

# Evaluation of Hylleraas-CI atomic integrals by integration over the coordinates of one electron. I. Three-electron integrals

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**Abstract** A method to evaluate the nonrelativistic electron-repulsion, nuclear attraction and kinetic energy three-electron integrals over Slater orbitals appearing in Hylleraas-CI (Hy-CI) electron structure calculations on atoms is shown. It consists on the direct integration over the interelectronic coordinate  $r_{ij}$  and the successive integration over the coordinates of one of the electrons. All the integrals are expressed as linear combinations of basic two-electron integrals. These last are solved in terms of auxiliary two-electron integrals which are easy to compute and have high accuracy. The use of auxiliary three-electron ones is avoided, with great saving of storage memory. Therefore this method can be used for Hy-CI calculations on atoms with number of electrons  $N \geq 5$ . It has been possible to calculate the kinetic energy also in terms of basic two-electron integrals by using the Hamiltonian in Hylleraas coordinates, for this purpose some mathematical aspects like derivatives of the spherical harmonics with respect to the polar angles and recursion relations are treated and some new relations are given.

**Keywords** Hylleraas-CI · Three-electron integrals · Kinetic energy · Slater orbitals

## 1 Introduction

Mathematical and computational developments in the analytical calculations of integrals play a key role in the successful extension and future applications of the explicitly correlated methods. A recent book is devoted to the analytical evaluation of atomic and molecular correlated and uncorrelated integrals over Slater orbitals [1].

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Among the highly accurate methods, the Configuration Interaction method (CI) using Slater orbitals suffers from slow convergence and requires a very large number of configurations, what reduces its applicability to small atoms. As it is well known, the CI wave function includes implicitly  $r_{ij}^2$  terms. These are known not to be as efficient as the linear  $r_{ij}$  ones, which fulfill the so-called Kato cusp condition [2]. As a consequence, explicitly correlated wave functions with linear  $r_{ij}$  like the Hylleraas-type wave functions [3] converge faster to the exact solution of the Schrödinger equation [4]. Wave functions which include also negative powers of the radial coordinates of the electrons and logarithmic terms show very good convergence to the exact solution, as it has been the case in recent calculations on helium atom [5].

Hylleraas-type wave functions led recently to highly accurate energy results in calculations of light atoms, i.e. helium [6], lithium [7], and beryllium [8] and the two-electron molecules  $H_2$  [9], and  $HeH^+$  [10]. They were also applied to the larger atom Ne [11], and the LiH molecule [12]. The challenge in the future is the application of the Hylleraas-type methods to calculate with high accuracy the nonrelativistic energy of the first row of atoms and further.

Hylleraas-type wave functions can be used to calculate a wide range of properties, to obtain closed form expressions of the exact one-electron density-matrix [13], to get the analytical representation of the exchange-correlation potential [14] in density functional theory (DFT), and as trial wave functions for quantum Monte Carlo methods.

The motivation of this paper was to overcome the demanding memory problem in calculations on boron atom using a large set of exponents. Clary and Handy [11] concerning the Ne atom, pointed out the problem to store all the integrals in core: *“It is thus clear that further investigations in the CI-Hy method are necessary, with particular reference to the development of programs and methods of efficiently calculate the three- and four-electron integrals before an extensive configuration search and a subsequent improvement in the neon energy reported here can be made”*. Indeed, the number of three- and four-electron auxiliary integrals, which should be stored in order to calculate efficiently the matrix elements, according to our computer program, grows as  $n_{orb}^6 \times n_{pow}^3$  and  $n_{orb}^8 \times n_{pow}^4$ , respectively, where  $n_{orb}$  is the number of atomic orbitals with different exponents and  $n_{pow}$  is the maximal value of the sum of the powers of the charge distributions and operators. Consequently, conventional Hy-CI calculations of atoms with  $N \geq 5$  request huge computer memory. This was the case in calculations on boron atom which are in progress [15].

In the standard Hylleraas method all possible interelectronic distances  $r_{ij}$  may be included simultaneously in a configuration with the symmetry of the ground state. Until now it has been applied using only  $s$ -type orbitals, therefore all the resulting integrals have been of radial symmetry. Excitations to angular orbitals are not included in this wave function. The resulting matrix elements contain nevertheless many-electron integrals, which are difficult to evaluate for  $N \geq 4$  electrons. For  $N = 4$  the four-electron integrals have not been fully solved yet. Integrals for double-linked wave functions were worked out by Kleindienst et al. [16], the most general four-electron integrals were given by King [17]. For  $N \geq 5$  one would have to solve generally five-electron integrals, six-electron ones, and so on.

The Hylleraas-CI (Hy-CI) wave function [18, 19] is a Configuration-Interaction wave function containing up to one linear  $r_{ij}$  per configuration. Excited configurations including  $r_{ij}$  are possible and theoretically replace the many- $r_{ij}$  configurations of the standard Hylleraas wave function.

Due to the presence of only one  $r_{ij}$  per configuration and to the form of the operators in the Hamiltonian, the Hy-CI wave function leads only to two-, three- and four-electron integrals, for any atom or system, which can be classified in the following types: two- and three-electron integrals:<sup>1</sup>

$$\langle r_{12} \rangle, \quad \langle r_{12}r_{13} \rangle, \quad \left\langle \frac{r_{12}}{r_{13}} \right\rangle, \quad \left\langle \frac{r_{12}r_{13}}{r_{23}} \right\rangle, \quad (1)$$

and three kinds of four-electron integrals, which evaluation will be shown in a forthcoming paper II of this series [20]:

$$\left\langle \frac{r_{12}r_{13}}{r_{14}} \right\rangle, \quad \left\langle \frac{r_{12}r_{13}}{r_{34}} \right\rangle, \quad \left\langle \frac{r_{12}r_{34}}{r_{23}} \right\rangle. \quad (2)$$

The classical method to solve the three- and four-electron integrals appearing in non-relativistic Hylleraas-type calculations is to expand them in terms of auxiliary three-electron integrals [18, 21–33], and four-electron auxiliary integrals [8, 18, 17, 34, 35], respectively, by the use of the Laplace expansion [36]. Radial four-electron integrals were also evaluated analytically [37]. The three-electron integral with fully linked indices  $\langle r_{12}r_{13}r_{23}^{-1} \rangle$ , has been calculated by expansion in three-electron auxiliary integrals [29, 30, 38], and analytically [39–42].

The method of this paper consists on integrating directly over the interelectronic distances  $r_{ij}$ , taken as integration coordinates. The expansion of  $r_{ij}$  into  $s_{ij}$  and  $g_{ij}$  (smaller and greater of  $r_1$  and  $r_2$ ) is avoided, which produced the great number of auxiliary integrals. Instead a successive integration over the coordinates of one electron is done, and an integral of lower order results. The three-electron integrals are broken down in linear combinations of two-electron integrals and consequently, the calculation of three-electron auxiliary integrals is entirely avoided. This method of integration is based on the theory of Calais and Löwdin [43], who evaluated radial and angular two-electron integrals. The fully linked three-electron integral was evaluated by Szász [44] in the year 1962, parallelly to Calais and Löwdin, essentially using the same method. The Szász's method is similar to the method used here, he used a similar rotation formula and direct integration over  $r_{ij}$ . Drake treated the case of general angular two-electron integrals [45], and relativistic two-electron integrals [46]. Perkins [47] extended the method to evaluate three- and four-electron radial integrals (restricted to  $s$ -type orbitals). In this paper the method is extended: (1) to the calculation of integrals where one of the interelectronic distances  $r_{ij}$  has a negative power,

<sup>1</sup> The notation e.g.  $\langle r_{12}r_{13} \rangle$  represents the integral where the left and right hand orbitals of electrons 1, 2 and 3 are involved:  $\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)|r_{12}r_{13}|\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3) \rangle$ . The indices of the integrals can be interchanged to write them in these forms. The usual CI integrals  $\langle 1/r_{12} \rangle$  are obviated as so as the integral  $\langle r_{12}^2 \rangle$ .

i.e.  $\langle r_{12}r_{13}^{-1} \rangle$ , and (2) to correlated angular integrals, that is, for any Slater orbital  $s, p, d, f, \dots$ . The angular four-electron integrals were until now never done by this method of integration, they will be presented in a following paper of these series.

The kinetic energy three-electron integrals are solved in terms of two-electron ones. The derivatives in the kinetic energy operator would have made it necessary to expand  $r_{ij}$  in  $s_{ij}$  and  $g_{ij}$ , which would lead to three-electron auxiliary integrals. The use of the Hamiltonian in Hylleraas coordinates [48] allows to differentiate separately with respect to every coordinate, leading to three-electron integrals which can be evaluated in terms of two-electron ones. For this it has been necessary to perform the derivatives of the spherical harmonics with respect to the polar angles. Some new recursion relations are given in the Appendix C. The resulting equations for the angular kinetic energy look somehow cumbersome, but they can be directly programmed, many terms cancel, leading to one or few radial three-electron integrals.

Finally, this integration method can be straightforward extended to higher powers  $\nu$  of  $r_{ij}^\nu$  appearing in the standard Hylleraas method. Also this method can be used to reduce five-, six-, and many-electron integrals with an unlinked electron index to integrals of one order less.

Along this work many of the integrals were first solved by using the algebraic program Maple [49]. The kinetic energy results have been checked with the ones of Sims and Hagstrom [33] showing complete agreement. The integrals have been calculated using a Fortran 90 program code which uses quadruple precision (in our machine, an accuracy of about 30 decimal digits). The program code has been thoroughly compared with the three-electron and kinetic energy codes from Sims and Hagstrom showing full agreement of 30 decimal digits (J. S. Sims, personal communication).

## 2 Theory

Let us define the Slater orbitals specified by the quantum numbers  $n, m$  and  $l$  with an unnormalized radial part and orthonormal spherical harmonics:

$$\begin{aligned}\phi^*(\mathbf{r}) &= r^{n-1} e^{-\alpha r} Y_l^{m*}(\theta, \phi), \\ \phi'(\mathbf{r}) &= r^{n'-1} e^{-\alpha' r} Y_l^{m'}(\theta, \phi).\end{aligned}\quad (3)$$

The spherical harmonics in Condon and Shortley phases [50, p. 52] are given by:

$$Y_l^m(\theta, \phi) = (-1)^m \left[ \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}, \quad (4)$$

with the associated Legendre functions  $P_l^m(\cos \theta)$  defined:

$$P_l^m(\cos \theta) = \sin^m \theta \frac{d^{m+l}}{d(\cos \theta)^m} (\cos^2 \theta - 1)^l. \quad (5)$$

The spherical harmonics and associated Legendre functions used along this work are written explicitly in [51, p. 14], and defined as in Ref. [18]. They obey the condition:

$$Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi). \quad (6)$$

We define the one-electron charge distributions by expanding or linearizing the products of spherical harmonics with equal argument using the formula [18, Eq. 12]:

$$Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \sum_{L=|l-l'|}^{l+l'} \left[ \frac{2L+1}{4\pi} \right]^{1/2} C^L(l', m'; l, m) Y_L^{m'-m}(\theta, \phi), \quad (7)$$

where the Condon–Shortley coefficients [50, Eqs. 6–11] are defined by:

$$C^L(l', m', l, m) = \left[ \frac{4\pi}{2L+1} \right] \int Y_L^{m'-m}(\theta, \phi) Y_{l'}^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) \sin \theta d\theta d\phi, \quad (8)$$

$L_i$  satisfies the triangular condition  $|l_i - l'_i| \leq L \leq l_i + l'_i$  and the restriction  $L_i \geq |M_i|$ . The summation is done in steps of two:  $L_i = |l_i - l'_i|, |l_i - l'_i| + 2, \dots, l_i + l'_i - 2, l_i + l'_i$  and  $M_i = m'_i - m_i$ . The lowest value of  $L_i$  depends also on  $m_i$ , for simplicity we will use the notation  $|l - l'|$  to recall on  $l$  and  $l'$ . For discussion about the use of the Condon and Shortley coefficients, see Appendix B and and Appendix in Ref. [33].

The charge distributions are:

$$\begin{aligned} \Omega_{N,L,M}(\mathbf{r}) &= \phi^*(\mathbf{r}) \phi'(\mathbf{r}) \\ &= \sum_{L=|l-l'|}^{l+l'} (2L+1)^{1/2} C^L(l', m'; l, m) r^{N-1} e^{-\omega r} Y_L^M(\theta, \phi), \end{aligned} \quad (9)$$

where  $N = n + n' - 1$ , and the exponents  $\omega = \alpha + \alpha'$ . In the next we will use capital letters  $N, L, M$  for the quantum numbers of charge distributions, while low letters  $n, l, m$  for the quantum numbers of the orbitals will be used.

The two-electron integrals are then defined:

$$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} = \int \Omega_{N_1, L_1, M_1}(\mathbf{r}_1) \Omega_{N_2, L_2, M_2}(\mathbf{r}_2) r_{12}^\nu d\mathbf{r}_1 d\mathbf{r}_2, \quad (10)$$

with the cases  $\nu = -1, 1, 2$  appearing in the Hy-CI method. After expanding the charge distributions, the two-electron integrals are:

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} \\ = \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \prod_{i=1}^2 \frac{(2L_i+1)^{1/2}}{4\pi} C^{L_i}(l'_i, m'_i; l_i, m_i) \end{aligned}$$

$$\begin{aligned}
 & \times \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \\
 & \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \\
 & \times \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
 & \times \int_0^\pi \int_0^{2\pi} r_{12}^\nu Y_{L_2}^{M_2}(\theta_2, \phi_2) \sin \theta_2 d\theta_2 d\phi_2, \tag{11}
 \end{aligned}$$

where radial and angular integrations have to be made. The three-electron integrals are defined:

$$\begin{aligned}
 & J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \\
 & = \int \Omega_{N_1, L_1, M_1}(\mathbf{r}_1) \Omega_{N_2, L_2, M_2}(\mathbf{r}_2) \Omega_{N_3, L_3, M_3}(\mathbf{r}_3) r_{12} r_{13}^\mu d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \tag{12}
 \end{aligned}$$

with  $\mu = -1, 1$ . After expanding the charge distributions, the three-electron integrals are:

$$\begin{aligned}
 & J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \\
 & = \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \sum_{L_3=|l_3-l'_3|}^{l_3+l'_3} \prod_{i=1}^3 \frac{(2L_i + 1)^{1/2}}{(4\pi)^{3/2}} C^{L_i}(l'_i, m'_i; l_i, m_i) \\
 & \times \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \\
 & \times \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \int_0^\pi \int_0^{2\pi} r_{12} Y_{L_2}^{M_2}(\theta_2, \phi_2) \sin \theta_2 d\theta_2 d\phi_2 \\
 & \times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_0^\pi \int_0^{2\pi} r_{13}^\mu Y_{L_3}^{M_3}(\theta_3, \phi_3) \sin \theta_3 d\theta_3 d\phi_3. \tag{13}
 \end{aligned}$$

The method of evaluation used here differs from the classical one. There are two steps, the first is a rotation.

Consider the triangle formed by  $r_1$  and  $r_2$ , see Fig. 1. The original idea from Calais and Löwdin consisted on making a rotation of one coordinate axis, which allows to

make a change of variable in the integral. Letting pass for a moment the  $z$ -axis through the  $r_1$  coordinate, the variables are transformed as  $\theta_2 \rightarrow \theta_{12}$ , and  $\phi_2 \rightarrow \phi_{12}$ . This may be understood graphically in Fig. 1. The volume element of electron 2 may be then written:

$$d\tau_2 = r_2^2 dr_2 \sin \theta_{12} d\theta_{12} d\phi_{12}. \quad (14)$$

As  $\theta_{12}$  is related to  $r_{12}$  through the cosine theorem:

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}, \quad (15)$$

we can differentiate on the left hand side of the equation with respect to  $r_{12}$ , and in the other side with respect to  $\theta_{12}$ :

$$2r_{12} dr_{12} = 2r_1 r_2 \sin \theta_{12} d\theta_{12}, \quad (16)$$

obtaining the relation, which will be used to change the variable of integration:

$$\sin \theta_{12} d\theta_{12} = \frac{r_{12}}{r_1 r_2} dr_{12}. \quad (17)$$

This equation will be used in the direct integration over the variable  $r_{12}$ . With the change of integration variable  $\theta_{12} \rightarrow r_{12}$ , the integration domain changes as  $\int_0^\pi \rightarrow \int_{|r_1-r_2|}^{r_1+r_2}$ . There are two regions of integration: when  $r_1 < r_2$  then  $|r_1 - r_2| = r_2 - r_1$  and when  $r_2 < r_1$  then  $|r_1 - r_2| = r_1 - r_2$ . The separation of domains of integration proposed by Perkins [47] has proved to be the best way. Other strategies lead to the same type of formulas. The domain of integration is divided into two parts:

$$J = D_1 - D_2 \quad (18)$$

with:

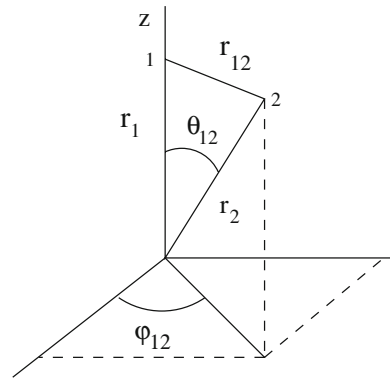
$$D_1 \rightarrow \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} + \int_{r_1}^{\infty} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} \rightarrow \int_0^{\infty} dr_2 \int_{r_1-r_2}^{r_2+r_1} dr_{12}, \quad (19)$$

$$D_2 \rightarrow \int_{r_1}^{\infty} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} - \int_{r_1}^{\infty} dr_2 \int_{r_2-r_1}^{r_1+r_2} dr_{12}. \quad (20)$$

The direct integration over the  $r_{12}$  coordinate [47] leads to the separation of the variables  $r_1$  and  $r_2$ :

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^v dr_{12} = \frac{1}{(v+1)} \sum_{i=1}^{\lfloor (v+2)/2 \rfloor} \binom{v+1}{2i-1} r_1^{v+2-2i} r_2^{2i-1}, \quad (21)$$

**Fig. 1** Definition and rotation of the coordinates of two electrons in an atomic center



where  $\lfloor (v + 2)/2 \rfloor$  is the floor function and denotes the integral part of  $(\delta + 2)/2$ .

The rotation of the axis produces a rotation of the functions, in this case, spherical harmonics. They suffer a transformation given by the rotation matrices, which can be written:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \left( \frac{4\pi}{2l + 1} \right)^{1/2} \sum_{m'_2=-l_2}^{l_2} Y_{l_2}^{m_2}(\theta_1, \phi_1) Y_{l_2}^{m'_2}(\theta_{12}, \phi_{12}), \tag{22}$$

In Appendix A this formula will be proved.  $Y_{l_2}^{m'_2}(\theta_{12}, \phi_{12})$  can be written according to Eq. 4 in terms of Legendre functions and  $e^{m'_2\phi_{12}}$ . It is then possible to integrate first over  $\phi_{12}$  which is an independent variable of integration (see in Fig. 1, that for a fixed  $r_{12}$ ,  $\phi_{12}$  may vary from 0 to  $2\pi$ ). This leads to  $m'_2 = 0$  and the summation reduces to one term containing  $P_L(\cos \theta_{12})$ , a Legendre polynomial. The Rodrigues representation [52] provides the formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l, \tag{23}$$

which yields upon expansion:

$$P_l(x) = \frac{1}{2^l} \sum_{k=0}^{\lfloor l/2 \rfloor} (-1)^k \binom{l}{k} \binom{2l - 2k}{l} x^{l-2k}, \tag{24}$$

where  $\lfloor l/2 \rfloor$  is the floor function. The argument  $x = \cos \theta_{12}$  can be expressed in radial coordinates:

$$\cos \theta_{12} = \frac{(r_1^2 + r_2^2 - r_{12}^2)}{2r_1 r_2}. \tag{25}$$

In the next sections the integrations will be carried out in more detail.



## 2.1 Three-electron integrals

The three-electron integrals are defined in Eqs. 12 and 13. Let us rotate the axis so that  $r_1$  coincides with the  $z$  axis, use Eq. 17 and the angular function of electrons 2 and 3 transformed according to Eq. 22. Substituting into the integral Eq. 13, it is possible to integrate first over  $\phi_{12}$  and  $\phi_{13}$  because they are independent. This leads to  $M'_2 = 0$  and  $M'_3 = 0$  and factors  $2\pi$ :

$$\begin{aligned}
 & J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \\
 &= \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \sum_{L_3=|l_3-l'_3|}^{l_3+l'_3} \prod_{i=1}^3 [(4\pi)(2L_i + 1)]^{1/2} \\
 &\quad \times C^{L_i}(l'_i, m'_i; l_i, m_i) \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
 &\quad \times \int_0^\pi \frac{1}{2} r_{12} P_{L_2}(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} \\
 &\quad \times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_0^\pi \frac{1}{2} r_{13}^\mu P_{L_3}(\cos \theta_{13}) \sin \theta_{13} d\theta_{13} \\
 &\quad \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1. \quad (26)
 \end{aligned}$$

This equation is valid for  $\mu = -1, 1$  and  $P_L(\cos \theta)$  are the Legendre Polynomials. At this point we could integrate over  $\theta_{12}$  and  $\theta_{13}$ , but as their integrations are independent of  $\theta_1$ , we solve first the three-fold integral over  $\theta_1$  and  $\phi_1$ . Using Eq. 6 we write the integral in the Condon and Shortley form Eq. 8. In addition, note that  $M_1 = -M_2 - M_3$  is fulfill:

$$\begin{aligned}
 & (-1)^{M_2} \int_0^\pi \int_0^{2\pi} Y_{L_2}^{-M_2*}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_1}^{M_1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \\
 &= (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) C^{L_1}(L_2, -M_2; L_3, M_3) \left[ \frac{2L_1 + 1}{4\pi} \right]^{1/2}. \quad (27)
 \end{aligned}$$

Finally the three-electron integral:

$$J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} = (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0)$$

$$\begin{aligned}
 & \times \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \sum_{L_3=|l_3-l'_3|}^{l_3+l'_3} \prod_{i=1}^3 (2L_i + 1)^{1/2} \\
 & \times C^{L_i}(l'_i, m'_i; l_i, m_i) (2L_1 + 1)^{1/2} C^{L_1}(L_2, -M_2; L_3, M_3) \\
 & \times J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu; L_2, L_3), \tag{28}
 \end{aligned}$$

where the angular integration has been performed and the radial three-electron introduced. In the programmable expression Eq. 28 only some terms of the summations will remain because of the Kronecker  $\delta$  factors and the  $C^k$  coefficients.

The radial three-electron integrals can be defined in two ways, for  $\mu = -1, 1$ :

$$\begin{aligned}
 & J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu; L_2, L_3) \\
 & = \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
 & \quad \times \int_0^\pi \frac{1}{2} r_{12} P_{L_2}(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \\
 & \quad \times \int_0^\pi \frac{1}{2} r_{13}^\mu P_{L_3}(\cos \theta_{13}) \sin \theta_{13} d\theta_{13}, \\
 & = \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^2}{r_1 r_2} P_{L_2}(\cos \theta_{12}) dr_{12} \\
 & \quad \times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2} \frac{r_{13}^{\mu+1}}{r_1 r_3} P_{L_3}(\cos \theta_{13}) dr_{13}, \tag{29}
 \end{aligned}$$

We are going to integrate over the coordinates of one electron in order to obtain an integral of lower order, a two-electron integral. As we are interested in the integrals of type  $\langle r_{12} r_{13} \rangle$ , and  $\langle \frac{r_{12}}{r_{13}} \rangle$ , we will integrate over electron 2, whose position does not vary in both cases. Note that Perkins [47] did not discuss the second kind of integral, but it has been proven by the author, that Perkins’ formulas are valid for the case  $\langle \frac{r_{12}}{r_{13}} \rangle$ . During the integration we are not interested in the coordinates of electron 3 which will not be affected.

Expanding the Legendre Polynomials  $P_{L_2}(\cos \theta_{12})$  according to Eq. 24, using the Binomial theorem twice, with indices  $q, p$ , we can directly integrate over the  $r_{12}$  variable. We treat  $D_1$  and  $D_2$  of Eqs. 19, 20 separately. For the first part  $D_1$  we have to evaluate the  $r_{12}$  integral:

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{2+2q} dr_{12} = \frac{1}{(2q+3)} \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} r_1^{2q+4-2i} r_2^{2i-1}. \quad (30)$$

$r_2$  is not linked to any other variable, and therefore the integration over  $r_2$  can be carried out leading to a  $A(n, \alpha)$  integral defined in Sect. 2.4. Substituting into  $D_1$  and rewriting the integral over  $r_1$  and  $r_3$  as a two-electron integral, which will be defined in the next Sect. 2.3, we finally have:

$$\begin{aligned} D_1 = & \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \\ & \times \binom{L_2-2k-q}{p} \times \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2-1+2k+2p+2i-L_2, \omega_2) \\ & \times I(N_1+L_2+2-2k-2p-2i, N_3; \omega_1, \omega_2; \mu; L_3). \end{aligned} \quad (31)$$

To calculate the part  $D_2$  we perform the direct integration of  $r_{12}$ , which leads to:

$$\frac{1}{(2q+3)} \frac{1}{2} \left[ (r_2-r_1)^{2q+3} - (r_1-r_2)^{2q+3} \right], \quad (32)$$

which leads upon expansion:

$$\frac{1}{(2q+3)} (r_2-r_1)^{2q+3}. \quad (33)$$

Substituting this into Eq. 29 and making the change of variable  $r_2-r_1 = y$ , we use the Binomial theorem to expand the powers of  $r_2$  with  $r_2 = y+r_1$ :

$$\begin{aligned} (r_1+y)^{N_2+2k+2p-L_2} = & \sum_{j=1}^{N_2+2k+2p+1-L_2} \binom{N_2+2k+2p+1-L_2}{j-1} \\ & \times r_1^{N_2+2k+2p-L_2-j} y^{j-1}. \end{aligned} \quad (34)$$

Note that now the integral over  $y$  leads to a  $A(n, \beta)$  integral. As the integrals over  $r_1$  and  $r_3$  can be rewritten as a basic two-electron integral, we obtain the part  $D_2$ , which together with  $D_1$  lead to:

$$\begin{aligned} & J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu; L_2, L_3) \\ & = \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\ & \quad \times \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \binom{L_2-2k-q}{p} \end{aligned}$$

$$\begin{aligned}
 & \times \left\{ \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2 - 1 + 2k + 2p + 2i - L_2, \omega_2) \right. \\
 & \times I(N_1 + L_2 + 2 - 2k - 2p - 2i, N_3; \omega_1, \omega_2; \mu; L_3) \\
 & - \sum_{j=1}^{N_2+2k+2p+1-L_2} \binom{N_2+2k+2p-L_2}{j-1} A(2q+2+j; \omega_2) \\
 & \left. \times I(N_1 + N_2 - 2q - j - 1, N_3; \omega_1 + \omega_2, \omega_3; \mu; L_3) \right\} \tag{35}
 \end{aligned}$$

The three-electron radial integral is a linear combination of two-electron ones. For  $L_2 = 0$ , then  $k = q = p = 0$ , the integral reduces to a radial one and agrees with Eq. 20 of Perkins [47]. Eq. 54 together with Eq. 40 give the total three-electron integral.

The occurring  $A(n, \alpha)$  auxiliary integrals in Eq. 35 have always a positive argument  $n$  because by definition  $N_2 \geq L_2 + 1$ , and therefore these integrals have solution. The first arguments of the  $I$  integrals can be negative, but nevertheless they can be evaluated as we will in Sect. 2.3. Equations 28 and 35 allow to calculate integrals including  $s$ -,  $p$ -,  $d$ -,  $f$ -,  $g$ -,  $h$ - ... Slater orbitals with great accuracy. In Table 1, a number of calculations of Hy-CI three-electron integrals are shown. The integral values have been thoroughly compared with the ones of Sims and Hagstrom (J. S. Sims, personal communication), which were obtained using auxiliary three-electron integrals, showing fully agreement in more than 30 digits. Many integrals have also been calculated with a Maple [49] program using 100 digits of accuracy.

### 2.2 Two-electron integrals

The two-electron integrals occurring in the Hy-CI method from Eqs. 10 to 11 after doing the rotation of the spherical harmonics in Eq. 22 as in the case of three-electron integrals are:

$$\begin{aligned}
 & I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} \\
 & = \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \\
 & \times \prod_{i=1}^2 (2L_i + 1)^{1/2} C^{L_i}(l'_i, m'_i; l_i, m_i) \\
 & \times \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
 & \times \int_0^\pi \frac{1}{2} r_{12}^\nu P_{L_2}(\cos \theta_{12}) \sin \theta_{12} d\theta_{12}
 \end{aligned}$$

**Table 1** Three-electron integrals ( $r_{12}^{\nu_1, \nu_2, \nu_3}$ ): the charge distributions are constructed with the exponents  $\alpha = 1.40$  for orbitals with  $\nu$ , otherwise  $\alpha = 2.86$

Charge distribution	$N_1$	$N_2$	$N_3$	$\omega_1$	$\omega_2$	$\omega_3$	$\nu$	$\mu$	$J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; \nu, \mu)_{1,1,1; 2,2,2; 3,3,3}^{m_1, m_1', m_2, m_2', m_3, m_3'}$
(1s1s, 1s2s'', 2s1s'')	1	2	2	5.72	4.26	4.26	1	1	0.43360 35040 31628 96644 48861 48030 $\times 10^{-5}$
(2p'' <sub>0</sub> 2p'' <sub>0</sub> , 1s1s, 2s''2s'')	3	1	3	2.80	5.72	2.80	1	1	0.10739 78306 79424 68755 47273 71639 $\times 10^{-2}$
(1s2s, 2p <sub>1</sub> 1s'', 2s''2p'' <sub>1</sub> )	2	2	3	5.72	4.26	2.80	1	1	0.59252 28510 41682 36719 83703 10602 $\times 10^{-6}$
(3p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p'' <sub>0</sub> )	4	3	3	5.72	5.72	4.26	1	1	0.49948 55683 00037 99144 99168 01541 $\times 10^{-6}$
(1s3d'' <sub>0</sub> , 1s1s, 1s3d'' <sub>0</sub> )	3	1	3	4.26	5.72	4.26	1	1	-0.13239 00165 89545 99710 26215 19568 $\times 10^{-6}$
(3d <sub>2</sub> 3d <sub>2</sub> , 1s1s, 3d <sub>2</sub> 3d'' <sub>2</sub> )	5	1	5	5.72	5.72	4.26	1	1	0.30436 13541 39604 44980 47650 22825 $\times 10^{-5}$
(3d <sub>0</sub> 3d <sub>0</sub> , 3d <sub>0</sub> 4d <sub>0</sub> , 4d <sub>0</sub> 4d'' <sub>0</sub> )	5	6	7	5.72	5.72	4.26	1	1	0.60815 81672 25805 84347 35665 61211 $\times 10^{-5}$
(4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f'' <sub>0</sub> )	7	7	7	5.72	5.72	4.26	1	1	0.18668 10714 43643 30085 62633 86625 $\times 10^{-4}$
(5g <sub>4</sub> 5g <sub>-4</sub> , 5g <sub>0</sub> 5g <sub>0</sub> , 5g <sub>-4</sub> 5g'' <sub>4</sub> )	9	9	9	5.72	5.72	4.26	1	1	-0.38139 83741 23940 87301 25483 13573 $\times 10^{-6}$
(6h <sub>5</sub> 6h <sub>5</sub> , 6h <sub>5</sub> 6h <sub>5</sub> , 6h <sub>5</sub> 6h'' <sub>5</sub> )	11	11	11	5.72	5.72	4.26	1	1	0.16580 01348 56801 11415 40854 65832
(1s1s, 1s2s'', 1s2s'')	1	2	2	5.72	4.26	4.26	1	-1	0.46067 93755 92941 44439 91694 42996 $\times 10^{-5}$
(2p'' <sub>-1</sub> 2p'' <sub>-1</sub> , 1s1s, 2s''2s'')	3	1	3	2.80	5.72	2.80	1	-1	0.17961 56183 43780 79836 75585 24594 $\times 10^{-3}$
(1s2s, 1s2p'' <sub>0</sub> , 2s''2p'' <sub>0</sub> )	2	2	3	5.72	4.26	2.80	1	-1	-0.29325 70321 56326 76315 76754 18333 $\times 10^{-6}$
(3s3s, 3p <sub>1</sub> 3p'' <sub>1</sub> , 3p'' <sub>-1</sub> 3p'' <sub>-1</sub> )	5	5	5	5.72	4.26	2.80	1	-1	0.48775 40916 66583 96596 86914 74376 $\times 10^{-4}$
(3d <sub>1</sub> 3d <sub>1</sub> , 1s1s, 3d <sub>1</sub> 3d'' <sub>1</sub> )	5	1	5	5.72	5.72	4.26	1	-1	0.88580 21951 81417 74242 20122 35173 $\times 10^{-6}$
(3d <sub>2</sub> 3d <sub>2</sub> , 3d <sub>2</sub> 3d <sub>2</sub> , 3d <sub>2</sub> 3d'' <sub>2</sub> )	5	5	5	5.72	5.72	4.26	1	-1	0.39119 62943 71525 23817 56562 34654 $\times 10^{-6}$
(4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f'' <sub>0</sub> )	7	7	7	5.72	5.72	4.26	1	-1	0.35801 59306 27837 55059 08860 35787 $\times 10^{-5}$
(5g <sub>4</sub> 5g <sub>4</sub> , 5g <sub>0</sub> 5g <sub>0</sub> , 5g <sub>4</sub> 5g'' <sub>4</sub> )	9	9	9	5.72	5.72	4.26	1	-1	0.13868 80908 21566 75419 70323 50220 $\times 10^{-3}$
(6h <sub>-5</sub> 6h <sub>-5</sub> , 6h <sub>0</sub> 6h <sub>0</sub> , 6h <sub>-3</sub> 6h'' <sub>-3</sub> )	11	11	11	5.72	5.72	4.26	1	-1	0.15001 30480 05940 35455 89341 87986 $\times 10^{-1}$

$$\times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1. \tag{36}$$

In the integrations over  $\theta_1$  and  $\phi_1$  we use the complex conjugate relation (6) and the orthogonality property of the spherical harmonics:

$$\int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 = (-1)^{M_1} \delta(M_1 + M_2, 0) \delta(L_1, L_2). \tag{37}$$

After angular integration the two-electron integrals are:

$$\begin{aligned} & I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} \\ &= (-1)^{M_1} \delta(M_1 + M_2, 0) \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \delta(L_1, L_2) \\ & \times \prod_{i=1}^2 (2L_i + 1)^{1/2} C^{L_i}(l'_i, m'_i; l_i, m_i) \\ & \times I(N_1, N_2; \omega_1, \omega_2; \nu; L_2) \end{aligned} \tag{38}$$

where  $I(N_1, N_2; \omega_1, \omega_2; \nu; L_2)$  are the basic radial two-electron integrals defined in the next section.

The powers which are of interest for the calculations are  $\nu = -1, 1, 2$ . The integration of the angular part leads to angular coefficients and basic two-electron integrals. Due to the presence of Kronecker  $\delta$  and Condon and Shortley coefficients many terms of the summation vanish.

The computer program for the two-electron integrals has been checked by comparison with values of Sims and Hagstrom (J. S. Sims, personal communication), showing full agreement. In Table 2, values of two-electron integrals including  $s$ -,  $p$ -,  $d$ -,  $f$ -,  $g$ -,  $h$ - ... Slater orbitals are given.

### 2.3 Basic two-electron integrals

The basic two-electron integrals are defined:

$$\begin{aligned} & I(N_1, N_2; \omega_1, \omega_2; \nu; L) \\ &= \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \end{aligned}$$

**Table 2** Two-electron integrals ( $r_{12}^{\nu}$ ): the charge distributions are constructed with the exponents  $\alpha = 1.40$  for orbitals with  $''$ , otherwise  $\alpha = 2.86$ 

Charge distribution	$N_1$	$N_2$	$\omega_1$	$\omega_2$	$\nu$	$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'}$
(1s 1s, 1s 1s)	1	1	5.72	5.72	1	0.87350 59088 73392 66795 94434 16545 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> '', 1s 1s)	3	1	4.26	5.72	1	0.23712 77012 83727 94893 45982 27493 $\times 10^{-3}$
(2p <sub>0</sub> 1s, 1s 2p <sub>0</sub> '')	2	2	5.72	4.26	1	-0.17796 44617 73516 30848 86700 45323 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> '')	3	3	5.72	4.26	1	0.97016 96970 53409 80887 31889 20964 $\times 10^{-4}$
(2p <sub>1</sub> 2p <sub>-1</sub> , 2p <sub>-1</sub> 2p <sub>1</sub> '')	3	3	5.72	4.26	1	-0.20051 32729 67598 61632 25838 25468 $\times 10^{-5}$
(2p <sub>1</sub> 2p <sub>1</sub> , 2p <sub>-1</sub> 2p <sub>-1</sub> '')	3	3	5.72	4.26	1	0.98019 53607 01789 73968 93181 12237 $\times 10^{-4}$
(3d <sub>0</sub> 3d <sub>0</sub> , 1s 1s)	5	1	5.72	5.72	1	0.51354 54639 45183 11307 64076 09391 $\times 10^{-4}$
(3d <sub>0</sub> 1s, 1s 3d <sub>0</sub> )	3	3	5.72	5.72	1	-0.34621 04251 31584 12117 51062 53522 $\times 10^{-6}$
(3d <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 3d <sub>0</sub> )	4	4	5.72	5.72	1	-0.23450 66528 11406 61493 93940 12732 $\times 10^{-5}$
(3d <sub>1</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 3d <sub>1</sub> )	4	4	5.72	5.72	1	-0.17686 25593 82904 43026 15541 43680 $\times 10^{-5}$
(3d <sub>0</sub> 3d <sub>0</sub> , 3d <sub>0</sub> 3d <sub>0</sub> )	5	5	5.72	5.72	1	0.21880 39161 87383 57280 73971 78995 $\times 10^{-4}$
(3d <sub>2</sub> 3d <sub>2</sub> , 3d <sub>2</sub> 3d <sub>2</sub> )	5	5	5.72	5.72	1	0.21914 51787 67998 99418 86552 06912 $\times 10^{-4}$
(4f <sub>0</sub> 1s'', 4f <sub>0</sub> 1s'')	4	4	4.26	4.26	1	-0.42288 64432 50031 61694 57281 30649 $\times 10^{-5}$
(4f <sub>3</sub> 2p <sub>1</sub> '', 2p <sub>1</sub> ''4f <sub>3</sub> )	5	5	4.26	4.26	1	-0.47240 74550 54197 25212 29823 18397 $\times 10^{-4}$
(4f <sub>0</sub> 3d <sub>0</sub> '', 4f <sub>0</sub> 3d <sub>0</sub> '')	6	6	4.26	4.26	1	-0.76004 44446 71947 13346 18437 83074 $\times 10^{-3}$
(4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f <sub>0</sub> )	7	7	5.72	5.72	1	0.81786 53166 09740 77823 76900 79206 $\times 10^{-4}$
(5g <sub>4</sub> 4f <sub>3</sub> , 5g <sub>-4</sub> 4f <sub>-3</sub> )	8	8	5.72	5.72	1	0.53430 52020 93629 62168 95761 47448 $\times 10^{-4}$
(5g <sub>-4</sub> 5g <sub>-4</sub> , 5g <sub>-4</sub> 5g <sub>-4</sub> )	9	9	5.72	5.72	1	0.74714 59475 99715 71165 95876 90193 $\times 10^{-3}$
(5g <sub>0</sub> 6h <sub>0</sub> , 6h <sub>0</sub> 5g <sub>0</sub> )	10	10	5.72	5.72	1	-0.42035 43165 82386 40055 84672 50207 $\times 10^{-3}$
(6h <sub>-5</sub> 6h <sub>-5</sub> , 6h <sub>-5</sub> 6h <sub>-5</sub> )	11	11	5.72	5.72	1	0.14275 01974 66940 02242 59848 77916 $\times 10^{-1}$
(1s 2p <sub>-1</sub> '', 1s 2p <sub>1</sub> )	2	2	4.26	5.72	2	0.44699 54319 37036 34511 44302 75528 $\times 10^{-4}$
(3d <sub>1</sub> 3d <sub>1</sub> , 3d <sub>-1</sub> 3d <sub>-1</sub> )	5	5	5.72	5.72	2	0.63160 92982 07984 62679 48473 21628 $\times 10^{-4}$
(4f <sub>0</sub> 4f <sub>0</sub> , 4f <sub>0</sub> 4f <sub>0</sub> )	7	7	5.72	5.72	2	0.49113 62805 26346 16780 00079 84461 $\times 10^{-3}$
(5g <sub>4</sub> 5g <sub>4</sub> , 5g <sub>4</sub> 5g <sub>4</sub> )	9	9	5.72	5.72	2	0.41906 26280 30062 29737 33646 47985 $\times 10^{-2}$

$$\begin{aligned}
& \times \int_0^{\pi} \frac{1}{2} r_{12}^{\nu} P_L(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} \\
& = \int_0^{\infty} r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
& \quad \times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^{\nu+1}}{r_1 r_2} P_L(\cos \theta_{12}) dr_{12}, \quad (39)
\end{aligned}$$

the second definition is obtained after the change of variable Eq. 17. For  $L = 0$ , the integrals reduce to the Perkins' two-electron radial integrals [47, Eq. 1]. The Eq. 39 agree up to a factor 1/2 with Drake's [45, Eqs. 7,42] and Yan and Drake's [46, Eq. 4] formulas obtained after angular integration in two-electron integrals. In this paper Eq. 39 have been obtained independently by integrating the three-electron integrals over the coordinates of one electron. Also we will evaluate these integrals in terms of auxiliary  $V$  integrals. Yan and Drake [46] solved  $I$  integrals with negative powers of  $r_i$  using hypergeometric functions.

The most important cases are the powers  $\nu = -1, 1, 2$ , and they are here derived separately to obtain efficient programmable expressions. Although general expressions of two-electron integrals can be found in the literature, it is of great importance to use those ones which do not lead to unwanted integrals like  $A(n, \alpha)$  with  $n < 0$ . In the first case,  $\nu = 1$ , we expand  $r_{12}$  in terms of Legendre Polynomials [36], collecting the terms in the form [47,53]:

$$r_{12} = \sum_{q=0}^{\infty} \left( -\frac{1}{2q-1} \frac{s_{12}^q}{g_{12}^{q-1}} + \frac{1}{2q+3} \frac{s_{12}^{q+2}}{g_{12}^{q+1}} \right) P_q(\cos \theta_{12}) \tag{40}$$

where  $s_{12}$  is the smallest of  $r_1$  and  $r_2$  and  $g_{12}$  is the greatest of  $r_1$  and  $r_2$ . There are two regions of integration:  $r_1 < r_2$  and  $r_2 < r_1$ . Substituting  $r_{12}$  into the integral and integrating over  $\theta_{12}$ , only the term  $q = L$  of the expansion remains. Grouping the powers together and writing the resulting integrals in the form of  $V$  auxiliary ones:

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; 1; L) = & \frac{\delta(L, q)}{(2L+2)} \\ & \times \left[ -\frac{1}{(2L-1)} [V(N_1+L+1, N_2-L+2; \omega_1, \omega_2) \right. \\ & + V(N_2+L+1, N_1-L+2; \omega_2, \omega_1)] \\ & + \frac{1}{(2L+3)} [V(N_1+L+3, N_2-L; \omega_1, \omega_2) \\ & \left. + V(N_2+L+3, N_1-L; \omega_2, \omega_1)] \right] \tag{41} \end{aligned}$$

The  $I(N_1, N_2; \omega_1, \omega_2; 1; L)$  are defined for  $N_1 + L \geq -1$  and  $N_2 + L \geq -1$  so that the first argument  $k$  of  $V(k, l; \alpha, \beta)$  is positive while the second  $l$  can be negative, with the restriction  $k + l \leq -1$ . In the calculation of all two-electron Hy-CI integrals these conditions are fulfilled. As the three-electron integrals are linear combinations of basic  $I(N_1, N_2; \omega_1, \omega_2; 1; L)$ , note that  $N_1$  can take negative values, but these in the practice, for three-electron integrals, are such that  $N_1 + L \geq -1$  is always fulfilled.

In the case  $\nu = -1$ , the integrals  $I(N_1, N_2; \omega_1, \omega_2; -1; L)$  are the usual two-electron integrals of the CI method.

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; -1; L) = & \int_0^{\infty} r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\ & \times \int_0^{\pi} \frac{1}{2} P_L(\cos \theta_{12}) \frac{1}{r_{12}} \sin \theta_{12} d\theta_{12}. \tag{42} \end{aligned}$$



Using the Laplace expansion written as [36]:

$$\frac{1}{r_{12}} = \sum_{q=0}^{\infty} P_q(\cos \theta_{12}) \frac{s_{12}^q}{g_{12}^{q+1}}, \quad (43)$$

and doing similar steps as in the case before, we finally have:

$$I(N_1, N_2; \omega_1, \omega_2; -1; L) = \frac{\delta(L, q)}{2(2L+2)} [V(N_1+L+1, N_2-L; \omega_1, \omega_2) + V(N_2+L+1, N_1-L; \omega_2, \omega_1)]. \quad (44)$$

Also here the integrals are defined for  $N_1+L \geq -1$  and  $N_2+L \geq -1$ . In the practice, this condition is always fulfilled in the calculations of two-, and three-electron integrals.

If  $\nu = 2$  we use the cosine law written as [47]:

$$r_{12}^2 = (s_{12}^2 + g_{12}^2)P_0(\cos \theta_{12}) - 2s_{12}g_{12}P_1(\cos \theta_{12}) \quad (45)$$

after integration over  $\theta_{12}$  only the terms  $L = 0, 1$  remain, respectively. We finally obtain:

$$I(N_1, N_2; \omega_1, \omega_2; 2; L) = \delta(L, 0) [A(N_1+3, \omega_1) A(N_2+1, \omega_2) + A(N_2+3, \omega_2) A(N_1+1, \omega_1) - \frac{2}{3} A(N_1+2, \omega_1) A(N_2+2, \omega_2)]. \quad (46)$$

The  $A(n, \alpha)$  integrals can always be calculated because by definition  $N_1, N_2 \geq 0$ , for  $L = 0$ .

The basic integrals show the symmetry property:

$$I(N_1, N_2; \omega_1, \omega_2; \nu; L) = I(N_2, N_1; \omega_2, \omega_1; \nu; L), \quad (47)$$

therefore  $N_1$  or  $N_2$  can be negative. If both  $N_1$  and  $N_2$  are negative at the same time, the conditions of  $V(k, l; \alpha, \beta)$ :  $k > 0$  and  $k+l \geq -1$  lead to  $N_1+N_2 \geq -2$ .

Using Eqs. 41, 44, 46 it is possible to calculate integrals including  $s$ -,  $p$ -,  $d$ -,  $f$ -,  $g$ -, ... Slater orbitals with great accuracy. No integrals  $A(n, \alpha)$  with  $n < 0$  appear, and therefore there is no loss of precision. Values of the basic two-electron integrals used in the calculations of three-electron integrals are given in Table 3. The integrals  $I$  appear repeatedly during the calculations. Computationally favorable would be to figure out the exponent combinations, calculate them a priori and store all necessary  $I$  integrals.

The radial  $J$  three-electron integrals calculated using the basic two-electron  $I$  integrals in terms of  $V(k, l; \alpha, \beta)$  auxiliary integrals, have 30 digits accuracy, when comparing with values obtained with Maple.

**Table 3** Some examples of calculation of basic two-electron integrals

$N_1$	$N_2$	$\omega_1$	$\omega_2$	$\nu$	$L$	$I(N_1, N_2; \omega_1, \omega_2; \nu; L)$
1	2	5.72	4.26	1	0	$0.13179\ 11369\ 69018\ 83310\ 68706\ 84572 \times 10^{-3}$
0	2	9.98	4.26	1	0	$0.17682\ 81603\ 30135\ 79087\ 03366\ 70515 \times 10^{-3}$
2	1	5.72	4.26	1	0	$0.14718\ 99890\ 51889\ 92488\ 52346\ 77136 \times 10^{-3}$
3	4	5.72	4.26	1	1	$-0.18998\ 03914\ 43413\ 57815\ 12859\ 36347 \times 10^{-4}$
-1	4	5.72	4.26	1	1	$-0.19826\ 83457\ 14215\ 25274\ 04093\ 73665 \times 10^{-3}$
-3	4	5.72	4.26	1	1	$-0.13036\ 00068\ 45803\ 00241\ 35411\ 44804 \times 10^{-4}$
6	5	5.72	4.26	1	2	$-0.52265\ 20625\ 88995\ 64851\ 83471\ 95040 \times 10^{-5}$
-1	4	5.72	4.26	1	3	$-0.16818\ 38115\ 88958\ 59965\ 24969\ 05666 \times 10^{-5}$
-3	4	5.72	4.26	1	3	$-0.13036\ 00068\ 45803\ 00241\ 35411\ 44804 \times 10^{-4}$
6	5	5.72	4.26	1	4	$-0.56347\ 95909\ 58278\ 20534\ 47071\ 54913 \times 10^{-6}$
4	5	5.72	4.26	-1	0	$0.62620\ 99559\ 50048\ 60166\ 25857\ 84776 \times 10^{-4}$
4	5	5.72	4.26	-1	2	$0.56268\ 78161\ 98078\ 67208\ 72797\ 57339 \times 10^{-5}$
8	5	5.72	4.26	-1	4	$0.58184\ 85531\ 61345\ 14905\ 89423\ 73621 \times 10^{-5}$

### 2.4 Auxiliary integrals

A characteristic of this method of integration is that for low quantum numbers of  $N_1$  and high quantum numbers of  $N_2, N_3$  in the three-electron integrals  $J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu; L_2, L_3)$  of Eq. 35, the integral  $I(n, m; \omega_1, \omega_2; \nu; l)$ , may take negative powers of  $n$  or  $m$ . Perkins repeated the integration procedure in the two-electron integrals and obtained a sum of products of two  $A(n, \alpha)$  auxiliary integrals, one of them with negative  $n$ . The auxiliary integrals  $A(n, \alpha)$  are defined for  $n \geq 0$ :

$$A(n, \alpha) = \int_0^\infty r_1^n e^{-\alpha r_1} dr_1 = \frac{n!}{\alpha^{n+1}}. \tag{48}$$

$A(n, \alpha)$  auxiliary integrals with negative  $n$  have no solution alone, but appropriate combinations of them lead to a solution including logarithmic terms [47]. In this method we have overcome this difficulty by calculating the  $I(n, m; \omega_1, \omega_2; \nu; l)$  integrals in terms of auxiliary two-electron integrals  $V(k, l; \alpha, \beta)$  with negative  $l$  and  $k + l \geq -1$ , which we call here *non-trivial* to distinguish them from the ones with both positive  $k, l$ .

The basic integrals  $I(n, m; \omega_1, \omega_2; \nu; l)$  are then defined for  $n+l \geq -1, m+l \geq -1$  and  $n+m \geq -2$ . The  $A(n, \alpha)$  integrals appearing in Eq. 35 never have a negative  $n$  as  $N_2 - 1 \leq L_2$  is always fulfilled. Therefore the need of logarithms is avoided, gaining in speed and accuracy (although logarithms can be also calculated accurately within the used computer precision [54]). In paper II, we will see that in some cases of one type of four-electron integrals it is necessary to combine groups of  $A(n, \alpha)$  integrals with negative  $n$ . Fortunately, the major part of four-electron integrals can be solved in terms of *non-trivial*  $V(k, l; \alpha, \beta)$ .

Also it is important for the total accuracy that we can calculate the positive integrals with more than 30–32 digits accuracy. If we use the technique of expanding

$I(n, m; \omega_1, \omega_2; \nu; l)$  in terms of  $A(n, \alpha)$  there is a subtraction of values of similar order (see Eq. 35) and the accuracy reduces to 26–28 digits.

The two-electron  $V(k, l; \alpha, \beta)$  auxiliary integrals are defined:

$$\begin{aligned} V(k, l; \alpha, \beta) &= \int_{0 < r_1 < r_2 < \infty} \int r_1^k r_2^l e^{-\alpha r_1} e^{-\beta r_2} dr_1 dr_2 \\ &= \int_0^\infty r_1^k e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^l e^{-\beta r_2} dr_2. \end{aligned} \quad (49)$$

for  $k, l$  positive, these integrals are easier and well-known. The  $V(k, l; \alpha, \beta)$  integrals were usually calculated using recursion relations first given by James and Coolidge [22], which due to subtraction were not always absolutely stable. We have used the more recent direct calculation of  $V(k, l; \alpha, \beta)$  auxiliary integrals from Frolov and Smith [55, Eq. 5] that consists on an explicit sum of products of  $A(n, \alpha)$  auxiliary integrals. The formula is very stable because it consists on a summation and therefore no loss of precision can appear:

$$V(k, l; \alpha, \beta) = \sum_{l'=0}^l \binom{l}{l'} A(l', \alpha) A(k+l-l', \alpha+\beta), \quad k, l \geq 0 \quad (50)$$

The formula was obtained by integrating over the coordinates of  $v$  after the substitution  $u = x$  and  $y = u + v$  on Eq. 49:

$$V(k, l; \alpha, \beta) = \int_0^\infty u^k e^{-(\alpha+\beta)u} du \int_0^\infty (u+v)^l e^{-\beta v} dv, \quad (51)$$

and turning back the substitution of  $u$ , see Eqs. 4–6 of [55].

The second type of auxiliary integrals are the *non-trivial* ones defined for  $k+l \geq -1$  and  $k > 0$  and used for the case  $l$  negative. They have been evaluated by Sims and Hagstrom [38, Eq. 33] with high accuracy using the so-called Larsson sum [21, Eq. 34],

$$V(k, l; \alpha, \beta) = \sum_{q=1}^{\infty} \frac{\alpha^{q-1} k!}{(k+q)!} A(k+l+q; \alpha+\beta), \quad k+l \geq -1, \quad k > 0, \quad l < 0 \quad (52)$$

Sims and Hagstrom checked these integrals for large positive and negative powers as so as for a large spectrum of  $s = \alpha/(\alpha+\beta)$ , when  $s$  was very close to 1 and 0, being  $\alpha, \beta$  exponents. Further, the author has checked the non-trivial  $V(k, l; \alpha, \beta)$  calculated with the Larsson sum against direct integration using the Maple program [49] at the required accuracy of the following equivalent formula of  $V(k, l; \alpha, \beta)$ :

$$V(k, l; \alpha, \beta) = \int_0^{\infty} r_2^l e^{-\beta r_2} dr_2 \int_0^{r_2} r_1^k e^{-\alpha r_1} dr_1 \quad (53)$$

the first integration over  $r_1$  leads to a polynomial in  $r_2$ , which combined with the negative  $l$  leads to an integrable expression. The accuracy of more than 30 decimal digits of the Larsson sum was confirmed. In addition, Eq. 52 is computationally very stable. For extreme values of  $s$  the summation converges slower, the sum limit in the program has to be put very high to ensure convergence.

More details of the non-trivial  $V(k, l; \alpha, \beta)$  integral can be found in Ref. [38]. We have used in this paper a computer program Vkl from Sims and Hagstrom to evaluate these integrals. In paper II of this series the four-electron integrals occurring in Hy-CI calculations will be evaluated in terms of these two kinds of  $V(k, l; \alpha, \beta)$  auxiliary integrals.

These integrals avoid the use of combinations of  $A(n, \alpha)$  with  $n < 0$  [47] which have the disadvantages: (1) they lead to logarithmic terms which reduce the speed of the program; (2) they lead to subtractions which reduce the accuracy of the calculations; and the not less important (3) these combinations are difficult to be programmed, because they have to be recognized, extracted from the computations and calculated appropriately, leading to many unwanted errors. The non-trivial  $V(k, l; \alpha, \beta)$  provide a powerful algorithm to calculate the basic  $I(n, m; \omega_1, \omega_2; \nu; l)$  integrals.

In an actual calculation, the  $V(k, l; \alpha, \beta)$  auxiliary integrals should be computed for the necessary exponents at the beginning of the calculation and stored in matrices or vectors.

### 3 Kinetic energy and nuclear attraction three-electron integrals

In this section we treat the kinetic energy integrals appearing in the Hy-CI method, the power of  $r_{ij}$  in the basis function set to 1. For any atomic number  $N \geq 3$  the kinetic energy integrals are of three-electron type. The method used here is to apply the Hamiltonian as defined in Ref. [48, Eq. 36] to the wave function. Sims and Hagstrom [33] developed the kinetic energy integrals using the transformation of Kolos and Roothaan [56] which partially avoids the differentiation with respect to  $r_{ij}$  terms appearing on the right hand side of the matrix elements. Here we will use the Hamiltonian written in polar and interelectronic coordinates and will solve the resulting integrals in terms of basic two-electron integrals.

Some terms of the Hamiltonian Ref. [48, Eq. 36] vanish when the wave function does not contain any, or more than one  $r_{ij}$ , or this one is set to the power 1. The kinetic energy terms are separable into a sum of one-electron kinetic energy terms. Following the technique of Ref. [33] we evaluate the kinetic energy of electron 1.

$$\hat{H}_1 = \hat{T}_{R_1} + \hat{T}_{\theta_1} + \hat{V}_1 \quad (54)$$

Let us separate the kinetic energy operator into radial and angular parts. The radial kinetic energy operator of electron 1 for a Hy-CI wave function [48, Eq. 21]:<sup>2</sup>

$$\hat{T}_{R_1} = -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1} \frac{\partial}{\partial r_1} - \sum_{j=2}^n \frac{2}{r_{1j}} \frac{\partial}{\partial r_{1j}} - \frac{1}{2} \sum_{j=2}^n \frac{r_1^2 + r_{1j}^2 - r_j^2}{r_1 r_{1j}} \frac{\partial^2}{\partial r_1 \partial r_{1j}} \quad (55)$$

and the angular one:<sup>3</sup>

$$\begin{aligned} \hat{T}_{\theta_1} = & \frac{1}{2} \frac{\hat{L}_1^2}{r_1^2} - \sum_{j=2}^n \left( \frac{r_j}{r_1 r_{1j}} \frac{\cos \theta_j}{\sin \theta_1} + \frac{1}{2} \cot \theta_1 \frac{r_{1j}^2 - r_1^2 - r_j^2}{r_1^2 r_{1j}} \right) \frac{\partial^2}{\partial \theta_1 \partial r_{1j}} \\ & - \sum_{j=2}^n \frac{r_j}{r_1 r_{1j}} \frac{\sin \theta_j}{\sin \theta_1} \sin(\phi_1 - \phi_j) \frac{\partial^2}{\partial \phi_1 \partial r_{1j}}. \end{aligned} \quad (56)$$

If the wave function on the right hand side has no  $r_{ij}$  term, the cross terms of the operator vanish. The angular momentum operator for electron 1 is:

$$\hat{L}_1^2 = -\frac{\partial^2}{\partial \theta_1^2} - \frac{1}{\sin^2 \theta_1} \frac{\partial^2}{\partial \phi_1^2} - \cot \theta_1 \frac{\partial}{\partial \theta_1}, \quad (57)$$

and the potential energy operator is:

$$V_1 = -\frac{Z}{r_1}. \quad (58)$$

Let us evaluate as an example the potential and kinetic energy integrals where on the right hand side a term with  $r_{13}$  appears and on the left hand side after permutations, for example, a term  $r_{12}$  appears. The orbitals are defined in Eq. 3 and the charge distributions in Eq. 9. Note that the operator does not affect the electrons which are not involved. To evaluate the nuclear attraction potential energy is simple:

$$\begin{aligned} I_{PE_1} = & \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{12} \mid \hat{V}_1 \mid \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{13} \right\rangle \\ = & -ZJ(N_1 - 1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3}, \end{aligned} \quad (59)$$

with  $Z$  the atomic nuclear charge (see Table 4).

<sup>2</sup> The radial kinetic energy operator [48, Eq. 22] is obtained summing up the kinetic energy operators of the single electrons [48, Eq. 21]. Unfortunately there is a typo in Eqs. 21 and 22 of Ref. [48], the correct factor is 2 and the term is  $-\sum_{j \neq 1}^5 \frac{2}{r_{1j}} \frac{\partial \psi}{\partial r_{1j}}$ , following Eq. 18. Also the angular part of the kinetic energy is a sum of the angular kinetic energy of the single electrons, see [48, Eqs. 34,35].

<sup>3</sup> Note that the kinetic energy operator can be separated into radial and angular parts although it contains  $r_{ij}$ . Only when the wave function contains simultaneously  $r_{ij}$  and angular orbitals, the cross angular terms of Eq. 74 will not vanish.

**Table 4** Potential energy three-electron integrals of electron 1.  $\alpha = 1.40$  for orbitals with  $''$ , otherwise  $\alpha = 2.86$ . Nuclear charge  $Z = 5$

Charge distribution	$\omega_1$	$\omega_2$	$\omega_3$	$I_{PE}$
(1s1s, 1s1s'', 1s1s'')	5.72	4.26	4.26	-0.69100 95936 46419 09356 13655 99564 × 10 <sup>-4</sup>
(1s1s, 1s2s'', 1s2s'')	5.72	4.26	4.26	-0.53283 14868 67595 50711 36514 66127 × 10 <sup>-4</sup>
(2p02p0, 1s1s, 2s''2s'')	5.72	5.72	2.80	-0.73313 52900 41262 72453 96580 78579 × 10 <sup>-4</sup>
(1s1s, 1s2p0'', 1s2p0'')	5.72	4.26	4.26	-0.68999 63860 56840 93636 96339 64867 × 10 <sup>-6</sup>
(1s2p0, 1s1s, 1s2p0'')	5.72	5.72	4.26	0.12500 51749 17197 56097 52328 50070 × 10 <sup>-5</sup>
(1s3d0'', 1s1s, 1s3d0'')	4.26	5.72	4.26	0.52719 55897 60854 52339 56333 42107 × 10 <sup>-6</sup>
(2p02p0'', 1s1s, 2p02p0'')	4.26	5.72	4.26	-0.29216 32946 78764 19887 16235 79072 × 10 <sup>-4</sup>
(1s1s, 2p02p0'', 2p02p0'')	5.72	4.26	4.26	-0.68762 04243 12947 45439 50115 40877 × 10 <sup>-4</sup>
(2p02p0, 2p02p0, 2p02p0)	5.72	5.72	5.72	-0.55447 61504 49669 84754 16741 12410 × 10 <sup>-6</sup>
(3d03d0'', 1s1s, 3d03d0'')	4.26	5.72	4.26	-0.10336 75817 73370 27913 80923 00882 × 10 <sup>-3</sup>
(3d03d0'', 3d03d0, 3d03d0'')	4.26	5.72	4.26	-0.41413 54719 97577 10716 12343 88915 × 10 <sup>-4</sup>
(2p12p1'', 1s1s, 1s1s)	4.26	5.72	5.72	-0.14174 70275 44922 47771 29056 60314 × 10 <sup>-4</sup>
(3d23d2, 1s1s'', 2s2s'')	5.72	4.26	4.26	-0.15996 14680 55114 15682 12521 84200 × 10 <sup>-5</sup>
(2p12p1'', 1s1s, 2p12p1'')	4.26	5.72	4.26	-0.29532 64682 17329 32601 19973 79124 × 10 <sup>-4</sup>
(2p12p1, 2p12p1'', 2p12p1'')	5.72	4.26	4.26	-0.15693 52016 51117 37368 62915 15878 × 10 <sup>-4</sup>
(3d13d1, 2p12p1'', 3d13d1'')	5.72	4.26	4.26	-0.25764 29358 27244 72887 46299 85635 × 10 <sup>-4</sup>
(3d23d2, 3d13d1'', 3d23d2'')	5.72	4.26	4.26	-0.51838 65767 18146 23857 27470 71550 × 10 <sup>-5</sup>
(2p02p0, 2p02p0'', 2p02p0'')	5.72	4.26	4.26	0.32031 53239 96744 65098 34059 34450 × 10 <sup>-8</sup>
(3d03d0, 3p03p0'', 3d03d1'')	5.72	4.26	4.26	0.36055 48794 79114 51535 69167 69702 × 10 <sup>-8</sup>
(2p-12p-1, 1s1s, 1s1s)	4.26	5.72	5.72	-0.14174 70275 44922 47771 29056 60314 × 10 <sup>-5</sup>
(3d-23d-2, 1s1s, 3d-23d-2'')	5.72	5.72	4.26	-0.12195 71137 43742 70748 10915 97961 × 10 <sup>-5</sup>

For the kinetic energy we have to evaluate:

$$I_{KE_1} = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12}|\hat{T}_{R_1} + \hat{T}_{\theta_1}|\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle. \tag{60}$$

The radial part:

$$I_{KE,R_1} = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12}|\hat{T}_{R_1}|\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle, \tag{61}$$

performing the derivatives given by the operator Eq. 55, combining terms, and using the definition of the three-electron integrals Eqs. 12 and 13, it can be straightforward obtained:

$$\begin{aligned} I_{KE,R_1} = & -\frac{(n_1'^2 - 1)}{2} J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ & + \frac{(2n_1' + 1)\alpha_1'}{2} J(N_1 - 1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ & - \frac{\alpha_1'^2}{2} J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ & - \frac{(n_1' + 1)}{2} J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \end{aligned}$$

$$\begin{aligned}
& + \frac{\alpha'_1}{2} J(N_1 + 1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1)_{l'_1, l'_1, l'_2, l'_2, l'_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \\
& - \frac{(1 - n'_1)}{2} J(N_1 - 2, N_2, N_3 + 2; \omega_1, \omega_2, \omega_3; 1, -1)_{l'_1, l'_1, l'_2, l'_2, l'_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \\
& - \frac{\alpha'_1}{2} J(N_1 - 1, N_2, N_3 + 2; \omega_1, \omega_2, \omega_3; 1, -1)_{l'_1, l'_1, l'_2, l'_2, l'_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \quad (62)
\end{aligned}$$

The  $J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, \mu; L_2, L_3)$  integrals are given by Eqs. 28 and 35. The first term of the angular kinetic operator can be easily evaluated by means of the eigenvalue equation of the square of the angular momentum operator:

$$\begin{aligned}
I_{KE, \theta_1, L} & = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \left| \frac{1}{2} \frac{\hat{L}_1^2}{r_1^2} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle \\
& = \frac{1}{2} l'_1(l'_1 + 1) J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l'_1, l'_1, l'_2, l'_2, l'_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3}, \quad (63)
\end{aligned}$$

where  $l'_1$  is the quantum number of  $\phi(\mathbf{r}_1)$ .

More difficult is the evaluation of the cross terms of Eq. 56. For our example, the summation cancels except for  $j = 3$ . Separating radial from angular differentiation, we have to calculate the derivatives of the angular part of electron 1 on the right hand side wave function using the operators of Eq. 56 and to solve the integrals:

$$I_{KE, \theta_1, 1} = - \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \left| \frac{r_3}{r_1 r_{13}} \frac{\cos \theta_3}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{13}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle, \quad (64)$$

$$\begin{aligned}
I_{KE, \theta_1, 2} & = - \frac{1}{2} \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \left| \frac{(r_{13}^2 - r_1^2 - r_3^2)}{r_1^2 r_{13}} \cot \theta_1 \right. \right. \\
& \quad \left. \left. \times \frac{\partial^2}{\partial \theta_1 \partial r_{13}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle, \quad (65)
\end{aligned}$$

$$\begin{aligned}
I_{KE, \phi_1, 3} & = - \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \left| \frac{r_3}{r_1 r_{13}} \frac{\sin \theta_3}{\sin \theta_1} \sin(\phi_1 - \phi_3) \right. \right. \\
& \quad \left. \left. \times \frac{\partial^2}{\partial \phi_1 \partial r_{13}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \right\rangle. \quad (66)
\end{aligned}$$

To evaluate these contributions to the kinetic energy, it is necessary to make the derivatives of the spherical harmonics with respect to the interelectronic coordinates and afterwards to use recursion relations. To avoid singularities we have to distinguish the cases of the quantum number  $m$  of the electron in which the operator acts:  $m'_1 = 0$  and  $m'_1 \neq 0$ . We make for the integrals Eqs. 64–66 the restriction  $l'_1 = 1, 2$  in order to avoid extremely large expressions in this paper. The extension to higher  $l'_1$  is straightforward. The rest of the quantum numbers can take any value.

Using the first term of Eq. C.9, substituting into the integral Eq. 64 and using the recursion relation Eq. C.1 we have:

$$\begin{aligned}
 I_{KE,\theta_1,1} = R & \left[ \frac{(2l'_1 + 1)(2l'_1 - 1)}{(2l'_3 + 1)} \right]^{1/2} \\
 & \times \int_0^\pi \int_0^{2\pi} Y_{l'_1}^{m_1*}(\theta_1, \phi_1) Y_{l'_1-1}^0(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \\
 & \times \int_0^\pi \int_0^{2\pi} Y_{l'_2}^{m_2*}(\theta_2, \phi_2) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \sin(\theta_2) d\theta_2 d\phi_2 \\
 & \times \left\{ \left[ \frac{(l'_3 + m'_3)(l'_3 - m'_3)}{(2l'_3 - 1)} \right]^{1/2} \right. \\
 & \times \int_0^\pi \int_0^{2\pi} Y_{l'_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3-1}^{m'_3}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \\
 & + \left[ \frac{(l'_3 + m'_3 + 1)(l'_3 - m'_3 + 1)}{(2l'_3 + 3)} \right]^{1/2} \\
 & \left. \times \int_0^\pi \int_0^{2\pi} Y_{l'_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3+1}^{m'_3}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \right\}, \\
 & m'_1 = 0, \quad l'_1 = 1, 2 \quad (67)
 \end{aligned}$$

$R$  denote the corresponding radial part. Now performing the rotations and expressing the integral in terms of radial three-electron integrals, we obtain the final expression of  $I_{KE,\theta_1,1}$ :

$$\begin{aligned}
 I_{KE,\theta_1,1} = & (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \left[ \frac{(2l'_1 + 1)(2l'_1 - 1)}{(2l'_3 + 1)} \right]^{1/2} \\
 & \times \sum_{L_1=|l'_1-1-l_1|}^{l'_1-1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} (2L_1 + 1)(2L_2 + 1)^{1/2} \\
 & \times C^{L_1}(l'_1 - 1, m'_1; l_1, m_1) C^{L_2}(l'_2, m'_2; l_2, m_2) \\
 & \times \left[ \frac{(l'_3 - m'_3)(l'_3 + m'_3)}{(2l'_3 - 1)} \right]^{1/2} \sum_{L_3=|l'_3-1-l_3|}^{l'_3-1+l_3} (2L_3 + 1)^{1/2} \\
 & \times C^{L_1}(L_2, -M_2; L_3, M_3) C^{L_3}(l'_3 - 1, m'_3; l_3, m_3)
 \end{aligned}$$



$$\begin{aligned}
& \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
& + \left[ \frac{(l'_3 - m'_3 + 1)(l'_3 + m'_3 + 1)}{(2l'_3 + 3)} \right]^{1/2} \sum_{L'_3=|l'_3+1-l_3|}^{l'_3+1+l_3} (2L'_3 + 1)^{1/2} \\
& \times C^{L_1}(L_2, -M_2; L'_3, M_3) C^{L'_3}(l'_3 + 1, m'_3; l_3, m_3) \\
& \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L'_3) \left. \vphantom{\sum} \right\}. \\
& m'_1 = 0, \quad l'_1 = 1, 2 \quad (68)
\end{aligned}$$

We have obtained a linear combination of radial three-electron integrals multiplied by some factors. In the practice many terms vanish due to the Condon and Shortley coefficients.

Combining Eq. C.1 and Eq. C.9 for the case  $l'_1 = 1, 2$  and substituting into Eq. 65 we get:

$$\begin{aligned}
I_{KE,\theta_1,2} &= R \frac{1}{2} \int_0^\pi \int_0^{2\pi} Y_{l_2}^{m_2*}(\theta_2, \phi_2) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \sin(\theta_2) d\theta_2 d\phi_2 \\
& \times \int_0^\pi \int_0^{2\pi} Y_{l_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3}^{m'_3}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \\
& \times \left\{ (l'_1 - 1) \left[ \frac{(2l'_1 + 1)}{(2l'_1 - 3)} \right]^{1/2} \right. \\
& \times \int_0^\pi \int_0^{2\pi} Y_{l_1}^{m_1*}(\theta_1, \phi_1) Y_{l'_1-2}^0(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \\
& \left. + l'_1 \int_0^\pi \int_0^{2\pi} Y_{l_1}^{m_1*}(\theta_1, \phi_1) Y_{l'_1}^0(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \right\}, \\
& m'_1 = 0, \quad l'_1 = 1, 2 \quad (69)
\end{aligned}$$

which after rotation expressed in terms of radial three-electron integrals leads to:

$$\begin{aligned}
I_{KE,\theta_1,2} &= \frac{1}{2} (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \\
& \times \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} (2L_2 + 1)^{1/2} (2L_3 + 1)^{1/2} \\
& \times C^{L_2}(l'_2, m'_2; l_2, m_2) C^{L_3}(l'_3, m'_3; l_3, m_3)
\end{aligned}$$

$$\begin{aligned}
 & \times \left\{ (l'_1 - 1) \left[ \frac{(2l'_1 + 1)}{(2l'_1 - 3)} \right]^{1/2} \sum_{L_1=|l'_1-2-l_1|}^{l'_1-2+l_1} (2L_1 + 1) \right. \\
 & \quad \times C^{L_1}(l'_1 - 2, m'_1; l_1, m_1) C^{L_1}(L_2, -M_2; L_3, M_3) \\
 & \quad + l'_1 \sum_{L'_1=|l'_1-l_1|}^{l'_1+l_1} (2L'_1+1)^{1/2} C^{L'_1}(l'_1, m'_1; l_1, m_1) \\
 & \quad \left. \times C^{L'_1}(L_2, -M_2; L_3, M_3) \right\} \\
 & \times [J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1; L_2, L_3) \\
 & \quad - J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
 & \quad - J(N_1 - 2, N_2, N_3 + 2; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3)]. \\
 & \qquad \qquad \qquad m'_1 = 0, \quad l'_1 = 1, 2 \quad (70)
 \end{aligned}$$

The derivative of the spherical harmonic with  $m'_1 = 0$  with respect to  $\phi_1$  vanishes:

$$I_{KE,\phi_1,3} = 0 \tag{71}$$

Now we treat the case  $m'_1 \neq 0$  for integrals Eqs. 64–66. Let us evaluate first the integral Eq. 65 using Eq. C.7, applying the  $\cot \theta_1$  over the complex conjugate  $Y_{l'_1}^{m'_1*}(\theta_1, \theta_1)$  and using the complex conjugate of Eq. C.3 we get:

$$\begin{aligned}
 & -\frac{1}{2} \cot \theta_1 Y_{l'_1}^{m'_1*}(\theta_1, \phi_1) \frac{\partial Y_{l'_1}^{m'_1}(\theta_1, \phi_1)}{\partial \theta_1} = -\frac{1}{8m_1} \\
 & \quad \times \left\{ [(l_1 + m_1 + 1)(l_1 - m_1)(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} \right. \\
 & \quad \times e^{2i\phi_1} Y_{l_1}^{m_1+1*}(\theta_1, \phi_1) Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1) \\
 & \quad - [(l_1 + m_1 + 1)(l_1 - m_1)(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} Y_{l_1}^{m_1+1*}(\theta_1, \phi_1) Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) \\
 & \quad + [(l_1 - m_1 + 1)(l_1 + m_1)(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} Y_{l_1}^{m_1-1*}(\theta_1, \phi_1) Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1) \\
 & \quad - [(l_1 - m_1 + 1)(l_1 + m_1)(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} \\
 & \quad \left. \times e^{-2i\phi_1} Y_{l_1}^{m_1-1*}(\theta_1, \phi_1) Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) \right\}. \qquad m_1 \neq 0 \quad (72)
 \end{aligned}$$

Expanding the spherical harmonics and using the integrals obtained at the end of Appendix C, a expression can be obtained without restrictions on  $l_1, l'_1$ :

$$\begin{aligned}
 I_{KE,\theta_1,2} &= \frac{(-1)^{M_2}}{8m_1} \delta(M_1 + M_2 + M_3, 0) \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} (2L + 1) \\
 & \quad \times [(2L_2 + 1)(2L_3 + 1)]^{1/2} C^{L_2}(l'_2, m'_2; l_2, m_2) C^{L_3}(l'_3, m'_3; l_3, m_3)
 \end{aligned}$$

$$\begin{aligned}
& \times C^{L_1}(L_2, -M_2; L_3, M_3) \\
& \times \left\{ -\delta(M_1, 1) [(l_1 + m_1 + 1)(l_1 - m_1)(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} \right. \\
& \quad \times C^{L_1}(l'_1, m'_1 - 1; l_1, m_1 + 1) + [(l_1 + m_1 + 1)(l_1 - m_1)(l'_1 + m'_1 + 1) \\
& \quad \times (l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1, m_1 + 1) \\
& \quad - [(l_1 - m_1 + 1)(l_1 + m_1)(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1, m_1 - 1) \\
& \quad \left. + \delta(M_1, -1) [(l_1 - m_1 + 1)(l_1 + m_1)(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} \right. \\
& \quad \times C^{L_1}(l'_1, m'_1 + 1; l_1, m_1 - 1) \left. \right\} [J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1; L_2, L_3) \\
& \quad - J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
& \quad - J(N_1 - 2, N_2, N_3 + 2; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3)], \quad m_1 \neq 0. \quad (73)
\end{aligned}$$

In order to avoid large expressions in the evaluation of  $I_{KE,\theta_1,1}$  and  $I_{KE,\phi_1,3}$  for  $m_1 \neq 0$ , we should distinguish between  $m_1 > 0$ , and  $m_1 < 0$ . Afterwards, the expressions can be combined. The expressions given here, although they look complicated, they vanish except for one, or several terms.

We evaluate Eq. 64 making the derivative of the spherical harmonic Eq. C.7 and applying the complex conjugate of relation Eq. C.13 on the left hand side for  $m_1 > 0$ , and Eq. C.14 for  $m_1 < 0$ , respectively, and using also Eq. C.1 we get:

$$\begin{aligned}
I_{KE,\theta_1,1} = & -R \frac{1}{2} \left[ \frac{(2l_1 + 1)(2l_1 - 1)}{(l_1 + |m_1|)(l_1 + |m_1| - 1)(2l'_3 + 1)} \right]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{l_2}^{m_2*}(\theta_2, \phi_2) \\
& \times Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \sin(\theta_2) d\theta_2 d\phi_2 \left\{ \left[ \frac{(l'_3 - m'_3)(l'_3 + m'_3)}{(2l'_3 - 1)} \right]^{1/2} \right. \\
& \times \int_0^\pi \int_0^{2\pi} Y_{l_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3-1}^{m'_3}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \\
& \times \left( [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} \int_0^\pi \int_0^{2\pi} F(l_1, m_1, \theta_1, \phi_1) \right. \\
& \times Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 - [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} \\
& \left. \times \int_0^\pi \int_0^{2\pi} F'(l_1, m_1, \theta_1, \phi_1) Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \right) \\
& \left. + \left[ \frac{(l'_3 - m'_3 + 1)(l'_3 + m'_3 + 1)}{(2l'_3 + 3)} \right]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{l_3}^{m_3*}(\theta_3, \phi_3) \right.
\end{aligned}$$

$$\begin{aligned}
 & \times Y_{l'_3+1}^{m'_3}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \left( [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} \right. \\
 & \times \int_0^\pi \int_0^{2\pi} F(l_1, m_1, \theta_1, \phi_1) Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \\
 & - [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} \int_0^\pi \int_0^{2\pi} F'(l_1, m_1, \theta_1, \phi_1) \\
 & \left. \times Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \right) \} \tag{74}
 \end{aligned}$$

with:

$$\begin{aligned}
 F(l_1, m_1, \theta_1, \phi_1) &= Y_{l_1-1}^{m_1-1*}(\theta_1, \phi_1), \\
 F'(l_1, m_1, \theta_1, \phi_1) &= e^{-2i\phi_1} Y_{l_1-1}^{m_1-1*}(\theta_1, \phi_1), \quad m_1 > 0 \\
 F(l_1, m_1, \theta_1, \phi_1) &= e^{2i\phi_1} Y_{l_1-1}^{m_1+1*}(\theta_1, \phi_1), \\
 F'(l_1, m_1, \theta_1, \phi_1) &= Y_{l_1-1}^{m_1+1*}(\theta_1, \phi_1), \quad m_1 < 0. \tag{75}
 \end{aligned}$$

After rotation and angular integration we obtain:

$$\begin{aligned}
 I_{KE,\theta_1,1} &= -\frac{1}{2} (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \left[ \frac{(2l_1 + 1)(2l_1 - 1)}{(l_1 + |m_1|)(l_1 + |m_1| - 1)(2l'_3 + 1)} \right]^{1/2} \\
 & \times \sum_{L_1=|l'_1-1-l_1|}^{l'_1-1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} (2L_1 + 1)(2L_2 + 1)^{1/2} C^{L_2}(l'_2, m'_2; l_2, m_2) \\
 & \times \left\{ \left[ \frac{(l'_3 - m'_3)(l'_3 + m'_3)}{(2l'_3 - 1)} \right]^{1/2} \sum_{L_3=|l'_3-1-l_3|}^{l'_3-1+l_3} (2L_3 + 1)^{1/2} \right. \\
 & \times C^{L_3}(l'_3 - 1, m'_3; l_3, m_3) C^{L_1}(L_2, -M_2; L_3, M_3) f(l_1, m_1, l'_1, m'_1) \\
 & \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
 & + \left[ \frac{(l'_3 - m'_3 + 1)(l'_3 + m'_3 + 1)}{(2l'_3 + 3)} \right]^{1/2} \sum_{L'_3=|l'_3+1-l_3|}^{l'_3+1+l_3} (2L'_3 + 1)^{1/2} \\
 & \times C^{L'_3}(l'_3 + 1, m'_3; l_3, m_3) C^{L_1}(L_2, -M_2; L'_3, M_3) f'(l_1, m_1, l'_1, m'_1) \\
 & \left. \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L'_3) \right\}, \tag{76}
 \end{aligned}$$

where the functions  $f$  and  $f'$  are for the case  $m_1 > 0$ :

$$\begin{aligned} f(l_1, m_1, l'_1, m'_1) &= [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1 - 1, m_1 - 1) \\ &\quad + \delta(M_1, -1) [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1 - 1, m_1 - 1), \\ f'(l_1, m_1, l'_1, m'_1) &= [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1 - 1, m_1 - 1) \\ &\quad + \delta(M_1, -1) [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1 - 1, m_1 - 1), \end{aligned} \quad (77)$$

and for the case  $m_1 < 0$ :

$$\begin{aligned} f(l_1, m_1, l'_1, m'_1) &= \delta(M_1, 1) [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1 - 1, m_1 + 1) \\ &\quad + [(l'_1 + m'_1 + 1)(l'_1 - m'_1)] C^{L_1}(l'_1, m'_1 + 1; l_1 - 1, m_1 + 1), \\ f'(l_1, m_1, l'_1, m'_1) &= \delta(M_1, 1) [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1 - 1, m_1 + 1) \\ &\quad + [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1 - 1, m_1 + 1). \end{aligned} \quad (78)$$

Now we evaluate Eq. 64 for  $m'_1 \neq 0$  using firstly Eq. C.8.  $\sin(\phi_1 - \phi_3)$  can be expanded and written as exponential:

$$\sin(\phi_1 - \phi_3) = \frac{1}{2i} \left( e^{i\phi_1} e^{-i\phi_3} - e^{-i\phi_1} e^{i\phi_3} \right), \quad (79)$$

$$\begin{aligned} I_{KE, \phi_1, 3} &= R(-1)^{M_2 + \rho} \frac{m'_1}{2} \left[ \frac{(2l_1 - 1)(2l_1 + 1)}{(l_1 + |m_1|)(l_1 + |m_1| - 1)} \right]^{1/2} \\ &\quad \times \int_0^\pi \int_0^{2\pi} F(\theta_1, \phi_1) Y_{l'_1}^{m'_1}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \\ &\quad \times \int_0^\pi \int_0^{2\pi} Y_{l'_2}^{m_2*}(\theta_2, \phi_2) Y_{l'_2}^{l'_2}(\theta_2, \phi_2) \sin(\theta_2) d\theta_2 d\phi_2 \\ &\quad \times \left\{ \left( \left[ \frac{(l'_3 - m'_3 + 1)(l'_3 - m'_3 + 2)}{(2l'_3 + 1)(2l'_3 + 3)} \right]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{l'_3}^{m_3*}(\theta_3, \phi_3) \right. \right. \\ &\quad \times Y_{l'_3+1}^{m'_3-1}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 - \left. \left[ \frac{(l_3 - m_3 + 1)(l_3 - m_3 + 2)}{(2l_3 + 1)(2l_3 + 3)} \right]^{1/2} \right. \\ &\quad \left. \left. \times \int_0^\pi \int_0^{2\pi} Y_{l'_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3+1}^{m'_3-1}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \right) \right\} \end{aligned}$$

$$\begin{aligned}
 & - \left( \left[ \frac{(l_3 + m_3 + 1)(l_3 + m_3)}{(2l_3 + 1)(2l_3 - 1)} \right]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{l_3+1}^{m_3-1*}(\theta_3, \phi_3) \right. \\
 & \times Y_{l_3}^{m_3'}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 - \left[ \frac{(l_3' + m_3' + 1)(l_3' + m_3')}{(2l_3' + 1)(2l_3' - 1)} \right]^{1/2} \\
 & \left. \times \int_0^\pi \int_0^{2\pi} Y_{l_3-1}^{m_3-1*}(\theta_3, \phi_3) Y_{l_3}^{m_3'}(\theta_3, \phi_3) \sin(\theta_3) d\theta_3 d\phi_3 \right) \Bigg\}, \tag{80}
 \end{aligned}$$

with

$$\begin{aligned}
 F(\theta_1, \phi_1) &= Y_{l_1-1}^{m_1-1*}(\theta_1, \phi_1), \quad \rho = 0, \quad m_1 > 0 \\
 F(\theta_1, \phi_1) &= Y_{l_1-1}^{m_1+1*}(\theta_1, \phi_1), \quad \rho = 1, \quad m_1 < 0.
 \end{aligned} \tag{81}$$

A general expression for Eq. 80 can be obtained using the recursion relation Eq. C.5 for  $Y_{l_1}^{m_1}(\theta_1, \phi_1)$  and Eq. C.2 for  $Y_{l_3}^{m_3}(\theta_3, \phi_3)$ , or the corresponding complex conjugate relations.

Similarly the evaluation of  $I_{KE,\phi_1,3}$  for  $m_1' \neq 0$ , with the two cases  $m_1 > 0$  and  $m_1 < 0$  leads to:

$$\begin{aligned}
 I_{KE,\phi_1,3} &= (-1)^{M_2+\rho} \frac{m_1'}{2} \left[ \frac{(2l_1 - 1)(2l_1 + 1)}{(l_1 + |m_1|)(l_1 + |m_1| - 1)} \right]^{1/2} \\
 & \times \sum_{L_1=|l_1'-1-l_1|}^{l_1'-1+l_1} \sum_{L_2=|l_2'-l_2|}^{l_2'+l_2} (2L_1 + 1)(2L_2 + 1)^{1/2} C^{L_2}(l_2', m_2'; l_2, m_2) \\
 & \times \left\{ \sum_{L_3=|l_3'-1-l_3|}^{l_3'-1+l_3} (2L_3 + 1)^{1/2} C^{L_3}(l_3' + 1, m_3' - 1; l_3, m_3) \right. \\
 & \times \left( \left[ \frac{(l_3' - m_3' + 1)(l_3' - m_3' + 2)}{(2l_3' + 1)(2l_3' + 3)} \right]^{1/2} f(L_1, M_1, L_2, M_2, L_3, M_3) \right. \\
 & \left. \left. - \left[ \frac{(l_3 - m_3 + 1)(l_3 - m_3 + 2)}{(2l_3 + 1)(2l_3 + 3)} \right]^{1/2} f'(L_1, M_1, L_2, M_2, L_3, M_3) \right) \right. \\
 & \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
 & \left. + \sum_{L_3'=|l_3'+1-l_3|}^{l_3'+1+l_3} (2L_3' + 1)^{1/2} C^{L_3'}(l_3', m_3'; l_3 - 1, m_3 - 1) \right)
 \end{aligned}$$

$$\begin{aligned} & \times \left( \left[ \frac{(l_3 + m_3 + 1)(l_3 + m_3)}{(2l_3 + 1)(2l_3 - 1)} \right]^{1/2} f'(L_1, M_1, L_2, M_2, L'_3, M_3) \right. \\ & \left. - \left[ \frac{(l'_3 + m'_3 + 1)(l'_3 + m'_3)}{(2l'_3 + 1)(2l'_3 - 1)} \right]^{1/2} f(L_1, M_1, L_2, M_2, L'_3, M_3) \right) \\ & \times J(N_1 - 1, N_2, N_3 + 1; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L'_3) \Bigg\}, \quad (82) \end{aligned}$$

where the functions  $f, f'$  for the case  $m'_1 > 0$  with  $\rho = 0$  are:

$$\begin{aligned} f(L_1, M_1, L_2, M_2, L_3, M_3) &= \delta(M_1 + M_2 + M_3, 0) \\ &\times C^{L_1}(l'_1, m'_1; l_1 - 1, m_1 - 1) C^{L_1}(L_2, -M_2; L_3, M_3 - 1), \\ f'(L_1, M_1, L_2, M_2, L_3, M_3) &= \delta(M_1, 0) \delta(M_1 + M_2 + M_3, 0) \\ &\times C^{L_1}(l'_1, m'_1; l_1 - 1, m_1 - 1) C^{L_1}(L_3, M_3 + 1; L_2, -M_2), \quad (83) \end{aligned}$$

and for  $m'_1 < 0$  with  $\rho = 1$  are:

$$\begin{aligned} f(L_1, M_1, L_2, M_2, L_3, M_3) &= \delta(M_1 + M_2 + M_3, 2) \\ &\times C^{L_1}(l'_1, m'_1; l_1 - 1, m_1 + 1) C^{L_1}(L_2, -M_2; L_3, M_3 - 1), \\ f'(L_1, M_1, L_2, M_2, L_3, M_3) &= \delta(M_1, 1) \delta(M_1 + M_2 + M_3, 0) \\ &\times C^{L_1}(l'_1, m'_1; l_1 - 1, m_1 + 1) C^{L_1}(L_3, M_3 + 1; L_2, -M_2). \quad (84) \end{aligned}$$

Due to the Kronecker  $\delta$ ,  $C^k$  and cancelation of products of  $C^k$ ,  $I_{KE, \phi_1, 3}$  is zero for most of the cases. This fact cannot be demonstrated a priori, therefore the equations are given.

The total kinetic energy is the sum of the radial, angular momentum and angular contributions:

$$I_{KE_1} = I_{KE, R_1} + I_{KE, \theta_1, L} + I_{KE, \theta_1, 1} + I_{KE, \theta_1, 2} + I_{KE, \phi_1, 3} \quad (85)$$

Results of all these integrals are given in the partitioning of the kinetic energy in Table 5. The recursion relations and derivatives of spherical harmonics are given in the Appendix C. In Table 6 values of the kinetic energy are given for several cases of orbitals involved with more than 30 figures. Using our computer program, we have been able to reproduce all the recent kinetic energy values given by Sims and Hagstrom [33] with full accuracy. Further, thousands of kinetic energy integrals have been computed and compared with the Sims and Hagstrom's program code (J. S. Sims, personal communication) showing full agreement. All the formulas have been checked with the Fortran 90 computer program and Maple.

**Table 5** Partitioning of some kinetic energy three-electron integrals.  $\alpha = 1.40$  for orbitals with  $''$ , otherwise  $\alpha = 2.86$ . Missing contributions are zero

Charge distribution	$\omega_1$	$\omega_2$	$\omega_3$	Value
(1s1s, 1s2s'', 2s1s'')				
$I_{KE,R_1}$	5.72	4.26	4.26	0.13126 72235 19561 47025 67125 92522 $\times 10^{-4}$
$I_{KE_1}$	5.72	4.26	4.26	0.13126 72235 19561 47025 67125 92522 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 1s1s, 2s''2s'')				
$I_{KE,R_1}$	5.72	5.72	2.80	0.11173 73454 25881 89473 77487 07305 $\times 10^{-4}$
$I_{KE,\theta_1,L}$	5.72	5.72	2.80	0.23121 46000 74224 80076 39627 66290 $\times 10^{-4}$
$I_{KE,\theta_1,1}$	5.72	5.72	2.80	0.11361 37233 59884 44695 67616 73635 $\times 10^{-5}$
$I_{KE,\theta_1,2}$	5.72	5.72	2.80	-0.11361 37233 59884 44695 67616 73635 $\times 10^{-5}$
$I_{KE_1}$	5.72	5.72	2.80	0.34295 19455 00106 69550 17114 73595 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> )				
$I_{KE,R_1}$	5.72	5.72	5.72	0.27412 63595 41602 41619 16234 12903 $\times 10^{-6}$
$I_{KE,\theta_1,L}$	5.72	5.72	5.72	-0.13319 27053 15727 61426 77155 24170 $\times 10^{-6}$
$I_{KE,\theta_1,1}$	5.72	5.72	5.72	0.30768 29932 79821 64018 64233 64324 $\times 10^{-7}$
$I_{KE,\theta_1,2}$	5.72	5.72	5.72	0.89066 97099 50921 45397 24746 94767 $\times 10^{-7}$
$I_{KE_1}$	5.72	5.72	5.72	0.26076 89245 48949 11133 97976 94642 $\times 10^{-6}$
(3d <sub>1</sub> 3d <sub>1</sub> , 2p <sub>1</sub> 2p <sub>1</sub> '', 3d <sub>1</sub> 3d <sub>1</sub> '')				
$I_{KE,R_1}$	5.72	4.26	4.26	0.37715 96048 76198 86984 97258 71928 $\times 10^{-5}$
$I_{KE,\theta_1,L}$	5.72	4.26	4.26	0.15731 01714 18448 93148 08711 44597 $\times 10^{-4}$
$I_{KE,\theta_1,1}$	5.72	4.26	4.26	-0.62869 65273 66595 59716 58684 73496 $\times 10^{-6}$
$I_{KE,\theta_1,2}$	5.72	4.26	4.26	0.34501 95075 21632 95846 87756 98358 $\times 10^{-6}$
$I_{KE_1}$	5.72	4.26	4.26	0.19218 93617 07619 19207 88728 04038 $\times 10^{-4}$

**Table 6** Kinetic energy three-electron integrals of electron 1. The charge distributions are constructed with the exponents  $\alpha = 1.40$  for orbitals with  $''$ , otherwise  $\alpha = 2.86$

Charge distribution	$\omega_1$	$\omega_2$	$\omega_3$	$I_{KE}$
(1s1s, 1s1s'', 1s1s'')	5.72	4.26	4.26	0.15659 17112 60607 62842 78921 37447 $\times 10^{-4}$
(1s1s, 1s2s'', 1s2s'')	5.72	4.26	4.26	0.13126 72235 19561 47025 67125 92522 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 1s1s, 2s''2s'')	5.72	5.72	2.80	0.34295 19455 00106 69550 17114 73595 $\times 10^{-4}$
(1s1s, 1s2p <sub>0</sub> '', 1s2p <sub>0</sub> '')	5.72	4.26	4.26	0.45769 77948 50777 26085 44884 85868 $\times 10^{-6}$
(1s2p <sub>0</sub> , 1s1s, 1s2p <sub>0</sub> '')	5.72	5.72	4.26	-0.12906 22778 17056 65339 27233 71594 $\times 10^{-6}$
(1s3d <sub>0</sub> '', 1s1s, 1s3d <sub>0</sub> '')	4.26	5.72	4.26	0.79465 21564 41320 36387 60727 96090 $\times 10^{-7}$
(2p <sub>0</sub> 2p <sub>0</sub> '', 1s1s, 2p <sub>0</sub> 2p <sub>0</sub> '')	4.26	5.72	4.26	0.81495 98738 32346 11143 47248 05787 $\times 10^{-5}$
(1s1s, 2p <sub>0</sub> 2p <sub>0</sub> '', 2p <sub>0</sub> 2p <sub>0</sub> '')	5.72	4.26	4.26	0.17800 68839 29555 22718 57902 99996 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> )	5.72	5.72	5.72	0.26076 89245 48949 11133 97976 94642 $\times 10^{-6}$
(3d <sub>0</sub> 3d <sub>0</sub> '', 1s1s, 3d <sub>0</sub> 3d <sub>0</sub> '')	4.26	5.72	4.26	0.46916 53824 00611 40864 14255 65967 $\times 10^{-4}$
(3d <sub>0</sub> 3d <sub>0</sub> '', 3d <sub>0</sub> 3d <sub>0</sub> , 3d <sub>0</sub> 3d <sub>0</sub> '')	4.26	5.72	4.26	0.19195 81649 30384 83368 39585 45964 $\times 10^{-4}$
(2p <sub>1</sub> 2p <sub>1</sub> '', 1s1s, 1s1s)	4.26	5.72	5.72	0.33657 95725 13801 82596 65603 91000 $\times 10^{-5}$
(3d <sub>2</sub> 3d <sub>2</sub> , 1s1s'', 2s2s'')	5.72	4.26	4.26	0.11417 77154 84591 52206 92069 39983 $\times 10^{-4}$
(2p <sub>1</sub> 2p <sub>1</sub> '', 1s1s, 2p <sub>1</sub> 2p <sub>1</sub> '')	4.26	5.72	4.26	0.82384 74233 55412 57794 19375 09453 $\times 10^{-5}$
(2p <sub>1</sub> 2p <sub>1</sub> , 2p <sub>1</sub> 2p <sub>1</sub> '', 2p <sub>1</sub> 2p <sub>1</sub> '')	5.72	4.26	4.26	0.78369 38975 20372 96896 51687 01558 $\times 10^{-5}$
(3d <sub>1</sub> 3d <sub>1</sub> , 2p <sub>1</sub> 2p <sub>1</sub> '', 3d <sub>1</sub> 3d <sub>1</sub> '')	5.72	4.26	4.26	0.19218 93617 07619 19207 88728 04038 $\times 10^{-4}$
(3d <sub>2</sub> 3d <sub>2</sub> , 3d <sub>1</sub> 3d <sub>1</sub> '', 3d <sub>2</sub> 3d <sub>2</sub> '')	5.72	4.26	4.26	0.40399 59434 35959 51311 79010 05972 $\times 10^{-4}$
(2p <sub>0</sub> 2p <sub>0</sub> , 2p <sub>0</sub> 2p <sub>0</sub> '', 2p <sub>0</sub> 2p <sub>0</sub> '')	5.72	4.26	4.26	-0.34528 36595 44116 76923 18333 94309 $\times 10^{-8}$
(3d <sub>0</sub> 3d <sub>0</sub> , 3p <sub>0</sub> 3p <sub>0</sub> '', 3d <sub>0</sub> 3d <sub>0</sub> '')	5.72	4.26	4.26	-0.58364 96884 44425 76337 00583 35223 $\times 10^{-8}$
(2p <sub>-1</sub> 2p <sub>-1</sub> '', 1s1s, 1s1s)	4.26	5.72	5.72	0.33657 95725 13801 82596 65603 91000 $\times 10^{-5}$
(3d <sub>-2</sub> 3d <sub>-2</sub> , 1s1s, 3d <sub>-2</sub> 3d <sub>-2</sub> '')	5.72	5.72	4.26	0.87337 99889 07121 70685 75959 02696 $\times 10^{-5}$



## 4 Conclusions

A new method is presented which combines the advantages of the direct integration of the interelectronic coordinate, with the new developments in the calculation of non-trivial auxiliary integrals employed in the classical method. The method has the advantage that only auxiliary one- and two-electron integrals have to be computed and stored in memory during the calculation of matrix elements. The number of these integrals is about  $n_{orb}^4 \times n_{pow}^2$ , reduced compared with the number of three-electron integrals, and dramatically reduced compared with the four-electron ones.

Also according to the development of the computers it seems more reasonable to perform direct calculations (always faster processors) than larger core memory. Therefore this method of integration would allow to extend the applicability of the Hy-CI method to atoms with higher number of electrons as the first row of elements.

This method can be used to evaluate all kinds of three-electron integrals (the triangle integral was evaluated by Szász) and two-electron integrals containing any angular functions (*s*-, *p*-, *d*-, *f*-, *g*-, ... orbitals) in terms of two-electron integrals. Basic two-electron integrals with a negative power are calculated in terms of auxiliary two-electron integrals instead of using logarithms. This fact means a winning in speed, and in accuracy because a loss of several digits could occur due to the substractions appearing together with the logarithmic expressions. This method achieves the highest accuracy at quadruple precision (by our computer about 30 decimal digits). For these reasons, the method is an extension of Perkins' method of integration to angular orbitals, taking care of accuracy aspects important in modern calculations.

As the method is conceptually completely different to the classical one, it can be useful for comparison purposes. Speed and performance of the computer program by this method was not studied in this paper, although these issues seem very promising. This will be discussed with actual calculations.

The kinetic energy is calculated using the Hamiltonian in Hylleraas coordinates, for first time to our knowledge. Therefore the angular part of the formula of the Hamiltonian has been with these calculations proved. The kinetic and potential energy integrals are also solved finally as linear combinations of auxiliary two-electron integrals. While the radial part is straightforward, to evaluate some contributions of the angular part, the derivatives of the spherical harmonics are done and recursion relations among spherical harmonics are used. A new derivative of spherical harmonics containing the inverse of the sinus is given, and so as some compact derivatives for the first quantum numbers, which make the expressions shorter. The lengthy resulting expressions are nevertheless computationally very fast, as they consist on factors and coefficients, which most of them vanish, and only one or two radial three-electron integrals remain, which are calculated in terms of basic two-electron ones.

Highly accurate results of the integrals are given in the tables of the paper. Thousands of all these integrals have been calculated with the program described here and the computer program of Sims and Hagstrom showing fully agreement to high accuracy. In a following paper the four-electron integrals will be evaluated using this method.

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integrals with the ones obtained by his program code. Also the high precision Vkl and Condon and Shortley coefficients programs of James Sims and Stanley Hagstrom are greatly acknowledged. Philip Hoggan is thanked for reading the manuscript and for his helpful comments to improve it. Finally, the author is very grateful to Peter Otto for supporting this project.

### Appendix A: The rotation of spherical harmonics

In Fig. 1 the z-axis has been rotated to coincide momentarily with  $r_1$ . This is a rotation of the Euler angles  $\alpha = \phi_1, \beta = \theta_1$  and  $\gamma = 0$ . One can see in Fig. 1 the transformation of the polar angles:  $\theta_2 \rightarrow \theta_{12}$ , and  $\phi_2 \rightarrow \phi_{12}$ . The index 2 stands for any electron different of 1. The angular function  $Y_{l_2}^{m_2}(\theta_2, \phi_2)$  has been transformed. There is a coupling with the function of  $\theta_1$  and  $\phi_1$  because the linked electron 1. We propose a transformation of the type:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \left(\frac{4\pi}{2l_2 + 1}\right)^{1/2} \sum_{m_2'=-l_2}^{l_2} Y_{l_2}^{m_2}(\theta_1, \phi_1) Y_{l_2}^{m_2'}(\theta_{12}, \phi_{12}). \tag{A.1}$$

When we integrate over  $\phi_{12}$  in the integrals we will get  $m_2' = 0$ , and the sum will be effectively reduced to:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) \longrightarrow Y_{l_2}^{m_2}(\theta_1, \phi_1) P_{l_2}(\cos \theta_{12}). \tag{A.2}$$

This relation has been obtained first empirically. We can demonstrate the validity of Eq. A.1. The rotation of a spherical harmonic is related to the rotation matrices [57, Eq. 204], [58, Eq. 4.1.(5)]. For our case:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \sum_{m_2'=-l_2}^{l_2} \mathbf{D}_{m_2, m_2'}^{(l_2)*}(\alpha, \beta, \gamma) Y_{l_2}^{m_2'}(\theta_{12}, \phi_{12}). \tag{A.3}$$

This equation was used by Drake [45, Eq. 6]. A particular case of Eq. A.3 is when the rotated z-axis coincides with  $r_1$ , the coordinates of electron 1 are then  $\theta_1 = 0$  and therefore  $\cos \theta = 1$ . For  $\theta = 0$ , all the Legendre functions have the value 1,  $P_l^{m'}(\cos \theta) = P_l^{m'}(1) = 1$ , that is the same that  $P_l^0(1)$ , then  $m' = 0$ . We can rewrite the definition Eq. 4 of a spherical harmonic:

$$Y_{l_2}^{m_2'}(0, \phi_1) = \left(\frac{2l_2 + 1}{4\pi}\right)^{1/2} \left[\frac{(l_2 - m_2')!}{(l_2 + m_2')!}\right]^{1/2} e^{im_2'\phi_1} \delta_{m_2', 0}, \tag{A.4}$$

substituting into Eq. A.3:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \sum_{m_2'=-l_2}^{l_2} \mathbf{D}_{m_2, m_2'}^{(l_2)*}(\alpha, \beta, \gamma) \left(\frac{2l_2 + 1}{4\pi}\right)^{1/2} \left[\frac{(l_2 - m_2')!}{(l_2 + m_2')!}\right]^{1/2} e^{im_2'\phi_1} \delta_{m_2', 0}, \tag{A.5}$$

simplifying:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \mathbf{D}_{m_2, m_2'}^{(l_2)*}(\alpha, \beta, \gamma) \left( \frac{2l_1 + 1}{4\pi} \right)^{1/2} \delta_{m_2', 0}, \quad (\text{A.6})$$

turning around:

$$\mathbf{D}_{m_2, m_2'}^{(l_2)*}(\alpha, \beta, \gamma) = \left( \frac{4\pi}{2l_2 + 1} \right)^{1/2} Y_{l_2}^{m_2}(\theta_1, \phi_1) \delta_{m_2', 0}. \quad (\text{A.7})$$

This equation shows the connection between the rotation operator and the spherical harmonics. Finally, substituting Eq. A.7 into Eq. A.3:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \left( \frac{4\pi}{2l_1 + 1} \right)^{1/2} \sum_{m_2'=-l_2}^{l_2} Y_{l_2}^{m_2}(\theta_1, \phi_1) Y_{l_2}^{m_2'}(\theta_{12}, \phi_{12}), \quad (\text{A.8})$$

this equation has the form of an addition theorem. We have checked the transformation Eq. A.1 in the angular integration after rotation of the two-electron integrals and obtained the same final expression than Calais and Lowdin [43], and Drake [45], respectively.

## Appendix B: Condon and Shortley coefficients

We have defined the one-electron radial charge distributions by expanding the products of spherical harmonics from Eq. 7, where the Condon and Shortley coefficients are given by Eq. 8. The expression Eq. 8 is equivalent to Condon and Shortley's original definition [50, Eq. 6, p. 175]. These coefficients are explicitly tabulated [50, pp. 178, 179]. The angular momentum quantum numbers  $L_i$  satisfy the triangular condition  $||l_i - l_i'| \leq L \leq l_i + l_i'$  and the restriction  $L_i \geq |M_i|$ .  $M_i$  is defined as  $M_i = m_i' - m_i$ . In Sect. 2, we have defined  $L_i$  and stated that it depends also on  $m_i$ . More precisely,  $L_i$  takes values in steps of 2,  $L_i = l_i^{\min}, l_i^{\min} + 2, \dots, l_i^{\max} - 2, l_i^{\max}$ , where:

$$\begin{aligned} l_i^{\max} &= l_i + l_i' \\ l_i^{\min} &= \max(|l_i - l_i'|, |m_i|) \quad \text{if } \max(|l_i - l_i'|, |m_i|) + l_i^{\max} \text{ even,} \\ l_i^{\min} &= \max(|l_i - l_i'|, |m_i|) + 1 \quad \text{if } \max(|l_i - l_i'|, |m_i|) + l_i^{\max} \text{ odd.} \end{aligned} \quad (\text{B.1})$$

These relations are the selection rules [59]. If these are not satisfied, the coefficients are zero, which greatly reduces the computational effort.

The Condon and Shortley coefficients are closely related to the Gaunt function [62, Eq. 9, p. 194] and to the Wigner  $3jm$ -symbols [61]. In fact in the program we have used, the Condon and Shortley coefficients are calculated with the Gaunt's formula [52, Eq. 11, p. 176].

Gaunt coefficients [60] are the coefficients of the expansion:

$$Y_l^{m*}(\theta, \phi)Y_{l'}^{m'}(\theta, \phi) = \sum_{L=|l-l'|}^{l+l'} \langle l', m'|l, m|L, M \rangle Y_L^M(\theta, \phi), \quad M = m' - m \tag{B.2}$$

and they are the result of the evaluation of the three-fold spherical harmonics integral:

$$\langle l', m'|l, m|L, M \rangle = \int_0^\pi \int_0^{2\pi} Y_{l'}^{m'*}(\theta, \phi)Y_l^m(\theta, \phi)Y_L^M(\theta, \phi) \sin \theta d\theta d\phi. \tag{B.3}$$

The Gaunt coefficients can be calculated making use of the expression of the 3jm-symbols [62]:

$$\begin{aligned} \langle l', m'|l, m|L, M \rangle &= (-1)^{m'} \left[ \frac{(2l' + 1)(2l + 1)(2L + 1)}{4\pi} \right]^{1/2} \\ &\times \begin{pmatrix} l' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & L \\ m' & m & -M \end{pmatrix}. \end{aligned} \tag{B.4}$$

For extremely large  $l$  quantum numbers, some difficulties appear due to the exact calculation of factorials of very large numbers. In our case, the expansions over spherical harmonic in atomic calculations do not need high values of  $l$ , and the use of the Gaunt function with quadruple precision arithmetic is sufficient.

The Gaunt coefficients are related to the Condon and Shortley coefficients. Comparing Eqs. B.2 and B.5 we get:

$$C^L(l', m', l, m) = \left( \frac{4\pi}{2L + 1} \right)^{1/2} \langle l', m'|l, m|L, M \rangle \tag{B.5}$$

in agreement with [59, Eq. 1.4]. Therefore, Gaunt coefficients and Condon and Shortley coefficients are equivalent up to a factor.

Alternatively, the integration of the three-fold spherical harmonics integral could have been carried out in terms of Clebs–Gordan coefficients, using Eq. [58, Eq. 5.9.4]:

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} Y_{l'}^{m'*}(\theta, \phi)Y_l^m(\theta, \phi)Y_L^M(\theta, \phi) \sin \theta d\theta d\phi &= \left[ \frac{(2l + 1)(2L + 1)}{4\pi(2l' + 1)} \right] \\ &\times C_{l0L0}^{l'0} C_{lmLM}^{l'm'} \end{aligned} \tag{B.6}$$

We have used in this work the computer program in quadruple precision by Sims and Hagstrom, for more information on the computational details, see Appendix A of Ref. [33].

### Appendix C: Recursion and differential relations of spherical harmonics

The angular kinetic energy is the sum of the contributions given by the operator Eq. 56, see [48, Eqs. 34, 35]. After performing the derivative with respect to the interparticle coordinate, we have to evaluate the integrals Eqs. 64–66. For this we have to make the derivatives of the spherical harmonics with respect to the angles, and also to express the products of the angular functions and spherical harmonics into spherical harmonics using recursion relations. Some necessary recursion relations<sup>4</sup> in terms of spherical harmonics are [64, 5.7.]:

$$\begin{aligned} \cos \theta Y_l^m(\theta, \phi) &= \left[ \frac{(l+m)(l-m)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1}^m(\theta, \phi) \\ &+ \left[ \frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)} \right]^{1/2} Y_{l+1}^m(\theta, \phi), \end{aligned} \quad (\text{C.1})$$

$$\begin{aligned} \sin \theta Y_l^m(\theta, \phi) &= \left[ \frac{(l-m+1)(l-m+2)}{(2l+3)(2l+1)} \right]^{1/2} e^{i\phi} Y_{l+1}^{m-1}(\theta, \phi) \\ &- \left[ \frac{(l+m-1)(l+m)}{(2l+1)(2l-1)} \right]^{1/2} e^{i\phi} Y_{l-1}^{m-1}(\theta, \phi), \end{aligned} \quad (\text{C.2})$$

$$\begin{aligned} -\cot \theta Y_l^m(\theta, \phi) &= \frac{1}{2m} [(l+m+1)(l-m)]^{1/2} e^{-i\phi} Y_l^{m+1}(\theta, \phi) \\ &+ \frac{1}{2m} [(l-m+1)(l+m)]^{1/2} e^{i\phi} Y_l^{m-1}(\theta, \phi). \end{aligned} \quad (\text{C.3})$$

We also need recursion relations with the factor  $\frac{1}{\sin \theta}$ . From Ref. [63] we subtract Eq. 3 from Eq. 2, and the recursion relation is found be:

$$\frac{1}{\sin \theta} P_l^m(\cos \theta) = \frac{1}{2m} \left[ (l-m+2)(l-m+1) P_{l+1}^{m-1}(\theta) + P_{l+1}^{m+1}(\theta) \right], \quad m \neq 0 \quad (\text{C.4})$$

which written in terms of spherical harmonics is:

$$\begin{aligned} \frac{Y_l^m(\theta, \phi)}{\sin \theta} &= -\frac{1}{2m} \left[ \frac{(2l+1)}{(2l+3)} \right]^{1/2} \left[ [(l-m+2)(l-m+1)]^{1/2} e^{i\phi} Y_{l+1}^{m-1}(\theta, \phi) \right. \\ &\left. + ((l+m+1)(l+m+2))^{1/2} e^{-i\phi} Y_{l+1}^{m+1}(\theta, \phi) \right], \quad m \neq 0. \end{aligned} \quad (\text{C.5})$$

<sup>4</sup> In the following, the quantum number  $m$  in the relations can be positive or negative, only when it is explicitly written  $|m|$  is the absolute value.

The derivative of a spherical harmonic with respect to the angle  $\theta$  expressed in terms of spherical harmonics is [58, Eq. 5.8.2.(1)]:

$$\frac{\partial Y_l^m(\theta, \phi)}{\partial \theta} = m \cot \theta Y_l^m(\theta, \phi) + [(l - m)(l + m + 1)]^{1/2} e^{-i\phi} Y_l^{m+1}(\theta, \phi), \quad (C.6)$$

and inserting Eq. C.3 into Eq. C.6:

$$\begin{aligned} \frac{\partial Y_l^m(\theta, \phi)}{\partial \theta} &= \frac{1}{2} [(l + m + 1)(l - m)]^{1/2} e^{-i\phi} Y_l^{m+1}(\theta, \phi) \\ &\quad - \frac{1}{2} [(l - m + 1)(l + m)]^{1/2} e^{i\phi} Y_l^{m-1}(\theta, \phi). \end{aligned} \quad (C.7)$$

The derivative of a spherical harmonic with respect to  $\phi$  is simple:

$$\frac{\partial Y_l^m(\theta, \phi)}{\partial \phi} = im Y_l^m(\theta, \phi). \quad (C.8)$$

To evaluate the integrals Eqs. 64–66, using Eq. C.5 we have distinguished between  $m = 0$  and  $m \neq 0$ , to avoid singularities. As the case  $m = 0$  is not defined, some relations have been investigated and the derivative is found to be:

$$-\frac{1}{\sin(\theta)} \frac{\partial Y_l^0(\theta, \phi)}{\partial \theta} = \sum_{i=1}^l [(2l + 1)(2l - i)]^{1/2} Y_{l-i}^0(\theta, \phi) \quad (C.9)$$

In order to evaluate Eq. 64 avoiding lengthly expressions, we look for shorter expressions involving the inverse of  $\sin(\theta)$ . For  $l \leq 2$  and some cases when  $l - m \leq 1$ , the following relations have been found:

$$\frac{1}{\sin(\theta)} Y_l^m(\theta, \phi) = - \left[ \frac{(2l - 1)(2l + 1)}{(l + m)(l + m - 1)} \right]^{1/2} Y_{l-1}^{m-1}(\theta, \phi) e^{i\phi}, \quad m > 0 \quad (C.10)$$

$$\frac{1}{\sin(\theta)} Y_l^m(\theta, \phi) = \left[ \frac{(2l - 1)(2l + 1)}{(l + |m|)(l + |m| - 1)} \right]^{1/2} Y_{l-1}^{m+1}(\theta, \phi) e^{-i\phi}, \quad m < 0 \quad (C.11)$$

Finally there are some integrals among spherical harmonics containing  $e^{2i\phi_1}$  and  $e^{-2i\phi_1}$  which deserve to be evaluated separately. Two examples are given:

$$\begin{aligned}
& \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) e^{2i\phi_1} \sin(\theta_1) d\theta_1 d\phi_1 \\
&= (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta_1, \phi_1) Y_{L_2}^{-M_2*}(\theta_1, \phi_1) \\
&\quad \times Y_{L_3}^{M_3}(\theta_1, \phi_1) e^{2i\phi_1} \sin(\theta_1) d\theta_1 d\phi_1 \\
&= (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \sum_{L=|L_2-L_3|}^{L_2+L_3} \left[ \frac{2L+1}{4\pi} \right]^{1/2} C^L(L_3, M_3; L_2, -M_2) \\
&\quad \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta_1, \phi_1) Y_L^M(\theta_1, \phi_1) e^{2i\phi_1} \sin(\theta_1) d\theta_1 d\phi_1 \\
&= 2\pi (-1)^{M_2} \delta(M_1 + M_2 + M_3, 0) \sum_{L=|L_2-L_3|}^{L_2+L_3} \left[ \frac{2L+1}{4\pi} \right]^{1/2} C^L(L_3, M_3; L_2, -M_2) \\
&\quad \times \left[ \frac{2L_1+1}{4\pi} \right]^{1/2} \left[ \frac{(L_1 - M_1 + 2)!}{(L_1 + M_1 - 2)!} \right]^{1/2} \left[ \frac{2L+1}{4\pi} \right]^{1/2} \left[ \frac{(L - M)!}{(L + M)!} \right]^{1/2} \\
&\quad \times \int_0^\pi P_{L_1}^{M_1-2} P_L^M \sin(\theta_1) d\theta_1 \\
&= (-1)^{M_2} \delta(M_1, 1) \delta(M_1 + M_2 + M_3, 0) \left[ \frac{(2L_1+1)}{4\pi} \right]^{1/2} C^{L_1}(L_3, M_3; L_2, -M_2), \tag{C.12}
\end{aligned}$$

with  $M = M_2 + M_3$  and

$$\int_0^\pi P_{L_1}^{M_1-2} P_L^M \sin(\theta_1) d\theta_1 = \delta(L, L_1) \delta(M_1 - 2, M) \frac{2(L+M)!}{(2L+1)(L-M)!}. \tag{C.13}$$

Similarly

$$\begin{aligned}
& \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+2}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) e^{-2i\phi_1} \sin(\theta_1) d\theta_1 d\phi_1 \\
&= (-1)^{M_2} \delta(M_1, -1) \delta(M_1 + M_2 + M_3, 0) \left[ \frac{2L_1+1}{4\pi} \right]^{1/2} C^{L_1}(L_3, M_3; L_2, -M_2). \tag{C.14}
\end{aligned}$$

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