IEPA:
Independent Electron Pair Approximation

$$E_c = \sum_{r<s}\sum_{a<b} c_{ab}^{rs} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle = \frac{1}{4}\sum_{rs}\sum_{ab} c_{ab}^{rs} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle$$

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

- je to jako CI počítáno „po párech“
- N elektronový problém rozdělen => N(N-1)/2 párů $\boldsymbol{e_{ab}}$

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

vlnová funkce obsahuje pouze základní stav a double-excitace

$$\sum_{rs} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle = E_{ab} = E_0 + e_{ab}$$

$$E_{ab}\, c_{ab}^{rs} = \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_{ab}^{tu} \right\rangle$$

....

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

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

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

$$\begin{pmatrix} 0 & B_{ab}^{+} \\ B_{ab} & D_{ab} \end{pmatrix} \begin{pmatrix} 1 \\ c_{ab} \end{pmatrix} = E_{ab} \begin{pmatrix} 1 \\ c_{ab} \end{pmatrix}$$

platí pro každý pár ***ab***

$$E_{corr}(IEPA) = \sum_{a<b} e_{ab} \qquad \left\langle \Psi_{ab}^{rs} \middle| H \middle| \Psi_{ab}^{tu} \right\rangle$$

- IEPA není aproximací k DCI
- ale má vztah k poruchové teorii   z DCI .. Tr(D): t = r u= s

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

$$\sum_{t<u} c_{ab}^{tu} \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{tu} \right\rangle = e_{ab}$$

$$e_{ab} = -\sum_{r<s} \frac{\left| \left\langle \Psi_0 \middle| H \middle| \Psi_{ab}^{rs} \right\rangle \right|^2}{\left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{ab}^{rs} \right\rangle - e_{ab}}$$

Epstein
Nesbet

$$E_{corr}(EN) = \sum_{a<b} e_{ab}$$

$$\left\langle \Psi_{ab}^{rs} \middle| H - E_0 \middle| \Psi_{ab}^{rs} \right\rangle = \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$$

$$e_{ab}^{FO} : E_{corr}(FO) = \sum_{r<s}\sum_{a<b} \frac{\left|\langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle\right|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} = \sum_{r<s}\sum_{a<b} \frac{\left|\langle ab || rs \rangle\right|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- ekvivalent k MP2

Příklad 1: výpočet molekuly H_2 metodou IEPA v minimální bázi

IEPA ⇔ DCI ⇔ FCI

$$\Delta = (\varepsilon_2 - \varepsilon_1) + \frac{1}{2}\left(J_{11} + J_{22} - 4J_{12} + 2K_{12}\right)$$

$$^1E_c = \Delta - (\Delta^2 + K_{12}^2)^{\frac{1}{2}}$$

Ukažte, že:

a) $^1E_{corr}(FO) = \dfrac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)}$

b) v $\boldsymbol{^1E_c}$ aproximujte $\Delta \doteq (\varepsilon_2 - \varepsilon_1)$ $\sqrt{1+x} \cong 1 + \frac{1}{2}x \longrightarrow {}^1E_c(FO)$

Například: dvě ne-interagující molekuly H_2 v minimální bázi

$$\left|\Psi_0\right\rangle = \left|1_1\bar{1}_1 1_2\bar{1}_2\right\rangle$$

6 párových korelačních energií: $e_{1_1\bar{1}_1}, e_{1_2\bar{1}_2}, \ldots$

jen $e_{1_1\bar{1}_1}, e_{1_2\bar{1}_2} \neq 0$

$$\left\langle\Psi_0\right|H\left|\Psi_{1_i\bar{1}_j}^{2_k\bar{2}_l}\right\rangle = \left\langle 1_i\bar{1}_j \| 2_k\bar{2}_l\right\rangle =$$

$$= \begin{cases} \left\langle 1_i\bar{1}_j \| 2_k\bar{2}_l\right\rangle = K_{12} & i = j = k = l \\ \mathbf{0} & \end{cases}$$

$$\left|\Psi_{1_i\bar{1}_j}\right\rangle = \left|\Psi_0\right\rangle + c_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|1_i\bar{1}_i 2_i\bar{2}_i\right\rangle$$

$$K_{12}c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i}$$

$$K_{12} + 2\Delta c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = c\, e_{1_i\bar{1}_i}$$

Příklad 2: odvoď!

$$^2E_c = e_{1_1\bar{1}_1} + e_{1_2\bar{1}_2} = 2\,^1E_c$$

IEPA je size konsistentní
DCI není size konsistentní

Příklad 3: ověřte, že platí: $^{2}E_{corr}(FO) = \dfrac{K_{12}^{2}}{(\varepsilon_2 - \varepsilon_1)}$

Invariance vůči unitární transformaci

$U\{\chi_a\} \to \Psi_0$ se nemění

Jak to je s IEPA a invariancí? $E_c(IEPA)$

Lokalizované MO: $1_1 2_1 1_2 2_2$

delokalizované MO:

	1.H$_2$	2.H$_2$	
$a = \frac{1}{\sqrt{2}}(1_1 + 1_2)$	$++$	$++$	g
$b = \frac{1}{\sqrt{2}}(1_1 - 1_2)$	$++$	$--$	u
$r = \frac{1}{\sqrt{2}}(2_1 - 2_2)$	$+-$	$-+$	g
$s = \frac{1}{\sqrt{2}}(2_1 + 2_2)$	$+-$	$+-$	u

$$\Psi_0 = \left| 1_1 \bar{1}_1 1_2 \bar{1}_2 \right\rangle == \left| a\bar{a}b\bar{b} \right\rangle$$

Příklad 4: ukažte:

$$(aa|aa)=(aa|bb)=(bb|bb)=(ab|ab)=\frac{1}{2}J_{11}$$

$$(rr|rr)=(rr|ss)=(ss|ss)=(rs|rs)=\frac{1}{2}J_{22}$$

$$(rr|aa)=(ss|bb)=(rr|bb)=(ss|bb)=\frac{1}{2}J_{12}$$

$$(ra|ra)=(sb|sb)=(rb|rb)=(sa|sa)=$$

$$=(ra|sb)=(rb|sa)=\frac{1}{2}K_{12}$$

$$\varepsilon_a=\varepsilon_b=\varepsilon_1$$

$$\varepsilon_r=\varepsilon_s=\varepsilon_2$$

$$\left|\Psi_{a\bar{a}}\right\rangle_g=\left|\Psi_0\right\rangle+c_1\left|\Psi_{a\bar{a}}^{r\bar{r}}\right\rangle+c_2\left|\Psi_{a\bar{a}}^{s\bar{s}}\right\rangle+c_?\xcancel{\left|\Psi_{a\bar{a}}^{r\bar{s}}\right\rangle_u}$$

$$\left\langle\Psi_0\right|H\left|\Psi_{a\bar{a}}^{r\bar{r}}\right\rangle=\left\langle a\bar{a}\|r\bar{r}\right\rangle=(ar|ar)=\frac{1}{2}K_{12}$$

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

$$\left\langle\Psi_0\right|H\left|\Psi_{a\bar{a}}^{s\bar{s}}\right\rangle=\frac{1}{2}K_{12}$$

$$\left|\Psi_{a\bar{a}}\right\rangle=\left|\Psi_0\right\rangle+\left|\Psi_{a\bar{a}}^{*\bar{*}}\right\rangle c$$

$e_{a\bar{a}}$:

$$\left\langle \Psi_0 \middle| H \middle| \Psi_{a\bar{a}}^{**} \right\rangle = \frac{1}{\sqrt{2}} K_{12}$$

$$\left\langle \Psi_{a\bar{a}}^{**} \middle| H - E_0 \middle| \Psi_{a\bar{a}}^{**} \right\rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{22} + \frac{1}{2}(J_{11} - 4J_{12} + 2K_{12}) \equiv 2\Delta'$$

Příklad 5:
dokažte!

$$e_{a\bar{a}} = \frac{1}{\sqrt{2}} K\, c$$

$$e_{a\bar{a}}\, c = \frac{1}{\sqrt{2}} K + 2\Delta' c$$

....

$$e_{a\bar{a}} = \Delta' + \left(\Delta'^2 + K^2/2\right)^{\frac{1}{2}}$$

$$e_{b\bar{b}} = \ldots = e_{a\bar{a}} \qquad e_{ab} = e_{\bar{a}\bar{b}} = 0$$

$$\left|\Psi_{\bar{a}\bar{b}}\right\rangle = \left|\Psi_0\right\rangle + c_1\left|\Psi_{\bar{a}\bar{b}}^{\bar{r}\bar{s}}\right\rangle$$

$$\left\langle\Psi_0\right|H\left|\Psi_{\bar{a}\bar{b}}^{\bar{r}\bar{s}}\right\rangle = \left\langle\bar{a}\bar{b}\middle|\middle|\bar{r}\bar{s}\right\rangle = \left(ar\middle|bs\right) - \left(as\middle|br\right) = 0$$

$$e_{a\bar{b}},\, e_{\bar{a}b}$$

$$\left|\Psi_{a\bar{b}}\right\rangle = \left|\Psi_0\right\rangle + c_1\left|\Psi_{a\bar{b}}^{r\bar{s}}\right\rangle + c_2\left|\Psi_{a\bar{b}}^{s\bar{r}}\right\rangle = \left|\Psi_0\right\rangle + c\left|\Psi_{a\bar{b}}^{*}\right\rangle$$

$$\left|\Psi_{a\bar{b}}^{*\bar{*}}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\Psi_{a\bar{b}}^{r\bar{s}}\right\rangle + \left|\Psi_{a\bar{b}}^{s\bar{r}}\right\rangle\right)$$

$$\left\langle\Psi_0\right|H\left|\Psi_{a\bar{b}}^{r\bar{s}}\right\rangle = \left\langle a\bar{b}\middle|\middle|r\bar{s}\right\rangle = \left(ar\middle|bs\right) = K/2$$

$$e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$$

Příklad 6: dokažte platnost.

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

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

Báze sto-3g, R = 1.4 a

${}^{2}E_{c}(L)$ = -0.0411 a.u.

${}^{2}E_{c}(D)$ = -0.0275 a.u.

pro větší báze je Δ(L-D) menší: BH_3

kanonické (D) MO: -0,0141

kanonické (L) MO: -0,0129

Příklad 7: ukažte, že DCI je invariantní vůči unitární transformaci

a) $$\left|\Psi_{DCI}\right\rangle = \left|\Psi_0\right\rangle + c_1\left|\Psi^*_{a\bar{a}}\right\rangle + c_2\left|\Psi^*_{b\bar{b}}\right\rangle + c_3\left|\Psi^*_{a\bar{b}}\right\rangle + c_4\left|\Psi^*_{\bar{a}b}\right\rangle$$

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}}K & \frac{1}{\sqrt{2}}K & \frac{1}{\sqrt{2}}K & \frac{1}{\sqrt{2}}K \\ \frac{1}{\sqrt{2}}K & 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K - J_{12} & \frac{1}{2}K - J_{12} \\ \frac{1}{\sqrt{2}}K & --- & 2\Delta' & \frac{1}{2}K - J_{12} & \frac{1}{2}K - J_{12} \\ \frac{1}{\sqrt{2}}K & --- & --- & 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{\sqrt{2}}K & --- & --- & --- & 2\Delta' \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = {}^2E_c(DCI) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

b) $$c_1 = c_2 = c_3 = c_4 \qquad {}^2E_c(DCI) = \Delta - \left(\Delta^2 + 2K^2\right)^{\frac{1}{2}} \neq {}^2E_c(FCI)$$

$^2E_c(FO)$:

$$^2E_c(IEPA) = 4[\,(\varepsilon_2-\varepsilon_1)-(\varepsilon_2-\varepsilon_1)\left(1+\frac{K^2}{2(\varepsilon_2-\varepsilon_1)^2}\right)^{\frac{1}{2}}\,]$$

$$\Delta' = \varepsilon_2-\varepsilon_1 \qquad \sqrt{1+x} \cong 1+\frac{1}{2}x$$

$$^2E_c(FO) = 4\left(\frac{-K^2}{4(\varepsilon_2-\varepsilon_1)}\right) = 2\left(\frac{-K^2}{2(\varepsilon_2-\varepsilon_1)}\right) = 2\ {}^1E_c(FO)$$

$$^2E_c(FO) = 2\ {}^1E_c(FO)$$

Příklad 8: odvoďte následující vztahy:

$$^2E_c(EN)(L) = -\frac{K^2}{\Delta}$$

$$^2E_c(EN)(D) = -\frac{K^2}{\Delta'}$$