Appendix D

Derivatives and Series Expansion for the New Form of ΔT

The new form of ΔT in GHA-QM is

$$\Delta T = O \cdot T + \frac{dd}{1 - S^2}$$

where

$$T \equiv \frac{3}{2}\frac{1}{s_1^2} + \frac{3}{2}\frac{1}{s_2^2} - \frac{6}{s_1^2 + s_2^2} + \frac{4R_{12}^2}{(s_1^2 + s_2^2)^2}.$$

The following shows the useful equations for its practical implementation.

D.1 Derivatives of the New Form

$$\frac{\partial \Delta T}{\partial R_{12}} = \frac{\partial O}{\partial R_{12}} T + O \frac{\partial T}{\partial R_{12}} + \frac{dd \cdot 2S}{(1 - S^2)^2} \frac{\partial S}{\partial R_{12}}$$

$$\frac{\partial \Delta T}{\partial s_1} = \frac{\partial O}{\partial s_1} T + O \frac{\partial T}{\partial s_1} + \frac{dd \cdot 2S}{(1 - S^2)^2} \frac{\partial S}{\partial s_1}$$

$$\frac{\partial \Delta T}{\partial s_2} = \frac{\partial O}{\partial s_2} T + O \frac{\partial T}{\partial s_2} + \frac{dd \cdot 2S}{(1 - S^2)^2} \frac{\partial S}{\partial s_2}$$

D.2 Series Expansion for the New Form

Define

$$a \equiv \frac{2s_1 s_2}{s_1^2 + s_2^2}, \quad x \equiv \frac{R_{12}^2}{s_1 s_2}$$

When $S \to 1$, $s_1 \to s_2$ and $R_{12} \to 0$, we have

$$
\begin{aligned}
\Delta T &\equiv \frac{a^3 \exp(-ax)(\frac{3}{a} - 3a + a^2 x)\frac{1}{s_1 s_2} + dd}{1 - a^3 \exp(-ax)} \\
&= \frac{\exp(-x)x\frac{1}{s_1 s_2} + dd}{1 - \exp(-x)} \text{ when } a \to 1 \\
&= \frac{x}{\exp(x) - 1}\frac{1}{s_1 s_2} + \frac{dd}{1 - \exp(-x)} \\
&= \frac{x}{\sum_{k=0}^{\infty} \frac{x^k}{k!} - 1}\frac{1}{s_1 s_2} + dd \sum_{n=-1}^{\infty} \frac{x^n B_{1+n}(1)}{(1+n)!} \\
&= \frac{1}{s_1 s_2}\left(1 - \frac{x}{2} + \frac{x^2}{12} - \frac{x^4}{720} + O(x^6)\right) + dd\left(\frac{1}{x} + \frac{1}{2} + \frac{x}{12} - \frac{x^3}{720} + \frac{x^5}{30240} + O(x^6)\right) \\
&= \frac{1}{s_1 s_2}\left(1 - \frac{x}{2} + \frac{x^2}{12} + O(x^4)\right) + dd\left(\frac{1}{x} + \frac{1}{2} + \frac{x}{12} - \frac{x^3}{720} + O(x^4)\right) \\
&= \left(\frac{1}{s_1 s_2} - \frac{R_{12}^2}{2s_1^2 s_2^2} + \frac{R_{12}^4}{12 s_1^3 s_2^3} + O(x^4)\right) + dd\left(\frac{s_1 s_2}{R_{12}^2} + \frac{1}{2} + \frac{R_{12}^2}{12 s_1 s_2} - \frac{R_{12}^6}{720 s_1^3 s_2^3} + O(x^4)\right)
\end{aligned}
$$

$$\frac{\partial x}{\partial R_{12}} = \frac{2R_{12}}{s_1 s_2} \equiv 2R$$

$$\frac{\partial x}{\partial s_1} = -\frac{R_{12}^2}{s_1^2 s_2} \equiv -R^2 s_2$$

$$\frac{\partial x}{\partial s_2} = -\frac{R_{12}^2}{s_1 s_2^2} \equiv -R^2 s_1$$

$$\frac{\partial \Delta T}{\partial R_{12}} = -\frac{R}{s_1 s_2} + \frac{R^3}{3} + dd\left(-\frac{2R}{x^2} + \frac{R}{6} - \frac{x^2 R}{120}\right)$$

$$\frac{\partial \Delta T}{\partial s_1} = -\frac{1}{s_1^2 s_2} + \frac{R^2}{s_1} - \frac{R^4 s_2}{4} + dd\left(\frac{s_2}{R_{12}} - \frac{x}{12 s_1} + \frac{x^3}{240 s_1}\right)$$