Discussion 4

CNDO/2 SCF

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:

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

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

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

$$t^{w}_{\mu\nu} = -\frac{1}{2}(\beta_A + \beta_B) S_{\mu\nu} - P^{w}_{\mu\nu}\gamma_{AB} \qquad (\mu \neq \nu)$$

I_μ, A_μ : parameter for orbitals

β_A : parameter for atoms

t depends on P.
P depends on C.
C depends on t
need to be solved self-consistently

$$P^{\alpha}_{\mu\nu} = \sum_{i=1}^{n^{\alpha}_{occ}} C^{\alpha}_{\mu i} C^{\alpha}_{\nu i} \qquad P^{\beta}_{\mu\nu} = \sum_{i=1}^{n^{\beta}_{occ}} C^{\beta}_{\mu i} C^{\beta}_{\nu i}$$

$$P^{tot}_{\mu\nu} = P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu} \qquad P^{tot}_{AA} = \sum_{\mu\in A} P^{tot}_{\mu\mu}$$

$S_{\mu\nu}$: AO overlap, same thing as in HW3

$$\gamma_{AB} = \int d\vec{r}_1 d\vec{r}_2 \left[S_A(\vec{r}_1)\right]^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \left[S_B(\vec{r}_2)\right]^2$$

s orbital located on atom A

s orbital located on atom B

$$S_A(\vec{r}) = \sum_{k=1}^{3} \underbrace{\left(d_{k,s_A} N^{s}_{k}\right)}_{d'_{k,s_A}} \underbrace{\omega^{s}_{k}(\vec{r} - \vec{R}_A)}_{\exp(-\alpha_k(\vec{r}-\vec{R}_A)^2)}$$

$$= \sum_{k=1}^{3} d'_{k,s_A} \exp(-\alpha_k(\vec{r}-\vec{R}_A)^2)$$

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

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

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

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))