

# Discussion 6

tock matrix

$$E_{\text{AOs}/2} = \frac{1}{2} \sum_{\mu\nu}^{\text{AO}} P_{\mu\nu}^{\alpha} (h_{\mu\nu} + t_{\mu\nu}^{\alpha}) + \frac{1}{2} \sum_{\mu\nu}^{\text{AO}} P_{\mu\nu}^{\beta} (h_{\mu\nu} + t_{\mu\nu}^{\beta}) + V_{\text{nuc}}$$

$$= \frac{1}{2} \sum_{\mu\nu}^{\text{AO}} P_{\mu\nu}^{\alpha} (\underbrace{h_{\mu\nu} + g_{\mu\nu}^{\alpha}}_{t_{\mu\nu}^{\alpha}} + h_{\mu\nu}) + \frac{1}{2} \sum_{\mu\nu}^{\text{AO}} P_{\mu\nu}^{\beta} (\underbrace{h_{\mu\nu} + g_{\mu\nu}^{\beta}}_{t_{\mu\nu}^{\beta}} + h_{\mu\nu}) + V_{\text{nuc}}$$

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

valence atomic number

$$\begin{array}{ll} Z_H = 1 & Z_O = 6 \\ Z_C = 4 & Z_N = 5 \dots \end{array}$$

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

$$\frac{\partial}{\partial \vec{R}_A} E_{\text{Endo12}} = E_{\text{Endo12}}^{\vec{R}_A} = \sum_{A \neq B} X_{AB} Y_{AB}^{\vec{R}_A} + \sum_{\mu \neq \nu} Y_{\mu\nu} S_{\mu\nu}^{\vec{R}_A} + V_{\text{nuc}}^{\vec{R}_A}$$

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

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

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

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

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

$S_{\mu\nu}^{\vec{R}_A}$  : non-zero only if  $\mu \in A, \nu \in B \neq A$

let's look at  $S_{\mu\nu}^{X_A}$  :  $S_{\mu\nu} = \sum_k^{\frac{3}{2}} \sum_l^{\frac{3}{2}} d_{k\mu} d_{l\nu} S_{kl}$

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

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

$$\times \int dz (z - z_A)^{l_A} (z - z_B)^{l_B} \exp[-\alpha(z - z_A)^2 - \beta(z - z_B)^2]$$

$$= I_x I_y I_z$$

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

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

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

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

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

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

$$\gamma_{AB}^{\vec{R}_A} : \quad \gamma_{AB} = \sum_k \sum_{k'} \sum_l \sum_{l'} d_{k's_A} d_{k's_A} d_{l's_B} d_{l's_B} [0]$$

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

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

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

$$\begin{aligned}
[0]^{R_A} &= \\
U_A U_B \left[ -d_{AB}^{-2} \cdot \frac{(\vec{P}_A - \vec{P}_B)}{d_{AB}} \operatorname{erf}(\sqrt{T}) + \frac{2}{\sqrt{\pi}} \frac{1}{d_{AB}} \cdot \exp(-T) \cdot \frac{(\vec{G}_A + \vec{G}_B)}{2\sqrt{T}} \cdot \cancel{\frac{1}{d_{AB}} \cdot \frac{(\vec{P}_A - \vec{P}_B)}{d_{AB}}} \right] \\
&= U_A U_B \left[ -d_{AB}^{-2} \frac{(\vec{P}_A - \vec{P}_B)}{d_{AB}} \operatorname{erf}(\sqrt{T}) + \frac{2}{\sqrt{\pi}} \frac{1}{d_{AB}^2} \exp(-T) V(\vec{P}_A - \vec{P}_B) \right] \\
&= \frac{U_A U_B}{d_{AB}^2} \left[ \frac{2V}{\sqrt{\pi}} \exp(-T) - \frac{\operatorname{erf}(\sqrt{T})}{d_{AB}} \right] (\vec{P}_A - \vec{P}_B)
\end{aligned}$$