UNIVERSITY OF CALIFORNIA BERKELEY

Numerical Algorithms Applied to Computational Quantum Chemistry
Homework 5: Evaluate the analytic gradient of your SCF energy

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1 DERIVING THE THEORY YOURSELF.

$$E_{\mathrm{CNDO/2}} = \frac{1}{2}\sum_{\mu\nu} p^{\alpha}_{\nu\mu}\left(h_{\mu\nu} + f^{\alpha}_{\mu\nu}\right) + \frac{1}{2}\sum_{\mu\nu} p^{\beta}_{\nu\mu}\left(h_{\mu\nu} + f^{\beta}_{\mu\nu}\right) + \sum_{A}\sum_{B<A}\frac{Z_A Z_B}{R_{AB}} \tag{1.1}$$

$$\begin{aligned}
E^{\alpha R_A}_{\mathrm{CNDO/2}} =& \frac{\partial}{\partial R_A}\frac{1}{2}\sum_{\mu\nu} p^{\alpha}_{\nu\mu}\left(h_{\mu\nu} + f^{\alpha}_{\mu\nu}\right) \\
=& \frac{1}{2}\sum_{\mu\in A}\sum_{\nu\neq\mu} p^{\alpha}_{\nu\mu}\left(h^{R_A}_{\mu\nu} + f^{\alpha R_A}_{\mu\nu}\right) + \frac{1}{2}\sum_{\nu\in A}\sum_{\mu\neq\nu} p^{\alpha}_{\nu\mu}\left(h^{R_A}_{\mu\nu} + f^{\alpha R_A}_{\mu\nu}\right) + \frac{1}{2}\frac{\partial}{\partial R_A}\sum_{\mu} p^{\alpha}_{\mu\mu}\left(h_{\mu\mu} + f^{\alpha}_{\mu\mu}\right) \\
=& \frac{1}{2}\sum_{\mu\in A}\sum_{\nu}\left[p^{\alpha}_{\nu\mu}\left(h^{R_A}_{\mu\nu} + f^{\alpha R_A}_{\mu\nu}\right) + p^{\alpha}_{\mu\nu}\left(h^{R_A}_{\nu\mu} + f^{\alpha R_A}_{\nu\mu}\right)\right] + \frac{1}{2}\frac{\partial}{\partial R_A}\sum_{\mu} p^{\alpha}_{\mu\mu}\left(h_{\mu\mu} + f^{\alpha}_{\mu\mu}\right) \\
=& \sum_{\mu\in A}\sum_{\nu} p^{\alpha}_{\nu\mu}(h^{R_A}_{\mu\nu} + f^{\alpha R_A}_{\mu\nu}) + \frac{1}{2}\sum_{\mu\in A} p^{\alpha}_{\mu\mu}\left(h^{R_A}_{\mu\mu} + f^{\alpha R_A}_{\mu\mu}\right) + \frac{1}{2}\sum_{\mu\in B, B\neq A} p^{\alpha}_{\mu\mu}\left(h^{R_A}_{\mu\mu} + f^{\alpha R_A}_{\mu\mu}\right)
\end{aligned} \tag{1.2}$$

$$h_{\mu\mu} = -\frac{1}{2}\left(I_\mu + A_\mu\right) - \left(Z_A - \frac{1}{2}\right)\gamma_{AA} - \sum_{B\neq A} Z_B\gamma_{AB} \tag{1.3}$$

$$f^{\alpha}_{\mu\mu} = -\frac{1}{2}\left(I_\mu + A_\mu\right) + \left[\left(p^{\mathrm{tot}}_{AA} - Z_A\right) - \left(p^{\alpha}_{\mu\mu} - \frac{1}{2}\right)\right]\gamma_{AA} + \sum_{B\neq A}\left(p^{\mathrm{tot}}_{BB} - Z_B\right)\gamma_{AB} \tag{1.4}$$

$$h_{\mu\nu} = \frac{1}{2}\left(\beta_A + \beta_B\right)s_{\mu\nu} \tag{1.5}$$

$$f^{\alpha}_{\mu\nu} = \frac{1}{2}\left(\beta_A + \beta_B\right)s_{\mu\nu} - p^{\alpha}_{\mu\nu}\gamma_{AB} \tag{1.6}$$

$$h_{\mu\mu}^{R_A} = -\sum_{B\neq A} Z_B \gamma_{AB}^{R_A}, \quad \mu \in A \tag{1.7}$$

$$f_{\mu\mu}^{\alpha R_A} = \sum_{B\neq A} \left(p_{BB}^{\text{tot}} - Z_B\right) \gamma_{AB}^{R_A}, \quad \mu \in A \tag{1.8}$$

$$h_{\mu\mu}^{R_A} = -Z_A \gamma_{BA}^{R_A} = -Z_A \gamma_{AB}^{R_A}, \quad \mu \notin A \tag{1.9}$$

$$f_{\mu\mu}^{\alpha R_A} = \left(p_{AA}^{\text{tot}} - Z_A\right) \gamma_{AB}^{R_A}, \quad \mu \notin A \tag{1.10}$$

$$h_{\mu\nu}^{R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\mu\nu}^{R_A} \tag{1.11}$$

$$f_{\mu\nu}^{\alpha R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\mu\nu}^{R_A} - p_{\mu\nu}^{\alpha} \gamma_{AB}^{R_A} \tag{1.12}$$

$$h_{\nu\mu}^{R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\nu\mu}^{R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\mu\nu}^{R_A} \tag{1.13}$$

$$f_{\nu\mu}^{\alpha R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\nu\mu}^{R_A} - p_{\nu\mu}^{\alpha} \gamma_{BA}^{R_A} = \frac{1}{2}\left(\beta_A + \beta_B\right) s_{\mu\nu}^{R_A} - p_{\mu\nu}^{\alpha} \gamma_{AB}^{R_A} \tag{1.14}$$

$$\begin{aligned} E_{\text{CNDO/2}}^{\alpha R} = &\sum_{\mu\in A}\sum_{\nu} p_{\mu\nu}^{\alpha} \left(\left(\beta_A + \beta_B\right) s_{\mu\nu}^{R} - p_{\mu\nu}^{\alpha} \gamma_{AB}^{R}\right) \\ &+ \frac{1}{2} p_{AA}^{\alpha} \sum_{B\neq A} \left(p_{BB}^{\text{tot}} - 2Z_B\right) \gamma_{AB}^{R} + \frac{1}{2} \sum_{B\neq A} p_{BB}^{\alpha} \left(p_{AA}^{\text{tot}} - 2Z_A\right) \gamma_{AB}^{R} \end{aligned} \tag{1.15}$$

The gradient can be written in the following general form:

$$E_{\text{CNDO/2}}^{\mathbf{R}_A} = \sum_{\mu\in A}\sum_{\nu\notin A} x_{\mu\nu} s_{\mu\nu}^{\mathbf{R}_A} + \sum_{B\neq A} y_{AB} \gamma_{AB}^{\mathbf{R}_A} + V_{\text{nuc}}^{\mathbf{R}_A} \tag{1.16}$$

$$x_{\mu\nu} = (\beta_A + \beta_B) p_{\mu\nu} \tag{1.17}$$

$$y_{AB}^{R} = p_{AA}^{\text{tot}} p_{BB}^{\text{tot}} - Z_B p_{AA}^{\text{tot}} - Z_A p_{BB}^{\text{tot}} - \sum_{\mu\in A}\sum_{\nu\in B} (p_{\mu\nu}^{\alpha} p_{\mu\nu}^{\alpha} + p_{\mu\nu}^{\beta} p_{\mu\nu}^{\beta}) \tag{1.18}$$

Integral Calculation:

$$\gamma_{AB}^{R} = \sum_{k}^{3}\sum_{k'}^{3}\sum_{l}^{3}\sum_{l'}^{3} d'_{ks_A} d'_{k's_A} d'_{ls_B} d'_{l's_B} [0]^{R} \tag{1.19}$$

$$[0]^{(0)} = U_A U_B \sqrt{\frac{1}{(\mathbf{R}_A - \mathbf{R}_B)^2}} \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{T}} \exp\left(-v^2\right) dv \tag{1.20}$$

$$\begin{aligned} [0]^{R_A} &= \frac{U_A U_B}{|\mathbf{R}_A - \mathbf{R}_B|} \left[\frac{-(\mathbf{R}_A - \mathbf{R}_B)}{|\mathbf{R}_A - \mathbf{R}_B|^2} \operatorname{erf}\left(\sqrt{T}\right) + \frac{2}{\sqrt{\pi}} \exp^{-T} \frac{V(\mathbf{R}_A - \mathbf{R}_B)}{|\mathbf{R}_A - \mathbf{R}_B|} \right] \\ &= \frac{U_A U_B}{|\mathbf{R}_A - \mathbf{R}_B|^2} \left[\frac{2V}{\sqrt{\pi}} \exp^{-T} - \frac{\operatorname{erf}\left(\sqrt{T}\right)}{|\mathbf{R}_A - \mathbf{R}_B|} \right] (\mathbf{R}_A - \mathbf{R}_B) \end{aligned} \tag{1.21}$$

$$S_{\mu\nu}^{R_A} = \sum_{k}^{3}\sum_{l}^{3} d_{k\mu} d_{l\nu} N_{k\mu} N_{l\nu} S^{kl,R_A} \tag{1.22}$$

$$S_x^{AB,x_A} = \frac{\partial}{\partial R_A} \int_x (x - X_A)^{l_A} (x - X_B)^{l_B} \exp\left[-\alpha (x - X_A)^2 - \beta (x - X_B)^2\right] \tag{1.23}$$

$$= -l_A \int_x (x - X_A)^{l_A - 1} (x - X_B)^{l_B} \exp\left[-\alpha (x - X_A)^2 - \beta (x - X_B)^2\right] \tag{1.24}$$

$$+2\alpha \int_x (x - X_A)^{l_A + 1} (x - X_B)^{l_B} \exp\left[-\alpha (x - X_A)^2 - \beta (x - X_B)^2\right] \tag{1.25}$$