CC: Coupled Clusters

- v IEPA není ***ab..cd*** coupling
- v DCI je ***ab..cd*** coupling, ale DCI zase není size-conzistentní

$$\left|\Phi_0\right\rangle = c_0\left|\Psi_0\right\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \sum_{\substack{a<b<c<d\\r<s<t<u}} c_{abcd}^{rstu}\left|\Psi_{abcd}^{rstu}\right\rangle + \ldots$$

$c_a^r, c_{abc}^{rst}, \ldots$ zanedbáme

$$(H - E_0)\left|\Phi_0\right\rangle = E_c\left|\Phi_0\right\rangle$$

fCI schéma

....

$$\sum_{\substack{c<d\\t<u}} \left\langle\Psi_0\right|H - E_0\left|\Psi_{cd}^{tu}\right\rangle c_{cd}^{tu} = E_c$$

$$\left\langle\Psi_{ab}^{rs}\right|H\left|\Psi_0\right\rangle + \sum_{\substack{c<d\\t<u}} \left\langle\Psi_{ab}^{rs}\right|H - E_0\left|\Psi_{cd}^{tu}\right\rangle c_{cd}^{tu} + \sum_{\substack{c<d\\t<u}} \left\langle\Psi_{ab}^{rs}\right|H\left|\Psi_{abcd}^{rstu}\right\rangle c_{abcd}^{rstu} = c_{ab}^{rs} E_c$$

Teorie vázaných klastrů – Coupled Cluster Theory

Introduction

The purpose of all many-body methods is to describe *electron correlation*.

- Löwdin definition of correlation energy

$$\Delta E = E_{exact} - E_{HF}. \quad (1)$$

Since the variationally optimized Hartree-Fock energy is an upper bound to the exact energy, the correlation energy must be a negative value.

- There are three main methods for calculating electron correlation:
  - Configuration Interaction (CI)
  - Many-Body Perturbation Theory (MBPT) or (MPPT)
  - Coupled-Cluster Theory (CC)

HF theory recovers 99% of overall energy.

But,

lots of important chemistry happen in the remaining 1%.

Základní idea vázaných klastrů spočívá v rozvoji vlnové funkce základního stavu $|\Psi_{CC}\rangle$ ve formě exponenciální řady:

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

$$=\left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots\right)|\Psi_0\rangle.$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$

$$\hat{T}_1\ |\Psi_0\rangle = \sum_{a,r} t_a^r \Psi_a^r,$$

$$\hat{T}_2\ |\Psi_0\rangle = \sum_{\substack{a>b\\r>s}} t_{ab}^{rs} \Psi_{ab}^{rs}, \qquad \hat{T}_2^2|\Psi_0\rangle = \sum_{\substack{a>b\\r>s}} \sum_{\substack{c>d\\u>v}} t_{ab}^{rs} t_{cd}^{uv}\, \Psi_{abcd}^{rsuv},$$

$$\hat{T}_3\ |\Psi_0\rangle = \sum_{\substack{a>b>c\\r>s>u}} t_{abc}^{rsu} \Psi_{abc}^{rsu},$$

Cluster Expansion (rozvoj vlnové funkce)

$$\left|\Psi_{ab}^{rs}\right\rangle = a_r^+ a_s^+ a_b a_a \left|\Psi_0\right\rangle \Longrightarrow \left|\Psi(DCI)\right\rangle = \left(1 + \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a\right)\left|\Psi_0\right\rangle$$

$$\left|\Psi(CC)\right\rangle = \exp(\tau_2)\left|\Psi_0\right\rangle$$

$$\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \dots$$

$$\tau_1 = \sum_{a,r} c_a^r\, a_r^+ a_a$$

$$\exp(x) = 1 + x + \frac{1}{2}x^2 + \dots$$

$$\tau_2 = \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a$$

$$\left|\Psi_{CC}\right\rangle = \left(1 + \frac{1}{4}\sum c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a + \frac{1}{32}\sum c_{ab}^{rs} c_{cd}^{tu}\, a_r^+ a_s^+ a_b a_a a_t^+ a_u^+ a_d a_c + \dots\right)\left|\Psi_0\right\rangle$$

$$\left|\Psi_{CC}\right\rangle == \left|\Psi_0\right\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \sum_{\substack{a<b<c<d\\ r<s<t<u}} c_{ab}^{rs} * c_{cd}^{tu}\left|\Psi_{abcd}^{rstu}\right\rangle + \dots$$

Pak lze Schodingerovu rovnici :

$$\hat{H}\ |\Psi\rangle = \mathrm{E}\ |\Psi\rangle$$

lze přepsat do tvaru:

$$\hat{H} e^{\hat{T}} |\Psi_0\rangle = \mathrm{E}\ e^{\hat{T}} |\Psi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Psi_0\rangle = \mathrm{E}\ e^{-\hat{T}} e^{\hat{T}} |\Psi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Psi_0\rangle = \mathrm{E}\ |\Psi_0\rangle$$

a tedy

$$\left\langle \Psi_0 \middle| e^{-\hat{T}} \hat{H} e^{\hat{T}} \middle| \Psi_0 \right\rangle \quad = \mathrm{E}$$

$$\left\langle \Psi_{ab}^{rs} \middle| e^{-\hat{T}} \hat{H} e^{\hat{T}} \middle| \Psi_0 \right\rangle \quad = 0$$

CC: Coupled Clusters

- v IEPA není ***ab..cd*** coupling
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$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c<d\\r<s<t<u}} c_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \ldots$$

$c_a^r, c_{abc}^{rst}, \ldots$ zanedbáme

$$(H - E_0)|\Phi_0\rangle = E_c|\Phi_0\rangle$$

fCI schéma

$$\sum_{\substack{c<d\\t<u}} \langle\Psi_0|H - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = E_c$$

$$\langle\Psi_{ab}^{rs}|H|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|H - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|H|\Psi_{abcd}^{rstu}\rangle c_{abcd}^{rstu} = c_{ab}^{rs} E_c$$

jiná cesta pro zahrnutí ***ab..cd*** coupling **CC aproximace**

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fCI: $2H_2$ molekula

$$\left|\Phi_0\right\rangle = \left|1_1\bar{1}_1 1_2\bar{1}_2\right\rangle + c_{1\bar{1}}^{2\bar{2}}\left(\left|2_1\bar{2}_1 1_2\bar{1}_2\right\rangle + \left|1_1\bar{1}_1 2_2\bar{2}_2\right\rangle\right) + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2}\left|2_1\bar{2}_1 2_2\bar{2}_2\right\rangle$$

Příklad 1: ověřte, zda-li platí: $c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} = \left(c_{1\bar{1}}^{2\bar{2}}\right)^2$?

$$\left|\Phi_0\right\rangle \doteq \left[\left|1_1\bar{1}_1\right\rangle + c_{1\bar{1}}^{2\bar{2}}\left|2_1\bar{2}_1\right\rangle\right]\left[\left|1_2\bar{1}_2\right\rangle + c_{1\bar{1}}^{2\bar{2}}\left|2_2\bar{2}_2\right\rangle\right] =$$

$$= \left|1_1\bar{1}_1\right\rangle\left|1_2\bar{1}_2\right\rangle + c_{1\bar{1}}^{2\bar{2}}\left|2_1\bar{2}_1\right\rangle\left|1_2\bar{1}_2\right\rangle + \ldots$$

$$c_{----}^{----} = c^2 \quad \sim \quad c_{----}^{----} = c_x * c_y \quad \Longrightarrow \quad \boxed{c_{abcd}^{rstu} \cong c_{ab}^{rs} * c_{cd}^{tu}}$$

$$\boxed{c_{abcd}^{rstu} \cong c_{ab}^{rs} * c_{cd}^{tu}}$$

$$*? \quad \begin{matrix} a \to r & c \to t \\ b \to s & d \to u \end{matrix} \quad |....abcd....\rangle \to |....rstu....\rangle$$

$$\begin{matrix} a \to r & c \to s \\ b \to t & d \to u \end{matrix} \quad \sim> |....rtsu....\rangle = -|....rstu....\rangle = ...$$

$$c_{abcd}^{rstu} \simeq c_{ab}^{rs}.c_{cd}^{tu} \vee c_{ab}^{rt}.c_{cd}^{su} \vee ...$$ celkem 18 členů

$$c_{abcd}^{rstu} = c_{ab}^{rs}.c_{cd}^{tu} - \left\langle c_{ab}^{rs} * c_{cd}^{tu} \right\rangle =$$

$$= c_{ab}^{rs}.c_{cd}^{tu} - c_{ac}^{rs}.c_{bd}^{tu} + c_{ad}^{rs}.c_{bc}^{tu} - c_{ab}^{rt}.c_{cd}^{su} + c_{ac}^{rt}.c_{bd}^{su} - c_{ad}^{rt}.c_{bc}^{su} + ...$$

$$c_{abcd}^{rstu} \cong c_{ab}^{rs} * c_{cd}^{tu}$$

$$*? \quad \begin{matrix} a \to r & c \to t \\ b \to s & d \to u \end{matrix} \quad |....abcd....\rangle \to |....rstu....\rangle$$

$$\begin{matrix} a \to r & c \to s \\ b \to t & d \to u \end{matrix} \quad \sim> |....rtsu....\rangle = -|....rstu....\rangle = ...$$

$$c_{abcd}^{rstu} \simeq c_{ab}^{rs} . c_{cd}^{tu} \vee c_{ab}^{rt} . c_{cd}^{su} \vee ... \quad \text{celkem 18 členů}$$

$$c_{abcd}^{rstu} = c_{ab}^{rs} . c_{cd}^{tu} - \left\langle c_{ab}^{rs} * c_{cd}^{tu} \right\rangle =$$

$$= c_{ab}^{rs} . c_{cd}^{tu} - c_{ac}^{rs} . c_{bd}^{tu} + c_{ad}^{rs} . c_{bc}^{tu} - c_{ab}^{rt} . c_{cd}^{su} + c_{ac}^{rt} . c_{bd}^{su} - c_{ad}^{rt} . c_{bc}^{su} + ...$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H | \Psi_{abcd}^{rstu} \rangle c_{abcd}^{rstu} = c_{ab}^{rs} E_c$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H | \Psi_{abcd}^{rstu} \rangle \left(c_{ab}^{rs} . c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle \right) = c_{ab}^{rs} E_c$$

$$E_c c_{ab}^{rs} = \left(\sum_{\substack{c<d \\ t<u}} \langle \Psi_0 | H - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs}$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | H | \Psi_{abcd}^{rstu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0$$

CP MET

+	-
- ne expl. $\boldsymbol{E_c}$ - v ***c*** nelineární - coupling mezi páry - size-conzistentní - invariantní vůči unitární tranf.	- není variační

N-molekul $\mathbf{H_2}$ v minimální bázi:

$$\left|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle \quad i=1,....N \quad \left\langle\Psi_0\middle|H\middle|\Psi_{11}^{22}\right\rangle = K_{12}$$

$$\left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\middle|H\middle|\Psi_{1_i\bar{1}_i1_j\bar{1}_j}^{2_i\bar{2}_i2_j\bar{2}_j}\right\rangle = \langle 0\|j\rangle = K_{12}$$

$$^{N}E_c = NcK_{12}$$

$$K + 2\Delta c + (N-1)Kc^2 = {}^{N}E_c c = (NcK)c$$

$$K + 2\Delta c - Kc^2 = 0$$

$$c = \frac{\Delta - \sqrt{\Delta^2 + K^2}}{K} \qquad {}^{N}E_c = N\left(\Delta - \sqrt{\Delta^2 + K^2}\right) = {}^{N}E_c(fCI)$$

$$c_{1_i\bar{1}_i1_j\bar{1}_j}^{2_i\bar{2}_i2_j\bar{2}_j} = c^2 \Longrightarrow$$ kolik **%** ?

Cluster Expansion (rozvoj)

$$\left|\Psi_{ab}^{rs}\right\rangle = a_r^+ a_s^+ a_b a_a \left|\Psi_0\right\rangle \Longrightarrow \left|\Psi(DCI)\right\rangle = (1 + \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a)\left|\Psi_0\right\rangle$$

$$\left|\Psi(CC)\right\rangle = \exp(\tau_2)\left|\Psi_0\right\rangle$$

$$\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \ldots$$

$$\tau_1 = \sum_{a,r} c_a^r\, a_r^+ a_a$$

$$\tau_2 = \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a$$

$$\exp(x) = 1 + x + \frac{1}{2}x^2 + \ldots$$

$$\left|\Psi_{CC}\right\rangle = (1 + \frac{1}{4}\sum c_{ab}^{rs}\, a_r^+ a_s^+ a_b a_a + \frac{1}{32}\sum c_{ab}^{rs} c_{cd}^{tu}\, a_r^+ a_s^+ a_b a_a a_t^+ a_u^+ a_d a_c + \ldots)\left|\Psi_0\right\rangle$$

$$\left|\Psi_{CC}\right\rangle == \left|\Psi_0\right\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \sum_{\substack{a<b<c<d\\ r<s<t<u}} c_{ab}^{rs} * c_{cd}^{tu}\left|\Psi_{abcd}^{rstu}\right\rangle + \ldots$$

Příklad 2: platí pro **$2H_2$** v minimální bázi?

$$\left|\Phi_0\right\rangle = \exp\left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^+ a_{\bar{2}_1}^+ a_{1_1} a_{\bar{1}_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^+ a_{\bar{2}_2}^+ a_{1_2} a_{\bar{1}_2}\right)\left|1_1\bar{1}_1 1_2\bar{1}_2\right\rangle$$

L-CCA

Aproximace CC, která je lineární v ***c*** koeficinetech: $c_{ab}^{rs} * c_{cd}^{tu} = c_{ab}^{rs} . c_{cd}^{tu}$

$$\left\langle\Psi_{ab}^{rs}\right|H\left|\Psi_0\right\rangle + \sum_{\substack{c<d\\t<u}} \left\langle\Psi_{ab}^{rs}\right|H - E_0\left|\Psi_{cd}^{tu}\right\rangle c_{cd}^{tu} = 0$$

$$\left\langle c_{ab}^{rs} * c_{cd}^{tu}\right\rangle = 0$$

Pozor!! $c_{ab}^{rs} * c_{cd}^{tu} \neq 0$

$$B + Dc = 0$$

$$B^+ c \quad = E_c$$

- -

$$E_c^{L-CCA} = -B^+ D^{-1} B$$

- -

Příklad 3: dokažte!

- je-li ***D*** diagonální => Epstein-Nesbet. metoda
- L-CCA je size-konzistentní

CEPA

$$\left\langle c_{ab}^{rs} * c_{cd}^{tu} \right\rangle \sim> \left\langle c_{ab}^{rs} * c_{ab}^{tu} \right\rangle = c_{ab}^{rs} . c_{ab}^{tu}$$

$$\left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle + \sum_{\substack{c<d \\ t<u}} \left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{cd}^{tu} \right\rangle c_{cd}^{tu} = \Big(\underbrace{\sum_{t<u} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{tu} \right\rangle c_{ab}^{tu}}_{e_{ab}} \Big) c_{ab}^{rs}$$

$$\left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle + \sum_{\substack{c<d \\ t<u}} \left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{cd}^{tu} \right\rangle c_{cd}^{tu} = e_{ab} c_{ab}^{rs}$$

$$\boxed{E_c(CEPA) = \sum_{ab} e_{ab}}$$

$$\sum_{\substack{c<d \\ t<u}} \sim> \sum_{t<u} \Rightarrow IEPA$$

$$e_{ab} \sim> E_c \Rightarrow DCI$$

- size-konzistentní,
- rychlá
- není variační, iterace c_{cd} v c_{ab}
- není invariant. k unitar.tr. - lepší než IEPA

$2H_2$: lokalizované MO: $$\left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \middle| H \middle| \Psi^{2_j\bar{2}_j}_{1_j\bar{1}_j} \right\rangle = 0$$ není rozdíl mezi IEPA a CEPA

$$^2E_c(L) = 2\left[\Delta + \left(\Delta^2 + K^2\right)^{\frac{1}{2}}\right] = E(FCI)$$

$2H_2$: delokalizované MO:
odvození formálně z DCI $\boldsymbol{E_c}$ -> $\boldsymbol{e_{ab}}$

$$^2E_c = \frac{1}{\sqrt{2}}K\left(c_1 + c_2 + c_3 + c_4\right) = e_{a\bar{a}} + e_{a\bar{b}} + e_{\bar{a}b} + e_{b\bar{b}}$$

např. pro $\boldsymbol{e_{aa}}$

$$\frac{1}{\sqrt{2}}K + 2\Delta' c_1 + \frac{1}{2}J_{11}c_2 + \left(\frac{1}{2}K - J_{12}\right)c_3 + \left(\frac{1}{2}K - J_{12}\right)c_4 = e_{a\bar{a}}c_1$$

$$^2E_c = 4e = 4\frac{Kc}{\sqrt{2}}$$

$$^2E_c(D) = e_{a\bar{a}} + e_{b\bar{b}} + e_{ab} + e_{a\bar{b}} + e_{\bar{a}b} + e_{\bar{a}\bar{b}} = 4\left[\Delta' + \left(\Delta'^2 + K^2/2\right)^{\frac{1}{2}}\right]$$

skoro inv.vůči UI

$$\frac{1}{\sqrt{2}}K + \left(2\Delta' + \frac{1}{2}J_{11} + K - 2J_{12}\right)c = ec$$

$$\frac{1}{\sqrt{2}}K + 2\Delta' c = ec \qquad \frac{K^2}{2} + 2\Delta e = e^2$$

$$\Longrightarrow \quad ^2E = 4\left(\Delta - \sqrt{\Delta^2 + \frac{K^2}{2}}\right)$$

Kalkulace:

H_2O v rozšířené bázi

metoda	CISD	IEPA	L-CCA	CCA	fCI	Exp
$\boldsymbol{E_c}$	-0.216	-0.327	-0.291	-0.286	-0.296	-0.37

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

$$\left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle + \sum_{\substack{c<d \\ t<u}} \left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{cd}^{tu} \right\rangle c_{cd}^{tu} = X$$

$$X(DCI) = E_{cor} c_{ab}^{rs}$$

$$X(L-CCA) = 0$$

$$X(CEPA) = e_{ab} c_{ab}^{rs}$$

$$X(CCA) = \sum_{\substack{c<d \\ t<u}} \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_{abcd}^{rstu} \right\rangle \left\langle c_{ab}^{rs} * c_{cd}^{tu} \right\rangle$$