$$E_{CNDO/2} = \underbrace{\frac{1}{2}\sum_{\mu\nu} P^{\alpha}_{\mu\nu}\left(H_{\mu\nu}+F^{\alpha}_{\mu\nu}\right)}_{\equiv E^{\alpha}} + \underbrace{\frac{1}{2}\sum_{\mu\nu} P^{\beta}_{\mu\nu}\left(H_{\mu\nu}+F^{\beta}_{\mu\nu}\right)}_{\equiv E^{\beta}} + V_{nuc}$$

$$\frac{\partial E^{\alpha}}{\partial R_A} = \frac{1}{2}\frac{\partial}{\partial R_A}\left(\sum_{\mu\in A}\sum_{\nu\in B\neq A} + \sum_{\nu\in A}\sum_{\mu\in B\neq A} + \sum_{\mu\in A,\, \nu=\mu} + \sum_{\mu\in B\neq A,\, \nu=\mu}\right) P^{\alpha}_{\mu\nu}\left(H_{\mu\nu}+F^{\alpha}_{\mu\nu}\right)$$

$$= \frac{1}{2}\Bigg[\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^{\alpha}_{\mu\nu}\left(\frac{\partial H_{\mu\nu}}{\partial R_A}+\frac{\partial F^{\alpha}_{\mu\nu}}{\partial R_A}\right) + \sum_{\nu\in A}\sum_{\mu\in B\neq A} P^{\alpha}_{\mu\nu}\left(\frac{\partial H_{\mu\nu}}{\partial R_A}+\frac{\partial F^{\alpha}_{\mu\nu}}{\partial R_A}\right)$$

$$+ \sum_{\mu\in A} P^{\alpha}_{\mu\mu}\left(\frac{\partial H_{\mu\mu}}{\partial R_A}+\frac{\partial F^{\alpha}_{\mu\mu}}{\partial R_A}\right) + \sum_{\mu\in B\neq A} P^{\alpha}_{\mu\mu}\left(\frac{\partial H_{\mu\mu}}{\partial R_A}+\frac{\partial F^{\alpha}_{\mu\mu}}{\partial R_A}\right)\Bigg]$$

$$\frac{\partial F^{\alpha}_{\mu\mu}}{\partial R_A} = \sum_{B\neq A}\left(P_{BB}-Z_B\right)\frac{\partial \gamma_{AB}}{\partial R_A} \qquad \mu\in A$$

$$\frac{\partial H_{\mu\mu}}{\partial R_A} = -\sum_{B\neq A} Z_B \frac{\partial \gamma_{AB}}{\partial R_A} \qquad \mu\in A$$

$$\frac{\partial F^{\alpha}_{\mu\nu}}{\partial R_A} = \frac{1}{2}\left(\beta_A+\beta_B\right)\frac{\partial S_{\mu\nu}}{\partial R_A} - P^{\alpha}_{\mu\nu}\frac{\partial \gamma_{AB}}{\partial R_A}$$

μ, ν belong to different atoms

$$\frac{\partial H^{\alpha}_{\mu\nu}}{\partial R_A} = \frac{1}{2}\left(\beta_A+\beta_B\right)\frac{\partial S_{\mu\nu}}{\partial R_A}$$

<u>x term</u>: extract all terms relate to $\frac{\partial S_{\mu\nu}}{\partial R_A}$

$$\frac{1}{2}\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^{\alpha}_{\mu\nu}\left[\frac{1}{2}\left(\beta_A+\beta_B\right)+\frac{1}{2}\left(\beta_A+\beta_B\right)\right]\frac{\partial S_{\mu\nu}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\nu\in A}\sum_{\mu\in B\neq A} P^{\alpha}_{\mu\nu}\left[\frac{1}{2}\left(\beta_A+\beta_B\right)+\frac{1}{2}\left(\beta_A+\beta_B\right)\right]\frac{\partial S_{\mu\nu}}{\partial R_A}$$

$\because$ ν, μ are dummy variables
$\therefore$ switch them won't influence anything

$$= \sum_{\mu\in A}\sum_{\nu\in B\neq A} P^{\alpha}_{\mu\nu}\left(\beta_A+\beta_B\right)\frac{\partial S_{\mu\nu}}{\partial R_A}$$

similar for E^{β}: $\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^{\beta}_{\mu\nu}\left(\beta_A+\beta_B\right)$

$$\Rightarrow \sum_{\mu\in A}\sum_{\nu\in B\neq A} x_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial R_A} = \sum_{\mu\in A}\sum_{\nu\in B\neq A} \underbrace{\left(P^{\alpha}_{\mu\nu}+P^{\beta}_{\mu\nu}\right)}_{\equiv P^{tot}_{\mu\nu}}\left(\beta_A+\beta_B\right)\frac{\partial S_{\mu\nu}}{\partial R_A}$$

$$\Rightarrow x_{\mu\nu} = P^{tot}_{\mu\nu}\left(\beta_A+\beta_B\right)$$

$\underline{\gamma \text{ term}}$: extract all terms relate to $\frac{\partial \gamma_{AB}}{\partial R_A}$ in $\frac{\partial E^\alpha}{\partial R_A}$

$$-\frac{1}{2}\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^\alpha_{\mu\nu} P^\alpha_{\mu\nu} \frac{\partial \gamma_{AB}}{\partial R_A} - \frac{1}{2}\sum_{\nu\in A}\sum_{\mu\in B\neq A} P^\alpha_{\mu\nu} P^\alpha_{\mu\nu} \frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in A} P^\alpha_{\mu\mu} \sum_{B\neq A}(-Z_B + P^{tot}_{BB} - Z_B)\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in B\neq A} P^\alpha_{\mu\mu} \sum(-Z_A + P^{tot}_{AA} - Z_A)\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$= -\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^\alpha_{\mu\nu} P^\alpha_{\mu\nu} \frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in A}\sum_{B\neq A} P^\alpha_{\mu\mu} P^{tot}_{BB}\frac{\partial \gamma_{AB}}{\partial R_A} - \sum_{\mu\in A}\sum_{B\neq A} Z_B P^\alpha_{\mu\mu}\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in B\neq A}\sum P^\alpha_{\mu\mu} P^{tot}_{AA}\frac{\partial \gamma_{AB}}{\partial R_A} - \sum_{\mu\in B\neq A}\sum Z_A P^\alpha_{\mu\mu}\frac{\partial \gamma_{AB}}{\partial R_A}$$

Similarly, for E^β:

$$-\sum_{\mu\in A}\sum_{\nu\in B\neq A} P^\beta_{\mu\nu} P^\beta_{\mu\nu} \frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in A}\sum_{B\neq A} P^\beta_{\mu\mu} P^{tot}_{BB}\frac{\partial \gamma_{AB}}{\partial R_A} - \sum_{\mu\in A}\sum_{B\neq A} Z_B P^\beta_{\mu\mu}\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$+\frac{1}{2}\sum_{\mu\in B\neq A}\sum P^\beta_{\mu\mu} P^{tot}_{AA}\frac{\partial \gamma_{AB}}{\partial R_A} - \sum_{\mu\in B\neq A}\sum Z_A P^\beta_{\mu\mu}\frac{\partial \gamma_{AB}}{\partial R_A}$$

$\Rightarrow$ sum them up:

$$\sum_{B\neq A} y_{AB}\frac{\partial \gamma_{AB}}{\partial R_A} = \Big[-\sum_{\mu\in A}\sum_{\nu\in B\neq A}(P^\alpha_{\mu\nu}P^\alpha_{\mu\nu} + P^\beta_{\mu\nu}P^\beta_{\mu\nu})$$

$$+\frac{1}{2}\sum_{\mu\in A}\sum_{B\neq A} P^{tot}_{\mu\mu}P^{tot}_{BB} - \sum_{\mu\in A}\sum_{B\neq A} Z_B P^{tot}_{\mu\mu}$$

$$+\frac{1}{2}\sum_{\mu\in B\neq A}\sum_{A\neq B} P^{tot}_{\mu\mu} P^{tot}_{AA} - \sum_{\mu\in B\neq A}\sum_{A\neq B} Z_A P^{tot}_{\mu\mu}\Big]\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$= \sum_{B\neq A}\Big[-\sum_{\mu\in A}\sum_{\nu\in B}(P^\alpha_{\mu\nu}P^\alpha_{\mu\nu} + P^\beta_{\mu\nu}P^\beta_{\mu\nu}) + P^{tot}_{AA}P^{tot}_{BB}$$

$$- Z_B P^{tot}_{AA} - Z_A P^{tot}_{BB}\Big]\frac{\partial \gamma_{AB}}{\partial R_A}$$

$$\Rightarrow y_{AB} = -\sum_{\mu\in A}\sum_{\nu\in B}(P^\alpha_{\mu\nu}P^\alpha_{\mu\nu} + P^\beta_{\mu\nu}P^\beta_{\mu\nu}) + P^{tot}_{AA}P^{tot}_{BB} - Z_B P^{tot}_{AA} - Z_A P^{tot}_{BB}$$