

RESEARCH ARTICLE

Multicenter Molecular Integrals over Dirac Wave Functions for Relativistic Kinetic Energy Terms

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Abstract

Multicenter molecular integrals over Dirac wave functions can be derived by using the Gaussian-transform for the Dirac wave function, which was derived by the author, for relativistic kinetic energy integrals; i.e., the integral for $\vec{A} \cdot \vec{A}$, where $\vec{A}$ is the vector potential of the magnetic field due to the nuclear spin, that for $\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}$, where $\vec{p} = -i\hbar\nabla$ is the momentum of the electron, and that for $i\vec{\sigma} \cdot (\vec{p} \times \vec{A} + \vec{A} \times \vec{p})$, where $\vec{\sigma}$ is the Pauli spin matrices. These integral formulas can be derived for the first time.

Keywords: Molecular integrals, Relativistic kinetic energy, Dirac wave function, NMR spectra.

1. Introduction

Recently, Sun et al. [1] derived the gauge invariant Dirac equation given by

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

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 of the electron, $\vec{A}$ is the vector potential of the magnetic field 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 use the atomic units throughout the present article ($m_e = 1$, $e = 1$, $\hbar = 1$, $4\pi\epsilon_0 = 1$, $c = 137.035999139$). However, we describe m_e , e , and $\hbar$ explicitly, for the readers convenience when one converts the units to the natural units. The gauge invariant Dirac equation has no rigorous solution. 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

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

Where $E = E_0 - m_e c^2$. To solve the Dirac equation, we may use a proper basis set, $\{\chi_\mu\}$. The large component spinor can be expressed as a linear combination in terms of these basis functions as given by

$$\Psi_i^L = \sum_\mu C_{i\mu}^L \chi_\mu \quad (1.3)$$

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

$$\Psi_i^S = \sum_\mu C_{i\mu}^S \vec{\sigma} \cdot (\vec{p} + \vec{A}) \chi_\mu \quad (1.4)$$

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

$$\begin{pmatrix} \vec{V} & \vec{T}_m \\ \vec{T}_m & \vec{W}_m - \vec{T}_m \end{pmatrix} \begin{pmatrix} \vec{C}_-^L & \vec{C}_+^L \\ \vec{C}_-^S & \vec{C}_+^S \end{pmatrix} = \begin{pmatrix} \vec{S} & \vec{0} \\ \vec{0} & \frac{1}{2m_e c^2} \vec{T}_m \end{pmatrix} \begin{pmatrix} \vec{C}_-^L & \vec{C}_+^L \\ \vec{C}_-^S & \vec{C}_+^S \end{pmatrix} \begin{pmatrix} \vec{\epsilon}_- & \vec{0} \\ \vec{0} & \vec{\epsilon}_+ \end{pmatrix} \quad (1.5)$$

Where $\vec{C}_-^L$ is the coefficient matrix of the large component spinor for the energy matrix $\vec{\epsilon}_-$, $\vec{C}_+^L$ is that for

$\vec{\epsilon}_+$, $\vec{C}_-^S$ and $\vec{C}_+^S$ are those for the small component spinor, $\vec{0}$ is the zero matrix,

$$V_{\mu\nu} = \langle \chi_\mu | V | \chi_\nu \rangle \quad (1.6)$$

$$(T_m)_{\mu\nu} = \frac{1}{2m_e} \langle \chi_\mu | \vec{\sigma} \cdot (\vec{p} + \vec{A}) \vec{\sigma} \cdot (\vec{p} + \vec{A}) | \chi_\nu \rangle \quad (1.7)$$

$$(W_m)_{\mu\nu} = \frac{1}{4m_e^2 c^2} \langle \chi_\mu | \vec{\sigma} \cdot (\vec{p} + \vec{A}) V \vec{\sigma} \cdot (\vec{p} + \vec{A}) | \chi_\nu \rangle \quad (1.8)$$

and

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \quad (1.9)$$

Many researchers extend the matrix Dirac equation to the molecule [2-17]. Especially, many are for relativistic calculations of NMR spectra [2,3,13-17]. It is natural to use the atomic Dirac wave function as one of basis functions. However, it has been not used yet, because there are no molecular integral formulas. In previous articles, the author derived the Gaussian-transform formulas for the Dirac wave function [18] and for its derivative [19]. One can derive any integral formula over Dirac wave functions by the use of the Gaussian-transform formulas.

In a previous article [18], using the Gaussian-transform, the author derived the integral formula over Dirac wave functions for the physical quantity $i\vec{\sigma} \cdot (\vec{p} \times V\vec{A} + \vec{A} \times V\vec{p})$, where $\times$ denotes the vector product. In a previous article [20], the author showed that the use of the Gaussian-type-orbital (GTO) is not suitable for the calculation of that quantity, which is necessary in the relativistic calculation of the NMR spectra. Also, in a previous article [19], the author derived molecular integrals over Dirac wave functions for the fundamental properties; i.e., the overlap integral, denoted by $S_{\mu\nu}$, the kinetic energy one, denoted by $\langle$

$\chi_\mu | \frac{1}{2m_e} \vec{p} \cdot \vec{p} | \chi_\nu \rangle$, and the nuclear attraction ones, denoted by $V_{\mu\nu}$, for the point-like nucleus ($V = -\frac{Ze^2}{r}$)

and for the finite-sized nucleus with the Gauss-type charge density distribution (GCDD) model [21] ($V =$

$-\frac{2Ze^2}{\sqrt{\pi}r_0}F_0)$, where $F_m(x) = \int_0^1 dt \, t^{2m} \exp(-xt^2)$ is the molecular incomplete gamma function, and the electron-repulsion integrals (which are the two-electron integrals of the potential one denoted as $V_{\mu\nu}$) for $V = \frac{e^2}{r_{12}}$ and for $V = \frac{2e^2}{\sqrt{\pi}r_e}F_0(\frac{r_{12}^2}{r_e^2})$ which is for the finite-sized electron with the classical radius of the electron r_e . The author derived these integral formulas for the first time. In the present article, we derive integrals over Dirac wave functions for the relativistic kinetic energy terms $(T_m)_{\mu\nu} = \frac{1}{2m_e} \langle \vec{\sigma} \cdot (\vec{p} + \vec{A}) \vec{\sigma} \cdot (\vec{p} + \vec{A}) | \chi_\nu \rangle$ in the next section.

2. Relativistic Kinetic Energy Integrals

The relativistic kinetic energy is given by Eq. (1.7). Using the Dirac identity [22], equation (1.7) can be rewritten as

$$\begin{aligned} (T_m)_{\mu\nu} &= \frac{1}{2m_e} \langle \chi_\mu | (\vec{p} + \vec{A}) \cdot (\vec{p} + \vec{A}) + i\vec{\sigma} \cdot (\vec{p} + \vec{A}) \times (\vec{p} + \vec{A}) | \chi_\nu \rangle \\ &= \frac{1}{2m_e} \langle \chi_\mu | \vec{p} \cdot \vec{p} + \vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} + \vec{A} \cdot \vec{A} + i\vec{\sigma} \cdot (\vec{p} \times \vec{A} + \vec{A} \times \vec{p}) | \chi_\nu \rangle \end{aligned} \quad (2.1)$$

We know that the term, $\frac{1}{2m_e} \langle \chi_\mu | \vec{p} \cdot \vec{p} | \chi_\nu \rangle$, is the usual kinetic energy, which has been evaluated in a previous article [19]. We evaluate terms other than it as follows:

2.1 The Term $\vec{A} \cdot \vec{A}$

We first evaluate the term $\vec{A} \cdot \vec{A}$. For the point-like nucleus, we have

$$\vec{A} = \frac{Ze}{c^2 r^3} \vec{\mu} \times \vec{r} \quad (2.1.1)$$

where Ze is the nuclear charge, $\vec{\mu}$ is the nuclear magnetic moment and $\vec{r}$ is the coordinate of the electron. Thus, we have

$$\vec{A} \cdot \vec{A} = \frac{Z^2 e^2}{c^4 r^6} (\vec{\mu} \times \vec{r}) \cdot (\vec{\mu} \times \vec{r}). \quad (2.1.2)$$

This term is singular at the nucleus (at origin), because of $1/r^6$. So, the integral of it is divergent. Some experiment shows [21] that the real nucleus is not the point-like one but a finite-sized one. There are several models for the finite-sized nucleus [21]. We use the Gauss-type charge density distribution (GCDD) model here. Then, we have [21]

$$\vec{A} = \frac{Ze}{c^2} \frac{4}{\sqrt{\pi} r_0^3} F_1\left(\frac{r^2}{r_0^2}\right) \vec{\mu} \times \vec{r} \quad (2.1.3)$$

and

$$\vec{A} \cdot \vec{A} = \frac{Z^2 e^2}{c^4} \frac{16}{\pi r_0^6} F_1 F_1 (\vec{\mu} \times \vec{r}) \cdot (\vec{\mu} \times \vec{r}) \quad (2.1.4)$$

where r_0 is the scale parameter of the GCDD model. The integral to be evaluated is, in the bra- and ket-notation by Dirac [22], given by

$$\langle \chi_{\mu A} | \vec{A} \cdot \vec{A} | \chi_{\nu B} \rangle = \frac{Z^2 e^2}{c^4} \sum_{\xi} \sum_{\eta} \mu_{M\xi} \mu_{M\eta} I_{\xi\eta} \quad [\xi, \eta \in (x, y, z)] \quad (2.1.5)$$

where μ_{Mz} is the z component of nuclear magnetic moment of the M-th nucleus located at $\vec{M} = (0, 0, 0)$, $\chi_{\mu A}$ is the Dirac wave function centered at A given by

$$\chi_{\mu A} = r_A^{-\varepsilon_A} \exp(-\zeta_A r_A) \quad (2.1.6)$$

in which $-\varepsilon_A = \sqrt{1 - (\alpha Z_A)^2} - 1$, $\alpha = 1/137.035999139$ is the fine structure constant, Z_A is nuclear charge of the atom or cation centered at A, ζ_A is the exponent, we may take $\zeta_A = Z_A$, and

$$I_{\xi\eta} = \frac{16}{\pi r_0^6} \int d\vec{r} F_1 F_1 (\delta_{\xi\eta} r_M^2 - \xi_M \eta_M) r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp(-\zeta_A r_A - \zeta_B r_B) \quad (2.1.7)$$

where we use the operator notation throughout the present article. Thus, we use $\int d\vec{r}$ as the integral operator. The integrand follows it in its right-hand side as in Eq. (2.1.7). We evaluate I_{zz} given by

$$I_{zz} = \frac{16}{\pi r_0^6} \int d\vec{r} F_1 F_1 (r_M^2 - z_M^2) r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp(-\zeta_A r_A - \zeta_B r_B) \quad (2.1.8)$$

First, we use the Gaussian-transform for the Dirac wave function derived in a previous article [18] given by

$$r_A^{-\varepsilon_A} \exp(-\zeta_A r_A) = \frac{\zeta_A^{1+\varepsilon_A}}{2\sqrt{\pi}\Gamma(1+\varepsilon_A)} \int_0^\infty dS_1 S_1^{-3/2} \exp(-S_1 r_A^2) \left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \quad (2.1.9)$$

where $\Gamma(x)$ is the gamma function [23]. Using the transform formula, we have

$$I_{zz} = \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{4\pi\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)} \int_0^\infty dS_1 \int_0^\infty dS_2 (S_1 S_2)^{-3/2} \left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \left[\frac{\zeta_B^2}{2S_2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) I_1 \quad (2.1.10)$$

where

$$I_1 = \frac{16}{\pi r_0^6} \int d\vec{r} F_1 F_1 (r_M^2 - z_M^2) \exp(-S_1 r_A^2 - S_2 r_B^2) \quad (2.1.11)$$

We use the Gaussian product rule given by

$$\exp(-S_1 r_A^2 - S_2 r_B^2) = \exp\left(-\frac{S_1 S_2}{S_{12}} \overline{AB}^2 - S_{12} r_P^2\right) \quad (2.1.12)$$

where $S_{12} = S_1 + S_2$ and $\vec{P} = \frac{S_1}{S_{12}} \vec{A} + \frac{S_2}{S_{12}} \vec{B}$.

Next, we use the Sack's formula [24] given by

$$\exp(-S_{12} r_P^2) = 4\pi \exp[-S_{12} r_M^2 - S_{12} \overline{MP}^2] \sum_{l=0}^\infty i_l (2S_{12} \overline{MP} r_M) \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r_M}) \quad (2.1.13)$$

where $i_l(x)$ is the modified spherical Bessel function of the first kind [23] and $Y_l^m(\hat{r})$ is the spherical harmonics [25]. We use the Gaussian product rule again as given by

$$\exp\left(-\frac{S_1 S_2}{S_{12}} \overline{AB}^2\right) \exp(-S_{12} \overline{MP}^2) = \exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2) \quad (2.1.14)$$

We know that $r_M^2 - z_M^2 = \frac{2}{3}r_M^2 - \frac{2}{3}S_{20}(\vec{r}_M)$, where $S_{20}(\vec{r}_M)$ is the solid harmonics [25]. Using the above relations, we can evaluate I_1 as given by

$$I_1 = 4\pi \exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2)(I_{1a} + I_{1b}) \quad (2.1.15)$$

where

$$\begin{aligned} I_{1a} &= \frac{32}{3\pi r_0^6} \int d\vec{r}_M r_M^2 F_1 F_1 \exp(-S_{12} r_M^2) \\ &\quad \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) \\ &= \frac{32}{3\pi r_0^6} \int_0^\infty dr_M r_M^4 F_1 F_1 \exp(-S_{12} r_M^2) \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \\ &\quad \int d\widehat{r}_M \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) \end{aligned} \quad (2.1.16)$$

and

$$\begin{aligned} I_{1b} &= -\frac{32}{3\pi r_0^6} \int d\vec{r}_M F_1 F_1 \exp(-S_{12} r_M^2) \\ &\quad \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) S_{20}(\vec{r}_M) \\ &= -\frac{32}{3\pi r_0^6} \int_0^\infty dr_M r_M^2 F_1 F_1 \exp(-S_{12} r_M^2) \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \\ &\quad \int d\widehat{r}_M \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) S_{20}(\vec{r}_M) \end{aligned} \quad (2.1.17)$$

We know the angular part can be evaluated as in a previous article [26] as given by

$$\int d\widehat{r}_M \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) = \delta_{l0} \delta_{m0} \quad (2.1.18)$$

and

$$\int d\widehat{r}_M \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) S_{20}(\vec{r}_M) = r_M^2 \delta_{l2} \frac{S_{20}(\overline{MP})}{\overline{MP}^2} \quad (2.1.19)$$

Then, we have

$$I_{1a} = \frac{32}{3\pi r_0^6} \int_0^\infty dr_M r_M^4 F_1 F_1 \exp(-S_{12} r_M^2) i_0 (2S_{12} \overline{MP} r_M) \quad (2.1.20)$$

and

$$I_{1b} = -\frac{32}{3\pi r_0^6} \frac{S_{20}(\overline{MP})}{\overline{MP}^2} \int_0^\infty dr_M r_M^4 F_1 F_1 \exp(-S_{12} r_M^2) i_2 (2S_{12} \overline{MP} r_M) \quad (2.1.21)$$

In order to evaluate these integrals, we separate inner and outer part of the finite nucleus, because r_0 is not the radius of the nucleus. As describing it in a previous article [18], we use $R_0 = br_0$ with $b = 7$ for the critical radius. For the outer part, we calculate F_m ($m \leq 2$) by its asymptotic value as given by

$$F_m \left(\frac{r_M^2}{r_0^2} \right) = \frac{\Gamma(m+1/2)}{2} \left(\frac{r_0}{r_M} \right)^{2m+1} \quad (r_M \geq R_0) \quad (2.1.22)$$

For the inner part we do it by the power series as given by

$$\begin{aligned} F_m \left(\frac{r_M^2}{r_0^2} \right) &= \frac{1}{2m+1} {}_1F_1 \left(m + \frac{1}{2}; m + \frac{3}{2}; -\frac{r_M^2}{r_0^2} \right) = \frac{1}{2m+1} \sum_{k=0} \frac{(m+1/2)_k}{k!(m+3/2)_k} \left(-\frac{r_M^2}{r_0^2} \right)^k \\ &\quad (r_M \leq R_0) \end{aligned} \quad (2.1.23)$$

where ${}_1F_1(a_1; c_1; x)$ is the confluent hypergeometric function [23] and

$(a)_j = a(a+1)\cdots(a+j-1)$ is the Pochhammer symbol. Then, we have

$$I_{1a} = I_{1a}^{in} + I_{1a}^{out} \quad (2.1.24)$$

where

$$I_{1a}^{in} = \frac{32}{3\pi r_0^6} \int_0^{R_0} dr_M r_M^4 F_1 F_1 \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M) \quad (2.1.25)$$

and

$$I_{1a}^{out} = \frac{32}{3\pi r_0^6} \int_{R_0}^{\infty} dr_M r_M^4 F_1 F_1 \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M) \quad (2.1.26)$$

We evaluate I_{1a}^{in} . We use Eq. (2.1.23) and the power series of the modified spherical Bessel function as given by [23]

$$i_l(x) = \frac{x^l}{(2l+1)!!} \sum_{j=0}^{\infty} \frac{(x^2/4)^j}{j!(l+\frac{3}{2})_j} \quad (2.1.27)$$

Then, we have

$$I_{1a}^{in} = \frac{32}{27\pi r_0^6} \sum_{k_1=0}^{\infty} \sum_{k_2=0}^{\infty} \frac{(-1/r_0^2)^{k_1+k_2} (3/2)_{k_1} (3/2)_{k_2}}{k_1! k_2! (5/2)_{k_1} (5/2)_{k_2}} \sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} I_{2a}^{in} \quad (2.1.28)$$

where

$$\begin{aligned} I_{2a}^{in} &= \int_0^{R_0} dr_M r_M^{2j+2k_1+2k_2+4} \exp(-S_{12} r_M^2) \\ &= \frac{1}{2} \int_0^{R_0^2} dx x^{j+k_1+k_2+3/2} \exp(-s_{12} x) = \frac{\gamma(j+k_{12}+5/2; S_{12} R_0^2)}{2(S_{12})^{j+k_{12}+5/2}} \end{aligned} \quad (2.1.29)$$

in which $k_{12} = k_1 + k_2$ and $\gamma(a; x)$ is the incomplete gamma function of the first kind [23]. It is easy to derive the following relation:

$$\gamma(a; x) = x^a \frac{\Gamma(a)}{\Gamma(a+1)} {}_1F_1(a; a+1; -x) \quad (2.1.30)$$

Using Eq. (2.1.30) for (2.1.29), we have

$$I_{2a}^{in} = \frac{1}{2} R_0^{2j+2k_{12}+5} \frac{\Gamma(j+k_{12}+5/2)}{\Gamma(j+k_{12}+7/2)} {}_1F_1\left(j+k_{12}+\frac{5}{2}; j+k_{12}+\frac{7}{2}; -S_{12} R_0^2\right) \quad (2.1.31)$$

Substituting Eq. (2.1.31) into Eq. (2.1.28), we have

$$\begin{aligned} I_{1a}^{in} &= \frac{16b^5}{27\pi r_0^6} \sum_{k_1=0}^{\infty} \sum_{k_2=0}^{\infty} \frac{(-b^2)^{k_{12}} (3/2)_{k_1} (3/2)_{k_2}}{k_1! k_2! (5/2)_{k_1} (5/2)_{k_2}} \\ &\quad \sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2 R_0^2)^j}{j!(3/2)_j} \frac{\Gamma(j+k_{12}+5/2)}{\Gamma(j+k_{12}+7/2)} {}_1F_1\left(j+k_{12}+\frac{5}{2}; j+k_{12}+\frac{7}{2}; -S_{12} R_0^2\right) \end{aligned} \quad (2.1.32)$$

Because $S_{12} R_0^2$ is very small value [S_1 and S_2 are not large, because of the factor of $\exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2)$ in Eq. (2.1.15)], we can use

$$\begin{aligned} &\sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2 R_0^2)^j}{j!(3/2)_j} \frac{\Gamma(j+k_{12}+5/2)}{\Gamma(j+k_{12}+7/2)} {}_1F_1\left(j+k_{12}+\frac{5}{2}; j+k_{12}+\frac{7}{2}; -S_{12} R_0^2\right) \\ &= \frac{\Gamma(k_{12}+5/2)}{\Gamma(k_{12}+7/2)} + \left(\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12}\right) R_0^2 \frac{\Gamma(k_{12}+7/2)}{\Gamma(k_{12}+9/2)} + O(R_0^4) \end{aligned} \quad (2.1.33)$$

The error term is in the order of $R_0^4 = 0.53179747(-15)$ for hydrogen atom, which is very small. Then, we have

$$I_{1a}^{in} = \frac{16b^5}{27\pi r_0} \sum_{k_1=0} \sum_{k_2=0} \frac{(-b^2)^{k_{12}} (3/2)_{k_1} (3/2)_{k_2}}{k_1! k_2! (5/2)_{k_1} (5/2)_{k_2}} \left\{ \frac{\Gamma(k_{12}+5/2)}{\Gamma(k_{12}+7/2)} + \left(\frac{3}{2} S_{12}^2 \overline{MP}^2 - S_{12} \right) R_0^2 \frac{\Gamma(k_{12}+7/2)}{\Gamma(k_{12}+9/2)} + O(R_0^4) \right\} \quad (2.1.34)$$

In a previous article [20], the author derived these summations as given by

$$Sum_1 = \sum_{k_1=0} \sum_{k_2=0} \frac{(-b^2)^{k_{12}} (3/2)_{k_1} (3/2)_{k_2}}{k_1! k_2! (5/2)_{k_1} (5/2)_{k_2}} \frac{\Gamma(k_{12}+5/2)}{\Gamma(k_{12}+7/2)} = -\frac{9\pi}{8b^6} + \frac{9\sqrt{2}\pi}{8b^5} \quad (2.1.35)$$

and

$$Sum_2 = \sum_{k_1=0} \sum_{k_2=0} \frac{(-b^2)^{k_{12}} (3/2)_{k_1} (3/2)_{k_2}}{k_1! k_2! (5/2)_{k_1} (5/2)_{k_2}} \frac{\Gamma(k_{12}+7/2)}{\Gamma(k_{12}+9/2)} = \frac{9\pi}{8b^6} - \frac{63\sqrt{2}\pi}{22b^7} \quad (2.1.36)$$

Substituting Eq. (2.1.35) and (2.1.36) into Eq. (2.1.34), we have

$$I_{1a}^{in} = -\frac{2}{3R_0} + \frac{2\sqrt{2}}{3\sqrt{\pi}r_0} + \left(\frac{3}{2} S_{12}^2 \overline{MP}^2 - S_{12} \right) \left(\frac{2}{3} R_0 - \frac{7\sqrt{2}}{6\sqrt{\pi}} r_0 \right) + O(R_0^3) \quad (2.1.37)$$

Next, we evaluate I_{1a}^{out} . We use the asymptotic value of $F_1 = \frac{\sqrt{\pi}r_0^3}{4r_M^3}$, Eq. (2.1.22), and Eq. (2.1.27) for Eq.

(2.1.26) and have

$$\begin{aligned} I_{1a}^{out} &= \frac{2}{3} \sum_{j=0} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} \int_{R_0}^{\infty} dr_M r_M^{2j-2} \exp(-S_{12} r_M^2) \\ &= \frac{2}{3} \int_{R_0}^{\infty} dr_M \frac{1}{r_M^2} \exp(-S_{12} r_M^2) + \frac{2}{3} \sum_{j=1} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} \int_{R_0}^{\infty} dr_M r_M^{2j-2} \exp(-S_{12} r_M^2) \\ &= \frac{1}{3} \int_{R_0^2}^{\infty} dx x^{-3/2} \exp(-S_{12} x) + \frac{4}{9} S_{12}^2 \overline{MP}^2 \sum_{j'=0} \frac{(S_{12}^2 \overline{MP}^2)^{j'}}{(2)_{j'} (5/2)_{j'}} \int_{R_0}^{\infty} dr_M r_M^{2j'} \exp(-S_{12} r_M^2) \end{aligned} \quad (2.1.38)$$

where $j' = j - 1$. Then, we have

$$I_{1a}^{out} = \frac{\sqrt{S_{12}}}{3} \Gamma\left(-\frac{1}{2}; -S_{12} R_0^2\right) + \frac{2}{9} S_{12}^2 \overline{MP}^2 \sum_{j'=0} \frac{(S_{12}^2 \overline{MP}^2)^{j'}}{(2)_{j'} (5/2)_{j'}} \frac{\Gamma(j'+1/2; -S_{12} R_0^2)}{(S_{12})^{j'+1/2}} \quad (2.1.39)$$

where $\Gamma(a, x)$ is the incomplete gamma function of the second kind [23]. It is easy to derive the relation given by

$$\Gamma(a, x) = \Gamma(a) - \frac{x^a}{a} + \frac{x^{a+1}}{a+1} + \dots \quad (x \ll 1) \quad (2.1.40)$$

Using Eq. (2.1.40), we have

$$\begin{aligned} I_{1a}^{out} &= \frac{2}{3R_0} - \frac{2}{3} \sqrt{\pi S_{12}} + \frac{2}{3} S_{12} + O(R_0^3) \\ &+ \frac{2}{9} S_{12}^{3/2} \overline{MP}^2 \sqrt{\pi} {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; S_{12} \overline{MP}^2\right) - \frac{4}{9} S_{12}^2 \overline{MP}^2 R_0 + O(R_0^3) \end{aligned} \quad (2.1.41)$$

Substituting Eq. (2.1.37) and (2.1.41) into (2.1.24), we have

$$\begin{aligned} I_{1a} &= \frac{2\sqrt{2}}{3\sqrt{\pi}r_0} - \frac{2}{3} \sqrt{\pi S_{12}} + \frac{2}{9} \sqrt{\pi S_{12}^3} \overline{MP}^2 {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; S_{12} \overline{MP}^2\right) \\ &+ \frac{7\sqrt{2}}{6\sqrt{\pi}} S_{12} r_0 - \frac{7\sqrt{2}}{9\sqrt{\pi}} S_{12}^2 \overline{MP}^2 r_0 + O(R_0^3) \end{aligned} \quad (2.1.42)$$

where ${}_2F_2(a_1, a_2; c_1, c_2; x)$ is one of the generalized hypergeometric functions [25]. The error term is in the order of $R_0^3 = 0.3501948(-11)$, which is very small.

With a similar derivation to the above, we have

$$I_{1b} = -\frac{4\sqrt{\pi}}{45} S_{12}^{3/2} S_{20}(\overrightarrow{MP}) {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; S_{12}\overrightarrow{MP}^2\right) + \frac{14\sqrt{2}}{45\sqrt{\pi}} S_{12}^2 S_{20}(\overrightarrow{MP}) r_0 + O(R_0^3) \quad (2.1.43)$$

Substituting Eq. (2.1.42) and (2.1.43) into Eq. (2.1.15), and doing the resulting equation into Eq. (2.1.10), we have

$$I_{zz} = \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)} \int_0^\infty dS_1 \int_0^\infty dS_2 (S_1 S_2)^{-3/2} \exp[-S_1 \overrightarrow{MA}^2 - S_2 \overrightarrow{MB}^2] \left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \left[\frac{\zeta_B^2}{2S_2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) (I_{1a} + I_{1b}) \quad (2.1.44)$$

Next, we change integral variables as follows: $S_{12} = z$ and $w = S_1/S_{12}$. The Jacobian is given by

$$\frac{\partial(z, w)}{\partial(S_1, S_2)} = z. \text{ Then, we have}$$

$$I_{zz} = \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)} \int_0^1 dw [w(1-w)]^{-3/2} \int_0^\infty dz z^{-2} \exp[-wz \overrightarrow{MA}^2 - (1-w)z \overrightarrow{MB}^2] \left[\frac{\zeta_A^2}{2wz} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wz t_1^2}\right) \left[\frac{\zeta_B^2}{2(1-w)z} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)z t_2^2}\right) (I_{1a} + I_{1b}) \quad (2.1.45)$$

where

$$I_{1a} + I_{1b} = \frac{2\sqrt{2}}{3\sqrt{\pi}r_0} - \frac{2}{3}\sqrt{\pi}z + \frac{2}{9}\sqrt{\pi}z^{3/2}x_0 {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; zx_0\right) - \frac{4\sqrt{\pi}}{45}z^{3/2}y_0 {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; zx_0\right) + \frac{7\sqrt{2}}{6\sqrt{\pi}}zr_0 - \frac{7\sqrt{2}}{9\sqrt{\pi}}z^2x_0r_0 + \frac{14\sqrt{2}}{45\sqrt{\pi}}z^2y_0r_0 + O(R_0^3) \quad (2.1.46)$$

in which

$$x_0 = w^2 \overrightarrow{MA}^2 + (1-w)^2 \overrightarrow{MB}^2 + 2w(1-w) \overrightarrow{MA} \cdot \overrightarrow{MB} \quad (2.1.47)$$

and

$$y_0 = w^2 S_{20}(\overrightarrow{MA}) + (1-w)^2 S_{20}(\overrightarrow{MB}) + w(1-w) S_{20}(\overrightarrow{MA}, \overrightarrow{MB}; 1). \quad (2.1.48)$$

In a previous article [27], the author defined the mixed solid harmonics given by

$$S_{20}(\overrightarrow{MA}, \overrightarrow{MB}; 1) = 2MA_z MB_z - (MA_x MB_x + MA_y MB_y). \quad (2.1.49)$$

Next, we separate the integral over z as follows: $\int_0^\infty dz = \int_0^{a^2} dz + \int_{a^2}^\infty dz = a^2 \int_0^1 du + a^2 \int_0^1 du \frac{1}{u^2}$,

where a^2 can be chosen arbitrary. We choose $a^2 = 4$ here. At the first term, we change integral variable from z to $u = z/a^2$. At the second term, we do z to $u = a^2/z$. Then, we have the final formula given by

$$\begin{aligned}
 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} \\
 & \left\{ \int_0^1 du \frac{1}{a^2 u^2} \exp[-wua^2 \overline{MA}^2 - (1-w)ua^2 \overline{MB}^2] \right. \\
 & \left[\frac{\zeta_A^2}{2wua^2} \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^2 t_1^2}\right) \\
 & \left[\frac{\zeta_B^2}{2(1-w)ua^2} \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{2\sqrt{2}}{3\sqrt{\pi}r_0} - \frac{2a}{3}\sqrt{\pi}u + \frac{2a^3}{9}\sqrt{\pi}u^{3/2}x_0 \quad {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; ua^2x_0\right) \right. \\
 & \left. - \frac{4\sqrt{\pi}a^3}{45}u^{3/2}y_0 \quad {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; ua^2x_0\right) + \frac{7\sqrt{2}}{6\sqrt{\pi}}ua^2r_0 - \frac{7\sqrt{2}}{9\sqrt{\pi}}a^4u^2x_0r_0 + \frac{14\sqrt{2}}{45\sqrt{\pi}}a^4u^2y_0r_0 \right] \\
 & + \int_0^1 du \frac{1}{a^2} \exp\left[-\frac{w}{u}a^2\overline{MA}^2 - \frac{1-w}{u}a^2\overline{MB}^2\right] \\
 & \left[\frac{u\zeta_A^2}{2wa^2} \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) \\
 & \left[\frac{u\zeta_B^2}{2(1-w)a^2} \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{2\sqrt{2}}{3\sqrt{\pi}r_0} - \frac{2\sqrt{\pi}a}{3\sqrt{u}} + \frac{2a^3}{9}\sqrt{\pi}u^{-3/2}x_0 \quad {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; \frac{a^2}{u}x_0\right) \right. \\
 & \left. - \frac{4\sqrt{\pi}a^3}{45u^{3/2}}y_0 \quad {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; ua^2x_0\right) + \frac{7\sqrt{2}}{6\sqrt{\pi}}\frac{a^2}{u}r_0 - \frac{7\sqrt{2}}{9\sqrt{\pi}}\frac{a^4}{u^2}x_0r_0 + \frac{14\sqrt{2}}{45\sqrt{\pi}}\frac{a^4}{u^2}y_0r_0 \right] \left. \right\} \quad (2.1.50)
 \end{aligned}$$

The integral I_{yy} can be given by replacing y_0 by $\frac{-1}{2}(y_0 + \sqrt{3}y_2)$ in Eq. (2.1.50), where $y_2 =$

$$w^2 S_{22}(\overrightarrow{MA}) + (1-w)^2 S_{22}(\overrightarrow{MB}) + w(1-w) S_{22}(\overrightarrow{MA}, \overrightarrow{MB}; 1). \quad (2.1.51)$$

The I_{xx} can be given by doing y_0 by $\frac{-1}{2}(y_0 - \sqrt{3}y_2)$ in Eq. (2.1.50).

With a similar derivation to the above, we have the final formula of I_{xy} as given by

$$\begin{aligned}
 I_{xy} = & \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(1+\varepsilon_B)} \int_0^1 dw [w(1-w)]^{-3/2} \\
 & [wMA_x + (1-w)MB_x][wMA_y + (1-w)MB_y] \\
 & \left\{ \int_0^1 du \frac{1}{a^2 u^2} \exp[-wua^2 \overline{MA}^2 - (1-w)ua^2 \overline{MB}^2] \right. \\
 & \left[\frac{\zeta_A^2}{2wua^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wua^2 t_1^2}\right) \\
 & \left[\frac{\zeta_B^2}{2(1-w)a^2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)a^2 t_2^2}\right) \\
 & \left[\frac{2\sqrt{2}}{3\sqrt{\pi}r_0} - \frac{2\sqrt{\pi}a}{3\sqrt{u}} + \frac{2a^3}{9}\sqrt{\pi}u^{-3/2}x_0 \quad {}_2F_2\left(\frac{1}{2}, 1; \frac{5}{2}, 2; \frac{a^2}{u}x_0\right) \right. \\
 & \left. - \frac{4\sqrt{\pi}a^3}{45u^{3/2}}y_0 \quad {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; ua^2x_0\right) + \frac{7\sqrt{2}}{6\sqrt{\pi}}\frac{a^2}{u}r_0 - \frac{7\sqrt{2}}{9\sqrt{\pi}}\frac{a^4}{u^2}x_0r_0 + \frac{14\sqrt{2}}{45\sqrt{\pi}}\frac{a^4}{u^2}y_0r_0 \right] \left. \right\}
 \end{aligned}$$

$$\begin{aligned}
& \left[\frac{\zeta_B^2}{2(1-w)ua^2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2t_2^2}\right) \\
& \left[-\frac{2\sqrt{\pi}a^3}{15} u^{3/2} {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; ua^2x_0\right) + \frac{7\sqrt{2}a^4}{15\sqrt{\pi}} r_0 \right] \\
& + \int_0^1 du \frac{1}{a^2} \exp\left[-\frac{w}{u} a^2 \overline{MA}^2 - \frac{1-w}{u} a^2 \overline{MB}^2\right] \\
& \left[\frac{u\zeta_A^2}{2wa^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{u\zeta_A^2}{4wa^2t_1^2}\right) \\
& \left[\frac{u\zeta_B^2}{2(1-w)a^2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2t_2^2}\right) \\
& \left[-\frac{2\sqrt{\pi}a^3}{15u^{3/2}} {}_1F_1\left(\frac{1}{2}; \frac{7}{2}; ua^2x_0\right) + \frac{7\sqrt{2}a^4}{15\sqrt{\pi}u^2} r_0 \right] \} \quad (2.1.52)
\end{aligned}$$

The I_{yz} can be obtained by replacing (x, y) by (y, z) in Eq. (2.1.52). The I_{zx} can be done by doing (x, y) by (z, x) . Of course, $I_{\eta\xi} = I_{\xi\eta}$ [$\xi, \eta \in (x, y, z)$].

The integrals for $[0, 1]$ can be evaluated numerically by using the Gauss-Legendre quadrature. We use the 64-point quadrature and obtain $\frac{e^2}{c^4} I_{zz} = 0.50938677(-5)$, $\frac{e^2}{c^4} I_{yy} = 0.50938637(-5)$, $\frac{e^2}{c^4} I_{xx} =$

$0.50938567(-5)$, $\frac{e^2}{c^4} I_{xy} = \frac{e^2}{c^4} I_{yz} = 0$, and $\frac{e^2}{c^4} I_{zx} = 0.15545769(-10)$ for the case of three hydrogen atoms located at $\vec{M} = (0, 0, 0)$, $\vec{A} = (-\sqrt{8}/3, -\sqrt{8}/3, 2/3)$, and $\vec{B} = (-\sqrt{8}/3, \sqrt{8}/3, 2/3)$. Thus, we have 8 significant figure precision.

2.2 The term $\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}$

Next, we evaluate the term $\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}$. We have

$$\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} = \frac{-i\hbar Ze}{c^2} \frac{8}{\sqrt{\pi}r_0^3} F_1\left(\frac{r_M^2}{r_0^2}\right) \sum_{\xi} \mu_{M\xi} (\vec{r} \times \nabla)_{\xi} \quad [\xi \in (x, y, z)] \quad (2.2.1)$$

and

$$\langle \chi_{\mu A} | \vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} | \chi_{\nu B} \rangle = \frac{-i\hbar Ze}{c^2} \sum_{\xi} \mu_{M\xi} I_{\xi} \quad (2.2.2)$$

where

$$I_{\xi} = \frac{8}{\sqrt{\pi}r_0^3} \langle \chi_{\mu A} | F_1(\vec{r} \times \nabla)_{\xi} | \chi_{\nu B} \rangle \quad (2.2.3)$$

We evaluate I_z given by

$$I_z = \frac{8}{\sqrt{\pi}r_0^3} \int d\vec{r}_M r_A^{-\varepsilon_A} \exp(-\zeta_A r_A) F_1(x_M \frac{\partial}{\partial y} - y_M \frac{\partial}{\partial x}) r_B^{-\varepsilon_B} \exp(-\zeta_B r_B) \quad (2.2.4)$$

We use the Gaussian-transform for the derivative of the Dirac wave function derived in a previous article [19] as given by

$$\begin{aligned}
\nabla r_B^{-\varepsilon_B} \exp(-\zeta_B r_B) &= -\vec{r}_B \frac{\zeta_B^{3+\varepsilon_B}}{2\sqrt{\pi}\Gamma(2+\varepsilon_B)} \int_0^{\infty} dS_2 S_2^{-3/2} \exp(-S_2 r_B^2) \\
&\left[\varepsilon_B \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} + \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{3+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) \quad (2.2.5)
\end{aligned}$$

Using Eq. (2.1.9) and (2.2.5) for Eq. (2.2.4), we have

$$I_Z = -\frac{\zeta_A^{1+\varepsilon_A}\zeta_B^{3+\varepsilon_B}}{4\pi\Gamma(1+\varepsilon_A)\Gamma(2+\varepsilon_B)}\int_0^\infty dS_1\int_0^\infty dS_2(S_1S_2)^{-3/2}$$

$$\left[\frac{\zeta_A^2}{2S_1}\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}}-\int_0^1 dt_1\frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}}\right]\exp\left(-\frac{\zeta_A^2}{4S_1t_1^2}\right)$$

$$\left[\varepsilon_B\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}}+\int_0^1 dt_2\frac{(1-t_2)^{\varepsilon_B}}{t_2^{3+\varepsilon_B}}\right]\exp\left(-\frac{\zeta_B^2}{4S_2t_2^2}\right)I_1^{(2)} \quad (2.2.6)$$

where

$$I_1^{(2)} = \frac{8}{\sqrt{\pi}r_0^3}\int d\vec{r}_M F_1(x_M y_B - y_M x_B)\exp(-S_1 r_A^2 - S_2 r_B^2) \quad (2.2.7)$$

We use the Gaussian product rule, Eq. (2.1.12), Sack's formula, Eq. (2.1.13), and Eq. (2.1.14). Then, we have

$$I_1^{(2)} = 4\pi\exp(-S_1\overline{MA}^2 - S_2\overline{MB}^2)I_2 \quad (2.2.8)$$

where

$$I_2 = \frac{8}{\sqrt{\pi}r_0^3}\int_0^\infty dr_M r_M^2 F_1\exp(-S_{12}r_M^2)\sum_{l=0}^\infty i_l(2S_{12}\overline{MP}r_M)$$

$$\int d\widehat{r}_M (x_M y_B - y_M x_B)\sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) \quad (2.2.9)$$

We know $y_B = y_M + BM_y$ and $x_M y_B - y_M x_B = x_M BM_y - y_M BM_x$. Then the angular part can be evaluated as in a previous article [26] as given by

$$\int d\widehat{r}_M (x_M y_B - y_M x_B)\sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M)$$

$$= r_M \delta_{l1} \frac{MP_x BM_y - MP_y BM_x}{\overline{MP}} = r_M \delta_{l1} \frac{S_{12}}{S_{12}} \frac{MA_y MB_x - MA_x MB_y}{\overline{MP}} \quad (2.2.10)$$

Substituting Eq. (2.2.10) into Eq. (2.2.9), we have

$$I_2 = \frac{S_{12}}{S_{12}} \frac{MA_y MB_x - MA_x MB_y}{\overline{MP}} \frac{8}{\sqrt{\pi}r_0^3} \int_0^\infty dr_M r_M^3 F_1 \exp(-S_{12}r_M^2) i_1(2S_{12}\overline{MP}r_M) \quad (2.2.11)$$

Using Eq. (2.1.27) for (2.2.11), we have

$$I_2 = \frac{16}{3} S_{12} (MA_y MB_x - MA_x MB_y) \sum_{j=0}^\infty \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(5/2)_j} I_3 \quad (2.2.12)$$

where

$$I_3 = \frac{1}{\sqrt{\pi}r_0^3} \int_0^\infty dr_M r_M^{2j+4} F_1 \exp(-S_{12}r_M^2) = I_3^{in} + I_3^{out} \quad (2.2.13)$$

in which

$$I_3^{in} = \frac{1}{\sqrt{\pi}r_0^3} \int_0^{R_0} dr_M r_M^{2j+4} F_1 \exp(-S_{12}r_M^2) \quad (2.2.14)$$

and

$$I_3^{out} = \frac{1}{\sqrt{\pi}r_0^3} \int_{R_0}^\infty dr_M r_M^{2j+4} F_1 \exp(-S_{12}r_M^2) \quad (2.2.15)$$

We evaluate I_3^{in} . We use Eq. (2.1.23) for (2.2.14) and have

$$I_3^{in} = \frac{1}{3\sqrt{\pi}r_0^3} \sum_{k=0}^\infty \frac{(-1/r_0^2)^k (3/2)_k}{k!(5/2)_k} \int_0^{R_0} dr_M r_M^{2j+2k+4} \exp(-S_{12}r_M^2)$$

$$= \frac{1}{6\sqrt{\pi}r_0^3} \sum_{k=0}^{\infty} \frac{(-1/r_0^2)^k (3/2)_k}{k!(5/2)_k} \int_0^{R_0^2} dx \, x^{j+k+3/2} \exp(-S_{12}x) \quad (2.2.16)$$

Similarly to as in Eq. (2.1.29), we have

$$I_3^{in} = \frac{1}{6\sqrt{\pi}r_0^3} \sum_{k=0}^{\infty} \frac{(-1/r_0^2)^k (3/2)_k}{k!(5/2)_k} R_0^{j+k+5/2} \frac{\Gamma(j+k+5/2)}{\Gamma(j+k+7/2)} {}_1F_1\left(j+k+\frac{5}{2}; j+k+\frac{7}{2}; -S_{12}R_0^2\right) \quad (2.2.17)$$

Using the power series of the function ${}_1F_1$, Eq. (2.1.23), we have

$$\begin{aligned} I_3^{in} &= \frac{b^3 R_0^{2j+2}}{6\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{(-b^2)^k (3/2)_k}{k!(5/2)_k} \frac{\Gamma(j+k+5/2)}{\Gamma(j+k+7/2)} + O(R_0^{2j+4}) \\ &= \delta_{j0} \frac{b^3 R_0^2}{6\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{(-b^2)^k (3/2)_k}{k!(5/2)_k} \frac{\Gamma(k+5/2)}{\Gamma(k+7/2)} + O(R_0^4) \\ &= \delta_{j0} \frac{b^3 R_0^2}{6\sqrt{\pi}} \frac{\Gamma(5/2)}{\Gamma(7/2)} {}_1F_1\left(\frac{3}{2}; \frac{7}{2}; -b^2\right) + O(R_0^4) \end{aligned} \quad (2.2.18)$$

Using the asymptotic expansion of the function ${}_1F_1$ [23], we have

$$I_3^{in} = \delta_{j0} \frac{b^3 R_0^2}{6\sqrt{\pi}} \frac{\Gamma(5/2)}{\Gamma(7/2)} \frac{\Gamma(7/2)}{b^3} \left(1 - \frac{3}{2b^2}\right) + O(R_0^4) = \delta_{j0} \left(\frac{R_0^2}{8} - \frac{3r_0^2}{16}\right) + O(R_0^4) \quad (2.2.19)$$

Thus, we have

$$\sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(5/2)_j} I_3^{in} = \left(\frac{R_0^2}{8} - \frac{3r_0^2}{16}\right) + O(R_0^4) \quad (2.2.20)$$

Next, we evaluate I_3^{out} . Using Eq. (2.1.22) with $m=1$ for (2.2.15), we have

$$I_3^{out} = \frac{1}{4} \int_{R_0^2}^{\infty} dr_M \, r_M^{2j+1} \exp(-S_{12}r_M^2) = \frac{1}{8} \int_{R_0^2}^{\infty} dx \, x^j \exp(-S_{12}x) = \frac{\Gamma(j+1, S_{12}R_0^2)}{8S_{12}^{j+1}} \quad (2.2.21)$$

Using the formula number 8.352.2 of the mathematical formula book [28], we have

$$\Gamma(j+1, S_{12}R_0^2) = \Gamma(j+1) \exp(-S_{12}R_0^2) \sum_{m=0}^j \frac{(S_{12}R_0^2)^m}{m!} = \Gamma(j+1) [1 - \delta_{j0} S_{12}R_0^2 + O(R_0^4)] \quad (2.2.22)$$

Substituting Eq. (2.2.22) into Eq. (2.2.21), we have

$$I_3^{out} = \frac{1}{8S_{12}^{j+1}} \Gamma(j+1) [1 - \delta_{j0} S_{12}R_0^2 + O(R_0^4)] \quad (2.2.23)$$

Thus, we have

$$\sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(5/2)_j} I_3^{out} = \frac{1}{8S_{12}} {}_1F_1\left(1; \frac{5}{2}; S_{12} \overline{MP}^2\right) - \frac{R_0^2}{8} + O(R_0^4) \quad (2.2.24)$$

Substituting Eq. (2.2.20) and (2.2.24) into Eq. (2.2.13) and doing the resulting equation into Eq. (2.2.12), we have

$$I_2 = \frac{2}{3} S_1 (MA_y MB_x - MA_x MB_y) \left[\frac{1}{S_{12}} {}_1F_1\left(1; \frac{5}{2}; S_{12} \overline{MP}^2\right) - \frac{3}{2} r_0^2 + O(R_0^4) \right] \quad (2.2.25)$$

Substituting Eq. (2.2.25) into Eq. (2.2.8) and the resulting equation into Eq. (2.2.6), we have

$$I_z = -\frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{3+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(2+\varepsilon_B)} \int_0^{\infty} dS_1 \int_0^{\infty} dS_2 (S_1 S_2)^{-3/2} \exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2)$$

$$\begin{aligned} & \left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \\ & \left[\varepsilon_B \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} + \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{3+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) \\ & \frac{2}{3} S_1 (MA_y MB_x - MA_x MB_y) \left[\frac{1}{S_{12}} {}_1F_1\left(1; \frac{5}{2}; S_{12} \overline{MP^2}\right) - \frac{3}{2} r_0^2 \right] + O(R_0^4) \end{aligned} \quad (2.2.26)$$

We change integral variables as follows: $S_{12} = z$, $\frac{S_1}{S_{12}} = w$, and Jacobian is $\frac{\partial(z,w)}{\partial(S_1,S_2)} = z$. We further separate

the integral over z as follows: $\int_0^\infty dz = \int_0^{a^2} dz + \int_{a^2}^\infty dz = a^2 \int_0^1 du + a^2 \int_0^1 du \frac{1}{u^2}$ with a similar manner as in the previous section. Then, we have the final formula as given by

$$\begin{aligned} I_z &= (MA_x MB_y - MA_y MB_x) \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{3+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(2+\varepsilon_B)} \int_0^1 dw w^{-1/2} (1-w)^{-3/2} \\ & \left\{ \int_0^1 du \frac{a^2}{(ua^2)^2} \exp[-wua^2 \overline{MA^2} - (1-w)ua^2 \overline{MB^2}] \right. \\ & \left[\frac{\zeta_A^2}{2wua^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wua^2 t_1^2}\right) \\ & \left[\varepsilon_B \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} + \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{3+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2 t_2^2}\right) \\ & \left[\frac{2}{3} {}_1F_1\left(1; \frac{5}{2}; ua^2 x_0\right) - ua^2 r_0^2 \right] \\ & + \int_0^1 du \frac{a^2}{u^2} \left(\frac{u}{a^2}\right)^2 \exp\left[-\frac{w}{u} a^2 \overline{MA^2} - \frac{1-w}{u} a^2 \overline{MB^2}\right] \\ & \left[\frac{u\zeta_A^2}{2wa^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{u\zeta_A^2}{4wa^2 t_1^2}\right) \\ & \left[\varepsilon_B \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} + \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{3+\varepsilon_B}} \right] \exp\left(-\frac{u\zeta_B^2}{4(1-w)a^2 t_2^2}\right) \\ & \left. \left[\frac{2}{3} {}_1F_1\left(1; \frac{5}{2}; \frac{a^2}{u} x_0\right) - \frac{a^2}{u} r_0^2 \right] \right\} + O(R_0^4) \end{aligned} \quad (2.2.27)$$

where x_0 is given by Eq. (2.1.47). The I_y can be given with replacing $MA_x MB_y - MA_y MB_x$ by $MA_z MB_x - MA_x MB_z$ in Eq. (2.2.27). The I_x can be given by doing that by $MA_y MB_z - MA_z MB_y$ in Eq. (2.2.27). The integral for $[0, 1]$ can be evaluated numerically with using the Gauss-Legendre quadrature. We use 64-point quadrature and obtain eight significant-figure precision as follows: $-\frac{i\hbar e}{c^2} I_z = 0.87572795(-5)i$, $-\frac{i\hbar e}{c^2} I_y = 0.0i$, and $-\frac{i\hbar e}{c^2} I_x = 0.61923317(-5)i$ for the case of three hydrogen atoms located at $\vec{M} = (0, 0, 0)$, $\vec{A} = (-\sqrt{8}/3, -\sqrt{8}/3, 2/3)$, and $\vec{B} = (-\sqrt{8}/3, \sqrt{8}/3, 2/3)$.

2.3 The term $i\vec{\sigma} \cdot (\vec{p} \times \vec{A} + \vec{A} \times \vec{p})$

We have

$$\langle \chi_{\mu A} | i\vec{\sigma} \cdot (\vec{p} \times \vec{A} + \vec{A} \times \vec{p}) | \chi_{\nu B} \rangle = \frac{Ze\hbar}{c^2} \sum_{\xi} \sum_{\eta} \sigma_{\xi} \mu_{M\eta} I_{\xi\eta}^{(3)} [\xi, \eta \in (x, y, z)] \quad (2.3.1)$$

where

$$I_{\xi\eta}^{(3)} = \frac{8}{\sqrt{\pi}r_0^5} \int d\vec{r}_M [\delta_{\xi\eta}(r_M^2 F_2 + r_0^2 F_1) - \xi\eta F_2] r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp(-\zeta_A r_A - \zeta_B r_B) \quad (2.3.2)$$

We evaluate $I_{zz}^{(3)}$ given by

$$I_{zz}^{(3)} = I_1^{(3)} + I_2^{(3)} \quad (2.3.3)$$

where

$$I_1^{(3)} = \frac{8}{\sqrt{\pi}r_0^5} \int d\vec{r}_M [(r_M^2 - z_M^2) F_2] r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp(-\zeta_A r_A - \zeta_B r_B) \quad (2.3.4)$$

and

$$I_2^{(3)} = \frac{8}{\sqrt{\pi}r_0^3} \int d\vec{r}_M F_1 r_A^{-\varepsilon_A} r_B^{-\varepsilon_B} \exp(-\zeta_A r_A - \zeta_B r_B) \quad (2.3.5)$$

The $I_1^{(3)}$ is very similar to Eq. (2.1.8). So, with a similar derivation to that from Eq. (2.1.8) to (2.1.45), we have

$$\begin{aligned} I_1^{(3)} &= \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)} \int_0^1 dw [w(1-w)]^{-3/2} \\ &\int_0^\infty dz z^{-2} \exp[-wz\overline{MA}^2 - (1-w)z\overline{MB}^2] \\ &\left[\frac{\zeta_A^2}{2wz} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wzt_1^2}\right) \\ &\left[\frac{\zeta_B^2}{2(1-w)z} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)zt_2^2}\right) \\ &\left\{ -[\gamma + \ln(zR_0^2)] + \frac{2}{3}zx_0 {}_2F_2\left(1, 1; 2, \frac{5}{2}; zx_0\right) \right. \\ &+ \frac{4b^5}{3\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{3/2} \exp(-b^2 uv) - \frac{5}{2}r_0^2 \left[\frac{2}{3}z^2x_0 - z\right] \\ &\left. - \frac{4}{15}zy_0 {}_1F_1\left(1; \frac{7}{2}; zx_0\right) \right\} + O(R_0^4) \end{aligned} \quad (2.3.6)$$

where $\gamma = 0.577215664901532860606512$ is the Euler constant, x_0 is given by Eq. (2.1.47) and y_0 is given by Eq. (2.1.48). The derivation for $I_2^{(3)}$ is also similar to the above. Thus, we use the Gaussian-transform, Eq. (2.1.9), and have

$$\begin{aligned} I_2^{(3)} &= \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{4\pi\Gamma(1+\varepsilon_A)\Gamma(1+\varepsilon_B)} \int_0^\infty dS_1 \int_0^\infty dS_2 (S_1 S_2)^{-3/2} \\ &\left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \\ &\left[\frac{\zeta_B^2}{2S_2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) I_{2a}^{(3)} \end{aligned} \quad (2.3.7)$$

where

$$I_{2a}^{(3)} = \frac{8}{\sqrt{\pi}r_0^3} \int d\vec{r}_M F_1 \exp(-S_1 r_A^2 - S_2 r_B^2) \quad (2.3.8)$$

We use the Gaussian product rule, Eq. (2.1.12), the Sack's formula, Eq. (2.1.13), and the Gaussian product rule again, Eq. (2.1.14). Then, we have

$$I_{2a}^{(3)} = 4\pi \exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2) I_{2b}^{(3)} \quad (2.3.9)$$

where

$$\begin{aligned} I_{2b}^{(3)} &= \frac{8}{\sqrt{\pi} r_0^3} \int d\vec{r}_M F_1 \exp(-S_{12} r_M^2) \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) \\ &= \frac{8}{\sqrt{\pi} r_0^3} \int_0^\infty dr_M r_M^2 F_1 \exp(-S_{12} r_M^2) \sum_{l=0} i_l (2S_{12} \overline{MP} r_M) \\ &\quad \int d\widehat{r}_M \sum_{m=-l}^l Y_l^m(\widehat{MP})^* Y_l^m(\widehat{r}_M) \end{aligned} \quad (2.310)$$

The angular part can be evaluated by using Eq. (2.1.18), thus, we have

$$I_{2b}^{(3)} = \frac{8}{\sqrt{\pi} r_0^3} \int_0^\infty dr_M r_M^2 F_1 \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M) \quad (2.3.11)$$

We separate inner and outer part as described as following to Eq. (2.1.21) and have

$$I_{2b}^{(3)} = I_{2b}^{(3)in} + I_{2b}^{(3)out} \quad (2.3.12)$$

where

$$I_{2b}^{(3)in} = \frac{8}{\sqrt{\pi} r_0^3} \int_0^{R_0} dr_M r_M^2 F_1 \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M) \quad (2.3.13)$$

and

$$I_{2b}^{(3)out} = \frac{8}{\sqrt{\pi} r_0^3} \int_{R_0}^\infty dr_M r_M^2 F_1 \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M) \quad (2.3.14)$$

We evaluate $I_{2b}^{(3)in}$. Using Eq. (2.1.23) and (2.1.27) for (2.3.13), we have

$$I_{2b}^{(3)in} = \sum_{k=0} \frac{(-1/r_0^2)^k (3/2)_k}{k! (5/2)_k} \sum_{j=0} \frac{(S_{12}^2 \overline{MP}^2)^j}{j! (3/2)_j} I_{2c}^{(3)in} \quad (2.3.15)$$

where

$$\begin{aligned} I_{2c}^{(3)in} &= \frac{8}{3\sqrt{\pi} r_0^3} \int_0^{R_0} dr_M r_M^{2k+2j+2} \exp(-S_{12} r_M^2) = \frac{4}{3\sqrt{\pi} r_0^3} \int_0^{R_0^2} dx x^{k+j+1/2} \exp(-S_{12} x) \\ &= \frac{4}{3\sqrt{\pi} r_0^3} \frac{\gamma(k+j+3/2)}{S_{12}^{k+j+3/2}} \end{aligned} \quad (2.3.16)$$

Using Eq. (2.1.30) for (2.3.16), we have

$$I_{2c}^{(3)in} = \frac{4}{3\sqrt{\pi} r_0^3} R_0^{2k+2j+3} \frac{\Gamma(k+j+3/2)}{\Gamma(k+j+5/2)} {}_1F_1\left(j+k+\frac{3}{2}; j+k+\frac{5}{2}; -S_{12} R_0^2\right) \quad (2.3.17)$$

Substituting Eq. (2.3.17) into (2.3.15), we have

$$\begin{aligned} I_{2b}^{(3)in} &= \frac{4b^3}{3\sqrt{\pi}} \sum_{k=0} \frac{(-b^2)^k (3/2)_k}{k! (5/2)_k} \sum_{j=0} \frac{(S_{12}^2 \overline{MP}^2 R_0^2)^j}{j! (3/2)_j} \left\{ \frac{\Gamma(k+j+3/2)}{\Gamma(k+j+5/2)} + \left[\delta_{j1} \frac{2}{3} S_{12}^2 \overline{MP}^2 \frac{\Gamma(k+j+3/2)}{\Gamma(k+j+5/2)} - \right. \right. \\ &\quad \left. \delta_{j0} S_{12} \frac{\Gamma(k+j+5/2)}{\Gamma(k+j+7/2)} \right] R_0^2 + O(R_0^4) \left\} = \frac{4b^3}{3\sqrt{\pi}} \sum_{k=0} \frac{(-b^2)^k (3/2)_k}{k! (5/2)_k} \left\{ \frac{\Gamma(k+3/2)}{\Gamma(k+5/2)} + \left[\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12} \right] R_0^2 \frac{\Gamma(k+5/2)}{\Gamma(k+7/2)} + \right. \\ &\quad \left. O(R_0^4) \right\} = \frac{4b^3}{3\sqrt{\pi}} \left\{ \frac{\Gamma(3/2)}{\Gamma(5/2)} {}_2F_2\left(\frac{3}{2}, \frac{3}{2}; \frac{5}{2}, \frac{5}{2}; -b^2\right) \right. \\ &\quad \left. + \frac{\Gamma(3/2)}{\Gamma(7/2)} {}_1F_1\left(\frac{3}{2}; \frac{7}{2}; -b^2\right) \left[\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12} \right] R_0^2 + O(R_0^4) \right\} \end{aligned} \quad (2.3.18)$$

It is easy to derive the integral representation of the function, ${}_2F_2$ as given by

$$\frac{\Gamma(3/2)}{\Gamma(5/2)} {}_2F_2\left(\frac{3}{2}, \frac{3}{2}; \frac{5}{2}, \frac{5}{2}; -b^2\right) = \frac{\Gamma(5/2)}{\Gamma(3/2)} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv) \quad (2.3.19)$$

Using the asymptotic expansion of the function ${}_1F_1$ [23], we have

$$\frac{\Gamma(3/2)}{\Gamma(7/2)} {}_1F_1\left(\frac{3}{2}; \frac{7}{2}; -b^2\right) = \frac{\Gamma(3/2)}{b^3} \left(1 - \frac{3}{2b^2}\right) \quad (2.3.20)$$

Substituting Eq. (2.3.19) and (2.3.20) into (2.3.18), we have

$$I_{2b}^{(3)in} = \frac{2b^2}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv)$$

$$\left[\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12}\right] R_0^2 \left(1 - \frac{3}{2b^2}\right) + O(R_0^4) \quad (2.3.21)$$

Next, we evaluate $I_{2b}^{(3)out}$. Using Eq. (2.1.22) with $m=1$ and (2.1.27) for (2.3.14), we have

$$I_{2b}^{(3)out} = 2 \int_{R_0}^{\infty} dr_M \frac{1}{r_M} \exp(-S_{12} r_M^2) i_0(2S_{12} \overline{MP} r_M)$$

$$= 2 \sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} \int_{R_0}^{\infty} dr_M r_M^{2j-1} \exp(-S_{12} r_M^2)$$

$$= \sum_{j=0}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} \int_{R_0^2}^{\infty} dx x^{j-1} \exp(-S_{12} x)$$

$$= \Gamma(0, S_{12} R_0^2) + \sum_{j=1}^{\infty} \frac{(S_{12}^2 \overline{MP}^2)^j}{j!(3/2)_j} \frac{\Gamma(j, S_{12} R_0^2)}{S_{12}^j}$$

$$= \Gamma(0, S_{12} R_0^2) + \frac{2}{3} S_{12} \overline{MP}^2 \sum_{j'=0}^{\infty} \frac{(S_{12} \overline{MP}^2)^{j'}}{(2)_{j'} (5/2)_{j'}} \Gamma(j' + 1, S_{12} R_0^2) \quad (2.3.22)$$

Using the formula number 8.352.5 of the mathematical formula book [28], we have

$$\Gamma(0, S_{12} R_0^2) = -E_i(-S_{12} R_0^2), \quad (2.3.23)$$

where $E_i(-x)$ is the exponential integral, which can be written as [23]

$$E_i(-x) = \gamma + \ln(x) + \sum_{n=1}^{\infty} \frac{(-x)^n}{n n!} \quad (2.3.24)$$

Then, we have

$$\Gamma(0, S_{12} R_0^2) = -E_i(-S_{12} R_0^2) = -[\gamma + \ln(S_{12} R_0^2)] - S_{12} R_0^2 + O(R_0^4) \quad (2.3.25)$$

Using Eq. (2.1.40) for the second term of Eq. (2.3.22), we have

$$\Gamma(j' + 1, S_{12} R_0^2) = \Gamma(j' + 1) - \frac{(S_{12} R_0^2)^{j'+1}}{j'+1} + O(R_0^4) \quad (2.3.26)$$

Substituting Eq. (2.3.25) and (2.3.26) into (2.3.22), we have

$$I_{2b}^{(3)out} = -[\gamma + \ln(S_{12} R_0^2)] - S_{12} R_0^2$$

$$+ \frac{2}{3} S_{12} \overline{MP}^2 {}_2F_2\left(1, 1; 2, \frac{5}{2}; S_{12} R_0^2\right) - \frac{2}{3} S_{12}^2 \overline{MP}^2 R_0^2 + O(R_0^4) \quad (2.3.27)$$

Substituting Eq. (2.3.21) and (2.3.27) into (2.3.12), we have

$$I_{2b}^{(3)} = -[\gamma + \ln(S_{12} R_0^2)] + \frac{2}{3} S_{12} \overline{MP}^2 {}_2F_2\left(1, 1; 2, \frac{5}{2}; S_{12} R_0^2\right) + \frac{2b^2}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv) -$$

$$\frac{3}{2} \left[\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12}\right] R_0^2 + O(R_0^4) \quad (2.3.28)$$

Substituting Eq. (2.3.28) into (2.3.9), and doing the resulting equation into (2.3.7), we have

$$\begin{aligned}
 I_2^{(3)} &= \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(1+\varepsilon_B)} \int_0^\infty dS_1 \int_0^\infty dS_2 (S_1 S_2)^{-3/2} \exp(-S_1 \overline{MA}^2 - S_2 \overline{MB}^2) \\
 &\left[\frac{\zeta_A^2}{2S_1} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4S_1 t_1^2}\right) \\
 &\left[\frac{\zeta_B^2}{2S_2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4S_2 t_2^2}\right) \\
 &\left\{ -[\gamma + \ln(S_{12} R_0^2)] + \frac{2}{3} S_{12} \overline{MP}^2 {}_2F_2\left(1, 1; 2, \frac{5}{2}; S_{12} R_0^2\right) \right. \\
 &\left. + \frac{2b^2}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv) - \frac{3}{2} \left[\frac{2}{3} S_{12}^2 \overline{MP}^2 - S_{12} \right] r_0^2 \right\} \quad (2.3.29)
 \end{aligned}$$

We change integral variables as follows: $S_{12} = z$ and $\frac{S_1}{S_{12}} = w$, and Jacobian is $\frac{\partial(z,w)}{\partial(S_1,S_2)} = z$. Then, we have

a similar equation to Eq. (2.3.6). Substituting the resulting equation and (2.3.6) into (2.3.3), we have

$$\begin{aligned}
 I_{zz}^{(3)} &= \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(1+\varepsilon_B)} \int_0^1 dw [w(1-w)]^{-3/2} \\
 &\int_0^\infty dz z^{-2} \exp[-wz \overline{MA}^2 - (1-w)z \overline{MB}^2] \\
 &\left[\frac{\zeta_A^2}{2wz} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wz t_1^2}\right) \\
 &\left[\frac{\zeta_B^2}{2(1-w)z} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)z t_2^2}\right) \\
 &\left[-2\gamma - 2\ln(z R_0^2) + \frac{4}{3} z x_0 {}_2F_2\left(1, 1; 2, \frac{5}{2}; z x_0\right) - \frac{4}{15} z y_0 {}_1F_1\left(1; \frac{7}{2}; z x_0\right) \right. \\
 &\left. + \frac{2b^3}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv) + \frac{4b^5}{3\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{3/2} \exp(-b^2 uv) \right. \\
 &\left. - 4r_0^2 \left[\frac{2}{3} z^2 x_0 - z \right] \right] + O(R_0^4) \quad (2.3.30)
 \end{aligned}$$

The value of the integral $\frac{2b^3}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv)$ is a constant, which can be evaluated 512-point Gauss-Legendre quadrature and we obtained previously [20] as

$$\frac{2b^3}{\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{1/2} \exp(-b^2 uv) = 3.855330324 \quad (2.3.31)$$

Also, we did that [20]

$$\frac{4b^5}{3\sqrt{\pi}} \int_0^1 du \int_0^1 dv (uv)^{3/2} \exp(-b^2 uv) = 3.188663658 \quad (2.3.32)$$

So, we set $C_0 = 3.855330720 + 3.188663658 - 2\gamma = 5.889562652$. We separate the integral over z as follows $\int_0^\infty dz = \int_0^{a^2} dz + \int_{a^2}^\infty dz = a^2 \int_0^1 du + a^2 \int_0^1 du \frac{1}{u^2}$ as doing at Eq. (2.1.50) and have the final

formula as given by

$$\begin{aligned}
 I_{zz}^{(3)} &= \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} \\
 &\left\{ \int_0^1 du \frac{a^2}{(ua^2)^2} \exp[-wua^2 \overline{MA}^2 - (1-w)ua^2 \overline{MB}^2] \right. \\
 &\left[\frac{\zeta_A^2}{2wua^2} \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^2 t_1^2}\right) \\
 &\left[\frac{\zeta_B^2}{2(1-w)ua^2} \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[-2 \ln(ua^2 R_0^2) + \frac{4}{3} ua^2 x_0 {}_2F_2\left(1, 1; 2, \frac{5}{2}; ua^2 x_0\right) \right. \\
 &\left. - \frac{4}{15} ua^2 y_0 {}_1F_1\left(1; \frac{7}{2}; ua^2 x_0\right) + C_0 - 4r_0^2 \left[\frac{2}{3} u^2 a^4 x_0 - ua^2\right] \right] \\
 &+ \int_0^1 du \frac{a^2}{u^2} \left(\frac{u}{a^2}\right)^2 \exp\left[-\frac{w}{u} a^2 \overline{MA}^2 - \frac{1-w}{u} a^2 \overline{MB}^2\right] \\
 &\left[\frac{u\zeta_A^2}{2wa^2} \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) \\
 &\left[\frac{u\zeta_B^2}{2(1-w)a^2} \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[-2 \ln\left(\frac{a^2}{u} R_0^2\right) + \frac{4}{3} \frac{a^2}{u} x_0 {}_2F_2\left(1, 1; 2, \frac{5}{2}; \frac{a^2}{u} x_0\right) \right. \\
 &\left. - \frac{4}{15} \frac{a^2}{u} y_0 {}_1F_1\left(1; \frac{7}{2}; \frac{a^2}{u} x_0\right) + C_0 - 4r_0^2 \left[\frac{2}{3} \frac{a^4}{u^2} x_0 - \frac{a^2}{u}\right] \right] \left. \right\} \quad (2.3.33)
 \end{aligned}$$

where x_0 is given by Eq. (2.1.47) and y_0 is given by Eq. (2.1.48).

The $I_{yy}^{(3)}$ can be given by replacing y_0 by $\frac{-1}{2}(y_0 + \sqrt{3}y_2)$ in Eq. (2.3.33), where y_2 is given by Eq. (2.1.51). The $I_{xx}^{(3)}$ can be given by doing y_0 by $\frac{-1}{2}(y_0 - \sqrt{3}y_2)$ in Eq. (2.3.33). With a similar derivation to the above, we have the final formula of $I_{xy}^{(3)}$ as given by

$$\begin{aligned}
 I_{xy}^{(3)} &= \frac{\zeta_A^{1+\varepsilon_A} \zeta_B^{1+\varepsilon_B}}{\Gamma(1+\varepsilon_A) \Gamma(1+\varepsilon_B)} \int_0^1 dw [w(1-w)]^{-3/2} \\
 &[wMA_x + (1-w)MB_x][wMA_y + (1-w)MB_y] \\
 &\left\{ \int_0^1 du \frac{a^2}{(ua^2)^2} \exp[-wua^2 \overline{MA}^2 - (1-w)ua^2 \overline{MB}^2] \right. \\
 &\left[\frac{\zeta_A^2}{2wua^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp\left(-\frac{\zeta_A^2}{4wua^2 t_1^2}\right) \\
 &\left[\frac{\zeta_B^2}{2(1-w)ua^2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp\left(-\frac{\zeta_B^2}{4(1-w)ua^2 t_2^2}\right) \\
 &\left[-\frac{2}{5} ua^2 {}_1F_1\left(1; \frac{7}{2}; ua^2 x_0\right) - u^2 a^4 r_0^2 \right] \left. \right\}
 \end{aligned}$$

$$\begin{aligned}
& + \int_0^1 du \frac{a^2}{u^2} \left(\frac{u}{a^2} \right)^2 \exp \left[-\frac{w}{u} a^2 \overline{MA}^2 - \frac{1-w}{u} a^2 \overline{MB}^2 \right] \\
& \left[\frac{u \zeta_A^2}{2wa^2} \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{4+\varepsilon_A}} - \int_0^1 dt_1 \frac{(1-t_1)^{\varepsilon_A}}{t_1^{2+\varepsilon_A}} \right] \exp \left(-\frac{u \zeta_A^2}{4wa^2 t_1^2} \right) \\
& \left[\frac{u \zeta_B^2}{2(1-w)a^2} \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{4+\varepsilon_B}} - \int_0^1 dt_2 \frac{(1-t_2)^{\varepsilon_B}}{t_2^{2+\varepsilon_B}} \right] \exp \left(-\frac{u \zeta_B^2}{4(1-w)a^2 t_2^2} \right) \\
& \left[-\frac{2}{5} \frac{a^2}{u} {}_1F_1 \left(1; \frac{7}{2}; ua^2 x_0 \right) - \frac{a^4}{u^2} r_0^2 \right] \} \quad (2.3.34)
\end{aligned}$$

The $I_{yz}^{(3)}$ can be given with replacing $[wMA_x + (1-w)MB_x][wMA_y + (1-w)MB_y]$ by $[wMA_y + (1-w)MB_y][wMA_z + (1-w)MB_z]$ in Eq. (2.3.34). The $I_{zx}^{(3)}$ can be given with doing that by $[wMA_z + (1-w)MB_z][wMA_x + (1-w)MB_x]$. Of course, $I_{\eta\xi}^{(3)} = I_{\xi\eta}^{(3)}$. The integral for $[0, 1]$ can be evaluated numerically with using the Gauss-Legendre quadrature. We use 64-point quadrature and obtain $\frac{\hbar e}{c^2} I_{zz}^{(3)} = 0.18611832(-3)$, $\frac{\hbar e}{c^2} I_{yy}^{(3)} = 0.18588045(-3)$, $\frac{\hbar e}{c^2} I_{xx}^{(3)} = 0.18556659(-3)$, $\frac{\hbar e}{c^2} I_{xy}^{(3)} = \frac{\hbar e}{c^2} I_{yz}^{(3)} = 0.0$, and $\frac{\hbar e}{c^2} I_{zx}^{(3)} = 0.78026306(-6)$ for the case of three hydrogen atoms located at $\vec{M} = (0, 0, 0)$, $\vec{A} = (-\sqrt{8}/3, -\sqrt{8}/3, 2/3)$, and $\vec{B} = (-\sqrt{8}/3, \sqrt{8}/3, 2/3)$. Thus, we have eight significant-figure precision.

3. Conclusion

The author derived the Gaussian-transform for the Dirac wave function in a previous article [18] and for the derivative of the Dirac wave function in a previous article [19]. Using these transform formulas, multicenter molecular integrals over Dirac wave functions can be derived for the relativistic kinetic energy terms. These integral formulas can be derived for the first time.

In order to solve the molecular matrix Dirac equation, necessary integral formulas to be derived are remaining, which are written as $(W_m)_{\mu\nu} = \frac{1}{4m_e^2 c^2} \langle \chi_\mu | \vec{\sigma} \cdot (\vec{p} + \vec{A}) V \vec{\sigma} \cdot (\vec{p} + \vec{A}) | \chi_\nu \rangle$. Projects to derive such integral formulas are in progress.

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