PROOF OF LINKED CLUSTER THEOREM (continued)

So far, we have demonstrated that

$$
\begin{aligned}
(\mathcal{H}_0 - K_0)\,|\Psi_0\rangle
&= (\mathcal{H}_0 - K_0)\left[\,|\Phi_0\rangle + \sum_{n=1}^{\infty} \left\{ (R^{(0)}W)^n \right\}_L |\Phi_0\rangle \right] \\
&= \sum_{n=0}^{\infty} \left\{ W \left\{ (R^{(0)}W)^n \right\}_L \right\}_{L_{ext}} |\Phi_0\rangle
\end{aligned}
$$

linked

linked with external lines

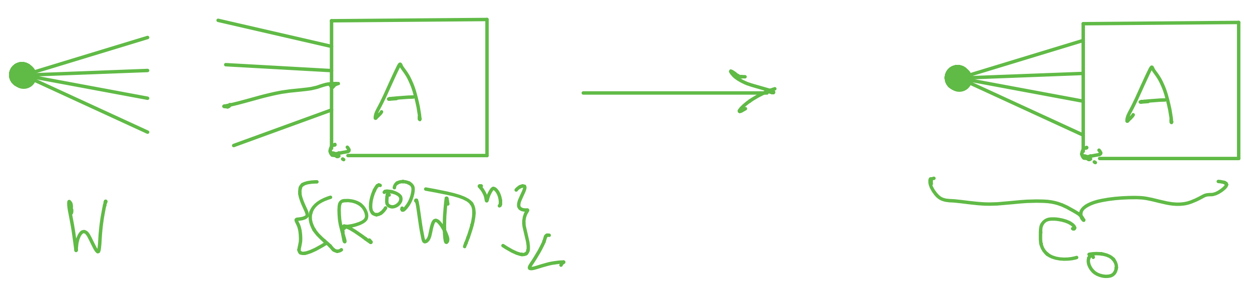
Let us calculate

$$\sum_{n=0}^{\infty} W\{(R^{(0)}W)^n\}_L |\Phi\rangle$$

$$= \sum_{n=0}^{\infty} \{W\{(R^{(0)}W)^n\}_L\}_{C_0} |\Phi\rangle$$

connected with no external lines

Case I: W is used to close all external lines of $\{(R^{(0)}W)^n\}_L$, as in



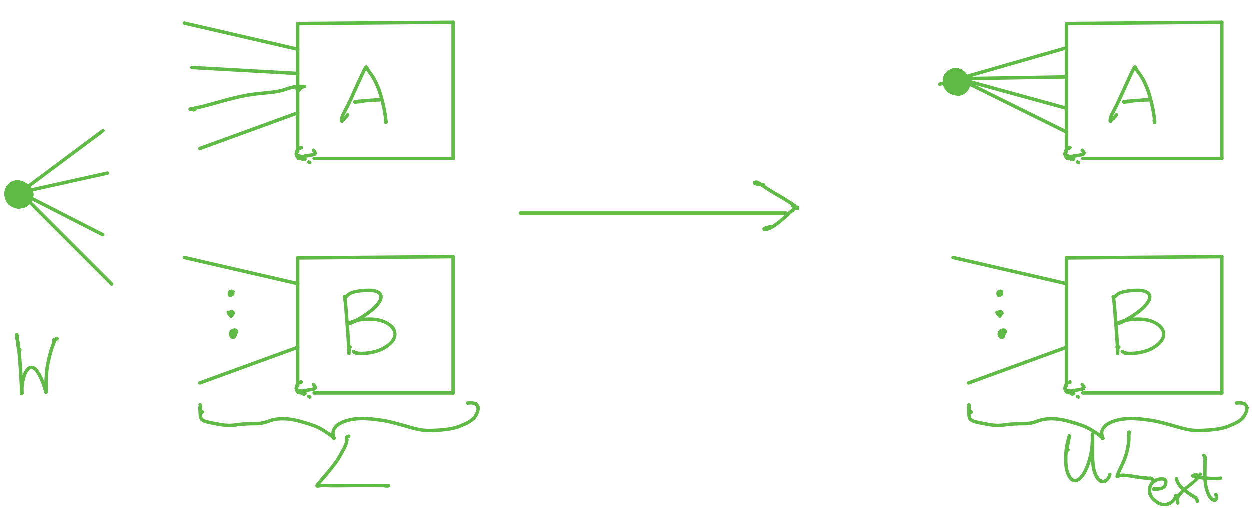
Case II: Two cases, where W does not close all the lines of $\{(R^{(0)}W)^n\}_L$

Case IIA:

$$+\sum_{n=0}^{\infty}\Big\{W\{(R^{(0)}W)^n\}_L\Big\}_{UL_{ext}}|\Phi_0\rangle$$

unlinked with external lines

W closes the lines of one (or more) of the disconnected parts of $\{(R^{(0)}W)^n\}_L$, producing the vacuum component(s), resulting in unlinked diagrams with external lines, as in



Case II B:

$$+\sum_{n=0}^{\infty}\left\{W\left\{\left(R^{(0)}W\right)^{n}\right\}_{L}\right\}_{L_{ext}}\left|\Phi_0\right\rangle$$

linked with external lines

W does not close lines of any of the parts of $\left\{\left(R^{(0)}W\right)^{n}\right\}_{L}$ completely, leaving us with linked diagrams with external lines

As a result of the above analysis, we obtain:

$$(\mathcal{E}_0 - K_0)|\Psi_0\rangle = \sum_{n=0}^{\infty} \{W\{(R^{(0)}W)^n\}_L\}_{L_{ext}}|\Phi_0\rangle$$

$$= W \sum_{n=0}^{\infty} \{(R^{(0)}W)^n\}_L |\Phi_0\rangle \qquad (A)$$

$$- \sum_{n=0}^{\infty} \{W\{(R^{(0)}W)^n\}_L\}_{C_0} |\Phi_0\rangle \qquad (B)$$

$$- \sum_{n=0}^{\infty} \{W\{(R^{(0)}W)^n\}_L\}_{UL_{ext}} |\Phi_0\rangle \qquad (C)$$

(A):

$$W \sum_{n=0}^{\infty} \{(R^{(0)}W)^n\}_L |\Phi_0\rangle$$

$$= W|\Psi_0\rangle \qquad \checkmark$$

(B):

$$\sum_{n=0}^{\infty} \overbrace{\left\{W\left\{(R^{(0)}W)^n\right\}_L\right\}_{c_0}}^{\text{a number } \langle\Phi_0|\dots|\Phi_0\rangle} |\Phi_0\rangle$$

$$= \sum_{n=0}^{\infty} \left\{W(R^{(0)}W)^n\right\}_{c_0} |\Phi_0\rangle$$

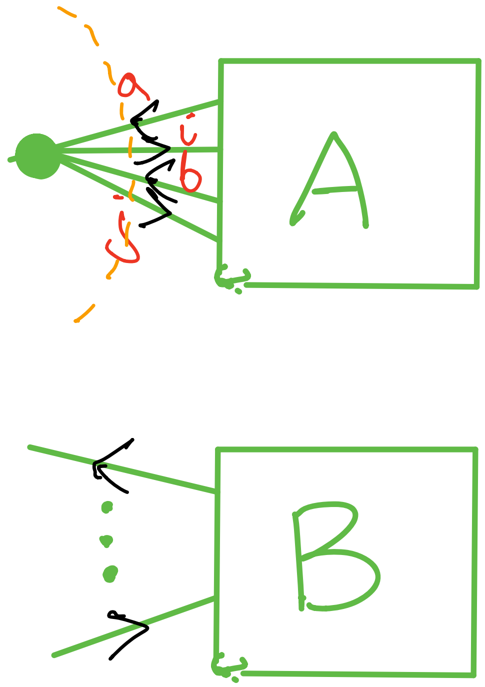
$$= (K_0 - \varepsilon_0)|\Phi_0\rangle$$

(C):

$$\sum_{n=0}^{\infty} \left\{W\left\{(R^{(0)}W)^n\right\}_L\right\}_{uL_{ext}} |\Phi_0\rangle$$

$$= \sum_{n=2}^{\infty} \left\{W\left\{(R^{(0)}W)^n\right\}_L\right\}_{uL_{ext}} |\Phi_0\rangle$$

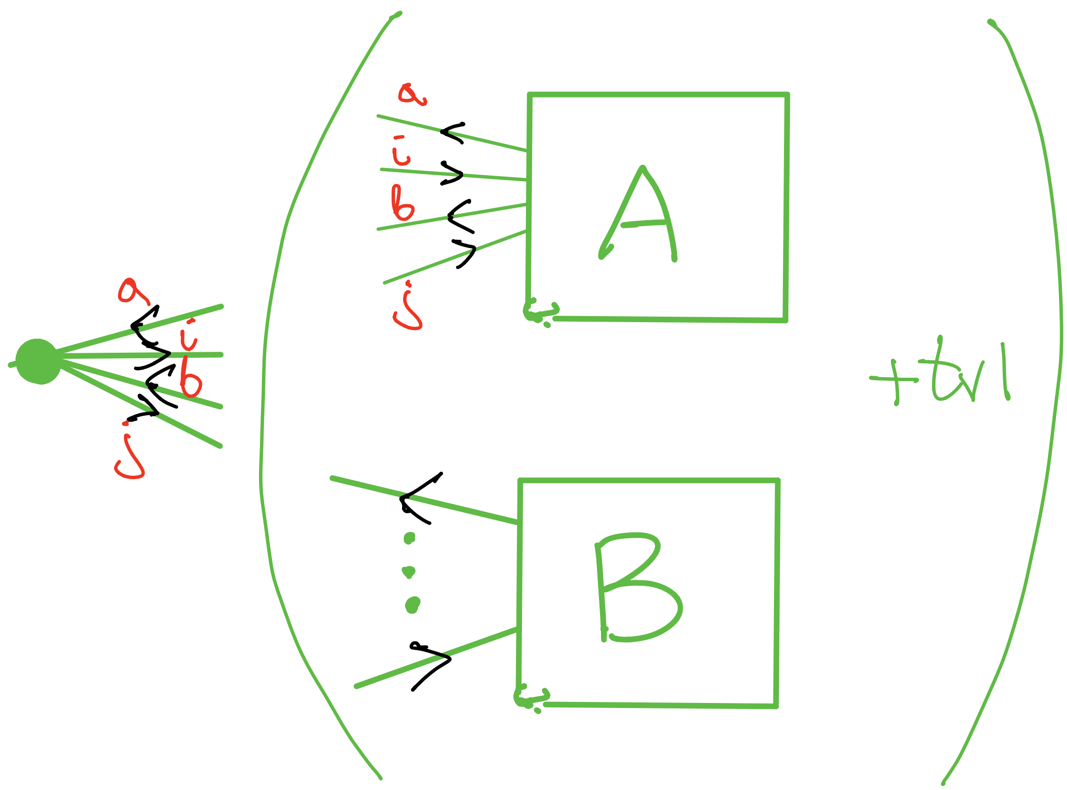
$\sum_{a,b,i,j}$



There is at least one W in A and at least one W in B

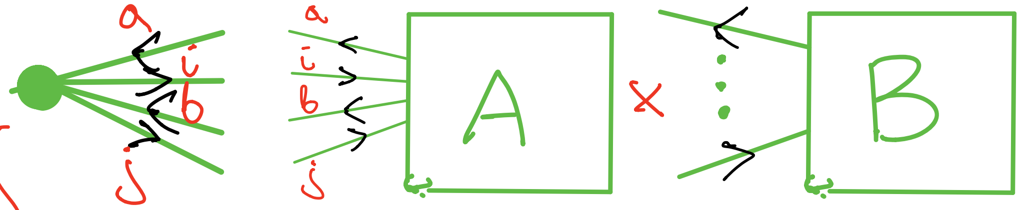
+ all time versions of the first kind (tvl)

$= \sum_{a,b,i,j}$

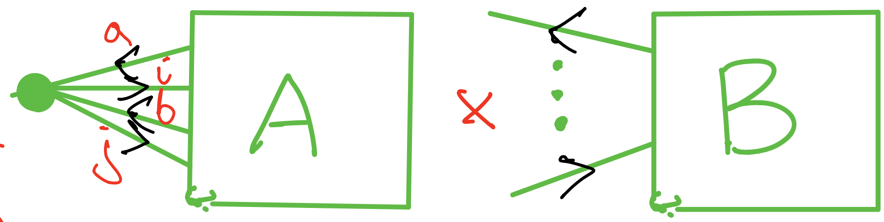


F2 = factorization lemma

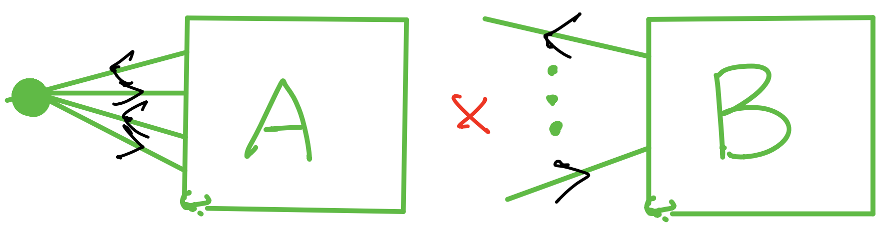
$$FL = \sum_{a,b,i,j}$$



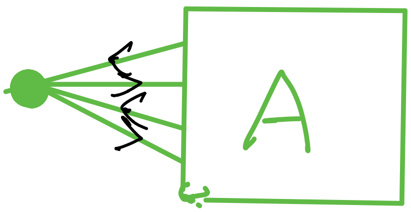
$$= \sum_{a,b,i,j}$$



$$=$$

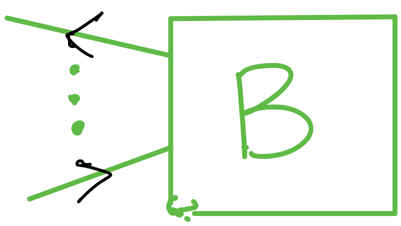


Since all of the above is done in all orders, we can write



$$= \sum_{n=1}^{\infty} \left\{ W \left\{ \left(R^{(0)} W \right)^n \right\}_L \right\}_{C_0}$$

$$= \sum_{n=1}^{\infty} \left\{ W \left(R^{(0)} W \right)^n \right\}_{C_0} = K_0 - \mathcal{E}_0$$



$$= \sum_{n=1}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_L |\Phi\rangle$$

$$= |\Psi_0\rangle - |\Phi_0\rangle$$

This means that (C) is:

$$\sum_{n=0}^{\infty} \left\{ W \left\{ \left(R^{(0)} W\right)^n \right\}_L \right\}_{UL_{ext}} |\Phi_0\rangle$$

$$= \sum_{n=2}^{\infty} \left\{ W \left\{ \left(R^{(0)} W\right)^n \right\}_L \right\}_{UL_{ext}} |\Phi_0\rangle$$

$$= \left(K_0 - \mathcal{E}_0\right)\left(|\Psi_0\rangle - |\Phi_0\rangle\right) \checkmark$$

Substituting (A), (B), and (C) into the equation for $(\mathcal{E}_0 - K_0)|\Psi_0\rangle$ produces

$$(\varepsilon_0 - K_0)|\Psi_0\rangle$$

$$= W|\Psi_0\rangle - \cancel{(K_0-\varepsilon_0)|\Phi_0\rangle}$$

$$-(K_0-\varepsilon_0)(|\Psi_0\rangle - \cancel{|\Phi_0\rangle})$$

$$(\cancel{\varepsilon_0} - K_0)|\Psi_0\rangle = W|\Psi_0\rangle$$

$$-(K_0 - \cancel{\varepsilon_0})|\Psi_0\rangle$$

$$-K_0|\Psi_0\rangle = W|\Psi_0\rangle$$

$$-K_0|\Psi_0\rangle$$

$$(K_0+W)|\Psi_0\rangle = K_0|\Psi_0\rangle,$$

where

$$|\Psi_0\rangle = \sum_{n=0}^{\infty} \{(R^{(0)} W)^n\}_L |\Phi_0\rangle$$

and

$$K_0 = \underbrace{\mathcal{E}_0}_{=0} + \sum_{n=0}^{\infty} \langle\Phi_0|\{W(R^{(0)}W)^n\}_C|\Phi_0\rangle$$

in reality, $n=1$, since $\langle W\rangle = 0$ ∴

$$\boxed{\begin{aligned} |\Psi_0^{(n)}\rangle &= \{(R^{(0)}W)^n\}_L|\Phi_0\rangle \\ K_0^{(n+1)} &= \langle\Phi_0|\{W(R^{(0)}W)^n\}_C|\Phi_0\rangle \end{aligned}}$$

Linked-cluster theorem (Brueckner, 1955; Goldstone, 1957)

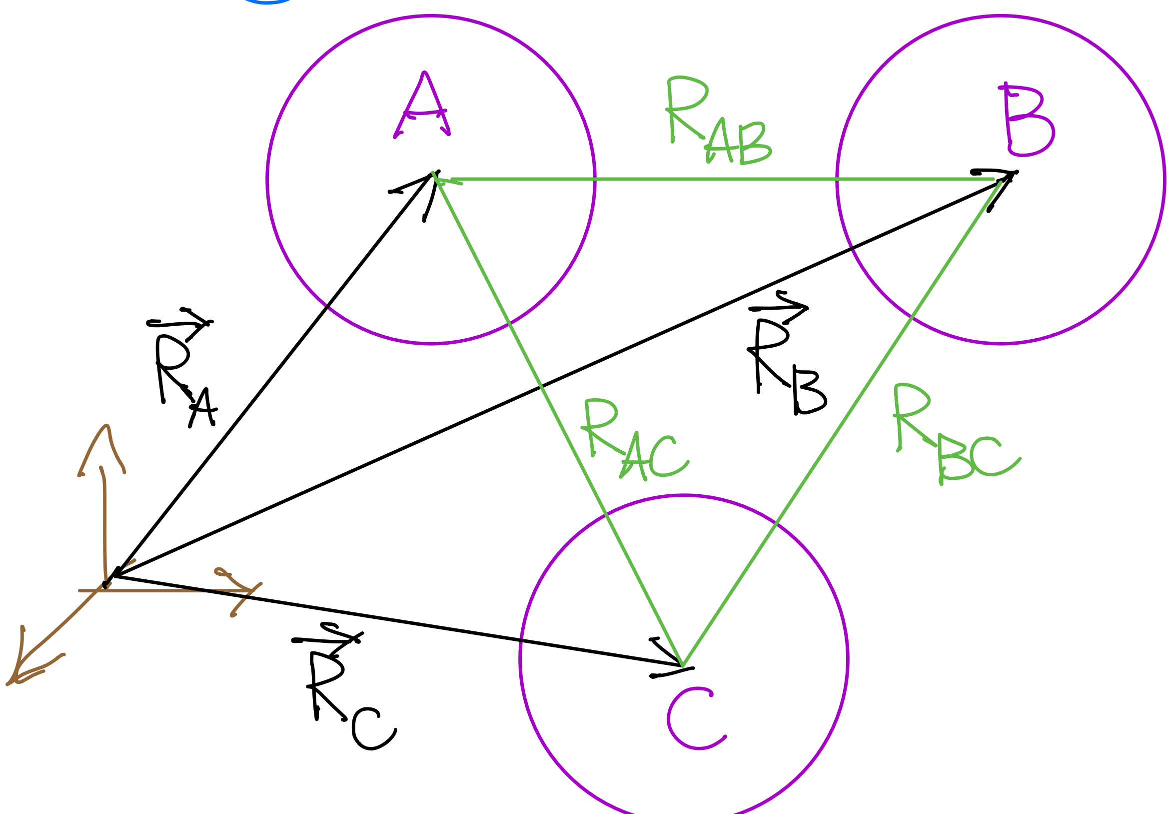
Consequences of the linked cluster theorem:

SIZE EXTENSIVITY OF ENERGY CORRECTIONS

Each finite-order MBPT calculation uses only connected diagrams in energy corrections,

$$\langle \Phi_0 | \{ W (R^{(0)} W)^n \}_C | \Phi_0 \rangle .$$

Let us try to understand what happens to connected quantities (of the $\langle \Phi_0 | \{ W (R^{(0)} W)^n \}_C | \Phi_0 \rangle$ or $\{ (R^{(0)} W)^n \}_C | \Phi_0 \rangle$ type) when the system separates into noninteracting fragments.



$$R_{AB}, R_{AC}, R_{BC}, \ldots \longrightarrow \infty$$

$$\text{System} \rightarrow A + B + \ldots$$

$$= \sum_{C} C$$

fragments

Single-particle states of the entire system:

$$|p\rangle \longrightarrow |p_A\rangle, |p_B\rangle, \ldots$$

$\chi_p(x)$ $\chi_{p_A}(x)$ $\chi_{p_B}(x)$

(in general, $|p_C\rangle$)

$\chi_{p_C}(x)$

Within a fragment, single-particle states are orthonormal.

In the non-interacting limit,

$$\chi_{p_A}(x)^* \chi_{q_B}(x) = 0$$

if $A \neq B$

(Zero Differential Overlap or ZDO).

Integrating,

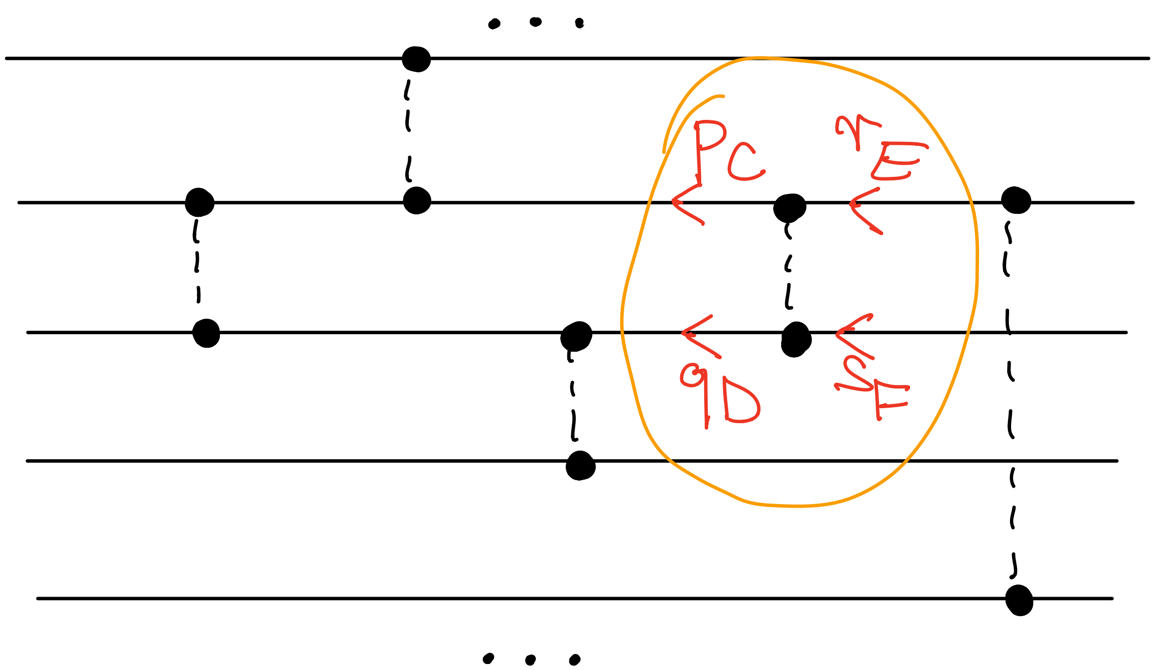
$$\langle p_A | q_B \rangle = 0 \quad \text{if} \quad A \neq B.$$

Thus,

$|p_A\rangle, |p_B\rangle, \ldots$ is an orthonormal basis.

connected quantity

$$\Lambda = \sum_{\dots C, D, E, F, \dots} \; \sum_{\dots p_C, q_D, r_E, s_F, \dots}$$



$$\langle p_C \, q_D | \hat{v} | r_E \, s_F \rangle \qquad \checkmark$$

$$\langle \overset{1}{p_C}\,\overset{2}{q_D} | \hat{v} | \overset{1}{r_E}\,\overset{2}{s_F} \rangle \underset{\hat{v}=\frac{1}{r_{12}}}{\overset{\text{assuming}}{=}}$$

$$= \int \frac{\psi^*_{p_C}(x_1)\,\psi^*_{q_D}(x_2)\,\psi_{r_E}(x_1)\,\psi_{s_F}(x_2)}{r_{12}}\,dx_1\,dx_2$$

$$\checkmark \quad \psi^*_{p_C}(x_1)\,\psi_{r_E}(x_1) \xrightarrow[R_{CE}\to\infty]{} 0$$

$$\checkmark \quad \psi^*_{q_D}(x_2)\,\psi_{s_F}(x_2) \xrightarrow[R_{DF}\to\infty]{} 0$$

In the non-interacting limit,

$$C = E, \quad D = F$$

We are left with

$$\langle p_C q_D | \hat{v} | r_C s_D \rangle$$

$$= \int \frac{\chi^*_{p_C}(x_1)\,\chi^*_{q_D}(x_2)\,\chi_{r_C}(x_1)\,\chi_{s_D}(x_2)}{r_{12}}\, dx_1\, dx_2$$

$$\vec{r}_1 \approx \vec{R}_C \, , \quad \vec{r}_2 \approx \vec{R}_D$$

If $C \neq D$, $R_{CD} \to \infty$,

$r_{12} \to \infty$,

$$\langle p_C q_D | \hat{v} | r_C s_D \rangle = 0$$

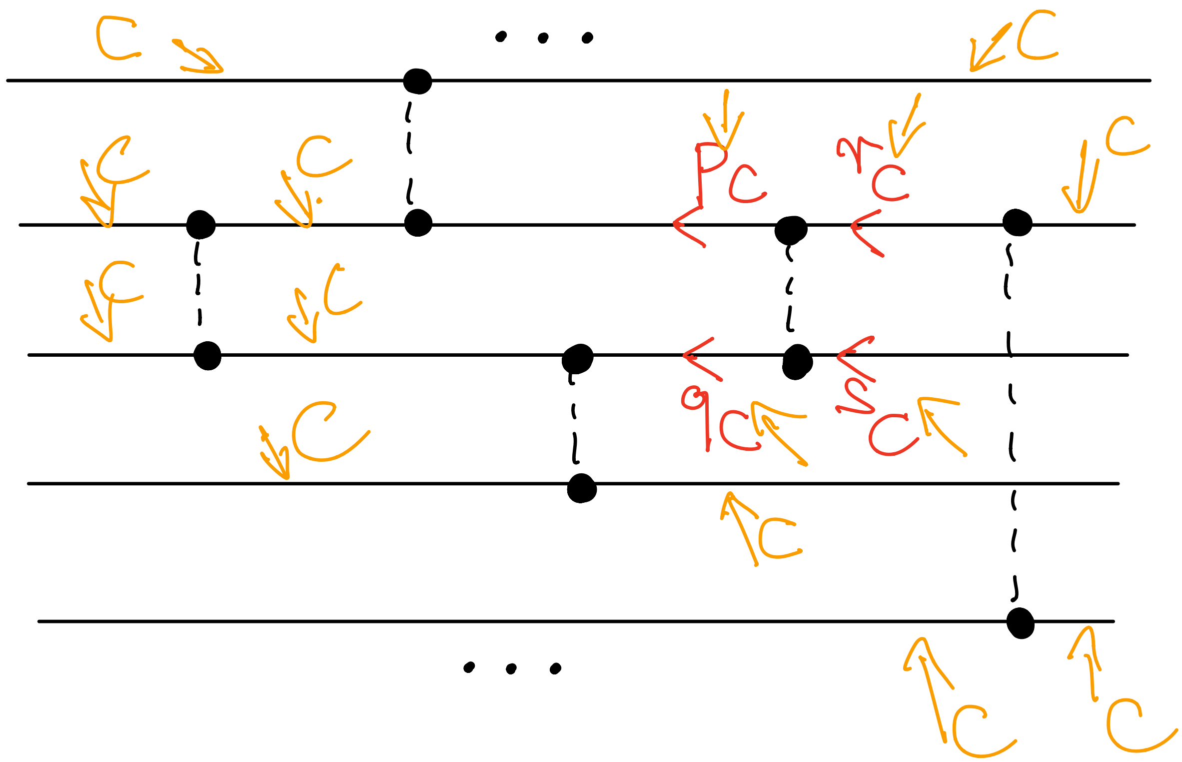
C must equal to D.

We are down to

$$\langle p_C q_C | \hat{v} | r_C s_C \rangle,$$

$C = D = E = F$ or we get a zero.

$$\Lambda = \sum_{\ldots C \ldots} \; \sum_{\ldots p_C, q_C, r_C, s_C, \ldots}$$



$$\Lambda = \sum_C \Lambda_C ,$$

where Λ_C is Λ drawn for fragment C. Also,

$$[\Lambda_C, \Lambda_D] = 0 .$$

Going back to MBPT corrections to energy,

$$K_0^{(n+1)} = \langle \Phi_0 | \{ W (R^{(0)} W)^n \}_C | \Phi_0 \rangle$$

$$= K_0^{(n+1)}(A) + K_0^{(n+1)}(B) + \ldots$$

i.e., finite-order MBPT calculations are size-extensive for energy.

Connected quantities scale as N, e.g., MBPT energy of N H_2 molecules,

$$\Delta E(N\, H_2) \underset{\substack{\text{noninteracting}\\ \text{limit}}}{=} N\, \Delta E(H_2).$$

For comparison, in truncated CI (e.g., CISD), we have disconnected terms in energy,

connected $\sim N$,

disconnected with 2 parts $\sim N^2$,

disconnected with 3 parts $\sim N^3$, etc.

For NH_2,

$$\Delta E^{(GFSD)} \sim \sqrt{N},$$

$$\frac{\Delta E^{(GFSD)}}{N} \xrightarrow[N\to\infty]{} 0.$$

Problems with MBPT:
wave function obtained in finite-order calculations does not satisfy the separability condition,

$$|\Psi_0^{(AB)}\rangle \xrightarrow[R_{AB}\to\infty]{} |\Psi_0^{(A)}\rangle\, |\Psi_0^{(B)}\rangle.$$

Other problems: convergence.

There is a theory that can satisfy separability condition, while being size extensive. That theory is called

COUPLED-CLUSTER THEORY.

Connected-cluster theorem

(Hubbard, 1957; Hugenholtz; 1957)

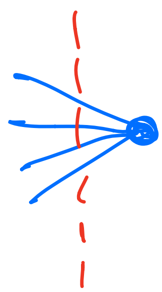
$$|\Psi_0\rangle = \sum_{n=0}^{\infty} \left\{ \left(R^{(0)} W\right)^n \right\}_{\mathcal{L}} |\Phi\rangle$$

Let us organize all linked d-ms according to the number of connected pieces in them.

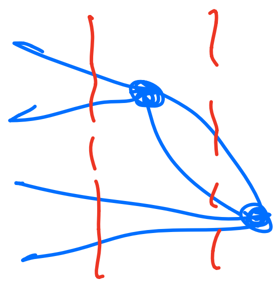
$\mathcal{L}_r$ = linked d-ms with exactly r connected components

Examples:

$\mathcal{L}_1$, $r=1$, connected d-ms,

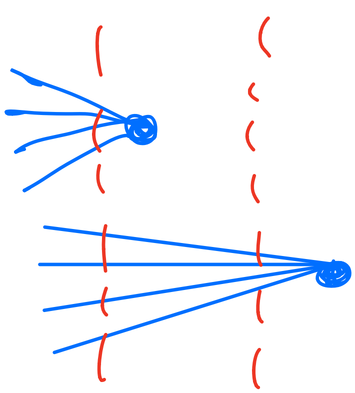


,

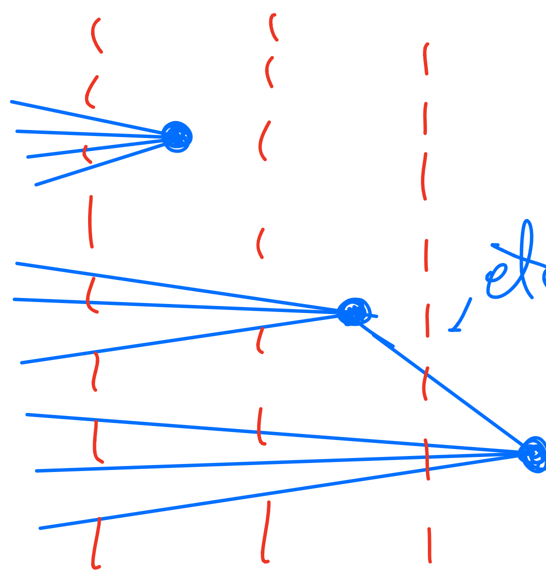


, etc.

$\mathcal{L}_2$, $r=2$,

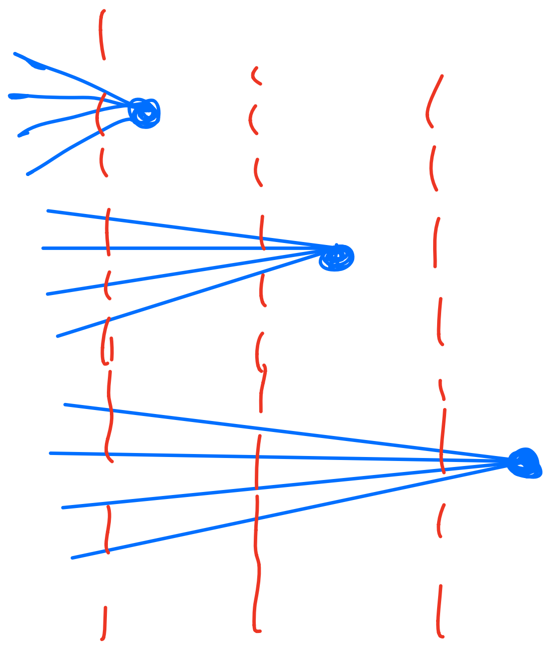


,



, etc.

$L_3, \ r=3,$



, etc.

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=1}^{\infty} |\Psi_0^{(n)}\rangle$$

$$= |\Phi_0\rangle + \sum_{n=1}^{\infty} \sum_{r=1}^{n} \left\{ R^{(0)} W \right\}^{n}_{L_r} |\Phi_0\rangle$$

$$\sum_{n=1}^{\infty}\left\{\left(R^{(0)}W\right)^n\right\}_{L}|\Phi_0\rangle$$

$$= \sum_{n=1}^{\infty}\left\{\left(R^{(0)}W\right)^n\right\}_{C}|\Phi_0\rangle$$

$$= T|\Phi_0\rangle$$

T = cluster operator

We will show that

$$|\Psi_0\rangle = e^{T}|\Phi_0\rangle$$

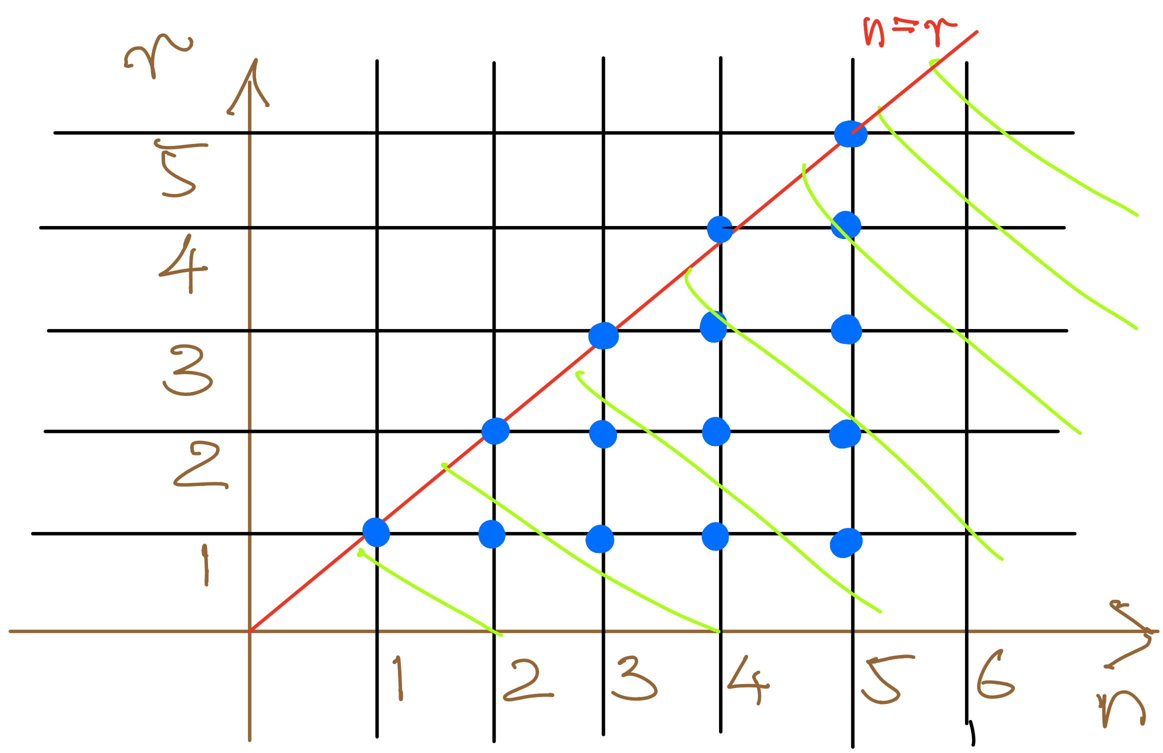
$$= \sum_{r=0}^{\infty}\frac{1}{r!}T^{r}|\Phi_0\rangle$$

|

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=1}^{\infty} |\Psi_0^{(n)}\rangle$$

$$= |\Phi_0\rangle + \sum_{n=1}^{\infty} \sum_{r=1}^{n} \left\{ \left(R^{(0)} W \right)^n \right\}_r |\Phi_0\rangle$$

$$= |\Phi_0\rangle + \sum_{r=1}^{\infty} \sum_{n=r}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_r |\Phi_0\rangle$$



$$\sum_{n=r}^{\infty}\{R^{(0)}W)^n\}_{L_r}|\Phi_0\rangle = \frac{1}{r!}T^r|\Phi_0\rangle \quad \checkmark$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{r=1}^{\infty}\sum_{n=r}^{\infty}\{R^{(0)}W)^n\}_{L_r}|\Phi_0\rangle$$

$r=1$, T

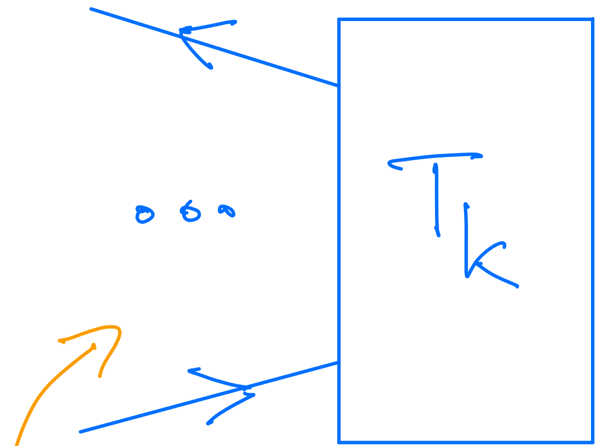
$r=2$, $\frac{1}{2!}T^2$

$r=3$, $\frac{1}{3!}T^3$

etc.

T generates connected d-ms, powers of T generate linked, dis-connected d-ms

$$T|\Phi\rangle = \sum_{n=1}^{\infty}\left\{\left(R^{(0)}W\right)^n\right\}_c |\Phi\rangle$$



2k external lines

$$T = \sum_{k=1}^{N} T_k$$

k-body component of T (kp-kh excitation operator)

$$T_k = \sum_{n=1}^{\infty} T_k^{(n)}$$

$$T_k^{(n)} |\Phi_0\rangle = \underbrace{\left\{ \left(R^{(0)} W \right)^n \right\}_{C,k}}_{\text{all connected d-ms resulting from } n\ W \text{ vertices having } 2k \text{ external lines}} |\Phi_0\rangle$$

$$T_k^{(n)} = \left(\frac{1}{k!} \right)^2 \sum_{\substack{i_1,\dots,i_k \\ a_1,\dots,a_k}} \langle a_1 \dots a_k | t_k^{(n)} | i_1 \dots i_k \rangle_A$$

$t^{(n)\,i_1 \dots i_k}_{a_1 \dots a_k}$

$$\times\ E^{a_1 \dots a_k}_{i_1 \dots i_k}$$

$N[X^\dagger_{a_1} X_{i_1} \dots X^\dagger_{a_k} X_{i_k}]$

$$= \left(\frac{1}{k!}\right)^2 {}^{(n)}t^{i_1 \ldots i_k}_{a_1 \ldots a_k} E^{a_1 \ldots a_k}_{i_1 \ldots i_k}$$

$$T_k = \sum_{n=1}^{\infty} T_k^{(n)}$$

$$T_k = \left(\frac{1}{k!}\right)^2 \sum_{\substack{i_1, \ldots, i_k \\ a_1, \ldots, a_k}} \langle a_1 \ldots a_k | t_k | i_1 \ldots i_k \rangle_A$$

$$\times E^{a_1 \ldots a_k}_{i_1 \ldots i_k}$$

$$= \left(\frac{1}{k!}\right)^2 t^{i_1 \ldots i_k}_{a_1 \ldots a_k} E^{a_1 \ldots a_k}_{i_1 \ldots i_k}$$

cluster amplitudes

$$t^{i_1\ldots i_k}_{a_1\ldots a_k} = \sum_{n=1}^{\infty} {}^{(n)}t^{i_1\ldots i_k}_{a_1\ldots a_k}$$

$${}^{(n)}t^{i_1\ldots i_k}_{a_1\ldots a_k} = \left\langle \Phi^{a_1\ldots a_k}_{i_1\ldots i_k} \right| \left\{ \left(R^{(0)} W\right)^n \right\}_{C,k} \left| \Phi \right\rangle$$

Let us consider the lowest MBPT orders that produce nonzero $T_k^{(n)}$ contributions.

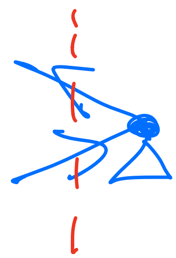
$$T_1^{(n)} |\Phi\rangle = \left\{ \left(R^{(0)} W\right)^n \right\}_{C,1} |\Phi\rangle$$

$$W = Q_N + V_N$$

$n=1$:

$$T_1^{(1)}|\Phi\rangle = \{(R^{(0)}W)\}_{C,1}|\Phi\rangle$$

$$= (R^{(0)}Q_N)_{C,1}|\Phi\rangle$$

$=$  , possible only if $|\Phi\rangle$ is not a H-F state ($Q_N \neq 0$).

In a H-F case,

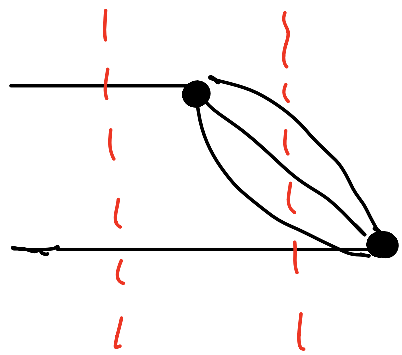
$$T_1^{(1)} = 0.$$

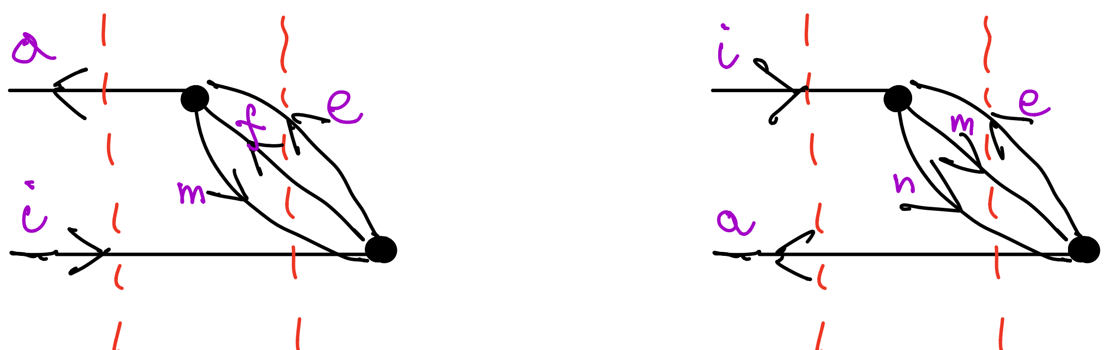
$n=2$:

$$T_1^{(2)}|\Phi_0\rangle = \{(R^{(0)}W)^2\}_{C,1}|\Phi_0\rangle$$

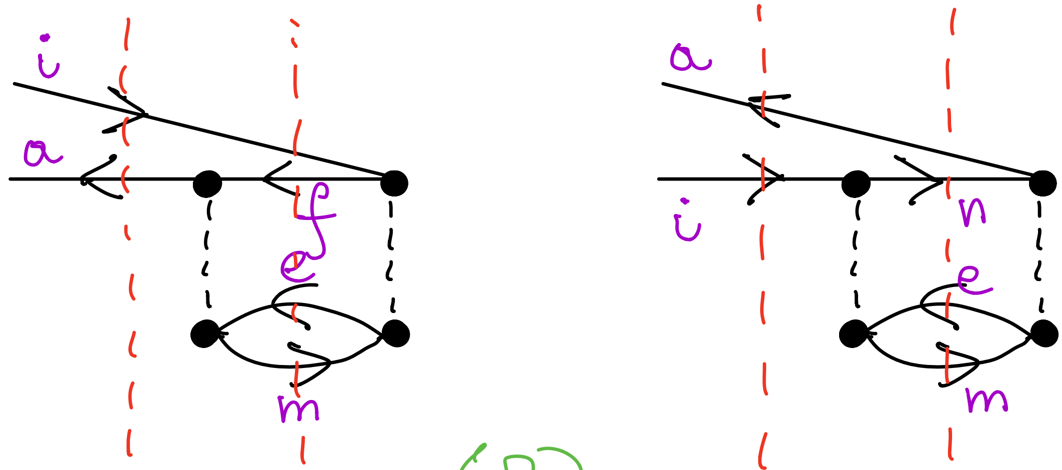
Let us consider $W = V_N$,

$$T_1^{(2)}|\Phi_0\rangle = \{(R^{(0)}V_N)^2\}_{C,1}|\Phi_0\rangle$$





(H)



(B)

$$T_1^{(2)} |\Phi\rangle = \sum_{a,i} (\ldots) |\Phi_i^a\rangle$$

$$T_1^{(2)} = \sum_{a,i} (\ldots) E_i^a$$

$\langle a | t_1^{(2)} | i \rangle$

What is $\langle a | t_1^{(2)} | i \rangle \equiv {}^{(1)}t_a^i$?

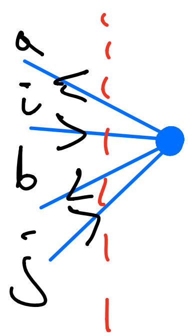
$$T_2^{(n)}|\Phi_0\rangle = \left\{\left(R^{(0)}W\right)^n\right\}_{C,2}|\Phi_0\rangle$$

$n=1$:

$$T_2^{(1)}|\Phi_0\rangle = \left\{\left(R^{(0)}W\right)\right\}_{C,2}|\Phi_0\rangle$$

$$W = \Omega_N + V_N$$

$$T_2^{(1)}|\Phi_0\rangle = \left(R^{(0)}V_N\right)_{C,2}|\Phi_0\rangle$$

$=$ 

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

$$= \sum_{a<b,i<j} \frac{\langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i-\varepsilon_a+\varepsilon_j-\varepsilon_b} |\Phi_{ij}^{ab}\rangle$$

$$T_2^{(1)} = \sum_{a<b,i<j} \langle ab|t_2^{(1)}|ij\rangle_A E_{ij}^{ab}$$

$$\langle ab|t_2^{(1)}|ij\rangle_A = \frac{\langle ab|\hat{v}|ij\rangle_A}{\varepsilon_i-\varepsilon_a+\varepsilon_j-\varepsilon_b}$$

$$^{(1)}t_{ab}^{ij} = \frac{v_{ab}^{ij}}{\varepsilon_i-\varepsilon_a+\varepsilon_j-\varepsilon_b}$$

In general,

$$v_{pq}^{rs} = \langle pq|\hat{v}|rs\rangle_A, \text{ etc.}$$

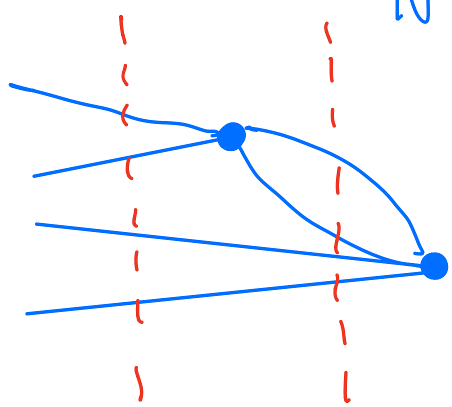
$$H_N = f_p^q N[X^p X_q] + \frac{1}{4} v_{pq}^{rs} N[X^p X^q X_s X_r]$$

$(X^p = X_p^{\dagger})$

Continuing on T_2:

$$T_2^{(2)} | \Phi \rangle = \{ (R^{(2)} W)^2 \}_{c,2} | \Phi \rangle$$

$$W = V_N$$



(3 d-ms)

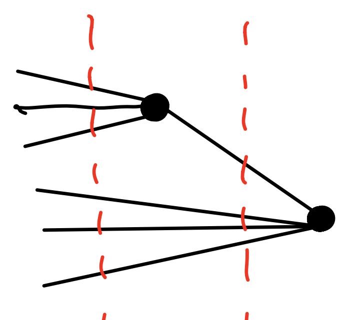
etc.

$$T_1 = T_1^{(1)} + \ldots$$ when a non-HF $|\Phi_0\rangle$ is used

$$T_1 = T_1^{(2)} + \ldots$$ when $|\Phi_0\rangle$ is a H-F state

$$T_2 = T_2^{(1)} + \ldots$$

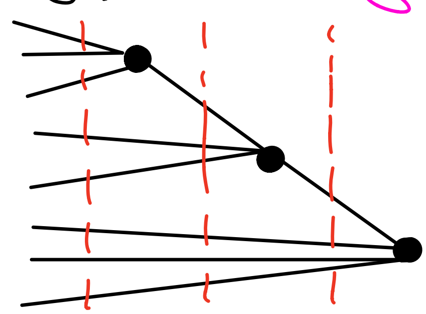
$$T_3 = T_3^{(2)} + \ldots$$



$T_3^{(2)}$

e.g.,

$$T_4 = T_4^{(3)} + \ldots$$



$$|\Psi_0\rangle = e^{T_1 + T_2 + \dots} |\Phi_0\rangle$$

$$= \Big(1 + \underbrace{T_1}_{\text{Singles}} + \underbrace{T_2 + \frac{1}{2!} T_1^2}_{\text{Doubles}}$$

$$+ \underbrace{T_3 + T_1 T_2 + \frac{1}{3!} T_1^3}_{\text{Triples}}$$

$$\left. \begin{aligned} &+ T_4 + T_1 T_3 + \frac{1}{2} T_2^2 \\ &+ \frac{1}{2} T_1^2 T_2 + \frac{1}{4!} T_1^4 \end{aligned} \right\} \text{Quadruples}$$

$$+ \dots$$

$$= \big(1 + C_1 + C_2 + C_3 + C_4 + \dots \big) |\Phi_0\rangle$$

(cluster analysis)

$$C_1 = T_1$$

$$C_2 = T_2 + \frac{1}{2}T_1^2$$

$$C_3 = T_3 + T_1T_2 + \frac{1}{6}T_1^3$$

$$C_4 = T_4 + \frac{1}{2}T_2^2 + T_1T_3 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4$$

$$\cdots$$

Suppose we use H-F orbitals ($C_N^1 = 0$).

In green, lowest MBPT orders in the wave function

$$C_1 = T_1^{(2)}$$

$$C_2 = T_2^{(1)} + \frac{1}{2}\left(T_1^2\right)^{(4)}$$

$$C_3 = T_3^{(2)} + \left(T_1 T_2\right)^{(3)} + \frac{1}{6}\left(T_1^3\right)^{(6)}$$

$$C_4 = T_4^{(3)} + \frac{1}{2}\left(T_2^2\right)^{(2)} + \left(T_1 T_3\right)^{(4)} + \frac{1}{2}\left(T_1^2 T_2\right)^{(5)} + \frac{1}{24}\left(T_1^4\right)^{(8)}$$

In weaker correlations,

$$T_3 > T_1 T_2,\ T_1^3$$

$$\frac{1}{2} T_2^2 > T_4, \ldots$$

The rest in videos 42, I, II, III.

Back to the connected cluster theorem.

We must prove the following:

$$\sum_{n=r}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_{L_r} |\Phi_0\rangle = \frac{1}{r!} T^r |\Phi_0\rangle \quad \checkmark$$

Proof:

$T|\Phi_0\rangle$

$r = 1$

$$\sum_{n=1}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_{L_1} |\Phi_0\rangle = \frac{1}{1!} T |\Phi_0\rangle$$

C

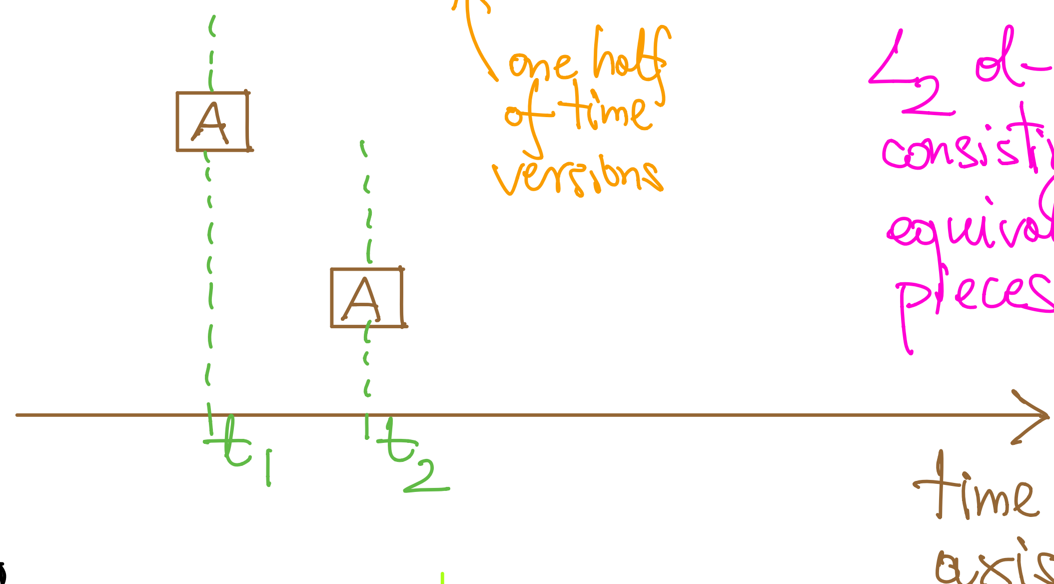
$r=2$

$$\sum_{n=2}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_{L_2} |\Phi_0\rangle$$

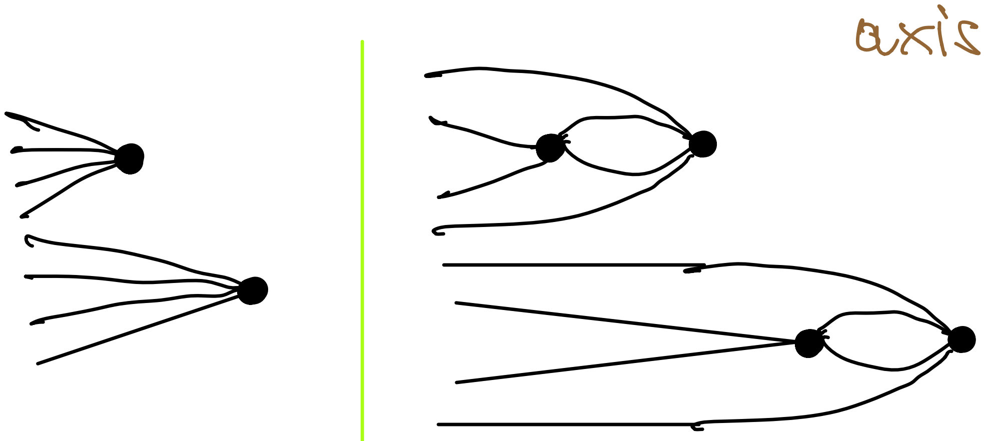
$$= \sum_{n=2}^{\infty} \sum_{[A]} \sum_{t_1<t_2} \left\{ \left(R^{(0)} W \right)^n \right\}_{[A]_{t_1}[A]_{t_2}} |\Phi_0\rangle$$

one half of time versions

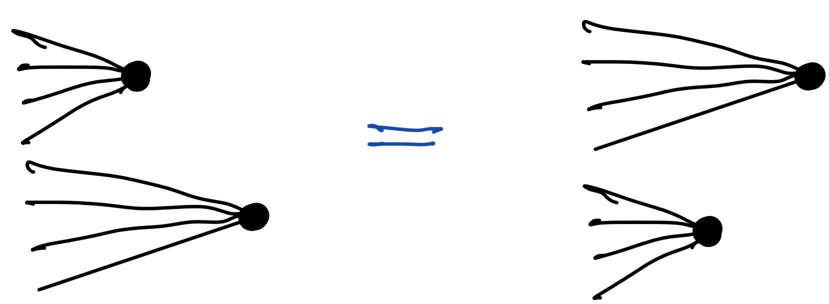
L_2 d-ms consisting of equivalent pieces



e.g.,



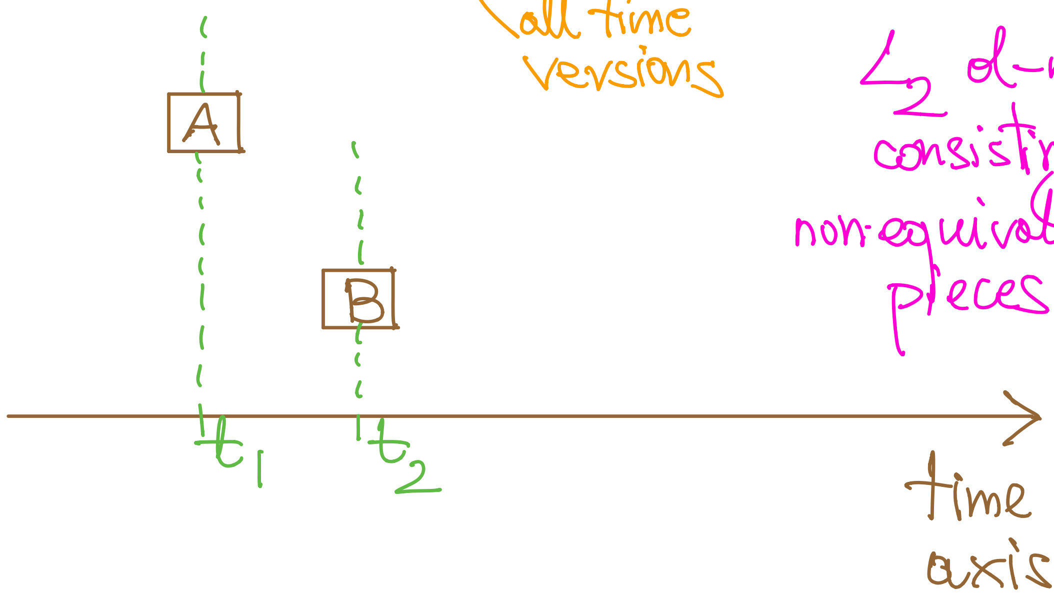
We do not have to consider all time versions, only one half of them, because



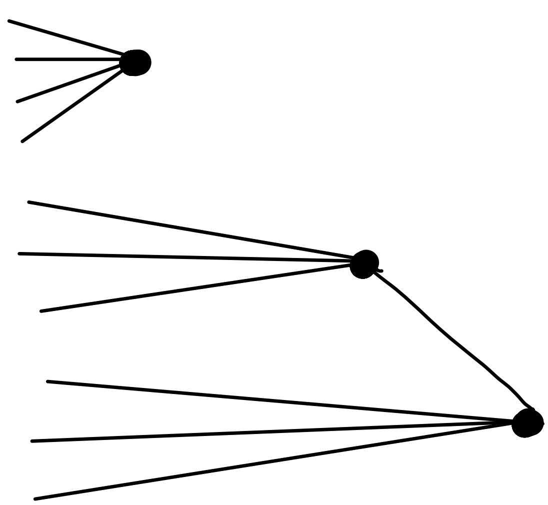
$$+\sum_{n=2}^{\infty}\ \sum_{[A]<[B]}\ \sum_{t_1,t_2}\left\{\left(R^{(0)}W\right)^n\right\}_{[A]_{t_1},[B]_{t_2}}|\Phi_0\rangle$$

all time versions

↳ 2 d-ms consisting of non-equivalent pieces



e.g.,



We can limit ourselves to $[A]<[B]$, since

$$\begin{array}{ccc} \boxed{A} & & \\ & \boxed{B} & \end{array} \quad = \quad \begin{array}{ccc} & & \boxed{B} \\ & \boxed{A} & \end{array},$$

but we need all time versions.

$$\sum_{n=2}^{\infty}\left\{\left(R^{(0)}W\right)^{n}\right\}_{\leq 2}|\Phi_0\rangle$$

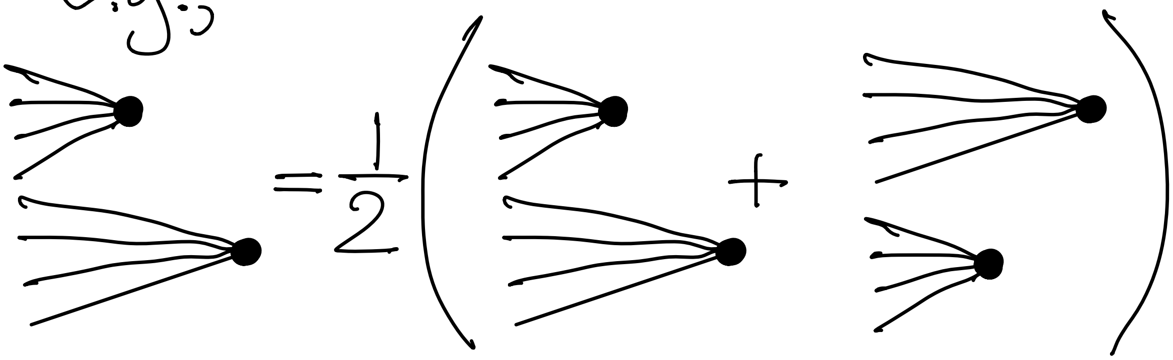
$$= \sum_{n=2}^{\infty}\sum_{[A]}\sum_{t_1<t_2}\left\{\left(R^{(0)}W\right)^{n}\right\}_{[A]_{t_1}[A]_{t_2}}|\Phi_0\rangle$$

$$+ \sum_{n=2}^{\infty}\sum_{[A]<[B]}\sum_{t_1,t_2}\left\{\left(R^{(0)}W\right)^{n}\right\}_{[A]_{t_1}[B]_{t_2}}|\Phi_0\rangle$$

$$= \frac{1}{2} \sum_{n=2}^{\infty} \sum_{[A]} \sum_{t_1, t_2} \left\{ \left(R^{(0)} W \right)^n \right\}_{[A]_{t_1} [A]_{t_2}} |\Phi_0\rangle$$

$$\uparrow \; [A]=[B]$$

e.g.,



$$+ \frac{1}{2} \sum_{n=2}^{\infty} \sum_{[A] \neq [B]} \sum_{t_1, t_2} \left\{ \left(R^{(0)} W \right)^n \right\}_{[A]_{t_1} [B]_{t_2}} |\Phi_0\rangle$$

$$= \frac{1}{2} \sum_{n=2}^{\infty} \sum_{[A], [B]} \sum_{t_1, t_2} \left\{ \left(R^{(0)} W \right)^n \right\}_{[A]_{t_1} [B]_{t_2}} |\Phi_0\rangle$$

$k, l = 1, \ldots, \infty$

$n = k + l$

k vertices W

l vertices W

$$= \frac{1}{2} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \sum_{[A]} \sum_{[B]} \sum_{t_1, t_2} \times \left\{ \left(R^{(0)} W\right)^k \left(R^{(0)} W\right)^l \right\}_{[A]_{t_1} [B]_{t_2}} |\Phi_0\rangle$$

$$\overset{\mathrm{FL}}{=} \frac{1}{2} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \sum_{[A]} \sum_{[B]} \times \left\{ \left(R^{(0)} W\right)^k \right\}_{[A]} \left\{ \left(R^{(0)} W\right)^l \right\}_{[B]} |\Phi_0\rangle$$

$$= \frac{1}{2} \underbrace{\sum_{k=1}^{\infty} \sum_{[A]} \left\{ \left(R^{(0)} W\right)^k \right\}_{[A]}}_{=T} \times \underbrace{\sum_{l=1}^{\infty} \sum_{[B]} \left\{ \left(R^{(0)} W\right)^l \right\}_{[B]}}_{T} |\Phi_0\rangle$$

all connected

all connected

$$= \frac{1}{2} T^2 |\Phi_0\rangle$$

General case:

$$\sum_{n=r}^{\infty} \left\{ \left(R^{(0)} W\right)^n \right\}_{L_r} |\Phi_0\rangle$$

$$= \underbrace{\frac{1}{r!}}_{\text{to remove redundancies}} \sum_{n=r}^{\infty} \sum_{\underbrace{[A_1], \dots, [A_r]}_{\text{connected components}}} \sum_{\underbrace{t_1, \dots, t_r}_{\text{all time versions}}}$$

$$\times \left\{ \left(R^{(0)} W\right)^n \right\}_{[A_1]_{t_1} \cdots [A_r]_{t_r}} |\Phi_0\rangle$$

k_1 vertices W

k_r vertices W

$$= \frac{1}{r!} \sum_{k_1=1}^{\infty} \cdots \sum_{k_r=1}^{\infty} \sum_{[A_1], \dots, [A_r]}$$

$n = k_1 + \dots + k_r$

$$\times \sum_{t_1,\ldots,t_r} \left\{ (R^{(0)}W)^{k_1} \cdots (R^{(0)}W)^{k_r} \right\}_{[A_1]_{t_1}\cdots[A_r]_{t_r}} |\Phi_0\rangle$$

$$\overset{\text{FL}}{=} \frac{1}{r!} \underbrace{\sum_{k_1=1}^{\infty} \sum_{\underset{\text{connected}}{[A_1]}} \left\{ (R^{(0)}W)^{k_1} \right\}_{[A_1]}}_{=T}$$

$$\times \cdots \times \underbrace{\sum_{k_r=1}^{\infty} \sum_{\underset{\text{connected}}{[A_r]}} \left\{ (R^{(0)}W)^{k_r} \right\}_{[A_r]}}_{=T} |\Phi_0\rangle$$

$$= \frac{1}{r!} T^r |\Phi_0\rangle$$

We already demonstrated that the summations over n and r in $|\Psi_0\rangle$ can be written as

$$
\begin{aligned}
|\Psi_0\rangle &= |\Phi_0\rangle \\
&\quad + \sum_{r=1}^{\infty} \underbrace{\sum_{n=r}^{\infty} \left\{ \left(R^{(0)} W \right)^n \right\}_r}_{\frac{1}{r!} T^r} |\Phi_0\rangle \\
&= |\Phi_0\rangle + \sum_{r=1}^{\infty} \frac{1}{r!} T^r |\Phi_0\rangle \\
&= e^T |\Phi_0\rangle .
\end{aligned}
$$

$\therefore$

One can propose other arguments in favor of the exponential ansatz,

$$
|\Psi_0\rangle = (c_0 + C)|\Phi_0\rangle,
$$

$$C = C_1 + C_2 + \ldots$$

Using the intermediate normalization, $\langle \Phi_0 | \Psi_0 \rangle = 1$,

$c_0 = 1$,

$$|\Psi_0\rangle = (1 + C)|\Phi_0\rangle.$$

full CI

Define

$$T = \ln(1 + C)$$

$$\ln(1+x) = \sum_{m=1}^{\infty} (-1)^{m+1} \frac{x^m}{m}, \quad |x| < 1$$

$$T = \ln(1+C) = \sum_{m=1}^{\infty} (-1)^{m+1} \frac{C^m}{m}$$

may not exist, but it does,

because

$$C^m = 0 \quad \text{for } m > N.$$

$$T = \ln(1+C) = \sum_{m=1}^{N} (-1)^{m+1} \frac{C^m}{m}$$

Another argument :

SEPARABILITY

$$AB = A + B$$

$$H_{AB} = H_A + H_B \quad \text{(noninteracting limit)}$$

Let us assume

$$|\Phi_0^{(AB)}\rangle = |\Phi_0^{(A)}\rangle |\Phi_0^{(B)}\rangle$$

$$|\Psi_0^{(AB)}\rangle = e^{T^{(AB)}}|\Phi_0^{(AB)}\rangle$$

$T^{(AB)}$ is connected, so

$$T^{(AB)} = T^{(A)} + T^{(B)},$$

$$[T^{(A)}, T^{(B)}] = 0$$

$$e^{X+Y} = e^X e^Y \text{ if } [X,Y]=0$$

$$|\Psi_0^{(AB)}\rangle = e^{T^{(A)}+T^{(B)}}|\Phi_0^{(A)}\rangle|\Phi_0^{(B)}\rangle$$

$$= e^{T^{(A)}}|\Phi_0^{(A)}\rangle\, e^{T^{(B)}}|\Phi_0^{(B)}\rangle$$

$$= |\Psi_0^{(A)}\rangle\, |\Psi_0^{(B)}\rangle$$

$$
\begin{aligned}
E^{(AB)} &= \langle \Phi_0^{(AB)} | H_{AB} | \Psi_0^{(AB)} \rangle \\
&= \langle \Phi_0^{(A)} | \langle \Phi_0^{(B)} | \left(H_A + H_B \right) | \Psi_0^{(A)} \rangle | \Psi_0^{(B)} \rangle \\
&= \langle \Phi_0^{(A)} | H_A | \Psi_0^{(A)} \rangle \overbrace{\langle \Phi_0^{(B)} | \Psi_0^{(B)} \rangle}^{=1} \\
&\quad + \langle \Phi_0^{(B)} | H_B | \Psi_0^{(B)} \rangle \underbrace{\langle \Phi_0^{(A)} | \Psi_0^{(A)} \rangle}_{=1} \\
&= \langle \Phi_0^{(A)} | H_A | \Psi_0^{(A)} \rangle \\
&\quad + \langle \Phi_0^{(B)} | H_B | \Psi_0^{(B)} \rangle \\
&= E^{(A)} + E^{(B)}
\end{aligned}
$$

For more information about the exponential ansatz and coupled-cluster theory, see videos 42, I, II, III.