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ORIGINAL PAPER

Evaluation of Hylleraas-CI atomic integrals. III. Two-electron kinetic energy integrals

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Abstract This paper is the part III of a series about the evaluation of Hylleraas-Configuration Interaction (Hy-CI) integrals by the method of direct integration over the interelectronic coordinates. The two-electron kinetic-energy integrals have been derived using the Hamiltonian in Hylleraas coordinates. We have improved the algorithm used in part II of this series and obtained general expressions. The method used for the two-electron integrals can be used in the same fashion for the evaluation of the three-electron ones. The formulas shown here have been tested in actual Hy-CI calculations of two-electron systems. The two-electron kinetic energy integrals values agree with the ones obtained using the Kolos and Roothaan transformation. The effectiveness of the different methods is discussed.

Keywords Hylleraas-Configuration Interaction · Two-electron integrals · Kinetic-energy integrals · Slater orbitals

1 Introduction

The Hylleraas-Configuration Interaction (Hy-CI) wave functions [1,2] are of great interest in Quantum Chemistry because they lead to highly accurate energy values, or benchmark calculations, which usually serve to test or calibrate other Quantum Mechanical methods. This possibility of achieving high accuracy has been demonstrated with recent calculations of the helium atom [3], the H_2 molecule [4], the lithium [5], and beryllium atoms [6,7]. The application of the Hy-CI method can be extended to the calculation of the states of the second period of elements. Hy-CI calculations

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on the B atom [8] are in progress. Also Hy-CI have been successfully used for the calculation excited states. One example of their applications is the study of atomic excitations during β^--decay processes of atoms and ions, and the calculation of the final state probabilities [9]. In the future Hy-CI wave functions may be applied to modern problems of Physical Chemistry as confined atoms [10] , and Nuclear Physics like the study of excitations during nuclear reactions [11]. Some of these nuclear reactions are important in Nuclear Medicine, like the Boron Neutron Capture Therapy [12], a promising therapy against head and many types of cancer. For all these reasons it is important to provide to future workers in the field with different analytical methods to solve all occurring Hy-CI integrals and to compare their effectiveness in practical calculations.

The kinetic energy integrals, which are generated by the kinetic energy operator part of the Hamiltonian, are not as complex as the repulsion four-electron integrals, but their evaluation is also difficult. Note that the two-electron kinetic-energy integrals are needed not only in computer programs for two-electron systems, but in any program code for larger atoms.

In paper I [13] of this series we have derived analytical expressions for the three-electron kinetic-energy integrals occurring in the Hy-CI method. The Hamiltonian in Hylleraas coordinates was used [14]. The method of derivation consisted in the direct application of the differential operators on the wave function. This included to perform derivatives over spherical harmonics and the use of recursion relations over these functions. We distinguished between the cases of one quantum number $m = 0$, $m > 0$, and $m < 0$. In this paper we obtain general expressions for any m quantum number. The most important fact is that the method employed here can be extended in the same fashion to the three-electron case.

The advantage of our method is due to the direct integration over the interelectronic distances and the coordinates of one of the electrons, reducing the integral to a lower order. The three- and two-electron kinetic energy integrals are reduced to a linear combination of usual two-electron integrals. In "Appendix A" the two-electron integrals are derived in detail.

In the method by Sims and Hagstrom [15] the interelectronic distance is expanded into one-electron distances. The treatment is the same than the one employed in the repulsion integrals. The three-electron kinetic energy integrals are then special cases of the repulsion integrals and therefore they are evaluated in terms of three-electron auxiliary integrals W. In our method the three-electron kinetic energy integrals are also special cases of the repulsion integrals and they are reduced to two-electron integrals.

We have also checked the two-electron kinetic energy integrals using the Kolos and Roothaan transformation [16], obtaining completely agreement of the integrals to more than 30 decimal digits. Along this work we have used quadruple precision (30 decimal digits in our computer). In "Appendix B", the Kolos and Roothaan transformation for two-electron kinetic energy integrals is derived. A similar transformation for the three-electron case can not be done, as it will be shown in a forthcoming paper. The Kolos and Roothaan transformation has shown to be a factor of times computationally faster than the integrals shown here, with identical memory requirements.

The resulting formulas have been programmed and used in highly accurate calculations on the ground and excited states of He atom with an accuracy $> 1 \cdot 10^{-10}$ a.u., to

obtain some benchmark calculations for the n^1S, $n = 2 - 4$ of the ion Li^+ [9] and in preliminary calculations on the B atom [8]. We shall see that the Kolos and Roothaan transformation provides an effective computational method for the two-electron case. Whereas the integrals and method showed here shall help us to better understanding of the underlying relations in the kinetic energy integrals and it can be used as a method for the three-electron case.

2 The Hylleraas-CI wave function

The Hy-CI wave function [1,2] is a linear combination of configurations built up with Slater-type atomic orbitals with higher angular momentum as in the regular Configuration-Interaction (CI) procedure and configurations including one interelectronic distance r_{ij} as for Hylleraas-type trial wave functions [17]. The Hy-CI and CI wave functions for an n-electron systems are defined as:

$$\Psi = \sum_{q=1}^{N} C_q \Phi_q, \qquad \Phi_q = \hat{O}(\hat{L}^2)\hat{\mathcal{A}}\phi_q \chi, \tag{1}$$

where Φ_q are symmetry adapted configurations, N is the number of configurations and the constants C_q are determined variationally. The operator $\hat{O}(\hat{L}^2)$ projects over the proper spatial space, so that every configuration is eigenfunction of the square of the angular momentum operator $\hat{L}^2$.$\hat{\mathcal{A}}$ is the n-particle antisymmetrization operator, and χ is the spin eigenfunction:

$$\chi = [(\alpha\beta - \beta\alpha)\cdots(\alpha\beta - \beta\alpha)\alpha] \tag{2}$$

where for even electron systems the last α spin function is omitted. The spatial part of the basis functions are Hartree products of Slater orbitals:

$$\phi_q = r_{ij}^{\nu} \prod_{k=1}^{n} \phi_k(r_k, \theta_k, \phi_k). \tag{3}$$

The powers ν take the values 0, or 1. For $\nu = 0$ the wave function reduces effectively to a CI wave function. To understand the meaning of the Hy-CI wave function, note that even powers of the interelectronic coordinate are equivalent to products of p-, d-,... type one-electron orbitals, for instance:

$$r_{ij}^2 \equiv p(i)p(j). \tag{4}$$

Furthermore, higher odd powers can be expressed as $r_{ij}r_{ij}^{2n}$. It can be demonstrated using the addition theorem of spherical harmonics that a configuration times r_{ij}

is equivalent to an infinite expansion of higher angular momentum one-electron orbitals:

$$s(i)s(j)r_{ij} \equiv s(i)s(j) + p(i)p(j) + d(i)d(j) + f(i)f(j) + \cdots \tag{5}$$

In this way a single Hy-CI configuration is equivalent to infinite sum of CI configurations containing the excitations of the involved electrons to all higher momentum orbitals.

3 Hylleraas-CI two-electron kinetic energy integrals

In this section the two-electron kinetic energy integrals occurring in the Hy-CI method when using the Hamiltonian in Hylleraas coordinates [14] shall be derived. For any atomic number $N \geq 2$ two kinds of kinetic energy integrals occur: two- and three-electron ones. The three-electron kinetic energy integrals can be found in refs. [13,15]. In this work we will differentiate directly over the variable r_{ij} and use Hamiltonian written in polar and interelectronic coordinates proving its correctness, and will solve the resulting integrals in terms of radial two-electron integrals.

For a two-electron system the effective Hamiltonian in Hylleraas coordinates may be written[1] [14]:

$$\begin{aligned}
\hat{H} = & -\frac{1}{2}\sum_{i=1}^{2}\frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^{2}\frac{1}{r_i}\frac{\partial}{\partial r_i} - \sum_{i=1}^{2}\frac{2}{r_i} + \frac{1}{r_{12}} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \\
& -\frac{1}{2}\sum_{i\neq j}^{2}\frac{r_i^2 + r_{12}^2 - r_j^2}{r_i r_{12}}\frac{\partial^2}{\partial r_i \partial r_{12}} \\
& -\frac{1}{2}\sum_{i=1}^{2}\frac{1}{r_i^2}\frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2}\sum_{i=1}^{2}\frac{1}{r_i^2 \sin^2\theta_i}\frac{\partial^2}{\partial \phi_i^2} - \frac{1}{2}\sum_{i=1}^{2}\frac{\cot\theta_i}{r_i^2}\frac{\partial}{\partial \theta_i} \\
& -\sum_{i\neq j}^{2}\left(\frac{r_j}{r_i r_{12}}\frac{\cos\theta_j}{\sin\theta_i} + \frac{1}{2}\cot\theta_i\frac{r_{12}^2 - r_i^2 - r_j^2}{r_i^2 r_{12}}\right)\frac{\partial^2}{\partial\theta_i \partial r_{12}} \\
& -\sum_{i\neq j}^{2}\frac{r_j}{r_i r_{12}}\frac{\sin\theta_j}{\sin\theta_i}\sin(\phi_i - \phi_j)\frac{\partial^2}{\partial\phi_i \partial r_{12}}.
\end{aligned} \tag{6}$$

The angular momentum operator can be extracted:

$$\sum_{i=1}^{2}\frac{1}{r_i^2}\hat{L}_i^2 = -\frac{1}{2}\sum_{i=1}^{2}\frac{1}{r_i^2}\frac{\partial^2}{\partial\theta_i^2} - \frac{1}{2}\sum_{i=1}^{2}\frac{1}{r_i^2\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2} - \frac{1}{2}\sum_{i=1}^{2}\frac{\cot\theta_i}{r_i^2}\frac{\partial}{\partial\theta_i}, \tag{7}$$

[1] As the Hy-CI wave function consists on only one r_{ij} per configuration and treating now a two electron atom/ion, the terms of the Hamiltonian including $\frac{\partial^2}{\partial r_{12}^2}$ and $\frac{\partial^2}{\partial r_{12}\partial r_{12}}$ vanish.

and its eigenvalue equation used:

$$\hat{L}_i^2 \phi_i = l_i(l_i + 1)\phi_i, \tag{8}$$

with l_i the angular quantum number of the orbital ϕ_i. From the variational principle one obtains the matrix eigenvalue problem:

$$(\mathbf{H} - E\boldsymbol{\Delta})\mathbf{C} = \mathbf{0}, \tag{9}$$

where the matrix elements are:

$$H_{kl} = \int \Phi_k H \Phi_l d\tau, \tag{10}$$

$$\Delta_{kl} = \int \Phi_k \Phi_l d\tau. \tag{11}$$

The Hamiltonian in Hylleraas coordinates can be separated in a sum of one-electron potential and kinetic energy operators.

$$\hat{H} = \sum_{i=1}^{n} \hat{H}(i), \qquad \hat{H}(1) = \hat{T}(1) + \hat{V}(1) = \hat{T}_R(1) + \hat{T}_\theta(1) + \hat{V}(1). \tag{12}$$

The kinetic energy operator can be again separated into radial and angular parts. Let us evaluate the kinetic energy of electron 1:

$$\hat{T}(1) = \hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1) + \hat{T}_L(1) + \hat{T}_{\theta_1}(1) + \hat{T}_{\theta_2}(1) + \hat{T}_{\theta_3}(1). \tag{13}$$

The radial operators are:

$$\hat{T}_{R_1}(1) = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1}, \tag{14}$$

$$\hat{T}_{R_2}(1) = -\frac{1}{2}\frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}}, \tag{15}$$

$$\hat{T}_{R_3}(1) = -\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}}, \tag{16}$$

and the angular ones:

$$\hat{T}_L(1) = \frac{1}{2}\frac{\hat{L}^2(1)}{r_1^2}, \qquad \hat{L}^2(1) = -\frac{\partial^2}{\partial \theta_1^2} - \cot\theta_1 \frac{\partial}{\partial \theta_1} - \frac{1}{\sin\theta_1{}^2}\frac{\partial^2}{\partial \phi_1^2}, \tag{17}$$

$$\hat{T}_{\theta_1}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\cos\theta_2}{\sin\theta_1} \frac{\partial^2}{\partial\theta_1 \partial r_{12}}, \tag{18}$$

$$\hat{T}_{\theta_2}(1) = -\frac{1}{2} \cot\theta_1 \frac{r_{12}^2 - r_1^2 - r_2^2}{r_1^2 r_{12}} \frac{\partial^2}{\partial\theta_1 \partial r_{12}}, \tag{19}$$

$$\hat{T}_{\theta_3}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\sin\theta_2}{\sin\theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial\phi_1 \partial r_{12}}, \tag{20}$$

the potential energy operator is:

$$\hat{V}(1) = -\frac{Z}{r_1}. \tag{21}$$

In the two-electron kinetic energy integrals we may encounter CI configurations $\nu = 0$ and configurations of Hy-CI type with $\nu = 1$. In the following, we will use ν for a power of r_{12} in the left hand side basis functions and ν' on the right ones. The inter-electronic distance in the integral has then the power $r_{12}^{\nu+\nu'}$. The two-electron integrals $I(N_1, N_2; \omega_1, \omega_2; \nu+\nu')_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'}$ are defined in "Appendix A", Eq. (A.3) and their value can be calculated using Eqs. (A.12, A.27).

The nuclear attraction potential energy is:

$$\begin{aligned} I_{PE}(1) &= \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} | \hat{V} | \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle \\ &= -Z I(N_1 - 1, N_2; \omega_1, \omega_2; \nu+\nu')_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'}, \qquad \nu, \nu' = 0, 1 \end{aligned} \tag{22}$$

with Z the atomic nuclear charge.

The radial kinetic energy integral is:

$$I_{KE,R}(1) = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} | \hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1) | \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle \tag{23}$$

The radial part can be separated into three contributions. The resulting integrals can be straightforward evaluated using the operators Eqs. (14–16) and the definition of the two-electron integrals Eq. (A.3):

$$\begin{aligned} I_{KE,R_1}(1) = &-\frac{(n_1'^2 - n_1')}{2} I(N_1 - 2, N_2; \omega_1, \omega_2; \nu+\nu')_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'} \\ &+ n_1'\omega_1' I(N_1 - 1, N_2; \omega_1, \omega_2; \nu+\nu')_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'} \\ &- \frac{\omega_1'^2}{2} I(N_1, N_2; \omega_1, \omega_2; \nu+\nu')_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'}, \end{aligned} \tag{24}$$

$$
\begin{aligned}
I_{KE,R_2}(1) = -\nu' \frac{n_1' - 1}{2} \Big[& I(N_1, N_2; \omega_1, \omega_2; \nu + \nu' - 2)^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \\
& + I(N_1 - 2, N_2; \omega_1, \omega_2; \nu + \nu')^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \\
& - I(N_1 - 2, N_2 + 2; \omega_1, \omega_2; \nu + \nu' - 2)^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \Big] \\
+ \nu' \frac{\omega_1'}{2} \Big[& I(N_1 + 1, N_2; \omega_1, \omega_2; \nu + \nu' - 2)^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \\
& + I(N_1 - 1, N_2; \omega_1, \omega_2; \nu + \nu')^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \\
& - I(N_1 - 1, N_2 + 2; \omega_1, \omega_2; \nu + \nu' - 2)^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'} \Big], \qquad (25)
\end{aligned}
$$

$$
I_{KE,R_3}(1) = -\nu' I(N_1, N_2; \omega_1, \omega_2; \nu + \nu' - 2)^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'}. \qquad (26)
$$

The factor ν' ensures that CI configurations will not contribute and a Hy-CI will contribute: $\nu' = 1$.

Now let us evaluate the angular kinetic energy. The integral containing the square of the angular momentum operator can be easily calculated by means of its eigenvalue equation:

$$
\begin{aligned}
I_{KE,\theta_1,L} &= \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} \middle| \frac{1}{2} \frac{\hat{L}_1^2}{r_1^2} \middle| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle \\
&= \frac{1}{2} l_1'(l_1' + 1) I(N_1 - 2, N_2; \omega_1, \omega_2; \nu + \nu')^{m_1, m_1', m_2, m_2'}_{l_1, l_1', l_2, l_2'}, \qquad (27)
\end{aligned}
$$

where l_1' is the quantum number of $\phi(\mathbf{r}_1)$.

The evaluation of the other angular kinetic energy contributions is more involving. The following integrals should be evaluated:

$$
I_{KE,\theta 1} = -\left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} \middle| \frac{r_2}{r_1 r_{12}} \frac{\cos\theta_2}{\sin\theta_1} \frac{\partial^2}{\partial\theta_1 \partial r_{12}} \middle| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle, \qquad (28)
$$

$$
I_{KE,\theta 2} = -\frac{1}{2} \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} \middle| \frac{(r_{12}^2 - r_1^2 - r_2^2)}{r_1^2 r_{12}} \cot\theta_1 \frac{\partial^2}{\partial\theta_1 \partial r_{12}} \middle| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle, \qquad (29)
$$

$$
I_{KE,\phi 3} = -\left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} \middle| \frac{r_2}{r_1 r_{12}} \frac{\sin\theta_2}{\sin\theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial\phi_1 \partial r_{12}} \middle| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle. \qquad (30)
$$

3.1 Evaluation of $I_{KE,\theta 1}$

Let us perform first the angular integration. The derivatives of a spherical harmonic $Y_{l_1}^{m_1}(\theta_1, \phi_1)$ with respect to the polar angle θ_1 [18, Eq. (5.7.)] is:

$$\frac{\partial Y_{l_1'}^{m_1'}(\theta_1, \phi_1)}{\partial \theta_1} = f_{1a} e^{-i\phi_1} Y_{l_1'}^{m_1'+1}(\theta_1, \phi_1) - f_{1b} e^{i\phi_1} Y_{l_1'}^{m_1'-1}(\theta_1, \phi_1), \tag{31}$$

where:

$$f_{1a} = \frac{1}{2}[(l_1' + m_1' + 1)(l_1' - m_1')]^{1/2}, \qquad f_{1b} = \frac{1}{2}[(l_1' - m_1' + 1)(l_1' + m_1')]^{1/2} \tag{32}$$

multiplying by the complex conjugate $Y_{l_1}^{m_1 *}(\theta_1, \phi_1)$ and linearizing the product using Eq. (A.4) we obtain:

$$\begin{aligned} Y_{l_1}^{m_1 *}(\theta_1, \phi_1) \frac{\partial Y_{l_1'}^{m_1'}(\theta_1, \phi_1)}{\partial \theta_1} &= \sum_{L_1 = |l_1' - l_1|}^{l_1' + l_1} \left[\frac{2L_1 + 1}{4\pi}\right]^{1/2} \\ &\times \left\{ f_{1a} c_{1a} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) e^{-i\phi_1} - f_{1b} c_{1b} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) e^{i\phi_1} \right\} \end{aligned} \tag{33}$$

with

$$c_{1a} = C^{L_1}(l_1', m_1' + 1; l_1, m_1), \qquad c_{1b} = C^{L_1}(l_1', m_1' - 1; l_1, m_1). \tag{34}$$

On the other side using the cosine recursion relation:

$$\cos\theta_2 Y_{l_2'}^{m_2'}(\theta_2, \phi_2) = f_{2a} Y_{l_2'-1}^{m_2'}(\theta_2, \phi_2) + f_{2b} Y_{l_2'+1}^{m_2'}(\theta_2, \phi_2), \tag{35}$$

with

$$f_{2a} = \left[\frac{(l_2' + m_2')(l_2' - m_2')}{(2l_2' + 1)(2l_2' - 1)}\right]^{1/2}, \quad f_{2b} = \left[\frac{(l_2' + m_2' + 1)(l_2' - m_2' + 1)}{(2l_2' + 1)(2l_2' + 3)}\right]^{1/2}, \tag{36}$$

multiplying by $Y_{l_2}^{m_2 *}(\theta_2, \phi_2)$ and linearizing the products:

$$\begin{aligned} Y_{l_2}^{m_2 *}(\theta_2, \phi_2) \cos\theta_2 Y_{l_2'}^{m_2'}(\theta_2, \phi_2) &= \sum_{L_2 = |l_2' - 1 - l_2|}^{l_2' - 1 + l_2} \left[\frac{2L_2 + 1}{4\pi}\right]^{1/2} f_{2a} c_{2a} Y_{L_2}^{M_2}(\theta_2, \phi_2) \\ &+ \sum_{L_2' = |l_2' + 1 - l_2|}^{l_2' + 1 + l_2} \left[\frac{2L_2' + 1}{4\pi}\right]^{1/2} f_{2b} c_{2b} Y_{L_2'}^{M_2}(\theta_2, \phi_2) \end{aligned} \tag{37}$$

with

$$c_{2a} = C^{L_2}(l_2' - 1, m_2'; l_2, m_2), \qquad c_{2b} = C^{L_2'}(l_2' + 1, m_2'; l_2, m_2). \tag{38}$$

The rotation of $Y_{L_2}^{M_2}(\theta_2, \phi_2)$, see Eq. (A.7), and integration over ϕ_{12} leads to $4\pi Y_{L_2}^{M_2}(\theta_1, \phi_1)$. Altogether:

$$\begin{aligned}
&\left(Y_{l_2}^{m_2 *}(\theta_2, \phi_2)\left(\cos\theta_2 Y_{l_2'}^{m_2'}(\theta_2, \phi_2)\right)\right)\left(Y_{l_1}^{m_1 *}(\theta_1, \phi_1)\frac{\partial Y_{l_1'}^{m_1'}(\theta_1, \phi_1)}{\partial \theta_1}\right) \\
&= \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} [2L_1+1]^{1/2} \left\{ \sum_{L_2=|l_2'-1-l_2|}^{l_2'-1+l_2} [2L_2+1]^{1/2} \right. \\
&\times \left(f_{1a}c_{1a}f_{2a}c_{2a} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) e^{-i\phi_1}\right. \\
&\left. -f_{1b}c_{1b}f_{2a}c_{2a} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) e^{i\phi}\right) \\
&+ \sum_{L_2'=|l_2'+1-l_2|}^{l_2'+1+l_2} [2L_2'+1]^{1/2} \left(f_{1a}c_{1a}f_{2b}c_{2b} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L_2'}^{M_2}(\theta_1, \phi_1) e^{-i\phi_1}\right. \\
&\left.\left. -f_{1b}c_{1b}f_{2b}c_{2b} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L_2'}^{M_2}(\theta_1, \phi_1) e^{i\phi_1}\right)\right\}
\end{aligned} \tag{39}$$

Now the spherical harmonics with the same arguments are linearized again, see Eq. (A.4). Note we need the complex conjugate in Eq. (A.10).

$$\begin{aligned}
&\frac{1}{4\pi} \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} [2L_1+1]^{1/2} \left\{ \sum_{L_2=|l_2'-1-l_2|}^{l_2'-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} [(2L_2+1)(2L+1)]^{1/2} \right. \\
&\times \left((-1)^{M_1+1} f_{1a}c_{1a}f_{2a}c_{2a}c_{3a} Y_L^{M_1+M_2+1}(\theta_1, \phi_1) e^{-i\phi_1}\right. \\
&\left. -(-1)^{M_1-1} f_{1b}c_{1b}f_{2a}c_{2a}c_{3b} Y_L^{M_1+M_2-1}(\theta_1, \phi_1) e^{i\phi}\right) \\
&+ \sum_{L_2'=|l_2'+1-l_2|}^{l_2'+1+l_2} \sum_{L'=|L_2'-L_1|}^{L_1+L_2} [(2L_2'+1)(2L'+1)]^{1/2} \\
&\times \left((-1)^{M_1+1} f_{1a}c_{1a}f_{2b}c_{2b}c_{3c} Y_{L'}^{M_1+M_2+1}(\theta_1, \phi_1) e^{-i\phi_1}\right. \\
&\left.\left. -(-1)^{M_1-1} f_{1b}c_{1b}f_{2b}c_{2b}c_{3d} Y_{L'}^{M_1+M_2-1}(\theta_1, \phi_1) e^{i\phi_1}\right)\right\}
\end{aligned} \tag{40}$$

with

$$c_{3a} = C^{L}(L_2, M_2; L_1, -M_1 - 1), \quad c_{3b} = C^{L}(L_2, M_2; L_1, -M_1 + 1)$$
$$c_{3c} = C^{L'}(L_2', M_2; L_1, -M_1 - 1), \quad c_{3d} = C^{L'}(L_2', M_2; L_1, -M_1 + 1) \tag{41}$$

Finally, the recursion relation containing the sine function is applied [13, C7]:

$$\frac{Y_l^m(\theta_1, \phi_1)}{\sin\theta_1} = -\frac{1}{2m}\left[\frac{(2l+1)}{(2l+3)}\right]^{1/2}\Big[[(l-m+2)(l-m+1)]^{1/2} e^{i\phi_1} Y_{l+1}^{m-1}(\theta_1, \phi_1) + ((l+m+1)(l+m+2))^{1/2} e^{-i\phi_1} Y_{l+1}^{m+1}(\theta_1, \phi_1)\Big], \tag{42}$$

The relation is valid for $m \neq 0$. This condition is fulfill in our cases $M = M_1 + M_2 + 1$ and $M' = M_1 + M_2 - 1$. Multiplying $1/\sin\theta_1$ and Eq. (40) we have:

$$\begin{aligned}
I_{KE,\theta_1}(1) = \frac{1}{4\pi} \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} [2L_1+1]^{1/2} \Bigg\{ \sum_{L_2=|l_2'-1-l_2|}^{l_2'-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} \frac{(2L+1)\,[2L_2+1]^{1/2}}{[2L+3]^{1/2}} \\
\times \Bigg(f_{1a}c_{1a}f_{2a}c_{2a}f_{3a}c_{3a} \int_0^{\pi}\int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1,\phi_1)\,d\Omega_1 \\
+ f_{1a}c_{1a}f_{2a}c_{2a}f_{3b}c_{3a} \int_0^{\pi}\int_0^{2\pi} Y_{L+1}^{M_1+M_2+2}(\theta_1,\phi_1) e^{-2i\phi_1}\,d\Omega_1 \\
- f_{1b}c_{1b}f_{2a}c_{2a}f_{3c}c_{3b} \int_0^{\pi}\int_0^{2\pi} Y_{L+1}^{M_1+M_2-2}(\theta_1,\phi_1) e^{2i\phi}\,d\Omega_1 \\
- f_{1b}c_{1b}f_{2a}c_{2a}f_{3d}c_{3b} \int_0^{\pi}\int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1,\phi_1)\,d\Omega_1 \Bigg) \\
\times I(N_1-1, N_2+1; \omega_1, \omega_2; \nu+\nu'-2; L_2) \\
+ \sum_{L_2'=|l_2'+1-l_2|}^{l_2'+1+l_2} \sum_{L'=|L_2'-L_1|}^{L_1+L_2} \frac{(2L'+1)\left[2L_2'+1\right]^{1/2}}{\left[2L'+3\right]^{1/2}} \\
\times \Bigg(f_{1a}c_{1a}f_{2b}c_{2b}f_{3a}c_{3c} \int_0^{\pi}\int_0^{2\pi} Y_{L'+1}^{M_1+M_2}(\theta_1,\phi_1)\,d\Omega_1 \\
+ f_{1a}c_{1a}f_{2b}c_{2b}f_{3b}c_{3c} \int_0^{\pi}\int_0^{2\pi} Y_{L'+1}^{M_1+M_2+2}(\theta_1,\phi_1) e^{-2i\phi_1}\,d\Omega_1 \\
- f_{1b}c_{1b}f_{2b}c_{2b}f_{3c}c_{3d} \int_0^{\pi}\int_0^{2\pi} Y_{L'+1}^{M_1+M_2-2}(\theta_1,\phi_1) e^{2i\phi_1}\,d\Omega_1
\end{aligned}$$

$$-f_{1b}c_{1b}f_{2b}c_{2b}f_{3d}c_{3d}\int_0^{\pi}\int_0^{2\pi}Y_{L'+1}^{M_1+M_2}(\theta_1,\phi_1)\Bigg)d\Omega_1$$
$$\times I(N_1-1,N_2+1;\omega_1,\omega_2;\nu+\nu'-2;L_2')\Bigg\} \tag{43}$$

with

$$\begin{aligned}
f_{3a} &= \frac{(-1)^{M_1+1}}{2M}[(L-M+2)(L-M+1)]^{1/2},\\
f_{3b} &= \frac{(-1)^{M_1+1}}{2M}[(L+M+2)(L+M+1)]^{1/2},\\
f_{3c} &= \frac{(-1)^{M_1-1}}{2M'}[(L-M'+2)(L-M'+1)]^{1/2},\\
f_{3d} &= \frac{(-1)^{M_1-1}}{2M'}[(L+M'+2)(L+M'+1)]^{1/2}.
\end{aligned} \tag{44}$$

The first kind of integrals over spherical harmonics are:

$$\int_0^{\pi}\int_0^{2\pi}Y_{L+1}^{M_1+M_2}(\theta_1,\phi_1)d\Omega_1=\delta(L+1,0)\delta(M_1+M_2,0)=0. \tag{45}$$

The following integrals are evaluated integrating over the associate Legendre functions:

$$\begin{aligned}
A_{Y1}(L,M+n,-n) &= \int_0^{\pi}\int_0^{2\pi}Y_L^{M+n}(\theta_1,\phi_1)e^{-ni\phi_1}d\Omega_1\\
&= \delta(M,0)\pi^{1/2}(2L+1)^{1/2}\left[\frac{(L-M-n)!}{(L+M+n)!}\right]^{1/2}\int_0^{\pi}P_L^{M+n}(\cos\theta_1)\sin\theta_1 d\theta_1
\end{aligned} \tag{46}$$

using the algorithm developed by Wong [19], in which the overlap integral over Associate Legendre functions is:

$$\begin{aligned}
&\int_0^{\pi}P_{L_1}^{M_1}(\cos\theta)P_{L_2}^{M_2}(\cos\theta)\sin(\theta)d\theta=\sum_{p_1=0}^{p_{1\max}}\sum_{p_2=0}^{p_{2\max}}a_{L_1,M_1}^{p_1}a_{L_2,M_2}^{p_2}\\
&\times\frac{\Gamma\left(\frac{1}{2}(L_1+L_2-M_1-M_2-2p_1-2p_2+1)\right)\Gamma\left(\frac{1}{2}(M_1+M_2+2p_1+2p_2+2)\right)}{\Gamma\left(\frac{1}{2}(L_1+L_2+3)\right)}.
\end{aligned} \tag{47}$$

Γ is the Gamma function. $p_{\max} = [(l-m)/2]$ the integral part of $(l-m)/2$. This formula is valid for $0 \le M_1 \le L_1$ and $0 \le M_2 \le L_2$. For $M_1 \le L_1$ or $M_1 \le L_1$ the integral is zero, see ref. [19]. If M is negative the formula is used:

$$P_L^{-M}(\cos\theta_1) = (-1)^M \frac{(L-M)!}{(L+M)!} P_L^M(\cos\theta_1). \tag{48}$$

For even $L_1 + L_2 - M_1 - M_2$ the integral vanishes. The coefficients are:

$$a_{L,M}^p = \frac{(-1)^p (L+M)!}{2^{M+2p}(M+p)!p!(L-M-2p)!}. \tag{49}$$

Finally the programmable expression is:

$$\begin{aligned} I_{KE,\theta_1}(1) = \frac{1}{4\pi}\delta(M_1+M_2,0) \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} [2L_1+1]^{1/2} \Bigg\{ \sum_{L_2=|l_2'-1-l_2|}^{l_2'-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} \frac{(2L+1)\,[2L_2+1]^{1/2}}{[2L+3]^{1/2}} \\ [f_{1a}c_{1a}f_{2a}c_{2a}f_{3b}c_{3a}A_{Y1}(L+1,M+1,-2) - f_{1b}c_{1b}f_{2a}c_{2a}f_{3c}c_{3b}A_{Y1}(L+1,M'-1,2)] \\ \times I(N_1-1,N_2+1;\omega_1,\omega_2;\nu+\nu'-2;L_2) + \sum_{L_2'=|l_2'+1-l_2|}^{l_2'+1+l_2} \sum_{L'=|L_2'-L_1|}^{L_1+L_2} \frac{(2L'+1)\left[2L_2'+1\right]^{1/2}}{[2L'+3]^{1/2}} \\ [f_{1a}c_{1a}f_{2b}c_{2b}f_{3b}c_{3c}A_{Y1}(L'+1,M+1,-2) - f_{1b}c_{1b}f_{2b}c_{2b}f_{3c}c_{3d}A_{Y1}(L'+1,M'-1,2)] \\ \times I(N_1-1,N_2+1;\omega_1,\omega_2;\nu+\nu'-2;L_2') \Bigg\} \end{aligned} \tag{50}$$

3.2 Evaluation of $I_{KE,\theta 2}$

For the evaluation of $I_{KE,\theta 2}$, the same steps than for $I_{KE,\theta 1}$ Eqs. (31–34) are needed. Afterwards the product of spherical harmonics of electron 2 should be linearized. Then a rotation like in Eq. (A.7) is performed and the complex conjugate of $Y_{L_1}^{M_1-1}(\theta_1,\phi_1)$ used. The new products of $Y_{L_1}^{-M_1+1*}(\theta_1,\phi_1)Y_{L_2}^{M_2}(\theta_1,\phi_1)$ lead to:

$$\begin{aligned} &\left(Y_{l_2}^{m_2*}(\theta_2,\phi_2)Y_{l_2'}^{m_2'}(\theta_2,\phi_2)\right)\left(Y_{l_1}^{m_1*}(\theta_1,\phi_1)\frac{\partial Y_{l_1'}^{m_1'}(\theta_1,\phi_1)}{\partial\theta_1}\right) \\ &= \frac{1}{(4\pi)^{1/2}} \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} \sum_{L_2=|l_2'-l_2|}^{l_2'+l_2} \sum_{L=|L_1-L_2|}^{L_1+L_2} [(2L_1+1)(2L_2+1)(2L+1)]^{1/2} c_{2L} \end{aligned}$$

$$\times \Big\{ (-1)^{M_1+1} f_{1a} c_{1a} c_{2a} Y_L^{M_1+M_2+1}(\theta_1, \phi_1) e^{-i\phi_1} - (-1)^{M_1-1} f_{1b} c_{1b} c_{2b} Y_L^{M_1+M_2-1}(\theta_1, \phi_1) e^{i\phi_1} \Big\} \tag{51}$$

where

$$c_{2L} = C^{L_2}(l_2', m_2'; l_2, m_2)$$
$$c_{2a} = C^{L}(L_2, M_2; L_1, -M_1 - 1), \qquad c_{2b} = C^{L}(L_2, M_2; L_1, -M_1 + 1) \tag{52}$$

Now we apply the recursion relation including the $\cot\theta$ function [18, 5.7.]:

$$-\cot\theta_1 Y_l^m(\theta_1, \phi_1) = \frac{1}{2m}[(l+m+1)(l-m)]^{1/2} e^{-i\phi_1} Y_l^{m+1}(\theta_1, \phi_1) + \frac{1}{2m}[(l-m+1)(l+m)]^{1/2} e^{i\phi_1} Y_l^{m-1}(\theta_1, \phi_1) \tag{53}$$

which leads to:

$$\begin{aligned} I_{KE,\theta_1,2} = \frac{1}{4\sqrt{\pi}} \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} \sum_{L_2=|l_2'-l_2|}^{l_2'+l_2} \sum_{L=|L_1-L_2|}^{L_1+L_2} [(2L_1+1)(2L_2+1)(2L+1)]^{1/2} c_{2L} \\ \times \Bigg\{ f_{1a} c_{1a} f_{2a} c_{2a} \int_0^{\pi}\int_0^{2\pi} Y_L^{M_1+M_2+2}(\theta_1, \phi_1) e^{-2i\phi_1} d\Omega_1 \\ + f_{1a} c_{1a} f_{2b} c_{2a} \int_0^{\pi}\int_0^{2\pi} Y_L^{M_1+M_2}(\theta_1, \phi_1) d\Omega_1 \\ - f_{1b} c_{1b} f_{2c} c_{2b} \int_0^{\pi}\int_0^{2\pi} Y_L^{M_1+M_2}(\theta_1, \phi_1) d\Omega_1 \\ - f_{1b} c_{1b} f_{2d} c_{2b} \int_0^{\pi}\int_0^{2\pi} Y_L^{M_1+M_2-2}(\theta_1, \phi_1) e^{2i\phi_1} d\Omega_1 \Bigg\} \\ \times \big[I(N_1-2, N_2; \omega_1, \omega_2; \nu+\nu'-2; L_2) - I(N_1, N_2; \omega_1, \omega_2; \nu+\nu'-2; L_2) \\ - I(N_1-2, N_2+2; \omega_1, \omega_2; \nu+\nu'-2; L_2) \big], \end{aligned} \tag{54}$$

with $M = M_1 + M_2 + 1$ and $M' = M_1 + M_2 - 1$. Integrating:

$$
\begin{aligned}
f_{2a} &= \frac{(-1)^{M_1+1}}{2M}[(L+M+1)(L-M)]^{1/2},\\
f_{2b} &= \frac{(-1)^{M_1+1}}{2M}[(L-M+1)(L+M)]^{1/2},\\
f_{2c} &= \frac{(-1)^{M_1-1}}{2M'}[(L+M'+1)(L-M')]^{1/2},\\
f_{2d} &= \frac{(-1)^{M_1-1}}{2M'}[(L+M'+1)(L+M')]^{1/2}
\end{aligned}
\tag{55}
$$

Using Eqs. (46–49), the final programmable expression is:

$$
\begin{aligned}
I_{KE,\theta_1,2} = \frac{1}{4\sqrt{\pi}}\delta(M_1+M_2,0) &\sum_{L_1=|l_1'-l_1|}^{l_1'+l_1}\ \sum_{L_2=|l_2'-l_2|}^{l_2'+l_2}\ \sum_{L=|L_1-L_2|}^{L_1+L_2}\\
&\times[(2L_1+1)(2L_2+1)(2L+1)]^{1/2}\,c_{2L}\\
&\times\Big\{f_{1a}c_{1a}f_{2a}c_{2a}A_{Y1}(L,M+1,-2)+f_{1a}c_{1a}f_{2b}c_{2a}A_{Y1}(L,M-1)\\
&\quad -f_{1b}c_{1b}f_{2c}c_{2b}A_{Y1}(L,M'+1)-f_{1b}c_{1b}f_{2d}c_{2b}A_{Y1}(L,M'-1,2)\Big\}\\
&\times\big[I(N_1-2,N_2;\omega_1,\omega_2;\nu+\nu';L_2)-I(N_1,N_2;\omega_1,\omega_2;\nu+\nu'-2;L_2)\\
&\quad -I(N_1-2,N_2+2;\omega_1,\omega_2;\nu+\nu'-2;L_2)\big],
\end{aligned}
\tag{56}
$$

3.3 Evaluation of $I_{KE,\phi 3}$

The derivative of the spherical harmonic with $m_1' = 0$ with respect to ϕ_1 vanishes:

$$
I_{KE,\phi_1,3} = 0. \tag{57}
$$

In case of $m_1 \neq 0$:

$$
\frac{\partial Y_l^m(\theta,\phi)}{\partial\phi} = imY_l^m(\theta,\phi). \tag{58}
$$

In this section we evaluate Eq. (30). The function $\sin(\phi_1-\phi_2)$ can be written in exponential form:

$$
\sin(\phi_1-\phi_2) = \frac{1}{2i}\left(e^{i\phi_1}e^{-i\phi_2} - e^{-i\phi_1}e^{i\phi_2}\right), \tag{59}
$$

and the following functions can be written as spherical harmonics:

$$
\sin\theta_2 e^{-i\phi_2} = \sqrt{\frac{8\pi}{3}}Y_1^{-1}(\theta_2,\phi_2), \qquad \sin\theta_2 e^{i\phi_2} = -\sqrt{\frac{8\pi}{3}}Y_1^{1}(\theta_2,\phi_2). \tag{60}
$$

The products of spherical harmonics can be linearized:

$$\sqrt{\frac{8\pi}{3}}Y_{l_2}^{m_2^*}(\theta_2,\phi_2)Y_1^{-1}(\theta_2,\phi_2)=\sqrt{\frac{2}{3}}\sum_{L_2=|l_2-1|}^{l_2+1}(2L_2+1)^{1/2}c_{2a}Y_{L_2}^{-1-m_2}(\theta_2,\phi_2)$$
$$\sqrt{\frac{8\pi}{3}}Y_{l_2}^{m_2^*}(\theta_2,\phi_2)Y_1^{1}(\theta_2,\phi_2)=\sqrt{\frac{2}{3}}\sum_{L_2=|l_2-1|}^{l_2+1}(2L_2+1)^{1/2}c_{2b}Y_{L_2}^{1-m_2}(\theta_2,\phi_2) \quad (61)$$

with

$$c_{2a}=C^{L2}(1,-1;l_2,m_2),\qquad c_{2b}=C^{L2}(1,1;l_2,m_2). \quad (62)$$

Using the above derived expression, the product of angular functions is:

$$\begin{aligned}
&-Y_{l_1}^{m_1^*}(\theta_1,\phi_1)Y_{l_2}^{m_2^*}(\theta_2,\phi_2)\frac{\sin\theta_2}{\sin\theta_1}\sin(\phi_1-\phi_2)\frac{\partial Y_{l_1'}^{m_1'}(\theta_1,\phi_1)}{\partial\phi_1}Y_{l_2'}^{m_2'}(\theta_2,\phi_2)\\
&=\frac{m_1}{2}\sqrt{\frac{2}{3}}\sum_{L_2=|l_2-1|}^{l_2+1}(2L_2+1)^{1/2}\\
&\quad\times\left\{c_{2a}Y_{L_2}^{-1-m_2}(\theta_1,\phi_1)Y_{l_1}^{m_1^*}(\theta_1,\phi_1)\frac{e^{i\phi_1}}{\sin\theta_1}Y_{l_1'}^{m_1'}(\theta_1,\phi_1)Y_{l_2'}^{m_2'}(\theta_2,\phi_2)\right.\\
&\qquad\left.+c_{2b}Y_{L_2}^{1-m_2}(\theta_1,\phi_1)Y_{l_1}^{m_1^*}(\theta_1,\phi_1)\frac{e^{-i\phi_1}}{\sin\theta_1}Y_{l_1}^{m_1^*}(\theta_1,\phi_1)Y_{l_2'}^{m_2'}(\theta_2,\phi_2)\right\}, \quad (63)
\end{aligned}$$

using the recursion relation containing the sinus function Eq. (42) over $Y_{l_1'}^{m_1'}(\theta_1,\phi_1)$ and the factors defined as:

$$f_{1a}=[(l_1'-m_1'+2)(l_1'-m_1'+1)]^{1/2},\quad f_{1b}=[(l_1'+m_1'+2)(l_1'+m_1'+1)]^{1/2} \quad (64)$$

Equation (63) can be written:

$$\begin{aligned}
&(-1)^{m_2'}\frac{1}{4}\sqrt{\frac{2}{3}}\left[\frac{2l_1'+1}{2l_1'+3}\right]^{1/2}\sum_{L_2=|l_2-1|}^{l_2+1}(2L_2+1)^{1/2}\\
&\times\left\{c_{2a}Y_{l_2'}^{m_2'}(\theta_2,\phi_2)Y_{L_2}^{-1-m_2}(\theta_2,\phi_2)\right.\\
&\quad\times\left(f_{1a}Y_{l_1}^{m_1}(\theta_1,\phi_1)e^{2\phi_1}Y_{l_1'+1}^{m_1'+1}(\theta_1,\phi_1)+f_{1b}Y_{l_1}^{m_1}(\theta_1,\phi_1)Y_{l_1'+1}^{m_1'+1}(\theta_1,\phi_1)\right)\\
&\quad+c_{2b}Y_{l_2'}^{m_2'}(\theta_2,\phi_2)Y_{L_2}^{1-m_2}(\theta_2,\phi_2)\\
&\quad\times\left.\left(f_{1a}Y_{l_1}^{m_1}(\theta_1,\phi_1)Y_{l_1'+1}^{m_1'-1}(\theta_1,\phi_1)+f_{1b}Y_{l_1}^{m_1}(\theta_1,\phi_1)e^{-2\phi_1}Y_{l_1'+1}^{m_1'+1}(\theta_1,\phi_1)\right)\right\}
\end{aligned} \quad (65)$$

Combining $Y_{l_2'}^{m_2'}(\theta_2,\phi_2)Y_{L_2}^{-1-m_2}(\theta_2,\phi_2)$:

$$Y_{l_2'}^{m_2'}(\theta_2,\phi_2)Y_{L_2}^{-1-m_2}(\theta_2,\phi_2) = (-1)^{m_2'}\sum_{L_2'=|L_2-l_2'|}^{L_2+l_2'}\frac{(2L_2'+1)^{1/2}}{(4\pi)^{1/2}}c_{2L'a}Y_{L_2'}^{M_2-1}(\theta_2,\phi_2)$$

$$Y_{l_2'}^{m_2'}(\theta_2,\phi_2)Y_{L_2}^{1-m_2}(\theta_2,\phi_2) = (-1)^{m_2'}\sum_{L_2'=|L_2-l_2'|}^{L_2+l_2'}\frac{(2L_2'+1)^{1/2}}{(4\pi)^{1/2}}c_{2L'b}Y_{L_2'}^{M_2+1}(\theta_2,\phi_2) \tag{66}$$

with

$$c_{2L'a} = C^{L_2'}(L_2,-1-m_2;l_2',-m_2'),\qquad c_{2L'b} = C^{L_2'}(L_2,1-m_2;l_2',-m_2') \tag{67}$$

Equation (65) can be rewritten as:

$$\begin{aligned}(-1)^{m_2'}\frac{1}{4\pi}\frac{1}{4}\sqrt{\frac{2}{3}}\left[\frac{2l_1'+1}{2l_1'+3}\right]^{1/2}&\sum_{L_2=|l_2-1|}^{l_2+1}\sum_{L_2'=|L_2-l_2'|}^{L_2+l_2'}\sum_{L_1=|l_1'+1-l_1|}^{l_1'+1+l_1}\\ &\times(2L_2+1)^{1/2}(2L_2'+1)^{1/2}(2L_1+1)^{1/2}\\ &\times\Big\{c_{2a}c_{2L'a}Y_{L_2'}^{M_2-1}(\theta_2,\phi_2)\left(f_{1a}c_{1a}Y_{L_1}^{M_1-1}(\theta_1,\phi_1)e^{2\phi_1}+f_{1b}c_{1b}Y_{L_1}^{M_1+1}(\theta_1,\phi_1)\right)\\ &\quad+c_{2b}c_{2L'b}Y_{L_2'}^{M_2+1}(\theta_2,\phi_2)\left(f_{1a}c_{1a}Y_{L_1}^{M_1-1}(\theta_1,\phi_1)+f_{1b}c_{1b}Y_{L_1}^{M_1+1}(\theta_1,\phi_1)e^{-2\phi_1}\right)\Big\},\end{aligned} \tag{68}$$

with

$$c_{1a} = C^{L_1}(l_1'+1,m_1'-1;l_1,m_1),\qquad c_{1b} = C^{L_1}(l_1'+1,m_1'+1;l_1,m_1). \tag{69}$$

After a rotation of the spherical harmonics of electron 2, see Eq. (A.7):

$$\begin{aligned}I_{KE,\phi_1,3} = (-1)^{m_2'}\frac{1}{4}\sqrt{\frac{2}{3}}\left[\frac{2l_1'+1}{2l_1'+3}\right]^{1/2}&\sum_{L_2=|l_2-1|}^{l_2+1}\sum_{L_2'=|L_2-l_2'|}^{L_2+l_2'}\sum_{L_1=|l_1'+1-l_1|}^{l_1'+1+l_1}\\ &\times(2L_2+1)^{1/2}(2L_2'+1)^{1/2}(2L_1+1)^{1/2}\Bigg\{c_{2a}c_{2L'a}\\ &\times\Bigg(f_{1a}c_{1a}\int_0^{\pi}\int_0^{2\pi}Y_{L_1}^{M_1-1}(\theta_1,\phi_1)Y_{L_2'}^{M_2-1}(\theta_1,\phi_1)e^{2\phi_1}d\Omega_1\\ &+f_{1b}c_{1b}\int_0^{\pi}\int_0^{2\pi}Y_{L_1}^{M_1+1}(\theta_1,\phi_1)Y_{L_2'}^{M_2-1}(\theta_1,\phi_1)d\Omega_1\Bigg)\end{aligned}$$

Table 1 Selected values of the two-electron kinetic energy integrals $I_{KE}(1) = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) r_{12}^{\nu} | \hat{T}(1) | \phi'(\mathbf{r}_1)\phi'(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle$

Charge distribution	ν	ν'	ω_1	ω_2	$I_{KE}(1)$
$(1s1s, 1s1s'')$	0	0	5.72	4.26	$0.11306\,94235\,96342\,29959\,53429\,49696 \times 10^{-2}$
$(1s1s, 1s1s''r_{12})$	0	1	5.72	4.26	$0.81163\,75268\,47031\,87529\,75146\,10704 \times 10^{-3}$
$(1s1sr_{12}, 1s1s''r_{12})$	1	1	5.72	4.26	$0.88589\,87406\,28402\,13650\,68426\,72554 \times 10^{-3}$
$(2p_02p_0r_{12}, 1s1s''r_{12})$	1	1	5.72	4.26	$0.45166\,59754\,56488\,45362\,54446\,78870 \times 10^{-3}$
$(1s2p_0r_{12}, 1s2p_0''r_{12})$	0	1	5.72	4.26	$-0.91406\,09587\,68045\,62212\,44984\,70428 \times 10^{-4}$
$(1s2p_{-1}, 1s2p_0''r_{12})$	0	1	5.72	4.26	$0.58757\,51233\,70769\,39483\,18989\,35356 \times 10^{-5}$
$(2p_12p_1, 1s1s''r_{12})$	0	1	5.72	4.26	$0.36884\,15178\,89976\,49027\,60208\,41471 \times 10^{-3}$
$(2p_02p_0r_{12}, 2p_02p_0''r_{12})$	0	1	5.72	4.26	$0.57064\,96111\,23526\,40585\,95972\,95882 \times 10^{-3}$
$(2p_12p_1, 2p_12p_1'')r_{12}$	0	1	5.72	4.26	$0.35077\,95770\,58879\,55483\,73439\,18144 \times 10^{-3}$
$(2p_02p_{-1}r_{12}, 2p_02p_1''r_{12})$	0	1	5.72	4.26	$0.24559\,87433\,35618\,42822\,76711\,54775 \times 10^{-5}$
$(1s3d_0, 1s3d_0''r_{12})$	1	0	5.72	4.26	$0.13702\,57071\,29853\,31857\,53170\,91604 \times 10^{-5}$
$(3d_13d_1r_{12}, 1s1s'')$	1	0	5.72	4.26	$0.43070\,01990\,44400\,85488\,65164\,35689 \times 10^{-3}$
$(3d_02p_0r_{12}, 3d_02p_0'')$	1	1	5.72	4.26	$-0.14778\,66269\,71181\,75795\,62356\,26373 \times 10^{-3}$
$(3d_13d_1r_{12}, 2p_12p_1''r_{12})$	1	1	5.72	4.26	$-0.11083\,99702\,28386\,31846\,71767\,19780 \times 10^{-3}$
$(3d_03d_0r_{12}, 3d_03d_0''r_{12})$	1	1	5.72	4.26	$0.16891\,38975\,77297\,18389\,89500\,38597 \times 10^{-2}$
$(3d_13d_1, 3d_13d_1''r_{12})$	0	1	5.72	4.26	$0.76466\,56134\,90021\,07948\,73046\,83233 \times 10^{-3}$
$(3d_{-2}3d_{-2}, 3d_{-2}3d_{-2}''r_{12})$	0	1	5.72	4.26	$0.76160\,52125\,54086\,06098\,28210\,16139 \times 10^{-3}$
$(4f_04f_0r_{12}, 4f_04f_0''r_{12})$	1	1	5.72	4.26	$0.14778\,79124\,60568\,69920\,97324\,37006 \times 10^{-1}$
$(1s4g_0, 1s4g_0''r_{12})$	0	1	5.72	4.26	$0.74695\,14050\,88089\,67105\,41034\,15793 \times 10^{-6}$
$(4g4g_0r_{12}, 4g4g_0''r_{12})$	1	1	5.72	4.26	$0.30204\,13172\,12481\,46784\,05670\,70694$

The charge distributions $(\phi(\mathbf{r}_1)\phi'(\mathbf{r}_1)r_{12}^{\nu}, \phi(\mathbf{r}_2)\phi'(\mathbf{r}_2)r_{12}^{\nu'})$ are constructed with the exponents $\omega_i = 1.40$ for orbitals with $''$, otherwise $\omega_i = 2.86$

$$+ c_{2b}c_{2L'b}\left(f_{1a}c_{1a}\int_0^{\pi}\int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1,\phi_1)Y_{L_2'}^{M_2+1}(\theta_1,\phi_1)d\Omega_1 \right.$$

$$\left. + \; f_{1b}c_{1b}\int_0^{\pi}\int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1,\phi_1)Y_{L_2'}^{M_2+1}(\theta_1,\phi_1)e^{-2\phi_1}d\Omega_1 \right)\Bigg\} \quad (70)$$

and defining the new auxiliary angular integral:

$$A_{Y2}(L_1, M_1+n, L_2, M_2+n, -2n) = \int_0^{\pi}\int_0^{2\pi} Y_{L_1}^{M_1+n}(\theta,\phi)Y_{L_2}^{M_2+n}(\theta,\phi)e^{-2ni\phi}d\Omega$$

$$= \frac{1}{2}\delta(M_1+M_2,0)\left[(2L_1+1)(2L_2+1)\right]^{1/2}\left[\frac{(L_1-M_1-n)!}{(L_1+M_1+n)!}\right]^{1/2}$$

$$\times \int_0^{\pi} P_{L_1}^{M_1+n}(\cos\theta)P_{L_2}^{M_2+n}(\cos\theta)\sin\theta d\theta \quad (71)$$

Table 2 Selected examples of the partitioning in kinetic energy two-electron integrals (see Table 1)

Charge distribution	ν	ν'	ω_1	ω_2	Value
$(1s1s, 1s1s''r_{12})$	0	1	5.72	4.26	$0.81163\ 75268\ 47031\ 87529\ 75146\ 10704 \times 10^{-3}$
$I_{KE,R_1}(1)$					$0.81163\ 75268\ 47031\ 87529\ 75146\ 10704 \times 10^{-3}$
$I_{KE,R_2}(1)$					$0.42008\ 31959\ 88661\ 01825\ 92441\ 65397 \times 10^{-3}$
$I_{KE,R_3}(1)$					$-0.42008\ 31959\ 88661\ 01825\ 92441\ 65397 \times 10^{-3}$
$I_{KE,KR}(1)$					$0.81163\ 75268\ 47031\ 87529\ 75146\ 10704 \times 10^{-3}$
$(2p_02p_0r_{12}, 1s1s''r_{12})$	1	1	5.72	4.26	$0.45166\ 59754\ 56488\ 45362\ 54446\ 78870 \times 10^{-3}$
$I_{KE,R_1}(1)$					$0.11675\ 57655\ 66243\ 81463\ 93205\ 81006 \times 10^{-3}$
$I_{KE,R_2}(1)$					$0.15209\ 80181\ 36635\ 51456\ 12244\ 03778 \times 10^{-3}$
$I_{KE,R_3}(1)$					$-0.10139\ 86787\ 57757\ 00970\ 74829\ 35852 \times 10^{-3}$
$I_{KE,R}(1)$					$0.16745\ 51049\ 45122\ 31949\ 30620\ 48932 \times 10^{-3}$
$I_{KE,L}(1)$					$0.28421\ 08705\ 11366\ 13413\ 23826\ 29938 \times 10^{-3}$
$I_{KE,KR}(1)$					$0.45166\ 59754\ 56488\ 45362\ 54446\ 78870 \times 10^{-3}$
$(1s2p_0r_{12}, 1s2p_0''r_{12})$	1	1	5.72	4.26	$-0.91406\ 09587\ 68045\ 62212\ 44984\ 70428 \times 10^{-4}$
$I_{KE,R_1}(1)$					$-0.60937\ 39725\ 12030\ 41474\ 96656\ 46952 \times 10^{-4}$
$I_{KE,R_2}(1)$					$-0.30468\ 69862\ 56015\ 20737\ 48328\ 23476 \times 10^{-4}$
$I_{KE,R}(1)$					$-0.91406\ 09587\ 68045\ 62212\ 44984\ 70428 \times 10^{-4}$
$I_{KE,L}(1)$					$-0.12187\ 47945\ 02406\ 08294\ 99331\ 29390 \times 10^{-3}$
$I_{KE,\theta 1}(1)$					$0.18281\ 21917\ 53609\ 12442\ 48996\ 94086 \times 10^{-3}$
$I_{KE,\theta 2}(1)$					$-0.60937\ 39725\ 12030\ 41474\ 96656\ 46952 \times 10^{-4}$
$I_{KE,\phi 3}(1)$					$0.12187\ 47945\ 02406\ 08294\ 99331\ 29390 \times 10^{-3}$
$I_{KE,KR}(1)$					$-0.91406\ 09587\ 68045\ 62212\ 44984\ 70428 \times 10^{-4}$
$(2p_02p_{-1}r_{12}, 2p_02p_1''r_{12})$	0	1	5.72	4.26	$0.24559\ 87433\ 35618\ 42822\ 76711\ 54775 \times 10^{-5}$
$I_{KE,R_1}(1)$					$0.89370\ 12617\ 79310\ 32306\ 17830\ 40472 \times 10^{-6}$
$I_{KE,R_2}(1)$					$0.14191\ 92133\ 57649\ 31359\ 95167\ 52558 \times 10^{-5}$
$I_{KE,R_3}(1)$					$0.32676\ 66381\ 15412\ 87416\ 49617\ 99624 \times 10^{-5}$
$I_{KE,R}(1)$					$0.55805\ 59776\ 50993\ 22007\ 06568\ 56230 \times 10^{-5}$
$I_{KE,L}(1)$					$0.15622\ 86171\ 57687\ 39592\ 14928\ 50727 \times 10^{-5}$
$I_{KE,\theta 1}(1)$					$0.69244\ 93742\ 25273\ 58975\ 85626\ 75011 \times 10^{-5}$
$I_{KE,\theta 2}(1)$					$-0.77056\ 36828\ 04117\ 28771\ 93091\ 00375 \times 10^{-5}$
$I_{KE,\phi 3}(1)$					$-0.39057\ 15428\ 94218\ 48980\ 37321\ 26819 \times 10^{-5}$
$I_{KE,ang}(1)$					$-0.46868\ 58514\ 73062\ 18776\ 44785\ 52182 \times 10^{-5}$
$I_{KE,KR}(1)$					$0.24559\ 87433\ 35618\ 42822\ 76711\ 54775 \times 10^{-5}$

The charge distributions exponents are $\omega_i = 1.40$ for orbitals with $''$, otherwise $\omega_i = 2.86$. Missing contributions are zero. Comparison with the result obtained using the Kolos and Roothaan transformation $I_{KE,KR}(1)$

This integral of the product of Legendre polynomials is solved according the Eq. (47) from Wong, finally the integral is:

$$I_{KE,\phi_1,3} = (-1)^{m'_2}\delta(M_1+M_2,0)\frac{1}{4}\sqrt{\frac{2}{3}}\left[\frac{2l'_1+1}{2l'_1+3}\right]^{1/2}\sum_{L_2=|l_2-1|}^{l_2+1}\sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2}\sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1}$$
$$\times(2L_2+1)^{1/2}(2L'_2+1)^{1/2}(2L_1+1)^{1/2}\{c_{2a}c_{2L'a}$$
$$\times\left(f_{1a}c_{1a}A_{Y2}(L_1,M_1-1,L'_2,M_2-1,2)\right.$$
$$\left.+f_{1b}c_{1b}A_{Y2}(L_1,M_1+1,L'_2,M_2-1,0)\right)$$
$$+c_{2b}c_{2L'b}\left(f_{1a}c_{1a}A_{Y2}(L_1,M_1-1,L'_2,M_2+1,0)\right.$$
$$\left.+\ f_{1b}c_{1b}A_{Y2}(L_1,M_1+1,L'_2,M_2+1,-2)\right)\} \tag{72}$$

We have developed a computer code and computed the radial integral equations (24–26) and angular integral contributions to the kinetic energy Eqs. (27, 50, 56, 72). The computer code has quadruple precision. In Table 1 we show some selected values of two-electron kinetic energy integrals calculated with high precision. The integrals of Table 1 have been checked with the ones calculated using the Kolos and Roothaan transformation, agreeing to more than 30 decimal digits. Finally, in Table 2 several kinetic energy integrals have been decomposed in all their components.

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Appendix A: The two-electron integrals

The complex Slater orbitals with quantum numbers n, l and m are defined by an unnormalized radial part and an angular orthonormal part which is a spherical harmonic:

$$\phi^*(\mathbf{r}) = r^{n-1}e^{-\alpha r}Y_l^{m*}(\theta,\phi),$$
$$\phi'(\mathbf{r}) = r^{n'-1}e^{-\alpha' r}Y_{l'}^{m'}(\theta,\phi). \tag{A.1}$$

The spherical harmonics in Condon and Shortley phases [20, p. 52] are given by:

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

where $P_l^m(\cos\theta)$ are the associated Legendre functions. The spherical harmonics and associated Legendre functions used along this work are written explicitly in [21, p. 14].

The two-electron integrals for any $\nu \geq -1$ are defined:

$$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'} = \int d\tau_1 r_1^{N_1-1} e^{-\omega_1 r_1} Y_{l_1}^{m_1 *}(\theta_1, \phi_1) Y_{l_1'}^{m_1'}(\theta_1, \phi_1) \times \int d\tau_2 r_2^{N_2-1} e^{-\omega_2 r_2} Y_{l_2}^{m_2 *}(\theta_2, \phi_2) Y_{l_2'}^{m_2'}(\theta_2, \phi_2) r_{12}^{\nu}, \tag{A.3}$$

where $N = n + n' - 1$, $M = m' - m$ and the exponents $\omega = \alpha + \alpha'$. We expand the products of spherical harmonics in Eq. (A.3) using the formula [1, Eq. (12)]:

$$Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \sum_{L=|l'-l|}^{l'+l} {}^{(2)} \frac{(2L+1)^{1/2}}{(4\pi)^{1/2}} C^L(l, m; l', m') Y_L^{m'-m}(\theta, \phi) \tag{A.4}$$

$\sum_{L=|l'-l|}^{l'+l} {}^{(2)}$ means that the summation goes in steps of 2 : $L = |l - l'|, |l - l'| + 2, \ldots, l + l' - 2, l + l'$, in the following the upper index (2) will be omitted. $C^L(l, m; l', m')$ is a Condon–Shortley coefficient [20, p. 175] defined by :

$$C^L(l, m; l', m') = \frac{(4\pi)^{1/2}}{(2L+1)^{1/2}} \int Y_L^{m'-m}(\theta, \phi) Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) d\Omega \tag{A.5}$$

with $M = m' - m.N$, L, M are the quantum numbers of the charge distributions. The volume element $d\Omega = \sin\theta d\theta d\phi$. We have to evaluate the following integral:

$$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'} = \frac{(-1)^{M_1+M_2}}{(4\pi)} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} \prod_{i=1}^{2} (2L_i+1)^{1/2} \times C^{L_1}(l_1, m_1; l_1', m_1') C^{L_2}(l_2, m_2; l_2' m_2') \int r_1^{N_1-1} e^{-\omega_1 r_1} r_1^2 dr_1 \int r_2^{N_2-1} e^{-\omega_2 r_2} r_2^2 dr_2 \times \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) d\Omega_1 \int_0^{\pi} \int_0^{2\pi} Y_{L_2}^{M_1}(\theta_2, \phi_2) r_{12}^{\nu} d\Omega_2 \tag{A.6}$$

A.1 Angular integration

The method of angular integration is the than the one used in papers I, and II [13,22] of this series. We consider the triangle formed by r_1, r_2 and r_{12}, see Fig. 1, and pass the z-axis along r_1, which is taken for a moment as a constant. A rotation has taken place.

As r_1 coincides with the z-axis, the angles transform as $\theta_2 \to \theta_{12}$, and $\phi_2 \to \phi_{12}$. The spherical harmonics are also transformed according to the formula [13]:

$$Y_{L_2}^{M_2}(\theta_2, \phi_2) = \sum_{M_2'} Y_{L_2}^{M_2}(\theta_1, \phi_1) P_{L_2}^{M_2'}(\cos\theta_{12}) e^{iM_2'\phi_{12}} \tag{A.7}$$

As ϕ_{12} is an independent variable, we first integrate over ϕ_{12} and we get a factor 2π for $m_2' = 0$, otherwise the integral vanishes. For convenience let us use a factor 4π and $\frac{1}{2}$. The two-electron integral is then:

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} &= (-1)^{M_1+M_2} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} \prod_{i=1}^{2} (2L_i+1)^{1/2} \\ &\times C^{L_1}(l_1, m_1; l_1', m_1') C^{L_2}(l_2, m_2; l_2' m_2') I(N_1, N_2; \omega_1, \omega_2; \nu; L_2) \\ &\times \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) d\Omega_1, \end{aligned} \tag{A.8}$$

where the radial two-electron integral is defined:

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; \nu; L_2) &= \int_0^{\infty} r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\ &\times \int_0^{\pi} \frac{1}{2} P_{L_2}(\cos\theta_{12}) \sin\theta_{12} d\theta_{12} r_{12}^{\nu} \end{aligned} \tag{A.9}$$

The radial two-electron integrals are very important in the method of direct integration over the interelectronic coordinates. The four- and three-electron integrals over Hy-CI wave functions are expressed as a linear combination of them [13,22]. Considering the property:

$$Y_L^{M*}(\theta_1, \phi_1) = (-1)^M Y_L^{-M}(\theta_1, \phi_1) \tag{A.10}$$

and the orthogonality relation of the spherical harmonics:

$$(-1)^{M_1} \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{-M_1*}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) d\Omega_1 = (-1)^{M_1} \delta(M_1 + M_2, 0) \delta(L_1, L_2). \tag{A.11}$$

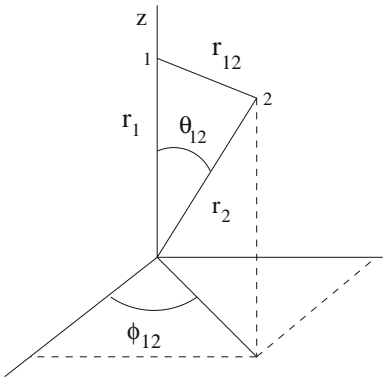

Fig. 1 Definition and rotation of the coordinates of two electrons in an atomic center

The two-electron integral is:

$$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1,l_1',l_2,l_2'}^{m_1,m_1',m_2,m_2'} = (-1)^{M_1}\delta_{(M_1+M_2,0)} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} \delta_{(L_1,L_2)}$$
$$\times \prod_{i=1}^{2}(2L_i+1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) I(N_1, N_2; \omega_1, \omega_2; \nu; L_2) \tag{A.12}$$

A.2 Radial integration

During the axis rotation, see Fig. 1, the variables are transformed as $\theta_2 \to \theta_{12}$, and $\phi_2 \to \phi_{12}$. The volume element of electron 2 is then $d\tau_2 = r_2^2 dr_2 \sin\theta_{12} d\theta_{12} d\phi_{12}$. The integration over the coordinate r_2 is replaced by an integration over the variable θ_{12}, which is related to the variable r_{12} by the cosine theorem:

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}. \tag{A.13}$$

By differentiating on both sides of the equation:

$$2r_{12}dr_{12} = 2r_1 r_2 \sin\theta_{12} d\theta_{12}, \tag{A.14}$$

the needed relation is obtained:

$$\sin\theta_{12} d\theta_{12} = \frac{r_{12}}{r_1 r_2} dr_{12}, \tag{A.15}$$

substituting it into Eq. (A.9) and rewriting appropriately the integration domain we have:

$$I(N_1, N_2; \omega_1, \omega_2; \nu; L) = \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^{\nu+1}}{r_1 r_2} P_{l_2}(\cos\theta_{12}) dr_{12} \tag{A.16}$$

with

$$\cos\theta_{12} = \frac{(r_1^2 + r_2^2 - r_{12}^2)}{2r_1 r_2}. \tag{A.17}$$

Substituting into Eq. (A.16) and using the Rodrigues formula [23]:

$$P_L(x) = \frac{1}{2^L} \sum_{k=0}^{[L/2]} (-1)^k \binom{L}{k} \binom{2L-2k}{L} x^{L-2k} \tag{A.18}$$

a expression in radial coordinates is obtained. $[L/2]$ means the integer part of $L/2$.

$$I(N_1, N_2; \omega_1, \omega_2; \nu; L) = \frac{1}{2^L} \sum_{k=0}^{[L/2]} (-1)^k \binom{L}{k} \binom{2L-2k}{L} \times \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^{\nu+1}}{r_1 r_2} \left(\frac{(r_1^2 + r_2^2 - r_{12}^2)}{2r_1 r_2} \right)^{L-2k} dr_{12} \tag{A.19}$$

Using the binomial theorem two times (indices q, p) and collecting powers:

$$I(N_1, N_2; \alpha, \beta; \nu; L) = \sum_{k=0}^{[L/2]} \sum_{q=0}^{L-2k} \sum_{p=0}^{L-2k-q} \frac{(-1)^{k+q}}{2^{2L-2k}} \binom{L}{k} \binom{2L-2k}{L} \binom{L-2k}{q} \binom{L-2k-q}{p} \times \int_0^\infty r_1^{N_1+L-2k-2q-2p} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+2k+2p-L} e^{-\omega_2 r_2} dr_2 \times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu+2q+1} dr_{12} \tag{A.20}$$

the direct integration over the r_{12} coordinate is possible. There are two regions of integration: $r_1 < r_2$ and $r_2 < r_1$, so that the integration domain can be divided into two:

$$\int dr_1 \int dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} = \int_0^{\infty} dr_1 \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} + \int_0^{\infty} r_1 dr_1 \int_{r_1}^{\infty} dr_2 \int_{r_2-r_1}^{r_1+r_2} dr_{12}. \tag{A.21}$$

For the case treated here, $\frac{1}{2} r_{12}^{\nu+2q+1}$, the integration over the r_{12} variable leads to:

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu+2q+1} dr_{12} = \frac{1}{2(\nu+2q+2)} \left[(r_1+r_2)^{\nu+2q+2} - (r_1-r_2)^{\nu+2q+2} \right], \tag{A.22}$$

and using the binomial theorem:

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu+2q+1} dr_{12} = \frac{1}{(\nu+2q+2)} \sum_{i=1}^{[(\nu+2q+3)/2]} \binom{\nu+2q+2}{2i-1} r_1^{\nu+2q+3-2i} r_2^{2i-1}. \tag{A.23}$$

The another integral is the same than Eq. (A.22) exchanging r_1 by r_2.$[(\nu+2q+3)/2]$ means the integral part of $(\nu+2q+3)/2$. Substituting Eq. (A.23) and the corresponding equation for the volume element $r_2 - r_1$ into Eq. (A.21) and writing explicitly the radial charge distributions:

$$\begin{aligned} \int dr_1 \int dr_2 \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu+2q+1} dr_{12} &= \frac{1}{(\nu+2q+2)} \sum_{i=1}^{[(\nu+2q+3)/2]} \binom{\nu+2q+2}{2i-1} \\ &\times \left\{ \int_0^{\infty} r_1^{N_1+L+\nu+3-2k-2p-2i} e^{-\omega_1 r_1} dr_1 \int_0^{r_1} r_2^{N_2+2k+2p+2i-L-1} e^{-\omega_2 r_2} dr_2 \right. \\ &\left. + \int_0^{\infty} r_1^{N_1-1+L+2i-2k-2q-2p} e^{-\omega_1 r_1} dr_1 \int_{r_1}^{\infty} r_2^{N_2+\nu+3+2k+2p+2q-2i-L} e^{-\omega_2 r_2} \right\} \end{aligned} \tag{A.24}$$

The integration limits may be transformed by the relation:

$$\int_0^{\infty} dr_1 \int_0^{r_1} dr_2 = \int_0^{\infty} dr_2 \int_{r_2}^{\infty} dr_1 \tag{A.25}$$

The integrals can be expressed as V-auxiliary integrals defined as:

$$V(m,n;\alpha,\beta)=\int_0^\infty r_1^m e^{-\alpha r_1}dr_1\int_{r_1}^\infty r_2^n e^{-\beta r_2}dr_2. \tag{A.26}$$

Finally, the general expression of the radial two-electron integral is:

$$\begin{aligned}I(N_1,N_2;\omega_1,\omega_2;\nu;L)=&\sum_{k=0}^{[L/2]}\sum_{q=0}^{L-2k}\sum_{p=0}^{L-2k-q}\sum_{i=1}^{[(\nu+2q+3)/2]}\frac{(-1)^{k+q}}{2^{2L-2k}(\nu+2q+2)}\\
&\times\binom{L}{k}\binom{2L-2k}{l}\binom{L-2k}{q}\binom{L-2k-q}{p}\binom{\nu+2q+2}{2i-1}\\
&\times\{V(N_1+L+2i-2k-2q-2p-1,N_2+\nu+3+2k+2p+2q-2i-L;\omega_1,\omega_2)\\
&+V(N_2+2k+2p+2i-L-1,N_1+L+\nu+3-2k-2p-2i;\omega_2,\omega_1)\}\end{aligned} \tag{A.27}$$

That is a programmable expression valid for $\nu\geq 1$. This formula is useful for the calculation of two-electron radial integrals with $\nu\geq 3$. For the cases $\nu=-1,0,1,2$ there are shorter expressions derived according to Sect. 2.3[2] ref. [13]. These expressions are:

$$\begin{aligned}I(N_1,N_2;\omega_1,\omega_2;1;L)=&-\frac{1}{(2L+1)(2L-1)}\\
&\times[V(N_1+L+1,N_2-L+2;\omega_1,\omega_2)\\
&+V(N_2+L+1,N_1-L+2;\omega_2,\omega_1)]+\frac{1}{(2L+1)(2L+3)}\\
&\times[V(N_1+L+3,N_2-L;\omega_1,\omega_2)\\
&+V(N_2+L+3,N_1-L;\omega_2,\omega_1)]\end{aligned} \tag{A.28}$$

$$\begin{aligned}I(N_1,N_2;\omega_1,\omega_2;-1;L)=&\frac{1}{(2L+1)}[V(N_1+L+1,N_2-L;\omega_1,\omega_2)\\
&+V(N_2+L+1,N_1-L;\omega_2,\omega_1)]\end{aligned} \tag{A.29}$$

$$\begin{aligned}I(N_1,N_2;\omega_1,\omega_2;2;0)=&A(N_1+3,\omega_1)A(N_2+1,\omega_2)\\
&+A(N_2+3,\omega_2)A(N_1+1,\omega_1)\end{aligned} \tag{A.30}$$

$$I(N_1,N_2;\omega_1,\omega_2;2;1)=-\frac{2}{3}A(N_1+2,\omega_1)\ A(N_2+2,\omega_2)] \tag{A.31}$$

$$I(N_1,N_2;\omega_1,\omega_2;0;0)=A(N_1+1,\omega_1)\ A(N_2+1,\omega_2)] \tag{A.32}$$

The auxiliary integrals $V(m,n;\alpha,\beta)$ for positive indices m,n consist on a sum of $A(n,\alpha)$ auxiliary integrals [24, Eq. (5)]:

$$V(m,n;\alpha,\beta)=\sum_{n'=0}^{n}\binom{n}{n'}A(n',\alpha)A(m+n-l',\alpha+\beta),\quad m,n\geq 0 \tag{A.33}$$

[2] The expressions are here rewritten correctly, unfortunately in ref. [13] there were several missprints.

This formula, developed by Frolov and Smith, is very useful because it is stable and very fast. For negative n but positive m and $m+n \geq -1$ the Sims and Hagstrom sum [25, Eq. (33)] is needed. In quantum mechanical calculations on two-electron systems this formula is employed to calculate the V-auxiliary integrals with the lowest index $n=-1$:

$$V(m,n;\alpha,\beta) = \sum_{q=1}^{\infty} \frac{\alpha^{q-1} m!}{(m+q)!} A(m+n+q;\alpha+\beta), \quad m+n \geq -1, \quad m>0, \quad n<0 \tag{A.34}$$

The $A(n,\alpha)$ auxiliary integrals are:

$$A(n,\alpha) = \frac{n!}{\alpha^{n+1}} \tag{A.35}$$

Appendix B: The Kolos and Roothaan transformation

The following transformation is a detailed derivation of Eq. (14) of ref. [16]:

$$\begin{aligned} &-\left\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) r_{12}^{\nu} | \nabla_1^2 | \phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle \\ &= \int \phi_2^*(\mathbf{r}_2)\phi_2'(\mathbf{r}_2) d\tau_2 \int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 \end{aligned} \tag{B.1}$$

using the turn over rule of the antihermitian operator nabla:

$$\nabla^* = -\nabla \tag{B.2}$$

$$\int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 \tag{B.3}$$

the derivative of a product:

$$\begin{aligned} \nabla_1^* \phi_1^*(\mathbf{r}_1) r_{12}^{\nu} &= r_{12}^{\nu} \nabla_1^* \phi_1^*(\mathbf{r}_1) + \phi_1^*(\mathbf{r}_1) \nabla_1^* r_{12}^{\nu} \\ \nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1) &= r_{12}^{\nu'} \nabla_1 \phi_1'(\mathbf{r}_1) + \phi_1'(\mathbf{r}_1) \nabla_1 r_{12}^{\nu'} \end{aligned} \tag{B.4}$$

$$\begin{aligned} &\int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 \\ &= \int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 + \int \phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1) \left[\nabla_1^* r_{12}^{\nu}\right] \left[\nabla_1 r_{12}^{\nu'}\right] d\tau_1 \\ &\quad + \int \left[\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)\right] \left[r_{12}^{\nu'} \nabla_1 r_{12}^{\nu}\right] d\tau_1 + \int \left[\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)\right] \left[r_{12}^{\nu} \nabla_1 r_{12}^{\nu'}\right] d\tau_1 \end{aligned} \tag{B.5}$$

using

$$\nabla_1 r_{12}^{\nu} = -\nabla_2 r_{12}^{\nu} = \nabla_{12} r_{12}^{\nu} = \nu r_{12}^{\nu-1} \tag{B.6}$$

$$\int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 = \nu\nu' \int \phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1) r_{12}^{\nu+\nu'-2} d\tau_1 + \int r_{12}^{\nu+\nu'} \left[\nabla_1 \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] r_{12}^{\nu+\nu'} d\tau_1 + \nu \int \left[\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)\right] r_{12}^{\nu+\nu'-1} d\tau_1 + \nu' \int \left[\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)\right] r_{12}^{\nu+\nu'-1} d\tau_1 \quad \text{(B.7)}$$

collecting terms

$$\int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 = \nu\nu' \int \phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1) r_{12}^{\nu+\nu'-2} d\tau_1 + \int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 + \frac{\nu}{\nu+\nu'} \int \left[\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 + \frac{\nu'}{\nu+\nu'} \int \left[\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 \quad \text{(B.8)}$$

$$\int \left[\phi_1^*(\mathbf{r}_1) r_{12}^{\nu} \nabla_1^*\right] \left[\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)\right] d\tau_1 = \nu\nu' \int \phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1) r_{12}^{\nu+\nu'-2} d\tau_1 + \frac{\nu}{\nu+\nu'} \int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 r + \frac{\nu}{\nu+\nu'} \int \left[\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 + \frac{\nu'}{\nu+\nu'} \int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 + \frac{\nu'}{\nu+\nu'} \int \left[\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 \quad \text{(B.9)}$$

we collect now the terms

$$\int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 + \int \left[\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 \quad \text{(B.10)}$$

$$\int r_{12}^{\nu+\nu'} \left[\nabla_1^* \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 \phi_1'(\mathbf{r}_1)\right] d\tau_1 + \int \left[\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)\right] \left[\nabla_1 r_{12}^{\nu+\nu'}\right] d\tau_1 \quad \text{(B.11)}$$

using the turn over rule Eq. (10) is

$$\int r_{12}^{\nu+\nu'}\left[\nabla_1^*\phi_1^*(\mathbf{r}_1)\right]\left[\nabla_1\phi_1'(\mathbf{r}_1)\right]d\tau_1-\int r_{12}^{\nu+\nu'}\left[\nabla_1^*\left(\phi_1^*(\mathbf{r}_1)\nabla_1\phi_1'(\mathbf{r}_1)\right)\right]d\tau_1 \tag{B.12}$$

using the Green's identity

$$-\nabla\left(\psi\nabla\phi\right)=-\psi\nabla^2\phi-\left(\nabla\psi\right)\left(\nabla\phi\right) \tag{B.13}$$

$$\begin{aligned}&\int r_{12}^{\nu+\nu'}\left[\nabla_1^*\phi_1^*(\mathbf{r}_1)\right]\left[\nabla_1\phi_1'(\mathbf{r}_1)\right]d\tau_1-\int r_{12}^{\nu+\nu'}\left[\nabla_1^*\left(\phi_1^*(\mathbf{r}_1)\nabla_1\phi_1'(\mathbf{r}_1)\right)\right]d\tau_1\\&=-\int r_{12}^{\nu+\nu'}\phi_1^*(\mathbf{r}_1)\nabla_1^2\phi_1'(\mathbf{r}_1)d\tau_1\end{aligned} \tag{B.14}$$

the other term

$$\begin{aligned}&\int r_{12}^{\nu+\nu'}\left[\nabla_1^*\phi_1^*(\mathbf{r}_1)\right]\left[\nabla_1\phi_1'(\mathbf{r}_1)\right]d\tau_1+\int\left[\nabla_1^*\phi_1'(\mathbf{r}_1)\nabla_1\phi_1^*(\mathbf{r}_1)\right]r_{12}^{\nu+\nu'}d\tau_1\\&=-\int\phi_1'(\mathbf{r}_1)\left[\nabla_1^2\phi_1^*(\mathbf{r}_1)\right]r_{12}^{\nu+\nu'}d\tau_1.\end{aligned} \tag{B.15}$$

Finally

$$\begin{aligned}\int\left[\phi_1^*(\mathbf{r}_1)r_{12}^{\nu}\nabla_1^*\right]\left[\nabla_1 r_{12}^{\nu'}\phi_1'(\mathbf{r}_1)\right]d\tau_1=\;&\nu\nu'\int\phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1)r_{12}^{\nu+\nu'-2}d\tau_1\\&-\frac{\nu}{\nu+\nu'}\int r_{12}^{\nu+\nu'}\phi_1^*(\mathbf{r}_1)\nabla_1^2\phi_1'(\mathbf{r}_1)d\tau_1\\&-\frac{\nu'}{\nu+\nu'}\int r_{12}^{\nu+\nu'}\phi_1^*(\mathbf{r}_1)\nabla_1^2\phi_1'(\mathbf{r}_1)d\tau_1\end{aligned} \tag{B.16}$$

Programmed is

$$\begin{aligned}-\frac{1}{2}\left\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)r_{12}|\nabla_1^2|\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)r_{12}\right\rangle=\;&\frac{1}{2}\left\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)|\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\right\rangle\\&-\frac{1}{4}\left\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)r_{12}^2|\nabla_1^2|\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\right\rangle\\&-\frac{1}{4}\left\langle\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)r_{12}^2|\nabla_1^2|\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\right\rangle\end{aligned} \tag{B.17}$$

Roothaan and Weiss [26] acknowledged this transformation to W. Kolos. Sims and Hagstrom wrote this expression in p. 1575 of ref. [25].

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