Discussion 6

fock matrix

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

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

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

valence atomic number

$Z_H = 1$ $Z_O = 6$

$Z_C = 4$ $Z_N = 5$ ...

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

$$\frac{\partial}{\partial \vec{R}_A} E_{CNDO/2} = E_{CNDO/2}^{\vec{R}_A} = \sum_{A \neq B}^{Atom} X_{AB}\, \gamma_{AB}^{\vec{R}_A} + \sum_{\mu \neq \nu}^{AO} Y_{\mu\nu}\, S_{\mu\nu}^{\vec{R}_A} + V_{nuc}^{\vec{R}_A}$$

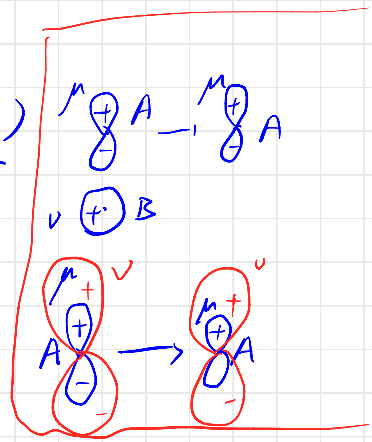
$$V_{nuc} = \sum_{B}^{Atom} \sum_{C \neq B}^{Atom} \frac{Z_B Z_C}{\sqrt{(\vec{R}_B - \vec{R}_C)^2}} \qquad \binom{5}{2} = 10$$

$$V_{nuc}^{\vec{R}_A} = \sum_{B \neq A}^{Atom} \frac{\partial}{\partial \vec{R}_A} \left[\frac{Z_A Z_B}{\sqrt{(\vec{R}_A - \vec{R}_B)^2}} \right] = \sum_{B \neq A}^{Atom} Z_A Z_B \frac{\partial}{\partial \vec{R}_A} \left[\frac{1}{d_{AB}} \right]$$

$$\frac{\partial d_{AB}}{\partial \vec{R}_A} = \frac{2(\vec{R}_A - \vec{R}_B)}{2 d_{AB}} = \frac{\vec{R}_A - \vec{R}_B}{d_{AB}}$$

$$\Rightarrow V_{nuc}^{\vec{R}_A} = \sum_{B \neq A}^{Atom} Z_A Z_B (-1)\, d_{AB}^{-2} \cdot \frac{(\vec{R}_A - \vec{R}_B)}{d_{AB}}$$

$$= \sum_{B \neq A}^{Atom} (-1) Z_A Z_B (\vec{R}_A - \vec{R}_B)\, d_{AB}^{-3}$$



$S_{\mu\nu}^{\vec{R}_A}$: none-zero only if $\mu \in A,\ \nu \in B \neq A$

let's look at $S_{\mu\nu}^{X_A}$: $S_{\mu\nu} = \sum_{k}^{3} \sum_{l}^{3} d_{k\mu}\, d_{l\nu}\, S_{kl}$

$$S_{kl} = \int dx\, (x - X_A)^{l_A} (x - X_B)^{l_B} \exp\left[-\alpha (x - X_A)^2 - \beta (x - X_B)^2\right]$$

$$\times \int dy\, (y - Y_A)^{l_A} (y - Y_B)^{l_B} \exp\left[-\alpha (y - Y_A)^2 - \beta (y - Y_B)^2\right]$$

$$\times \int dz\, (z-Z_A)^{l_A}(z-Z_B)^{l_B}\exp\left[-\alpha(z-Z_A)^2-\beta(z-Z_B)^2\right]$$

$$= I_x I_y I_z$$

$$S_{kl}^{X_A} = I_x^{X_A} I_y I_z$$

$$I_x^{X_A} = \int dx \frac{\partial}{\partial X_A}\left\{(x-X_A)^{l_A}(x-X_B)^{l_B}\exp\left[-\alpha(x-X_A)^2-\beta(x-X_B)^2\right]\right\}$$

$$= \int dx\, -l_A(x-X_A)^{l_A-1}(x-X_B)^{l_B}\exp\left[-\alpha(x-X_A)^2-\beta(x-X_B)^2\right]$$

$$+ \int dx\, 2\alpha(x-X_A)^{l_A+1}(x-X_B)^{l_B}\exp\left[-\alpha(x-X_A)^2-\beta(x-X_B)^2\right]$$

$$= -l_A\int dx\, (x-X_A)^{l_A-1}(x-X_B)^{l_B}\exp\left[-\alpha(x-X_A)^2-\beta(x-X_B)^2\right] \quad (=0 \text{ if } l_A=0)$$

$$+2\alpha\int dx\, (x-X_A)^{l_A+1}(x-X_B)^{l_B}\exp\left[-\alpha(x-X_A)^2-\beta(x-X_B)^2\right]$$

$\gamma_{AB}^{\vec{R}_A}$:

$$\gamma_{AB} = \sum_{k}^{3}\sum_{k'}^{3}\sum_{l}^{3}\sum_{l'}^{3} d_{ks_A} d_{k's_A} d_{ls_B} d_{l's_B}\,[0]$$

$$[0] = U_A U_B \frac{1}{d_{AB}}\frac{2}{\sqrt{\pi}}\int_0^{\sqrt{T}}\exp(-v^2)\,dv$$

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

$$V^2 = (\sigma_A+\sigma_B)^{-1}$$

$$[0]^{R_A} =$$

$$U_A U_B \left[-d_{AB}^{-2} \cdot \frac{(\vec{R}_A - \vec{R}_B)}{d_{AB}} \operatorname{erf}(\sqrt{T}) + \frac{2}{\sqrt{\pi}} \frac{1}{d_{AB}} \cdot \exp(-T) \cdot \frac{(\sigma_A + \sigma_B)^{-1}}{\cancel{2}\sqrt{T}} \cdot \cancel{2} \cancel{d_{AB}} \cdot \frac{\vec{R}_A - \vec{R}_B}{\cancel{d_{AB}}} \right]$$

$$= U_A U_B \left[-d_{AB}^{-2} \frac{(\vec{R}_A - \vec{R}_B)}{d_{AB}} \operatorname{erf}(\sqrt{T}) + \frac{2}{\sqrt{\pi}} \frac{1}{d_{AB}^2} \exp(-T) V (\vec{R}_A - \vec{R}_B) \right]$$

$$= \frac{U_A U_B}{d_{AB}^2} \left[\frac{2V}{\sqrt{\pi}} \exp(-T) - \frac{\operatorname{erf}(\sqrt{T})}{d_{AB}} \right] (\vec{R}_A - \vec{R}_B)$$

$$\frac{d}{dx} \int_{\text{Const}}^{x} dt \, f(t) = f(x)$$

$$\frac{d}{d\vec{R}_A} \int_0^{\sqrt{T}} \exp(-v^2) \, dv = \frac{d\sqrt{T}}{d\vec{R}_A} \underbrace{\frac{d}{d\sqrt{T}} \int_0^{\sqrt{T}} \exp(-v^2) \, dv}_{\exp(-T)}$$

$$\frac{dT}{d\vec{R}_A} \underbrace{\frac{d\sqrt{T}}{dT}}_{\frac{1}{2\sqrt{T}}}$$