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① Configuration interaction (CI) method

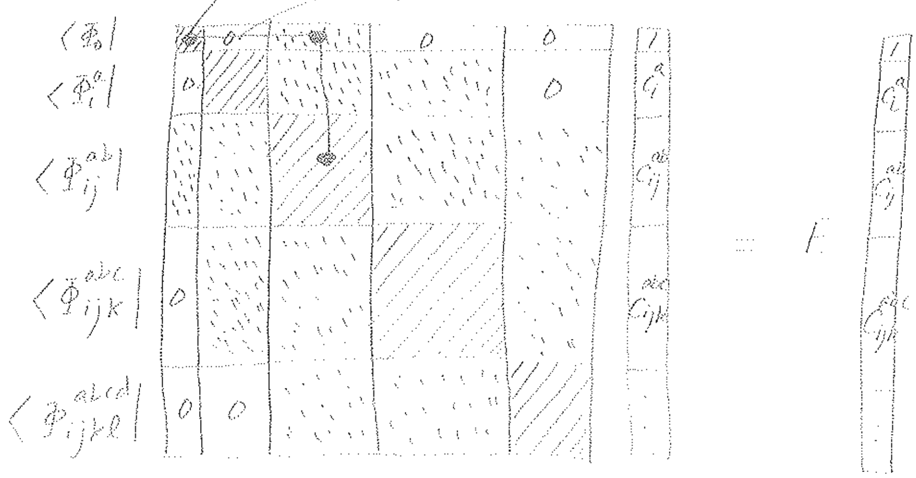
$$|\Psi\rangle = |\Phi_0\rangle + \sum_{a,i} C_i^a |\Phi_i^a\rangle + \sum_{\substack{i<j\\ a<b}} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \cdots$$

$$\frac{\partial}{\partial C} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = 0 \longrightarrow \begin{aligned} \langle\Phi_0|\hat{H}|\Psi\rangle &= E \,\langle\Phi_0|\Psi\rangle \\ \langle\Phi_i^a|\hat{H}|\Psi\rangle &= E\, C_i^a \,\langle\Phi_i^a|\Psi\rangle \\ \langle\Phi_{ij}^{ab}|\hat{H}|\Psi\rangle &= E\, C_{ij}^{ab} \,\langle\Phi_{ij}^{ab}|\Psi\rangle \\ &\vdots \end{aligned}$$

$\hat{H}|\Psi\rangle = E|\Psi\rangle$ is true in the spaces of $\langle\Phi_0|, \langle\Phi_i^a|, \langle\Phi_{ij}^{ab}|$

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

$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle i|\hat{f}|a\rangle = 0$



$$\sum_{pq} \langle p|\hat{f}|q\rangle \langle\Phi_0|\{\hat{p}^\dagger \hat{q}\}\{\hat{a}^\dagger \hat{i}\}|\Phi_0\rangle$$

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle\Phi_i^a|\hat{H}|\Phi_0\rangle^* = \langle i|\hat{f}|a\rangle = \langle a|\hat{f}|i\rangle^* = 0$$

(Brillouin theorem)

$$\langle\Phi_0|\hat{H}|\Phi_{ijk}^{abc}\rangle = \langle\Phi_{ijk}^{abc}|\hat{H}|\Phi_0\rangle^* = 0 \quad \text{(two-body nature of } \hat{H})$$

$\vdots$

CID should be cost-effective!

$$|\Psi_{CID}\rangle = |\Phi_0\rangle + \sum_{\substack{i<j\\ a<b}} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad \text{truncated CI.}$$

"Intermediate" normalization ($C_0 = 1$)
(in other words, $|\Psi_{CID}\rangle$ is <u>not</u> normalized)

Energy eq.

$$E_{CID} = \langle \Phi_0|\hat H|\Psi_{CID}\rangle = \underbrace{\langle\Phi_0|\hat H|\Phi_0\rangle}_{E_{HF}} + \underbrace{\sum_{\substack{i<j\\a<b}} C_{ij}^{ab}\langle\Phi_0|\hat H|\Phi_{ij}^{ab}\rangle}_{E^{CID}_{corr.}\ (=E_{CID}-E_{HF})}$$

$$\left(\frac{1}{4}\right)^2 \sum_{\substack{i,j\\a,b}} C_{ij}^{ab}\langle pq||rs\rangle\langle\Phi_0|\{\hat p^\dagger\hat q^\dagger\hat s\hat r\}\{\hat a^\dagger\hat b^\dagger\hat j\hat i\}|\Phi_0\rangle$$ and 3 other contractions

or

$$\left(\frac{1}{2}\right)^2\sum_{\substack{i,j\\a,b}}\langle ij||ab\rangle C_{ij}^{ab} \times(-1)^{2+2}$$

$$E^{CID}_{corr.} = \frac{1}{4}\sum_{\substack{i,j\\a,b}}\langle ij||ab\rangle C_{ij}^{ab}$$

C_2 amplitude eq.

$\frac{1}{4}\sum_{\substack{k,l\\c,d}}$ missing

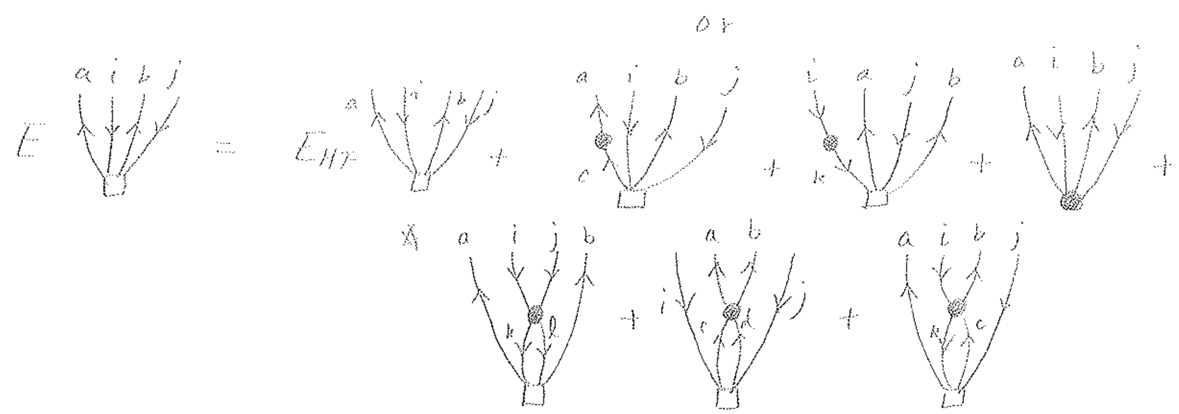
$$E\, C_{ij}^{ab} = \langle\Phi_{ij}^{ab}|\hat H|\Psi_{CID}\rangle = E_{HF}\langle\Phi_0|\{\hat i^\dagger\hat j^\dagger\hat b\hat a\}\{\hat c^\dagger\hat d^\dagger\hat l\hat k\}|\Phi_0\rangle C_{kl}^{cd}$$

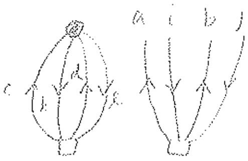
$$+\sum_{p,q}\langle p|\hat f|q\rangle\langle\Phi_0|\{\hat i^\dagger\hat j^\dagger\hat b\hat a\}\{\hat p^\dagger\hat q\}\{\hat c^\dagger\hat d^\dagger\hat l\hat k\}|\Phi_0\rangle C_{kl}^{cd}$$

$$+\frac{1}{4}\sum_{\substack{p,q\\r,s}}\langle pq||rs\rangle\langle\Phi_0|\{\hat i^\dagger\hat j^\dagger\hat b\hat a\}\{\hat p^\dagger\hat q^\dagger\hat s\hat r\}|\Phi_0\rangle$$

$$+\frac{1}{4}\sum_{\substack{p,q\\r,s}}\langle pq||rs\rangle\langle\Phi_0|\{\hat i^\dagger\hat j^\dagger\hat b\hat a\}\{\hat p^\dagger\hat q^\dagger\hat s\hat r\}\{\hat c^\dagger\hat d^\dagger\hat l\hat k\}|\Phi_0\rangle C_{kl}^{cd}$$

or

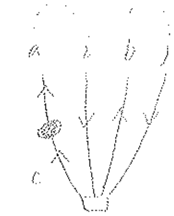




$E^{CID}_{corr.}$ $\quad C^{ab}_{ij}$

disconnected

$=$



a-b non equivalent

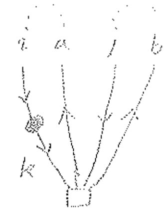
$$(-1)^{2+2} P_{a/b} \sum_c \langle a|\hat{f}|c\rangle C^{cb}_{ij}$$

$$= \sum_c \langle a|\hat{f}|c\rangle C^{cb}_{ij} - \sum_c \langle b|\hat{f}|c\rangle C^{ca}_{ij}$$

$$= (\epsilon_a+\epsilon_b) C^{ab}_{ij}$$

$P_{a/b} = \left(1 - \underset{a\leftrightarrow b}{\text{replace}}\right)$

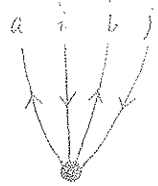
$+$



$$(-1)^{2+3} P_{i/j} \sum_k \langle k|\hat{f}|i\rangle C^{ab}_{kj}$$

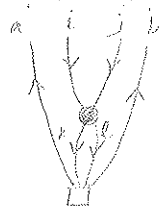
$$= -\sum_k \langle k|\hat{f}|i\rangle C^{ab}_{kj} + \sum_k \langle k|\hat{f}|j\rangle C^{ab}_{ki} = -(\epsilon_i+\epsilon_j) C^{ab}_{ij}$$

$+$



$$(-1)^{2+2} \langle ab||ij\rangle$$

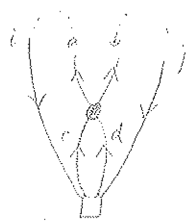
$+$



k-l equivalent

$$(-1)^{2+4} \left(\frac{1}{2}\right) \sum_{k,l} \langle kl||ij\rangle C^{ab}_{kl}$$

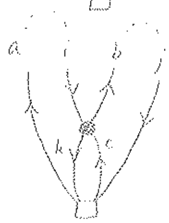
$+$



c-d

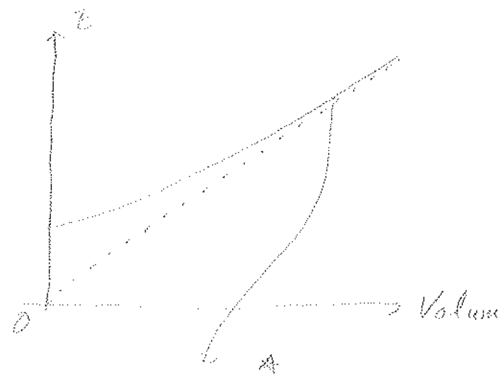
$$(-1)^{2+2} \left(\frac{1}{2}\right) \sum_{c,d} \langle ab||cd\rangle C^{cd}_{ij}$$

$+$



$$(-1)^{2+3} P_{a/b} P_{i/j} \sum_{k,c} \langle kb||ic\rangle C^{ac}_{kj}$$

Size consistency (size extensivity)



It's one of the foundations of statistical thermodynamics in chemsistry!

Energy is "asymptotically" proportional to Volume

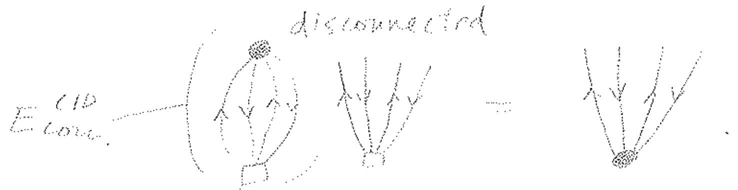
$\lim_{V\to\infty} \frac{E}{V} = \text{finite}$

$\lim_{V\to\infty} E \propto V^1$

Q: Is CID size consistent? *

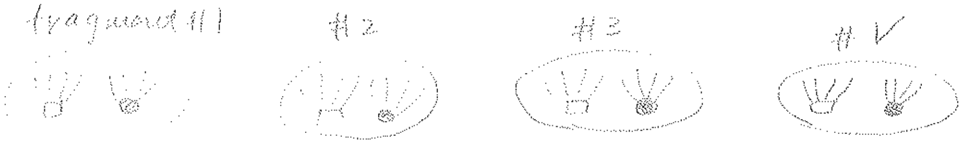
A: No! Thus, CID is a nonsensical method for total energy. (if not for excitations)

In the first approximation, CID eq. may be simplified to



This is what one gets in the first iteration of the iterative sln. of CID eq. with $C_{ij}^{ab} = 0$ initial guess.

In a local basis, we have local  and  for each fragment



$E^{CID}_{corr.} = V$  $_{local}$; Assume  $_{local} \propto V^n$

 $= \dfrac{\text{}}{E^{CID}_{corr}}$  $\propto \dfrac{V^0}{V^{n+1}} = V^{-n-1}$

$V^n \propto$  $_{local} \propto V^{-n-1} \rightarrow n = -\frac{1}{2}$, $E^{CID}_{corr.} = V \cdot V^{-\frac{1}{2}} = V^{\frac{1}{2}}$

<u>not</u> extensive