

## Appendix D

### Derivatives and Series Expansion for the New Form of $\Delta T$

The new form of  $\Delta T$  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  $S \rightarrow 1$ ,  $s_1 \rightarrow s_2$  and  $R_{12} \rightarrow 0$ , we have

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

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

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

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

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

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