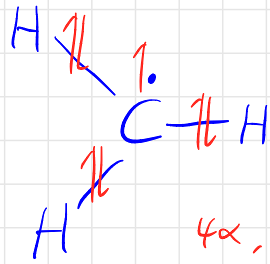
Discussion 5

CNDO/2 SCF

α : spin up

β : spin down



4α, 3β

Coupled SCF equation:

$$\begin{cases} \sum_{\nu}^{AO} f^{\alpha}_{\mu\nu} C^{\alpha}_{\nu i} = C^{\alpha}_{\mu i} \varepsilon^{\alpha}_{i} \\ \sum_{\nu}^{AO} f^{\beta}_{\mu\nu} C^{\beta}_{\nu i} = C^{\beta}_{\mu i} \varepsilon^{\beta}_{i} \end{cases}$$

in matrix form:

$$\begin{cases} AO\overset{AO}{\begin{bmatrix} f^{\alpha}_{\mu\nu} \end{bmatrix}} AO\overset{AO}{\begin{bmatrix} C^{\alpha} \end{bmatrix}} = AO\overset{AO}{\begin{bmatrix} C^{\alpha} \end{bmatrix}} AO\overset{AO}{\begin{bmatrix} \varepsilon^{\alpha}_{1} & & & 0 \\ & \varepsilon^{\alpha}_{2} & & \\ & & \varepsilon^{\alpha}_{3} & \\ 0 & & & \ddots & \\ & & & & \varepsilon^{\alpha}_{n} \end{bmatrix}} \\ AO\overset{AO}{\begin{bmatrix} f^{\beta}_{\mu\nu} \end{bmatrix}} AO\overset{AO}{\begin{bmatrix} C^{\beta} \end{bmatrix}} = AO\overset{AO}{\begin{bmatrix} C^{\beta} \end{bmatrix}} AO\overset{AO}{\begin{bmatrix} \varepsilon^{\beta}_{1} & & & 0 \\ & \varepsilon^{\beta}_{2} & & \\ & & \varepsilon^{\beta}_{3} & \\ 0 & & & \ddots & \\ & & & & \varepsilon^{\beta}_{n} \end{bmatrix}} \end{cases}$$

Energy:

$$E_{CNDO/2} = \frac{1}{2}\sum_{\mu\nu}^{AO} P^{\alpha}_{\mu\nu} \overbrace{(h_{\mu\nu} + g^{\alpha}_{\mu\nu})}^{f^{\alpha}_{\mu\nu}} + \frac{1}{2}\sum_{\mu\nu}^{AO} P^{\beta}_{\mu\nu} \underbrace{(h_{\mu\nu} + g^{\beta}_{\mu\nu})}_{f^{\beta}_{\mu\nu}} + V_{nuc}$$

$$V_{nuc} = \sum_{A \neq B} \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|}$$

$$\hat{P} = |\psi_i\rangle\langle\psi_i| = C_{\mu i}|\phi_\mu\rangle C_{\nu i}\langle\phi_\nu| = \underbrace{C_{\mu i}C_{\nu i}}_{P_{\mu\nu}}|\phi_\mu\rangle\langle\phi_\nu|$$

$$P_{\mu\nu} = \sum_i^{MO} C_{\mu i}C_{\nu i} = \sum_i^{MO} C_{\mu i}C^T_{i\nu} = (CC^T)_{\mu\nu}$$

$$P_{\mu\nu} = P_{\nu\mu} = (P^T)_{\mu\nu}$$

$$P = CC^T \Rightarrow P^T = (CC^T)^T = CC^T = P$$

$$\mathrm{tr}(ABC) = \mathrm{tr}(BCA) = \mathrm{tr}(CAB)$$

$$E_{CNDO/2} = \frac{1}{2}\sum_{\mu\nu}^{AO} P^\alpha_{\mu\nu} t^\alpha_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu}^{AO} P^\beta_{\mu\nu} t^\beta_{\mu\nu} + V_{nuc}$$

$$= \frac{1}{2}\sum_{\mu\nu}^{AO} \underline{P^\alpha_{\nu\mu} t^\alpha_{\mu\nu}} + \frac{1}{2}\sum_{\mu\nu}^{AO} \underline{P^\beta_{\nu\mu} t^\beta_{\mu\nu}} + V_{nuc}$$

$$= \frac{1}{2}\sum_{\nu}^{AO}(P^\alpha t^\alpha)_{\nu\nu} + \frac{1}{2}\sum_{\nu}^{AO}(P^\beta t^\beta)_{\nu\nu} + V_{nuc}$$

$$= \frac{1}{2}\mathrm{tr}(P^\alpha t^\alpha) + \frac{1}{2}\mathrm{tr}(P^\beta t^\beta) + V_{nuc}$$

$$= \frac{1}{2}\mathrm{tr}(C^\alpha C^{\alpha T} t^\alpha) + \frac{1}{2}\mathrm{tr}(C^\beta C^{\beta T} t^\beta) + V_{nuc}$$

$$= \frac{1}{2}\mathrm{tr}(t^\alpha C^\alpha C^{\alpha T}) + \frac{1}{2}\mathrm{tr}(t^\beta C^\beta C^{\beta T}) + \cdots$$

$$= \frac{1}{2}\mathrm{tr}(\underline{\varepsilon^\alpha C^\alpha C^{\alpha T}) + \frac{1}{2}\mathrm{tr}(\varepsilon^\beta} C^\beta C^{\beta T}) + \cdots$$

diagonal

$$= \frac{1}{2}\mathrm{tr}(\underbrace{C^{\alpha T} C^\alpha}_{I} \varepsilon^\alpha) + \frac{1}{2}\mathrm{tr}(\underbrace{C^{\beta T} C^\beta}_{I} \varepsilon^\beta) + \cdots$$

$$= \frac{1}{2}(\varepsilon^\alpha_1 + \varepsilon^\alpha_2 + \cdots + \varepsilon^\alpha_p) + \frac{1}{2}(\varepsilon^\beta_1 + \varepsilon^\beta_2 + \cdots + \varepsilon^\beta_q) + V_{nuc}$$

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

valence atomic number

$Z_H = 1$ $\quad Z_O = 6$

$Z_C = 4$ $\quad Z_N = 5$ ---

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

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

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

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

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

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

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

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

primitive gaussian exponents on A

primitive gaussian exponents on B

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

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

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

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

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

CH_4