1997

Computational methods for three-electron atomic systems in Hylleraas coordinates

Z. C. Yan

Gordon W. F. Drake
University of Windsor

Computational methods for three-electron atomic systems in Hylleraas coordinates

1997 J. Phys. B: At. Mol. Opt. Phys. 30 4723

(http://iopscience.iop.org/0953-4075/30/21/012)

J. Phys. B: At. Mol. Opt. Phys. **30** (1997) 4723–4750. Printed in the UK PII: S0953-4075(97)83525-0

Computational methods for three-electron atomic systems in Hylleraas coordinates

Zong-Chao Yan† and G W F Drake‡

† Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA
‡ Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Received 21 April 1997

Abstract. General methods for evaluating three-electron integrals in Hylleraas coordinates are given. Formulae are obtained for the matrix elements of various operators arising in Hylleraas-type variational calculations for states of arbitrary angular momentum. For the calculations of Breit interaction, a number of reduction relations are developed for the elimination of singularities in some singular integrals. A numerically stable scheme is presented for the case when one of the powers of r_{ij} is -2.

1. Introduction

In atomic structure calculations, one important issue is how to build electron–electron correlation into the basis sets. Variational calculations in Hylleraas coordinates, which include explicitly powers of the inter-electronic distances $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$, are well established as providing the most precise wavefunctions for two- and three-electron atomic systems. Recently, a series of high-precision Hylleraas-type calculations have been done [1–4] for the lithium energy levels in S, P, and D states and other properties, such as the oscillator strengths, the Fermi contact terms, the dispersion coefficients, etc. The success of these calculations relies largely on efficient algorithms for evaluating both radial and angular integrals. The radial integrals converge very slowly in general, ultimately leading to calculations that are extremely time consuming. For nonrelativistic eigenvalue calculations, the problem of slow convergence has been solved recently [5], using an asymptotic expansion method. This method has proven to be very successful in accelerating the rate of convergence. In calculations of the Breit interaction, one needs to deal with several types of singular integrals. One type is integrals containing r_{ij}^{-2} in the integrands. Although integrals of this type are convergent, they converge as slowly as the series $\sum_k k^{-2}$. Previous work on this problem can be found in [6–9]. However, problems of computational efficiency remain. Another type is those with integrands more singular than r_{ij}^{-2}. These integrals are generally divergent individually, but they always occur in combinations with other similar terms such that the sum is convergent. Thus, the main issues for the radial integrals are how to improve the rate of convergence for slowly convergent integrals, and how to eliminate the singularities analytically among divergent integrals. The remaining angular parts of the integrals are always convergent. However, the evaluation of these integrals involving high angular momentum could become very complicated. To the best of our knowledge, for the three-electron case in Hylleraas coordinates, there is no published work which discusses the reduction of singularities and the simplification of angular integrals with arbitrary angular momentum.

The purpose of this paper is to present a complete description for the variational calculations of three-electron systems in Hylleraas coordinates. The variational basis sets in Hylleraas coordinates are first introduced in section 2 for both doublet and quartet states. The explicit form of the Hamiltonian in Hylleraas coordinates is given. The evaluation of matrix elements of operators with various angular structures is presented in section 3. The singular integrals are discussed in section 4, including a derivation of a set of reduction formulae and schemes for computing integrals with r_{ij}^{-2} singularity. The appendix deals with two auxiliary infinite series.

2. Variational basis sets

2.1. Basis sets

The variational basis function is

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)\chi(1, 2, 3), \tag{1}$$

where the orbital part ϕ is constructed from Hylleraas-type coordinates

$$\phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} \mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) \tag{2}$$

with

$$\mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \sum_{\text{all } m_i} \langle \ell_1 m_1; \ell_2 m_2 | \ell_1 \ell_2; \ell_{12} m_{12}\rangle \times \langle \ell_{12} m_{12}; \ell_3 m_3 | \ell_{12}\ell_3; L M_L\rangle Y_{\ell_1 m_1}(\boldsymbol{r}_1) Y_{\ell_2 m_2}(\boldsymbol{r}_2) Y_{\ell_3 m_3}(\boldsymbol{r}_3) \tag{3}$$

being a vector-coupled product of spherical harmonics for the three electrons to form a state of total angular momentum L. The spin part χ can be either

$$\chi(1, 2, 3) = \chi^{(\mathrm{d})}(1, 2, 3) = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \tag{4}$$

for the spin angular momentum $\frac{1}{2}$ (doublet), or

$$\chi(1, 2, 3) = \chi^{(\mathrm{q})}(1, 2, 3) = \alpha(1)\alpha(2)\alpha(3) \tag{5}$$

for the spin angular momentum $\frac{3}{2}$ (quartet). The superscripts d and q are used to denote the doublet and quartet states. The variational wavefunction is a linear combination of the functions Φ antisymmetrized by the three-particle antisymmetrizer

$$\mathcal{A} = \sum_{i=1}^{6} \epsilon_i \mathcal{A}_i \tag{6}$$

where $\mathcal{A}_1 = (1)$, $\mathcal{A}_2 = (12)$, $\mathcal{A}_3 = (13)$, $\mathcal{A}_4 = (23)$, $\mathcal{A}_5 = (123)$, $\mathcal{A}_6 = (132)$, and $\epsilon_i = 1$ with $i = 1, 5, 6$; $\epsilon_i = -1$ with $i = 2, 3, 4$. The variational basis set can thus be formed by $\{\omega_i\}_{i=1}^{N}$, where N is the size of the basis set and ω_i is

$$\omega_i = \sum_{p=1}^{6} \phi_i^p \chi_p. \tag{7}$$

In (7), $\phi_i^p = \mathcal{A}_p \phi_i$ and $\chi_p = \epsilon_p \mathcal{A}_p \chi$. It is easy to show that, for a symmetric spin-independent operator O, the following expressions hold:

$$\langle \omega_i | O | \omega_j \rangle^{(\mathrm{d})} = 12 O_{ij}^{11} + 12 O_{ij}^{12} - 6 O_{ij}^{13} - 6 O_{ij}^{14} - 6 O_{ij}^{15} - 6 O_{ij}^{16} \tag{8}$$

$$\langle \omega_i | O | \omega_j \rangle^{(\mathrm{q})} = 6 O_{ij}^{11} - 6 O_{ij}^{12} - 6 O_{ij}^{13} - 6 O_{ij}^{14} + 6 O_{ij}^{15} + 6 O_{ij}^{16}, \tag{9}$$

where $O_{ij}^{p'p} = \langle \phi_i^{p'} | O | \phi_j^p \rangle$. Thus, only the direct–direct term and five direct–exchange terms need be calculated.

The explicit form of ϕ_i^p can be written in the form

$$\phi^p(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \mathcal{A}_p(r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3}) \times \sum_{\text{all } m_i} \Omega(\ell_1, \ell_2, \ell_{12}, \ell_3, L, M_L, m_1, m_2, m_3) Y_{\ell_a m_a}(\boldsymbol{r}_1) Y_{\ell_b m_b}(\boldsymbol{r}_2) Y_{\ell_c m_c}(\boldsymbol{r}_3), \tag{10}$$

where

$$\Omega(\ell_1, \ell_2, \ell_{12}, \ell_3, L, M_L, m_1, m_2, m_3) = (-1)^{\ell_1 - \ell_2 + m_{12} + \ell_{12} - \ell_3 + M_L} (\ell_{12}, L)^{1/2} \times \begin{pmatrix} \ell_1 & \ell_2 & \ell_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix} \begin{pmatrix} \ell_{12} & \ell_3 & L \\ m_{12} & m_3 & -M_L \end{pmatrix} \tag{11}$$

with the notation $(l, m, n, \ldots) = (2l+1)(2m+1)(2n+1)\ldots$. Here, the $3j$ symbol is related to the corresponding Clebsch–Gordan coefficient by [10]

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} = \frac{(-1)^{j_1 - j_2 + m}}{\sqrt{2j+1}} \langle j_1 m_1; j_2 m_2 | j_1 j_2; jm \rangle. \tag{12}$$

In (10), the subscripts a, b, and c can be determined according to the definition of antisymmetrizer (6) as follows:

$$\begin{aligned}
(a, b, c)^{p=1} &= (1, 2, 3) \\
(a, b, c)^{p=2} &= (2, 1, 3) \\
(a, b, c)^{p=3} &= (3, 2, 1) \\
(a, b, c)^{p=4} &= (1, 3, 2) \\
(a, b, c)^{p=5} &= (3, 1, 2) \\
(a, b, c)^{p=6} &= (2, 3, 1).
\end{aligned} \tag{13}$$

Note that the angular parts of ϕ^2, ϕ^5, and ϕ^6 can be formally obtained from the corresponding ϕ^1, ϕ^3, and ϕ^4 by simply interchanging ℓ_1 and ℓ_2 and by multiplying by a phase factor $(-1)^{\ell_1+\ell_2+\ell_{12}}$. As for the radial parts of basis functions, the operation of $\mathcal{A}_p$ is equivalent to permuting the powers of r_i and r_{ij} as well as the nonlinear coefficients of r_i. However, since the radial parts do not affect the evaluation of angular integrals, for the sake of simplicity, we may drop $\mathcal{A}_p$ in equation (10).

2.2. Hamiltonian

The nonrelativistic Hamiltonian for three-electron atoms, including the mass polarization terms, is given by

$$H = \sum_{i=1}^{3} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i>j}^{3} \frac{1}{r_{ij}} - \frac{\mu}{M} \sum_{i>j}^{3} \nabla_i \cdot \nabla_j, \tag{14}$$

in units of $2R_M$, where $R_M = (1 - \mu/M) R_\infty$, M is the nuclear mass, $\mu = mM/(m+M)$ is the electron reduced mass, and Z is the nuclear charge. For the basis set (1), the gradient operator ∇_1 can be separated according to

$$\nabla_1 = \frac{\boldsymbol{r}_1}{r_1} \frac{\partial}{\partial r_1} + \frac{\boldsymbol{r}_{12}}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{\boldsymbol{r}_{13}}{r_{13}} \frac{\partial}{\partial r_{13}} + \nabla_1^Y, \tag{15}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, and ∇_i^Y is understood to act only on spherical harmonics. Similarly, ∇_2 and ∇_3 can be obtained by cyclically permuting the indices 1, 2, 3. Applying (15) twice, the Laplacian operator for particle 1 can be written in the form

$$\begin{aligned}\nabla_1^2 = {}& \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{\partial^2}{\partial r_{31}^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{2}{r_{31}}\frac{\partial}{\partial r_{31}} + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} \\ & + \frac{r_1^2 - r_3^2 + r_{31}^2}{r_1 r_{31}}\frac{\partial^2}{\partial r_1 \partial r_{31}} + \frac{r_{12}^2 + r_{31}^2 - r_{23}^2}{r_{12} r_{31}}\frac{\partial^2}{\partial r_{12}\partial r_{31}} - \frac{\ell_1(\ell_1+1)}{r_1^2} \\ & - 2(\boldsymbol{r}_2 \cdot \nabla_1^Y)\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} - 2(\boldsymbol{r}_3 \cdot \nabla_1^Y)\frac{1}{r_{31}}\frac{\partial}{\partial r_{31}}. \end{aligned} \tag{16}$$

The corresponding results for ∇_2^2 and ∇_3^2 can be obtained by permuting the subscripts 1, 2, and 3. $\nabla_i \cdot \nabla_j$ can also be worked out in a similar way. Finally, the Hamiltonian can be expressed in the form

$$H = T - \sum_{i=1}^{3} \frac{Z}{r_i} + \sum_{i>j}^{3} \frac{1}{r_{ij}}, \tag{17}$$

where the operator T is

$$\begin{aligned} T = {}& -\frac{1}{2}\sum_{i=1}^{3}\left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} - \frac{\ell_i(\ell_i+1)}{r_i^2}\right) - \frac{1}{2}\left(1 - \frac{\mu}{M}\right)\left[\sum_{i>j}^{3}\left(2\frac{\partial^2}{\partial r_{ij}^2} + \frac{4}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right)\right. \\ & + \sum_{i\neq j}^{3} \frac{r_i^2 - r_j^2 + r_{ij}^2}{r_i r_{ij}}\frac{\partial^2}{\partial r_i \partial r_{ij}} + \frac{r_{31}^2 + r_{12}^2 - r_{23}^2}{r_{31} r_{12}}\frac{\partial^2}{\partial r_{31}\partial r_{12}} \\ & \left. + \frac{r_{12}^2 + r_{23}^2 - r_{31}^2}{r_{12} r_{23}}\frac{\partial^2}{\partial r_{12}\partial r_{23}} + \frac{r_{23}^2 + r_{31}^2 - r_{12}^2}{r_{23} r_{31}}\frac{\partial^2}{\partial r_{23}\partial r_{31}}\right] \\ & - \frac{\mu}{M}\sum_{i>j}^{3} \frac{r_i^2 + r_j^2 - r_{ij}^2}{2 r_i r_j}\frac{\partial^2}{\partial r_i \partial r_j} \\ & + \sum_{i>j}^{3}\left[\left(1 - \frac{\mu}{M}\right)\frac{r_i}{r_j r_{ij}}\frac{\partial}{\partial r_{ij}} - \frac{\mu}{M}\frac{1}{r_j}\frac{\partial}{\partial r_i}\right](\hat{\boldsymbol{r}}_i \cdot \hat{\nabla}_j^Y) \\ & + \sum_{i>j}^{3}\left[\left(1 - \frac{\mu}{M}\right)\frac{r_j}{r_i r_{ji}}\frac{\partial}{\partial r_{ji}} - \frac{\mu}{M}\frac{1}{r_i}\frac{\partial}{\partial r_j}\right](\hat{\boldsymbol{r}}_j \cdot \hat{\nabla}_i^Y) \\ & - \frac{\mu}{M}\sum_{i>j}^{3}\frac{1}{r_i r_j}(\hat{\nabla}_i^Y \cdot \hat{\nabla}_j^Y). \end{aligned} \tag{18}$$

In (18), $\hat{\boldsymbol{r}}_i = \boldsymbol{r}_i / r_i$ and $\hat{\nabla}_i^Y = r_i \nabla_i^Y$.

3. Evaluation of matrix elements

3.1. Basic integral

Consider the following basic integral

$$\begin{aligned} & I(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_1 m_1, \ell_2 m_2, \ell_3 m_3;\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31};\, \alpha, \beta, \gamma) \\ & \quad = \int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, \mathrm{d}\boldsymbol{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} \\ & \quad \times Y_{\ell_1' m_1'}^*(\boldsymbol{r}_1) Y_{\ell_2' m_2'}^*(\boldsymbol{r}_2) Y_{\ell_3' m_3'}^*(\boldsymbol{r}_3) Y_{\ell_1 m_1}(\boldsymbol{r}_1) Y_{\ell_2 m_2}(\boldsymbol{r}_2) Y_{\ell_3 m_3}(\boldsymbol{r}_3). \end{aligned} \tag{19}$$

The interelectron coordinates r_{ij} can be expanded according to

$$r_{12}^{j} = \sum_{q=0}^{M_{12}} P_q(\cos\theta_{12}) \sum_{k=0}^{L_{12}} C_{jqk} r_{12<}^{q+2k} r_{12>}^{j-q-2k}, \tag{20}$$

as derived by Perkins [11], where, for even values of j, $M_{12} = \frac{1}{2}j$, $L_{12} = \frac{1}{2}j - q$; for odd values of j, $M_{12} = \infty$, $L_{12} = \frac{1}{2}(j+1)$. Also in (20), $r_{12<} = \min(r_1, r_2)$, $r_{12>} = \max(r_1, r_2)$, and the coefficients are given by

$$C_{jqk} = \frac{2q+1}{j+2}\binom{j+2}{2k+1} \prod_{t=0}^{S_{qj}} \frac{2k+2t-j}{2k+2q-2t+1}, \tag{21}$$

where $S_{qj} = \min(q-1, \frac{1}{2}(j+1))$. After expanding each of the $r_{\mu\nu}^{j_{\mu\nu}}$ in (19), we obtain

$$\begin{aligned} & I(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_1 m_1, \ell_2 m_2, \ell_3 m_3; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma) \\ &\quad = \sum_{q_{12}=0}^{M_{12}} \sum_{q_{23}=0}^{M_{23}} \sum_{q_{31}=0}^{M_{31}} \sum_{k_{12}=0}^{L_{12}} \sum_{k_{23}=0}^{L_{23}} \sum_{k_{31}=0}^{L_{31}} \int_0^\infty \int_0^\infty \int_0^\infty \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r_3 r_1^{j_1+2} r_2^{j_2+2} r_3^{j_3+2} \\ &\quad \times \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} F(jqk)_{12} F(jqk)_{23} F(jqk)_{31} \\ &\quad \times I_{\mathrm{ang}}(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_1 m_1, \ell_2 m_2, \ell_3 m_3; q_{12}, q_{23}, q_{31}), \end{aligned} \tag{22}$$

where $F(jqk)_{ij}$ are defined by

$$F(jqk)_{12} = C_{j_{12}q_{12}k_{12}} r_{12<}^{q_{12}+2k_{12}} r_{12>}^{j_{12}-q_{12}-2k_{12}}, \text{ etc} \tag{23}$$

and I_{ang} is the angular integral defined by

$$\begin{aligned} & I_{\mathrm{ang}}(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_1 m_1, \ell_2 m_2, \ell_3 m_3; q_{12}, q_{23}, q_{31}) \\ &\quad = \int \mathrm{d}\Omega_1\,\mathrm{d}\Omega_2\,\mathrm{d}\Omega_3 Y^*_{\ell_1' m_1'}(\boldsymbol{r}_1) Y^*_{\ell_2' m_2'}(\boldsymbol{r}_2) Y^*_{\ell_3' m_3'}(\boldsymbol{r}_3) Y_{\ell_1 m_1}(\boldsymbol{r}_1) Y_{\ell_2 m_2}(\boldsymbol{r}_2) Y_{\ell_3 m_3}(\boldsymbol{r}_3) \\ &\quad \times P_{q_{12}}(\cos\theta_{12}) P_{q_{23}}(\cos\theta_{23}) P_{q_{31}}(\cos\theta_{31}). \end{aligned} \tag{24}$$

By applying the addition theorem for spherical harmonics to each of $P_{q_{ij}}(\cos\theta_{ij})$ and using the formula

$$Y_{\ell m}(\boldsymbol{r}) Y_{\ell' m'}(\boldsymbol{r}) = \sum_{LM} \sqrt{\frac{(\ell, \ell', L)}{4\pi}} \begin{pmatrix} \ell & \ell' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & L \\ m & m' & M \end{pmatrix} Y^*_{LM}(\boldsymbol{r}), \tag{25}$$

I_{ang} becomes

$$\begin{aligned} & I_{\mathrm{ang}}(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_1 m_1, \ell_2 m_2, \ell_3 m_3; q_{12}, q_{23}, q_{31}) \\ &\quad = (-1)^{m_1+m_2+m_3} (\ell_1', \ell_2', \ell_3', \ell_1, \ell_2, \ell_3)^{1/2} \\ &\quad \times \sum_{\text{all } m_{ij}} \sum_{n_1 n_2 n_3} (-1)^{m_{12}+m_{23}+m_{31}} (n_1, n_2, n_3) \begin{pmatrix} \ell_1' & \ell_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} \ell_2' & \ell_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_3' & \ell_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} \ell_1' & \ell_1 & n_1 \\ -m_1' & m_1 & m_1' - m_1 \end{pmatrix} \begin{pmatrix} \ell_2' & \ell_2 & n_2 \\ -m_2' & m_2 & m_2' - m_2 \end{pmatrix} \\ &\quad \times \begin{pmatrix} \ell_3' & \ell_3 & n_3 \\ -m_3' & m_3 & m_3' - m_3 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ -m_{12} & m_{31} & m_1 - m_1' \end{pmatrix} \end{aligned}$$

$$\times\begin{pmatrix} q_{23} & q_{12} & n_2 \\ -m_{23} & m_{12} & m_2-m_2' \end{pmatrix}\begin{pmatrix} q_{31} & q_{23} & n_3 \\ -m_{31} & m_{23} & m_3-m_3' \end{pmatrix}. \tag{26}$$

The summation over m_{ij} can be performed using [10]

$$\sum_{\mu_1\mu_2\mu_3}(-1)^{\ell_1+\ell_2+\ell_3+\mu_1+\mu_2+\mu_3}\begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix}\begin{pmatrix} \ell_1 & j_2 & \ell_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix}\begin{pmatrix} \ell_1 & \ell_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix}$$
$$= \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix}. \tag{27}$$

One finally obtains

$$I_{\rm ang}(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; q_{12}, q_{23}, q_{31})$$
$$= (-1)^{m_1'+m_2'+m_3'+q_{12}+q_{23}+q_{31}}(\ell_1', \ell_2', \ell_3', \ell_1, \ell_2, \ell_3)^{1/2}\sum_{n_1n_2n_3}(n_1, n_2, n_3)$$
$$\times\begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix}\begin{pmatrix} n_1 & n_2 & n_3 \\ m_1'-m_1 & m_2'-m_2 & m_3'-m_3 \end{pmatrix}$$
$$\times\begin{pmatrix} \ell_1' & \ell_1 & n_1 \\ -m_1' & m_1 & m_1'-m_1 \end{pmatrix}\begin{pmatrix} \ell_2' & \ell_2 & n_2 \\ -m_2' & m_2 & m_2'-m_2 \end{pmatrix}$$
$$\times\begin{pmatrix} \ell_3' & \ell_3 & n_3 \\ -m_3' & m_3 & m_3'-m_3 \end{pmatrix}\begin{pmatrix} \ell_1' & \ell_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \ell_2' & \ell_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} \ell_3' & \ell_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix}. \tag{28}$$

The radial part of the integral can be done by splitting the integration region into six parts according to the relative positions of r_1, r_2, and r_3 [11]. The final result for the whole integral I is

$$I(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma)$$
$$= \sum_{q_{12}=0}^{M_{12}}\sum_{q_{23}=0}^{M_{23}}\sum_{q_{31}=0}^{M_{31}}\sum_{k_{12}=0}^{L_{12}}\sum_{k_{23}=0}^{L_{23}}\sum_{k_{31}=0}^{L_{31}}$$
$$\times I_{\rm ang}(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; q_{12}, q_{23}, q_{31})$$
$$\times I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma), \tag{29}$$

where the radial part $I_{\rm R}$ is

$$I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma)$$
$$= C_{j_{12}q_{12}k_{12}}C_{j_{23}q_{23}k_{23}}C_{j_{31}q_{31}k_{31}}$$
$$\times W_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma). \tag{30}$$

In (30), $W_{\rm R}$ is further defined by

$$W_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma)$$
$$= W(j_1+2+s_{12}+s_{31}, j_2+2+j_{12}-s_{12}+s_{23}, j_3+2+j_{23}-s_{23}$$
$$+j_{31}-s_{31}; \alpha, \beta, \gamma) + W(j_1+2+s_{12}+s_{31}, j_3+2+s_{23}$$
$$+j_{31}-s_{31}, j_2+2+j_{12}-s_{12}+j_{23}-s_{23}; \alpha, \gamma, \beta) + W(j_2+2+s_{12}$$
$$+s_{23}, j_1+2+j_{12}-s_{12}+s_{31}, j_3+2+j_{23}-s_{23}+j_{31}-s_{31}; \beta, \alpha, \gamma)$$
$$+W(j_2+2+s_{12}+s_{23}, j_3+2+j_{23}-s_{23}+s_{31}, j_1+2+j_{12}-s_{12}$$
$$+j_{31}-s_{31}; \beta, \gamma, \alpha) + W(j_3+2+s_{23}+s_{31}, j_1+2+s_{12}$$

$$+j_{31}-s_{31},\, j_2+2+j_{12}-s_{12}+j_{23}-s_{23};\gamma,\alpha,\beta)+W(j_3+2+s_{23}$$
$$+s_{31},\, j_2+2+s_{12}+j_{23}-s_{23},\, j_1+2+j_{12}-s_{12}+j_{31}-s_{31};\gamma,\beta,\alpha) \quad (31)$$

with $s_{ij}=q_{ij}+2k_{ij}$. W is a subsidiary integral defined by

$$W(\ell,m,n;\alpha,\beta,\gamma)=\int_0^\infty \mathrm{d}x\, x^\ell \mathrm{e}^{-\alpha x}\int_x^\infty \mathrm{d}y\, y^m\mathrm{e}^{-\beta y}\int_y^\infty \mathrm{d}z\, z^n\mathrm{e}^{-\gamma z}. \quad (32)$$

A general analytic expression can be obtained [5]

$$\begin{aligned}W(\ell,m,n;\alpha,\beta,\gamma)&=\frac{\ell!}{(\alpha+\beta+\gamma)^{\ell+m+n+3}}\\ &\times\sum_{p=0}^\infty\frac{(\ell+m+n+p+2)!}{(\ell+1+p)!(\ell+m+2+p)}\left(\frac{\alpha}{\alpha+\beta+\gamma}\right)^p\\ &\times{}_2F_1\left(1,\ell+m+n+p+3;\ell+m+p+3;\frac{\alpha+\beta}{\alpha+\beta+\gamma}\right).\end{aligned} \quad (33)$$

An effective evaluation of the I_R integral can be found in [5]. (30) is valid when

$$\begin{aligned}&j_{12}\geqslant-1, \qquad j_{23}\geqslant-1, \qquad j_{31}\geqslant-1,\\ &j_1\geqslant-2, \qquad j_2\geqslant-2, \qquad j_3\geqslant-2,\\ &j_1+j_2+j_3+j_{12}+j_{23}+j_{31}\geqslant-8.\end{aligned} \quad (34)$$

A generalization to the singular case of $j_{12}=-2$ is discussed in section 4.

3.2. Overlap integral

The general form of the overlap integral is

$$I^p(1)=\langle\phi_\mathrm{L}^1|\phi_\mathrm{R}^p\rangle, \quad (35)$$

where

$$\begin{aligned}\phi_\mathrm{L}^1(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)&=r_1^{j_1'}r_2^{j_2'}r_3^{j_3'}r_{12}^{j_{12}'}r_{23}^{j_{23}'}r_{31}^{j_{31}'}\mathrm{e}^{-\alpha' r_1-\beta' r_2-\gamma' r_3}\\ &\times\sum_{\text{all } m_i'}\Omega(\ell_1',\ell_2',\ell_{12}',\ell_3',L',M_{L'},m_1',m_2',m_3')Y_{\ell_1'm_1'}(\boldsymbol{r}_1)Y_{\ell_2'm_2'}(\boldsymbol{r}_2)Y_{\ell_3'm_3'}(\boldsymbol{r}_3)\end{aligned} \quad (36)$$

and

$$\begin{aligned}\phi_\mathrm{R}^p(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)&=r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}\mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3}\\ &\times\sum_{\text{all } m_i}\Omega(\ell_1,\ell_2,\ell_{12},\ell_3,L,M_L,m_1,m_2,m_3)Y_{\ell_a m_a}(\boldsymbol{r}_1)Y_{\ell_b m_b}(\boldsymbol{r}_2)Y_{\ell_c m_c}(\boldsymbol{r}_3).\end{aligned} \quad (37)$$

Substituting (36) and (37) into (35) and using the basic integral (29), one obtains

$$\begin{aligned}I^p(1)=\sum_{\text{all } m_i'm_i}&\Omega(\ell_1',\ell_2',\ell_{12}',\ell_3',L',M_{L'},m_1',m_2',m_3')\\ &\times\Omega(\ell_1,\ell_2,\ell_{12},\ell_3,L,M_L,m_1,m_2,m_3)\\ &\times\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3\, r_1^{\tilde{j}_1}r_2^{\tilde{j}_2}r_3^{\tilde{j}_3}r_{12}^{\tilde{j}_{12}}r_{23}^{\tilde{j}_{23}}r_{31}^{\tilde{j}_{31}}\mathrm{e}^{-\tilde{\alpha}r_1-\tilde{\beta}r_2-\tilde{\gamma}r_3}\\ &\times Y^*_{\ell_1'm_1'}(\boldsymbol{r}_1)Y^*_{\ell_2'm_2'}(\boldsymbol{r}_2)Y^*_{\ell_3'm_3'}(\boldsymbol{r}_3)Y_{\ell_a m_a}(\boldsymbol{r}_1)Y_{\ell_b m_b}(\boldsymbol{r}_2)Y_{\ell_c m_c}(\boldsymbol{r}_3)\end{aligned}$$

$$= \sum_{q_{12}=0}^{M_{12}} \sum_{q_{23}=0}^{M_{23}} \sum_{q_{31}=0}^{M_{31}} \sum_{k_{12}=0}^{L_{12}} \sum_{k_{23}=0}^{L_{23}} \sum_{k_{31}=0}^{L_{31}} C^p(1) \times I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; \tilde{j}_1, \tilde{j}_2, \tilde{j}_3, \tilde{j}_{12}, \tilde{j}_{23}, \tilde{j}_{31}; \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}), \quad (38)$$

where $\tilde{j}_1 = j_1' + j_1$, etc and

$$C^p(1) = \sum_{\text{all } m_i' m_i} \Omega(\ell_1', \ell_2', \ell_{12}', \ell_3', L', M_{L'}, m_1', m_2', m_3') \times \Omega(\ell_1, \ell_2, \ell_{12}, \ell_3, L, M_L, m_1, m_2, m_3) \times I_{\rm ang}(\ell_1' m_1', \ell_2' m_2', \ell_3' m_3', \ell_a m_a, \ell_b m_b, \ell_c m_c; q_{12}, q_{23}, q_{31}). \quad (39)$$

By (11) and (28), $C^p(1)$ becomes

$$C^p(1) = U \sum_{n_1 n_2 n_3} (n_1, n_2, n_3) \begin{pmatrix} \ell_1' & \ell_a & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2' & \ell_b & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_3' & \ell_c & n_3 \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix} \tilde{C}^p(1), \quad (40)$$

where

$$U = (\ell_1', \ell_2', \ell_3', \ell_{12}', \ell_1, \ell_2, \ell_3, \ell_{12})^{1/2} (-1)^{q_{12}+q_{23}+q_{31}}, \quad (41)$$

and

$$\tilde{C}^p(1) = (L', L)^{1/2} \sum_{\text{all } m_i' m_i t_i} (-1)^{\ell_1'-\ell_2'+m_{12}'+\ell_{12}'-\ell_3'+M_{L'}+\ell_1-\ell_2+m_{12}+\ell_{12}-\ell_3+M_L+m_1'+m_2'+m_3'} \times \begin{pmatrix} \ell_1' & \ell_2' & \ell_{12}' \\ m_1' & m_2' & -m_{12}' \end{pmatrix} \begin{pmatrix} \ell_{12}' & \ell_3' & L' \\ m_{12}' & m_3' & -M_{L'} \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix} \times \begin{pmatrix} \ell_{12} & \ell_3 & L \\ m_{12} & m_3 & -M_L \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n_3 \\ t_1 & t_2 & t_3 \end{pmatrix} \begin{pmatrix} \ell_1' & \ell_a & n_1 \\ -m_1' & m_a & t_1 \end{pmatrix} \times \begin{pmatrix} \ell_2' & \ell_b & n_2 \\ -m_2' & m_b & t_2 \end{pmatrix} \begin{pmatrix} \ell_3' & \ell_c & n_3 \\ -m_3' & m_c & t_3 \end{pmatrix}. \quad (42)$$

Using the standard graphical methods of dealing with angular momentum [12], (42) can be recast into (we only need to discuss the cases of $p = 1$, $p = 3$, and $p = 4$)

$$\tilde{C}^1(1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{L+\ell_1+\ell_2+\ell_{12}} \begin{Bmatrix} \ell_3 & \ell_3' & n_3 \\ \ell_{12}' & \ell_{12} & L \end{Bmatrix} \begin{Bmatrix} \ell_1' & \ell_2' & \ell_{12}' \\ \ell_1 & \ell_2 & \ell_{12} \\ n_1 & n_2 & n_3 \end{Bmatrix}, \quad (43)$$

$$\tilde{C}^3(1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{L+\ell_1+\ell_2+\ell_{12}} \times \sum_\lambda (2\lambda+1) \begin{Bmatrix} \ell_3 & \ell_{12} & L \\ \lambda & \ell_1' & n_1 \end{Bmatrix} \begin{Bmatrix} \ell_1' & \ell_{12}' & \ell_2' \\ \ell_3' & \lambda & L \end{Bmatrix} \begin{Bmatrix} \ell_3' & \ell_2' & \lambda \\ \ell_1 & \ell_2 & \ell_{12} \\ n_3 & n_2 & n_1 \end{Bmatrix}, \quad (44)$$

$$\tilde{C}^4(1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{L+\ell_1'+\ell_2'+\ell_{12}'} \times \sum_\lambda (2\lambda+1) \begin{Bmatrix} \ell_3 & \ell_{12} & L \\ \lambda & \ell_2' & n_2 \end{Bmatrix} \begin{Bmatrix} \ell_2' & \ell_{12}' & \ell_1' \\ \ell_3' & \lambda & L \end{Bmatrix} \begin{Bmatrix} \ell_3' & \ell_1' & \lambda \\ \ell_2 & \ell_1 & \ell_{12} \\ n_3 & n_1 & n_2 \end{Bmatrix}. \quad (45)$$

For S states where all ℓ_i' and ℓ_i are zero, the angular part $C^p(1)$ can further be simplified to

$$C^p(1) = \frac{1}{(2q_{12}+1)^2} \delta_{q_{12}q_{23}} \delta_{q_{23}q_{31}}. \quad (46)$$

3.3. Integrals involving $\hat{\boldsymbol{r}}_i \cdot \hat{\nabla}_j^Y$, $\hat{\nabla}_i^Y \cdot \hat{\nabla}_j^Y$, $\hat{\boldsymbol{r}}_i \cdot \hat{\nabla}_j^{Y'}$, and $\hat{\nabla}_i^{Y'} \cdot \hat{\nabla}_j^{Y'}$

According to (18), one needs to evaluate the angular coefficients involving $\hat{\nabla}_i^Y$. Furthermore, in the use of various reduction formulae which will be derived in section 4 one also needs to evaluate the angular coefficients involving $\hat{\nabla}_i^{Y'}$. The superscripts Y and Y' indicate the operation of the operators on the right side and left side respectively. For ∇ acting only on spherical harmonics [12], we have the formula

$$\hat{\nabla}_\mu^Y Y_{\ell m}(\boldsymbol{r}) = \sum_{\lambda\tau} b(\ell;\lambda)(\ell,\lambda)^{1/2} \begin{pmatrix} 1 & \ell & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & \ell & \lambda \\ \mu & m & \tau \end{pmatrix} Y_{\lambda\tau}^*(\boldsymbol{r}), \tag{47}$$

where ∇ is written in the spherical component form with $\mu = -1$, 0, and 1, and the function $b(\ell;\lambda)$ is defined by

$$\begin{aligned} b(\ell;\ell-1) &= \ell+1 \\ b(\ell;\ell+1) &= -\ell. \end{aligned} \tag{48}$$

On the other hand, since

$$\hat{\boldsymbol{r}}_\mu = \sqrt{\frac{4\pi}{3}}\, Y_{1\mu}(\boldsymbol{r}), \tag{49}$$

we obtain by (25)

$$\hat{\boldsymbol{r}}_\mu Y_{\ell m}(\boldsymbol{r}) = \sum_{\lambda\tau} (\ell,\lambda)^{1/2} \begin{pmatrix} 1 & \ell & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & \ell & \lambda \\ \mu & m & \tau \end{pmatrix} Y_{\lambda\tau}^*(\boldsymbol{r}). \tag{50}$$

Comparing (47) with (50), one can see that the angular coefficients involving $\hat{\nabla}_\mu^Y$ can be obtained by first replacing $\hat{\nabla}_\mu^Y$ by $\hat{\boldsymbol{r}}_\mu$, evaluating the corresponding terms, and then inserting $b(\ell;\lambda)$'s appropriately. Also see [13] for a discussion. We thus first consider the following integral

$$I^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2) = \langle \phi_{\rm L}^1 | \hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2 | \phi_{\rm R}^p \rangle. \tag{51}$$

Since

$$\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2 = \sum_\mu (-1)^\mu \hat{r}_{1\mu} \hat{r}_{2-\mu} = \frac{4\pi}{3} \sum_\mu (-1)^\mu Y_{1\mu}(\boldsymbol{r}_1) Y_{1-\mu}(\boldsymbol{r}_2), \tag{52}$$

and using the same method which leads to (38), (51) can be simplified to

$$\begin{aligned} I^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2) = {}& \sum_{q_{12}=0}^{M_{12}} \sum_{q_{23}=0}^{M_{23}} \sum_{q_{31}=0}^{M_{31}} \sum_{k_{12}=0}^{L_{12}} \sum_{k_{23}=0}^{L_{23}} \sum_{k_{31}=0}^{L_{31}} \sum_{T_1 T_2} C^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2) \\ & \times I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; \tilde{j}_1, \tilde{j}_2, \tilde{j}_3, \tilde{j}_{12}, \tilde{j}_{23}, \tilde{j}_{31}; \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}), \end{aligned} \tag{53}$$

where

$$\begin{aligned} C^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2) = {}& U \sum_{n_1 n_2 n_3} (n_1, n_2, n_3, T_1, T_2) \begin{pmatrix} 1 & \ell_a & T_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & \ell_b & T_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1' & T_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} \ell_2' & T_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_3' & \ell_c & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix} \tilde{C}^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2). \end{aligned} \tag{54}$$

In (54),

$$\tilde{C}^1(\hat{\boldsymbol{r}}_1\cdot\hat{\boldsymbol{r}}_2) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_1'+\ell_2'+\ell_{12}'+\ell_{12}+L}\begin{Bmatrix}\ell_3' & \ell_3 & n_3\\ \ell_{12} & \ell_{12}' & L\end{Bmatrix} \times\begin{Bmatrix}T_1 & \ell_1 & 1\\ \ell_2 & T_2 & \ell_{12}\end{Bmatrix}\begin{Bmatrix}\ell_{12} & T_2 & T_1\\ n_3 & n_2 & n_1\\ \ell_{12}' & \ell_2' & \ell_1'\end{Bmatrix}, \tag{55}$$

$$\tilde{C}^3(\hat{\boldsymbol{r}}_1\cdot\hat{\boldsymbol{r}}_2) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_{12}+\ell_2'+\ell_3'}\sum_{\lambda_1\lambda_2}(\lambda_1,\lambda_2)(-1)^{\lambda_1+\lambda_2}\begin{Bmatrix}L & \ell_{12} & \ell_3\\ 1 & T_1 & \lambda_1\end{Bmatrix} \times\begin{Bmatrix}\ell_{12} & \ell_1 & \ell_2\\ T_2 & 1 & \lambda_1\end{Bmatrix}\begin{Bmatrix}T_1 & n_1 & \ell_1'\\ \lambda_2 & L & \lambda_1\end{Bmatrix}\begin{Bmatrix}\ell_{12}' & \ell_1' & \ell_2'\\ \lambda_2 & \ell_3' & L\end{Bmatrix}\begin{Bmatrix}n_1 & \lambda_1 & \lambda_2\\ n_3 & \ell_1 & \ell_3'\\ n_2 & T_2 & \ell_2'\end{Bmatrix}, \tag{56}$$

$$\tilde{C}^4(\hat{\boldsymbol{r}}_1\cdot\hat{\boldsymbol{r}}_2) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_2+\ell_1'+\ell_2'+\ell_{12}'}\sum_{\lambda_1\lambda_2}(\lambda_1,\lambda_2)\begin{Bmatrix}T_2 & \ell_3 & 1\\ \ell_{12} & \lambda_1 & L\end{Bmatrix}\begin{Bmatrix}1 & \ell_1 & T_1\\ \ell_2 & \lambda_1 & \ell_{12}\end{Bmatrix} \times\begin{Bmatrix}T_2 & n_2 & \ell_2'\\ \lambda_2 & L & \lambda_1\end{Bmatrix}\begin{Bmatrix}\ell_{12}' & \ell_2' & \ell_1'\\ \lambda_2 & \ell_3' & L\end{Bmatrix}\begin{Bmatrix}n_1 & T_1 & \ell_1'\\ n_3 & \ell_2 & \ell_3'\\ n_2 & \lambda_1 & \lambda_2\end{Bmatrix}. \tag{57}$$

Similarly,

$$I^p(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = \langle\phi_{\rm L}^1|\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3|\phi_{\rm R}^p\rangle = \sum_{q_{12}=0}^{M_{12}}\sum_{q_{23}=0}^{M_{23}}\sum_{q_{31}=0}^{M_{31}}\sum_{k_{12}=0}^{L_{12}}\sum_{k_{23}=0}^{L_{23}}\sum_{k_{31}=0}^{L_{31}}\sum_{T_2T_3}C^p(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) \times I_{\rm R}(q_{12},q_{23},q_{31},k_{12},k_{23},k_{31};\tilde{j}_1,\tilde{j}_2,\tilde{j}_3,\tilde{j}_{12},\tilde{j}_{23},\tilde{j}_{31};\tilde{\alpha},\tilde{\beta},\tilde{\gamma}), \tag{58}$$

where

$$C^p(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = U\sum_{n_1n_2n_3}(n_1,n_2,n_3,T_2,T_3)\begin{pmatrix}1 & \ell_b & T_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & \ell_c & T_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_1' & \ell_a & n_1\\ 0 & 0 & 0\end{pmatrix} \times\begin{pmatrix}\ell_2' & T_2 & n_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_3' & T_3 & n_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}q_{31} & q_{12} & n_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}q_{12} & q_{23} & n_2\\ 0 & 0 & 0\end{pmatrix} \times\begin{pmatrix}q_{23} & q_{31} & n_3\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}n_1 & n_2 & n_3\\ q_{23} & q_{31} & q_{12}\end{Bmatrix}\tilde{C}^p(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3), \tag{59}$$

with

$$\tilde{C}^1(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_{12}+\ell_1'+\ell_2'+\ell_{12}'}\sum_{\lambda}(2\lambda+1)(-1)^{\lambda}\begin{Bmatrix}T_3 & \ell_3 & 1\\ \ell_{12} & \lambda & L\end{Bmatrix} \times\begin{Bmatrix}\ell_3' & T_3 & n_3\\ \lambda & \ell_{12}' & L\end{Bmatrix}\begin{Bmatrix}\ell_{12} & \ell_2 & \ell_1\\ T_2 & \lambda & 1\end{Bmatrix}\begin{Bmatrix}\lambda & T_2 & \ell_1\\ n_3 & n_2 & n_1\\ \ell_{12}' & \ell_2' & \ell_1'\end{Bmatrix}, \tag{60}$$

$$\tilde{C}^3(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_1+\ell_2+L}\sum_{\lambda}(2\lambda+1)\begin{Bmatrix}\ell_1' & \ell_3 & n_1\\ \ell_{12} & \lambda & L\end{Bmatrix} \times\begin{Bmatrix}\ell_{12}' & \ell_1' & \ell_2'\\ \lambda & \ell_3' & L\end{Bmatrix}\begin{Bmatrix}T_2 & \ell_2 & 1\\ \ell_1 & T_3 & \ell_{12}\end{Bmatrix}\begin{Bmatrix}\lambda & \ell_{12} & n_1\\ \ell_3' & T_3 & n_3\\ \ell_2' & T_2 & n_2\end{Bmatrix}, \tag{61}$$

and

$$\tilde{C}^4(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_1+\ell_3+\ell_{12}+\ell_1'+\ell_{12}'}\sum_{\lambda_1\lambda_2}(\lambda_1,\lambda_2)(-1)^{\lambda_2}\begin{Bmatrix}T_2 & \ell_3 & 1\\ \ell_{12} & \lambda_1 & L\end{Bmatrix}$$

$$\times \begin{Bmatrix} \lambda_1 & \ell_{12} & 1 \\ \ell_2 & T_3 & \ell_1 \end{Bmatrix} \begin{Bmatrix} \ell_2' & T_2 & n_2 \\ \lambda_1 & \lambda_2 & L \end{Bmatrix} \begin{Bmatrix} \ell_{12}' & \ell_2' & \ell_1' \\ \lambda_2 & \ell_3' & L \end{Bmatrix} \begin{Bmatrix} n_2 & \lambda_1 & \lambda_2 \\ n_3 & T_3 & \ell_3' \\ n_1 & \ell_1 & \ell_1' \end{Bmatrix}. \tag{62}$$

$$I^p(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1) = \langle \phi_{\rm L}^1 | \hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1 | \phi_{\rm R}^p \rangle = \sum_{q_{12}=0}^{M_{12}} \sum_{q_{23}=0}^{M_{23}} \sum_{q_{31}=0}^{M_{31}} \sum_{k_{12}=0}^{L_{12}} \sum_{k_{23}=0}^{L_{23}} \sum_{k_{31}=0}^{L_{31}} \sum_{T_3 T_1} C^p(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1)$$
$$\times I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; \tilde{j}_1, \tilde{j}_2, \tilde{j}_3, \tilde{j}_{12}, \tilde{j}_{23}, \tilde{j}_{31}; \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}), \tag{63}$$

where

$$C^p(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1) = U \sum_{n_1 n_2 n_3} (n_1, n_2, n_3, T_3, T_1) \begin{pmatrix} 1 & \ell_c & T_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & \ell_a & T_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1' & T_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} \ell_2' & \ell_b & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_3' & T_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix} \tilde{C}^p(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1), \tag{64}$$

with

$$\tilde{C}^1(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{\ell_1} \sum_{\lambda} (2\lambda + 1)(-1)^{\lambda} \begin{Bmatrix} T_3 & \ell_3 & 1 \\ \ell_{12} & \lambda & L \end{Bmatrix} \begin{Bmatrix} \ell_3' & T_3 & n_3 \\ \lambda & \ell_{12}' & L \end{Bmatrix}$$
$$\times \begin{Bmatrix} T_1 & 1 & \ell_1 \\ \ell_{12} & \ell_2 & \lambda \end{Bmatrix} \begin{Bmatrix} \lambda & \ell_2 & T_1 \\ \ell_{12}' & \ell_2' & \ell_1' \\ n_3 & n_2 & n_1 \end{Bmatrix}, \tag{65}$$

$$\tilde{C}^3(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{1+\ell_2+\ell_2'+\ell_3'} \sum_{\lambda_1 \lambda_2} (\lambda_1, \lambda_2)(-1)^{\lambda_2} \begin{Bmatrix} T_1 & \ell_3 & 1 \\ \ell_{12} & \lambda_1 & L \end{Bmatrix}$$
$$\times \begin{Bmatrix} \lambda_1 & \ell_{12} & 1 \\ \ell_1 & T_3 & \ell_2 \end{Bmatrix} \begin{Bmatrix} T_1 & n_1 & \ell_1' \\ \lambda_2 & L & \lambda_1 \end{Bmatrix} \begin{Bmatrix} \ell_{12}' & \ell_1' & \ell_2' \\ \lambda_2 & \ell_3' & L \end{Bmatrix} \begin{Bmatrix} n_1 & \lambda_1 & \lambda_2 \\ n_3 & T_3 & \ell_3' \\ n_2 & \ell_2 & \ell_2' \end{Bmatrix}, \tag{66}$$

and

$$\tilde{C}^4(\hat{\boldsymbol{r}}_3 \cdot \hat{\boldsymbol{r}}_1) = \delta_{L'L} \delta_{M_{L'} M_L} (-1)^{1+L+\ell_{12}+\ell_1'+\ell_2'+\ell_{12}'} \begin{Bmatrix} T_1 & \ell_1 & 1 \\ \ell_2 & T_3 & \ell_{12} \end{Bmatrix} \sum_{\lambda} (2\lambda + 1)$$
$$\times \begin{Bmatrix} \ell_2' & \ell_3 & n_2 \\ \ell_{12} & \lambda & L \end{Bmatrix} \begin{Bmatrix} \ell_{12}' & \ell_2' & \ell_1' \\ \lambda & \ell_3' & L \end{Bmatrix} \begin{Bmatrix} \ell_{12} & T_3 & T_1 \\ n_2 & n_3 & n_1 \\ \lambda & \ell_3' & \ell_1' \end{Bmatrix}. \tag{67}$$

The angular coefficients containing $\hat{\nabla}_i^Y$ are obtained by the following replacements:

$$\begin{aligned} C^p(\hat{\boldsymbol{r}}_i \cdot \hat{\nabla}_s^Y) &\longrightarrow b(\ell_{a_s}; T_s) C^p(\hat{\boldsymbol{r}}_i \cdot \hat{\boldsymbol{r}}_s) \\ C^p(\hat{\nabla}_i^Y \cdot \hat{\nabla}_s^Y) &\longrightarrow b(\ell_{a_i}; T_i) b(\ell_{a_s}; T_s) C^p(\hat{\boldsymbol{r}}_i \cdot \hat{\boldsymbol{r}}_s), \end{aligned} \tag{68}$$

where $a_1 = a$, $a_2 = b$, and $a_3 = c$. It is obvious that

$$\hat{\boldsymbol{r}}_i \cdot \hat{\nabla}_i^Y = 0. \tag{69}$$

Finally, as mentioned in section 4, we will develop some reduction formulae which are needed to calculate the angular coefficients involving $\hat{\nabla}_i^{Y'}$. We list the expressions for the corresponding operators discussed above acting on the left-hand state. A subscript L is introduced in order to distinguish them from the above expressions.

$$I_{\rm L}^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2) = \sum_{q_{12}=0}^{M_{12}} \sum_{q_{23}=0}^{M_{23}} \sum_{q_{31}=0}^{M_{31}} \sum_{k_{12}=0}^{L_{12}} \sum_{k_{23}=0}^{L_{23}} \sum_{k_{31}=0}^{L_{31}} \sum_{T_1 T_2} C_{\rm L}^p(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2)$$
$$\times I_{\rm R}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; \tilde{j}_1, \tilde{j}_2, \tilde{j}_3, \tilde{j}_{12}, \tilde{j}_{23}, \tilde{j}_{31}; \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}), \tag{70}$$

where

$$C_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_1\cdot\hat{\boldsymbol r}_2)=U\sum_{n_1n_2n_3}(n_1,n_2,n_3,T_1,T_2)\begin{pmatrix}1&\ell_1'&T_1\\0&0&0\end{pmatrix}\begin{pmatrix}1&\ell_2'&T_2\\0&0&0\end{pmatrix}\begin{pmatrix}T_1&\ell_a&n_1\\0&0&0\end{pmatrix}$$
$$\times\begin{pmatrix}T_2&\ell_b&n_2\\0&0&0\end{pmatrix}\begin{pmatrix}\ell_3'&\ell_c&n_3\\0&0&0\end{pmatrix}\begin{pmatrix}q_{31}&q_{12}&n_1\\0&0&0\end{pmatrix}\begin{pmatrix}q_{12}&q_{23}&n_2\\0&0&0\end{pmatrix}$$
$$\times\begin{pmatrix}q_{23}&q_{31}&n_3\\0&0&0\end{pmatrix}\begin{Bmatrix}n_1&n_2&n_3\\q_{23}&q_{31}&q_{12}\end{Bmatrix}\tilde C_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_1\cdot\hat{\boldsymbol r}_2) \tag{71}$$

with

$$\tilde C_{\mathrm{L}}^{1}(\hat{\boldsymbol r}_1\cdot\hat{\boldsymbol r}_2)=\delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_2+\ell_{12}+L+\ell_{12}'+1}\begin{Bmatrix}\ell_3'&\ell_3&n_3\\\ell_{12}&\ell_{12}'&L\end{Bmatrix}$$
$$\times\begin{Bmatrix}\ell_1'&T_1&1\\T_2&\ell_2'&\ell_{12}'\end{Bmatrix}\begin{Bmatrix}n_3&\ell_{12}&\ell_{12}'\\n_2&\ell_2&T_2\\n_1&\ell_1&T_1\end{Bmatrix}, \tag{72}$$

$$\tilde C_{\mathrm{L}}^{3}(\hat{\boldsymbol r}_1\cdot\hat{\boldsymbol r}_2)=\delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_2+\ell_{12}+L+\ell_{12}'+1}\sum_{\lambda}(2\lambda+1)\begin{Bmatrix}T_1&\ell_3&n_1\\\ell_{12}&\lambda&L\end{Bmatrix}$$
$$\times\begin{Bmatrix}\lambda&T_2&\ell_3'\\\ell_{12}'&L&T_1\end{Bmatrix}\begin{Bmatrix}T_1&1&\ell_1'\\\ell_2'&\ell_{12}'&T_2\end{Bmatrix}\begin{Bmatrix}\ell_2&\ell_1&\ell_{12}\\T_2&\ell_3'&\lambda\\n_2&n_3&n_1\end{Bmatrix}, \tag{73}$$

$$\tilde C_{\mathrm{L}}^{4}(\hat{\boldsymbol r}_1\cdot\hat{\boldsymbol r}_2)=\delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_1'+\ell_2'+L}\sum_{\lambda}(2\lambda+1)\begin{Bmatrix}T_2&\ell_3&n_2\\\ell_{12}&\lambda&L\end{Bmatrix}$$
$$\times\begin{Bmatrix}1&T_1&\ell_1'\\\ell_{12}'&\ell_2'&T_2\end{Bmatrix}\begin{Bmatrix}T_2&\lambda&L\\\ell_3'&\ell_{12}'&T_1\end{Bmatrix}\begin{Bmatrix}\lambda&n_2&\ell_{12}\\T_1&n_1&\ell_1\\\ell_3'&n_3&\ell_2\end{Bmatrix}. \tag{74}$$

$$I_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3)=\sum_{q_{12}=0}^{M_{12}}\sum_{q_{23}=0}^{M_{23}}\sum_{q_{31}=0}^{M_{31}}\sum_{k_{12}=0}^{L_{12}}\sum_{k_{23}=0}^{L_{23}}\sum_{k_{31}=0}^{L_{31}}\sum_{T_2T_3}C_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3)$$
$$\times I_{\mathrm{R}}(q_{12},q_{23},q_{31},k_{12},k_{23},k_{31};\tilde j_1,\tilde j_2,\tilde j_3,\tilde j_{12},\tilde j_{23},\tilde j_{31};\tilde\alpha,\tilde\beta,\tilde\gamma), \tag{75}$$

where

$$C_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3)=U\sum_{n_1n_2n_3}(n_1,n_2,n_3,T_2,T_3)\begin{pmatrix}1&\ell_2'&T_2\\0&0&0\end{pmatrix}\begin{pmatrix}1&\ell_3'&T_3\\0&0&0\end{pmatrix}\begin{pmatrix}\ell_1'&\ell_a&n_1\\0&0&0\end{pmatrix}$$
$$\times\begin{pmatrix}T_2&\ell_b&n_2\\0&0&0\end{pmatrix}\begin{pmatrix}T_3&\ell_c&n_3\\0&0&0\end{pmatrix}\begin{pmatrix}q_{31}&q_{12}&n_1\\0&0&0\end{pmatrix}\begin{pmatrix}q_{12}&q_{23}&n_2\\0&0&0\end{pmatrix}$$
$$\times\begin{pmatrix}q_{23}&q_{31}&n_3\\0&0&0\end{pmatrix}\begin{Bmatrix}n_1&n_2&n_3\\q_{23}&q_{31}&q_{12}\end{Bmatrix}\tilde C_{\mathrm{L}}^{p}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3) \tag{76}$$

with

$$\tilde C_{\mathrm{L}}^{1}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3)=\delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_2+\ell_{12}+\ell_{12}'+\ell_1'}\sum_{\lambda}(2\lambda+1)(-1)^{\lambda}\begin{Bmatrix}T_3&\ell_3&n_3\\\ell_{12}&\lambda&L\end{Bmatrix}$$
$$\times\begin{Bmatrix}\ell_3'&T_3&1\\\lambda&\ell_{12}'&L\end{Bmatrix}\begin{Bmatrix}\lambda&T_2&\ell_1'\\\ell_2'&\ell_{12}'&1\end{Bmatrix}\begin{Bmatrix}n_3&\ell_{12}&\lambda\\n_2&\ell_2&T_2\\n_1&\ell_1&\ell_1'\end{Bmatrix}, \tag{77}$$

$$\tilde C_{\mathrm{L}}^{3}(\hat{\boldsymbol r}_2\cdot\hat{\boldsymbol r}_3)=\delta_{L'L}\delta_{M_{L'}M_L}(-1)^{1+\ell_2'+\ell_3'+L}\sum_{\lambda}(2\lambda+1)\begin{Bmatrix}\ell_3&n_1&\ell_1'\\\lambda&L&\ell_{12}\end{Bmatrix}$$

$$\times\begin{Bmatrix} \ell_1' & \ell_2' & \ell_{12}' \\ \ell_3' & L & \lambda \end{Bmatrix}\begin{Bmatrix} \ell_2' & T_2 & 1 \\ T_3 & \ell_3' & \lambda \end{Bmatrix}\begin{Bmatrix} n_1 & \ell_{12} & \lambda \\ n_3 & \ell_1 & T_3 \\ n_2 & \ell_2 & T_2 \end{Bmatrix}, \tag{78}$$

$$\tilde{C}^4_{\mathrm{L}}(\hat{\boldsymbol{r}}_2\cdot\hat{\boldsymbol{r}}_3) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1'+\ell_2'+L}\sum_\lambda(2\lambda+1)(-1)^\lambda\begin{Bmatrix} T_2 & \ell_3 & n_2 \\ \ell_{12} & \lambda & L \end{Bmatrix}$$
$$\times\begin{Bmatrix} T_2 & \lambda & L \\ 1 & T_3 & \ell_3' \\ \ell_2' & \ell_1' & \ell_{12}' \end{Bmatrix}\begin{Bmatrix} n_2 & n_1 & n_3 \\ \ell_{12} & \ell_1 & \ell_2 \\ \lambda & \ell_1' & T_3 \end{Bmatrix}. \tag{79}$$

$$I^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) = \sum_{q_{12}=0}^{M_{12}}\sum_{q_{23}=0}^{M_{23}}\sum_{q_{31}=0}^{M_{31}}\sum_{k_{12}=0}^{L_{12}}\sum_{k_{23}=0}^{L_{23}}\sum_{k_{31}=0}^{L_{31}}\sum_{T_3T_1} C^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1)$$
$$\times I_{\mathrm{R}}(q_{12},q_{23},q_{31},k_{12},k_{23},k_{31};\tilde{j}_1,\tilde{j}_2,\tilde{j}_3,\tilde{j}_{12},\tilde{j}_{23},\tilde{j}_{31};\tilde{\alpha},\tilde{\beta},\tilde{\gamma}), \tag{80}$$

where

$$C^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) = U\sum_{n_1n_2n_3}(n_1,n_2,n_3,T_3,T_1)\begin{pmatrix} 1 & \ell_3' & T_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & \ell_1' & T_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} T_1 & \ell_a & n_1 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} \ell_2' & \ell_b & n_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} T_3 & \ell_c & n_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} q_{31} & q_{12} & n_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} q_{23} & q_{31} & n_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix}\tilde{C}^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) \tag{81}$$

with

$$\tilde{C}^1_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1'}\sum_\lambda(2\lambda+1)(-1)^\lambda\begin{Bmatrix} \ell_3 & n_3 & T_3 \\ \lambda & L & \ell_{12} \end{Bmatrix}$$
$$\times\begin{Bmatrix} \ell_3' & T_3 & 1 \\ \lambda & \ell_{12}' & L \end{Bmatrix}\begin{Bmatrix} 1 & T_1 & \ell_1' \\ \ell_2' & \ell_{12}' & \lambda \end{Bmatrix}\begin{Bmatrix} n_3 & n_1 & n_2 \\ \ell_{12} & \ell_1 & \ell_2 \\ \lambda & T_1 & \ell_2' \end{Bmatrix}, \tag{82}$$

$$\tilde{C}^3_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_1+\ell_2+\ell_{12}+\ell_{12}'+L}\sum_\lambda(2\lambda+1)(-1)^\lambda\begin{Bmatrix} T_1 & \ell_3 & n_1 \\ \ell_{12} & \lambda & L \end{Bmatrix}$$
$$\times\begin{Bmatrix} \lambda & \ell_{12} & n_1 \\ T_3 & \ell_1 & n_3 \\ \ell_2' & \ell_2 & n_2 \end{Bmatrix}\begin{Bmatrix} T_1 & \lambda & L \\ 1 & T_3 & \ell_3' \\ \ell_1' & \ell_2' & \ell_{12}' \end{Bmatrix}, \tag{83}$$

$$\tilde{C}^4_{\mathrm{L}}(\hat{\boldsymbol{r}}_3\cdot\hat{\boldsymbol{r}}_1) = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{\ell_{12}+\ell_3+\ell_1'+\ell_{12}'+L+1}\sum_\lambda(2\lambda+1)\begin{Bmatrix} \ell_3 & n_2 & \ell_2' \\ \lambda & L & \ell_{12} \end{Bmatrix}$$
$$\times\begin{Bmatrix} \ell_{12}' & \ell_2' & \ell_1' \\ \lambda & \ell_3' & L \end{Bmatrix}\begin{Bmatrix} \ell_1' & T_1 & 1 \\ T_3 & \ell_3' & \lambda \end{Bmatrix}\begin{Bmatrix} n_2 & \ell_{12} & \lambda \\ n_3 & \ell_2 & T_3 \\ n_1 & \ell_1 & T_1 \end{Bmatrix}. \tag{84}$$

The corresponding angular coefficients containing $\hat{\nabla}_i^{Y'}$ can be obtained by the following replacements:

$$\begin{aligned} C^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_i\cdot\hat{\nabla}_s^{Y'}) &\longrightarrow b(\ell_s';T_s)C^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_i\cdot\hat{\boldsymbol{r}}_s) \\ C^p_{\mathrm{L}}(\hat{\nabla}_i^{Y'}\cdot\hat{\nabla}_s^{Y'}) &\longrightarrow b(\ell_i';T_i)b(\ell_s';T_s)C^p_{\mathrm{L}}(\hat{\boldsymbol{r}}_i\cdot\hat{\boldsymbol{r}}_s). \end{aligned} \tag{85}$$

4. Evaluation of singular integrals

The radial integrals containing r_{ij}^{-1} are discussed in [5]. However, in the calculation of the Breit interaction, one needs to deal with more singular integrals. Although the integrals containing r_{ij}^{-2} are convergent, effective evaluation of these integrals is still a problem. The integrals with powers more negative than -2 generally diverge individually. However, these integrals always occur in combinations with other similar terms, thus resulting in a cancellation of the singularity. For the two-electron case, these problems have been solved completely [13–15]. In this section, we extend the techniques developed for the two-electron systems to three-electron calculations.

4.1. Reduction formulae

Consider the matrix element of ∇_1^2

$$\langle\phi_{\rm L}|\nabla_1^2|\phi_{\rm R}\rangle, \tag{86}$$

where

$$\phi_{\rm L} = r_1^{j_1'} r_2^{j_2'} r_3^{j_3'} r_{12}^{j_{12}'} r_{23}^{j_{23}'} r_{31}^{j_{31}'} {\rm e}^{-\alpha' r_1 - \beta' r_2 - \gamma' r_3} \mathcal{Y}^{L'M_{L'}}_{(\ell_1'\ell_2')\ell_{12}',\ell_3'}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) \tag{87}$$

and

$$\phi_{\rm R} = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} {\rm e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} \mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3). \tag{88}$$

Since ∇_1^2 is Hermitian, the result must be the same whether ∇_1^2 operates to the left or right so that

$$\langle\nabla_1^2\phi_{\rm L}|\phi_{\rm R}\rangle = \langle\phi_{\rm L}|\nabla_1^2\phi_{\rm R}\rangle. \tag{89}$$

The application of formula (16) yields

$$\begin{aligned}\nabla_1^2|\phi_{\rm R}\rangle = \bigg\{&[j_1(j_1+1) - \ell_1(\ell_1+1)]\frac{1}{r_1^2} + j_{12}(j_{12}+1)\frac{1}{r_{12}^2}\\ &+ j_{31}(j_{31}+1)\frac{1}{r_{31}^2} + \alpha^2 - 2\alpha(j_1+1)\frac{1}{r_1} + 2j_{12}j_1\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}}{r_1^2 r_{12}^2}\\ &- 2j_{12}\alpha\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}}{r_1 r_{12}^2} + 2j_{31}j_1\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}}{r_1^2 r_{31}^2} - 2j_{31}\alpha\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}}{r_1 r_{31}^2} + 2j_{12}j_{31}\frac{\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{13}}{r_{12}^2 r_{31}^2}\\ &- 2j_{12}\frac{r_2}{r_1 r_{12}^2}(\hat{\boldsymbol{r}}_2\cdot\hat{\nabla}_1^Y) - 2j_{31}\frac{r_3}{r_1 r_{31}^2}(\hat{\boldsymbol{r}}_3\cdot\hat{\nabla}_1^Y)\bigg\}|\phi_{\rm R}\rangle.\end{aligned} \tag{90}$$

Introducing the following notations:

$$\begin{aligned}F_0 &= \langle\phi_{\rm L}|\phi_{\rm R}\rangle,\\ F_1 &= \langle\phi_{\rm L}|1/r_1^2|\phi_{\rm R}\rangle,\\ F_2 &= \langle\phi_{\rm L}|1/r_{12}^2|\phi_{\rm R}\rangle,\\ F_3 &= \langle\phi_{\rm L}|1/r_{31}^2|\phi_{\rm R}\rangle,\\ F_4 &= \langle\phi_{\rm L}|1/r_1|\phi_{\rm R}\rangle,\\ F_5 &= \langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}}{r_1^2 r_{12}^2}|\phi_{\rm R}\rangle,\\ F_6 &= \langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}}{r_1 r_{12}^2}|\phi_{\rm R}\rangle,\\ F_7 &= \langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}}{r_1^2 r_{31}^2}|\phi_{\rm R}\rangle,\end{aligned} \tag{91}$$

$$F_8 = \langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}}{r_1 r_{31}^2}|\phi_{\rm R}\rangle,$$

$$F_9 = \langle\phi_{\rm L}|\frac{\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{13}}{r_{12}^2 r_{31}^2}|\phi_{\rm R}\rangle,$$

$$g_1 = \langle\phi_{\rm L}|\frac{r_2}{r_1 r_{12}^2}(\hat{\boldsymbol{r}}_2\cdot\hat{\nabla}_1^{Y})|\phi_{\rm R}\rangle,$$

$$g_2 = \langle\phi_{\rm L}|\frac{r_3}{r_1 r_{31}^2}(\hat{\boldsymbol{r}}_3\cdot\hat{\nabla}_1^{Y})|\phi_{\rm R}\rangle,$$

$$g_1' = \langle\phi_{\rm L}|\frac{r_2}{r_1 r_{12}^2}(\hat{\boldsymbol{r}}_2\cdot\hat{\nabla}_1^{Y'})|\phi_{\rm R}\rangle,$$

$$g_2' = \langle\phi_{\rm L}|\frac{r_3}{r_1 r_{31}^2}(\hat{\boldsymbol{r}}_3\cdot\hat{\nabla}_1^{Y'})|\phi_{\rm R}\rangle,$$

one has

$$\begin{aligned}\langle\phi_{\rm L}|\nabla_1^2\phi_{\rm R}\rangle = {} & \alpha^2 F_0 + [j_1(j_1+1) - \ell_1(\ell_1+1)]F_1 + j_{12}(j_{12}+1)F_2 \\ & + j_{31}(j_{31}+1)F_3 - 2\alpha(j_1+1)F_4 + 2j_{12}j_1F_5 - 2j_{12}\alpha F_6 \\ & + 2j_{31}j_1F_7 - 2j_{31}\alpha F_8 + 2j_{12}j_{31}F_9 - 2j_{12}g_1 - 2j_{31}g_2.\end{aligned} \tag{92}$$

Similarly,

$$\begin{aligned}\langle\nabla_1^2\phi_{\rm L}|\phi_{\rm R}\rangle = {} & \alpha'^2 F_0 + [j_1'(j_1'+1) - \ell_1'(\ell_1'+1)]F_1 + j_{12}'(j_{12}'+1)F_2 \\ & + j_{31}'(j_{31}'+1)F_3 - 2\alpha'(j_1'+1)F_4 + 2j_{12}'j_1'F_5 - 2j_{12}'\alpha' F_6 \\ & + 2j_{31}'j_1'F_7 - 2j_{31}'\alpha' F_8 + 2j_{12}'j_{31}'F_9 - 2j_{12}'g_1' - 2j_{31}'g_2'.\end{aligned} \tag{93}$$

Put

$$\begin{aligned}\tilde{j}_1 &= j_1 + j_1', \\ \tilde{j}_{12} &= j_{12} + j_{12}', \\ \tilde{j}_{31} &= j_{31} + j_{31}', \\ \tilde{\alpha} &= \alpha + \alpha',\end{aligned} \tag{94}$$

and substitute $j_1' = \tilde{j}_1 - j_1$, etc in $\langle\nabla_1^2\phi_{\rm L}|\phi_{\rm R}\rangle$. If one fixes $\tilde{j}_1$, $\tilde{j}_{12}$, $\tilde{j}_{31}$, and $\tilde{\alpha}$ and notes that F_i, g_i, and g_i' only depend on $\tilde{j}_1$, $\tilde{j}_2$, $\tilde{j}_3$, $\tilde{j}_{12}$, $\tilde{j}_{23}$, $\tilde{j}_{31}$, $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$, then (89) must be true for arbitrary j_1, j_{12}, j_{31}, and α. Comparing the coefficients of j_1, j_{12}, j_{31}, and α gives the following identities:

$$(1+\tilde{j}_1)F_1 - \tilde{\alpha}F_4 + \tilde{j}_{12}F_5 + \tilde{j}_{31}F_7 = 0, \tag{95}$$

$$(1+\tilde{j}_{12})F_2 + \tilde{j}_1F_5 - \tilde{\alpha}F_6 + \tilde{j}_{31}F_9 - g_1 - g_1' = 0, \tag{96}$$

$$(1+\tilde{j}_{31})F_3 + \tilde{j}_1F_7 - \tilde{\alpha}F_8 + \tilde{j}_{12}F_9 - g_2 - g_2' = 0, \tag{97}$$

$$-\tilde{\alpha}F_0 + (\tilde{j}_1+2)F_4 + \tilde{j}_{12}F_6 + \tilde{j}_{31}F_8 = 0. \tag{98}$$

However (98) does not give rise to a new identity because letting $\tilde{j}_1 \to \tilde{j}_1 - 1$ in (98) reproduces (95). From (95), one has

$$\langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}}{r_1^2 r_{12}^2}|\phi_{\rm R}\rangle = -\frac{\tilde{j}_{31}}{\tilde{j}_{12}}\langle\phi_{\rm L}|\frac{\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}}{r_1^2 r_{31}^2}|\phi_{\rm R}\rangle + \frac{\tilde{\alpha}}{\tilde{j}_{12}}\langle\phi_{\rm L}|1/r_1|\phi_{\rm R}\rangle - \frac{1+\tilde{j}_1}{\tilde{j}_{12}}\langle\phi_{\rm L}|1/r_1^2|\phi_{\rm R}\rangle, \tag{99}$$

where $\tilde{j}_1 \neq -1$; otherwise, since $\langle\phi_{\rm L}|1/r_1^2|\phi_{\rm R}\rangle$ does not exist in general, the last term above is undetermined. On the right-hand side, the degree of singularity at $r_{12} = 0$ is reduced by 2 compared with that of the left-hand side. Using

$$\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12} = r_1^2 - \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 = \frac{r_1^2 - r_2^2 + r_{12}^2}{2}, \tag{100}$$

and making the transformations $\tilde{j}_{12} \to \tilde{j}_{12} + 2$ and $\tilde{j}_1 \to \tilde{j}_1 + 2$ in (99) yields

$$\begin{aligned}\langle\phi_{\rm L}|r_1^2 - r_2^2|\phi_{\rm R}\rangle = {} & -\frac{\tilde{j}_{31}}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|r_1^2 r_{12}^2/r_{31}^2|\phi_{\rm R}\rangle + \frac{\tilde{j}_{31}}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|r_3^2 r_{12}^2/r_{31}^2|\phi_{\rm R}\rangle \\ & + \frac{2\tilde{\alpha}}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|r_1 r_{12}^2|\phi_{\rm R}\rangle - \frac{\tilde{j}_{12}+\tilde{j}_{31}+2\tilde{j}_1+8}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|r_{12}^2|\phi_{\rm R}\rangle. \end{aligned} \tag{101}$$

Equation (99) can also be used to reduce the singularity at $r_{31} = 0$ by switching the left side with the first term of the right side:

$$\begin{aligned}\langle\phi_{\rm L}|r_1^2 - r_3^2|\phi_{\rm R}\rangle = {} & -\frac{\tilde{j}_{12}}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|r_1^2 r_{31}^2/r_{12}^2|\phi_{\rm R}\rangle + \frac{\tilde{j}_{12}}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|r_2^2 r_{31}^2/r_{12}^2|\phi_{\rm R}\rangle \\ & + \frac{2\tilde{\alpha}}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|r_1 r_{31}^2|\phi_{\rm R}\rangle - \frac{\tilde{j}_{31}+\tilde{j}_{12}+2\tilde{j}_1+8}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|r_{31}^2|\phi_{\rm R}\rangle. \end{aligned} \tag{102}$$

Similarly, making $\tilde{j}_{12} \to \tilde{j}_{12} + 2$ and $\tilde{j}_{31} \to \tilde{j}_{31} + 2$ in (96) and (97) gives rise to the following reduction formulae which reduce the singularities with respect to $r_{31} = 0$ and $r_{12} = 0$ respectively:

$$\begin{aligned}\langle\phi_{\rm L}|\boldsymbol{r}_{13}\cdot\boldsymbol{r}_{12}|\phi_{\rm R}\rangle = {} & \frac{\tilde{\alpha}}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|\frac{r_{31}^2}{r_1}\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}|\phi_{\rm R}\rangle - \frac{\tilde{j}_1}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|\frac{r_{31}^2}{r_1^2}\boldsymbol{r}_1\cdot\boldsymbol{r}_{12}|\phi_{\rm R}\rangle \\ & - \frac{\tilde{j}_{12}+3}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|r_{31}^2|\phi_{\rm R}\rangle + \frac{1}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|\frac{r_{31}^2 r_2}{r_1}(\hat{\boldsymbol{r}}_2\cdot\hat{\nabla}_1^{Y})|\phi_{\rm R}\rangle \\ & + \frac{1}{\tilde{j}_{31}+2}\langle\phi_{\rm L}|\frac{r_{31}^2 r_2}{r_1}(\hat{\boldsymbol{r}}_2\cdot\hat{\nabla}_1^{Y'})|\phi_{\rm R}\rangle, \end{aligned} \tag{103}$$

$$\begin{aligned}\langle\phi_{\rm L}|\boldsymbol{r}_{13}\cdot\boldsymbol{r}_{12}|\phi_{\rm R}\rangle = {} & \frac{\tilde{\alpha}}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|\frac{r_{12}^2}{r_1}\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}|\phi_{\rm R}\rangle - \frac{\tilde{j}_1}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|\frac{r_{12}^2}{r_1^2}\boldsymbol{r}_1\cdot\boldsymbol{r}_{13}|\phi_{\rm R}\rangle \\ & - \frac{\tilde{j}_{31}+3}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|r_{12}^2|\phi_{\rm R}\rangle + \frac{1}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|\frac{r_{12}^2 r_3}{r_1}(\hat{\boldsymbol{r}}_3\cdot\hat{\nabla}_1^{Y})|\phi_{\rm R}\rangle \\ & + \frac{1}{\tilde{j}_{12}+2}\langle\phi_{\rm L}|\frac{r_{12}^2 r_3}{r_1}(\hat{\boldsymbol{r}}_3\cdot\hat{\nabla}_1^{Y'})|\phi_{\rm R}\rangle. \end{aligned} \tag{104}$$

Equations (101), (102), (103), and (104) are a set of reduction formulae resulting from the Hermiticity of ∇_1^2. The corresponding results for ∇_2^2 and ∇_3^2 can be obtained by permuting the subscripts 1, 2, and 3.

4.2. Recursion relation

For the calculations of two-electron integrals in Hylleraas coordinates, there exist several recursion relations [13] which are particularly useful in the elimination of singularities. These recursion relations are derived by keeping r_1, r_2, and r_{12} as independent variables. For the three-electron integrals, the problem is complicated by the fact that there are three inter-electronic distances r_{12}, r_{23}, and r_{31}. However, it is possible to keep only r_{12} as an independent variable and expand r_{23} and r_{31}. Consider the basic integral (19) again. We expand $r_{23}^{j_{23}}$ and $r_{31}^{j_{31}}$ according to (20) and retain $r_{12}^{j_{12}}$. The volume elements can be written as [13]

$$\begin{aligned} \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 &= r_1\,\mathrm{d}r_1\,r_2\,\mathrm{d}r_2\,r_{12}\,\mathrm{d}r_{12}\,\mathrm{d}\Omega_{12},\\ \mathrm{d}\boldsymbol{r}_3 &= r_3^2\,\mathrm{d}r_3\,\mathrm{d}\Omega_3, \end{aligned} \tag{105}$$

with $\mathrm{d}\Omega_{12} = \sin\theta_1\,\mathrm{d}\theta_1\,\mathrm{d}\phi_1\,\mathrm{d}\chi$, where θ_1, ϕ_1 are the polar angles of the vector $\boldsymbol{r}_1$, χ is the angle of rotation of the rigid triangle formed by $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, $\boldsymbol{r}_{12}$ about the $\boldsymbol{r}_1$ direction, and Ω_3 is the solid angle of $\boldsymbol{r}_3$. Thus, the integral (19) becomes

$$\begin{aligned} &I(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma)\\ &\quad = \sum_{q_{23}q_{31}}\sum_{k_{23}k_{31}} \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2 \int_0^\infty \mathrm{d}r_3 \int_{|r_1-r_2|}^{r_1+r_2} \mathrm{d}r_{12} r_1^{j_1+1} r_2^{j_2+1} r_3^{j_3+2} r_{12}^{j_{12}+1}\\ &\qquad \times \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3} F(jqk)_{23} F(jqk)_{31} G, \end{aligned} \tag{106}$$

where $F(jqk)_{23}$ and $F(jqk)_{31}$ are defined in (23) and G is the angular integral

$$\begin{aligned} G = \int \mathrm{d}\Omega_{12}\,\mathrm{d}\Omega_3 P_{q_{23}}(\cos\theta_{23}) P_{q_{31}}(\cos\theta_{31}) Y^*_{\ell_1'm_1'}(\boldsymbol{r}_1) Y^*_{\ell_2'm_2'}(\boldsymbol{r}_2) Y^*_{\ell_3'm_3'}(\boldsymbol{r}_3)\\ \times Y_{\ell_1m_1}(\boldsymbol{r}_1) Y_{\ell_2m_2}(\boldsymbol{r}_2) Y_{\ell_3m_3}(\boldsymbol{r}_3). \end{aligned} \tag{107}$$

After applying the addition theorem of spherical harmonics to $P_{q_{23}}(\cos\theta_{23})$ and $P_{q_{31}}(\cos\theta_{31})$,

$$\begin{aligned} G = \frac{16\pi^2}{(q_{23}, q_{31})} \sum_{m_{23}m_{31}} \int \mathrm{d}\Omega_{12}\, Y^*_{\ell_1'm_1'}(\boldsymbol{r}_1) Y_{\ell_1m_1}(\boldsymbol{r}_1) Y_{q_{31}m_{31}}(\boldsymbol{r}_1) Y^*_{\ell_2'm_2'}(\boldsymbol{r}_2) Y_{\ell_2m_2}(\boldsymbol{r}_2) Y^*_{q_{23}m_{23}}(\boldsymbol{r}_2)\\ \times \int \mathrm{d}\Omega_3 Y^*_{\ell_3'm_3'}(\boldsymbol{r}_3) Y_{\ell_3m_3}(\boldsymbol{r}_3) Y_{q_{23}m_{23}}(\boldsymbol{r}_3) Y^*_{q_{31}m_{31}}(\boldsymbol{r}_3). \end{aligned} \tag{108}$$

The integration over $\mathrm{d}\Omega_3$ can easily be obtained by using (25) and the orthogonality relation of spherical harmonics. The result is

$$\begin{aligned} &\int \mathrm{d}\Omega_3 Y^*_{\ell_3'm_3'}(\boldsymbol{r}_3) Y_{\ell_3m_3}(\boldsymbol{r}_3) Y_{q_{23}m_{23}}(\boldsymbol{r}_3) Y^*_{q_{31}m_{31}}(\boldsymbol{r}_3)\\ &\quad = \frac{1}{4\pi}(-1)^{m_3'+m_{23}} \sum_{n_3s_3} (2n_3+1)(\ell_3', \ell_3, q_{23}, q_{31})^{1/2} \begin{pmatrix} \ell_3' & \ell_3 & n_3\\ 0 & 0 & 0 \end{pmatrix}\\ &\qquad \times \begin{pmatrix} q_{23} & q_{31} & n_3\\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_3' & \ell_3 & n_3\\ -m_3' & m_3 & s_3 \end{pmatrix} \begin{pmatrix} q_{23} & q_{31} & n_3\\ -m_{23} & m_{31} & s_3 \end{pmatrix}. \end{aligned} \tag{109}$$

As for the integration over $\mathrm{d}\Omega_{12}$, using (25) and the formula [13]

$$\int \mathrm{d}\Omega_{12} Y^*_{q_{12}\omega}(\boldsymbol{r}_1) Y_{E\epsilon}(\boldsymbol{r}_2) = \delta_{Eq_{12}}\delta_{\epsilon\omega} 2\pi P_{q_{12}}(\cos\theta_{12}), \tag{110}$$

one has

$$\begin{aligned} &\int \mathrm{d}\Omega_{12} Y^*_{\ell_1'm_1'}(\boldsymbol{r}_1) Y_{\ell_1m_1}(\boldsymbol{r}_1) Y_{q_{31}m_{31}}(\boldsymbol{r}_1) Y^*_{\ell_2'm_2'}(\boldsymbol{r}_2) Y_{\ell_2m_2}(\boldsymbol{r}_2) Y^*_{q_{23}m_{23}}(\boldsymbol{r}_2)\\ &\quad = \frac{1}{8\pi}(-1)^{m_1+m_2'}(\ell_1', \ell_2', \ell_1, \ell_2, q_{23}, q_{31})^{1/2} \sum_{n_1n_2q_{12}} \sum_{s_1s_2\omega} (n_1, n_2, q_{12})\\ &\qquad \times \begin{pmatrix} \ell_1' & \ell_1 & n_1\\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2' & \ell_2 & n_2\\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{31} & q_{12} & n_1\\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

$$\times\begin{pmatrix} q_{12} & q_{23} & n_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \ell_1' & \ell_1 & n_1 \\ m_1' & -m_1 & s_1 \end{pmatrix}\begin{pmatrix} \ell_2' & \ell_2 & n_2 \\ -m_2' & m_2 & s_2 \end{pmatrix}$$
$$\times\begin{pmatrix} n_1 & q_{31} & q_{12} \\ s_1 & m_{31} & \omega \end{pmatrix}\begin{pmatrix} n_2 & q_{23} & q_{12} \\ s_2 & m_{23} & \omega \end{pmatrix} P_{q_{12}}(\cos\theta_{12}). \tag{111}$$

In (111), $\cos\theta_{12}$ is a radial function given by

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1r_2}. \tag{112}$$

Substituting (109) and (111) into (108) and using formula (27) to the summation over m_{23}, m_{31}, and ω, one obtains

$$G = \tfrac{1}{2}\sum_{q_{12}}(2q_{12}+1) I_{\mathrm{ang}}(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; q_{12}, q_{23}, q_{31}) P_{q_{12}}(\cos\theta_{12}). \tag{113}$$

By introducing the following radial integral:

$$I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma)$$
$$= \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2 \int_0^\infty \mathrm{d}r_3 \int_{|r_1-r_2|}^{r_1+r_2} \mathrm{d}r_{12} r_1^{j_1+1} r_2^{j_2+1} r_3^{j_3+2} r_{12}^{j_{12}+1}$$
$$\times \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3} \tilde{F}(jqk)_{23} \tilde{F}(jqk)_{31} P_{q_{12}}(\cos\theta_{12}), \tag{114}$$

where the superscript '(1)' means that the above definition is derived from keeping r_{12} as an independent variable, and $\tilde{F}(jqk)_{23} = F(jqk)_{23}/C_{j_{23}q_{23}k_{23}}$, etc, the integral (19) can be written as

$$I(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3;\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma)$$
$$= \sum_{q_{12}q_{23}q_{31}} \sum_{k_{23}k_{31}} \tfrac{1}{2}(2q_{12}+1) C_{j_{23}q_{23}k_{23}} C_{j_{31}q_{31}k_{31}}$$
$$\times I_{\mathrm{ang}}(\ell_1'm_1', \ell_2'm_2', \ell_3'm_3', \ell_1m_1, \ell_2m_2, \ell_3m_3; q_{12}, q_{23}, q_{31})$$
$$\times I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma). \tag{115}$$

A recursion relation for $I^{(1)}_{q_{12}}$ can be derived using the same method of [13]

$$I^{(1)}_{q_{12}+1}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma)$$
$$= \frac{2q_{12}+1}{j_{12}+2} I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1-1, j_2-1, j_3, j_{12}+2, j_{23}, j_{31}, \alpha, \beta, \gamma)$$
$$+ I^{(1)}_{q_{12}-1}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma), \tag{116}$$

where $j_{12} \neq -2$. The case of $j_{12} = -2$ will be discussed in section 4.3. On the other hand, comparing (115) with (29), one can establish a relation between I_{R} and $I^{(1)}_{q_{12}}$

$$\sum_{k_{12}} I_{\mathrm{R}}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma) = \frac{2q_{12}+1}{2} C_{j_{23}q_{23}k_{23}} C_{j_{31}q_{31}k_{31}}$$
$$\times I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma), \tag{117}$$

or by (30)

$$I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma) = \frac{2}{2q_{12}+1} \sum_{k_{12}} C_{j_{12}q_{12}k_{12}}$$
$$\times W_{\mathrm{R}}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31};\, j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma). \tag{118}$$

The importance of the recursion relation (116) may be seen as follows. If the matrix element of an operator $\hat{O}$ can be written in the form

$$\langle\hat{O}\rangle = \sum_{q_{12}}\sum_{q_{23}}\sum_{q_{31}}\sum_{k_{12}}\sum_{k_{23}}\sum_{k_{31}} C(\hat{O}) \times I_{\mathrm{R}}(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma), \tag{119}$$

where $C(\hat{O})$ is the angular coefficient of $\langle\hat{O}\rangle$ which is dependent on q_{ij} and independent of k_{ij}, then from (117), one has

$$\langle\hat{O}\rangle = \frac{1}{2}\sum_{q_{23}}\sum_{q_{31}}\sum_{k_{23}}\sum_{k_{31}} C_{j_{23}q_{23}k_{23}} C_{j_{31}q_{31}k_{31}} \times\left[\sum_{q_{12}}(2q_{12}+1)C(\hat{O}) I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma)\right]. \tag{120}$$

In the case where

$$\sum_{q_{12}}(2q_{12}+1)C(\hat{O}) = 0 \tag{121}$$

for fixed q_{23} and q_{31}, using the recursion relation (116) the sum of q_{12} in (120) can be reduced to a sum over $I^{(1)}_{q_{12}}$ with j_1, j_2, and j_{12} replaced by $j_1 - 1$, $j_2 - 1$, and $j_{12} + 2$ respectively (see [14] for details). Thus the singularity at $r_{12} = 0$ is reduced by 2. Two examples of (121), which arise from the Breit interaction calculation, are

$$\sum_{q_{12}}(2q_{12}+1)C(\hat{\boldsymbol{r}}_1 \cdot \hat{\nabla}^Y_2) = 0 \tag{122}$$

and

$$\sum_{q_{12}}(2q_{12}+1)C(\hat{\boldsymbol{r}}_1 \cdot (\hat{\boldsymbol{r}}_2 \cdot \hat{\nabla}^Y_1)\hat{\nabla}^Y_2) = 0. \tag{123}$$

Equation (118) can be considered as the solution to the recursion relation (116). In fact, $I^{(1)}_{q_{12}}$ can be calculated directly in terms of W functions without the use of the recursion relation.

Before finishing this section, we introduce the following quantity:

$$\omega^{(1)}(q_{12}, q_{23}, q_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma) = \sum_{k_{23}}\sum_{k_{31}} C_{j_{23}q_{23}k_{23}} C_{j_{31}q_{31}k_{31}} I^{(1)}_{q_{12}}(q_{23}, q_{31}, k_{23}, k_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma), \tag{124}$$

which satisfies the same recursion relation as (116)

$$\omega^{(1)}(q_{12}+1, q_{23}, q_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma) = \frac{2q_{12}+1}{j_{12}+2}\omega^{(1)}(q_{12}, q_{23}, q_{31}; j_1 - 1, j_2 - 1, j_3, j_{12}+2, j_{23}, j_{31}, \alpha, \beta, \gamma) + \omega^{(1)}(q_{12}-1, q_{23}, q_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma). \tag{125}$$

Thus, (120) becomes

$$\langle\hat{O}\rangle = \frac{1}{2}\sum_{q_{12}}\sum_{q_{23}}\sum_{q_{31}}(2q_{12}+1)C(\hat{O})\omega^{(1)}(q_{12}, q_{23}, q_{31}; j_1, j_2, j_3, j_{12}, j_{23}, j_{31}, \alpha, \beta, \gamma), \tag{126}$$

where $\omega^{(1)}$ may be considered as the radial part of $\langle \hat{O} \rangle$. The reduction formula equation (101) can now be rewritten in the form

$$\begin{aligned}
&\tfrac{1}{2}\sum_{q_{12}}\sum_{q_{23}}\sum_{q_{31}}(2q_{12}+1)C(1)[\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+2,\, j_2,\, j_3,\, j_{12},\, j_{23},\, j_{31},\alpha,\beta,\gamma)\\
&\qquad -\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2+2,\, j_3,\, j_{12},\, j_{23},\, j_{31},\alpha,\beta,\gamma)]\\
&\quad = \tfrac{1}{2}\sum_{q_{12}}\sum_{q_{23}}\sum_{q_{31}}(2q_{12}+1)C(1)\\
&\qquad \times\bigg[-\frac{j_{31}}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+2,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31}-2,\alpha,\beta,\gamma)\\
&\qquad +\frac{j_{31}}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2,\, j_3+2,\, j_{12}+2,\, j_{23},\, j_{31}-2,\alpha,\beta,\gamma)\\
&\qquad +\frac{2\alpha}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+1,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31},\alpha,\beta,\gamma)\\
&\qquad -\frac{j_{12}+j_{31}+2j_1+8}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31},\alpha,\beta,\gamma)\bigg],
\end{aligned} \tag{127}$$

where $C(1)$ is the angular part of operator 1. Since the above equation is held for arbitrary q_{ij}, one arrives at

$$\begin{aligned}
&\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+2,\, j_2,\, j_3,\, j_{12},\, j_{23},\, j_{31},\alpha,\beta,\gamma)\\
&\qquad -\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2+2,\, j_3,\, j_{12},\, j_{23},\, j_{31},\alpha,\beta,\gamma)\\
&\quad = -\frac{j_{31}}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+2,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31}-2,\alpha,\beta,\gamma)\\
&\qquad +\frac{j_{31}}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2,\, j_3+2,\, j_{12}+2,\, j_{23},\, j_{31}-2,\alpha,\beta,\gamma)\\
&\qquad +\frac{2\alpha}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1+1,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31},\alpha,\beta,\gamma)\\
&\qquad -\frac{j_{12}+j_{31}+2j_1+8}{j_{12}+2}\omega^{(1)}(q_{12},q_{23},q_{31};\, j_1,\, j_2,\, j_3,\, j_{12}+2,\, j_{23},\, j_{31},\alpha,\beta,\gamma),
\end{aligned} \tag{128}$$

which reduces the singularity at $r_{12}=0$ by 2. Equation (128) is very useful in dealing with spin–other-orbit terms of the Breit interaction.

4.3. *Special case:* $j_{12}=-2$

For the case of $j_{12}=-2$, according to Sack's expansion [16], the upper limits L_{12} and M_{12} in (20) become infinite. Thus, (118) is an infinite series. Since [15]

$$C_{-2q_{12}k_{12}} = \frac{(2q_{12}+1)(2q_{12}+2k_{12})!!(2k_{12}-1)!!}{(2q_{12}+2k_{12}+1)!!(2k_{12})!!}, \tag{129}$$

with the understanding that $(-1)!!=(0)!!=1$, the numerical stability of this series can be assured by the fact that each term in the series is positive. The problem is that the series converges very slowly. Using Stirling's formula, the asymptotic behaviour of $C_{-2q_{12}k_{12}}$ is k_{12}^{-1}. The leading term in W_{R} is also k_{12}^{-1}. Thus, the series has an asymptotic dependence of k_{12}^{-2} and, therefore, the rate of convergence must be improved. It should be mentioned that, in the case where at least one of j_{23} and j_{31} is even, the summation over q_{ij} in (120) becomes finite. In the case where both j_{23} and j_{31} are odd, the summation over one of q_{23} and q_{31} in (120) becomes infinite. However, the infinite sum can be efficiently performed using the asymptotic-expansion method [5]. Therefore, the main issue for the case of $j_{12} = -2$ is how to deal with the slowly convergent summation over k_{12} in (118).

We have studied two methods to accelerate the series (118). The first method is a direct approach using the asymptotic-expansion method [5] with the leading term being order k_{12}^{-2}. In the case where both j_{23} and j_{31} are odd, the integral (120) contains doubly infinite sums over one of q_{23} and q_{31} as well as k_{12} in $I^{(1)}_{q_{12}}$. The asymptotic-expansion technique is generalized to the double sum by first making the following transformation [9]

$$\sum_{k_{12}=0}^{\infty}\sum_{q_{12}=0}^{\infty} f(k_{12}, q_{12}) = \sum_{p_{12}=0}^{\infty}\sum_{q_{12}=0}^{p_{12}} f(p_{12} - q_{12}, q_{12}). \tag{130}$$

The sum over p_{12} can then be performed by the asymptotic-expansion method in one variable. As an example, table 1 shows a convergence study for the integral with all $j_i = 1$, $j_{12} = -2$, $j_{23} = 1$, $j_{31} = 1$, $\alpha = 2.7$, $\beta = 2.7$, and $\gamma = 2.7$. We included 15 terms in the asymptotic expansion. In table 1, N is the number of terms included in the partial sum of the series (130). The second column of table 1 contains the values of $S_{\mathrm{d}}(N)$ calculated from the direct summation of the series. The third column contains the values obtained by the asymptotic-expansion method. It can be seen that at $N = 37$, the results in the third column have converged to about one part in 10^{16}, while the direct sum in the second column converges only to the second digit. This approach has been successfully applied to the calculations of the Li $1s^2 2p\,{}^2P_J$ fine-structure splitting with a computational precision of one part in 10^6, including relativistic and QED terms up to $O(\alpha^4 mc^2)$, $O((\mu/M)\alpha^4 mc^2)$, $O(\alpha^5 mc^2)$, and $O((\mu/M)\alpha^5 mc^2)$ [17].

The approach of the second method is to identify slowly convergent parts in $I^{(1)}_{q_{12}}$ and evaluate them analytically. The remaining summations over q_{23} and q_{31} in (120) are either finite when one of j_{23} and j_{31} is even, or rapidly convergent by the asymptotic-expansion method when both j_{23} and j_{31} are odd. The method has the advantage of absolute numerical stability, but a large number of analytic expressions is required. Consider a general term in (118)

$$T_1 = \frac{2}{2q_{12}+1}\sum_{k_{12}=0}^{\infty} C_{-2q_{12}k_{12}} W(\ell, m, n; \alpha, \beta, \gamma). \tag{131}$$

From (33), one can see that the k_{12} dependence of W is through ℓ and $\ell + m$ only. Writing

$$\begin{aligned} \ell &= \mathcal{L}_{12} + \mu_1 k_{12} \\ \ell + m &= \mathcal{M}_{12} + \mu_2 k_{12}, \end{aligned} \tag{132}$$

where $\mathcal{L}_{12}$ and $\mathcal{M}_{12}$ are independent of k_{12}, one has three possible cases:

$$\begin{aligned} &\text{case 1: } \mu_1 = 2, \qquad \mu_2 = 0, \\ &\text{case 2: } \mu_1 = 2, \qquad \mu_2 = 2, \\ &\text{case 3: } \mu_1 = 0, \qquad \mu_2 = 2. \end{aligned} \tag{133}$$

Substituting (33) into (131) yields

$$T_1 = \frac{2}{(2q_{12}+1)\varpi^{s+3}}\sum_{p=0}^{\infty}(s+p+2)!\,Z_\alpha^p V_p, \tag{134}$$

Table 1. Convergence study of the integral $\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{-2} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3}$ with $j_1 = 1,\ j_2 = 1,\ j_3 = 1,\ j_{23} = 1,\ j_{31} = 1,\ \alpha = 2.7,\ \beta = 2.7$, and $\gamma = 2.7$. $S_{\mathrm{d}}(N)$ is the partial sum of the first N terms for the series expansion of the integral, and $S_{\mathrm{a}}(N)$ is $S_{\mathrm{d}}(N)$ with the asymptotic expansion included.

N	$S_{\mathrm{d}}(N)$	$S_{\mathrm{a}}(N)$
15	7.045 679 719	7.187 646 245 105 896 11
16	7.054 036 549	7.187 646 245 097 782 92
17	7.061 464 752	7.187 646 245 094 629 91
18	7.068 110 894	7.187 646 245 093 284 10
19	7.074 092 252	7.187 646 245 092 644 67
20	7.079 503 778	7.187 646 245 092 314 22
21	7.084 423 170	7.187 646 245 092 132 13
22	7.088 914 620	7.187 646 245 092 026 57
23	7.093 031 624	7.187 646 245 091 962 77
24	7.096 819 120	7.187 646 245 091 922 81
25	7.100 315 135	7.187 646 245 091 897 02
26	7.103 552 061	7.187 646 245 091 879 93
27	7.106 557 664	7.187 646 245 091 868 33
28	7.109 355 882	7.187 646 245 091 860 29
29	7.111 967 458	7.187 646 245 091 854 62
30	7.114 410 458	7.187 646 245 091 850 54
31	7.116 700 693	7.187 646 245 091 847 58
32	7.118 852 054	7.187 646 245 091 845 38
33	7.120 876 800	7.187 646 245 091 843 74
34	7.122 785 786	7.187 646 245 091 842 49
35	7.124 588 663	7.187 646 245 091 841 54
36	7.126 294 038	7.187 646 245 091 840 81
37	7.127 909 610	7.187 646 245 091 840 23
Porras and King[a]		7.187 646 245 091 838 249

[a] [9].

where V_p is given by

$$V_p = \sum_{k_{12}=0}^{\infty} C_{-2q_{12}k_{12}} \frac{(\mathcal{L}_{12}+\mu_1 k_{12})!}{(\mathcal{L}_{12}+\mu_1 k_{12}+p+1)!(\mathcal{M}_{12}+\mu_2 k_{12}+p+2)} \times {}_2F_1(1, s+p+3; \mathcal{M}_{12}+\mu_2 k_{12}+p+3; Z_{\alpha\beta}) \tag{135}$$

with

$$\begin{aligned} s &= \ell + m + n \\ \varpi &= \alpha + \beta + \gamma \\ Z_\alpha &= \frac{\alpha}{\alpha+\beta+\gamma} \\ Z_{\alpha\beta} &= \frac{\alpha+\beta}{\alpha+\beta+\gamma}. \end{aligned} \tag{136}$$

Though (134) is an infinite series, the rate of convergence is now determined completely by Z_α which is a small number for most cases of practical interest. Thus, we only need to consider V_p. For case 1, substituting $\mu_1 = 2$, $\mu_2 = 0$, and (129) into (135), the sum over

k_{12} can be isolated

$$V_p = \frac{1}{\mathcal{M}_{12}+p+2}\, {}_2F_1(1, s+p+3; \mathcal{M}_{12}+p+3; Z_{\alpha\beta}) \times \sum_{k_{12}=0}^{\infty} C_{-2q_{12}k_{12}} \frac{(\mathcal{L}_{12}+2k_{12})!}{(\mathcal{L}_{12}+2k_{12}+p+1)!} = \frac{2q_{12}+1}{\mathcal{M}_{12}+p+2} A(p, q_{12}, \mathcal{L}_{12}+1)\, {}_2F_1(1, s+p+3; \mathcal{M}_{12}+p+3; Z_{\alpha\beta}), \tag{137}$$

where

$$A(m, q, n) = \sum_{k=0}^{\infty} \frac{(2q+2k)!!(2k-1)!!(n+2k-1)!}{(2q+2k+1)!!(2k)!!(n+2k+m)!}. \tag{138}$$

$A(m, q, n)$ can be summed analytically to a finite form with the help of symbolic manipulation programs [15] (for example, Maple). It can also be calculated using the following scheme. Since the general term in $A(m, q, n)$ is roughly proportional to k^{-m-2}, one can perform summation directly for large m. However, for small m, as derived in the appendix, $A(m, q, n)$ can be calculated using

$$A(m, q, n) = \sum_{\nu=0}^{q} \frac{(2\nu-1)!!(2q-2\nu-1)!!}{(2\nu)!!(2q-2\nu)!!} S_A(m, 2\nu+1, n), \tag{139}$$

where

$$S_A(m, p, c) = \sum_{k=0}^{m} \frac{(-1)^k}{k!(m-k)!} g_A(p, c+k) \tag{140}$$

with $g_A(p, c)$ being given by

$$g_A(p, p) = \tfrac{1}{4}\Psi'(p/2), \qquad g_A(p, c) = \frac{1}{2(c-p)}[\Psi(c/2) - \Psi(p/2)], \qquad \text{for } p \neq c. \tag{141}$$

In (141), $\Psi(x)$ is the digamma function and $\Psi'(x)$ is its first derivative.

For case 2 where $\mu_1 = 2$ and $\mu_2 = 2$, the general term in V_p is asymptotically k_{12}^{-p-3}. However, if we expand ${}_2F_1$ in (135) according to

$${}_2F_1(1, s+p+3; \mathcal{M}_{12}+2k_{12}+p+3; Z_{\alpha\beta}) = \sum_{\lambda=0}^{\Lambda} \frac{(s+p+3)_\lambda}{(\mathcal{M}_{12}+2k_{12}+p+3)_\lambda} Z_{\alpha\beta}^{\lambda} + F_\Lambda(1, s+p+3; \mathcal{M}_{12}+2k_{12}+p+3; Z_{\alpha\beta}), \tag{142}$$

where F_Λ is ${}_2F_1$ with the first $\Lambda+1$ terms omitted, and the notation $(s)_\lambda$ is the Pochhammer's symbol

$$(s)_\lambda = \frac{\Gamma(s+\lambda)}{\Gamma(s)}, \tag{143}$$

then V_p can be written in the form

$$V_p = (2q_{12}+1) \sum_{\lambda=0}^{\Lambda} (s+p+3)_\lambda Z_{\alpha\beta}^{\lambda} B(p, q_{12}, \lambda, \mathcal{L}_{12}, \mathcal{M}_{12})$$

$$+\sum_{k_{12}=0}^{\infty} C_{-2q_{12}k_{12}} \frac{(\mathcal{L}_{12}+2k_{12})!}{(\mathcal{L}_{12}+2k_{12}+p+1)!(\mathcal{M}_{12}+2k_{12}+p+2)} \times F_{\Lambda}(1, s+p+3; \mathcal{M}_{12}+2k_{12}+p+3; Z_{\alpha\beta}) \tag{144}$$

with B being defined by

$$B(p,q,\lambda,L,M) = \sum_{k=0}^{\infty} \frac{(2q+2k)!!(2k-1)!!(L+2k)!(M+2k+p+1)!}{(2q+2k+1)!!(2k)!!(L+2k+p+1)!(M+2k+p+\lambda+2)!}. \tag{145}$$

The asymptotic behaviour of the infinite series in (144) is now $k_{12}^{-p-4-\Lambda}$. The choice of $\Lambda = 15$–20 is just adequate to greatly improve the rate of convergence. As for B, since the general term in (145) is asymptotically proportional to $k^{-p-\lambda-3}$, one can calculate B directly using (145) for large $p+\lambda$. For small $p+\lambda$, as derived in the appendix, one can use the formula

$$B(p,q,\lambda,L,M) = \sum_{\nu=0}^{q} \frac{(2\nu-1)!!(2q-2\nu-1)!!}{(2\nu)!!(2q-2\nu)!!} S_B(2\nu+1, L+1, M+p+2, p, \lambda), \tag{146}$$

where S_B is given by

$$S_B(a,b,c,p,q) = \sum_{s=0}^{p}\sum_{k=0}^{q} \frac{(-1)^{k+s}}{k!(q-k)!s!(p-s)!} g_B(a, b+s, c+k). \tag{147}$$

In (147), $g_B(a,b,c)$ is a symmetric function of a, b, and c given by

$$\begin{aligned} g_B(a,b,c) &= \frac{\Psi(a/2)}{2(c-a)(a-b)} + \frac{\Psi(b/2)}{2(a-b)(b-c)} + \frac{\Psi(c/2)}{2(b-c)(c-a)}, \\ &\qquad a \neq b, b \neq c, c \neq a; \\ g_B(a,a,c) &= \frac{\Psi(a/2)}{2(a-c)^2} - \frac{\Psi(c/2)}{2(a-c)^2} - \frac{\Psi'(a/2)}{4(a-c)}, \qquad a \neq c; \\ g_B(a,a,a) &= -\tfrac{1}{16}\Psi''(a/2). \end{aligned} \tag{148}$$

Finally, for case 3 where $\mu_1 = 0$ and $\mu_2 = 2$, after using (142) V_p becomes

$$V_p = \frac{\mathcal{L}_{12}!}{(\mathcal{L}_{12}+p+1)!} \left[(2q_{12}+1) \sum_{\lambda=0}^{\Lambda} \frac{(s+p+\lambda+2)!}{(s+p+2)!} A(\lambda, q_{12}, \mathcal{M}_{12}+p+2) Z_{\alpha\beta}^{\lambda} + \sum_{k_{12}=0}^{\infty} \frac{C_{-2q_{12}k_{12}}}{(\mathcal{M}_{12}+2k_{12}+p+2)} F_{\Lambda}(1, s+p+3; \mathcal{M}_{12}+2k_{12}+p+3; Z_{\alpha\beta}) \right]. \tag{149}$$

The asymptotic behaviour of V_p in (149) is $k_{12}^{-\Lambda-3}$ and thus the rate of convergence is now improved from k_{12}^{-2} to $k_{12}^{-\Lambda-3}$.

Table 2 lists some values of the integral

$$\int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, \mathrm{d}\boldsymbol{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{-2} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3}. \tag{150}$$

Porras and King [9] also evaluated this integral using an expansion for r_{12}^{-2} in terms of the Gegenbauer polynominal. Some results included in table 2 reproduce their calculations.

Table 2. Values of $\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{-2} r_{23}^{j_{23}} r_{31}^{j_{31}} \mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3}$.

j_1	j_2	j_3	j_{23}	j_{31}	α	β	γ	Integral
0	0	0	3	1	0.65	2.9	2.7	405.798 619 419 015 8
0	0	0	1	−1	0.65	2.9	2.7	16.986 781 603 319 52
0	0	0	−1	−1	0.65	2.9	2.7	15.271 059 472 580 98
1	1	1	−1	−1	1	2	3	15.397 606 932 243 12
1	2	0	−1	−1	2	1	3	30.330 168 684 237 67
0	2	3	3	1	1	2	3	12 157.365 012 010 14
2	3	1	3	−1	4	3	2	12. 319 239 848 913 46
2	3	4	1	0	1	1	1	1 444 860 737.375 033
0	1	0	2	0	1	1	1	112 714.016 988 225 9
−2	1	0	1	1	1	1	1	56 715.028 924 051 61
−2	−1	2	1	3	1	1	1	100 998 106.483 377 9
−1	−1	0	3	1	1	1	1	837 298.166 941 531 8
1	1	1	1	1	1	1	1	1 078 827.141 800 905

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council of Canada. ZCY is also supported by the National Science Foundation through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory.

Appendix: The auxiliary series A and B

A.1. The series $A(m, q, n)$

Using the expression [7]

$$\frac{(2q+2k)!!(2k-1)!!}{(2q+2k+1)!!(2k)!!} = \sum_{\nu=0}^{q} \frac{(2\nu-1)!!(2q-2\nu-1)!!}{(2\nu)!!(2q-2\nu)!!} \frac{1}{2k+2\nu+1}, \tag{A1}$$

equation (138) becomes

$$A(m,q,n) = \sum_{\nu=0}^{q} \frac{(2\nu-1)!!(2q-2\nu-1)!!}{(2\nu)!!(2q-2\nu)!!} S_A(m, 2\nu+1, n), \tag{A2}$$

where

$$S_A(m,p,c) = \sum_{n=\mathrm{even}}^{\infty} \frac{1}{(n+p)(n+c)(n+c+1)\cdots(n+c+m)}. \tag{A3}$$

Then

$$\begin{aligned} S_A(1,p,c) &= \sum_{n=\mathrm{even}}^{\infty} \frac{1}{(n+p)(n+c)(n+c+1)} \\ &= \sum_{n=\mathrm{even}}^{\infty} \left[\frac{1}{(n+p)(n+c)} - \frac{1}{(n+p)(n+c+1)} \right] \\ &= g_A(p,c) - g_A(p,c+1) \\ &= \sum_{k=0}^{1} \frac{(-1)^k}{k!(1-k)!} g_A(p, c+k) \end{aligned} \tag{A4}$$

with g_A being defined by

$$g_A(p,c) = \sum_{n=\text{even}}^{\infty} \frac{1}{(n+p)(n+c)}. \tag{A5}$$

$$\begin{aligned} S_A(2,p,c) &= \sum_{n=\text{even}}^{\infty} \frac{1}{(n+p)(n+c)(n+c+1)(n+c+2)} \\ &= \frac{1}{2}\sum_{n=\text{even}}^{\infty}\left[\frac{1}{(n+p)(n+c)(n+c+1)} - \frac{1}{(n+p)(n+c+1)(n+c+2)}\right] \\ &= \tfrac{1}{2}[S_A(1,p,c) - S_A(1,p,c+1)] \\ &= \tfrac{1}{2}[g_A(p,c) - 2g_A(p,c+1) + g_A(p,c+2)] \\ &= \sum_{k=0}^{2} \frac{(-1)^k}{k!(2-k)!} g_A(p,c+k). \end{aligned} \tag{A6}$$

This can easily be generalized by the method of mathematical induction. The final result is

$$S_A(m,p,c) = \sum_{k=0}^{m} \frac{(-1)^k}{k!(m-k)!} g_A(p,c+k). \tag{A7}$$

Since for the digamma function $\Psi(x)$

$$\Psi(x) = -\gamma - \frac{1}{x} + \sum_{n=1}^{\infty}\left(\frac{1}{n} - \frac{1}{n+x}\right), \tag{A8}$$

one obtains

$$\sum_{n=0}^{\infty} \frac{1}{(n+x)(n+y)} = \frac{\Psi(x) - \Psi(y)}{x-y}. \tag{A9}$$

Thus

$$\begin{aligned} g_A(p,c) &= \sum_{n=0}^{\infty} \frac{1}{(2n+p)(2n+c)} \\ &= \frac{1}{4}\sum_{n=0}^{\infty} \frac{1}{(n+p/2)(n+c/2)} \\ &= \frac{\Psi(c/2) - \Psi(p/2)}{2(c-p)}. \end{aligned} \tag{A10}$$

It is obvious that for $c = p$,

$$g_A(p,p) = \tfrac{1}{4}\Psi'(p/2). \tag{A11}$$

A.2. The series $B(p,q,\lambda,L,M)$

By (A1), (145) becomes

$$B(p,q,\lambda,L,M) = \sum_{\nu=0}^{q} \frac{(2\nu-1)!!(2q-2\nu-1)!!}{(2\nu)!!(2q-2\nu)!!} S_B(2\nu+1, L+1, M+p+2, p, \lambda), \tag{A12}$$

where

$$S_B(a,b,c,p,q) = \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)\Pi_{i=0}^{p}(n+b+i)\Pi_{j=0}^{q}(n+c+j)}. \tag{A13}$$

Then

$$S_B(a,b,c,p,0) = \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)(n+c)\Pi_{i=0}^{p}(n+b+i)}, \tag{A14}$$

and

$$\begin{aligned}
S_B(a,b,c,p,1) &= \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)(n+c)(n+c+1)\Pi_{i=0}^{p}(n+b+i)} \\
&= \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)\Pi_{i=0}^{p}(n+b+i)} \left(\frac{1}{n+c} - \frac{1}{n+c+1}\right) \\
&= S_B(a,b,c,p,0) - S_B(a,b,c+1,p,0) \\
&= \sum_{k=0}^{1} \frac{(-1)^k}{k!(1-k)!} S_B(a,b,c+k,p,0).
\end{aligned} \tag{A15}$$

Similarly,

$$\begin{aligned}
&S_B(a,b,c,p,2) \\
&\quad= \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)(n+c)(n+c+1)(n+c+2)\Pi_{i=0}^{p}(n+b+i)} \\
&\quad= \tfrac{1}{2} \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)\Pi_{i=0}^{p}(n+b+i)} \\
&\qquad \times \left[\frac{1}{(n+c)(n+c+1)} - \frac{1}{(n+c+1)(n+c+2)}\right] \\
&\quad= \tfrac{1}{2}[S_B(a,b,c,p,1) - S_B(a,b,c+1,p,1)] \\
&\quad= \tfrac{1}{2} S_B(a,b,c,p,0) - S_B(a,b,c+1,p,0) + \tfrac{1}{2} S_B(a,b,c+2,p,0) \\
&\quad= \sum_{k=0}^{2} \frac{(-1)^k}{k!(2-k)!} S_B(a,b,c+k,p,0).
\end{aligned} \tag{A16}$$

By the method of mathematical induction, one can show that

$$S_B(a,b,c,p,q) = \sum_{k=0}^{q} \frac{(-1)^k}{k!(q-k)!} S_B(a,b,c+k,p,0). \tag{A17}$$

As for $S_B(a,b,c,p,0)$, application of the above procedure yields

$$S_B(a,b,c,p,0) = \sum_{s=0}^{p} \frac{(-1)^s}{s!(p-s)!} g_B(a,b+s,c), \tag{A18}$$

where g_B is defined by

$$g_B(a,b,c) = \sum_{n=\text{even}}^{\infty} \frac{1}{(n+a)(n+b)(n+c)}. \tag{A19}$$

g_B can be expressed in terms of the digamma function $\Psi(x)$ according to (A8). The final result is listed in (148).

References

[1] Yan Z-C and Drake G W F 1995 *Phys. Rev.* A **52** 3711
[2] Yan Z-C and Drake G W F 1995 *Phys. Rev.* A **52** R4316
[3] Yan Z-C, McKenzie D K and Drake G W F 1996 *Phys. Rev.* A **54** 1322
[4] Yan Z-C, Babb J F, Dalgarno A and Drake G W F 1996 *Phys. Rev.* A **54** 2824
[5] Drake G W F and Yan Z-C 1995 *Phys. Rev.* A **52** 3681
[6] King F W 1991 *Phys. Rev.* A **44** 7108
[7] Lüchow A and Kleindienst H 1992 *Int. J. Quantum Chem.* **41** 719
[8] Lüchow A and Kleindienst H 1993 *Int. J. Quantum Chem.* **45** 445
[9] Porras I and King F W 1994 *Phys. Rev.* A **49** 1637
[10] Edmonds A R 1985 *Angular Momentum in Quantum Mechanics* (Princeton, NJ: Princeton University)
[11] Perkins J F 1968 *J. Chem. Phys.* **48** 1985
[12] Brink D M and Satchler G R 1968 *Angular Momentum* 2nd edn (Oxford: Clarendon)
[13] Drake G W F 1978 *Phys. Rev.* A **18** 820
[14] Yan Z-C and Drake G W F 1994 *Can. J. Phys.* **72** 822
[15] Yan Z-C and Drake G W F 1996 *Chem. Phys. Lett.* **259** 96
[16] Sack R A 1964 *J. Math. Phys.* **5** 245
[17] Yan Z-C and Drake G W F 1997 *Phys. Rev. Lett.* **79** 1646