$$K|\Psi_0\rangle = k_0|\Psi_0\rangle$$

$$K = H - \langle\Phi_0|H|\Phi_0\rangle = H_N$$

$$k_0 = E_0 - \langle\Phi_0|H|\Phi_0\rangle = \Delta E_0$$

$$K = K_0 + W$$

$$K_0 = Z_N + U_N$$

$$(\hat{z} + \hat{u})|p\rangle = \varepsilon_p|p\rangle \quad \checkmark$$

$$K_0|\Phi_0\rangle = \varkappa_0|\Phi_0\rangle$$

$$\varkappa_0 = 0$$

$$K_0|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\rangle = \varkappa_{i_1\ldots i_n}^{a_1\ldots a_n}|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\rangle,$$

$$n = 1, \ldots, N$$

$$\varkappa_{i_1\ldots i_n}^{a_1\ldots a_n} = \sum_{g=1}^{n}(\varepsilon_{a_g} - \varepsilon_{i_g})$$

$$W = W_1 + W_2 \;(= K - K_0)$$

$$W_1 = \hat{Q}_N = \sum_{rs} \langle r|\hat{q}|s\rangle N[X_r^\dagger X_s]$$

$$\hat{q} = \hat{g} - \hat{u} = \hat{f} - (\hat{z} + \hat{u})$$

$$\langle r|\hat{q}|s\rangle = \langle r|\hat{g}|s\rangle - \langle r|\hat{u}|s\rangle$$

$$\langle r|\hat{g}|s\rangle = \sum_i \langle ri|\hat{v}|si\rangle_A$$

$$W_2 = V_N = \frac{1}{4}\sum_{rstu} \langle rs|\hat{v}|tu\rangle_A \times N[X_r^\dagger X_t X_s^\dagger X_u]$$

$$[R^{(0)}]^k = \sum_{n=1}^{N} [R_n^{(0)}]^k, \quad k = 1, 2, \ldots$$

$$[R_n^{(0)}]^k = \left(\frac{1}{n!}\right)^2 \times \sum_{\substack{i_1,\dots,i_n\\ a_1,\dots,a_n}} \frac{\overbrace{E_{i_1\dots i_n}^{a_1\dots a_n}|\Phi_0\rangle\langle\Phi_0|\left(E_{i_1\dots i_n}^{a_1\dots a_n}\right)^\dagger}^{|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle\langle\Phi_{i_1\dots i_n}^{a_1\dots a_n}|}}{\underbrace{\left(-\varkappa_{i_1\dots i_n}^{a_1\dots a_n}\right)^k}_{\left[\sum_\gamma\left(\varepsilon_{i_\gamma}-\varepsilon_{a_\gamma}\right)\right]^k}}$$

$$\langle W\rangle = \langle\Phi_0|W|\Phi_0\rangle = 0$$

W is in the N-product form

$$k_0^{(1)} = \langle W\rangle = 0 \quad ✓$$

$$k_0^{(2)} = \langle W R^{(0)} W\rangle \quad \leftarrow$$

$$k_0^{(3)} = \langle W R^{(0)} W R^{(0)} W \rangle - \cancelto{0}{\langle W \rangle} \langle W R^{(0)2} W \rangle$$

$$= \langle W R^{(0)} W R^{(0)} W \rangle$$

$$k_0^{(4)} = \langle W R^{(0)} W R^{(0)} W R^{(0)} W \rangle - \langle W R^{(0)} W \rangle \langle W R^{(0)2} W \rangle,$$

etc.

$$|\Psi_0^{(1)}\rangle = R^{(0)} W |\Phi_0\rangle$$

$$|\Psi_0^{(2)}\rangle = \left(R^{(0)} W\right)^2 |\Phi_0\rangle - \cancelto{0}{\langle W \rangle} R^{(0)2} W |\Phi_0\rangle$$

$$= \left(R^{(0)} W\right)^2 |\Phi_0\rangle$$

$$|\Psi_0^{(3)}\rangle = (R^{(0)}W)^3|\Phi_0\rangle$$

$$- \langle W R^{(0)} W\rangle R^{(0)2} W |\Phi_0\rangle,$$

etc.

Correlation energy contributions $k_0^{(n)}$ start with $n=2$.

Explanation (not referring to normal ordering):

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$H = H_0 + \tilde{W}$$

$$H_0 = Z + U, \quad \tilde{W} = V - U$$

$$H_0|\Phi_0\rangle = E_0^{(0)}|\Phi_0\rangle$$

$$E_0^{(0)} = \sum_i \varepsilon_i$$

$$H_0 |\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle = \mathcal{E}_{i_1 \ldots i_n}^{a_1 \ldots a_n} |\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle$$

$$\mathcal{E}_{i_1 \ldots i_n}^{a_1 \ldots a_n} = E_0^{(0)} + \sum_{g=1}^{n} (\varepsilon_{a_g} - \varepsilon_{i_g})$$

$$E_0 = \underbrace{E_0^{(0)} + E_0^{(1)}}_{\langle\Phi_0|H_0|\Phi_0\rangle + \langle\Phi_0|\tilde{W}|\Phi_0\rangle} + E_0^{(2)} + \ldots$$

$$\langle\Phi_0|H_0|\Phi_0\rangle + \langle\Phi_0|\tilde{W}|\Phi_0\rangle$$

$$= \langle\Phi_0| H_0 + \tilde{W} |\Phi_0\rangle$$

$$= \langle\Phi_0|H|\Phi_0\rangle$$

$$E_0 = \langle\Phi_0|H|\Phi_0\rangle + E_0^{(2)} + \ldots$$

DIAGRAMMATIC MBPT

$$\langle \Phi_0 | W \left(R^{(0)}\right)^{n_1} W \left(R^{(0)}\right)^{n_2} \cdots \left(R^{(0)}\right)^{n_g} W | \Phi_0 \rangle$$

energy corrections $\qquad n_1, n_2, \ldots \geq 1$

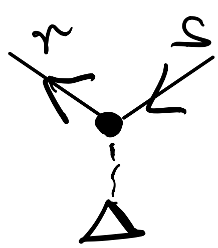
$$W = W_1 + W_2 = Q_N + V_N$$

wavefunction corrections

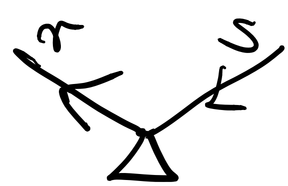
$$\left(R^{(0)}\right)^{n_1} W \left(R^{(0)}\right)^{n_2} \cdots \left(R^{(0)}\right)^{n_g} W | \Phi_0 \rangle$$

We must represent W_1, W_2, $\left[R_n^{(0)}\right]^k$.

$W_1 = \hat{Q}_N$:



Goldstone (G)



Hugenholtz (H)

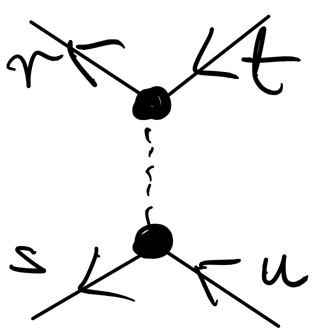
$$W_1^{(X)} = w_{\mathcal{Q}_N}^{(X)} \sum_{r,s} d_{rs}^{(X)} \hat{O}_{rs}$$

$X = G, H$

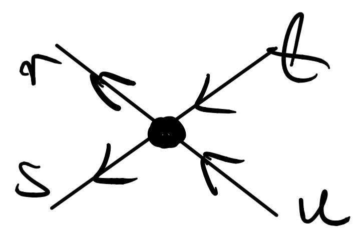
$w_{\mathcal{Q}_N}^{(X)} = 1, \quad d_{rs}^{(X)} = \langle r|\hat{q}|s\rangle,$

$$\hat{O}_{rs} = N[X_r^\dagger X_s]$$

$W_2 = V_N$:



(G)



(H)

$$W_2 = w_{v_N}^{(X)} \sum_{rstu} d_{rstu}^{(X)} \hat{O}_{rstu}$$

$$w_{v_N}^{(G)} = \frac{1}{2} \qquad w_{v_N}^{(H)} = \frac{1}{4}$$

$$d_{rstu}^{(G)} = \langle rs|\hat{o}|tu\rangle \qquad d_{rstu}^{(H)} = \langle rs|\hat{o}|tu\rangle_A$$

$$\hat{O}_{rstu} = N[X_r^\dagger X_s^\dagger X_u X_t]$$
$$= N[X_r^\dagger X_t X_s^\dagger X_u]$$

$[R_n^{(0)}]^k$:

$$[R_n^{(\infty)}]^k = \left(\frac{1}{n!}\right)^2$$

weight

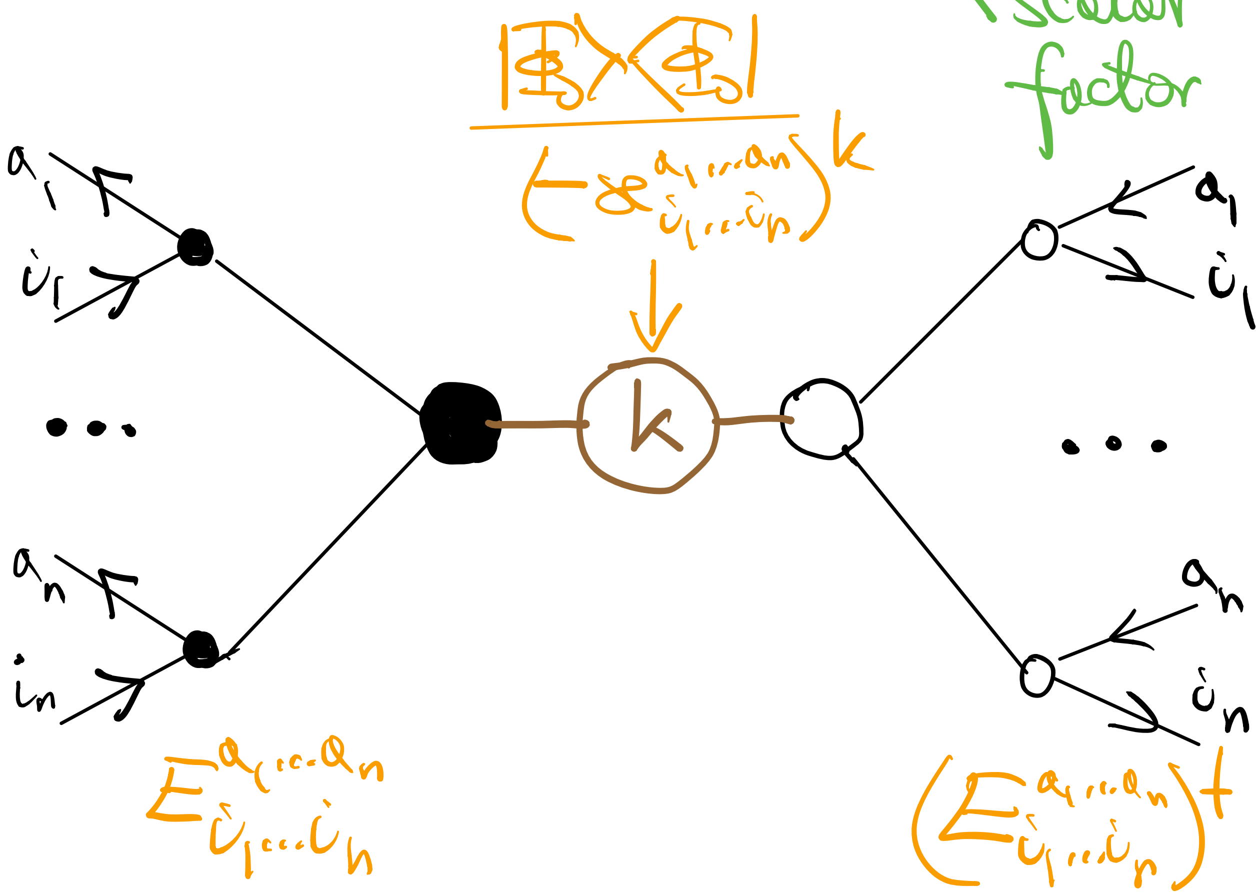
excitation operator

operator part

$$\times \sum_{\substack{i_1,\dots,i_n \\ a_1,\dots,a_n}} \frac{\underbrace{E^{a_1\dots a_n}_{i_1\dots i_n} |\Phi_0\rangle\langle\Phi_0| \left(E^{a_1\dots a_n}_{i_1\dots i_n}\right)^\dagger}_{\text{operator part}}}{\left(-\varkappa^{a_1\dots a_n}_{i_1\dots i_n}\right)^k}$$

deexcitation operator

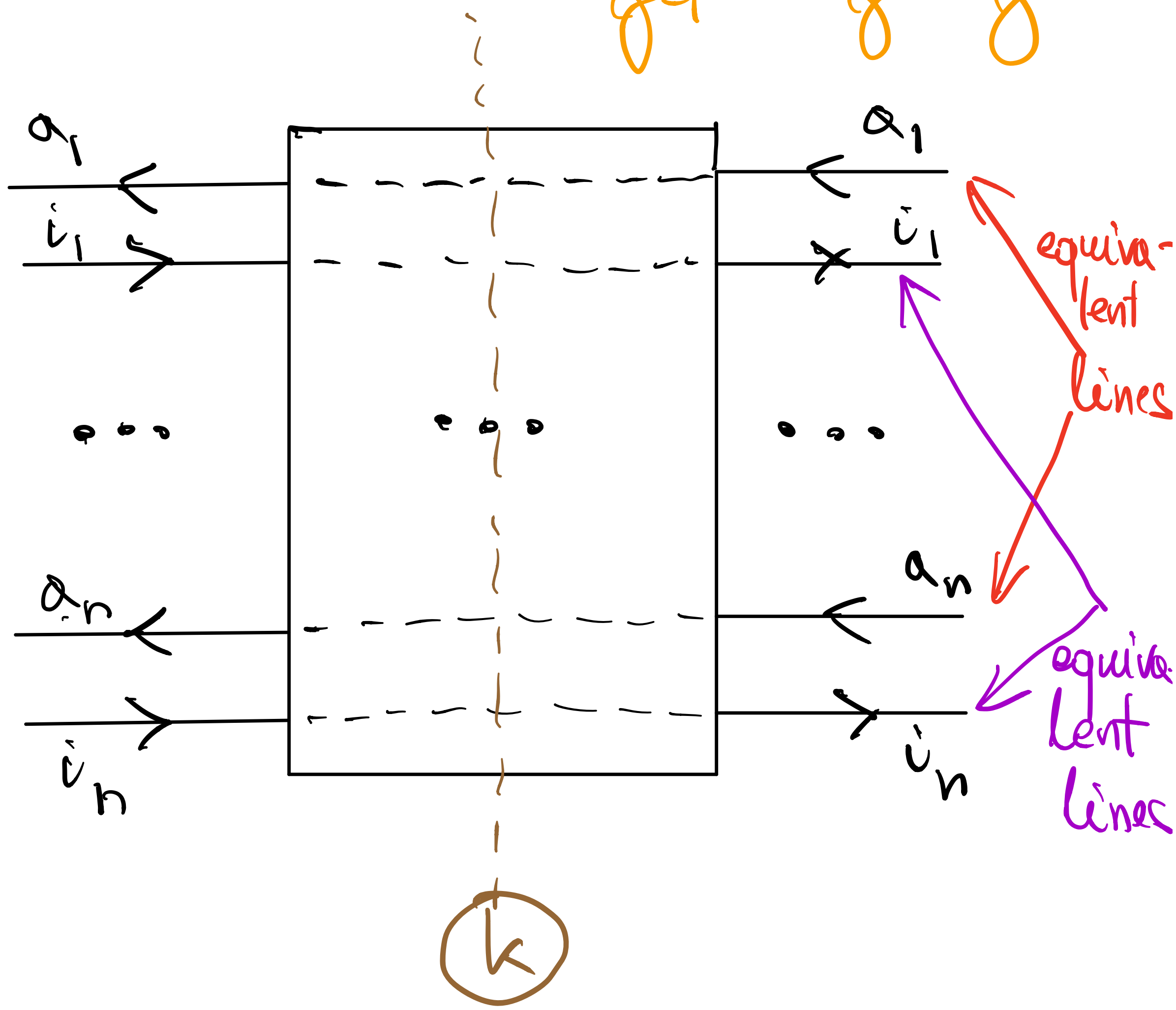
scalar factor



$$E^{a_1,\dots,a_n}_{i_1,\dots,i_n} = \prod_{g=1}^{n} X^{+}_{a_g} X_{i_g}$$

$$\left(E^{a_1,\dots,a_n}_{i_1,\dots,i_n}\right)^{+} = E^{i_1,\dots,i_n}_{a_1,\dots,a_n}$$

$$= \prod_{g=1}^{n} X^{+}_{i_g} X_{a_g}$$



$$w_R = \left(\frac{1}{n!}\right)^2$$

$$d^{(k)}_{i_1\ldots i_n a_1\ldots a_n} = \left(-\mathcal{E}^{a_1\ldots a_n}_{i_1\ldots i_n}\right)^{-k}$$

$$= \left[\sum_{\gamma=1}^{n} \left(\varepsilon_{i_\gamma} - \varepsilon_{a_\gamma}\right)\right]^{-k}$$

$$\hat{O}_{i_1\ldots i_n a_1\ldots a_n} = E^{a_1\ldots a_n}_{i_1\ldots i_n} |\Phi_0\rangle\langle\Phi_0| \left(E^{a_1\ldots a_n}_{i_1\ldots i_n}\right)^\dagger$$

$$\left[R^{(0)}_n\right]^k = w_R \sum_{\substack{i_1\ldots i_n \\ a_1\ldots a_n}} d^{(k)}_{i_1\ldots i_n a_1\ldots a_n}$$

$$\times \hat{O}_{i_1\ldots i_n a_1\ldots a_n}$$

$$K_0^{(2)} = \langle \Phi_0 | W R^{(0)} W | \Phi_0 \rangle$$

$$W = W_1 + W_2 = \mathcal{Q}_N + V_N$$

$$K_0^{(2)} = \langle \Phi_0 | (\mathcal{Q}_N + V_N) R^{(0)} (\mathcal{Q}_N + V_N) | \Phi_0 \rangle$$

$$= K_0^{(2)}(A) + K_0^{(2)}(B) + K_0^{(2)}(C) + K_0^{(2)}(D)$$

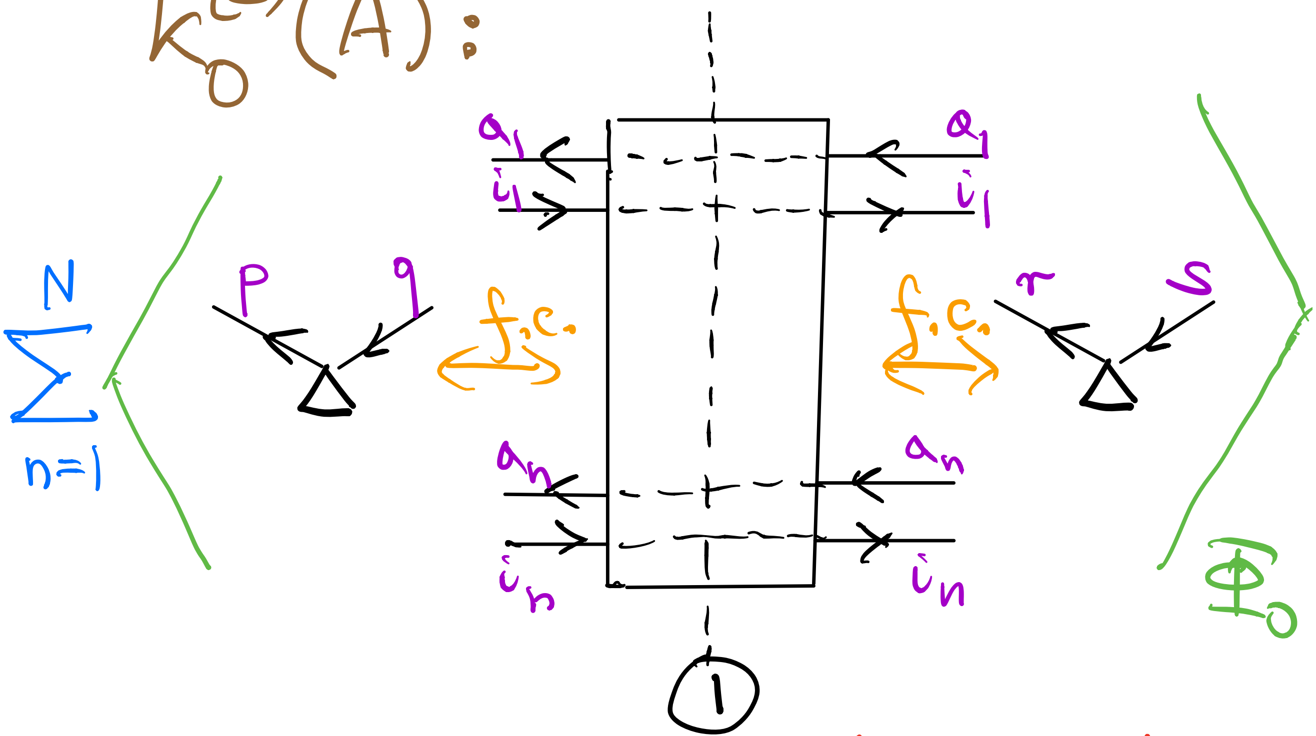
$$K_0^{(2)}(A) = \langle \Phi_0 | \mathcal{Q}_N R^{(0)} \mathcal{Q}_N | \Phi_0 \rangle \checkmark$$

$$K_0^{(2)}(B) = \langle \Phi_0 | \mathcal{Q}_N R^{(0)} V_N | \Phi_0 \rangle \checkmark$$

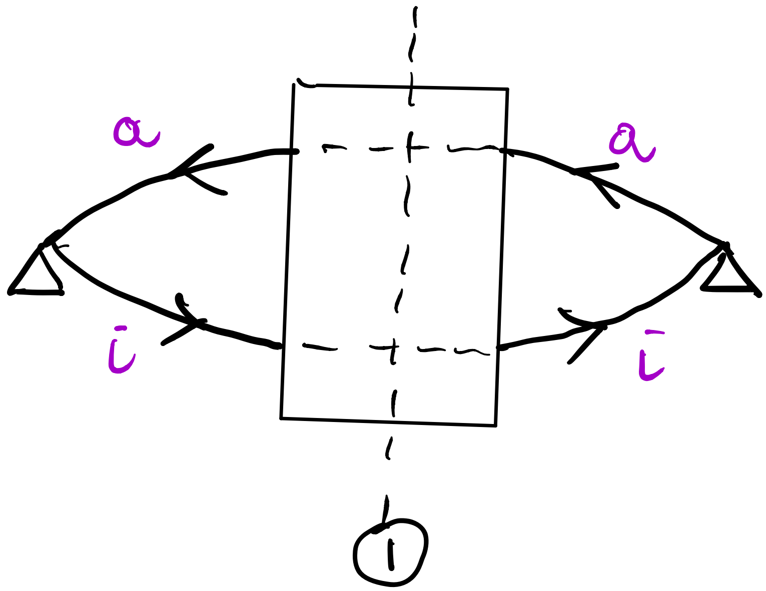
$$K_0^{(2)}(C) = \langle \Phi_0 | V_N R^{(0)} \mathcal{Q}_N | \Phi_0 \rangle \checkmark$$

$$K_0^{(2)}(D) = \langle \Phi_0 | V_N R^{(0)} V_N | \Phi_0 \rangle \checkmark$$

$k_0^{(2)}(A)$:



$$\underbrace{\langle \Phi_0 | \quad \cdots \quad \frac{|\Phi_0\rangle}{\left(-\epsilon^{a_1\ldots a_n}_{i_1\ldots i_n}\right)}}_{\text{full contraction } n=1} \underbrace{\langle\Phi_0| \quad \cdots \quad |\Phi_0\rangle}_{\text{full contraction } n=1}$$



a,i-free

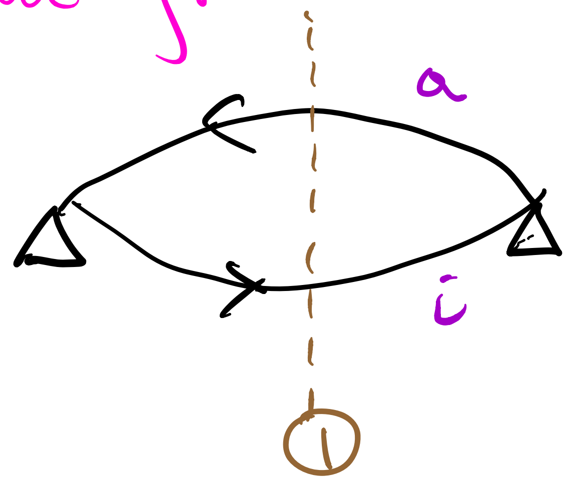
$w = 1$

$s = (-1)^{1+1} = +1$

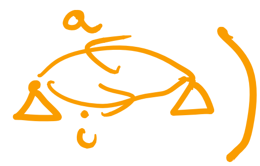
$d_{ia} = \langle i|\hat{q}|a\rangle\langle a|\hat{q}|i\rangle \times (\varepsilon_i - \varepsilon_a)^{-1}$

$$K_0^{(2)}(A) = \sum_{a,i} \frac{\langle i|\hat{q}|a\rangle\langle a|\hat{q}|i\rangle}{\varepsilon_i - \varepsilon_a}$$

We could obtain the same result from



(or, even



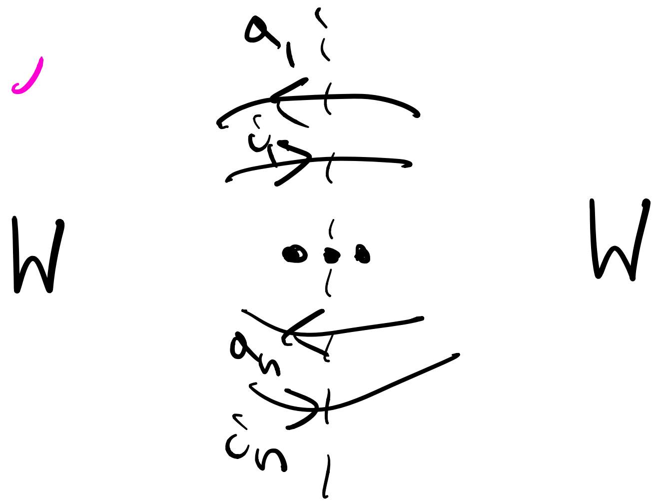
)

$$\sum_{i,a} \langle i|\hat{q}|a\rangle\langle a|\hat{q}|i\rangle(\varepsilon_i-\varepsilon_a)^{-1}$$

if we agreed that with each pair of neighboring W vertices we associate the energy denominator obtained by assigning

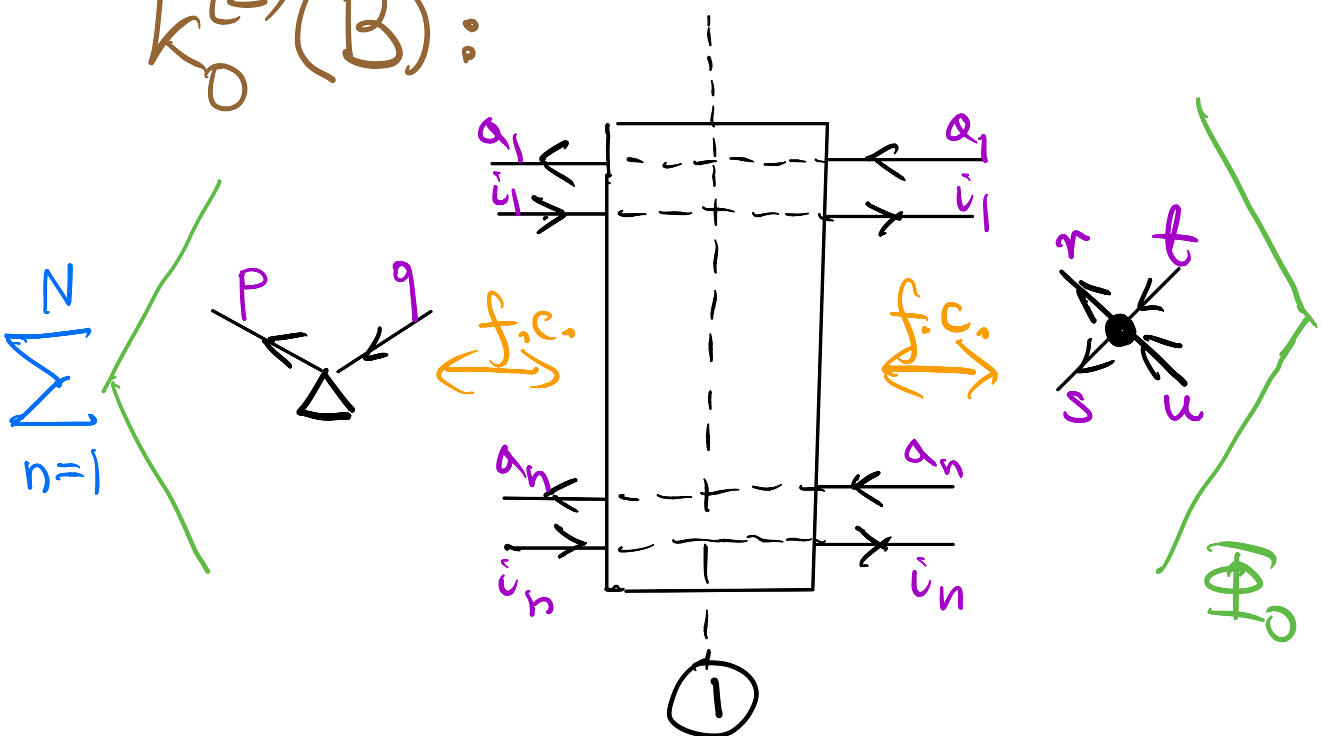
$$\left[(\varepsilon_{i_1}-\varepsilon_{a_1})+\ldots+(\varepsilon_{i_n}-\varepsilon_{a_n})\right]^{-k}$$

to the lines between these Ws,



We will call this new rule the denominator convention.

$k_0^{(2)}(B)$:



$$\underbrace{\langle \Phi_0 | \; \cdots \; \frac{|\Phi_B\rangle}{}}_{\text{full contraction } n=1}\!\!\!\!\underbrace{\frac{\langle \Phi_B|}{(-\varepsilon^{a_1 \ldots a_n}_{i_1 \ldots i_n})} \; \cdots \; |\Phi_0\rangle}_{\text{full contraction } n=2}$$

cannot be done at the same time

$$k_0^{(2)}(B) = 0$$

We could have obtained the same result by trying to form d-ms from

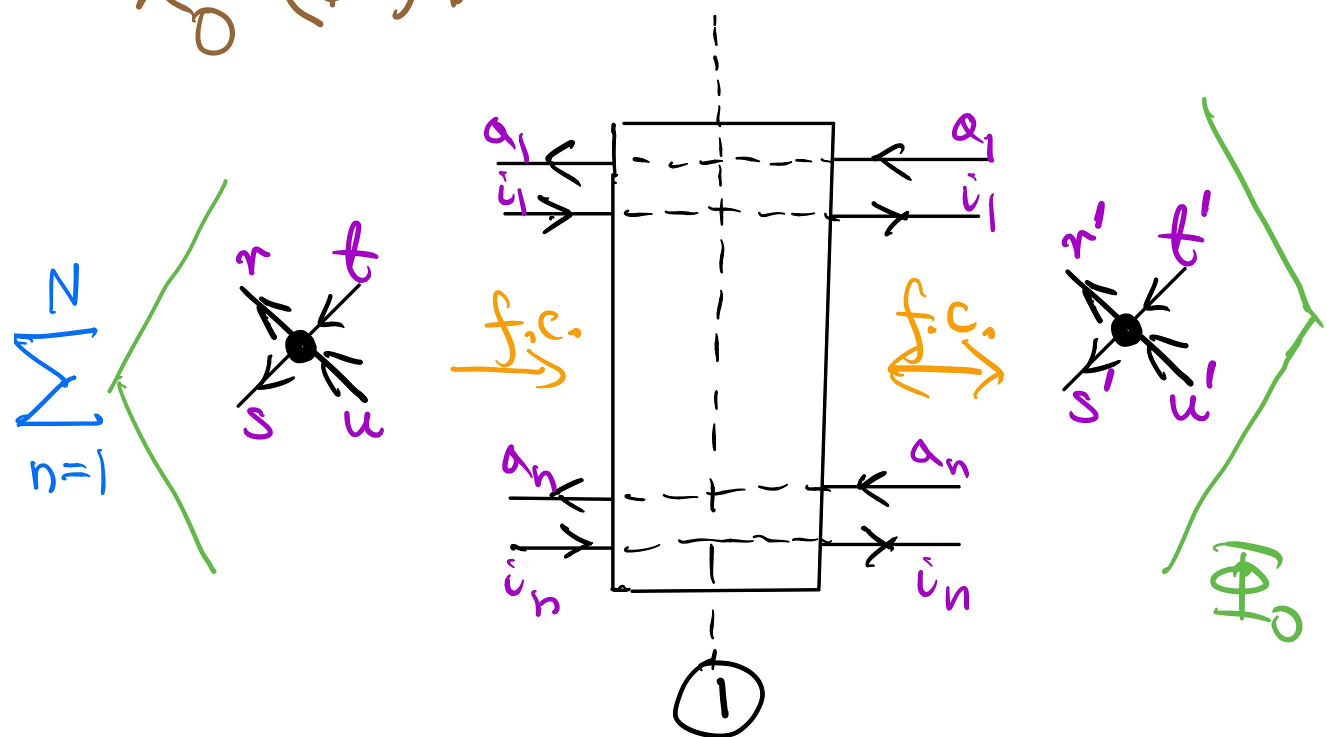
$\Big\langle$

$\Big\rangle_{\Phi_0} = 0$

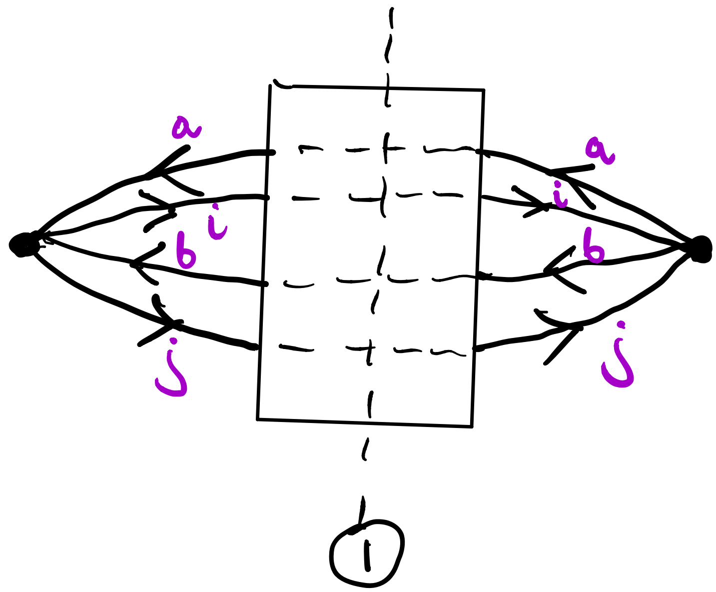
Similarly

$$k_0^{(2)}(C) = 0 .$$

$k_0^{(2)}(D)$:

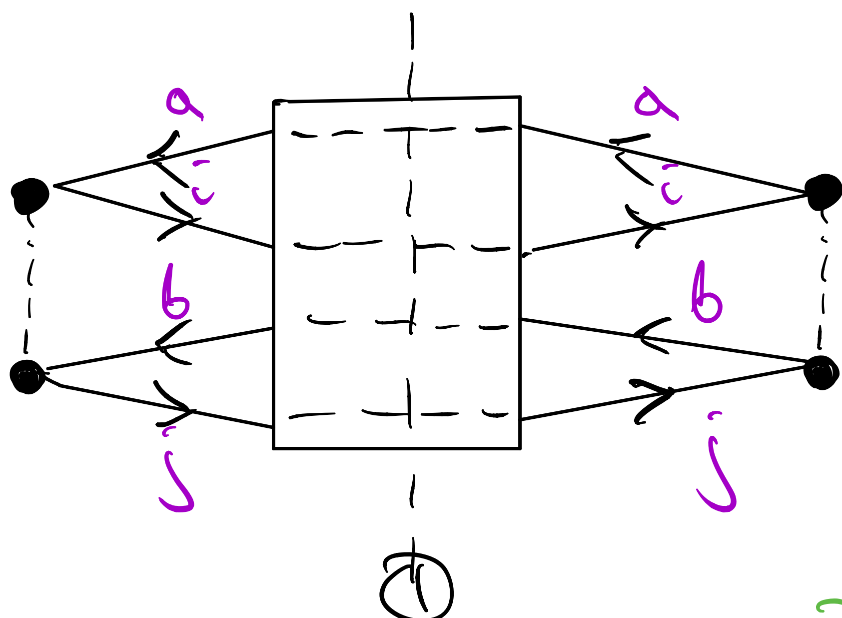


$$\underbrace{\langle \Phi_0 | \cdots \frac{|\Phi_0\rangle}{}}_{\text{full contraction}\atop n=2}\!\!\!\!\frac{\langle\Phi_0|}{\left(-\Delta\varepsilon^{a_1\ldots a_n}_{i_1\ldots i_n}\right)}\underbrace{\cdots |\Phi_0\rangle}_{\text{full contraction}\atop n=2}$$



Hugenholtz (H)

a, i, b, j - free



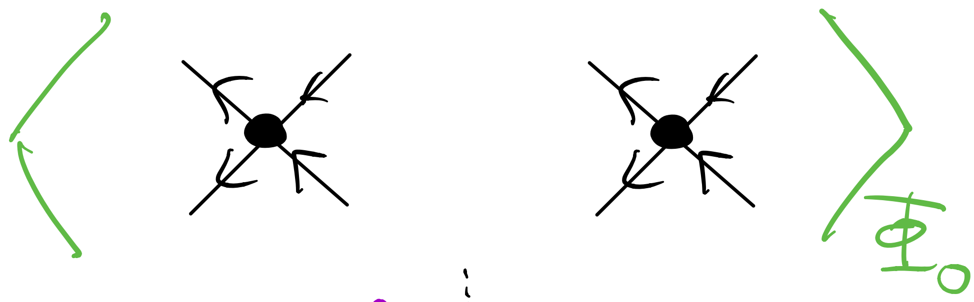
Brandon (B)

$$w^{(H)} = \frac{1}{4}, \quad s^{(B)} = (-1)^{2+2} = +1$$

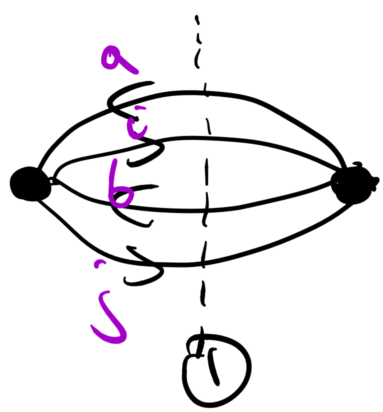
$$d^{(B)}_{ijab} = \langle ij|\hat{v}|ab\rangle_A \langle ab|\hat{v}|ij\rangle_A \times (\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b)^{-1}$$

$$K_0^{(2)}(D) = \frac{1}{4} \sum_{ijab} \frac{\langle ij|\hat{v}|ab\rangle_A \langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b}$$

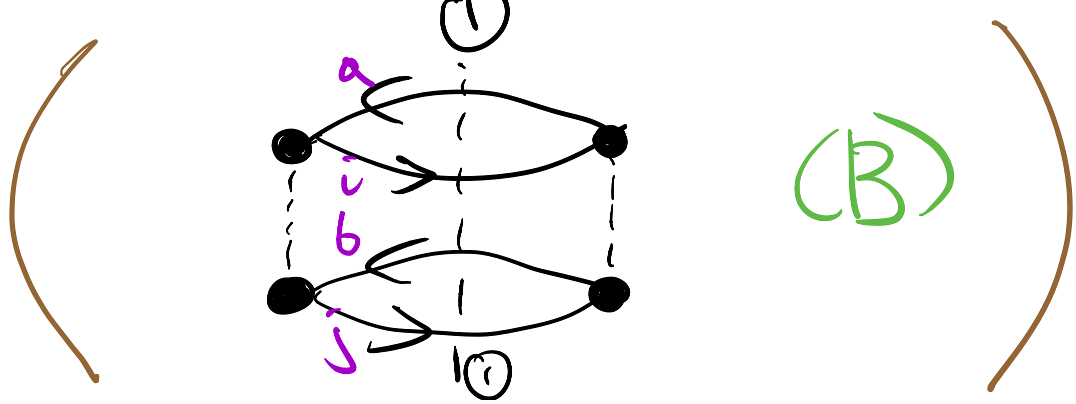
Again, we could have obtained the same result from



=



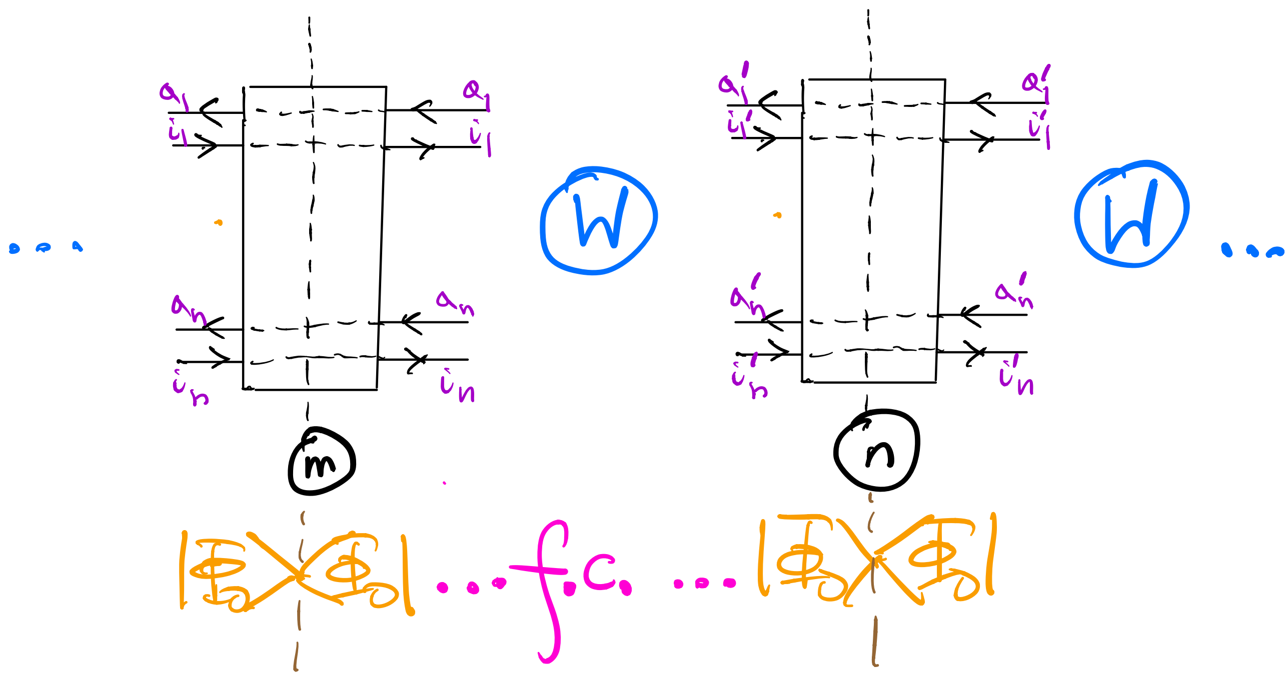
(H)



(B)

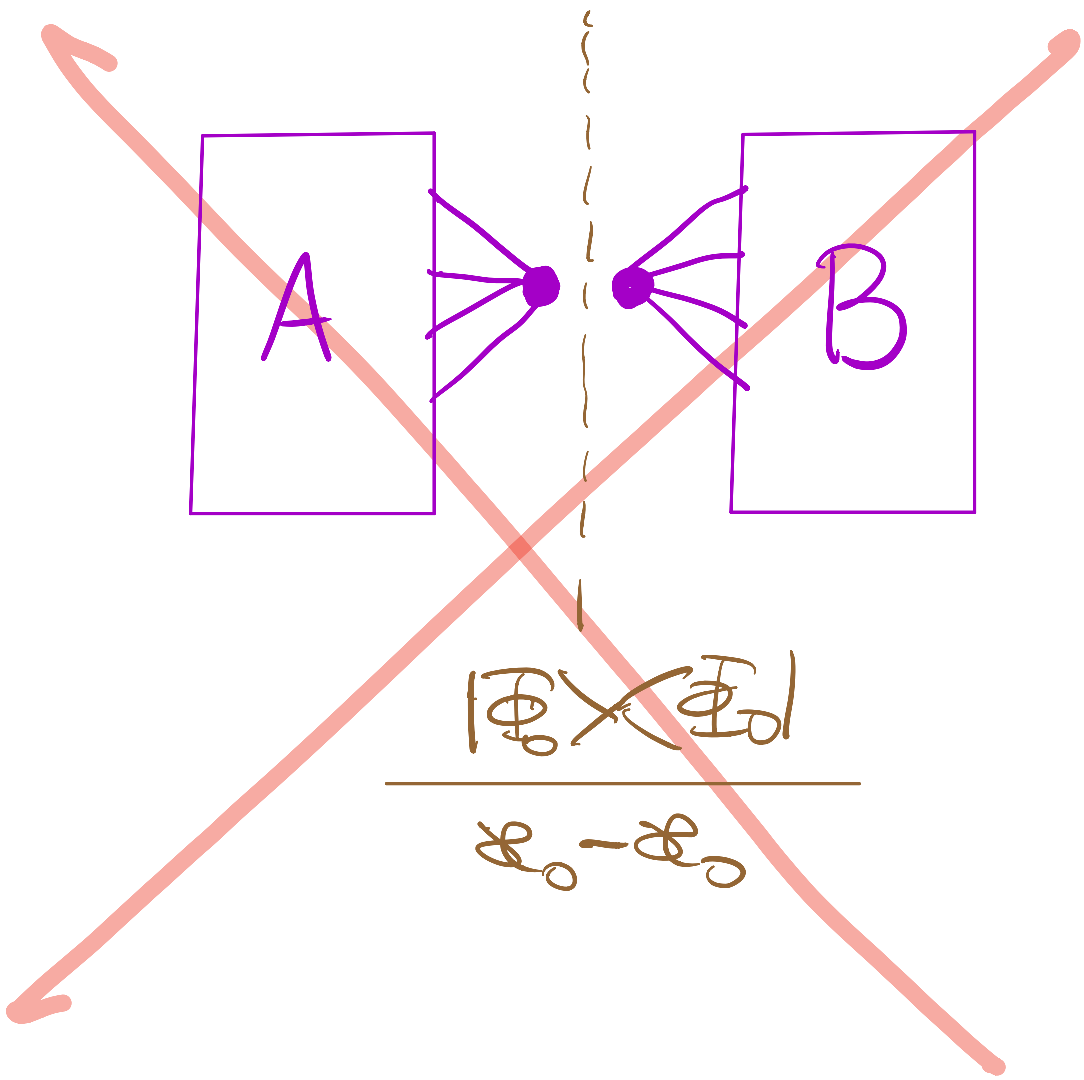
if we adopted the denominator convention.

$$\ldots \left(R^{(0)}\right)^m \underset{(Q_N \text{ or } V_N)}{W} \left(R^{(0)}\right)^n W \ldots$$



The above structure of MBPT expressions enforces the denominator convention.

DO NOT DRAW DIAGRAMS WITH "DANGEROUS DENOMINATORS":



$$\boxed{K_0^{(2)} = K_0^{(2)}(S) + K_0^{(2)}(D)}$$

$$K_0^{(2)}(S) = \sum_{i,a} \frac{\langle i|\hat{q}|a\rangle\langle a|\hat{q}|i\rangle}{\varepsilon_i - \varepsilon_a}$$

previously A

$$= \sum_{i,a} \langle i|\hat{q}|a\rangle\langle a|\hat{q}|i\rangle \times \Delta^{(1)}(i;a)$$

$$\Delta^{(k)}(i_1,\ldots,i_n;a_1,\ldots,a_n)$$

$$= \left(-\mathscr{E}^{a_1\ldots a_n}_{i_1\ldots i_n}\right)^{-k}$$

$$= \left[\sum_{g=1}^{n}\left(\varepsilon_{i_g} - \varepsilon_{a_g}\right)\right]^{-k}$$

(n=1, singles, S)

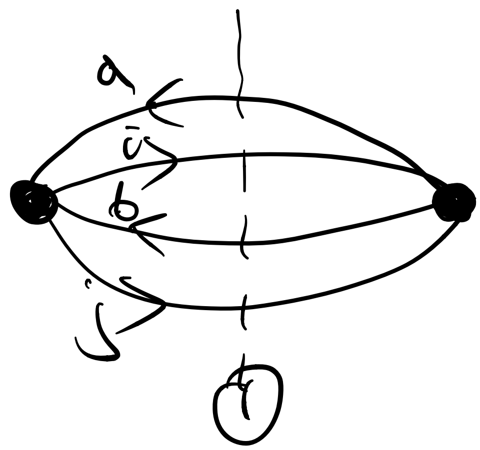
$k_0^{(2)}(S)$ contributes only if $\hat{g} \neq 0$ ($\hat{g} \neq u$; $\hat{\Sigma} + \hat{u} \neq \hat{f}$, non-H-F $|\Phi_0\rangle$ and orbitals

previously D

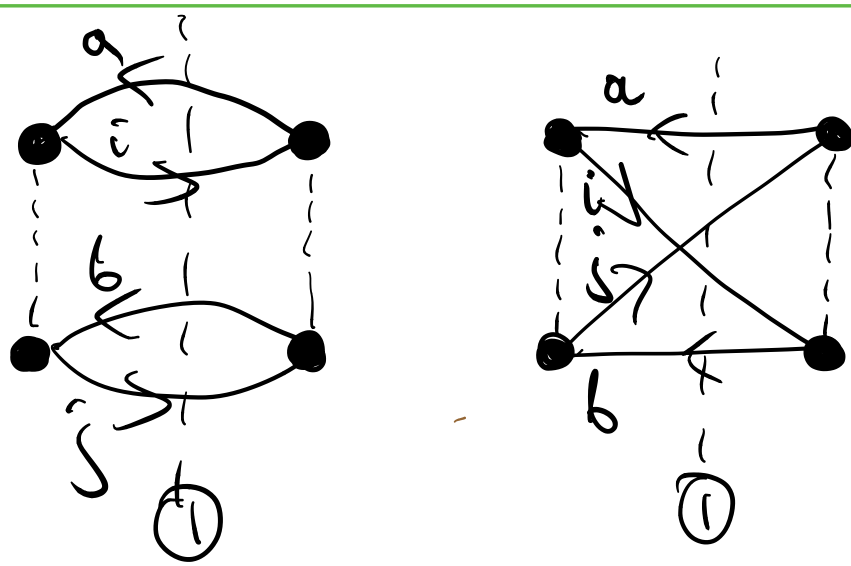
$$k_0^{(2)}(D) = \frac{1}{4} \sum_{ijab} \frac{\langle ij|\hat{v}|ab\rangle_A \langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b}$$

$$= \frac{1}{4} \sum_{ijab} \langle ij|\hat{v}|ab\rangle_A \langle ab|\hat{v}|ij\rangle_A \times \Delta^{(1)}(i,j;a,b)$$

$$= \frac{1}{2} \sum_{ijab} \langle ij|\hat{o}|ab\rangle\langle ab|\hat{v}|ij\rangle_A \times \Delta^{(1)}(i,j;a,b)$$



(H)



(G)

How about $|\Psi_0^{(1)}\rangle$?

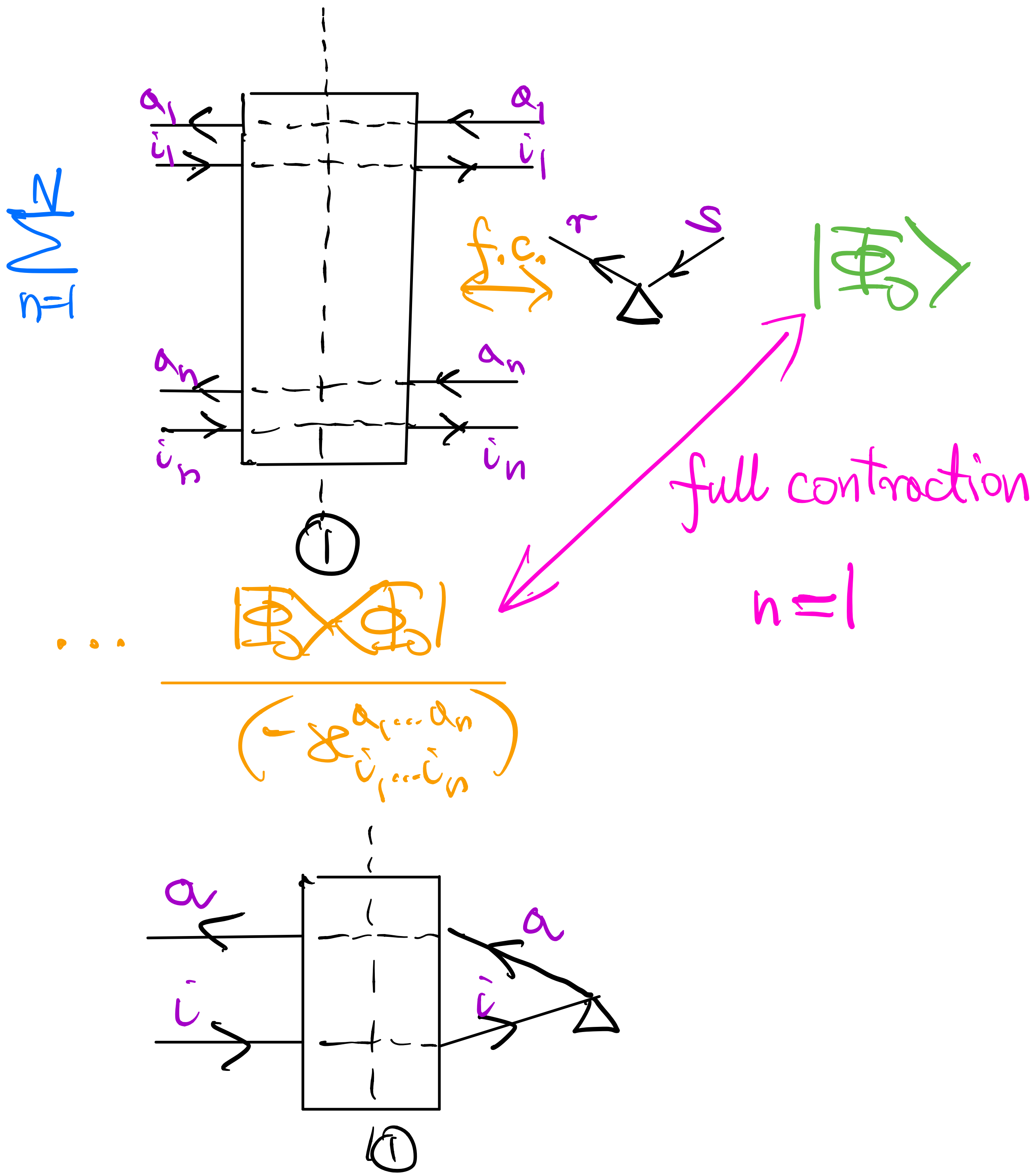
$$|\Psi_0^{(1)}\rangle = R^{(0)} W |\Phi_0\rangle$$

$$= |\Psi_0^{(1)}(S)\rangle + |\Psi_0^{(1)}(D)\rangle$$

$$|\Psi_0^{(1)}(S)\rangle = R^{(0)} \mathcal{L}_N |\Phi_0\rangle$$

$$|\Psi_0^{(1)}(D)\rangle = R^{(0)} V_N |\Phi_0\rangle$$

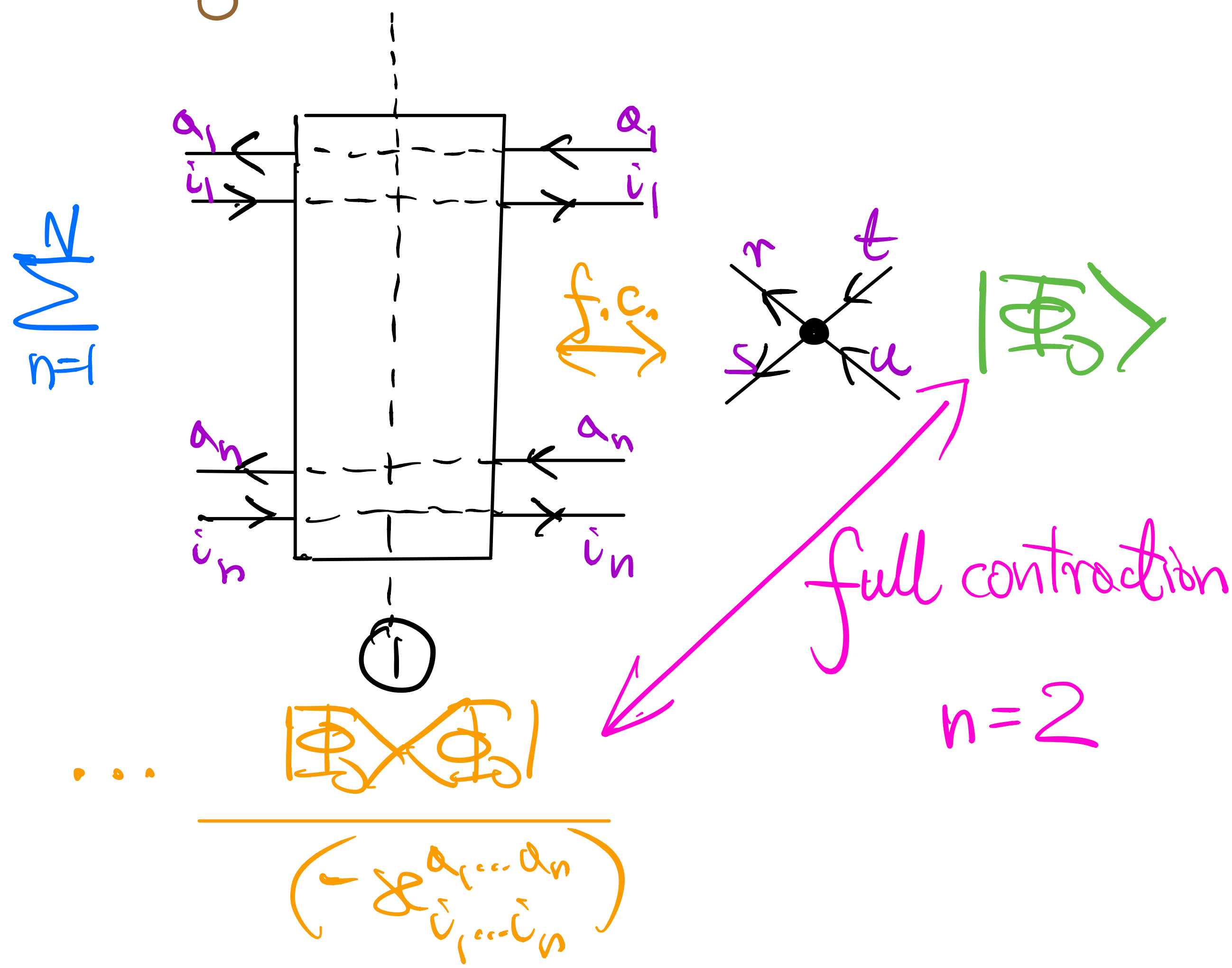
$|\Psi_0^{(n)}(S)\rangle$:

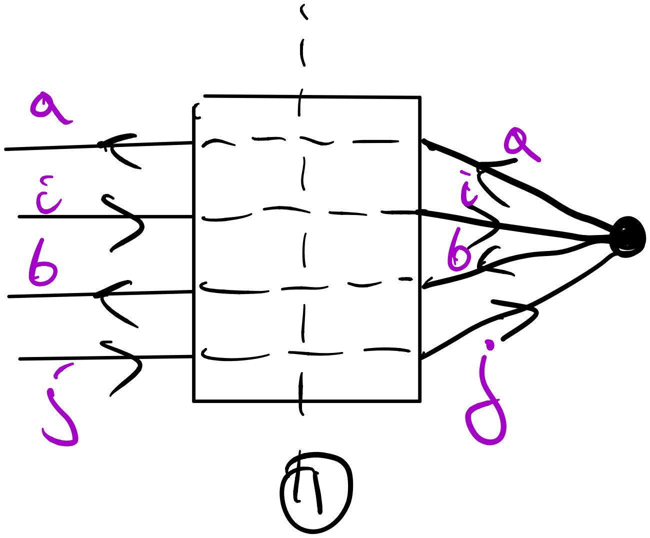


$$|\Psi_0^{(1)}(S)\rangle = \sum_{i,a} \frac{\langle a|\hat{q}|i\rangle}{\varepsilon_i - \varepsilon_a} N[X_a^{\dagger} X_i] |\Phi_0\rangle$$

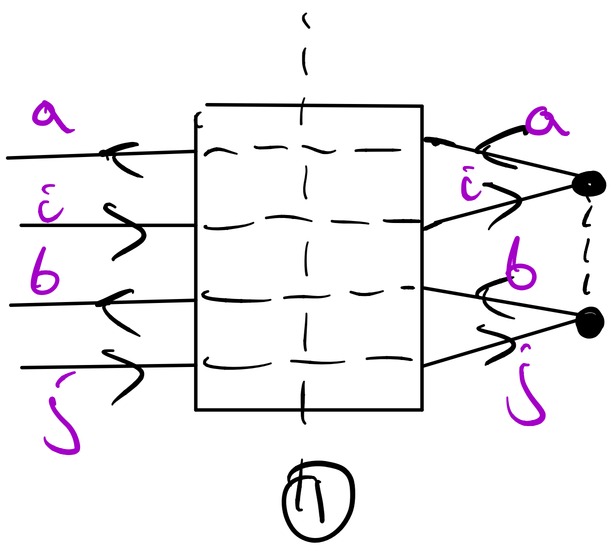
$$= \sum_{i,a} \frac{\langle a|\hat{q}|i\rangle}{\varepsilon_i - \varepsilon_a} |\Phi_i^a\rangle$$

$|\Psi_0^{(1)}(D)\rangle$:





(H)



(B)

$$|\Psi_0^{(1)}(D)\rangle = \frac{1}{4}\sum_{ijab} \frac{\langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i-\varepsilon_a+\varepsilon_j-\varepsilon_b}$$

$$\times N[X_a^\dagger X_i X_b^\dagger X_j]|\Phi\rangle$$

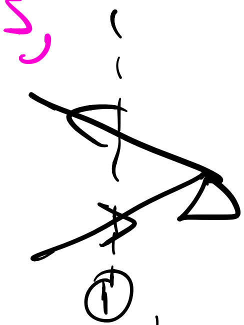
$$= \frac{1}{4} \sum_{ijab} \frac{\langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b} |\Phi_{ij}^{ab}\rangle$$

$$= \frac{1}{2} \sum_{ijab} \frac{\langle ab|\hat{v}|ij\rangle}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b} |\Phi_{ij}^{ab}\rangle$$

$|\Psi_0^{(1)}(S)\rangle$ contributes only if $\hat{q} \neq 0$ (non-HF $|\Phi_0\rangle$)

We could have obtained the same results from Q_N and V_N, without drawing reduced resolvents,

$|\Psi_0^{(1)}(S)\rangle$:

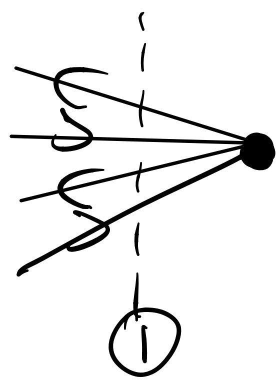


(H)

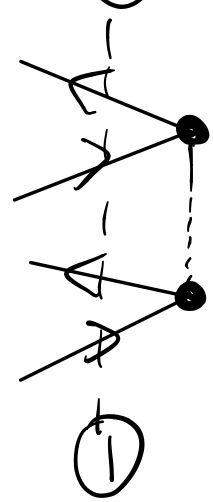
(or

(G))

$|\Psi_0^{(1)}(D)\rangle$:



(H)



(B) or (G)

if we adopted the denominator convention (in this case, read the denominators from the external lines extending to the left).

$$|\Psi_0^{(1)}\rangle = |\Psi_0^{(1)}(S)\rangle + |\Psi_0^{(1)}(D)\rangle$$

$$|\Psi_0^{(1)}(S)\rangle = \sum_{i,a} \langle a|\hat{q}|i\rangle \Delta^{(1)}(i;a) \times |\Phi_i^a\rangle$$

$$|\Psi_0^{(1)}(D)\rangle = \frac{1}{4}\sum_{ijab} \langle ab|\hat{v}|ij\rangle_A \times \Delta^{(1)}(i,j;a,b)\,|\Phi_{ij}^{ab}\rangle$$

$$= \frac{1}{2}\sum_{ijab} \langle ab|\hat{v}|ij\rangle \Delta^{(1)}(ij;a,b) \times |\Phi_{ij}^{ab}\rangle .$$

Note that $|\Psi_0^{(1)}(S)\rangle = R_1^{(0)} Q_N |\Phi_0\rangle$,
$|\Psi_0^{(1)}(D)\rangle = R_2^{(0)} V_N |\Phi_0\rangle$.

Similarly, $K_0^{(2)}(S) = \langle\Phi_0| Q_N R_1^{(0)} Q_N |\Phi_0\rangle$,
$K_0^{(2)}(D) = \langle\Phi_0| V_N R_2^{(0)} V_N |\Phi_0\rangle$.

This is not a surprise. For example,

$$\langle\Phi_0| V_N R^{(0)} V_N |\Phi_0\rangle$$

$$= \sum_{n=1}^{N} \sum_{\substack{i_1<\dots<i_n \\ a_1<\dots<a_n}} \frac{\langle\Phi_0|V_N|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle\langle\Phi_{i_1\dots i_n}^{a_1\dots a_n}|V_N|\Phi_0\rangle}{\left(-\mathcal{E}_{i_1\dots i_n}^{a_1\dots a_n}\right)}$$

nonzero only if $n=2$
($\langle\Phi_0|$ can only couple to doubly excited determinants via V_N)

$$\langle \Phi_0 | V_N R^{(0)} V_N | \Phi_0 \rangle = \langle \Phi_0 | V_N R_2^{(0)} V_N | \Phi_0 \rangle .$$

MBPT(2) energy and MBPT(1) wave function capture the leading correlations due to doubles and, if $\hat{q} \neq \hat{g}$, i.e., the non-Hartree-Fock reference and orbitals are used, singly excited contributions.

We must go to higher orders to see the emergence of higher-than-doubly excited contributions.

From now on, we will not be drawing diagrams representing reduced resolvent operators. Instead, we will rely on the denominator convention (slice the lines in regions between neighboring Ws and, in the case of wave function corrections, external lines extending to the left to read the denominators).