Generalized Born : Energies, Forces and Hessian

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1 Energy and Force Equations

Effective Born radii for atom i is given by

$$R_i^{-1} = \tilde{\rho}_i^{-1} - \rho_i^{-1} \tanh(\alpha\Psi_i - \beta{\Psi_i}^2 + \gamma{\Psi_i}^3). \tag{1}$$

or

$$R_i = \frac{\tilde{\rho}_i \rho_i}{\rho_i - \tilde{\rho}_i \tanh(\alpha\Psi_i - \beta{\Psi_i}^2 + \gamma{\Psi_i}^3)}. \tag{2}$$

where

$$\Psi_i = I_i \tilde{\rho}_i. \tag{3}$$

Note that,

$$\tilde{\rho}_i = \rho_i - p. \tag{4}$$

where p is dielectric offset and $p = 0.09\,\mathring{A}$ and ρ_i is the radius of atom i. I_i for atom i is given by (according to HCT paper)

$$I_i = \frac{1}{2}\sum_{j \neq i}\left(\left[\frac{1}{L_{ij}} - \frac{1}{U_{ij}} + \frac{r_{ij}}{4}\left(\frac{1}{U_{ij}^2} - \frac{1}{L_{ij}^2}\right) + \frac{1}{2r_{ij}}\log\frac{L_{ij}}{U_{ij}} + \frac{S_j^2{\tilde{\rho}_j}^2}{4r_{ij}}\left(\frac{1}{L_{ij}^2} - \frac{1}{U_{ij}^2}\right)\right] + C_{ij}\right), \tag{5}$$

where

$$L_{ij} = \left\{\begin{array}{cl} 1 & , \tilde{\rho}_i \geq r_{ij} + S_j\tilde{\rho}_j \\ \tilde{\rho}_i & , r_{ij} + S_j\tilde{\rho}_j \geq \tilde{\rho}_i \geq r_{ij} - S_j\tilde{\rho}_j \\ r_{ij} - S_j\tilde{\rho}_j & , r_{ij} - S_j\tilde{\rho}_j \geq \tilde{\rho}_i \end{array}\right. , \tag{6}$$

$$U_{ij} = \left\{\begin{array}{cl} 1 & , \tilde{\rho}_i \geq r_{ij} + S_j\tilde{\rho}_j \\ r_{ij} + S_j\tilde{\rho}_j & , \tilde{\rho}_i < r_{ij} + S_j\tilde{\rho}_j \end{array}\right. , \tag{7}$$

$$C_{ij} = \left\{\begin{array}{cl} 2(\frac{1}{\tilde{\rho}_i} - \frac{1}{L_{ij}}) & , \tilde{\rho}_i < (\tilde{\rho}_j S_j - r_{ij}) \\ 0 & \text{otherwise} \end{array}\right. , \tag{8}$$

and S_j are given constants.

Derivative of Born Radius R_i w.r.t. r_{ij} is given by (note that $\frac{\partial \tanh(x)}{\partial x} = (1 - \tanh^2(x))$)

$$\frac{\partial R_i}{\partial r_{ij}} = R_i^2\left(1 - \tanh^2\left(\alpha\Psi_i - \beta{\Psi_i}^2 + \gamma{\Psi_i}^3\right)\right)\left(\alpha - 2\beta\Psi_i + 3\gamma{\Psi_i}^2\right)\frac{\tilde{\rho}_i}{\rho_i}\frac{\partial I_i}{\partial r_{ij}}. \tag{9}$$

Derivative of the burial term in Equation (5) is given by

$$\begin{aligned}\frac{\partial I_i}{\partial r_{ij}} &= -\frac{1}{2}\frac{\partial L_{ij}}{\partial r_{ij}}\frac{1}{L_{ij}(r_{ij})^2} + \frac{1}{2}\frac{\partial U_{ij}}{\partial r_{ij}}\frac{1}{U_{ij}(r_{ij})^2} + \left(\frac{1}{8U_{ij}^2} - \frac{1}{8L_{ij}^2}\right) \\ &+ \frac{1}{8}r_{ij}\left(\frac{-2}{U_{ij}^3}\frac{\partial U_{ij}}{\partial r_{ij}} + \frac{2}{L_{ij}^3}\frac{\partial L_{ij}}{\partial r_{ij}}\right) - \frac{1}{4}\frac{1}{r_{ij}^2}\log\left(\frac{L_{ij}}{U_{ij}}\right) + \frac{U_{ij}}{4r_{ij}L_{ij}}\left(\frac{1}{U_{ij}}\frac{\partial L_{ij}}{r_{ij}} - \frac{L_{ij}}{U_{ij}^2}\frac{\partial U_{ij}}{\partial r_{ij}}\right) \\ &- \frac{1}{8}\frac{S_j^2\tilde{\rho}_j^2}{r_{ij}^2}\left(\frac{1}{L_{ij}^2} - \frac{1}{U_{ij}^2}\right) + \frac{1}{4}\frac{S_j^2\tilde{\rho}_j^2}{r_{ij}U_{ij}^3}\frac{\partial U_{ij}}{\partial r_{ij}} - \frac{1}{4}\frac{S_j^2\tilde{\rho}_j^2}{r_{ij}L_{ij}^3}\frac{\partial L_{ij}}{\partial r_{ij}} + \frac{\partial C_{ij}}{\partial r_{ij}}\end{aligned} \tag{10}$$

Derivative of L_{ij} (Equation (6)) w. r. t. r_{ij} is given by

$$\frac{\partial L_{ij}}{\partial r_{ij}} = \begin{cases} 1 & , r_{ij} - S_j\tilde{\rho}_j \geq \tilde{\rho}_i \\ 0 & , \text{otherwise} \end{cases} . \tag{11}$$

Derivative of U_{ij} (Equation (7)) w. r. t. r_{ij} is given by

$$\frac{\partial U_{ij}}{\partial r_{ij}} = \begin{cases} 1 & , \tilde{\rho}_i < r_{ij} + S_j\tilde{\rho}_j \\ 0 & , \text{otherwise} \end{cases} . \tag{12}$$

Derivative of C_{ij} (Equation (8)) w. r. t. r_{ij} is given by

$$\frac{\partial C_{ij}}{\partial r_{ij}} = \begin{cases} 2\frac{1}{L_{ij}^2}\frac{\partial L_{ij}}{\partial r_{ij}} & , \tilde{\rho}_i < (\tilde{\rho}_j S_j) - r_{ij} \\ 0 & , \text{otherwise} \end{cases} . \tag{13}$$

Question: Does $\partial C_{ij}/\partial r_{ij} = 0$?

ACE Solvation term The nonpolar ACE solvation energy is given by

$$G^{np}(\mathbf{r}) = \sum_i G_i^{np}(\mathbf{r}) = 4\pi\sigma \sum_i (\rho_i + \rho_s)^2 \left(\frac{\rho_i}{R_i}\right)^6, \tag{14}$$

where ρ_s is the radius of water probe sphere. Derivative of G^{np} is given by

$$\frac{\partial G^{np}}{\partial r_{ij}} = -24\pi\sigma\left((\rho_i + \rho_s)^2\frac{\rho_i^6}{R_i^7}\frac{\partial R_i}{\partial r_{ij}} + (\rho_j + \rho_s)^2\frac{\rho_j^6}{R_j^7}\frac{\partial R_j}{\partial r_{ij}}\right). \tag{15}$$

Generalized Born potential The Generalized-Born potential energy function in OpenMM is given by

$$E_{GB} = -\frac{1}{2}\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_w}\right)\sum_i\sum_{j\neq i}\frac{q_i q_j}{f_{ij}^{GB}(r_{ij}, R_i, R_j)}. \tag{16}$$

In Equation (16), ϵ_S is the solute dielectric, R_i and R_j are effective Born radii of atoms i and j respectively. Note we have not calculated the 'self' term as OpenMM assumes the derivative of the 'self' term is zero. The function f_{ij}^{GB} is given by,

$$f_{ij}^{GB} = \left(r_{ij}^2 + R_i R_j \exp\left(-\frac{r_{ij}^2}{4R_iR_j}\right)\right)^{\frac{1}{2}}. \tag{17}$$

The pairwise force term can be obtained by taking the negative of the derivative of E_{GB} w. r. t. r_{ij}.

$$\frac{\partial E_{GB}}{\partial r_{ij}} = \left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_w}\right) \left(\sum_{k \neq i,j} \frac{q_i q_k}{\left(f_{ik}^{GB}\right)^2} \frac{\partial f_{ik}^{GB}}{\partial r_{ij}} + \sum_{l \neq i,j} \frac{q_j q_l}{\left(f_{jl}^{GB}\right)^2} \frac{\partial f_{jl}^{GB}}{\partial r_{ij}} + \frac{q_i q_j}{\left(f_{ij}^{GB}\right)^2} \frac{\partial f_{ij}^{GB}}{\partial r_{ij}} \right). \tag{18}$$

Derivative of f_{ij}^{GB} (Equation (17)) w. r. t. r_{ij} can be written as

$$\begin{aligned} \frac{\partial f_{ij}^{GB}}{\partial r_{ij}} \quad &= \quad \frac{1}{2 f_{ij}^{GB}} \left[2 r_{ij} + \frac{\partial R_i}{\partial r_{ij}} R_j \exp\left(-\frac{r_{ij}^2}{4 R_i R_j}\right) + R_i \frac{\partial R_j}{\partial r_{ij}} \exp\left(-\frac{r_{ij}^2}{4 R_i R_j}\right) \right. \\ &\left. + R_i R_j \exp\left(-\frac{r_{ij}^2}{4 R_i R_j}\right) \left(-\frac{r_{ij}}{2 R_i R_j} + \frac{1}{4} \frac{r_{ij}^2}{R_i^2 R_j} \frac{\partial R_i}{\partial r_{ij}} + \frac{1}{4} \frac{r_{ij}^2}{R_i R_j^2} \frac{\partial R_j}{\partial r_{ij}}\right) \right]. \end{aligned} \tag{19}$$

Derivative of f_{ik}^{GB} w. r. t. r_{ij} is then

$$\frac{\partial f_{ik}^{GB}}{\partial r_{ij}} = \frac{1}{2 f_{ik}^{GB}} \left(R_k + \frac{r_{ik}^2}{4 R_i}\right) \exp\left(-\frac{r_{ik}^2}{4 R_i R_k}\right) \frac{\partial R_i}{\partial r_{ij}}. \tag{20}$$

Similarly, the derivative of f_{jl}^{GB} w. r. t. r_{ij} is

$$\frac{\partial f_{jl}^{GB}}{\partial r_{ij}} = \frac{1}{2 f_{jl}^{GB}} \left(R_l + \frac{r_{jl}^2}{4 R_j}\right) \exp\left(-\frac{r_{jl}^2}{4 R_j R_l}\right) \frac{\partial R_j}{\partial r_{ij}}. \tag{21}$$

1.1 Force in $\mathbf{r}_i$

To obtain the force we need to find

$$\frac{\mathrm{d} r_{ij}}{\mathrm{d} \mathbf{r}_i} = \frac{\mathrm{d} ||\mathbf{r}_j - \mathbf{r}_i||}{\mathrm{d} \mathbf{r}_i} \quad = \quad - \frac{||\mathbf{r}_j - \mathbf{r}_i||}{r_{ij}} \quad = \quad - \hat{\mathbf{r}}_{ij}, \tag{22}$$

and similarly for $\mathbf{r}_j$, then apply the chain rule to get

$$\nabla_{ij} E_{GB} \quad = \quad \frac{\partial E_{GB}}{\partial r_{ij}} \left[-\hat{\mathbf{r}}_{ij} \quad \hat{\mathbf{r}}_{ij} \right]. \tag{23}$$

For the force

$$\mathbf{F}_{ij} = -\nabla_{ij} E_{GB} \quad = \quad \frac{\partial E_{GB}}{\partial r_{ij}} \left[\ \hat{\mathbf{r}}_{ij} \quad - \hat{\mathbf{r}}_{ij} \ \right]. \tag{24}$$

2 Hessian

Second derivative of G_{np} is given by

$$\frac{\partial^2 G^{np}}{\partial r_{ij}^2} = 24 \pi \sigma \left[(\rho_i + \rho_s)^2 \frac{\rho_i{}^6}{R_i^7} \left(\frac{7}{R_i} \left(\frac{\partial R_i}{\partial r_{ij}} \right)^2 - \frac{\partial^2 R_i}{\partial r_{ij}^2} \right) + (\rho_j + \rho_s)^2 \frac{\rho_j{}^6}{R_j^7} \left(\frac{7}{R_j} \left(\frac{\partial R_j}{\partial r_{ij}} \right)^2 - \frac{\partial^2 R_j}{\partial r_{ij}^2} \right) \right]. \tag{25}$$

Second derivative of E_{GB} is given by

$$\frac{\partial^2 E_{GB}}{\partial r_{ij}^2} = \left[q_i q_j \left(\frac{1}{f_{ij}^{GB^2}} \frac{\partial^2 f_{ij}^{GB}}{\partial r_{ij}^2} - \frac{2}{f_{ij}^{GB^3}} \left(\frac{\partial f_{ij}^{GB}}{\partial r_{ij}} \right)^2 \right) + \sum_k \sum_l q_k q_l \left(\frac{1}{f_{kl}^{GB^2}} \frac{\partial^2 f_{kl}^{GB}}{\partial r_{ij}^2} - \frac{2}{f_{kl}^{GB^3}} \left(\frac{\partial f_{kl}^{GB}}{\partial r_{ij}} \right)^2 \right) \right]. \tag{26}$$

Second derivative of the Born Radius R_i (see Equation (25)) is given by

$$\begin{aligned} \frac{\partial^2 R_i}{\partial r_{ij}^2} &= 2(1-\tanh(\alpha\Psi-\beta\Psi^2+\gamma\Psi^3))^2(\frac{\partial \Psi}{\partial r_{ij}})^2(\alpha-2\beta\Psi+3\gamma\Psi^2)^2\frac{R_i^3}{\rho^2} \\ &\quad -2R_i^2\tanh(\alpha\Psi-\beta\Psi^2+\gamma\Psi^3)(1-\tanh(\alpha\Psi-\beta\Psi^2+\gamma\Psi^3)^2) \\ &\quad \left(\frac{\partial \Psi_i}{\partial r_{ij}}\right)^2(\alpha-2\beta\Psi+3\gamma\Psi^2)^2\frac{1}{\rho} \\ &\quad R_i^2(1-\tanh(\alpha\Psi-\beta\Psi^2+\gamma\Psi^3)^2)(\alpha\frac{\partial^2\Psi_i}{\partial r_{ij}^2}-2\beta(\frac{\partial\Psi_i}{\partial r_{ij}})^2-2\beta\Psi_i\frac{\partial^2\Psi_i}{\partial r_{ij}^2})\frac{1}{\rho_i} \\ &\quad +R_i^2(1-\tanh(\alpha\Psi-\beta\Psi^2+\gamma\Psi^3)^2)(6\gamma\Psi_i(\frac{\partial\Psi_i}{\partial r_{ij}})^2+3\gamma\Psi_i^2\frac{\partial^2\Psi_i}{\partial r_{ij}^2})\frac{1}{\rho_i}. \end{aligned} \tag{27}$$

Second derivative of f_{ij}^{GB} is given by

$$\begin{aligned} \frac{\partial^2 f_{ij}^{GB}}{\partial r_{ij}^2} &= -\frac{1}{4}\frac{1}{f_{ij}^{GB}}4\left(f_{ij}^{GB}\right)^2\left(\frac{\partial f_{ij}^{GB}}{\partial r_{ij}}\right)^2 \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[2+\frac{\partial^2 R_i}{\partial r_{ij}^2}R_j\exp(-\frac{r_{ij}^2}{4R_iR_j})+2\frac{\partial R_i}{\partial r_{ij}}\frac{\partial R_j}{\partial r_{ij}}\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[2\frac{\partial R_i}{\partial r_{ij}}R_j\left(-\frac{r_{ij}}{R_iR_j}+\frac{r_{ij}^2}{4R_i^2R_j}\frac{\partial R_i}{\partial r_{ij}}+\frac{r_{ij}^2}{4R_iR_j^2}\frac{\partial R_j}{\partial r_{ij}}\right)\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[R_i\frac{\partial^2 R_j}{\partial r_{ij}^2}\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[2R_j\frac{\partial R_i}{\partial r_{ij}}\left(-\frac{r_{ij}}{2R_iR_j}+\frac{r_{ij}^2}{4R_i^2R_j}\frac{\partial R_i}{\partial r_{ij}}+\frac{r_{ij}^2}{4R_iR_j^2}\frac{\partial R_j}{\partial r_{ij}}\right)\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[R_iR_j\left(-\frac{1}{2R_iR_j}+\frac{r_{ij}}{4R_i^2R_j}\frac{\partial R_i}{\partial r_{ij}}+\frac{r_{ij}}{4R_iR_j^2}\frac{\partial R_j}{\partial r_{ij}}-\frac{r_{ij}^2}{2R_i^2R_j^2}\frac{\partial R_i}{\partial r_{ij}}\frac{\partial R_j}{\partial r_{ij}}\right)\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[R_iR_j\left(\frac{r_{ij}^2}{4R_i^2R_j}\frac{\partial^2 R_i}{\partial r_{ij}^2}+\frac{r_{ij}^2}{4R_iR_j^2}\frac{\partial^2 R_j}{\partial r_{ij}^2}-\frac{r_{ij}^2}{2R_iR_j^3}(\frac{\partial R_j}{\partial r_{ij}})^2\right)\exp(-\frac{r_{ij}^2}{4R_iR_j})\right] \\ &\quad +\frac{1}{2f_{ij}^{GB}}\left[R_iR_j\left(-\frac{r_{ij}}{2R_iR_j}+\frac{r_{ij}^2}{4R_i^2R_j}\frac{\partial R_i}{\partial r_{ij}}+\frac{r_{ij}^2}{4R_iR_j^2}\frac{\partial R_j}{\partial r_{ij}}\right)\exp(-\frac{r_{ij}^2}{4R_iR_j})\right]. \end{aligned} \tag{28}$$

Similarly, we can find,

$$\frac{\partial^2 f_{il}^{GB}}{\partial r_{ij}^2} = \frac{1}{f_{il}^{GB}}\exp(-\frac{r_{il}^2}{4R_iR_l})(R_l+\frac{r_{il}^2}{4R_i})\left[\frac{\partial^2 R_i}{\partial r_{ij}} - \frac{\partial R_i}{\partial r_{ij}}\left(\frac{1}{f_{il}^{GB}}\right)\frac{\partial f_{il}^{GB}}{\partial r_{ij}}\right] + \frac{1}{f_{il}^{GB}}\exp(-\frac{r_{il}^2}{4R_iR_j})\left(\frac{\partial R_i}{\partial r_{ij}}\right)^2\left[(R_l+\left(-\frac{r_{il}^2}{4R_i}\right))\frac{-r_{il}^2}{4R_i^2R_l} - \frac{r_{il}^2}{4R_i}\right] \quad (29)$$

and

$$\frac{\partial^2 f_{jl}^{GB}}{\partial r_{ij}^2} = \frac{1}{f_{jl}^{GB}}\exp(-\frac{r_{jl}^2}{4R_jR_l})(R_l+\frac{r_{jl}^2}{4R_j})\left[\frac{\partial^2 R_j}{\partial r_{ij}} - \frac{\partial R_j}{\partial r_{ij}}\left(\frac{1}{f_{jl}^{GB}}\right)\frac{\partial f_{jl}^{GB}}{\partial r_{ij}}\right] + \frac{1}{f_{jl}^{GB}}\exp(-\frac{r_{jl}^2}{4R_jR_j})\left(\frac{\partial R_j}{\partial r_{ij}}\right)^2\left[(R_l+\left(-\frac{r_{jl}^2}{4R_j}\right))\frac{-r_{jl}^2}{4R_j^2R_l} - \frac{r_{jl}^2}{4R_j}\right] \quad (30)$$

Note that

$$\frac{\partial^2 \Psi_i}{\partial r_{ij}^2} = \frac{\partial^2 I_i}{\partial r_{ij}^2}\tilde{\rho}_i. \quad (31)$$

where

$$\begin{aligned}\frac{\partial^2 I_i}{\partial r_{ij}^2} = & \left[\frac{1}{L_{ij}^3}\left(\frac{\partial L_{ij}}{\partial r_{ij}}\right)^2 - \frac{1}{U_{ij}^3}\left(\frac{\partial U_{ij}}{\partial r_{ij}}\right)^2 + \left(\frac{1}{4L_{ij}^3}\frac{\partial L_{ij}}{\partial r_{ij}} - \frac{1}{4U_{ij}^3}\frac{\partial U_{ij}}{\partial r_{ij}}\right)\right] \\ & + \left[\frac{1}{8}\left(\frac{2}{L_{ij}^3}\frac{\partial L_{ij}}{\partial r_{ij}} - \frac{2}{U_{ij}^3}\frac{\partial U_{ij}}{\partial r_{ij}}\right) - \frac{r_{ij}}{4}\left(\frac{3}{U_{ij}^4}\left(\frac{\partial U_{ij}}{\partial r_{ij}}\right)^2 - \frac{3}{L_{ij}^4}\left(\frac{\partial L_{ij}}{\partial r_{ij}}\right)^2\right)\right] \\ & + \left[\frac{1}{2r_{ij}^3}\log(\frac{L_{ij}}{U_{ij}}) - \frac{1}{2}\frac{U_{ij}}{r_{ij}^2L_{ij}}\left(\frac{1}{U_{ij}}\frac{\partial L_{ij}}{\partial r_{ij}} - \frac{L_{ij}}{U_{ij}^2}\frac{\partial U_{ij}}{\partial r_{ij}}\right) + \frac{1}{4}\frac{U_{ij}}{r_{ij}L_{ij}}\left(\frac{2L_{ij}}{U_{ij}^3}\left(\frac{\partial U_{ij}}{\partial r_{ij}}\right)^2 - 2\frac{\frac{\partial L_{ij}}{\partial r_{ij}}\frac{\partial U_{ij}}{\partial r_{ij}}}{U_{ij}^2}\right)\right] \\ & - \left[\frac{1}{4}\frac{U_{ij}}{r_{ij}L_{ij}^2}\frac{\partial L_{ij}}{\partial r_{ij}}\left(\frac{1}{U_{ij}}\frac{\partial L_{ij}}{\partial r_{ij}} - \frac{L_{ij}}{U_{ij}^2}\frac{\partial U_{ij}}{\partial r_{ij}}\right) + \frac{1}{4}\frac{1}{r_{ij}L_{ij}}\frac{\partial U_{ij}}{\partial r_{ij}}\left(\frac{1}{U_{ij}}\frac{\partial L_{ij}}{\partial r_{ij}} - \frac{L_{ij}}{U_{ij}^2}\frac{\partial U_{ij}}{\partial r_{ij}}\right)\right] \\ & + \frac{S_j^2\tilde{\rho}_i^2}{4r_{ij}}\left[\frac{1}{r_{ij}^2}\left(\frac{1}{L_{ij}^2} - \frac{1}{U_{ij}^2}\right) - \frac{2}{r_{ij}^2U_{ij}^3}\frac{\partial U_{ij}}{\partial r_{ij}} - \frac{3}{U_{ij}^4}\left(\frac{\partial U_{ij}}{\partial r_{ij}}\right)^2\right]\end{aligned} \quad (32)$$

Hessian for $\mathbf{r}_i$.

We can now differentiate w.r.t. $\mathbf{r}_{ij}$ to get the Hessian for atoms i and j.

$$\mathbf{H}_{ij} = \frac{\partial E_{GB}}{\partial r_{ij}}\frac{1}{r_{ij}}\begin{bmatrix} \mathbf{I} & -\mathbf{I} \\ -\mathbf{I} & \mathbf{I}\end{bmatrix} + \left(\frac{\partial^2 E_{GB}}{\partial r_{ij}^2} - \frac{\partial E_{GB}}{\partial r_{ij}}\frac{1}{r_{ij}}\right)\begin{bmatrix} \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}} & -\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}} \\ -\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}} & \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}}\end{bmatrix}. \quad (33)$$