Konfigurační Interakce

FCI: Full Configuration Interaction

$$E_{cor} = \varepsilon_0 - E_0$$

E_0 ... energie na HF úrovni
ε_0 ... exaktní, nerelativistická energie
E_{corr} ... úplná korelační energie

CI ... diagonální N-elektronový Hamiltonian v N-elektronové funkci (SD)

2K N-elek. SD => N-násobné excitace FCI
N exaktní energie pro všechny stavy

HF => MO – jedno-elektronová funkce: báze pro SD n-násobná excitace

HF funkce ... $|\Psi_0\rangle$

CI základní stav ... $|\Phi_0\rangle$

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \ldots$$

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab\\ rs}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc\\ rst}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \ldots$$

$$c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle, \quad c_{ba}^{rs}, \quad c_{ab}^{sr}, \quad c_{ba}^{sr}$$

n-násobná excitace ... 2K-N... prázdných virtuálních orbitalů $\binom{2K-N}{n}$

N... okupovaných orbitalů $\binom{N}{n}$

δ^{state}, $\delta^{spin(N\alpha, N\beta)}$, báze pro korelační energii

$$\left|\Phi_0\right\rangle = c_0\left|\Psi_0\right\rangle + c_D\left|\Psi_D\right\rangle + c_T\left|\Psi_T\right\rangle + c_Q\left|\Psi_Q\right\rangle + \ldots$$

$\left\langle \Phi \middle| \mathrm{H} \middle| \Phi \right\rangle$:

1) $\left\langle \Psi_0 \middle| H \middle| \Psi_S \right\rangle = 0$ Brilliův teorém

2) $\left\langle \Psi_0 \middle| H \middle| \Psi_{T,Q} \right\rangle = 0$ Slater-Condon. pravidla

3) $\left\langle \Psi_D \middle| H \middle| \Psi_Q \right\rangle = \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_{abcd}^{rstu} \right\rangle$

4) D jsou nejdůležitější k Ψ_0, Q>T

$$
\begin{pmatrix}
\langle 0|H|0\rangle & 0 & \langle 0|H|D\rangle & 0 & .. & 0 \\
0 & \langle S|H|S\rangle & \langle S|H|D\rangle & \langle S|H|T\rangle & & . \\
\langle D|H|0\rangle & \langle D|H|S\rangle & \langle D|H|D\rangle & \langle D|H|T\rangle & \langle D|H|Q\rangle & . \\
0 & \langle T|H|S\rangle & \langle T|H|D\rangle & \langle T|H|T\rangle & \langle T|H|Q\rangle & 0 \\
.. & 0 & \langle Q|H|D\rangle & \langle Q|H|T\rangle & \langle Q|H|Q\rangle & ... \\
0 & . & . & 0 & ... & ...
\end{pmatrix} = \mathrm{FCI}
$$

N-rozměrná matice FCI (Full CI)

$$|\Psi_0\rangle, \quad |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, |\Psi_{abc}^{rst}\rangle, ...$$

$$|\Psi_0\rangle, \quad |\Psi_S\rangle, |\Psi_D\rangle, |\Psi_T\rangle, ...$$

$$|0\rangle, \quad |S\rangle, \quad |D\rangle, \quad |T\rangle, ...$$

- značení determinantů

Příklad 1:

Single excitace:

$$\left\langle \Psi_0 \middle| H \middle| {}^1\Psi_a^r \right\rangle = 0 \qquad < rb \| as >$$

$$\left\langle {}^1\Psi_a^r \middle| H - E_0 \middle| {}^1\Psi_b^s \right\rangle = (\varepsilon_r - \varepsilon_a)\delta_{rs}\delta_{ab} - (rs|ba) + 2(ra|bs)$$

$$\left| {}^1\Psi_a^r \right\rangle = \sqrt{\frac{1}{2}}\left(\left|..a\bar{r}..\right\rangle + \left|..r\bar{a}..\right\rangle\right)$$

Double excitace:

$$\left\langle \Psi_0 \middle| H \middle| {}^1\Psi_{aa}^{rr} \right\rangle = K_{ra}$$

$$\left\langle \Psi_0 \middle| H \middle| {}^1\Psi_{aa}^{rs} \right\rangle = \sqrt{2}\left(sa|ra\right)$$

$$\left\langle \Psi_0 \middle| H \middle| {}^1\Psi_{ab}^{rr} \right\rangle = \sqrt{2}\left(rb|ra\right)$$

$$\left\langle {}^1\Psi_{aa}^{rr} \middle| H - E_0 \middle| {}^1\Psi_{aa}^{rr} \right\rangle = (\varepsilon_r - \varepsilon_a) + J_{aa} + J_{rr} - 4J_{ra} + 2K_{ra}$$

$$\left\langle {}^1\Psi_{aa}^{rs} \middle| H - E_0 \middle| {}^1\Psi_{aa}^{rs} \right\rangle = \varepsilon_r + \varepsilon_s + 2\varepsilon_a + J_{aa} + J_{rs} + K_{rs} - 2J_{sa} - 2J_{ra} + K_{ra} + K_{sa}$$

Normalizace:

$$c_0 \gg c_a^r$$

$$\left|\Phi_0\right\rangle = c_0\left|\Psi_0\right\rangle + \sum_{ar} c_a^r \left|\Psi_a^r\right\rangle + \ldots$$

$$\left\langle\Phi_0\middle|\Phi_0\right\rangle = 1 + \sum_{ar}\left(c_a^r\right)^2 + \sum_{abrs}\left(c_{ab}^{rs}\right)^2$$

$$\left\langle\Psi_0\middle|\Phi_0\right\rangle = 1$$ <= intermediate normalization

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$$H\left|\Phi_0\right\rangle = \varepsilon_0\left|\Phi_0\right\rangle$$

$$H - E_0\left|\Phi_0\right\rangle = \left(\varepsilon_0 - E_0\right)\left|\Phi_0\right\rangle = E_{cor}\left|\Phi_0\right\rangle$$

$$\left\langle\Psi_0\middle|H - E_0\middle|\Phi_0\right\rangle = E_{cor}\left\langle\Psi_0\middle|\Phi_0\right\rangle$$

$$\left\langle\Psi_0\right|H - E_0\left(\left|\Psi_0\right\rangle + \sum_{ar} c_a^r\left|\Psi_a^r\right\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \ldots\right) = \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left\langle\Psi_0\middle|H\middle|\Psi_{ab}^{rs}\right\rangle$$

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

Příklad 2:

$$\sum_{\substack{b<c<d\\ s<t<u}} c_{bcd}^{stu} \langle \quad | \quad \rangle = \left(\frac{1}{3!}\right)^2 \sum_{\substack{bcd\\ stu}} c_{bcd}^{stu} \langle \quad | \quad \rangle$$

Molekula H$_2$: $\{\psi_1, \psi_2\}$

HF: $\left|\Psi_0\right\rangle = \left|\psi_1 \overline{\psi_1}\right\rangle = \left|\lambda_1 \lambda_2\right\rangle = \left|1\,\overline{1}\right\rangle$

$$\left|\Phi_0\right\rangle = \left|\Psi_0\right\rangle + c_1^2\left|2\,\overline{1}\right\rangle + c_{\overline{1}}^{\overline{2}}\left|1\overline{2}\right\rangle + c_{\overline{1}}^{2}\left|12\right\rangle + c_1^{\overline{2}}\left|\overline{2}\,\overline{1}\right\rangle + c_{1\overline{1}}^{2\overline{2}}\left|2\overline{2}\right\rangle$$

$$\left|\Phi_0\right\rangle = \left|\Psi_0\right\rangle_g + c_1^2\left|{}^1\Psi_1^2\right\rangle_u + c_{1\overline{1}}^{2\overline{2}}\left|2\overline{2}\right\rangle_g$$

$$\left|{}^1\Psi_1^2\right\rangle = \sqrt{\frac{1}{2}}\left(\left|1\overline{2}\right\rangle + \left|2\,\overline{1}\right\rangle\right)$$

$$H = \begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | {}^1\Psi_{11}^{22} \rangle \\ \langle \Psi_0 | H | {}^1\Psi_{11}^{22} \rangle & \langle {}^1\Psi_{11}^{22} | H | {}^1\Psi_{11}^{22} \rangle \end{pmatrix}$$

$$\langle \Psi_0 | H | \Psi_0 \rangle = E_0 = 2h_{11} + J_{11} = 2\varepsilon_1 - J_{11}$$

$$\langle \Psi_0 | H | {}^1\Psi_{11}^{22} \rangle = \langle 1\,\overline{1} \| 2\overline{2} \rangle = (12|12) = K_{12}$$

$$\langle {}^1\Psi_{1}^{2} | H | {}^1\Psi_{11}^{22} \rangle = 2h_{22} + J_{22} =$$

$$\begin{bmatrix} \varepsilon_1 = h_{11} + J_{11} \\ \varepsilon_2 = h_{22} + J_{12} - K_{12} \end{bmatrix} = 2\varepsilon_2 - 4J_{12} + 2K_{12} + J_{22}$$

$$(H-E_0)(|\Psi_0\rangle + c|\Psi_1^2\rangle) = E_{cor}(|\Psi_0\rangle + c|\Psi_1^2\rangle)$$

$$|\Psi_0\rangle \quad \rightarrow \quad E_{cor} = c\,K_{12}$$

$$|\Psi_1^2\rangle \quad \rightarrow \quad K_{12} + c2\Delta = c\,E_{cor}$$

$$2\Delta = \langle {}^1\Psi_1^2 | H - E_0 | {}^1\Psi_1^2 \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_{cor} \begin{pmatrix} 1 \\ c \end{pmatrix}$$

$$\left.\begin{aligned} c &= \frac{K}{E-2\Delta} \\ E &= \frac{K^2}{E-2\Delta} \end{aligned}\right\} E = \Delta - \sqrt{\Delta^2 + K^2}$$

$$\varepsilon_0 = E + E_0 = 2h_{11} + J_{11} + \Delta - \sqrt{\Delta^2 + K^2}$$

Výsledky pro dva oddalující se atomy vodíku:

$$R \to \infty : h_{11} = h_{22} \to E(H)$$

$$J_{22} = J_{11} = J_{12} = K_{12} = \frac{1}{2}\left(\phi_1\phi_1 \middle| \phi_1\phi_1\right) : \Delta \to 0 \quad E_{cor} = -\frac{1}{2}\left(\phi_1\phi_1 \middle| \phi_1\phi_1\right)$$

$$\varepsilon_0\left(R \to \infty\right) = 2E(H) = 2h_{11}$$