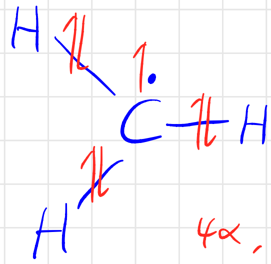
Discussion 5

CNDO/2 SCF

α : spin up

β : spin down



4α, 3β

Coupled SCF equation:

$$
\begin{cases}
\sum_{\nu}^{AO} f_{\mu\nu}^{\alpha} C_{\nu i}^{\alpha} = C_{\mu i}^{\alpha} \varepsilon_i^{\alpha} \\
\sum_{\nu}^{AO} f_{\mu\nu}^{\beta} C_{\nu i}^{\beta} = C_{\mu i}^{\beta} \varepsilon_i^{\beta}
\end{cases}
$$

in matrix form:

$$
\begin{cases}
\underbrace{\overbrace{\left[f_{\mu\nu}^{\alpha} \right]}^{AO}}_{AO} \underbrace{\overbrace{\left[C^{\alpha} \right]}^{AO}}_{AO} = \underbrace{\overbrace{\left[C^{\alpha} \right]}^{AO}}_{AO} \underbrace{\overbrace{\begin{bmatrix} \varepsilon_1^{\alpha} & & & 0 \\ & \varepsilon_2^{\alpha} & & \\ & & \varepsilon_3^{\alpha} & \\ 0 & & & \ddots \; \varepsilon_n^{\alpha} \end{bmatrix}}^{AO}}_{AO} \\
\underbrace{\overbrace{\left[f_{\mu\nu}^{\beta} \right]}^{AO}}_{AO} \underbrace{\overbrace{\left[C^{\beta} \right]}^{AO}}_{AO} = \underbrace{\overbrace{\left[C^{\beta} \right]}^{AO}}_{AO} \underbrace{\overbrace{\begin{bmatrix} \varepsilon_1^{\beta} & & & 0 \\ & \varepsilon_2^{\beta} & & \\ & & \varepsilon_3^{\beta} & \\ 0 & & & \ddots \; \varepsilon_n^{\beta} \end{bmatrix}}^{AO}}_{AO}
\end{cases}
$$

Energy:

$$
E_{CNDO/2} = \frac{1}{2} \sum_{\mu\nu}^{AO} P_{\mu\nu}^{\alpha} \overbrace{\left(h_{\mu\nu} + g_{\mu\nu}^{\alpha} \right)}^{f_{\mu\nu}^{\alpha}} + \frac{1}{2} \sum_{\mu\nu}^{AO} P_{\mu\nu}^{\beta} \underbrace{\left(h_{\mu\nu} + g_{\mu\nu}^{\beta} \right)}_{f_{\mu\nu}^{\beta}} + V_{nuc}
$$

Construction of $t^{\omega}_{\mu\nu}$ $(\omega = \alpha, \beta)$:

valence atomic number

$Z_H = 1 \quad Z_O = 6$

$Z_C = 4 \quad Z_N = 5 \; \cdots$

$$\begin{cases} t^{\omega}_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + \left[(P^{tot}_{AA} - Z_A) - (P^{\omega}_{\mu\mu} - \frac{1}{2}) \right] \gamma_{AA} \\ \qquad + \sum_{B \neq A}^{atoms} (P^{tot}_{BB} - Z_B) \gamma_{AB} \\ t^{\omega}_{\mu\nu} = + \frac{1}{2}(\beta_A + \beta_B) S_{\mu\nu} - P^{\omega}_{\mu\nu} \gamma_{AB} \qquad (\mu \neq \nu) \end{cases}$$

$$\begin{cases} t^{\omega}_{\mu\mu} = h_{\mu\mu} + g^{\omega}_{\mu\mu} \\ t^{\omega}_{\mu\nu} = h_{\mu\nu} + g^{\omega}_{\mu\nu} \qquad (\mu \neq \nu) \end{cases}$$

$$\begin{cases} h_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) - (Z_A - \frac{1}{2}) \gamma_{AA} - \sum_{B \neq A}^{atom} Z_B \gamma_{AB} \\ h_{\mu\nu} = + \frac{1}{2}(\beta_A + \beta_B) S_{\mu\nu} \qquad (\mu \neq \nu,\ \mu \in A,\ \nu \in B) \end{cases}$$

$$\begin{cases} g^{\omega}_{\mu\mu} = \left[P^{tot}_{AA} - P^{\omega}_{\mu\mu} \right] \gamma_{AA} + \sum_{B \neq A}^{atom} P^{tot}_{BB} \gamma_{AB} \\ g^{\omega}_{\mu\nu} = -P^{\omega}_{\mu\nu} \gamma_{AB} \qquad (\mu \neq \nu,\ \mu \in A,\ \nu \in B) \end{cases}$$

$$\gamma_{AB} = \sum_{k=1}^{3} \sum_{k'=1}^{3} \sum_{l=1}^{3} \sum_{l'=1}^{3} d'_{k,s_A} d'_{k',s_A} d'_{l,s_B} d'_{l',s_B} [0]^{(0)}$$

$$[0]^{(0)} = \frac{U_A U_B}{\sqrt{(\vec{R}_A - \vec{R}_B)^2}} \operatorname{erf}(\sqrt{T}) \qquad A \neq B$$

$$[0]^{(0)} = 2 U_A U_B \sqrt{\frac{(\sigma_A + \sigma_B)^{-1}}{\pi}} \qquad A = B$$

$$U_A = \left(\frac{\pi}{\alpha_k + \alpha_{k'}}\right)^{\frac{3}{2}} \qquad U_B = \left(\frac{\pi}{\beta_l + \beta_{l'}}\right)^{\frac{3}{2}}$$

primitive gaussian exponents on A

primitive gaussian exponents on B

$$\exp\left(-\beta_l (\vec{r} - \vec{R}_B)^2\right)$$

$$T = (\sigma_A + \sigma_B)^{-1} (\vec{R}_A - \vec{R}_B)^2$$

$$\sigma_A = (\alpha_k + \alpha_{k'})^{-1} \qquad \sigma_B = (\beta_l + \beta_{l'})^{-1}$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

(built in C++, just do
#include <cmath>
the function can be called as
erf(x))