DCI: Double excitation CI

$$\left|\Phi_{DCI}\right\rangle = \left|\Psi_0\right\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle$$

vlnová funkce obsahuje pouze základní stav a double-excitace

$$H - E_0\left|\Phi_{DCI}\right\rangle = E_{corr}\left|\Psi_0\right\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle \quad /. \quad \left\langle\Psi_0\right|, \left\langle\Psi_{ab}^{rs}\right|$$

$$\sum_{\substack{a<b\\r<s}} c_{ab}^{rs} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle = E_{corr}$$

$$\left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle + \sum_{\substack{a<b\\r<s}} c_{cd}^{tu} \left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{cd}^{tu} \right\rangle = c_{ab}^{rs} E_{corr}$$

$$\left(c_{rasb} \right) = c_{ab}^{rs}$$

$$\left(B_{rasb} \right) = \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle$$

$$\left(D_{rasb,tcud} \right) = \left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{cd}^{tu} \right\rangle$$

$$B^{+} c = E_{corr}$$

$$B + Dc = cE_{corr}$$

$$\begin{pmatrix} 0 & B^{+} \\ B & D \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_{corr} \begin{pmatrix} 1 \\ c \end{pmatrix}$$

$$B^{+}c = E_{corr}$$

$$B + Dc = cE_{corr}$$

$$c = -(D - 1E_{corr})^{-1} B$$

$$E_{corr} = -B^{+}(D - 1E_{corr})^{-1} B$$

$D >> 1E_{corr}$: $\quad E' = -B^{+}(D)^{-1} B \quad$ popř. $\quad E'' = -B^{+}(D - 1E')^{-1} B$

$$D \approx TrD \qquad D^{-1} = \frac{\delta_{ac}\delta_{bd}\delta_{rt}\delta_{su}}{\left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{ab}^{rs} \right\rangle}$$

$$E_{corr} \cong -\sum_{\substack{a<b \\ r<s}} \frac{\left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle}{\left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{ab}^{rs} \right\rangle}$$

Například:

H_2 R=1.4

Báze	DCI	SD-CI	
sto	-0,02056	-0,02056	0
4-31G	-0,02487	-0,02494	7
6-31G**	-0,03373	-0,03387	14
10s5p1d	-0,03954	-0,03969	15
E			-0,04090

BeH_2 (DZ)

S+D	T	Q	5	6	Σ	E
-,074033	-,000428	-,001439	-,000011	-,000006	-,075917	-,14

IP: N_2 (6s,4p,3d,2f)

$3\sigma_g$	,635	,580	,573
$1\Pi_u$	,615	,610	,624
	Koop.	CI-SD	Exp.

μ: CO (rozšířená STO báze)

	SCF	CI-D(138)	CI-D(200)	CI-SD (138D,62s)	Exp.
E	-112.788	-113.016	-113.034	-113.018	
μ	-.108	-.068	-.072	+.030	+.044

NO + ρ,γ - redukované matice hustoty

$$\rho(x_1) = N\int dx_2 \ldots dx_N \Phi(1\ldots N)\Phi^*(1\ldots N) \qquad \langle\Phi|\Phi\rangle = 1$$

$$\int dx_1 \rho(x_1) = N \qquad tr(\gamma) = \rho$$

$$\gamma(x_1, x_1') = N\int dx_2 \ldots dx_N \Phi(1\ldots N)\Phi^*(1', 2\ldots N)$$

$$\gamma(x_1, x_1') = \sum_{ij} \chi_i(x_1)\gamma_{ij}\chi^*{}_j(x_1')$$

$$\chi_i - HF$$

$$\gamma_{ij} = \int dx_1 dx_1' \chi_i(x_1)\gamma(x_1, x_1')\chi_j(x_1')$$

Příklad 1:

γ - je hermitovská, ***tr(γ)=N***

Příklad 2:

je-li $O_1 = \sum_i^N h(i)$

pak platí: ***a)*** $\langle \Phi | O_1 | \Phi \rangle = \int dx_1 \left[h(x_1) \gamma(x_1, x_1') \right]_{x_1 = x'}$

b) $\langle \Phi | O_1 | \Phi \rangle = tr(h\gamma)$

kde $h_{ij} = \langle \chi_i | h | \chi_j \rangle = \int dx_1 \, \chi_i^*(x_1) h(x_1) \chi_j(x_1)$

HF základní stav ~ Φ

$$\gamma^{HF}\left(x_1, x_1'\right) = \sum_a \chi_a\left(x_1\right) 1\, \chi_a^{\,*}\left(x_1'\right) \qquad\qquad \gamma_{ij}^{HF} = \delta_{ij}$$

Příklad 3:

ukažte, že platí:

$$O_1 = \sum_{ij} \left\langle i \middle| h \middle| j \right\rangle$$

$$a) \quad \gamma_{ij} = \left\langle \Phi \middle| a_j^{+} a_j \middle| \Phi \right\rangle$$

$$b) \quad \gamma_{ij}^{HF} = \delta_{ij}$$

$$\left|\Phi\right\rangle \neq \left|\Psi_0\right\rangle, \quad \gamma_{ij} - nediag.: \quad \forall\, hermit\ \exists U \rightarrow diag.: NO : \eta$$

$$\eta_i = \sum_k \chi_k U_{ik} \quad \rightarrow \quad \chi_i = \sum_k \eta_k U^{+}_{ki} = \sum_k \eta_k U^{*}_{ik}$$

$$\gamma(x_1, x_1') = \sum_{ijkl} \eta_k(x_1) U^{*}_{ik} \gamma_{ij} U_{jl} \eta^{*}_l(x_1') =$$

$$= \sum_{kl} \eta_k(x_1) \left[\sum_{ij} U^{+}_{ki} \gamma_{ij} U_{jl} \right] \eta^{*}_l(x_1') = \qquad / \, \lambda = U^{+} \gamma\, U$$

$$= \sum_{kl} \eta_k(x_1)\, \lambda_{kl}\, \eta^{*}_l(x_1')$$

$$\lambda_{kl} = \delta_{kl}\lambda_k$$ U taková, že diagonalizují γ $\lambda_{kl}=\delta_{kl}\lambda_k$

$\{\eta_i\} \ldots NO$ $$\gamma(x_1, x_1') = \sum_i \lambda_i \, \eta_i(x_1)\, \eta_i^*(x_1')$$

$\lambda_i \ldots occ \quad \in (0,1)$ $\lambda_i > \varepsilon$

Například: H_2O CI-SD 39-STO

# MO	14	52	140	351	617	1760
# NO	6	18	50	147	362	1652
% E_{corr}	20	40	60	80	90	99

Příklad 4:

$$\left|{}^1\Phi_0\right\rangle = c_0\left|1\,\overline{1}\right\rangle + \sum_{r=2}^{K} c_1^r\left|\psi_1^r\right\rangle + \sum_{rs}^{K} c_{11}^{rs}\left|\psi_{11}^{rs}\right\rangle, \quad \left|\psi_1^r\right\rangle = \frac{1}{\sqrt{2}}\left(\left|1\overline{r}\right\rangle + \left|r\,\overline{1}\right\rangle\right)$$

ukažte, že platí:

$$a)\quad \left|{}^1\Phi_0\right\rangle = \sum_{ij=1}^{K} c_{ij}\left|\psi_i\,\overline{\psi}_j\right\rangle \qquad C\ \ldots\ sym.\ KxK$$

$$b)\quad \gamma(x_1,x_1') = \sum_i \left(CC^+\right)_{ij}\left(\psi_i\,(1)\psi_j^*(1') + \overline{\psi}_i\,(1)\overline{\psi}_j^*(1')\right)$$

$$c)\quad \exists U:\quad U^+CU = d \quad d_{ij} = \delta_{ij}d_i \wedge U^+CC^+U = d^2$$

$$d)\quad \Rightarrow \gamma(x_1,x_1') = \sum_i d^2\left(\xi_i\,(x_1)\xi_i^*(x_1') + \overline{\xi}_i\,(x_1)\overline{\xi}_i^*(x_1')\right)$$

$$e)\quad C\ldots sym, U\ldots real, \quad \left|{}^1\Phi_0\right\rangle = \sum_i^K d_i\left|\xi_i\,\overline{\xi}_i\right\rangle \qquad kde\ \xi_i = \sum_k \psi_i U_{ki}$$