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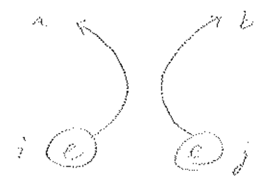
② Coupled-cluster method

Q: Can we truncate full CI more mildly? Without increasing the cost or the # parameters?

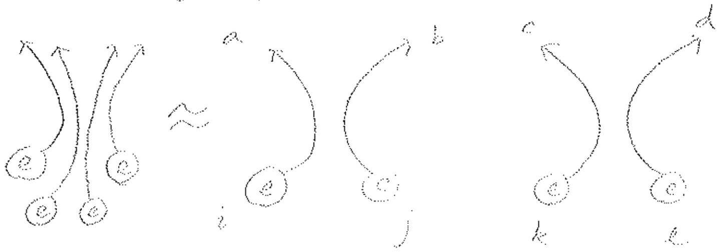
A: Yes — coupled-cluster

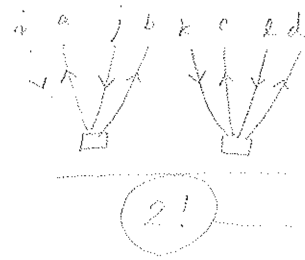
— CID accounts for only two-electron collision-like correlation



This is exact if there are only 2 electrons.

— If there are more than 2 electrons, there are four-electron, six-electron etc. collision-like correlation. It's reasonable to expect that they are largely simultaneous two-electron collisions.





$ij \to ab$, $kl \to cd$ $\equiv$ $kl \to cd$, $ij \to ab$

intermediate normalization

$$|\Psi_{CCD}\rangle = |\Phi_0\rangle + \sum_{\substack{i<j\\a<b}} t_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \frac{1}{2!}\sum_{\substack{i<j\\a<b}} t_{ij}^{ab} \sum_{\substack{k<l\\c<d}} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle$$

$$+ \frac{1}{3!}\sum_{\substack{i<j\\a<b}} t_{ij}^{ab} \sum_{\substack{k<l\\c<d}} t_{kl}^{cd} \sum_{\substack{m<n\\e<f}} t_{mn}^{ef} |\Phi_{ijklmn}^{abcdef}\rangle + \cdots$$

$$= \left(1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \frac{1}{4!}\hat{T}_2^4 \cdots\right)|\Phi_0\rangle$$

$$= \exp(\hat{T}_2)|\Phi_0\rangle$$

$$\hat{T}_2|\Phi_0\rangle = \sum_{\substack{i<j\\a<b}} t_{ij}^{ab}|\Phi_{ij}^{ab}\rangle = \left(\frac{1}{2}\right)^2 \sum_{\substack{ij\\ab}} t_{ij}^{ab}|\Phi_{ij}^{ab}\rangle$$

a) $$\frac{\partial}{\partial t}\frac{\langle\Psi_{CCD}|\hat H|\Psi_{CCD}\rangle}{\langle\Psi_{CCD}|\Psi_{CCD}\rangle}=0$$

unlike CID, b) doesn't follow from a)

b) $$\langle\Phi_0|\hat H|\Psi_{CCD}\rangle = \langle\Phi_0|E_{CCD}|\Psi_{CCD}\rangle$$
$$\langle\Phi_{ij}^{ab}|\hat H|\Psi_{CCD}\rangle = \langle\Phi_{ij}^{ab}|E_{CCD}|\Psi_{CCD}\rangle$$

eqs = # unknowns

a) Variational CC or expectation-value CC — not widely used so far

b) Projection CC or CC — highly successful (for good reasons related to size consistency see below)

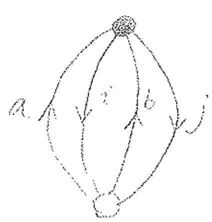
Energy eq.

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

$$+\frac{1}{2}\sum_{\substack{i<j\\a<b}} t_{ij}^{ab}\sum_{\substack{k<l\\c<d}} t_{kl}^{cd}\underbrace{\langle\Phi_0|\hat H|\Phi_{ijkl}^{abcd}\rangle}_{0}+\underbrace{\cdots\cdots}_{0}$$

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

or



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

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

T_2 amplitude eq.

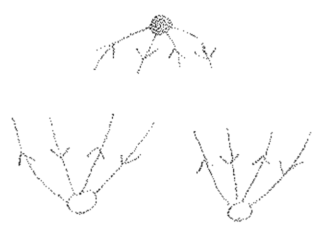
creates 6+ electron excited determinants.

$$E\, t_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_2 + \tfrac{1}{2!}\hat{T}_2^2 + \tfrac{1}{3!}\hat{T}_2^3 + \cdots) | \Phi_0 \rangle$$

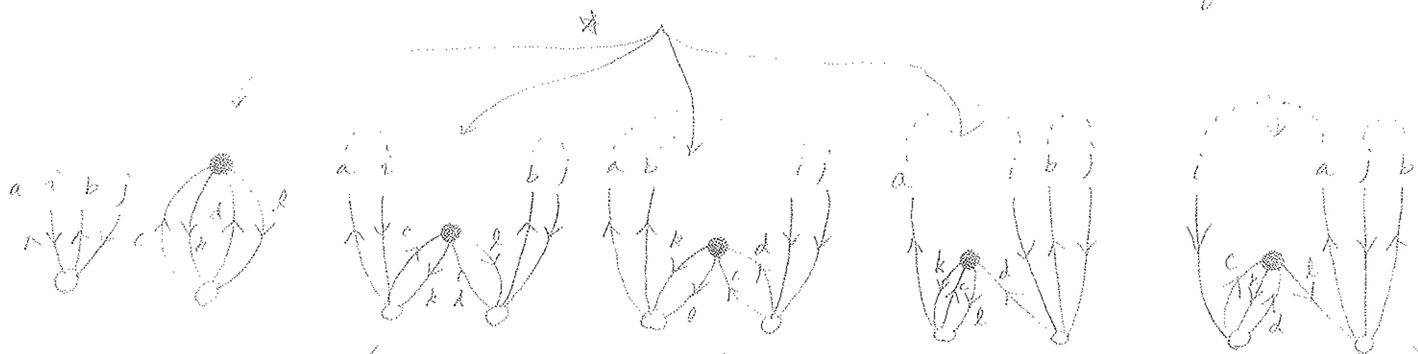
$$= \underbrace{\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle + \langle \Phi_{ij}^{ab} | \hat{H}\hat{T}_2 | \Phi_0 \rangle}_{\text{same as CID}} + \underbrace{\frac{1}{2!}\langle \Phi_{ij}^{ab} | \hat{H}\hat{T}_2^2 | \Phi_0 \rangle}_{\text{new}}$$

$$\frac{1}{2!}\,\frac{1}{4}\left(\frac{1}{4}\right)^2 \sum_{\substack{p,q\\r,s}} \sum_{\substack{k,l\\c,d}} \sum_{\substack{m,n\\e,f}} \langle pq||rs\rangle \langle \Phi_0 | \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\}\{\hat{e}^\dagger \hat{f}^\dagger \hat{n}\hat{m}\} | \Phi_0 \rangle$$

or



connect to form overall two-electron excited diagrams



equivalent vertexes

$$\frac{1}{2}(-1)^{4+4} P_{a/b} P_{i/j} \sum_{\substack{k,l\\c,d}} \langle kl||cd\rangle t_{ik}^{ac} t_{lj}^{db}$$

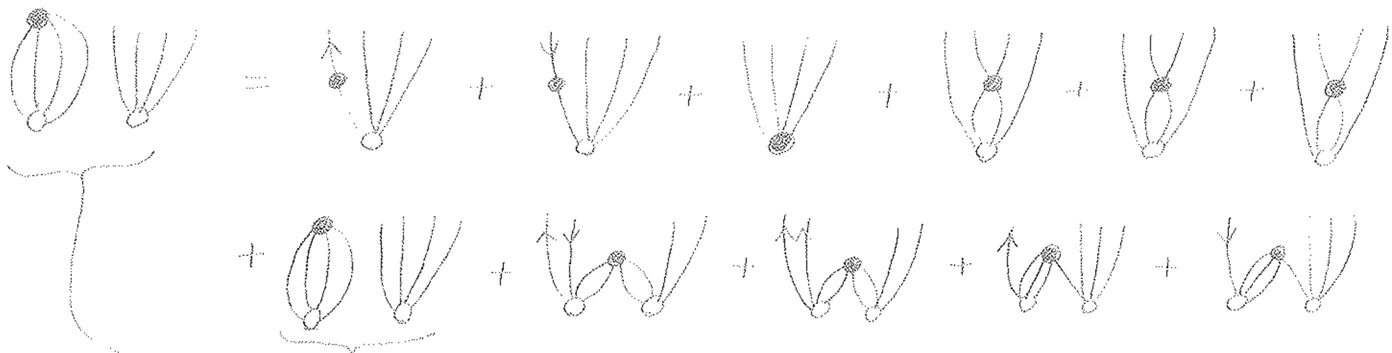
a-i-d-l-c-k/b-j

$$(-1)^{2+4}\left(\frac{1}{2}\right) P_{a/b} \sum_{\substack{k,l\\c,d}} \langle kl||cd\rangle t_{kl}^{ac} t_{ij}^{db}$$

$$(-1)^{2+4}\left(\frac{1}{2}\right)^2 \sum_{\substack{k,l\\c,d}} \langle kl||cd\rangle t_{kl}^{ab} t_{ij}^{cd}$$

$$(-1)^{2+4}\left(\frac{1}{2}\right) P_{i/j} \sum \langle kl||cd\rangle t_{lj}^{ab} t_{ik}^{cd}$$

a-i-c-k-d-l/b-j

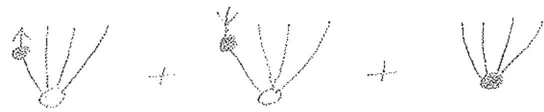


disconnected diagrams   cancel!

Q: Is CCD size consistent?

A: Yes!

$(\epsilon_a+\epsilon_b)\,t_{ij}^{ab} \quad -(\epsilon_i+\epsilon_j)\,t_{ij}^{ab} \quad \langle ab||ij\rangle$

In the first approx, $0 =$ 

or

$$t_{ij}^{ab} \simeq \frac{\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

fragment #1   #2   #3   #V

 $_{local} = t_{ij\,(local)}^{ab} \propto \dfrac{V^0}{V^0} = V^0$

$E_{corr.}^{CCD} = V$  $_{local} \propto V \cdot V^0 \cdot V^0 = V^1$

extensive!

Generally

$$|\Psi_{CC}\rangle = \exp(\hat{T})\,|\Phi_0\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n$$

$\hookrightarrow$ n-electron excitation

$$\langle \Phi_0 | \hat{H} \exp(\hat{T}) | \Phi_0 \rangle = E_{CCD} \longrightarrow \langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E_{corr}^{CCD}$$

$$\langle \Phi_i^a | \hat{H} \exp(\hat{T}) | \Phi_0 \rangle = E_{CCD}\, t_i^a \longrightarrow \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0$$

$$\vdots \qquad\qquad\qquad\qquad \vdots$$

$$\langle \Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n} | \hat{H} \exp(\hat{T}) | \Phi_0 \rangle = E_{CCD}\, t_{i_1 \cdots i_n}^{a_1 \cdots a_n} \longrightarrow \langle \Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n} | \bar{H} | \Phi_0 \rangle = 0$$

$$\bar{H} = \left[\hat{H} \exp(\hat{T})\right]_{connected}$$