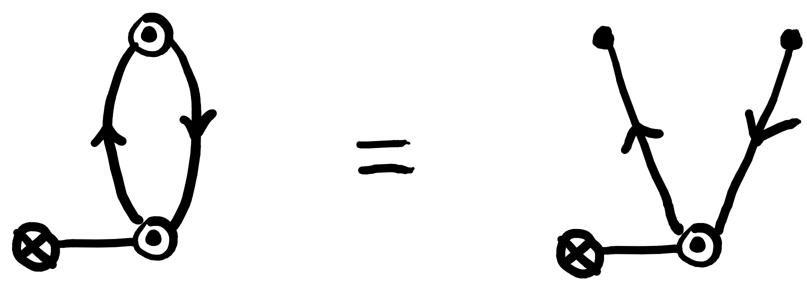

Coefficient Graphs

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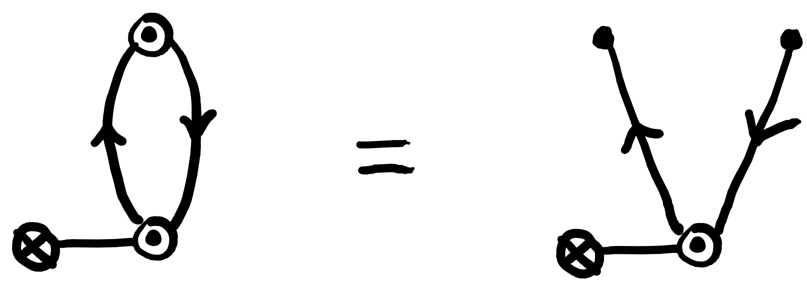

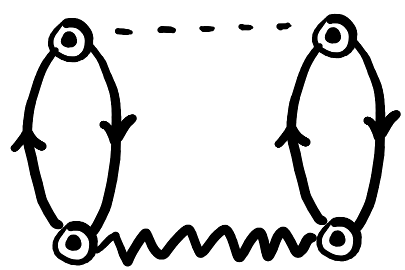

Coefficient Graphs

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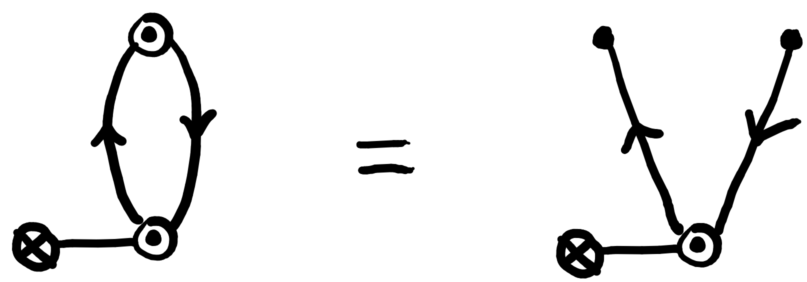

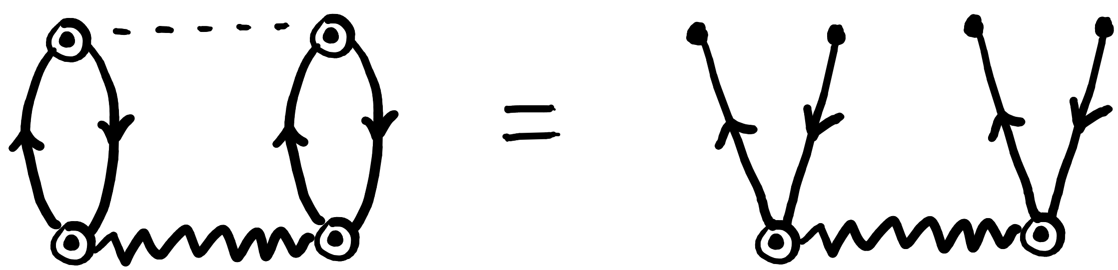

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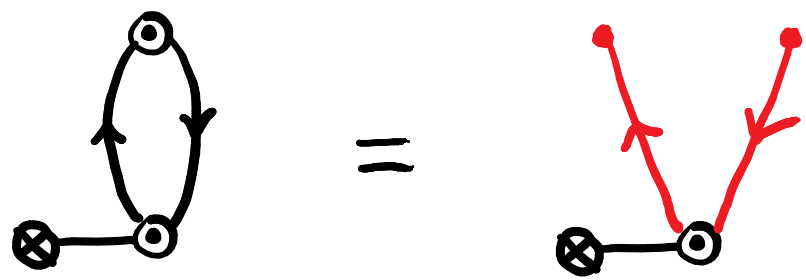

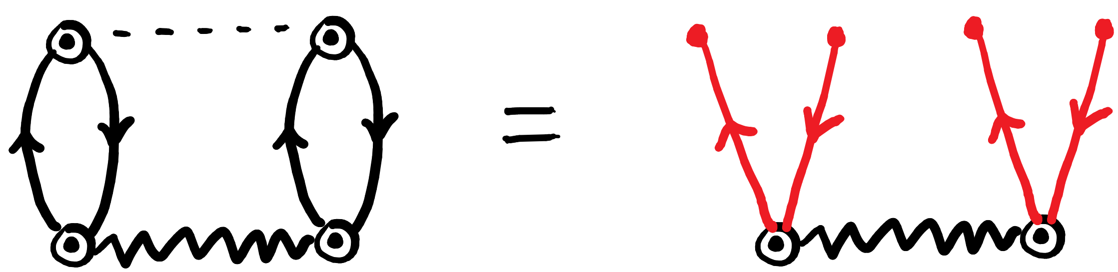

coefficient lines

Coefficient Graphs

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useful result:

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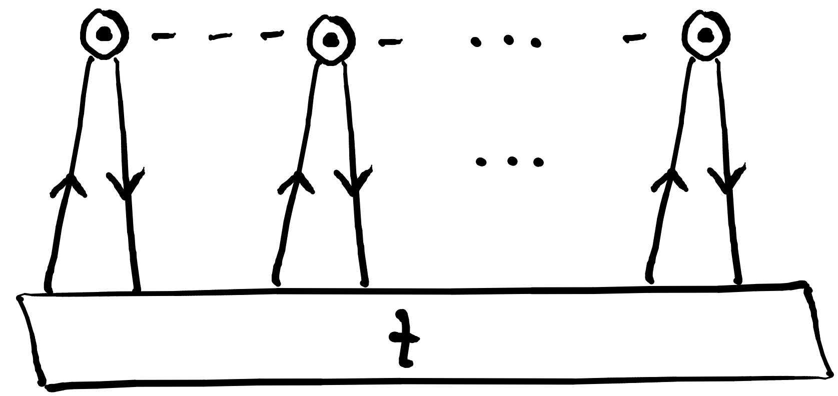
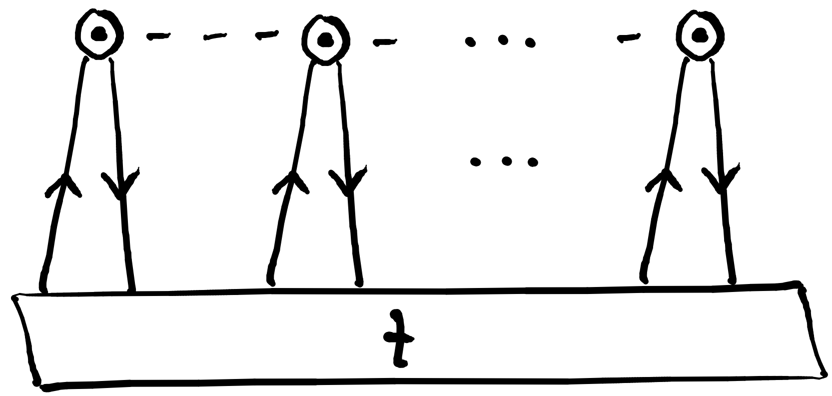


Coefficient Graphs

useful result:



$$\frac{1}{|P_1|! \cdots |P_n|!\,|Q_1|! \cdots |Q_k|!}\;\hat{P}^{(p_1/\cdots/p_m)}_{(q_1/\cdots/q_m)}\; t^{p_1 \cdots p_m}_{q_1 \cdots q_m}$$

Coefficient Graphs

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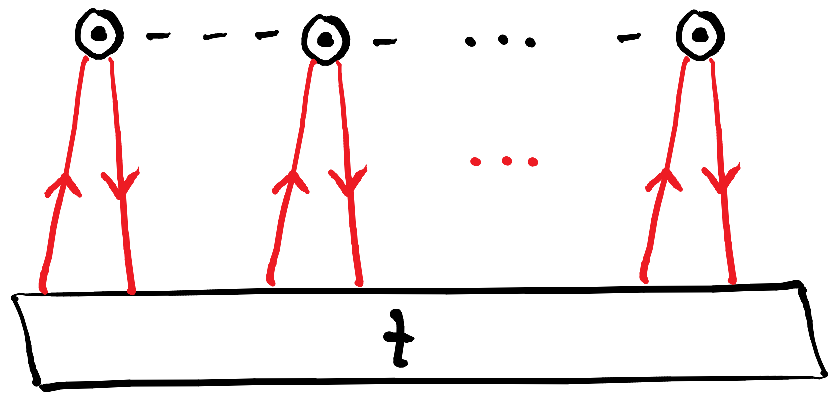

coeff lines

$$\frac{1}{|P_1|!\cdots|P_h|!\,|Q_1|!\cdots|Q_k|!}\,\hat{P}^{(p_1/\cdots/p_m)}_{(q_1/\cdots/q_m)}\, t^{p_1\cdots p_m}_{q_1\cdots q_m}$$

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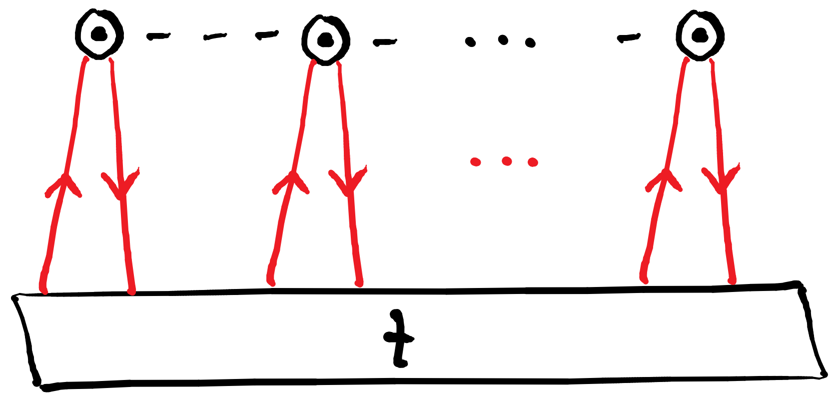

coeff lines

$$\frac{1}{|P_1|!\cdots|P_h|!\,|Q_1|!\cdots|Q_k|!}\,\hat{P}^{(p_1,\cdots,p_m)}_{(q_1,\cdots,q_m)}\,t^{p_1\cdots p_m}_{q_1\cdots q_m}$$

equiv. coeff lines factor

Coefficient Graphs

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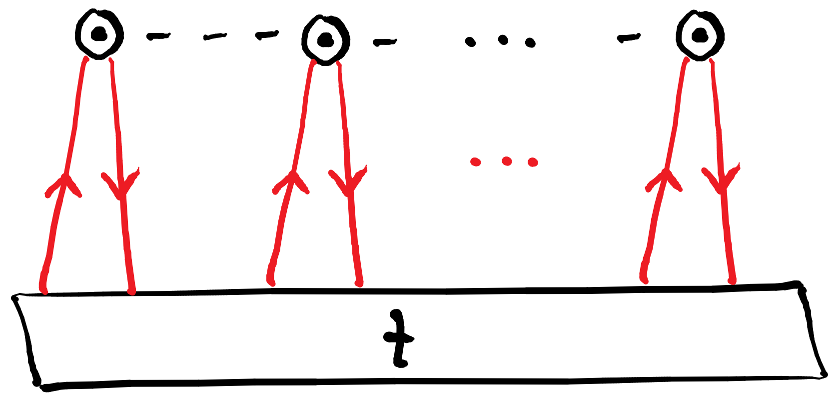

coeff lines

$$\frac{1}{|P_1|!\cdots|P_n|!\,|Q_1|!\cdots|Q_k|!}\,\hat{P}^{(p_1/\cdots/p_m)}_{(q_1/\cdots/q_m)}\,t^{p_1\cdots p_m}_{q_1\cdots q_m} = \hat{P}^{(P_1/\cdots/P_n)}_{(Q_1/\cdots/Q_k)}\,t^{p_1\cdots p_m}_{q_1\cdots q_m}$$

equiv. coeff lines factor

Coefficient Graphs

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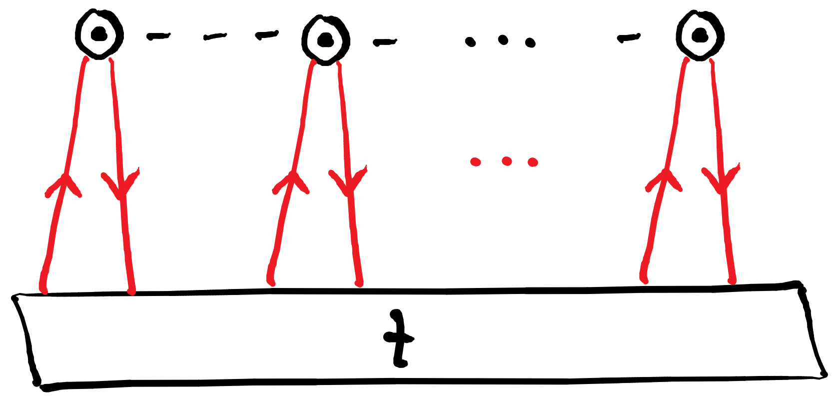

coeff lines

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equiv. coeff lines factor

antisymmetrize inequiv. coeff lines

Other useful rules:

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1. open cycle $= (-)^n a^p_q$

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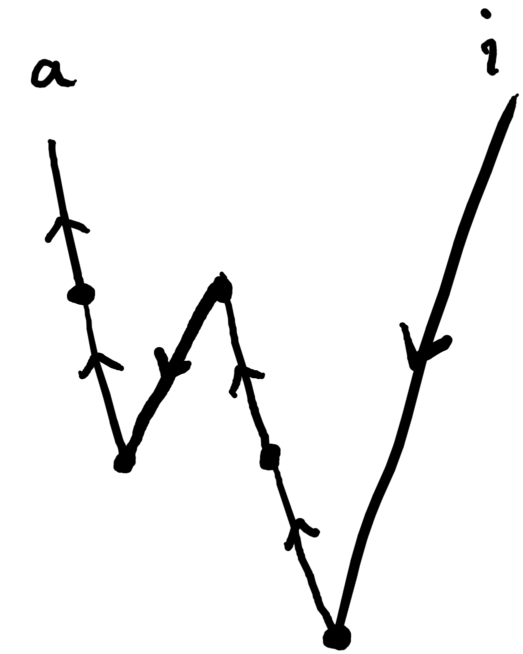
1. open cycle $= (-)^n a_q^p$ 

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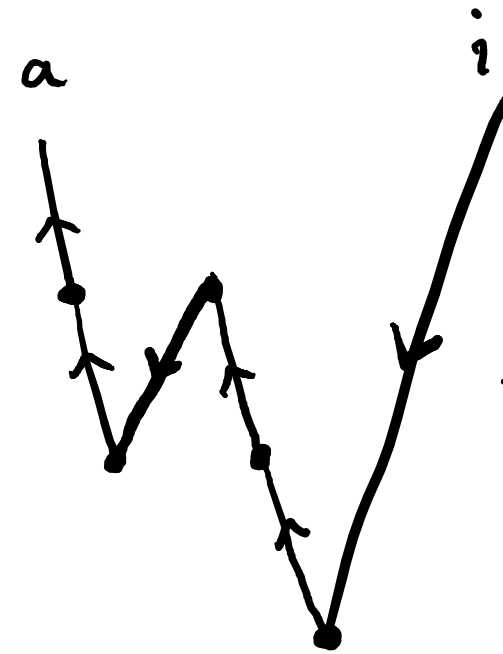

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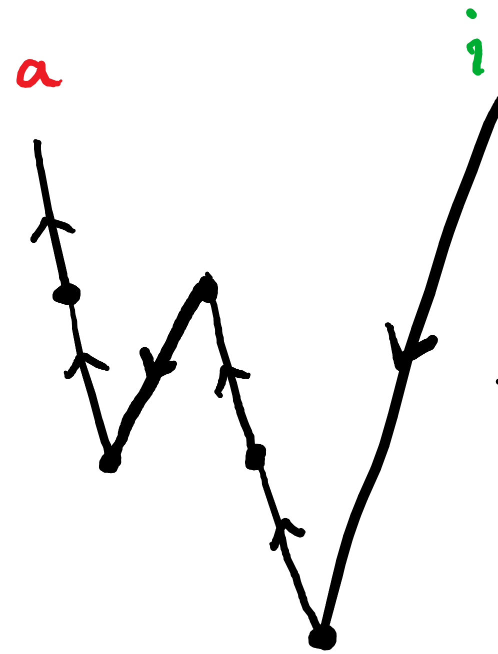

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Other useful rules:

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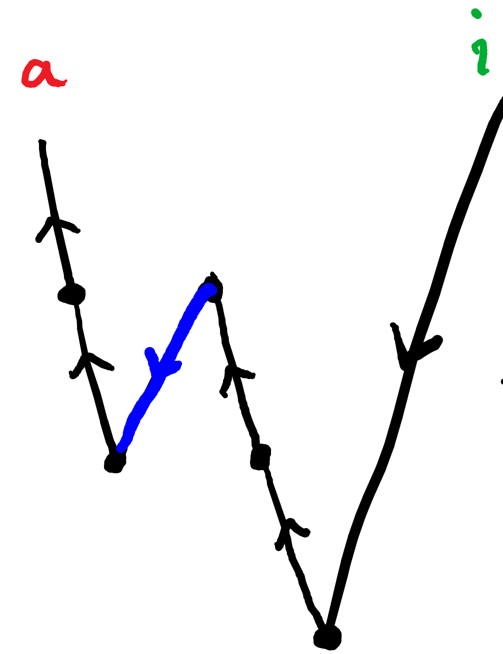
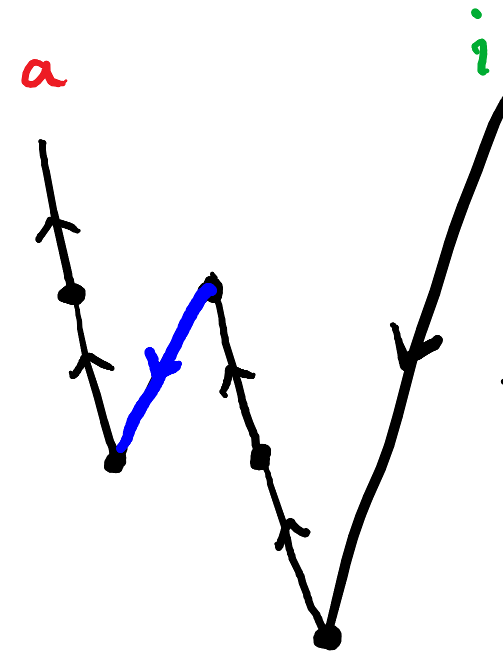


$= (-)^{1} a^{a}_{i}$

Other useful rules:

1. open cycle $= (-)^h a_q^p$



$= (-)^1 a_i^a$

2. loop $= (-)^{h+1}$

Wick's Thm for Graphs:

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$$G = :G: + \sum_{c}^{Ctr(G)} :c(G):$$

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$$G = :G: + \underbrace{\sum_{c}^{C\,\mathrm{tr}(G)} :c(G):}_{\text{unique graph contractions}}$$

CID/CCD

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CID/CCD

$$\Psi_{CID} = (1 + C_2)\Phi$$

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energy:

CID/CCD

$$H_c \Psi = E_c \Psi$$

$$\Psi_{CID} = (1 + C_2)\Phi$$

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energy: $\langle \Phi | H_c (1 + C_2) | \Phi \rangle = E_c$

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$$H_c \Psi = E_c \Psi$$

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energy: $\langle \Phi | H_c (1 + C_2) | \Phi \rangle = E_c$

coeff:

CID/CCD

$$H_c \Psi = E_c \Psi$$

$$\Psi_{CID} = (1 + C_2)\Phi$$

$$\Psi_{CCD} = \exp(C_2)\Phi$$

energy: $\langle \Phi | H_c (1 + C_2) | \Phi \rangle = E_c$

coeff: $\langle \Phi_{ij}^{ab} | H_c (1 + C_2) | \Phi \rangle = E_c \, c_{ab}^{ij}$

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$$+ \frac{1}{2} \langle \Phi_{ij}^{ab} | H_c C_2^2 | \Phi \rangle$$

CID/CCD energy

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E_c

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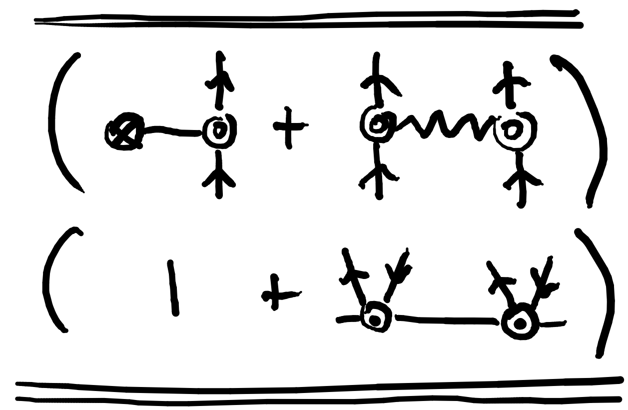

CID/CCD energy

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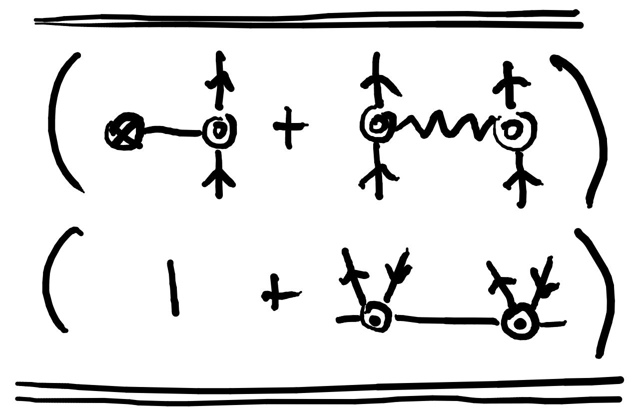
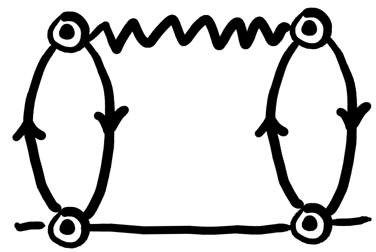


$$=$$



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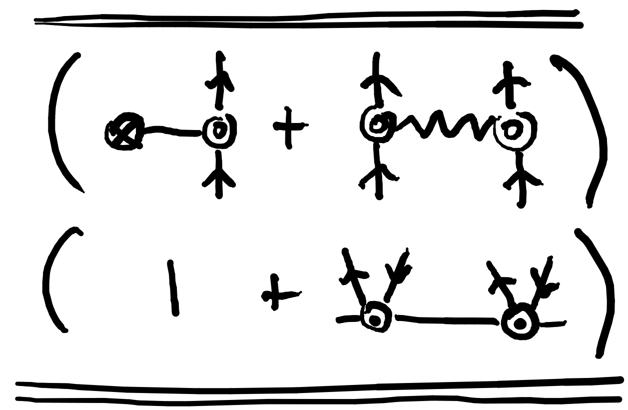

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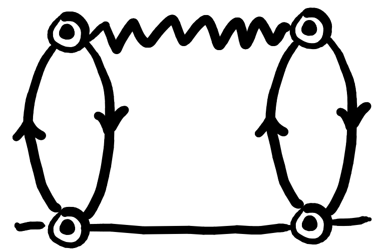

$$= \frac{1}{2 \cdot 2} \bar{g}^{ab}_{ij} c^{ij}_{ab}$$

CID coeff equations

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$$E_c C^{ij}_{ab}$$

CID coeff equations

$$E_c c^{ij}_{ab} = \langle \Phi^{ab}_{ij} | H_c (1 + C_2) | \Phi \rangle$$

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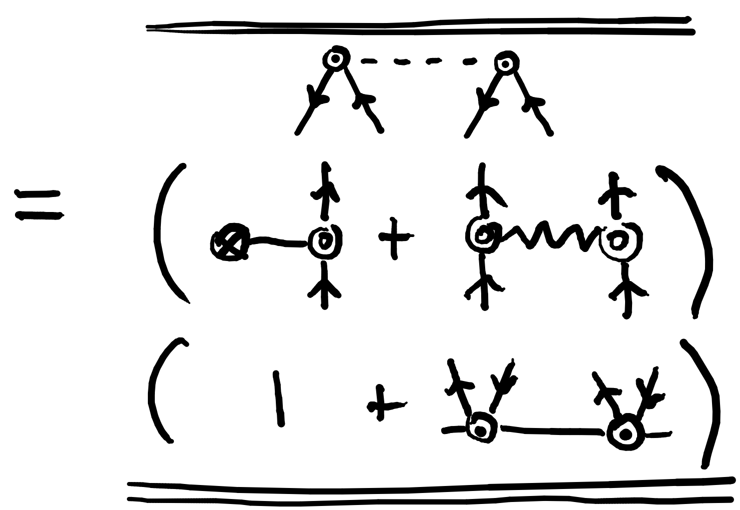

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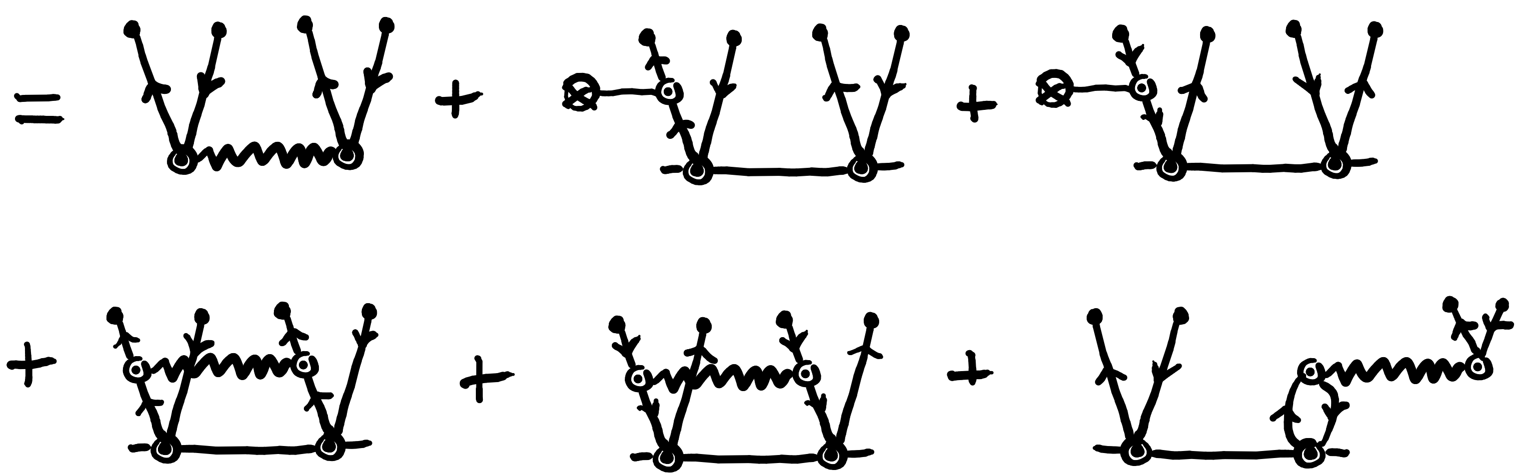

extra term in CCD:

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$$\frac{1}{2}\langle \Phi_{ij}^{ab} | H_c C_2^2 | \Phi \rangle$$

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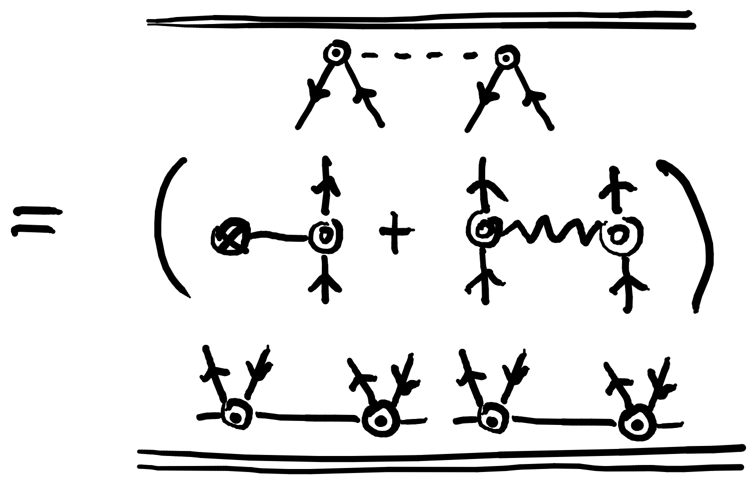

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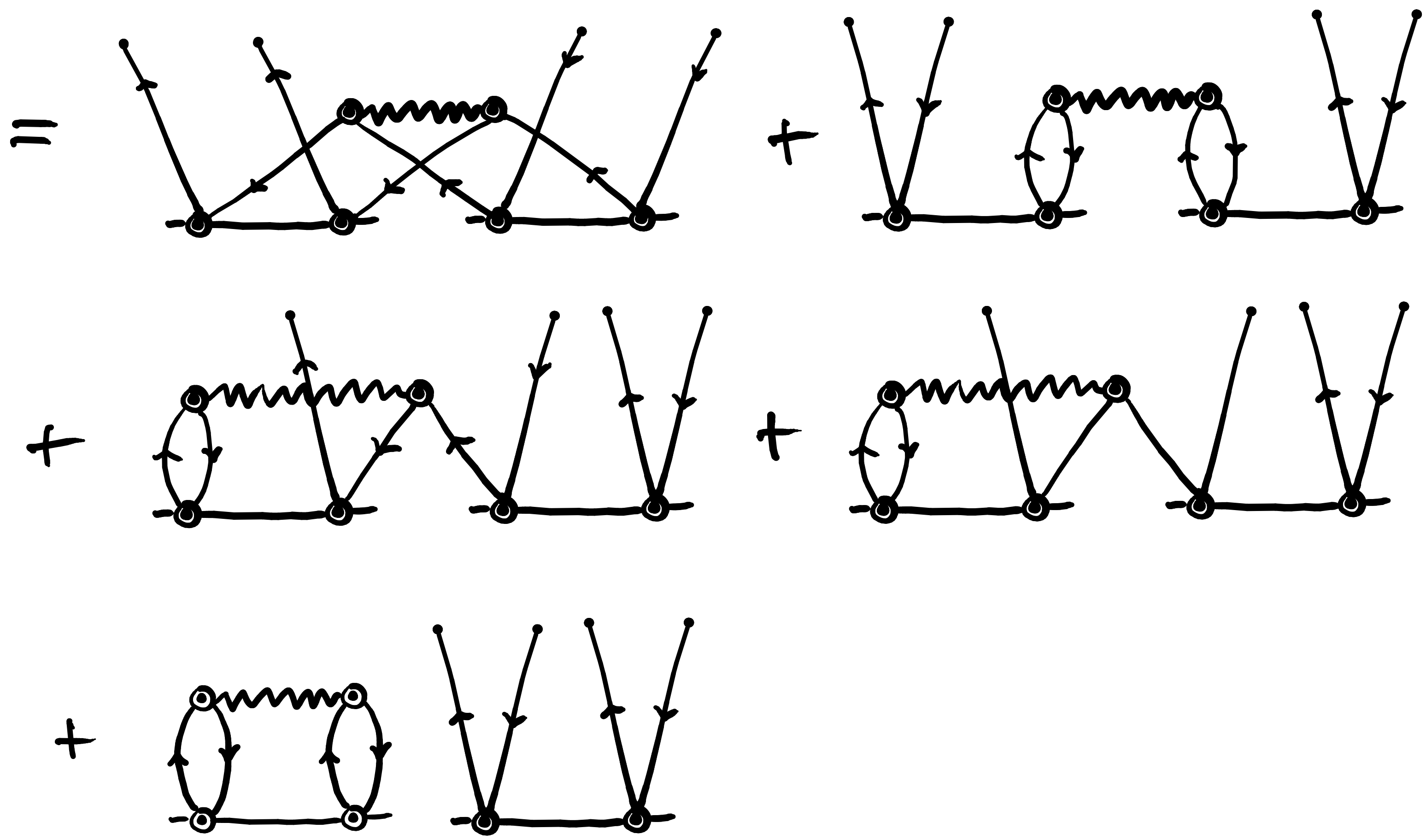

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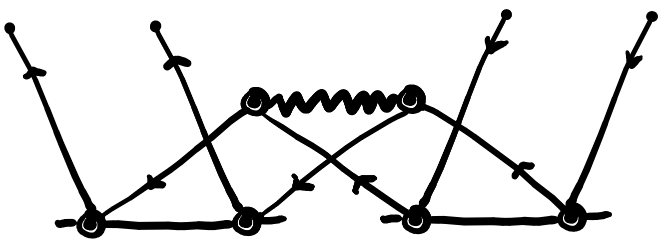
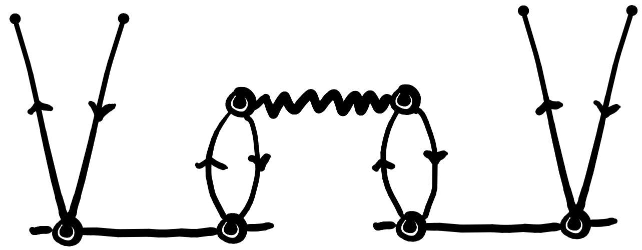
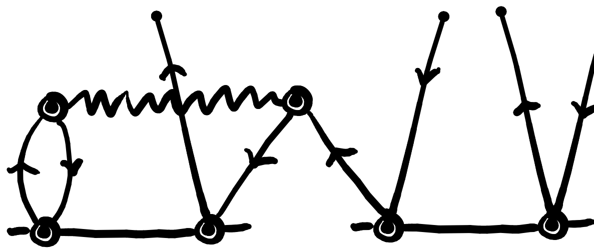
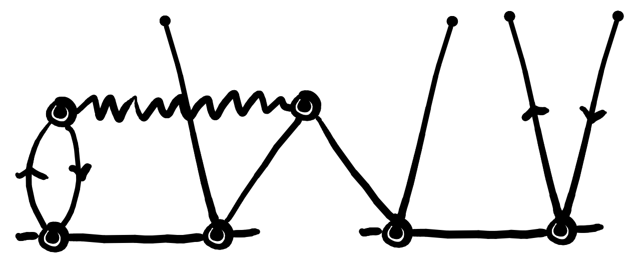
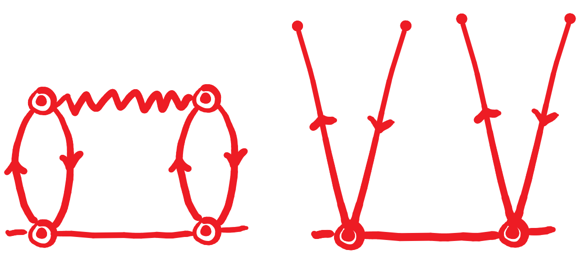
$=$  $+$ 

$+$  $+$ 

$+$ 

this is the only unlinked term

a closer look at the CCD equations:

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$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle$$

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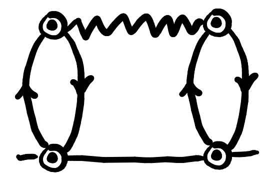
$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

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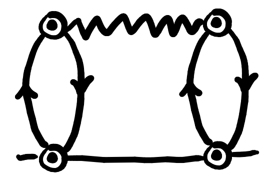
$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle = $$ 

$$E_c\, c^{ij}_{ab} = \langle \Phi^{ab}_{ij} | H_c \exp(C_2) | \Phi \rangle$$

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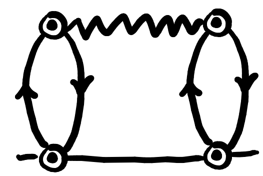
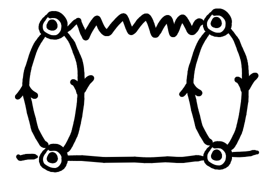
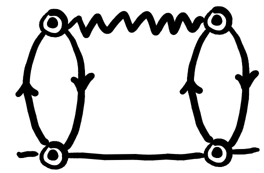
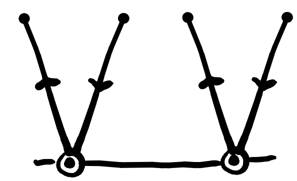
$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

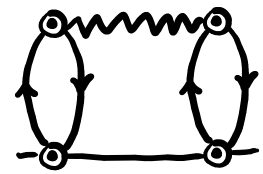
$$E_c\, c_{ab}^{ij} = \langle \Phi_{ij}^{ab} | H_c \exp(C_2) | \Phi \rangle_L$$

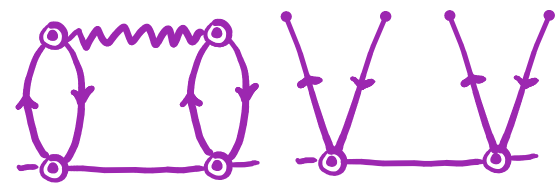
a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

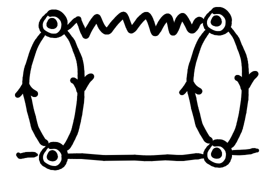
$$E_c \, c^{ij}_{ab} = \langle \Phi^{ab}_{ij} | H_c \exp(C_2) | \Phi \rangle_L +$$  

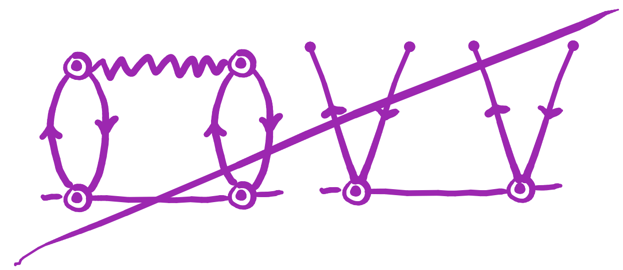
a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

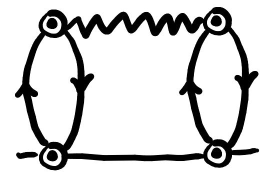
$$E_c \, c^{ij}_{ab} = \langle \Phi^{ab}_{ij} | H_c \exp(C_2) | \Phi \rangle_L +$$ 

a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

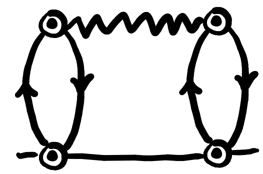
$$\cancel{E_c C^{ij}_{ab}} = \langle \Phi^{ab}_{ij} | H_c \exp(C_2) | \Phi \rangle_L +$$ 

a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle = $$ 

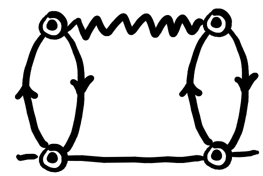
$$0 = \langle \Phi_{ij}^{ab} | H_c \exp(C_2) | \Phi \rangle_L$$

a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle = $$ 

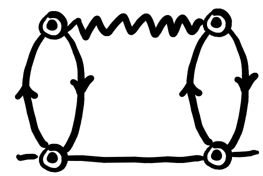
$$0 = \langle \Phi_{ij}^{ab} | F_c \exp(C_2) | \Phi \rangle_L$$

a closer look at the CCD equations:

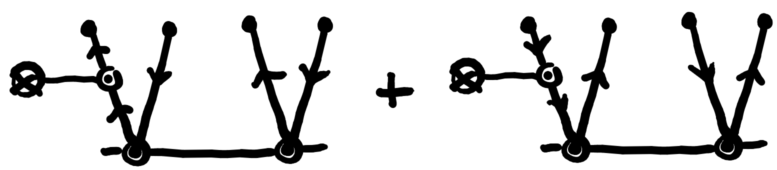
$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

$$0 = \langle \Phi_{ij}^{ab} | F_c \exp(C_2) | \Phi \rangle_L + \langle \Phi_{ij}^{ab} | V_c \exp(C_2) | \Phi \rangle_L$$

a closer look at the CCD equations:

$$E_c = \langle \Phi | H_c \exp(C_2) | \Phi \rangle =$$ 

$$0 = \underbrace{\langle \Phi_{ij}^{ab} | F_c \exp(C_2) | \Phi \rangle_L} + \langle \Phi_{ij}^{ab} | V_c \exp(C_2) | \Phi \rangle_L$$



a closer look at the CCD equations:

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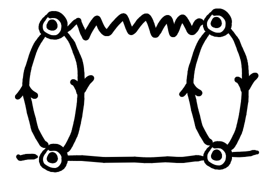
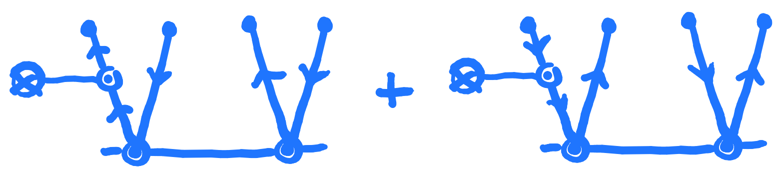


$$0 = \underbrace{\langle \Phi_{ij}^{ab} | F_c \exp(C_2) | \Phi \rangle_L}_{} + \langle \Phi_{ij}^{ab} | V_c \exp(C_2) | \Phi \rangle_L$$



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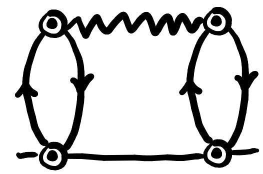

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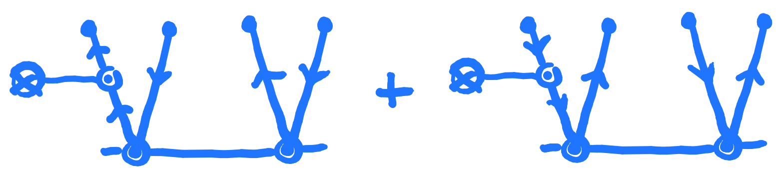
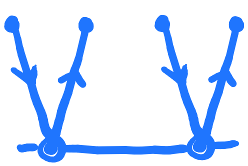


$$= -(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$$



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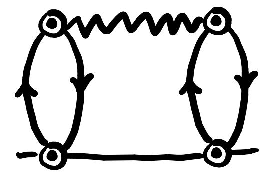

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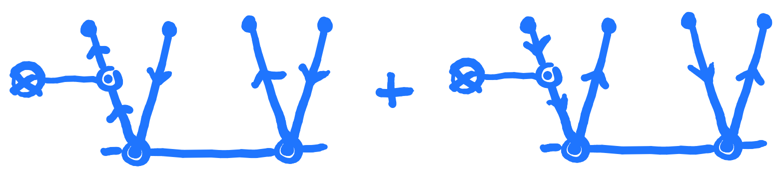
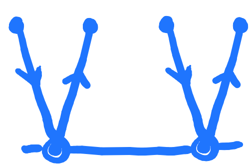
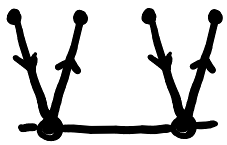
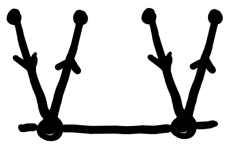


(assumes Brillouin's Thm. holds)

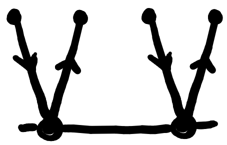
$$= -(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$$



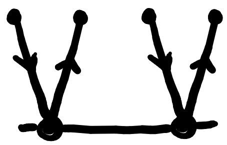




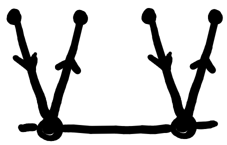
$$= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$$

 $= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$

CCD:

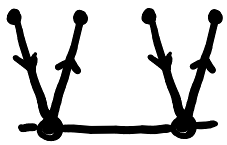
 $$= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$$

CCD: $$\Psi \rightarrow \left(1 + C_2 + \frac{1}{2} C_2^2 + \dots\right) \Phi$$

 $= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$

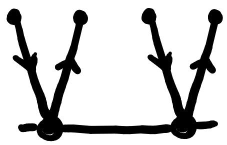
CCD: $\Psi \rightarrow (1 + C_2 + \frac{1}{2} C_2^2 + \ldots) \Phi$

CEPA$_0$:

 $= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$

CCD: $\Psi \to (1 + C_2 + \frac{1}{2} C_2^2 + \dots)\Phi$

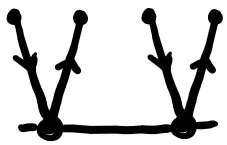
CEPA$_0$: $\Psi \to (1 + C_2)\Phi$

 $= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$

CCD: $\Psi \rightarrow (1 + C_2 + \frac{1}{2} C_2^2 + \ldots)\Phi$

CEPA$_0$: $\Psi \rightarrow (1 + C_2)\Phi$

MP2:

 $= (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle \Phi_{ij}^{ab} | V_c | \Psi \rangle_L$

CCD: $\Psi \rightarrow (1 + C_2 + \frac{1}{2} C_2^2 + \ldots)\,\Phi$

CEPA_0: $\Psi \rightarrow (1 + C_2)\,\Phi$

MP2: $\Psi \rightarrow \Phi$

resolvent line:

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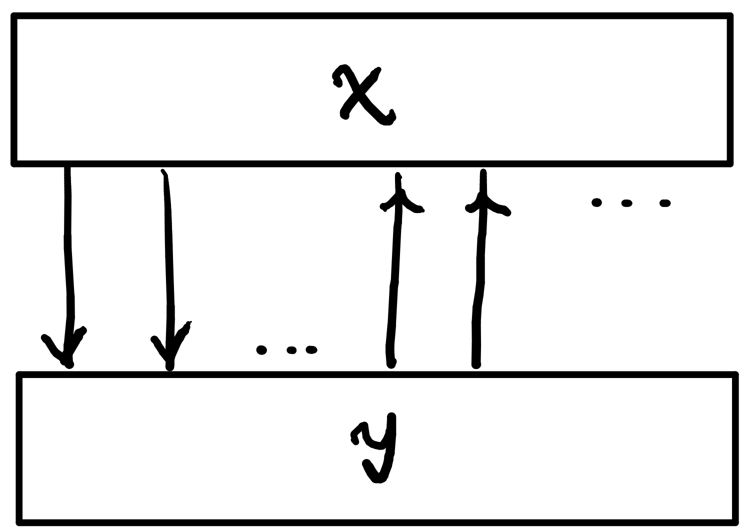
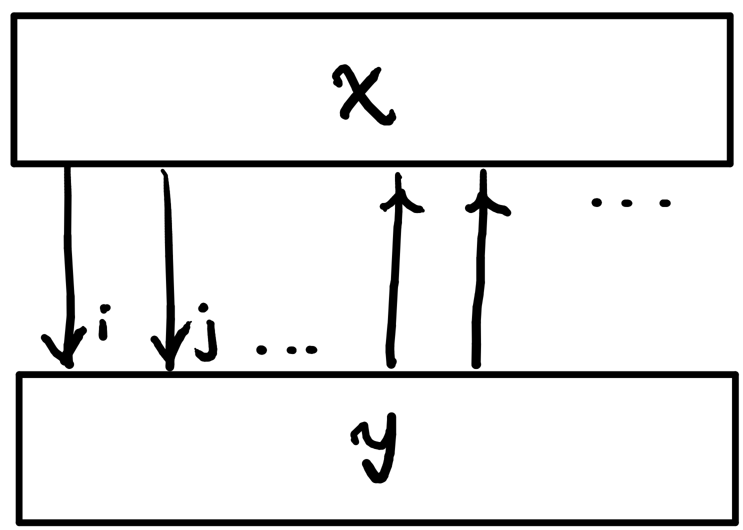
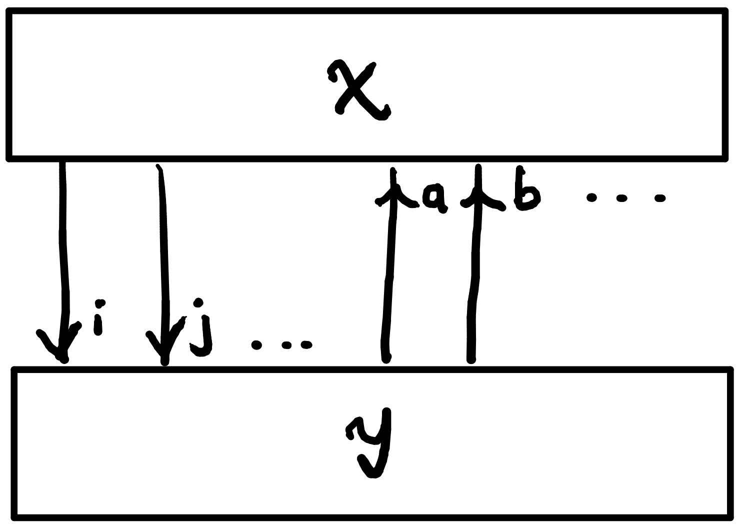


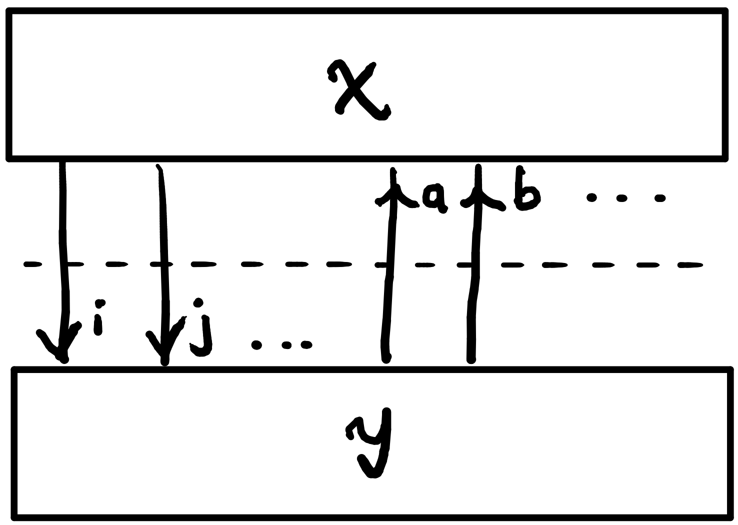
resolvent line:



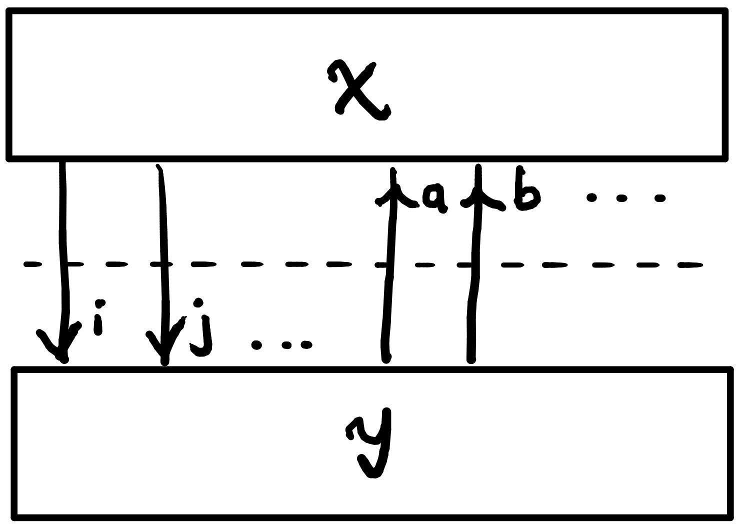
resolvent line:



resolvent line:

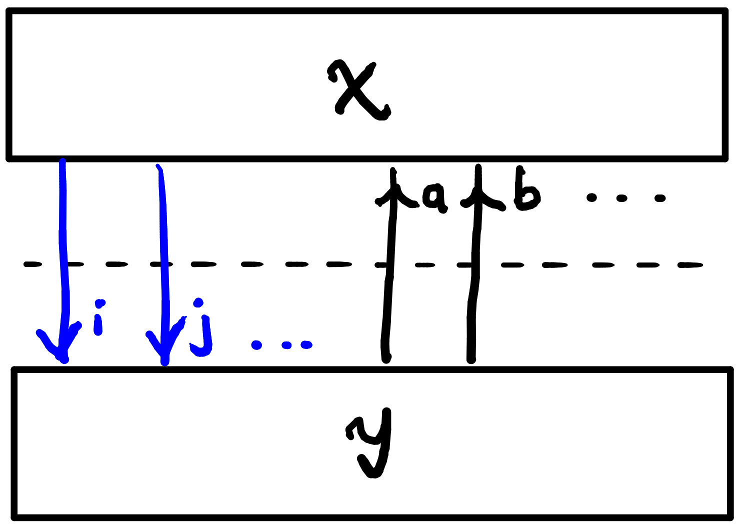


resolvent line:



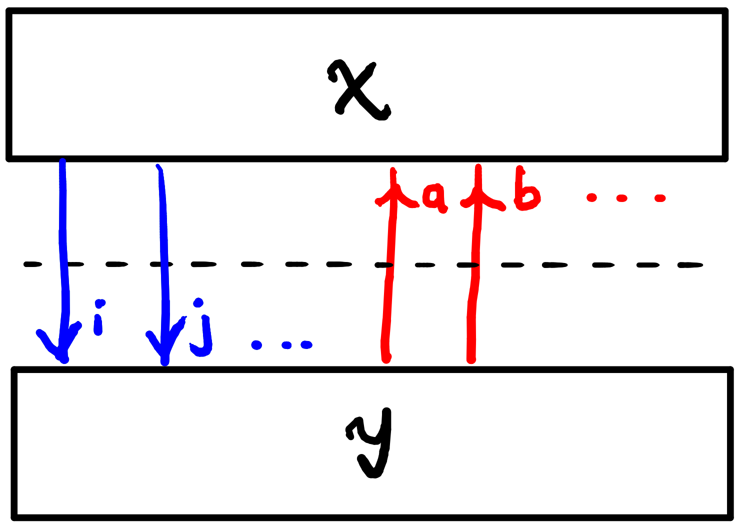
$$= \frac{x_{ij\cdots}^{ab\cdots}\, y_{ab\cdots}^{ij\cdots}}{\epsilon_i + \epsilon_j + \dots - \epsilon_a - \epsilon_b - \dots}$$

resolvent line:

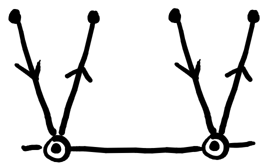


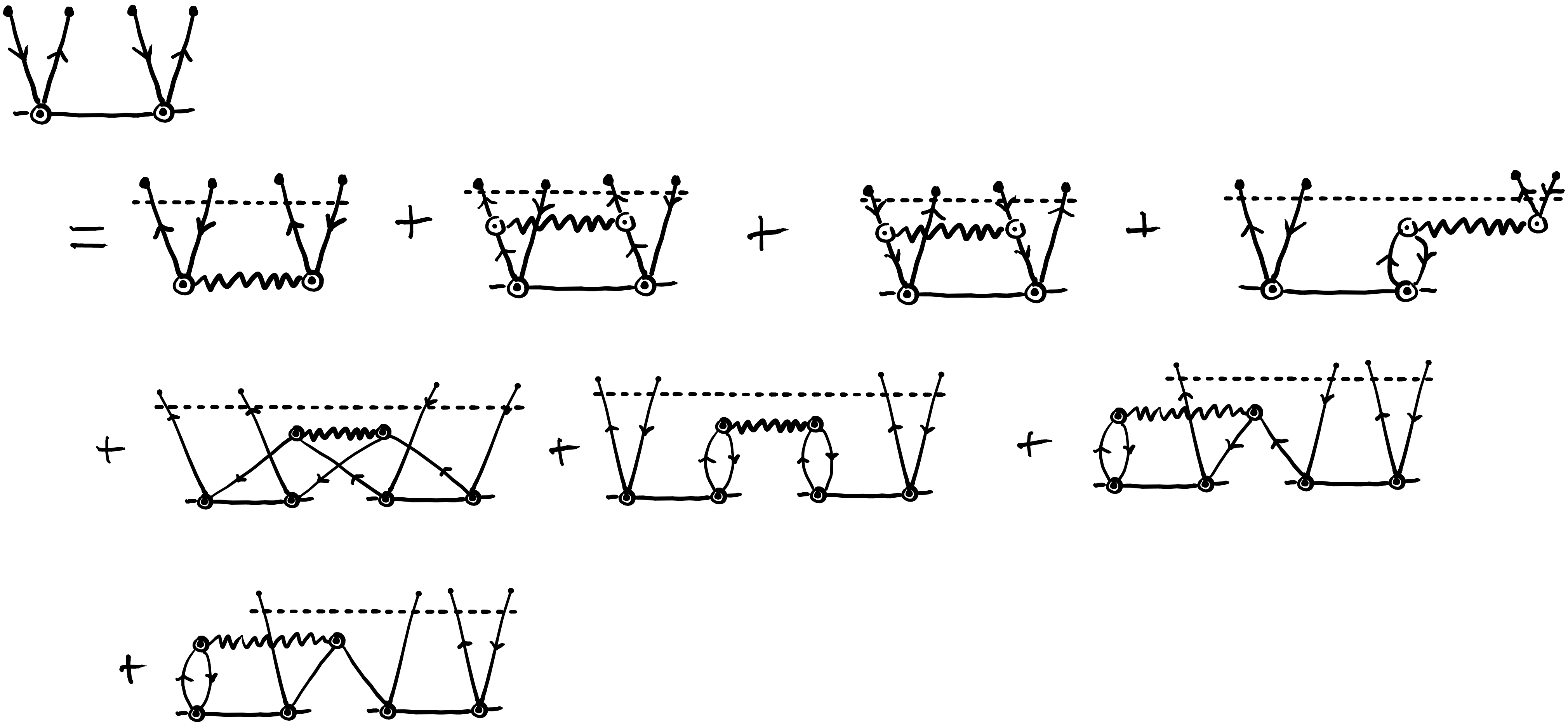
$$= \frac{x^{ab\cdots}_{ij\cdots}\, y^{ij\cdots}_{ab\cdots}}{\epsilon_i + \epsilon_j + \ldots - \epsilon_a - \epsilon_b - \ldots}$$

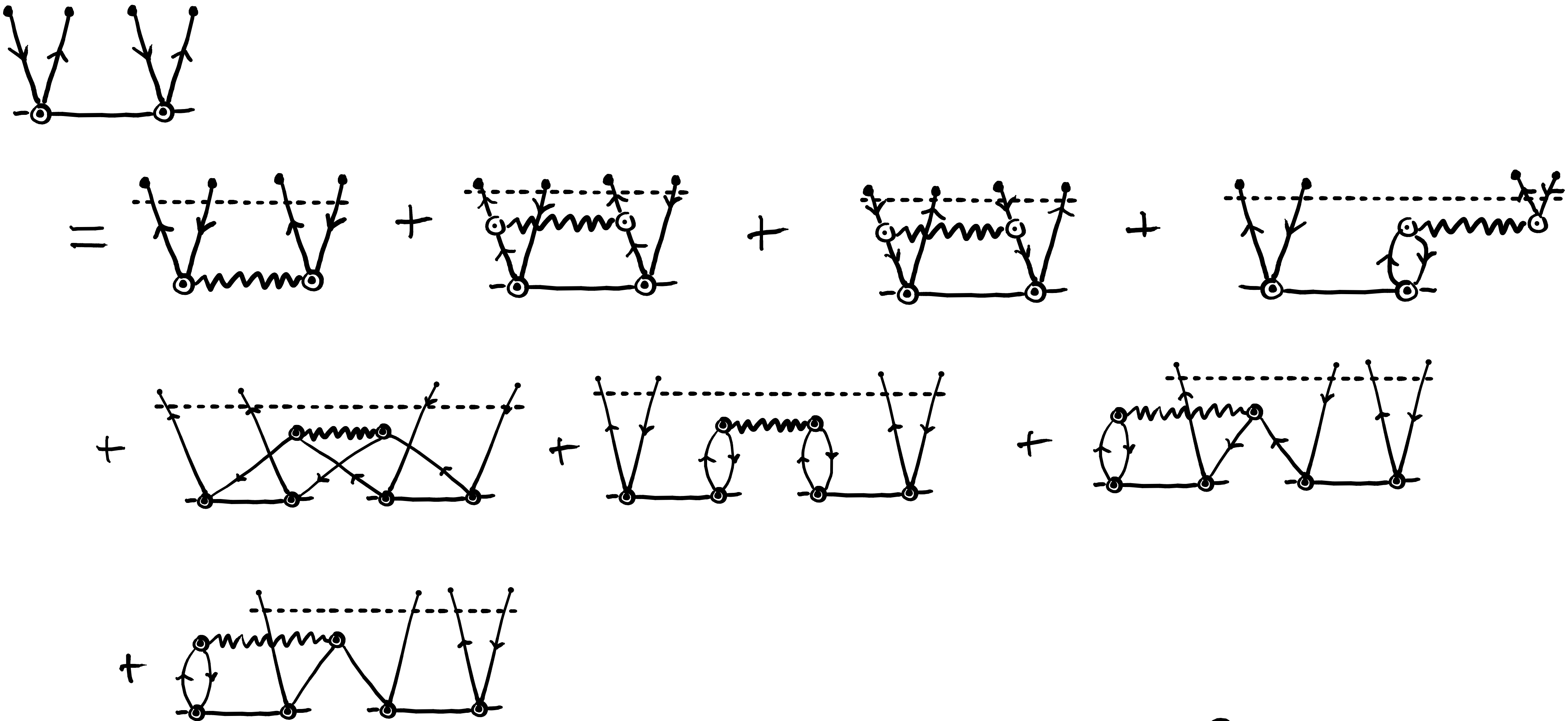
resolvent line:



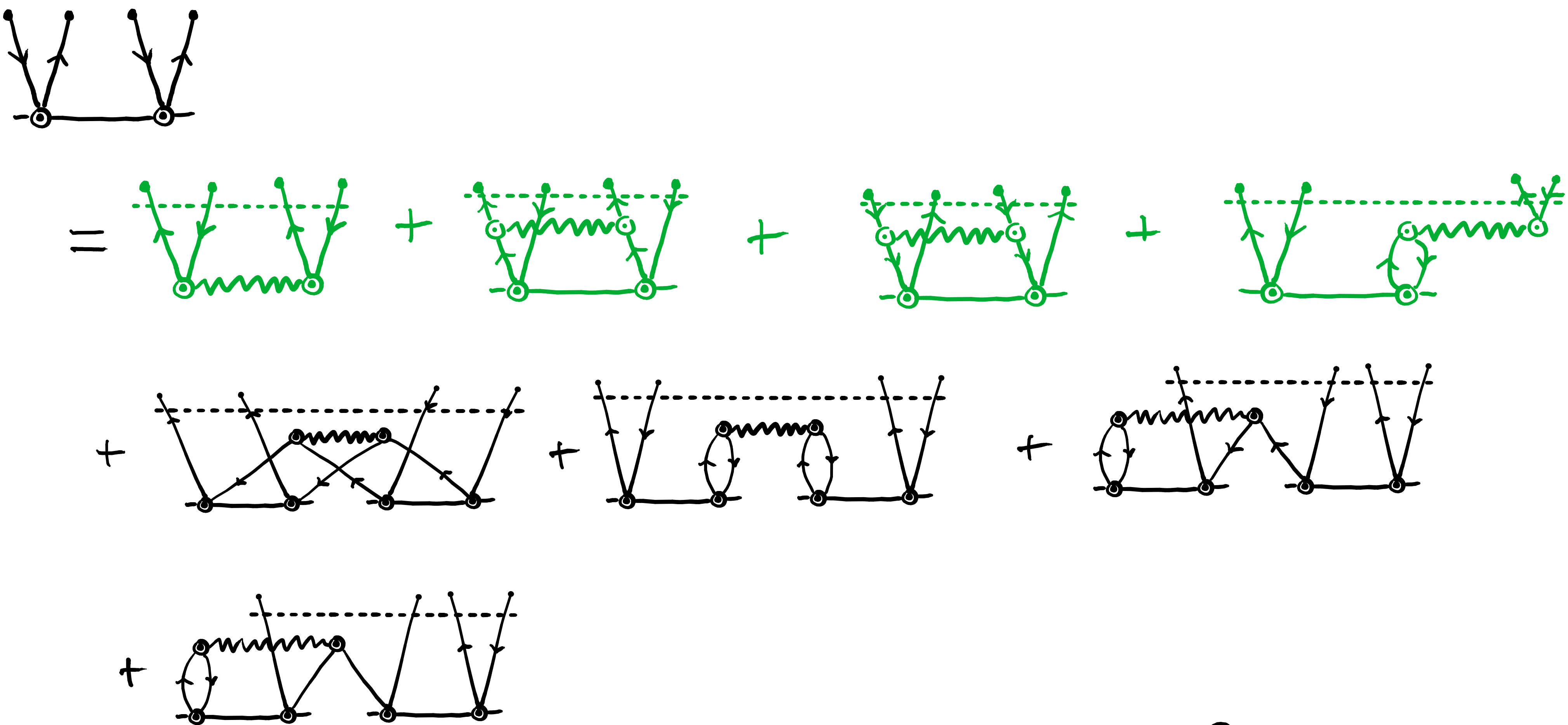
$$= \frac{x^{ab\cdots}_{ij\cdots}\, y^{ij\cdots}_{ab\cdots}}{\epsilon_i + \epsilon_j + \dots - \epsilon_a - \epsilon_b - \dots}$$





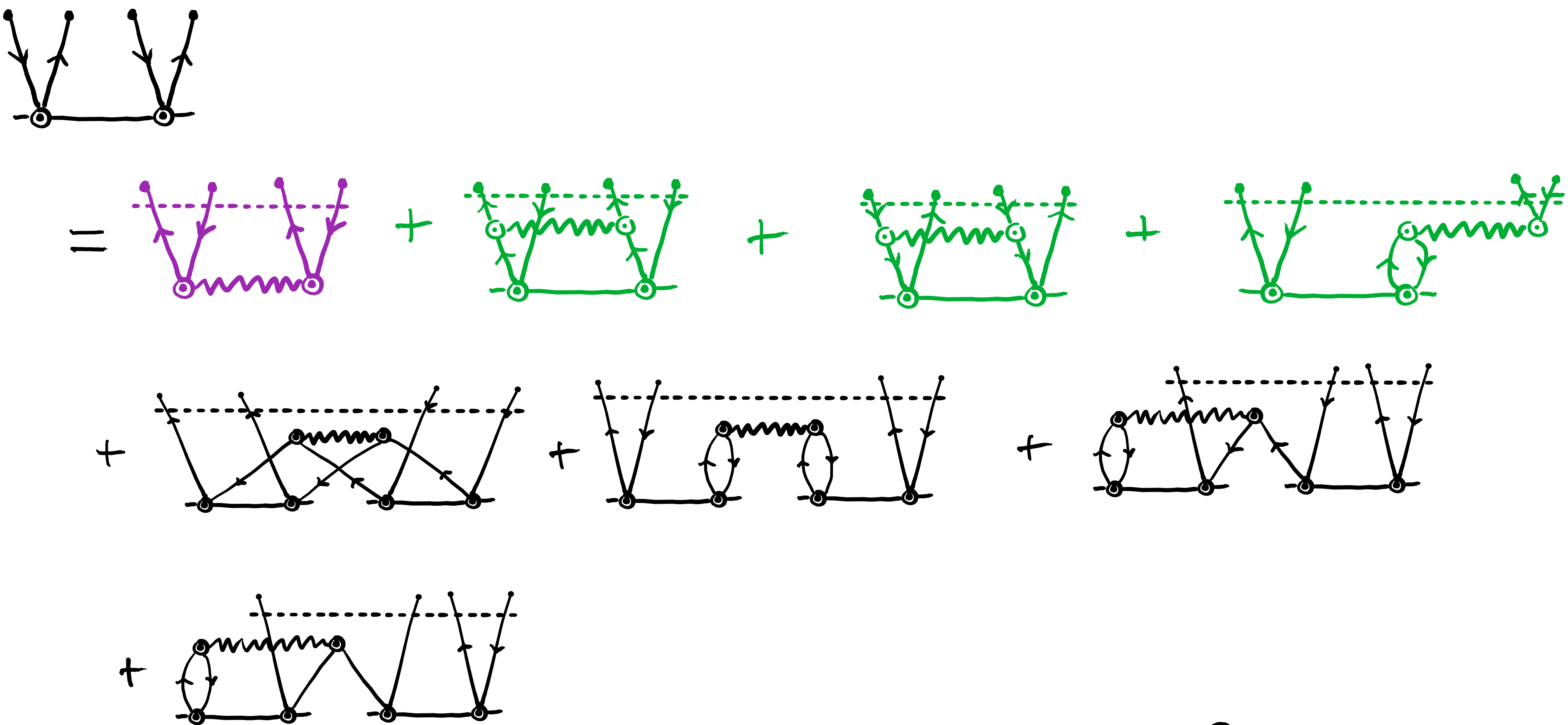


CCD



CCD

$CEPA_0$



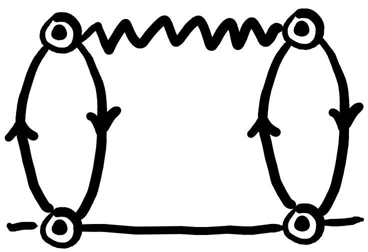
CCD

CEPA$_0$

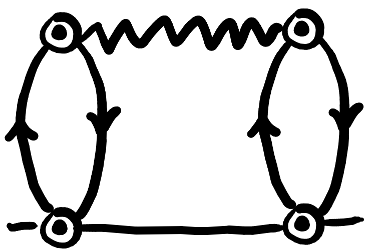
MP2

MP2 energy:

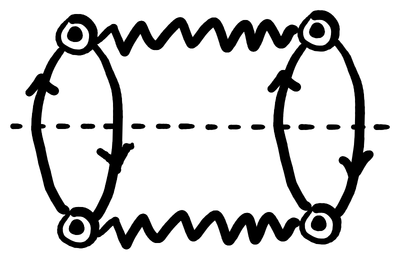
MP2 energy:

 (1)

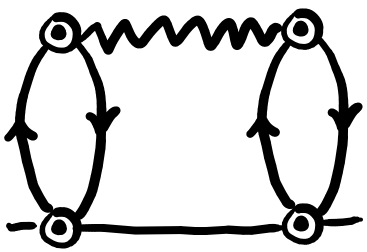
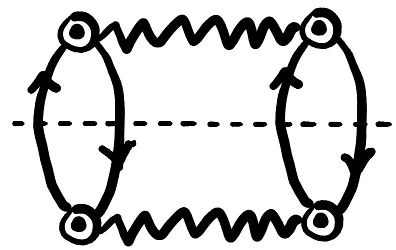
MP2 energy:



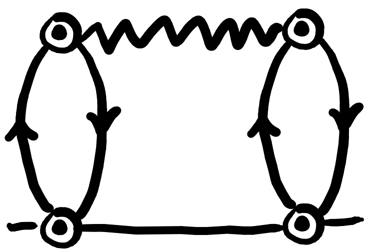
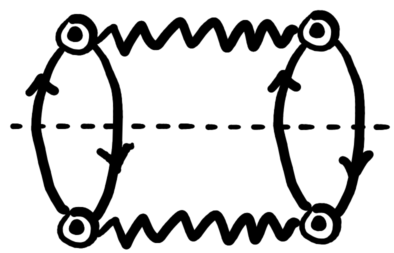
=



MP2 energy:

 (1) $=$  $= \dfrac{1}{4}\,\dfrac{\bar{g}^{ab}_{ij}\,\bar{g}^{ij}_{ab}}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$

MP2 energy:

 (1) $=$  $= \dfrac{1}{4} \dfrac{\bar{g}_{ij}^{ab}\,\bar{g}_{ab}^{ij}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$

(sloppy Einstein summation over i, j, a, b)

end.