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Research Article

Gaussian–Transform for the Dirac Wave Function and its Application to the Multicenter Molecular Integral Over Dirac Wave Functions for Solving the Molecular Matrix Dirac Equation

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Keywords: Gaussian-transform; Dirac wave function; Multicenter molecular integral; Relativistic calculation; Finite nucleus models; Restricted magnetic balance

Abstract

Gaussian-transform formula is derived for the Dirac wave function. Using it, one can derive the multicenter molecular integral over Dirac wave functions for any physical quantity. As the first application of it, multicenter molecular integrals over Dirac wave functions are derived for the homogeneous charge density distribution model and the Gauss-type charge density distribution model. Such integrals are necessary for solving the gauge-invariant molecular matrix Dirac equation with using the restricted magnetic balance.

1. Introduction

The real hydrogen atom has the vector potential of the magnetic field due to the nuclear spin because it has its nuclear spin. Sun, et al. [1] showed the gauge invariant Hamiltonian of the Dirac equation of the hydrogen atom must include the vector potential due to the nuclear spin. Generally speaking, the fundamental equation of physics must be gauge invariant. The gauge invariant Dirac equation, because it has the vector potential due to the nuclear spin, does not have a rigorous solution. The gauge invariant Dirac equation is given by

$$\begin{pmatrix} m_e c^2 + V & c\vec{\sigma}\bullet(\vec{p}+\vec{A}) \\ c\vec{\sigma}\bullet(\vec{p}+\vec{A}) & -m_e c^2 + V \end{pmatrix}\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} E_0 \tag{1.1}$$

Where m_e is the electron rest mass, c is the speed of light, V is the scalar potential, $\vec{\sigma}$ is the Pauli spin matrices, $\vec{p} = -i\hbar\nabla$ is the momentum, and $\vec{A}$ is the vector potential due to the nuclear spin, Ψ^L is the large component spinor, Ψ^S is the small component spinor, and E_0 is the energy. We subtract the rest-mass energy $m_e c^2$ from E_0 to align the energy scale to that of the Schrödinger equation. So Eq. (1.1) can be modified to

$$\begin{pmatrix} V & c\vec{\sigma}\bullet(\vec{p}+\vec{A}) \\ c\vec{\sigma}\bullet(\vec{p}+\vec{A}) & -2m_e c^2 + V \end{pmatrix}\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} E \quad E = E_0 - m_e c^2 \tag{1.2}$$

To solve this Dirac equation, Eq. (1.2), we may use a suitable basis set, $\{\chi_v\}$. The large component spinor can be expressed as a linear combination in terms of these basis functions as given by

$$\Psi_i^L = \Sigma_V C_{iV}^L \chi_V \tag{1.3}$$

However, the small component spinor is in the variational collapse until using the restricted magnetic balance (RMB) [2] as given by

$$\Psi_i^S = \Sigma_V C_{iV}^S \vec{\sigma} \bullet (\vec{p} + \vec{A}) \chi_V \tag{1.4}$$

Recently, Yoshizawa [3] derived the matrix Dirac equation with using the RMB as given by

$$\begin{pmatrix} \overleftrightarrow{V} & \overleftrightarrow{T_m} \\ \overleftrightarrow{T_m} & \overleftrightarrow{W} - \overleftrightarrow{T_m} \end{pmatrix} \begin{pmatrix} \overleftrightarrow{C_-^L} & \overleftrightarrow{C_+^L} \\ \overleftrightarrow{C_-^S} & \overleftrightarrow{C_+^S} \end{pmatrix} = \begin{pmatrix} \overleftrightarrow{S} & \overleftrightarrow{0} \\ \overleftrightarrow{0} & \frac{1}{2m_e c^2} \overleftrightarrow{T_m} \end{pmatrix} \begin{pmatrix} \overleftrightarrow{C_-^L} & \overleftrightarrow{C_+^L} \\ \overleftrightarrow{C_-^S} & \overleftrightarrow{C_+^S} \end{pmatrix} \begin{pmatrix} \overleftrightarrow{\varepsilon_-} & \overleftrightarrow{0} \\ \overleftrightarrow{0} & \overleftrightarrow{\varepsilon_+} \end{pmatrix} \tag{1.5}$$

where

$$V_{\mu\nu} = < \chi_\mu | V | \chi_\nu > \tag{1.6}$$

$$(T_m)_{\mu\nu} = \frac{1}{2m_e} < \chi_\mu | \vec{\sigma} \bullet (\vec{p} + \vec{A}) \vec{\sigma} \bullet (\vec{p} + \vec{A}) | \chi_\nu > \tag{1.7}$$

$$(W_m)_{\mu\nu} = \frac{1}{4m_e^2 c^2} < \chi_\mu | \vec{\sigma} \bullet (\vec{p} + \vec{A}) V \vec{\sigma} \bullet (\vec{p} + \vec{A}) | \chi_\nu > \tag{1.8}$$

and

$$S_{\mu\nu} = < \chi_\mu | \chi_\nu > \tag{1.9}$$

The above gauge-invariant Dirac equation may have the vector potential of the external magnetic field in addition to that due to the nuclear spin. We use the atomic units throughout the present article $(m_e = 1,\ e = 1,\ \hbar = 1,\ 4\pi\varepsilon_0 = 1,\ c = 137.035999139)$. However, we describe $m_e, e, \hbar$ explicitly for the reader's convenience when one converts the units to natural units. When one extends the matrix Dirac equation to the molecule, it is natural to use the Dirac wave function as the basis function for solving it. However, there is no molecular integral formula for that purpose. The author will derive all of the necessary molecular integrals over Dirac wave functions as the target shortly. As the first step, we select a physical quantity as follows: There is the physical quantity $\vec{\sigma} \bullet (\vec{p} + \vec{A}) V \vec{\sigma} \bullet (\vec{p} + \vec{A})$ in the Hamiltonian of the above matrix Dirac equation. Using the Dirac identity, we have

$$\vec{\sigma} \bullet (\vec{p} + \vec{A}) V \vec{\sigma} \bullet (\vec{p} + \vec{A}) = (\vec{p} + \vec{A}) \bullet V (\vec{p} + \vec{A}) + i\vec{\sigma} \bullet (\vec{p} + \vec{A}) \times V (\vec{p} + \vec{A}) \tag{1.10}$$

In the second term, we have the physical quantity $i\vec{\sigma} \bullet (\vec{p} \times V\vec{A} + \vec{A} \times V\vec{p})$ which is the target in the present article. The one-center integral of the target quantity is divergent for the point charge nucleus [4]. Theoretical chemists use the finite nucleus models [5] instead of the point charge one. Some experiment shows that the real nucleus is not the point charge one but the finite one [5]. The experimental radius (the root-mean-square radius) of the finite nucleus is given by [5].

$$RMS = 0.836\, A^{1/3} + 0.570\ (\pm 0.05)\ fm \tag{1.11}$$

where A is the atomic mass number (for example, A = 13 for ^{13}C an atom). We use the homogeneous charge density distribution (HCDD) model [5] and the Gauss-type charge density distribution (GCDD) model [5] here. Especially the GCDD model is used in several calculations using the finite nucleus model [6-8]. In a previous article [9], it is shown that the Gaussian-type-orbital (GTO) is not suitable for the calculation of the target quantity and the point charge nucleus is also not suitable as the theoretical model. In the next section, the Gaussian-transform formula of the Dirac wave function can be derived for the calculation of the multicenter molecular-integral over Dirac wave functions. As the first application of the formula, the multicenter molecular integral over Dirac wave functions for the target quantity can be derived in the third section for the HCDD model and for the GCDD model.

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2. Gaussian-transform formula for the Dirac wave function

Shavitt and Karplus [10] derived the Gaussian-transform formula for the 1s Slater-type orbital (STO) as given by

$$\exp(-\zeta_A r_A) = \frac{\zeta_A^2}{2\sqrt{\pi}} \int_0^\infty ds\, s^{-3/2} \exp\left(-\frac{\zeta_A^2}{4s} - s r_A^2\right) \tag{2.1}$$

Ishida [11] extends it to the integer n STO as given by

$$r_A^{n_A-1} \exp(-\zeta_A r_A) = \frac{\zeta_A^{n_A}}{2^{n_A}\sqrt{\pi}} \sum_{i_A} (-)^{i_A} (2i_A - 1)!! \binom{n_A}{2i_A} \left(\frac{2}{\zeta_A^2}\right)^{i_A} \int_0^\infty ds\, s^{-n_A+i_A-1/2} \exp\left[-\frac{\zeta_A^2}{4s} - s r_A^2\right] \tag{2.2}$$

We extend it to the non-integer n STO as follows: For a non-integer n_A^* with $n_A - 1 < n_A^* < n_A$ ($n_A = 1$ for the Dirac wave function), we have

$$r_A^{n_A^*-1} = \frac{r_A^{n_A}}{r_A^{n_A - n_A^* + 1}} \tag{2.3}$$

There is the identity given by [12]

$$\frac{\exp(-\beta)}{\beta^\nu} = \frac{1}{\Gamma(\nu)} \int_0^1 dt \frac{(1-t)^{\nu-1}}{t^{\nu+1}} \exp\left[-\frac{\beta}{t}\right] \quad (\beta = \zeta_A r_A > 0,\ \nu = n_A - n_A^* + 1 > 0) \tag{2.4}$$

Using Eqs. (2.3) and (2.4), we have

$$r_A^{n_A^*-1} \exp(-\zeta_A r_A) = \frac{\zeta_A^{n_A - n_A^* + 1}}{\Gamma(n_A - n_A^* + 1)\, 2^{n_a+1}\sqrt{\pi}} \sum_{i_A} (-)^{i_A} (2i_A - 1)!! \binom{n_A+1}{2i_A} \left(\frac{2}{\zeta_A^2}\right)^{i_A} \int_0^1 dt \frac{(1-t)^{n_A - n_A^*}}{t^{n_A - n_A^* + 2}} r_A^{n_A} \exp\left(-\frac{\zeta_A}{t} r_A\right) \tag{2.5}$$

Using Eq. (2.2) for Eq. (2.5), we have the final formula for the non-integer n STO given by

$$r_A^{n_A^*-1} \exp(-\zeta_A r_A) = \frac{\zeta_A^{2n_A - n_A^* + 2}}{\Gamma(n_A - n_A^* + 1)\, 2^{n_a+1}\sqrt{\pi}} \sum_{i_A} (-)^{i_A} (2i_A - 1)!! \binom{n_A+1}{2i_A} \left(\frac{2}{\zeta_A^2}\right)^{i_A} \int_0^1 dt \frac{(1-t)^{n_A - n_A^*}}{t^{2n_A - 2i_A - n_A^* + 3}} \int_0^\infty ds\, s^{-n_A + i_A - 3/2} \exp\left[-\frac{\zeta_A^2}{4st^2} - s r_A^2\right] \tag{2.6}$$

For the Dirac wave function (in the case of $n_A = 1$), we have

$$r_A^{-\varepsilon_A} \exp(-\zeta_A r_A) = \frac{\zeta_A^{1+\varepsilon_A}}{2\sqrt{\pi}\,\Gamma(1+\varepsilon_A)} \int_0^\infty ds\, s^{-3/2} \exp(-s r_A^2) \left[\left(\frac{\zeta_A^2}{2s}\right) \int_0^1 dt \frac{(1-t)^{\varepsilon_A}}{t^{4+\varepsilon_A}} - \int_0^1 dt \frac{(1-t)^{\varepsilon_A}}{t^{2+\varepsilon_A}}\right] \exp\left(-\frac{\zeta_A^2}{4st^2}\right) \tag{2.7}$$

where $\varepsilon_A = 1 - \sqrt{1-(Z_A\alpha)^2}$ in which α = 1/137.035999139 is the fine structure constant and $\zeta_A = Z_A$ in which $Z_A e$ is the nuclear charge. In the above derivation, Eq. (2.1) is taken from the reference. Equation (2.2) is the author's previous work. Equation (2.3) is derived by the author. Equation (2.4) is taken from the reference. Equations (2.5)-(2.7) are derived by the author. Note that the Dirac wave function is divergent at $r = 0$. Therefore, it is impossible to mimic it in terms of not only GTOs but also integer n STOs. For the molecular integral over the non-integer n STOs, several researchers developed it, for example, see [13-16]. However, their non-integer n STO does not include the Dirac wave function. The present Gaussian-transform, Eq. (2.7), is only one formula to treat the multicenter molecular integral over Dirac wave functions.

3. Application of the present Gaussian-transform formula

3.1 Three-center molecular integral over Dirac wave functions for the target quantity with the HCDD model

For the HCDD model, the distribution function of the nuclear charge is given by

$$\rho(r) = \rho_0 \Theta(r_H - r) \tag{3.1.1}$$

where $\rho_0 = \frac{3Ze}{4\pi r_H^3}$ and $\Theta(r_H - r)$ is the Heaviside step function given by

$$\Theta(r_H - r) = \begin{cases} 1 & (0 \le r < r_H) \\ 1/2 & (r = r_H) \\ 0 & (r > r_H) \end{cases} \tag{3.1.2}$$

in which r_H is the radius of the finite nucleus of the HCDD model. The value of r_H is given by $r_H = \sqrt{5/3}\,RMS$ [5], where RMS is the root-mean-square radius of the finite nucleus. The scalar potential is given by

$$V(r) = \begin{cases} -\dfrac{3Ze^2}{2r_H}\left(1 - \dfrac{1}{3}\dfrac{r^2}{r_H^2}\right) & (0 \le r \le r_H) \\ -\dfrac{Ze^2}{r} & (r > r_H) \end{cases} \tag{3.1.3}$$

The vector potential is given by

$$\vec{A} = \begin{cases} \dfrac{Ze}{c^2 r_H^3}\vec{\mu}\times\vec{r} & (0 \le r \le r_H) \\ \dfrac{Ze}{c^2 r^3}\vec{\mu}\times\vec{r} & (r > r_H) \end{cases} \tag{3.1.4}$$

where $\vec{\mu} = (\mu_x, \mu_y, \mu_z)$ is the nuclear magnetic moment. Note that each potential is the same as the corresponding one for the point charge nucleus in the outer part, $r > r_H$. The target quantity is given by

$$i\vec{\sigma}\bullet(\vec{p}\times V\vec{A} + \vec{A}\times V\vec{p}) = \begin{cases} \dfrac{Z^2 e^3 \hbar}{c^2}\sum_\xi \sum_\eta \sigma_\xi \mu_\eta X_{\xi\eta}^{in} & (0 \le r \le r_H) \\ \dfrac{Z^2 e^3 \hbar}{c^2}\sum_\xi \sum_\eta \sigma_\xi \mu_\eta X_{\xi\eta}^{out} & (r > r_H) \end{cases} \quad [\xi,\eta \in (x,y,z)] \tag{3.1.5}$$

where

$$X_{\xi\eta}^{in} = \delta_{\xi\eta}\left(-\frac{3}{r_H^4} + \frac{2r^2}{r_H^6}\right) - \frac{\xi\eta}{r_H^6} \tag{3.1.6}$$

and

$$X_{\xi\eta}^{out} = \delta_{\xi\eta}\frac{2}{r^4} - \frac{4\xi\eta}{r^6} \tag{3.1.7}$$

The matrix element of the target quantity over Dirac wave functions are given by

$$< \chi_A | i\vec{\sigma}\bullet(\vec{p}\times V\vec{A} + \vec{A}\times V\vec{p}) | \chi_B > = \frac{Z^2 e^3 \hbar}{c^2}\sum_\xi \sum_\eta \sigma_\xi \mu_\eta I_{\xi\eta} \tag{3.1.8}$$

where $\chi_A = r_A^{-\varepsilon_A}\exp(-\zeta_A r_A)$ and three-center molecular integral is given by, $I_{\xi\eta} = I_{\xi\eta}^{in} + I_{\xi\eta}^{out}$, in which

$$I_{\xi\eta}^{in} = \int d\vec{r}\left(-\frac{3\delta_{\xi\eta}}{r_H^4} + \frac{2r^2\delta_{\xi\eta} - \xi\eta}{r_H^6}\right) r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp\left(-\zeta_A r_A - \zeta_B r_B\right) \tag{3.1.9}$$

and

$$I_{\xi\eta}^{out} = \int d\vec{r}\left(\delta_{\xi\eta}\frac{2}{r^4} - \frac{4\xi\eta}{r^6}\right) r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp\left(-\zeta_A r_A - \zeta_B r_B\right) \tag{3.1.10}$$

First, let us evaluate I_{zz}^{in}. To evaluate the integral, we use the Gaussian-transform formula, Eq. (2.7), and have

$$I_{zz}^{in} = \frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{4\pi\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^\infty ds_1 \int_0^\infty ds_2 (s_1 s_2)^{-3/2} \left[\left(\frac{\zeta_A^2}{2s_1}\right)\int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4s_1 t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2s_2}\right)\int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4s_2 t_2^2}\right) \int d\vec{r}\left(-\frac{3}{r_H^4}+\frac{2r^2-z^2}{r_H^6}\right)\exp[-s_1 r_A^2 - s_2 r_B^2] \quad (3.1.11)$$

We know $2r^2 - z^2 = \frac{5}{3}r^2 - \frac{2}{3}S_{20}(\vec{r})$, where $S_{20}(\vec{r})$ is the solid harmonics. We use the Gaussian product rule and have

$$\exp[-s_1 r_A^2 - s_2 r_B^2] = \exp\left[-\frac{s_1 s_2}{s_1+s_2}\overline{AB}^2\right]\exp[-(s_1+s_2)r_P^2] \quad (3.1.12)$$

where $\vec{P} = \frac{s_1}{s_1+s_2}\vec{A} + \frac{s_2}{s_1+s_2}\vec{B}$. We use Sack's translation of GTO given by [17]

$$\exp[-(s_1+s_2)r_P^2] = 4\pi \exp[-(s_1+s_2)r_M^2 - (s_1+s_2)\overline{MP}^2] \sum_\ell i_\ell[2(s_1+s_2)\overline{MP}\, r_M] \sum_{m=-\ell}^{\ell} Y_\ell^m(M\hat{P}) Y_\ell^m(\hat{r}_M)^* \quad (3.1.13)$$

where $i_\ell(z)$ is the modified spherical Bessel function of the first kind [18]. The $\vec{M} = (0,0,0)$ denotes the origin of the molecular integral. We again use the Gaussian product rule as given by

$$\exp[-(s_1+s_2)\overline{MP}^2]\exp\left[-\frac{s_1 s_2}{s_1+s_2}\overline{AB}^2\right] = \exp[-s_1\overline{MA}^2 - s_2\overline{MB}^2] \quad (3.1.14)$$

Using these equations, we have

$$I_{zz}^{in} = \frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^\infty ds_1 \int_0^\infty ds_2 (s_1 s_2)^{-3/2}\exp[-s_1\overline{MA}^2 - s_2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2s_1}\right)\int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4s_1 t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2s_2}\right)\int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4s_2 t_2^2}\right)[I_1^{in} + I_2^{in}] \quad (3.1.15)$$

Where

$$I_1^{in} = \int_0^{r_H} dr_M \left(-\frac{3}{r_H^4} + \frac{5r_M^2}{3r_H^6}\right) r_M^2 \exp[-(s_1+s_2)r_M^2]\sum_\ell i_\ell[2(s_1+s_2)\overline{MP}\, r_M]\sum_{m=-\ell}^{\ell} Y_\ell^m(M\hat{P})\int d\hat{r}\, Y_\ell^m(\hat{r}_M)^* \quad (3.1.16)$$

And

$$I_2^{in} = \frac{-2}{3r_H^6}\int_0^{r_H} dr_M\, r_M^2 \exp[-(s_1+s_2)r_M^2] \sum_\ell i_\ell[2(s_1+s_2)\overline{MP}\, r_M]\sum_{m=-\ell}^{\ell} Y_\ell^m(M\hat{P})\int d\hat{r}\, Y_\ell^m(\hat{r}_M)^* S_{20}(\overrightarrow{r_M}) \quad (3.1.17)$$

For the angular part, we know the relations [11] given by

$$\sum_{m=-\ell}^{\ell} Y_\ell^m(M\hat{P})\int d\hat{r}\, Y_\ell^m(\hat{r}_M)^* = \delta_{\ell 0}\delta_{m0} \quad (3.1.18)$$

And

$$\sum_{m=-\ell}^{\ell} Y_\ell^m(M\hat{P})\int d\hat{r}\, Y_\ell^m(\hat{r}_M)^* S_{20}(\overrightarrow{r_M}) = r_M^2 \delta_{\ell 2}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2} \quad (3.1.19)$$

Using Eq. (3.1.18) for Eq. (3.1.16), we have

$$I_1^{in} = \int_0^{r_H} dr_M \left(-\frac{3}{r_H^4} + \frac{5r_M^2}{3r_H^6}\right) r_M^2 \exp[-(s_1+s_2)r_M^2]\, i_0[2(s_1+s_2)\overline{MP}\, r_M] \quad (3.1.20)$$

Using Eq. (3.1.19) for Eq. (3.1.17), we have

$$I_2^{in} = \frac{-2}{3r_H^6}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_0^{r_H} dr_M\, r_M^2 \exp[-(s_1+s_2)r_M^2]\, i_2[2(s_1+s_2)\overline{MP}\, r_M] \qquad (3.1.21)$$

Using the Taylor series of the modified spherical Bessel function of the first kind given by [18]

$$i_\ell(x) = \frac{x^\ell}{(2\ell+1)!!}\sum_{j=0}^{\infty}\frac{(x^2/4)^j}{j!(\ell+3/2)_j} \qquad (3.1.22)$$

(where $a_j = a(a+1)\bullet\bullet\bullet(a+j-1)$ is the Pochhammer symbol), we have

$$I_1^{in} = \sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\left\{\left(\frac{-3}{r_H^4}\right)\int_0^{r_H} dr_M\, r_M^{2j+2}\exp[-(s_1+s_2)r_M^2] + \frac{5}{3r_H^6}\int_0^{r_H} dr_M\, r_M^{2j+4}\exp[-(s_1+s_2)r_M^2]\right\}$$

$$= \sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\left\{\left(\frac{-3}{2r_H^4}\right)\int_0^{r_H^2} dx\, x^{j+1/2}\exp[-(s_1+s_2)x] + \frac{5}{6r_H^6}\int_0^{r_H^2} dx\, x^{j+3/2}\exp[-(s_1+s_2)x]\right\}$$

$$= \frac{-3}{2r_H^4}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+3/2}\gamma[j+3/2;(s_1+s_2)r_H^2] + \frac{5}{6r_H^6}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+5/2}\gamma[j+5/2;(s_1+s_2)r_H^2] \qquad (3.1.23)$$

We know the following relation [18] given by

$$\gamma(\alpha;x) = x^\alpha\frac{\Gamma(\alpha)}{\Gamma(\alpha+1)}\,{}_1F_1(\alpha;\alpha+1;-x) \qquad (3.1.24)$$

Using Eq. (3.1.24) for (3.1.23), we have

$$I_1^{in} = \frac{-3}{2r_H^4}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\, r_H^{2j+3}\frac{\Gamma(j+3/2)}{\Gamma(j+5/2)}\,{}_1F_1\left(j+\frac{3}{2};j+\frac{5}{2};-(s_1+s_2)r_H^2\right)$$

$$+\frac{5}{6r_H^6}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\, r_H^{2j+5}\frac{\Gamma(j+5/2)}{\Gamma(j+7/2)}\,{}_1F_1\left(j+\frac{5}{2};j+\frac{7}{2};-(s_1+s_2)r_H^2\right)$$

$$= \frac{-3}{2r_H}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2 r_H^2]^j}{j!(3/2)_j}\left[\frac{\Gamma(j+3/2)}{\Gamma(j+5/2)} - (s_1+s_2)r_H^2\frac{\Gamma(j+5/2)}{\Gamma(j+7/2)} + O(r_H^4)\right]$$

$$+\frac{5}{6r_H}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2 r_H^2]^j}{j!(3/2)_j}\left[\frac{\Gamma(j+5/2)}{\Gamma(j+7/2)} - (s_1+s_2)r_H^2\frac{\Gamma(j+7/2)}{\Gamma(j+9/2)} + O(r_H^4)\right]$$

$$= -\frac{2}{3r_H} - \frac{38}{105}\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2 - (s_1+s_2)\right]r_H + O(r_H^3) \qquad (3.1.25)$$

Also using Eq. (3.1.24), we have

$$I_2^{in} = \frac{-2}{3r_H^6}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\frac{4(s_1+s_2)^2\overline{MP}^2}{15}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}$$

$$\int_0^{r_H} dr_M\, r_M^{2j+6}\exp[-(s_1+s_2)r_M^2]$$

$$= \frac{-4}{45r_H^6}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\int_0^{r_H^2} dx\, x^{j+5/2}\exp[-(s_1+s_2)x]$$

$$=\frac{-4}{45\,r_H^6}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+7/2}\gamma[j+\frac{7}{2};(s_1+s_2)r_H^2]=\frac{-4}{45\,r_H^6}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}$$

$$r_H^{2j+7}\frac{\Gamma(j+7/2)}{\Gamma(j+9/2)}\,{}_1F_1\left(j+\frac{7}{2};j+\frac{9}{2};(s_1+s_2)r_H^2\right)=\frac{-4}{45}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\,r_H\frac{\Gamma(7/2)}{\Gamma(9/2)}+O(r_H^3)$$

$$=\frac{-8}{315}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\,r_H+O(r_H^3) \tag{3.1.26}$$

where $\gamma(\alpha;x)$ is the incomplete gamma function of the first kind [18] and ${}_1F_1(\alpha;\gamma;x)$ is the confluent hypergeometric function [18]. Next, let us evaluate I_{zz}^{out}. Similarly to I_{zz}^{in} of Eq. (3.1.15), we have

$$I_{zz}^{out}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^{\infty}ds_1\int_0^{\infty}ds_2(s_1s_2)^{-3/2}\exp[-s_1\overline{MA}^2-s_2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2s_1}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4s_1t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2s_2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4s_2t_2^2}\right)[I_1^{out}+I_2^{out}] \tag{3.1.27}$$

Where

$$I_1^{out}=\frac{2}{3}\int_{r_H}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]\sum_{\ell}i_{\ell}[2(s_1+s_2)\overline{MP}\,r_M]\sum_{m=-\ell}^{\ell}Y_{\ell}^m(\hat{MP})\int d\hat{r}\,Y_{\ell}^m(\hat{r}_M)^* \tag{3.1.28}$$

And

$$I_2^{out}=\frac{-8}{3}\int_{r_H}^{\infty}dr_M\frac{1}{r_M^4}\exp[-(s_1+s_2)r_M^2]\sum_{\ell}i_{\ell}[2(s_1+s_2)\overline{MP}\,r_M]\sum_{m=-\ell}^{\ell}Y_{\ell}^m(\hat{MP})\int d\hat{r}\,Y_{\ell}^m(\hat{r}_M)^*S_{20}(\overrightarrow{r_M}) \tag{3.1.29}$$

Using Eq. (3.1.18) and (3.1.19) for the angular part, we have

$$I_1^{out}=\frac{2}{3}\int_{r_H}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]\,i_0[2(s_1+s_2)\overline{MP}\,r_M] \tag{3.1.30}$$

and

$$I_2^{out}=\frac{-8}{3}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_{r_H}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]\,i_2[2(s_1+s_2)\overline{MP}\,r_M] \tag{3.1.31}$$

Using the Taylor series of the modified spherical Bessel function, Eq. (3.1.22), we have

$$I_1^{out}=\frac{2}{3}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\int_{r_H}^{\infty}dr_M\,r_M^{2j-2}\exp[-(s_1+s_2)r_M^2]=\frac{1}{3}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\int_{r_H^2}^{\infty}dx\,x^{j-3/2}\exp[-(s_1+s_2)x]$$

$$=\frac{1}{3}\int_{r_H^2}^{\infty}dx\,x^{-3/2}\exp[-(s_1+s_2)x]+\frac{2(s_1+s_2)^2\overline{MP}^2}{9}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{(2)_j(5/2)_j}\int_{r_H^2}^{\infty}dx\,x^{j-1/2}\exp[-(s_1+s_2)x]=\frac{\sqrt{s_1+s_2}}{3}\Gamma[-\frac{1}{2};(s_1+s_2)r_H^2]$$

$$+\frac{2(s_1+s_2)^2\overline{MP}^2}{9}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{(2)_j(5/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+1/2}\Gamma[j+1/2;(s_1+s_2)r_H^2] \tag{3.1.32}$$

We can easily derive the following relation given by

$$\Gamma(\alpha;x)=\Gamma(\alpha)-\frac{x^{\alpha}}{\alpha}+\frac{x^{\alpha+1}}{\alpha+1}-\frac{x^{\alpha+2}}{2(\alpha+2)}+\bullet\bullet\bullet\; x<<1 \tag{3.1.33}$$

Using Eq. (3.1.33) for (3.1.32), we have

$$I_1^{out}=\frac{2}{3r_H}-\frac{2}{3}\sqrt{\pi}(s_1+s_2)^{1/2}+\frac{2}{3}(s_1+s_2)r_H+O(r_H^3)+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)$$

$$-\frac{4}{9}(s_1+s_2)^2\overline{MP}^2 r_H+O(r_H^3) \qquad (3.1.34)$$

Also using Eq. (3.1.33), we have

$$I_2^{out}=\frac{-8}{3}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\frac{4(s_1+s_2)^2\overline{MP}^2}{15}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\int_{r_H}^{\infty}dr_M\, r_M^{2j}\exp[-(s_1+s_2)r_M^2]$$

$$=\frac{-16}{45}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\int_{r_H^2}^{\infty}dx\, x^{j-1/2}\exp[-(s_1+s_2)x]$$

$$=\frac{-16}{45}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+1/2}\Gamma(j+\frac{1}{2};(s_1+s_2)r_H^2)$$

$$=\frac{-16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};(s_1+s_2)\overline{MP}^2\right)+\frac{32}{45}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})r_H+O(r_H^3) \qquad (3.1.35)$$

where $\Gamma(\alpha;x)$ is the incomplete gamma function of the second kind [18]. With Eq. (3.1.25) and Eq. (3.1.34), we have

$$I_1^{in}+I_1^{out}=\frac{-2}{3}\sqrt{\pi}\sqrt{s_1+s_2}+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)$$

$$+\frac{36}{35}(s_1+s_2)r_H-\frac{24}{35}(s_1+s_2)^2\overline{MP}^2 r_H+O(r_H^3) \qquad (3.1.36)$$

Note that the largest term as $\frac{2}{3r_H}$ in Eq. (3.1.34) cancels that as $-\frac{2}{3r_H}$ in Eq. (3.1.25) out. With Eq. (3.1.26) and (3.1.35), we have

$$I_2^{in}+I_2^{out}=-\frac{16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})+\frac{24}{35}(s_1+s_2)^2 S_{20}(\overrightarrow{MP})r_H+O(r_H^3) \qquad (3.1.37)$$

Using Eq. (3.1.36) and (3.1.37) for Eq. (3.1.15) and (3.1.26), we have

$$I_{zz}=\frac{\varsigma_A^{1+\varepsilon_A}\varsigma_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^{\infty}ds_1\int_0^{\infty}ds_2(s_1s_2)^{-3/2}\exp[-s_1\overline{MA}^2-s_2\overline{MB}^2]\left[\left(\frac{\varsigma_A^2}{2s_1}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\varsigma_A^2}{4s_1t_1^2}\right)$$

$$\times\left[\left(\frac{\varsigma_B^2}{2s_2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\varsigma_B^2}{4s_2t_2^2}\right)$$

$$\left\{\frac{-2}{3}\sqrt{\pi}\sqrt{s_1+s_2}+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)\right.$$

$$\left.-\frac{16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};(s_1+s_2)\overline{MP}^2\right)+\frac{36}{35}(s_1+s_2)r_H-\frac{24}{35}(s_1+s_2)^2\overline{MP}^2r_H+\frac{24}{35}(s_1+s_2)^2S_{20}(\overrightarrow{MP})r_H\right\}+O(r_H^3) \qquad (3.1.38)$$

Note that all main terms come from the outer part, as seen in Eq. (3.1.34), (3.1.35), (3.1.36), and (3.1.37). Let us change the variables as $z=s_1+s_2$ and $w=s_1/(s_1+s_2)$. The Jacobian is $\frac{\partial(s_1,s_2)}{\partial(z,w)}=z$. Thus Eq. (3.1.38) can be rewritten as

$$I_{zz}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw\int_0^\infty dz\, z[w(1-w)z]^{-3/2}\exp[-wz\overline{MA}^2-(1-w)z\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2wz}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wzt_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2(1-w)z}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)zt_2^2}\right)\left\{\frac{-2}{3}\sqrt{\pi}z^{1/2}+\frac{2}{9}\sqrt{\pi}z^{3/2}x_0\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};zx_0\right)-\frac{16}{45}\sqrt{\pi}z^{3/2}y_0\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};zx_0\right)\right.$$

$$\left.+\frac{36}{35}zr_H-\frac{24}{35}z^2x_0r_H+\frac{24}{35}z^2y_0r_H\right\}+O(r_H^3) \tag{3.1.39}$$

where $x_0=w^2\overline{MA}^2+(1-w)^2\overline{MB}^2+2w(1-w)\overrightarrow{MA}\bullet\overrightarrow{MB}$ and

$y_m=w^2S_{2m}(\overrightarrow{MA})+(1-w)^2S_{2m}(\overrightarrow{MB})+w(1-w)S_{2m}(\overrightarrow{MA},\overrightarrow{MB};1)$ $(m=-2,-1,0,1,2)$ in which $S_{2m}(\overrightarrow{MA},\overrightarrow{MB};1)$ is the mixed solid harmonics defined by Ishida [19]. We separate the integral over z as follows:

$$\int_0^\infty dz=\int_0^{a^2}dz+\int_{a^2}^\infty dz \tag{3.1.40}$$

Where a^2 can be chosen arbitrarily. We choose as $a^2 = 4$, here. Next, we change the integral variable as follows: In the first term in Eq. (3.1.40), we do as $z=a^2u$. We do as $z=a^2/u$ in the last term in Eq. (3.1.40). Thus we have

$$\int_0^\infty dz=a^2\int_0^1 du+a^2\int_0^1 du\frac{1}{u^2} \tag{3.1.41}$$

Substituting Eq. (3.1.41) into Eq. (3.1.39), we have the final formula of the three-center molecular integral over Dirac wave functions for the HCDD model, which is given by

$$I_{zz}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-wua^2\overline{MA}^2-(1-w)ua^2\overline{MB}^2]$$

$$\times\left[\left(\frac{\zeta_A^2}{2wua^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wua^2t_1^2}\right)\left[\left(\frac{\zeta_B^2}{2(1-w)ua^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2t_2^2}\right)$$

$$\times\left\{\frac{-2}{3}\frac{\sqrt{\pi}}{au^{3/2}}+\frac{2}{9}\sqrt{\pi}\frac{ax_0}{u^{1/2}}\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};ua^2x_0\right)-\frac{16}{45}\sqrt{\pi}\frac{ay_0}{u^{1/2}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};ua^2x_0\right)+\frac{36}{35}\frac{r_H}{u}-\frac{24}{35}a^2x_0r_H+\frac{24}{35}a^2y_0r_H\right\}$$

$$+\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-\frac{w}{u}a^2\overline{MA}^2-\frac{1-w}{u}a^2\overline{MB}^2]\left[\left(\frac{u\zeta_A^2}{2wa^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{u\zeta_A^2}{4wa^2t_1^2}\right)$$

$$\times\left[\left(\frac{u\zeta_B^2}{2(1-w)a^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2t_2^2}\right)\left\{\frac{-2}{3}\frac{\sqrt{\pi}}{au^{1/2}}+\frac{2}{9}\sqrt{\pi}\frac{ax_0}{u^{3/2}}\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};\frac{a^2}{u}x_0\right)-\frac{16}{45}\sqrt{\pi}\frac{ay_0}{u^{3/2}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};\frac{a^2}{u}x_0\right)\right.$$

$$\left.+\frac{36}{35}\frac{r_H}{u}-\frac{24}{35}\frac{a^2x_0}{u^2}r_H+\frac{24}{35}\frac{a^2y_0}{u^2}r_H\right\}+O(r_H^3) \tag{3.1.42}$$

The error term is in the order of r_H^3. In Eq. (3.1.42), integrals over *w*, *u*, t_1, and t_2 can be performed numerically with using the 64-point Gauss-Legendre quadrature in the good precision of the 8 significant figures. With a similar derivation to that for I_{zz}, we obtain I_{xx} by replacing y_0 with $[-y_0+\sqrt{3}y_2]/2$ in the above Eq. (3.1.42) and I_{yy} by doing y_0 with $[-y_0-\sqrt{3}y_2]/2$. Also with a similar derivation to that for I_{zz}, we have

$$I_{xy}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-wua^2\overline{MA}^2-(1-w)ua^2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2wua^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wua^2t_1^2}\right)$$

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$$\left[\left(\frac{\zeta_B^2}{2(1-w)ua^2}\right)\int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2 t_2^2}\right)\left\{-\frac{8}{15}\sqrt{\pi}\frac{a}{u^{1/2}}\frac{y_{-2}}{\sqrt{3}}{}_1F_1\left(\frac{1}{2};\frac{7}{2};ua^2x_0\right)+\frac{36}{35}a^2\frac{y_{-2}}{\sqrt{3}}r_H\right\}$$

$$+\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du \exp[-\frac{w}{u}a^2\overline{MA}^2 - \frac{1-w}{u}a^2\overline{MB}^2]\left[\left(\frac{u\zeta_A^2}{2wa^2}\right)\int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{u\zeta_A^2}{4wa^2 t_1^2}\right)$$

$$\times\left[\left(\frac{u\zeta_B^2}{2(1-w)a^2}\right)\int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2 t_2^2}\right)\left\{-\frac{8}{15}\sqrt{\pi}\frac{a}{u^{3/2}}\frac{y_{-2}}{\sqrt{3}}{}_1F_1\left(\frac{1}{2};\frac{7}{2};ua^2x_0\right)+\frac{36}{35}\frac{a^2}{u^2}\frac{y_{-2}}{\sqrt{3}}r_H\right\}+O(r_H^3) \quad (3.1.43)$$

We obtain I_{yz} by replacing y_{-2} with y_1 in the above Eq. (3.1.41) and I_{zx} by doing y_{-2} with y_{-1}. Of course, $I_{\eta\xi} = I_{\xi\eta}$.

3.2 Three-center molecular integral over Dirac wave functions for the target quantity with the GCDD model

For the GCDD model, the distribution function of the nuclear charge is given by

$$\rho(r) = \rho_0 \exp\left(-\frac{r^2}{r_0^2}\right) \quad \rho_0 = \frac{1}{\Gamma(5/2)}\frac{3Ze}{4\pi r_0^3} \quad (3.2.1)$$

The value of the parameter r_0 is given by $r_0 = \sqrt{2/3}\,RMS$ [5]. The scalar potential of the GCDD model is given by

$$V(r) = -\frac{2Ze^2}{\sqrt{\pi}\, r_0}F_0\left(\frac{r^2}{r_0^2}\right) \quad (3.2.2)$$

Where $F_m(Z)$ is the molecular incomplete gamma function given by

$$F_m(z) = \int_0^1 dt\, t^{2m}\exp(-zt^2) \quad (3.2.3)$$

The vector potential due to the nuclear spin of this model is given by

$$\vec{A} = \frac{Ze}{c^2}\frac{4}{\sqrt{\pi}\, r_0^3}F_1\left(\frac{r^2}{r_0^2}\right)\vec{\mu}\times\vec{r} \quad (3.2.4)$$

The target quantity can be written as

$$i\vec{\sigma}\bullet\left(\vec{p}\times V\vec{A}+\vec{A}\times V\vec{p}\right) = \frac{Z^2e^3\hbar}{c^2}\sum_\xi\sum_\eta \sigma_\xi\mu_\eta X_{\xi\eta}[\xi,\eta\in(x,y,z)] \quad (3.2.5)$$

where

$$X_{\xi\eta} = \frac{16}{\pi r_0^6}\left\{\delta_{\xi\eta}\left[(F_1F_1+F_0F_2)r^2 - F_0F_1r_0^2\right]-(F_1F_1+F_0F_2)\xi\eta\right\} \quad (3.2.6)$$

The three-center molecular integral over Dirac wave functions for the target quantity is given by

$$I_{\xi\eta} = \int d\vec{r}\, X_{\xi\eta} r_A^{-\varepsilon_A} r_B^{-\varepsilon_B}\exp[-\zeta_A r_A - \zeta_B r_B] \quad (3.2.7)$$

First, we evaluate I_{zz} which is given by

$$I_{zz} = \int d\vec{r}\left[\frac{32}{3\pi r_0^6}r^2(F_1F_1+F_0F_2) - \frac{16}{\pi r_0^4}F_0F_1 - \frac{32}{3\pi r_0^6}S_{20}(\vec{r})(F_1F_1+F_0F_2)\right] r_A^{-\varepsilon_A} r_B^{-\varepsilon_B}\exp[-\zeta_A r_A - \zeta_B r_B] \quad (3.2.8)$$

Using the Gaussian transform for the Dirac wave function and Eq. (3.1.12)-(3.1.14), we have

$$I_{zz} = \frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^\infty ds_1\int_0^\infty ds_2 (s_1s_2)^{-3/2}\exp[-s_1\overline{MA}^2 - s_2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2s_1}\right)\int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4s_1t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2s_2}\right)\int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4s_2t_2^2}\right)(I_1+I_2) \quad (3.2.9)$$

Where

$$I_1 = \frac{32}{3\pi r_0^6}\int_0^\infty dr_M\ r_M^2[r_M^2(F_1F_1+F_0F_2)-\frac{3}{2}r_0^2F_0F_1]\exp[-(s_1+s_2)r_M^2]\sum_\ell i_\ell[2(s_1+s_2)\overline{MP}r_M]\sum_m Y_\ell^m(\hat{MP})\int d\hat{r}_M Y_\ell^m(\hat{r}_M)^* \quad (3.2.10)$$

and

$$I_2 = \frac{-32}{3\pi r_0^6}\int_0^\infty dr_M\ r_M^2(F_1F_1+F_0F_2)\exp[-(s_1+s_2)r_M^2]\sum_\ell i_\ell[2(s_1+s_2)\overline{MP}r_M]\sum_m Y_\ell^m(\hat{MP})\int d\hat{r}_M Y_\ell^m(\hat{r}_M)^* S_{20}(\overrightarrow{r_M}) \quad (3.2.11)$$

For the angular part, using Eq. (3.1.18) and (3.1.19), we have

$$I_1 = \frac{32}{3\pi r_0^6}\int_0^\infty dr_M\ r_M^2[r_M^2(F_1F_1+F_0F_2)-\frac{3}{2}r_0^2F_0F_1]\exp[-(s_1+s_2)r_M^2]i_0[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.12)$$

and

$$I_2 = \frac{-32}{3\pi r_0^6}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_0^\infty dr_M\ r_M^2(F_1F_1+F_0F_2)\exp[-(s_1+s_2)r_M^2]i_2[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.13)$$

We separate the inner and outer part of the finite nucleus of the GCDD model as follows: We use the asymptotic expansion of the molecular incomplete gamma function given by

$$F_m\left(\frac{r^2}{r_0^2}\right)=\frac{\Gamma(m+1/2)}{2}\left(\frac{r_0}{r}\right)^{2m+1}\quad (r\to\infty) \quad (3.2.14)$$

We know that $F_0(z)$ becomes its asymptotic value for $z > 36$ in the 15 significant precision and $F_1(z)$ does for $z > 40$ [20]. We choose $r > R_0 = br_0$ the outer part and $b = 7(b^2 = 49)$. . For $r > R_0$, the value of $F_0\left(\frac{r^2}{r_0^2}\right)$ is equal to $\frac{\sqrt{\pi}}{2}\frac{r_0}{r}$, so that the value of the scalar potential $V(r)=\frac{-2Ze^2}{\sqrt{\pi}\, r_0}F_0\left(\frac{r^2}{r_0^2}\right)$ is equal to $\frac{-Ze^2}{r}$, which is also equal to the outer part of that of the HCDD model as seen in Eq. (3.1.3), and the value of $F_1\left(\frac{r^2}{r_0^2}\right)$ is equal to $\frac{\sqrt{\pi}}{4}\frac{r_0^3}{r^3}$, so that the value of the vector potential $\vec{A}=\frac{Ze}{c^2}\frac{4}{\sqrt{\pi}\, r_0^3}F_1\left(\frac{r^2}{r_0^2}\right)\vec{\mu}\times\vec{r}$ is equal to $\frac{Ze}{c^2}\frac{1}{r^3}\vec{\mu}\times\vec{r}$, which is also equal to the outer part of that of the HCDD model as seen in Eq. (3.1.4). Thus, for the outer part, each scalar potential of both models coincides each other and also each vector potential does. Because we separate the inner and outer parts, we have

$$I_1 = I_1^{in}+I_1^{out} \quad (3.2.15)$$

and

$$I_2 = I_2^{in}+I_2^{out} \quad (3.2.16)$$

where

$$I_1^{in} = \frac{32}{3\pi r_0^6}\int_0^{R_0} dr_M\ r_M^2[r_M^2(F_1F_1+F_0F_2)-\frac{3}{2}r_0^2F_0F_1]\exp[-(s_1+s_2)r_M^2]i_0[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.17)$$

$$I_1^{out} = \frac{32}{3\pi r_0^6}\int_{R_0}^\infty dr_M\ r_M^2[r_M^2(F_1F_1+F_0F_2)-\frac{3}{2}r_0^2F_0F_1]\exp[-(s_1+s_2)r_M^2]i_0[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.18)$$

$$I_2^{in} = \frac{-32}{3\pi r_0^6}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_0^{R_0} dr_M\ r_M^2(F_1F_1+F_0F_2)\exp[-(s_1+s_2)r_M^2]i_2[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.19)$$

and

$$I_2^{out} = \frac{-32}{3\pi r_0^6}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_{R_0}^\infty dr_M\ r_M^2(F_1F_1+F_0F_2)\exp[-(s_1+s_2)r_M^2]i_2[2(s_1+s_2)\overline{MP}r_M] \quad (3.2.20)$$

To calculate the inner part, we use the power series of the molecular incomplete gamma function as given by

$$F_m(x)=\frac{1}{2m+1}\,{}_1F_1(m+\frac{1}{2};m+\frac{3}{2};-x)=\frac{1}{2m+1}\sum_{j=0}^{\infty}\frac{(m+1/2)_j}{(m+3/2)_j}\frac{(-x)^j}{j!} \tag{3.2.21}$$

Thus we have

$$I_1^{in}=\left\{\frac{1}{9}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-1/r_0^2)^{n_1+n_2}}{n_1!n_2!}+\frac{1}{5}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-1/r_0^2)^{n_1+n_2}}{n_1!n_2!}\right\}$$

$$\times\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\frac{32}{3\pi r_0^6}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+4}\exp[-(s_1+s_2)r_M^2]-\frac{1}{3}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(1/2)_{n_2}}{(5/2)_{n_1}(3/2)_{n_2}}\frac{(-1/r_0^2)^{n_1+n_2}}{n_1!n_2!}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}$$

$$\times\frac{16}{\pi r_0^4}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+2}\exp[-(s_1+s_2)r_M^2] \tag{3.2.22}$$

And

$$I_2^{in}=\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\frac{4(s_1+s_2)^2\overline{MP}^2}{15}\left\{\frac{1}{9}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-1/r_0^2)^{n_1+n_2}}{n_1!n_2!}\right.$$

$$\left.+\frac{1}{5}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-1/r_0^2)^{n_1+n_2}}{n_1!n_2!}\right\}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\frac{-32}{3\pi r_0^6}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+6}\exp[-(s_1+s_2)r_M^2] \tag{3.2.23}$$

We have

$$\frac{32}{3\pi r_0^6}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+4}\exp[-(s_1+s_2)r_M^2]=\frac{16}{3\pi r_0^6}\int_0^{R_0^2}dx\, x^{n_1+n_2+j+3/2}\exp[-(s_1+s_2)x]$$

$$=\frac{16}{3\pi r_0^6}\left(\frac{1}{s_1+s_2}\right)^{n_1+n_2+j+5/2}\gamma(n_1+n_2+j+\frac{5}{2};(s_1+s_2)R_0^2)$$

$$=\frac{16b^5}{3\pi r_0}R_0^{2(n_1+n_2+j)}\frac{\Gamma(n_1+n_2+j+5/2)}{\Gamma(n_1+n_2+j+7/2)}\,{}_1F_1\left(n_1+n_2+j+\frac{5}{2};n_1+n_2+j+\frac{7}{2};-(s_1+s_2)R_0^2\right)$$

$$=\frac{16}{3\pi}R_0^{2(n_1+n_2)}\left\{\frac{b^5}{r_0}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}\delta_{j0}+b^6R_0\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}\left[\delta_{j1}-(s_1+s_2)\delta_{j0}\right]+O(R_0^3)\right\} \tag{3.2.24}$$

Similarly to the above Eq. (3.2.24), we have

$$\frac{16}{\pi r_0^4}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+2}\exp[-(s_1+s_2)r_M^2]=\frac{8}{\pi}R_0^{2(n_1+n_2)}\left\{\frac{b^3}{r_0}\frac{\Gamma(n_1+n_2+3/2)}{\Gamma(n_1+n_2+5/2)}\delta_{j0}+b^4R_0\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}\left[\delta_{j1}-(s_1+s_2)\delta_{j0}\right]+O(R_0^3)\right\} \tag{3.2.25}$$

Similarly to the above Eq. (3.2.24), we have

$$\frac{-32}{3\pi r_0^6}\int_0^{R_0}dr_M\, r_M^{2(n_1+n_2+j)+6}\exp[-(s_1+s_2)r_M^2]=\frac{-16b^7R_0}{3\pi}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}+O(R_0^3) \tag{3.2.26}$$

Substituting Eq. (3.2.24) and (3.2.25) into Eq. (3.2.22), we have

$$I_1^{in}=\frac{16}{3\pi}\frac{b^5}{r_0}\left\{\frac{1}{9}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}\right.$$

$$\left.+\frac{1}{5}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}\right\}+\frac{16}{3\pi}b^6R_0\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2-(s_1+s_2)\right]$$

$$\times\left\{\frac{1}{9}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}+\frac{1}{5}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}\right\}+O(R_0^3)$$

$$-\frac{8}{3\pi}\frac{b^3}{r_0}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(1/2)_{n_2}}{(5/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+3/2)}{\Gamma(n_1+n_2+5/2)}-\frac{8}{3\pi}b^4R_0\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2-(s_1+s_2)\right]$$

$$\times\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(1/2)_{n_2}}{(5/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}+O(R_0^3) \tag{3.2.27}$$

Substituting Eq. (3.2.26) into Eq. (3.2.23), we have

$$I_2^{in}=-\frac{4(s_1+s_2)^2S_{20}(\overrightarrow{MP})}{15}\frac{16}{3\pi}b^2R_0\left\{\frac{1}{9}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}\right.$$

$$\left.+\frac{1}{5}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}\right\}+O(R_0^3) \tag{3.2.28}$$

We have

$$S=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}=\sum_{n_1=0}^{\infty}\frac{(3/2)_{n_1}}{(5/2)_{n_1}}\frac{\Gamma(n_1+5/2)(-b^2)^{n_1}}{n_1!\Gamma(n_1+7/2)}\,{}_2F_2\left(\frac{3}{2},n_1+\frac{5}{2};\frac{5}{2},n_1+\frac{7}{2};-b^2\right) \tag{3.2.29}$$

We can easily derive the following relation given by

$${}_2F_2(c_1,c_2;c_1+1,c_2+1;x)=\frac{c_1}{c_1-c_2}\,{}_1F_1(c_2;c_2+1;x)-\frac{c_2}{c_1-c_2}\,{}_1F_1(c_1;c_1+1;x) \tag{3.2.30}$$

Using Eq. (3.2.30), we have

$$S=\sum_{n_1=0}^{\infty}\frac{(3/2)_{n_1}}{(5/2)_{n_1}}\frac{\Gamma(n_1+5/2)(-b^2)^{n_1}}{n_1!\Gamma(n_1+7/2)}\left\{\frac{-3/2}{n_1+1}\,{}_1F_1\left(n_1+\frac{5}{2};n_1+\frac{7}{2};-b^2\right)+\frac{n_1+5/2}{n_1+1}\,{}_1F_1\left(\frac{3}{2};\frac{5}{2};-b^2\right)\right\} \tag{3.2.31}$$

We know the integral representation of the confluent hypergeometric function given by

$${}_1F_1(\alpha;\gamma;-x)=\frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\gamma-\alpha)}\int_0^1 dt\,t^{\alpha-1}(1-t)^{\gamma-\alpha-1}\exp(-xt) \tag{3.2.32}$$

and the asymptotic expansion of the confluent hypergeometric function given by

$${}_1F_1(\alpha;\alpha+1;-b^2)=\frac{\Gamma(\alpha+1)}{b^{2\alpha}}(b^2=49;\frac{1}{2}\le\alpha\le\frac{5}{2}) \tag{3.2.33}$$

Using Eq. (3.2.32) and (3.2.33), we have

$$S=-\frac{3}{2}\frac{\Gamma(1)}{\Gamma(2)}\int_0^1 dt\,t^{3/2}\exp(-b^2t)\,{}_2F_2\left(1,\frac{3}{2};2,\frac{5}{2};-tb^2\right)+\frac{3\sqrt{\pi}}{4b^3}\,{}_2F_2\left(1,\frac{3}{2};2,\frac{5}{2};-b^2\right)$$

$$=-\frac{3}{2}\int_0^1 dt\,t^{3/2}\exp(-b^2t)\left\{\frac{3/2}{1/2}\,{}_1F_1(1;2;-tb^2)-\frac{1}{1/2}\,{}_1F_1\left(\frac{3}{2};\frac{5}{2};-tb^2\right)\right\}+\frac{3\sqrt{\pi}}{4b^3}\left\{\frac{3/2}{1/2}\,{}_1F_1(1;2;-b^2)-\frac{1}{1/2}\,{}_1F_1\left(\frac{3}{2};\frac{5}{2};-b^2\right)\right\}$$

$$=-\frac{3}{2}\left\{3\int_0^1 ds\int_0^1 dt\,t^{3/2}\exp[-b^2t(1+s)]-\frac{2\Gamma(5/2)}{\Gamma(3/2)}\int_0^1 ds\,s^{1/2}\int_0^1 dt\,t^{3/2}\exp[-b^2t(1+s)]\right\}+\frac{3\sqrt{\pi}}{4b^3}\left\{\frac{3}{b^2}-\frac{3\sqrt{\pi}}{2b^3}\right\}$$

$$=-\frac{3}{2}\left\{3\frac{\Gamma(5/2)}{b^5}\int_0^1 ds\frac{1}{(1+s)^{5/2}}-3\frac{\Gamma(5/2)}{b^5}\int_0^1 ds\frac{s^{1/2}}{(1+s)^{5/2}}\right\}+\frac{9\sqrt{\pi}}{4b^5}-\frac{9\pi}{8b^6}=-\frac{27\sqrt{\pi}}{8b^5}\left(\frac{2}{3}-\frac{1}{3\sqrt{2}}-\frac{1}{3\sqrt{2}}\right)+\frac{9\sqrt{\pi}}{4b^5}-\frac{9\pi}{8b^6}=\frac{9\sqrt{2\pi}}{8b^5}-\frac{9\pi}{8b^6} \tag{3.2.34}$$

Similarly to the above derivation, we have

$$\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}=\frac{15\sqrt{\pi}}{4b^5}\ln(1+\sqrt{2})-\frac{5\sqrt{2\pi}}{8b^5}-\frac{15\pi}{8b^6} \quad (3.2.35)$$

$$\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(3/2)_{n_2}}{(5/2)_{n_1}(5/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}=\frac{9\pi}{8b^6}-\frac{63\sqrt{2\pi}}{32b^7} \quad (3.2.36)$$

$$\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(5/2)_{n_1}(1/2)_{n_2}}{(7/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+7/2)}{\Gamma(n_1+n_2+9/2)}=\frac{15\pi}{8b^6}-\frac{25\sqrt{2\pi}}{8b^7} \quad (3.2.37)$$

$$\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(1/2)_{n_2}}{(5/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+3/2)}{\Gamma(n_1+n_2+5/2)}=\frac{3\sqrt{\pi}}{2b^3}\ln(1+\sqrt{2})-\frac{3\pi}{4b^4} \quad (3.2.38)$$

and

$$\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(3/2)_{n_1}(1/2)_{n_2}}{(5/2)_{n_1}(3/2)_{n_2}}\frac{(-b^2)^{n_1+n_2}}{n_1!n_2!}\frac{\Gamma(n_1+n_2+5/2)}{\Gamma(n_1+n_2+7/2)}=\frac{3\pi}{4b^4}-\frac{9\sqrt{2\pi}}{8b^5} \quad (3.2.39)$$

Substituting Eq. (3.2.34)-(3.2.39) into Eq. (3.2.27), we have

$$I_1^{in}=\frac{16}{3\pi}\frac{b^5}{r_0}\frac{1}{9}\left(\frac{9\sqrt{2\pi}}{8b^5}-\frac{9\pi}{8b^6}\right)+\frac{16}{3\pi}\frac{b^5}{r_0}\frac{1}{5}\left(\frac{15\sqrt{\pi}}{4b^5}\ln(1+\sqrt{2})-\frac{5\sqrt{2\pi}}{8b^5}-\frac{15\pi}{8b^6}\right)+\frac{16}{3\pi}\frac{b^6R_0}{9}\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2-(s_1+s_2)\right]\left(\frac{9\pi}{8b^6}-\frac{63\sqrt{2\pi}}{32b^7}\right)$$

$$+\frac{16}{3\pi}\frac{b^6R_0}{5}\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2-(s_1+s_2)\right]\left(\frac{15\pi}{8b^6}-\frac{25\sqrt{2\pi}}{8b^7}\right)-\frac{8}{3\pi}\frac{b^3}{r_0}\left[\frac{3\sqrt{\pi}}{2b^3}\ln(1+\sqrt{2})-\frac{3\pi}{4b^4}\right]$$

$$-\frac{8}{3\pi}b^4R_0\left[\frac{2}{3}(s_1+s_2)^2\overline{MP}^2-(s_1+s_2)\right]\left(\frac{3\pi}{4b^4}-\frac{9\sqrt{2\pi}}{8b^5}\right)=-\frac{2}{3R_0}-\frac{2}{3}R_0(s_1+s_2)+\frac{4}{9}R_0(s_1+s_2)^2\overline{MP}^2$$

$$+\frac{3\sqrt{2}}{2\sqrt{\pi}}r_0(s_1+s_2)-\frac{2}{\sqrt{\pi}}r_0(s_1+s_2)^2\overline{MP}^2+O(R_0^3) \quad (3.2.40)$$

Note that each of the larger (in the absolute value) terms

$\frac{16}{3\pi}\frac{b^5}{r_0}\frac{1}{5}\left(\frac{15\sqrt{\pi}}{4b^5}\ln(1+\sqrt{2})-\frac{5\sqrt{2\pi}}{8b^5}-\frac{15\pi}{8b^6}\right)$ cancels the corresponding one of

$-\frac{8}{3\pi}\frac{b^3}{r_0}\left[\frac{3\sqrt{\pi}}{2b^3}\ln(1+\sqrt{2})-\frac{3\pi}{4b^4}\right]$ and $\frac{16}{3\pi}\frac{b^5}{r_0}\frac{1}{9}\frac{9\sqrt{2\pi}}{8b^5}$ out. Substituting Eq. (3.2.36) and (3.2.37) into Eq. (3.2.28), we have

$$I_2^{in}=-\frac{32(s_1+s_2)^2S_{20}(\overrightarrow{MP})}{45}R_0+\frac{6\sqrt{2}}{5\sqrt{\pi}}(s_1+s_2)^2S_{20}(\overrightarrow{MP})r_0+O(R_0^3) \quad (3.2.41)$$

To calculate the outer part, we use the asymptotic expansion of the molecular incomplete gamma function, Eq. (3.2.14). Thus we have

$$I_1^{out}=\frac{2}{3}\int_{R_0}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]i_0[2(s_1+s_2)\overline{MP}r_M]=\frac{2}{3}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(3/2)_j}\int_{R_0}^{\infty}dr_M\,r_M^{2j-2}\exp[-(s_1+s_2)r_M^2]=\frac{2}{3}\int_{R_0}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]$$

$$+\frac{4}{9}(s_1+s_2)^2\overline{MP}^2\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{(2)_j(5/2)_j}\int_{R_0}^{\infty}dr_M\,r_M^{2j}\exp[-(s_1+s_2)r_M^2]=\frac{1}{3}\int_{R_0^2}^{\infty}dx\,x^{-3/2}\exp[-(s_1+s_2)x]$$

$$+\frac{2}{9}(s_1+s_2)^2\overline{MP}^2\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{(2)_j(5/2)_j}\int_{R_0^2}^{\infty}dx\,x^{j-1/2}\exp[-(s_1+s_2)x]=\frac{1}{3}\left(\frac{1}{s_1+s_2}\right)^{-1/2}\Gamma\left(-\frac{1}{2},(s_1+s_2)R_0^2\right)$$

$$+\frac{2}{9}(s_1+s_2)^2\overline{MP}^2\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{(2)_j(5/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+1/2}\Gamma\left(j+\frac{1}{2},(s_1+s_2)R_0^2\right)=\frac{2}{3R_0}-\frac{2}{3}\sqrt{\pi}(s_1+s_2)+\frac{2}{3}(s_1+s_2)R_0+O(R_0^3)$$

$$+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)-\frac{4}{9}(s_1+s_2)^2\overline{MP}^2R_0+O(R_0^3) \quad (3.2.42)$$

and

$$I_2^{out}=\frac{-8}{3}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\int_{R_0}^{\infty}dr_M\frac{1}{r_M^2}\exp[-(s_1+s_2)r_M^2]i_2[2(s_1+s_2)\overline{MP}\,r_M]=-\frac{8}{3}\frac{S_{20}(\overrightarrow{MP})}{\overline{MP}^2}\frac{4(s_1+s_2)^2\overline{MP}^2}{15}\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\int_{R_0}^{\infty}dr_M\,r_M^{2j}\exp[-(s_1+s_2)r_M^2]$$

$$=-\frac{16}{45}(s_1+s_2)^2S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\int_{R_0^2}^{\infty}dx\,x^{j-1/2}\exp[-(s_1+s_2)x]$$

$$=-\frac{16}{45}(s_1+s_2)^2S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)^2\overline{MP}^2]^j}{j!(7/2)_j}\left(\frac{1}{s_1+s_2}\right)^{j+1/2}\Gamma\left(j+\frac{1}{2},(s_1+s_2)R_0^2\right)$$

$$=-\frac{16}{45}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\sum_{j=0}^{\infty}\frac{[(s_1+s_2)\overline{MP}^2]^j}{j!(7/2)_j}\Gamma\left(j+\frac{1}{2},(s_1+s_2)R_0^2\right)=-\frac{16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};(s_1+s_2)\overline{MP}^2\right)$$

$$+\frac{32}{45}(s_1+s_2)^2S_{20}(\overrightarrow{MP})R_0+O(R_0^3) \quad (3.2.43)$$

Adding Eq. (3.2.42) to Eq. (3.2.40), we have

$$I_1=I_1^{in}+I_1^{out}=-\frac{2}{3}\sqrt{\pi}(s_1+s_2)+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)$$

$$+\frac{3\sqrt{2}}{2\sqrt{\pi}}r_0(s_1+s_2)-\frac{2}{\sqrt{\pi}}r_0(s_1+s_2)^2\overline{MP}^2+O(R_0^3) \quad (3.2.44)$$

Note that the largest term as $\frac{2}{3R_0}$ in I_1^{out} cancels that as $\frac{-2}{3R_0}$ in I_i^{in} out. Adding Eq. (3.2.43) to Eq. (3.2.41), we have

$$I_2=I_2^{in}+I_2^{out}=-\frac{16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};(s_1+s_2)\overline{MP}^2\right)+\frac{6\sqrt{2}}{5\sqrt{\pi}}(s_1+s_2)^2S_{20}(\overrightarrow{MP})r_0+O(R_0^3) \quad (3.2.45)$$

Substituting Eq. (3.2.44) and (3.2.45) into Eq. (3.2.9), we have

$$I_{zz}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^{\infty}ds_1\int_0^{\infty}ds_2(s_1s_2)^{-3/2}\exp[-s_1\overline{MA}^2-s_2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2s_1}\right)\int_0^1dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4s_1t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2s_2}\right)\int_0^1dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4s_2t_2^2}\right)\left\{-\frac{2}{3}\sqrt{\pi}(s_1+s_2)+\frac{2}{9}\sqrt{\pi}(s_1+s_2)^{3/2}\overline{MP}^2\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};(s_1+s_2)\overline{MP}^2\right)\right.$$

$$\left.-\frac{16}{45}\sqrt{\pi}(s_1+s_2)^{3/2}S_{20}(\overrightarrow{MP})\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};(s_1+s_2)\overline{MP}^2\right)+\frac{3\sqrt{2}}{2\sqrt{\pi}}r_0(s_1+s_2)-\frac{2}{\sqrt{\pi}}r_0(s_1+s_2)^2\overline{MP}^2+\frac{6\sqrt{2}}{5\sqrt{\pi}}(s_1+s_2)^2S_{20}(\overrightarrow{MP})r_0\right\}+O(R_0^3) \quad (3.2.46)$$

Note that all main terms come from the outer part, as seen in Eq. (3.2.42) and (3.2.43). Let us change the variables as $z=s_1+s_2$ and $w=s_1/(s_1+s_2)$. The Jacobian is $\frac{\partial(s_1,s_2)}{\partial(z,w)}=z$. Thus Eq. (3.2.46) can be rewritten as

$$I_{zz}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1dw\int_0^{\infty}dz\,z[w(1-w)z]^{-3/2}\exp[-wz\overline{MA}^2-(1-w)z\overline{MB}^2]$$

$$\times\left[\left(\frac{\zeta_A^2}{2wz}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wzt_1^2}\right)\left[\left(\frac{\zeta_B^2}{2(1-w)z}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)zt_2^2}\right)$$

$$\left\{\frac{-2}{3}\sqrt{\pi}z^{1/2}+\frac{2}{9}\sqrt{\pi}z^{3/2}x_0\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};zx_0\right)-\frac{16}{45}\sqrt{\pi}z^{3/2}y_0\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};zx_0\right)+\frac{3\sqrt{2}}{2\sqrt{\pi}}zr_0-\frac{2}{\sqrt{\pi}}z^2x_0r_0+\frac{6\sqrt{2}}{5\sqrt{\pi}}z^2y_0\,r_0\right\}+O(R_0^3)\quad(3.2.47)$$

We separate the integral over z as follows:

$$\int_0^\infty dz=\int_0^{a^2}dz+\int_{a^2}^\infty dz\qquad(3.2.48)$$

Where a^2 can be chosen arbitrarily. We choose as $a^2 = 4$, here. Next, we change the integral variable as follows: In the first term in Eq. (3.2.48), we do as $z = a^2u$. We do as $z = a^2/u$ in the last term in Eq. (3.2.48). Thus we have

$$\int_0^\infty dz=a^2\int_0^1 du+a^2\int_1^\infty du\frac{1}{u^2}\qquad(3.2.49)$$

Substituting Eq. (3.2.49) into Eq. (3.2.47), we have the final formula of the three-center molecular integral over Dirac wave functions of the target quantity for the GCDD model as given by

$$I_{zz}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-wua^2\overline{MA}^2-(1-w)ua^2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2wua^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wua^2t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2(1-w)ua^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2t_2^2}\right)\left\{\frac{-2}{3}\frac{\sqrt{\pi}}{au^{3/2}}+\frac{2}{9}\sqrt{\pi}\frac{ax_0}{u^{1/2}}\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};ua^2x_0\right)-\frac{16}{45}\sqrt{\pi}\frac{ay_0}{u^{1/2}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};ua^2x_0\right)\right.$$

$$\left.+\frac{3\sqrt{2}}{2\sqrt{\pi}}\frac{r_0}{u}-\frac{2}{\sqrt{\pi}}a^2x_0r_0+\frac{6\sqrt{2}}{5\sqrt{\pi}}a^2y_0\,r_0\right\}+\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-\frac{w}{u}a^2\overline{MA}^2-\frac{1-w}{u}a^2\overline{MB}^2]$$

$$\times\left[\left(\frac{u\zeta_A^2}{2wa^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{u\zeta_A^2}{4wa^2t_1^2}\right)\left[\left(\frac{u\zeta_B^2}{2(1-w)a^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2t_2^2}\right)$$

$$\times\left\{\frac{-2}{3}\frac{\sqrt{\pi}}{au^{1/2}}+\frac{2}{9}\sqrt{\pi}\frac{ax_0}{u^{3/2}}\,{}_2F_2\left(1,\frac{1}{2};2,\frac{5}{2};\frac{a^2}{u}x_0\right)-\frac{16}{45}\sqrt{\pi}\frac{ay_0}{u^{3/2}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};\frac{a^2}{u}x_0\right)+\frac{3\sqrt{2}}{2\sqrt{\pi}}\frac{r_0}{u}-\frac{2}{\sqrt{\pi}}\frac{a^2x_0}{u^2}r_0+\frac{6\sqrt{2}}{5\sqrt{\pi}}\frac{a^2y_0}{u^2}r_0\right\}+O(R_0^3)\qquad(3.2.50)$$

The error term is in the order of $R_0^3=(7r_0)^3$. Note that Eq. (3.2.50) is almost the same as Eq. (3.1.42). These terms contained r_0 in Eq. (3.2.50) (in other words, terms in the order of r_0) are different from those r_H in Eq. (3.1.42) (terms in the order of r_H). For the hydrogen atom, r_0 = 0.216939446(-4) and r_H = (0.343011382(-4), which are small quantities. All main terms of Eq. (3.2.50) are the same as those in Eq. (3.1.42). As pointed out in the succeeding sentence after Eq. (3.2.14), for the outer part, each scalar potential of both models coincides with each other, and also each vector potential does. Also as pointed out in Eq. (3.1.38) and Eq. (3.2.46), all main terms come from the outer part. At the outer part, the value of the target quantity for the HCDD model coincides with that for the GCDD model, because of the coincidence of potentials. Therefore all main terms of the HCDD model are the same as those of the GCDD model. In Eq. (3.2.50), integrals over *w, u,* t_1, *and* t_2 can be performed numerically using the 64-point Gauss-Legendre quadrature in the good precision of 8 significant figures. With a similar derivation to that for I_{zz}, we obtain I_{xx} by replacing y_0 with $[-y_0+\sqrt{3}y_2]/2$ in the above Eq. (3.2.50) and I_{yy} by doing y_0 with $[-y_0-\sqrt{3}y_2]/2$. With a similar derivation to that for I_{zz}, we have

$$I_{xy}=\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-wua^2\overline{MA}^2-(1-w)ua^2\overline{MB}^2]\left[\left(\frac{\zeta_A^2}{2wua^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4wua^2t_1^2}\right)$$

$$\times\left[\left(\frac{\zeta_B^2}{2(1-w)ua^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2t_2^2}\right)\left\{-\frac{8}{15}\sqrt{\pi}\frac{a}{u^{1/2}}\frac{y_{-2}}{\sqrt{3}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};ua^2x_0\right)+\frac{9\sqrt{2}}{5\sqrt{\pi}}a^2\frac{y_{-2}}{\sqrt{3}}r_0\right\}$$

$$+\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)}\int_0^1 dw[w(1-w)]^{-3/2}\int_0^\infty du\exp[-\frac{w}{u}a^2\overline{MA}^2-\frac{1-w}{u}a^2\overline{MB}^2]$$

$$\times\left[\left(\frac{u\zeta_A^2}{2wa^2}\right)\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{u\zeta_A^2}{4wa^2t_1^2}\right)\left[\left(\frac{u\zeta_B^2}{2(1-w)a^2}\right)\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}-\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}}\right]\exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2t_2^2}\right)$$

$$\times\left\{-\frac{8}{15}\sqrt{\pi}\frac{a}{u^{3/2}}\frac{y_{-2}}{\sqrt{3}}\,{}_1F_1\left(\frac{1}{2};\frac{7}{2};\frac{a^2}{u}x_0\right)+\frac{9\sqrt{2}}{5\sqrt{\pi}}\frac{a^2}{u^2}\frac{y_{-2}}{\sqrt{3}}r_0\right\}+O(R_0^3) \qquad (3.2.51)$$

We obtain I_{yz} by replacing y_{-2} with y_1 in the above Eq. (3.2.51) and I_{zx} by doing y_{-2} with y_{-1}. Of course, $I_{\eta\xi}=I_{\xi\eta}$.

Table 1 shows new values (which are never published) for the three-center molecular integral over Dirac wave functions for both the HCDD and the GCDD models, which are expressed as $\frac{Z_M^2 e^3\hbar}{c^2}N_A N_B I_{\xi\eta}$ where $N_A=\left(\frac{(2-\varepsilon_A)Z_A^3}{\pi\Gamma(3-2\varepsilon_A)}\right)^{1/2}$ is the normalization

Table 1: Example values for the three-center molecular integral over Dirac wave function for both the HCDD and the GCDD models; $\frac{Z_M^2 e^3\hbar}{c^2}N_A N_B I_{\xi\eta}$.

Atom at M	Atoms at A and B	ξη	HCDD model[a]	GCDD model[b]
H(Z_M = 1)	H($\zeta_A=\zeta_B$ =1)	XX	-0.2273368(-5)	-0.2273373(-5)
		YY	-0.1745919(-5)	-0.1745922(-5)
		ZZ	-0.1447661(-5)	-0.1447664(-5)
		XY	0.0	0.0
		YZ	0.0	0.0
		ZX	0.1167725(-5)	0.1167728(-5)
C(Z_M = 6)		ZZ	-0.5211580(-4)	-0.5211591(-4)
Sn(Z_M = 50)		ZZ	-0.3619153(-2)	-0.3619161(-2)
Hg(Z_M = 80)		ZZ	-0.9265031(-2)	-0.9265052(-2)
C(Z_M = 6)	C($\zeta_A=\zeta_B$ =6)	XX	-0.5814495(-10)	-0.5814054(-10)
		YY	0.7153494(-9)	0.7153571(-9)
		ZZ	0.4495310(-9)	0.4495373(-9)
		XY	0.0	0.0
		YZ	0.0	0.0
		ZX	0.7179622(-9)	0.7179649(-9)
Sn(Z_M = 50)		ZZ	0.3121743(-7)	0.3121763(-7)
Hg(Z_M = 80)		ZZ	0.7991664(-7)	0.7991776(-7)

a) Eq. (3.1.42) and (3.1.43)
b) Eq. (3.2.50) and (3.2.51)

constant of the Dirac wave function at A and $\xi,\eta\in(x,y,z)$. The three centers are denoted by $\vec{M}=(0,0,0),\vec{A}=(-\sqrt{8}/3,-\sqrt{8/3},2/3)$, and, $\vec{B}=(-\sqrt{8}/3,\sqrt{8/3},2/3)$. Such is for the methane molecule with the C-H bond length is 2 bohr; i.e., the carbon atom is at M and two hydrogen atoms at A and B. In each example integrals, the target quantity is at M and the Dirac wave functions are at A and B. As seen in Table 1, each value of the HCDD model is very near to the corresponding one of the GCDD model, because the main term of the HCDD model is the same as that of the GCDD model as pointed out in Eq. (3.2.50).

Conclusion

The Gaussian-transform formula for the Dirac wave function is derived. Using this formula, one can derive the multicenter molecular integral over Dirac wave functions for any physical quantity. The present formula is useful, especially for the relativistic calculations of the NMR spectra, where those using the Dirac wave function as the basis function have been never reported yet. As the first application of the present formula, the three-center molecular integral is derived for the target quantity with two finite nucleus models (HCDD and GCDD), which is necessary for solving the molecular matrix Dirac equation using the restricted magnetic balance. The integral value of the HCDD model is very near to that of the GCDD model. The next application is the multicenter molecular integrals for all of the physical quantities appearing in the matrix Dirac equation, Eq. (1.5). For the molecule, of course, the scalar potential in the Hamiltonian includes not only one electron term but also two electron terms. Such a project is in progress.

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