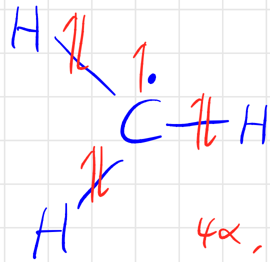
Discussion 5

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:

$$\begin{cases} \underbrace{\left[\, f^{\alpha}_{\mu\nu} \,\right]}_{AO \times AO} \underbrace{\left[\, C^{\alpha} \,\right]}_{AO \times AO} = \underbrace{\left[\, C^{\alpha} \,\right]}_{AO \times AO} \underbrace{\begin{bmatrix} \varepsilon^{\alpha}_1 & & & 0 \\ & \varepsilon^{\alpha}_2 & & \\ & & \varepsilon^{\alpha}_3 & \\ 0 & & & \ddots \ \varepsilon^{\alpha}_n \end{bmatrix}}_{AO \times AO} \\ \underbrace{\left[\, f^{\beta}_{\mu\nu} \,\right]}_{AO \times AO} \underbrace{\left[\, C^{\beta} \,\right]}_{AO \times AO} = \underbrace{\left[\, C^{\beta} \,\right]}_{AO \times AO} \underbrace{\begin{bmatrix} \varepsilon^{\beta}_1 & & & 0 \\ & \varepsilon^{\beta}_2 & & \\ & & \varepsilon^{\beta}_3 & \\ 0 & & & \ddots \ \varepsilon^{\beta}_n \end{bmatrix}}_{AO \times AO} \end{cases}$$

Energy:

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

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

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

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

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

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

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

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

$$= \frac{1}{2}\sum_{\mu\nu}^{AO} \underbrace{P^\alpha_{\nu\mu} f^\alpha_{\mu\nu}} + \frac{1}{2}\sum_{\mu\nu}^{AO} \underbrace{P^\beta_{\nu\mu} f^\beta_{\mu\nu}} + V_{nuc} + \frac{1}{2}\sum_{\mu\nu}^{AO} P^{tot}_{\mu\nu} h_{\mu\nu}$$

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

$$= \frac{1}{2}\mathrm{tr}(P^\alpha f^\alpha) + \frac{1}{2}\mathrm{tr}(P^\beta f^\beta) + V_{nuc} + \frac{1}{2}\sum_{\mu\nu}^{AO} P^{tot}_{\mu\nu} h_{\mu\nu}$$

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

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

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

diagonal

$$= \frac{1}{2}\mathrm{tr}(\underbrace{C^{\alpha T} C^\alpha}_{I} \varepsilon^\alpha) + \frac{1}{2}\mathrm{tr}(\underbrace{C^{\beta T} C^\beta}_{I} \varepsilon^\beta) + \cdots + \frac{1}{2}\sum_{\mu\nu}^{AO} P^{tot}_{\mu\nu} h_{\mu\nu}$$

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

$$\Rightarrow E_{CNDO/2} = \underbrace{\frac{1}{2}(\varepsilon_1^\alpha + \cdots + \varepsilon_p^\alpha) + \frac{1}{2}(\varepsilon_1^\beta + \cdots + \varepsilon_q^\beta) + \frac{1}{2}\operatorname{tr}(P^{tot} h)}_{E_{electronic}}$$

$$+ V_{nuc}$$

or you can do:

$$E_{electronic} = \frac{1}{2}\operatorname{tr}\left[P^\alpha(h + f^\alpha)\right] + \frac{1}{2}\operatorname{tr}\left[P^\beta(h + f^\beta)\right]$$

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

valence atomic number

$Z_H = 1 \quad Z_O = 6$

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

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

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

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

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

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

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

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

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

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)

CH_4