Notes on SCPISM.

In the following discussion paramiters $R_{i,COV}$, $\delta(+/-)$, γ, R_p, $R_{i,vdW}$, A, B, C and E are provided for each atom type. The self energy is dependent on the inter-atom distance which is denoted, for atoms i and j, $r_{ij} = ||\mathbf{r}_j - \mathbf{r}_i||$ for atomic position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$.

Born radius and its first derivatives.

We can write the Born radius defined by Hassan, for non-polar atoms, as

$$R_i = \zeta_i + \eta_i \sum_{j \neq i}^{N} f(r_{ij}) \exp(-C_i r_{ij}), \tag{1}$$

for

$$\zeta_i = R_{i,COV} + \delta(+/-) + \gamma - \frac{\gamma A_i}{4\pi(R_p + R_{i,vdW})^2}, \ \eta_i \ = \ \frac{\gamma B_i}{4\pi(R_p + R_{i,vdW})^2}, \tag{2}$$

and

$$f(r_{ij}) = \begin{cases} \left(1 - \frac{r_{ij}^4}{625}\right)^4 & 0 \leq r_{ij} < 5, \\ 0 & r_{ij} \geq 5. \end{cases} \tag{3}$$

For polar Hydrogens we have an additional term to give the modified Born radius

$$R_i^{H+} = R_i + \sum_{j \neq i}^{M} g_i g_j f(r_{ij}) \exp(-E_i r_{ij}). \tag{4}$$

For non-polar atoms the derivative of the Born radius w.r.t. the atom pair distance is

$$\frac{\mathrm{d}R_i}{\mathrm{d}r_{ij}} = \eta_i \left(\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij}) - f(r_{ij}) C_i \right) \exp(-C_i r_{ij}), \tag{5}$$

with (for $r_{ij} < 5$),

$$\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij}) = -\frac{16}{625} r_{ij}^3 \left(1 - \frac{r_{ij}^4}{625}\right)^3. \tag{6}$$

For polar Hydrogens

$$\frac{\mathrm{d}R_i^{H+}}{\mathrm{d}r_{ij}} = \frac{\mathrm{d}R_i}{\mathrm{d}r_{ij}} + g_i g_j \left(\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij}) - f(r_{ij}) E_i \right) \exp(-E_i r_{ij}). \tag{7}$$

Self energy and its first derivatives.

The self energy term, from Hassan, is

$$E_s = \frac{1}{2}\sum_{i=1}^{N}\frac{q_i^2}{R_i}\left(\frac{1}{D_s(R_i)} - 1\right), \tag{8}$$

where the screening function is given by

$$D_s = \frac{1+\epsilon_s}{1+k\exp(-\alpha_i R_i)} - 1, \tag{9}$$

where ϵ_s is the dielectric constant of the bulk solvent (assumed to be 80). Note in Hassans paper $k = (\epsilon_s - 1)/2$.

The first derivative of the self energy is

$$\begin{aligned}\frac{\delta E_s}{\delta r_{ij}} \quad = \quad & \frac{1}{2}\frac{q_i^2}{R_i^2}\frac{\mathrm{d}R_i}{\mathrm{d}r_{ij}}\left(1 - \frac{1}{D_s(R_i)} - \frac{R_i}{D_s^2(R_i)}\frac{\mathrm{d}D_s}{\mathrm{d}R}(R_i)\right) + \\ & \frac{1}{2}\frac{q_j^2}{R_j^2}\frac{\mathrm{d}R_j}{\mathrm{d}r_{ij}}\left(1 - \frac{1}{D_s(R_j)} - \frac{R_j}{D_s^2(R_j)}\frac{\mathrm{d}D_s}{\mathrm{d}R}(R_j)\right).\end{aligned} \tag{10}$$

Here

$$\frac{\mathrm{d}D_s}{\mathrm{d}R}(R_i) = \frac{(1+\epsilon_s)k\alpha_i\exp(-\alpha_i R_i)}{(1+k\exp(-\alpha_i R_i))^2}. \tag{11}$$

This can be written in compact form

$$\frac{\mathrm{d}D_s}{\mathrm{d}R}(R_i) = \frac{\alpha_i}{1+\epsilon_s}(1+D_s(R_i))(\epsilon_s - D_s(R_i)). \tag{12}$$

Self energy force.

To obtain the force we need to find

$$\frac{\mathrm{d}r_{ij}}{\mathrm{d}\mathbf{r}_i} = \frac{\mathrm{d}||\mathbf{r}_j - \mathbf{r}_i||}{\mathrm{d}\mathbf{r}_i} \quad = \quad -\frac{||\mathbf{r}_j - \mathbf{r}_i||}{r_{ij}} \quad = \quad -\hat{\mathbf{r}}_{ij}, \tag{13}$$

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

$$\nabla_{ij}E_s \quad = \quad \frac{\delta E_s}{\delta r_{ij}}\,[-\hat{\mathbf{r}}_{ij} \quad \hat{\mathbf{r}}_{ij}\,]. \tag{14}$$

For the force

$$\mathbf{F}_{ij} = -\nabla_{ij}E_s \quad = \quad \frac{\delta E_s}{\delta r_{ij}}\,[\,\hat{\mathbf{r}}_{ij} \quad -\hat{\mathbf{r}}_{ij}\,]. \tag{15}$$

Self energy second derivative.

The second derivative of the self energy is

$$\begin{aligned}\frac{\delta^2 E_s}{\delta r_{ij}^2} &= \frac{q_i^2}{R_i}\left[\left(\frac{\mathrm{d}R_i}{\mathrm{d}r_{ij}}\right)^2\left(\left(\frac{\mathrm{d}D_s}{\mathrm{d}R}\right)^2\frac{1}{D_s^3}-\frac{1}{2}\frac{\mathrm{d}^2 D_s}{\mathrm{d}R^2}\frac{1}{D_s^2}+\frac{\mathrm{d}D_s}{\mathrm{d}R}\frac{1}{D_s^2 R_i}+\frac{1}{D_s R_i^2}-\frac{1}{R_i^2}\right)\right.\\&\quad\left.\left.-\frac{1}{2}\frac{\mathrm{d}^2 R_i}{\mathrm{d}r_{ij}^2}\left(\frac{\mathrm{d}D_s}{\mathrm{d}R}\frac{1}{D_s^2}+\frac{1}{D_s R_i}-\frac{1}{R_i}\right)\right]\right|_{R_i}\\&\quad+\frac{q_j^2}{R_j}\left[\left(\frac{\mathrm{d}R_j}{\mathrm{d}r_{ij}}\right)^2\left(\left(\frac{\mathrm{d}D_s}{\mathrm{d}R}\right)^2\frac{1}{D_s^3}-\frac{1}{2}\frac{\mathrm{d}^2 D_s}{\mathrm{d}R^2}\frac{1}{D_s^2}+\frac{\mathrm{d}D_s}{\mathrm{d}R}\frac{1}{D_s^2 R_j}+\frac{1}{D_s R_j^2}-\frac{1}{R_j^2}\right)\right.\\&\quad\left.\left.-\frac{1}{2}\frac{\mathrm{d}^2 R_j}{\mathrm{d}r_{ij}^2}\left(\frac{\mathrm{d}D_s}{\mathrm{d}R}\frac{1}{D_s^2}+\frac{1}{D_s R_j}-\frac{1}{R_j}\right)\right]\right|_{R_j},\end{aligned} \tag{16}$$

where 'evaluated at' denotes the argument used in function D_s and its derivatives.

Here the second derivative of the screening function is

$$\frac{\mathrm{d}^2 D_s}{\mathrm{d}R^2}(R_i)=\frac{2(1+\epsilon_s)k^2\alpha_i^2\exp(-2\alpha_i R_i)}{(1+k\exp(-\alpha_i R_i))^3}-\frac{(1+\epsilon_s)k\alpha_i^2\exp(-\alpha_i R_i)}{(1+k\exp(-\alpha_i R_i))^2}. \tag{17}$$

From Eqn.(12) we can write this more compactly

$$\frac{\mathrm{d}^2 D_s}{\mathrm{d}R^2}(R_i)=\frac{\alpha_i}{1+\epsilon_s}\left(\epsilon_s-1-2D_s(R_i)\right)\frac{\mathrm{d}D_s}{\mathrm{d}R}(R_i). \tag{18}$$

The second derivative of the Bourn radius

$$\frac{\mathrm{d}^2 R_j}{\mathrm{d}r_{ij}^2}=\eta_i\left(\frac{\mathrm{d}2f}{\mathrm{d}r_{ij}^2}(r_{ij})-2\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij})C_i+f(r_{ij})C_i^2\right)\exp(-C_i r_{ij}), \tag{19}$$

where, for $r_{ij}<5$,

$$\frac{\mathrm{d}^2 f}{\mathrm{d}r_{ij}^2}(r_{ij})=r_{ij}^2\left(1-\frac{r_{ij}^4}{625}\right)^2\left(\frac{192}{390625}r_{ij}^4-\frac{48}{625}\left(1-\frac{r_{ij}^4}{625}\right)\right). \tag{20}$$

For polar Hydrogen we have the additional term

$$\frac{\mathrm{d}^2 R_i^{H+}}{\mathrm{d}r_{ij}^2}=\frac{\mathrm{d}^2 R_i}{\mathrm{d}r_{ij}^2}+g_i g_j\left(\frac{\mathrm{d}^2 f}{\mathrm{d}r_{ij}^2}(r_{ij})-2\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij})E_i+f(r_{ij})E_i^2\right)\exp(-E_i r_{ij}). \tag{21}$$

Self energy Hessian.

We can now differentiate Eq. (14) w.r.t. $\mathbf{r}_{ij}$ to get the Hessian for atoms i and j.

$$\mathbf{H}_{ij}=\frac{\delta E_s}{\delta r_{ij}}\frac{1}{r_{ij}}\begin{bmatrix}\mathbf{I} & -\mathbf{I}\\ -\mathbf{I} & \mathbf{I}\end{bmatrix}+\left(\frac{\delta^2 E_s}{\delta r_{ij}^2}-\frac{\delta E_s}{\delta r_{ij}}\frac{1}{r_{ij}}\right)\begin{bmatrix}\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}} & -\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}}\\ -\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}} & \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\mathrm{T}}\end{bmatrix}. \tag{22}$$

Original switch function.

In the papers by Hassan the original switch function was given by

$$f(r_{ij}) = \begin{cases} \left(1 - \frac{r_{ij}^2}{25}\right)^2 & 0 \leq r_{ij} < 5, \\ 0 & r_{ij} \geq 5. \end{cases} \tag{23}$$

This has first derivative, for $r_{ij} < 5$,

$$\frac{\mathrm{d}f}{\mathrm{d}r_{ij}}(r_{ij}) = -\frac{4}{25} r_{ij} \left(1 - \frac{r_{ij}^2}{25}\right). \tag{24}$$