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ORIGINAL PAPER

Evaluation of Hylleraas-CI atomic integrals by integration over the coordinates of one electron. II. Four-electron integrals

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Abstract An alternative procedure to the classical method for evaluating the four-electron Hylleraas-CI integrals is given. The method consists of direct integration over the r_{12} coordinate and integration over the coordinates of one of the electrons, reducing the integrals to lower order. The method based on the earlier work of Calais and Löwdin and of Perkins is extended to the general angular case. In this way it is possible to solve all of the four-electron integrals appearing in the Hylleraas-CI method. The four-electron integrals are expanded in three-electron ones which are in turn expanded in two-electron integrals. Finally the two-electron integrals are expanded into two-electron auxiliary integrals which usually have one negative power. The use of three- and four-electron electron auxiliary integrals is avoided. Some special cases lead to one- and two-electron auxiliary integrals with negative powers which do not converge individually but do converge in combination with others. These relations and their solutions are presented, together with results of various kinds of integrals.

Keywords Hylleraas-CI · Interelectronic distance · Four-electron integrals

1 Introduction

The highly accurate calculation of energy levels and properties of the atomic elements is still a challenge. The Configuration Interaction (CI) method is known to converge extremely slowly. As is well-known, the explicit inclusion of the interelectronic distance in the wave function accelerates the convergence of the wave function expansion [1] (which results in a dramatically smaller number of Slater determinants). Although

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the integrals occurring in the explicitly correlated methods are usually more difficult to evaluate and their calculation is more time consuming than the electron repulsion integral of the CI method, the number of integrals is smaller than in standard CI calculations. As a result, highly accurate explicit correlated calculations require less computer time than the corresponding CI calculation. It is therefore of importance to investigate mathematical algorithms of integral evaluation in order to facilitate the application of the explicitly correlated methods to large systems.

The integrals treated here are radial ones which contain s-orbitals and the so-called angular correlated integrals, i.e. integrals containing the interelectronic distances r_{ij} and non-zero angular momentum p-, d-, f-, $\cdots$ Slater orbitals. They arise in the method that combines the advantages of inclusion of the interelectronic distances in the wave function with easier integration techniques. This method is the Hylleraas-Configuration Interaction (Hy-CI) method introduced by Sims and Hagstrom [2,3], and independently by Woznicki [4], as Superposition of Correlated Configurations (SCC). As Woznicki [5] pointed out: *"The method represents some kind of generalization of the conventional CI procedure"*. In fact, the Hylleraas-CI method is an alternative to the CI method.

In a previous paper [6], we have evaluated some of the three-electron integrals of the Hy-CI method by integrating directly over r_{ij} and over the coordinates of one of the electrons. In this paper, the method is extended to the calculation of the four-electron integrals occurring in the Hy-CI method for any atomic system. Four-electron type is the highest order of integrals which may occur within the Hy-CI method. This is due to the form of the matrix elements when using a wave function which contains up to one r_{ij} per configuration. The four-electron integrals are of three types:[1]

$$\left\langle \frac{r_{12}r_{13}}{r_{14}} \right\rangle, \qquad \left\langle \frac{r_{12}r_{13}}{r_{34}} \right\rangle, \qquad \left\langle \frac{r_{12}r_{34}}{r_{23}} \right\rangle. \tag{1}$$

The literature about four-electron integrals is not as numerous as in the case of the three-electron ones. The first techniques to evaluate four-electron integrals appeared in the 60s: the direct integration over r_{ij} [7] in radial integrals, a mixture of direct integration and usage of auxiliary three-electron integrals [8], a method using derivatives from Roberts [9] without computational implementation, and a Fourier transform technique from Bonham [10], which also was not implemented in computer programs.

The classical method for solving the four-electron integrals consists in expanding them in terms of auxiliary four-electron integrals called X. The auxiliary integrals A, V, W and X are defined in Appendix A. The auxiliary four-electron integrals X were first introduced by Sims and Hagstrom [2] as a continuation of the James and Coolidge definitions of two- and three-electron auxiliary integrals V, W [11] (five-electron integrals, if necessary, would be Y, and six-electron ones, Z). More recently, Kleindienst and co-workers [12] evaluated linked four-electron integrals (containing

[1] The notation e.g. $\langle r_{12}r_{13}/r_{14}\rangle$ represents the integral where the left and right hand orbitals of electrons 1, 2, 3 and 4 are involved: $\langle\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)\phi(\mathbf{r}_4)|r_{12}r_{13}/r_{14}|\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)\phi(\mathbf{r}_4)\rangle$. The indices of the actual integrals can be interchanged to write them in these forms.

two r_{ij} per configuration) using auxiliary integrals X. A majority of the four-electron integrals arising in the Hylleraas four-electron problem were solved by King [13–15] by a reduction to auxiliary three-electron W integrals. Frolov [16] expressed the auxiliary X integrals as a limited sum of the three-electron ones W [16,17]. The author of this paper [18] also studied some cases of four-electron integrals for angular orbitals by the classical method. Recently, Sims and Hagstrom [19] have evaluated with high accuracy (more than 30 decimal digits) the angular correlated four-electron integrals of Eq. 1 in terms of four-electron auxiliary X integrals, and correlated three-electron ones in terms of W auxiliary integrals [20]. Those integral values (J.S. Sims, "Personal communication") have been used throughout this work to check the approach presented here.

In conventional Hy-CI calculations of the first row of atoms, the orbital basis may contain a large number of orbital exponents. In our computer program the number of X auxiliary integrals which are computed and stored in memory grows as $n_{orb}^8 \times n_{pow}^4$, 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. For atoms with $N \geq 5$ the number of integrals which have to be calculated would require huge amounts of memory to store. This was the case in calculations on boron atom which are in progress [21].

In this paper the integrals are evaluated by integrating directly over the interelectronic distance coordinates. In this way it is unnecessary to expand the r_{ij}s in r_i and r_j by the Laplace expansion, which produces a large number of auxiliary integrals. Instead a successive integration over the coordinates of one electron is done and integrals of lower order, of one electron less, are obtained. The four-electron integrals are then broken down into linear combinations of three-electron integrals. As shown in the previous paper, the three-electron integrals are evaluated in terms of two-electron ones and consequently, the calculation of auxiliary four- and three-electron integrals X and W is entirely avoided, with great saving of computer memory, especially in the case of the X auxiliary integrals which require the construction of very large tables whose dimensions depend on the number of different exponents.

Our method has its origin in Calais and Löwdin's [22] idea of direct integration over r_{ij}, which they applied to evaluate angular two-electron integrals in the year 1962. Also in 1962, Szasz [23] developed basically the same method of direct integration to evaluate linked three-electron integrals. Afterwards, Perkins [7] in 1969 extended and improved the method for the four-electron integrals containing radial s-orbitals. More recently, Yan and Drake [24] have generalized the angular two-electron integral case and solved some cases of relativistic two-electron integrals [25].

The concept of expanding an integral in others of lower order has been often used in the literature. King [13] integrated separately a part of a four-electron integral with many correlation factors and expressed it in terms of three-electron W auxiliary integrals. The expressions obtained are similar to the ones shown here. Other examples are expressing higher order auxiliary integrals in terms of lower order ones, as in Sims and Hagstrom's [2] and Frolov's methods [16,26] which expand a higher auxiliary integral in others of lower order.

Finally, the mathematical investigations have been done with the help of the algebraic package program Maple 9 [27]. For speed we have developed a Fortran 90

computer code which uses Quadruple Precision (QP), about 30 decimal digits of accuracy in our computer. Some examples of four-electron integral values are shown in the Tables 1–3. We have reproduced the recent values of Sims and Hagstrom [19,20] and thousands of other integrals were compared with ones obtained by Sims and Hagstrom. In all cases there was complete agreement.

The method can also be used for the evaluation of fully linked four-electron integrals and many-electron integrals to any power of the interelectronic coordinates. In this work we have, without loss of generality, restricted the expressions to the power 1. The extension to higher powers of r_{ij} is straightforward.

2 Theory

Let us define the Slater orbitals with an unnormalized radial part and orthonormal spherical harmonics as defined in Refs. [2,6].

$$\begin{aligned} \phi^*(\mathbf{r}) &= r^{n-1}e^{-\alpha r}Y_l^{m*}(\theta,\phi), \\ \phi'(\mathbf{r}) &= r^{n'-1}e^{-\alpha' r}Y_{l'}^{m'}(\theta,\phi). \end{aligned} \tag{2}$$

The one-electron charge distributions are written as in Ref. [20] as an expansion of Slater orbitals:

$$\Omega(\mathbf{r}) = \phi^*(\mathbf{r})\phi'(\mathbf{r}) = \sum_{L_i=|l_i-l_i'|}^{l_i+l_i'} {}^{(2)}(2L_i+1)^{1/2}C^{L_i}(l_i',m_i';l_i,m_i)\,f_i(\mathbf{r}), \tag{3}$$

with

$$f_i(\mathbf{r}) = r^{N_i-1}e^{-\omega_i r}Y_{L_i}^{M_i}(\theta_i,\phi_i), \tag{4}$$

where $N_i = n_i + n_i' - 1$ and the exponents are $\omega_i = \alpha_i + \alpha_i'$. The symbol $\sum^{(2)}$ means that summation is done in steps of two, i.e., $L_i = |l_i - l_i'|, |l_i - l_i'|+2, \ldots, l_i + l_i' - 2, l_i + l_i'$, and $M_i = m_i' - m_i$. The lowest value of L_i also depends on m_i, see Appendix B of [6]. From now on we will use capital letters N, L, M for the quantum numbers of charge distributions, while lower case letters n, l, m will be used for the quantum numbers of the orbitals.

In defining the charge distribution above, we have expanded the products of spherical harmonics in Eq. 2 using the formula [2, Eq. 12]:

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

Table 1 Four-electron integrals L, type $\langle r_{12} r_{13} / r_{14} \rangle$ with $\nu = 1, \mu = 1, \lambda = -1$

Charge distribution	ω_1	ω_2	ω_3	ω_4	$L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; \nu, \mu, \kappa)_{l_1,l_2,l_3,l_4}^{m_1,m_2,m_3,m_4}$
$(1s1s, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.16509 33690 91471 34726 17575 44135 $\times 10^{-4}$
$(2s2s, 2s2s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.13146 73615 28568 27727 38521 60655 $\times 10^{-5}$
$(2p_0 2p_0, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.49606 48449 22979 98156 05319 77607 $\times 10^{-5}$
$(1s1s, 1s1s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	0.16507 57402 75790 59750 36266 20897 $\times 10^{-4}$
$(2s2s, 2s2s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	0.13142 83133 68156 65055 41415 58624 $\times 10^{-5}$
$(2p_0 2p_0, 1s1s, 1s1s", 2p_0"2p_0")$	7.37	7.37	4.641	1.912	0.41151 69561 68770 34211 53634 04361 $\times 10^{-7}$
$(2p_0 3d_0, 1s1s, 1s1s", 2p_0"3d_0")$	7.37	7.37	4.641	1.912	0.96287 93608 57511 70944 44684 45982 $\times 10^{-8}$
$(2p_0 4f_0, 1s1s, 1s1s", 2p_0"4f_0")$	7.37	7.37	4.641	1.912	0.80762 56512 90742 21860 61923 77433 $\times 10^{-8}$
$(2p_0 2p_0, 2p_0 2p_0, 2p_0"2p_0", 2p_0 2p_0")$	7.37	7.37	1.912	1.912	0.13347 54141 57510 83043 91203 56254 $\times 10^{-5}$
$(2p_0 2p_0, 2p_0 2p_0, 3d_0 3d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	0.74063 89572 95482 26588 26433 51056 $\times 10^{-7}$
$(3p_0 3p_0, 3p_0 3p_0, 3d_0 3d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	0.33485 68986 29852 13308 55736 61429 $\times 10^{-7}$
$(3p_0 3p_0, 4d_0 4d_0, 4d_0 4d_0", 4d_0"4d_0")$	7.37	7.37	4.641	1.912	0.14228 88514 01287 78023 08231 73114 $\times 10^{-5}$
$(3d_0 3d_0, 3d_0 3d_0, 4d_0 4d_0", 4d_0"4d_0")$	7.37	7.37	4.641	1.912	0.12086 46488 78576 15340 42492 94343 $\times 10^{-5}$
$(3d_0 3d_0, 3d_0 3d_0, 4f_0 4f_0", 4f_0"4f_0")$	7.37	7.37	4.641	1.912	0.12079 14964 05616 13393 60564 41004 $\times 10^{-5}$
$(5g_0 5g_0, 1s1s, 6h_0 6h_0", 1s"1s")$	7.37	7.37	4.641	1.912	0.41416 81552 13027 31066 37318 03978 $\times 10^{-5}$
$(2p_{-1} 2p_{-1}, 2p_1 2p_1, 2s3s", 2s"2s")$	7.37	7.37	4.641	1.912	0.91553 40411 05335 77879 33203 64491 $\times 10^{-8}$
$(2p_{-1} 2p_{-1}, 2p_1 2p_1, 2p_{-1} 3p_1", 2p_1"2p_{-1}")$	7.37	7.37	4.641	1.912	-0.11667 01204 88271 98278 93040 14812 $\times 10^{-10}$
$(3d_{-2} 4d_0, 3d_1 4d_{-1}, 4d_1 4d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	0.54302 68764 93278 18104 77256 87055 $\times 10^{-11}$
$(3d_{-2} 3d_0, 3d_1 3d_{-1}, 4d_1 4d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	0.36266 61724 30362 74379 43359 73434 $\times 10^{-11}$
$(3d_{-2} 3f_0, 4f_1 4d_{-1}, 4d_1 4d_{-1}", 4f_{-2}"4f_0")$	7.37	7.37	4.641	1.912	0.41870 41919 27377 18499 08741 14258 $\times 10^{-11}$

The orbital exponents are $\alpha_i = 0.956$ for orbitals with ", otherwise $\alpha_i = 3.685$

Table 2 Four-electron integrals K_1, type $\langle r_{12} r_{13} / r_{34} \rangle$ with $\nu = 1$, $\mu = 1, \kappa = -1$

Charge distribution	ω_1	ω_2	ω_3	ω_4	$K_1(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; \nu, \mu, \kappa)_{l_1,l_2,l_3,l_4}^{m_1,m_2,m_3,m_4}$
$(1s1s, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.10920 77604 59562 12978 04886 77070 $\times 10^{-4}$
$(2s2s, 2s2s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.88667 45676 73784 06087 40018 40730 $\times 10^{-6}$
$(2p_0 2p_0, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	0.33546 12747 29117 78572 92964 29362 $\times 10^{-5}$
$(1s1s, 1s1s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	0.11765 21546 23838 07738 49011 19468 $\times 10^{-4}$
$(2s2s, 2s2s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	0.95514 89489 95832 26901 42563 01884 $\times 10^{-6}$
$(2p_0 2p_0, 1s1s, 1s1s", 2p_0"2p_0")$	7.37	7.37	4.641	1.912	0.39691 88001 49615 94358 38215 75910 $\times 10^{-7}$
$(2p_0 3d_0, 1s1s, 1s1s", 2p_0"3d_0")$	7.37	7.37	4.641	1.912	−0.98344 81780 40909 01670 17668 17315 $\times 10^{-9}$
$(2p_0 4f_0, 1s1s, 1s1s", 2p_0"4f_0")$	7.37	7.37	4.641	1.912	−0.61413 29426 14900 02656 97377 80802 $\times 10^{-10}$
$(2p_0 2p_0, 2p_0 2p_0, 2p_0"2p_0", 2p_0 2p_0")$	7.37	7.37	1.912	1.912	0.93556 14215 81734 86545 71520 22302 $\times 10^{-6}$
$(2p_0 2p_0, 2p_0 2p_0, 3d_0 3d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	0.73879 62901 61361 90127 50795 21610 $\times 10^{-7}$
$(3p_0 3p_0, 3p_0 3p_0, 3d_0 3d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	0.33286 72282 99124 06821 13613 43180 $\times 10^{-7}$
$(3p_0 3p_0, 3d_0 3d_0, 3d_0 3d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	0.14388 63188 48905 80405 46675 86615 $\times 10^{-5}$
$(3d_0 3d_0, 3d_0 3d_0, 4d_0 4d_0", 4d_0"4d_0")$	7.37	7.37	4.641	1.912	0.12238 03514 64172 07076 31777 65647 $\times 10^{-5}$
$(3d_0 3d_0, 3d_0 3d_0, 4f_0 4f_0", 4f_0"4f_0")$	7.37	7.37	4.641	1.912	0.12180 33377 30106 38098 00606 50996 $\times 10^{-5}$
$(5g_0 5g_0, 1s1s, 6h_0 6h_0", 1s"1s")$	7.37	7.37	4.641	1.912	0.26295 38179 48928 79306 19896 41088 $\times 10^{-5}$
$(2p_{-1} 2p_{-1}, 2p_1 2p_1, 2s3s", 2s"2s")$	7.37	7.37	4.641	1.912	0.84365 10925 65022 43129 81005 70942 $\times 10^{-8}$
$(2p_{-1} 2p_{-1}, 2p_1 2p_1, 2p_{-1} 3p_1", 2p_1"2p_{-1}")$	7.37	7.37	4.641	1.912	0.84423 35250 59613 57835 35764 27846 $\times 10^{-9}$
$(3d_{-2} 4d_0, 3d_1 4d_{-1}, 4d_1 4d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	−0.26639 13976 15667 34697 02989 03236 $\times 10^{-9}$
$(3d_{-2} 3d_0, 3d_1 3d_{-1}, 4d_1 4d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	−0.24677 81081 89328 42631 12765 49502 $\times 10^{-9}$
$(3d_{-2} 3f_0, 4f_1 4d_{-1}, 4d_1 4d_{-1}", 4f_{-2}"4f_0")$	7.37	7.37	4.641	1.912	−0.43715 44882 76299 92188 13995 57759 $\times 10^{-9}$

The orbital exponents are $\alpha_i = 0.956$ for orbitals with ", otherwise $\alpha_i = 3.685$

Table 3 Four-electron integrals K_2, type $\langle r_{12} r_{34} / r_{23} \rangle$ with $\nu = 1, \mu = 1, \kappa = -1$

Charge distribution	ω_1	ω_2	ω_3	ω_4	$K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; \nu, \mu, \kappa)_{l_1,l_2,l_3,l_4}^{m_1,m_2,m_3,m_4}$
$(1s1s, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	$0.20966\,42029\,13192\,17029\,49820\,32819 \times 10^{-4}$
$(2s2s, 2s2s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	$0.16397\,32206\,51482\,17686\,41381\,77842 \times 10^{-5}$
$(2p_02p_0, 1s1s, 2s"2s", 2s"2s")$	7.37	7.37	1.912	1.912	$0.62585\,69753\,87716\,83265\,70394\,61698 \times 10^{-5}$
$(1s1s, 1s1s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	$0.20680\,85497\,22492\,55676\,51323\,04244 \times 10^{-4}$
$(2s2s, 2s2s, 2p_0"2p_0", 2p_0"2p_0")$	7.37	7.37	1.912	1.912	$0.16172\,32963\,05492\,37319\,66031\,08040 \times 10^{-5}$
$(2p_02p_0, 1s1s, 1s1s", 2p_0"2p_0")$	7.37	7.37	4.641	1.912	$0.37874\,95164\,15215\,28880\,73462\,36156 \times 10^{-6}$
$(2p_03d_0, 1s1s, 1s1s", 2p_0"3d_0")$	7.37	7.37	4.641	1.912	$0.92942\,76221\,98892\,91968\,95047\,65074 \times 10^{-9}$
$(2p_04f_0, 1s1s, 1s1s", 2p_0"4f_0")$	7.37	7.37	4.641	1.912	$0.38307\,04904\,16891\,15753\,36026\,24405 \times 10^{-11}$
$(2p_02p_0, 2p_02p_0, 2p_0"2p_0", 2p_02p_0")$	7.37	7.37	1.912	1.912	$0.16428\,17680\,84802\,62220\,01742\,26606 \times 10^{-5}$
$(2p_02p_0, 2p_02p_0, 3d_03d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	$0.40825\,79821\,20306\,97706\,10672\,87727 \times 10^{-6}$
$(3p_03p_0, 3p_03p_0, 3d_03d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	$0.16436\,17150\,80544\,00181\,95794\,97776 \times 10^{-6}$
$(3p_03p_0, 3d_03d_0, 3d_03d_0", 3d_0"3d_0")$	7.37	7.37	4.641	1.912	$0.78032\,39544\,28682\,54048\,70192\,98641 \times 10^{-5}$
$(3d_03d_0, 3d_03d_0, 4d_04d_0", 4d_0"4d_0")$	7.37	7.37	4.641	1.912	$0.67674\,51976\,21844\,73971\,86440\,40157 \times 10^{-5}$
$(3d_03d_0, 3d_03d_0, 4f_04f_0", 4f_0"4f_0")$	7.37	7.37	4.641	1.912	$0.67176\,86880\,16208\,22757\,85937\,75359 \times 10^{-5}$
$(5g_05g_0, 1s1s, 6h_06h_0", 1s"1s")$	7.37	7.37	4.641	1.912	$0.27876\,76913\,85453\,64053\,87471\,05351 \times 10^{-5}$
$(2p_{-1}2p_{-1}, 2p_12p_1, 2s3s", 2s"2s")$	7.37	7.37	4.641	1.912	$0.31736\,53355\,09448\,45371\,62145\,23933 \times 10^{-7}$
$(2p_{-1}2p_{-1}, 2p_12p_1, 2p_{-1}3p_1", 2p_1"2p_{-1}")$	7.37	7.37	4.641	1.912	$-0.41772\,53104\,86504\,42083\,63126\,23245 \times 10^{-9}$
$(3d_{-2}4d_0, 3d_14d_{-1}, 4d_14d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	$0.26120\,08218\,63182\,20959\,27070\,77701 \times 10^{-9}$
$(3d_{-2}3d_0, 3d_13d_{-1}, 4d_14d_{-1}", 4d_{-2}"4d_0")$	7.37	7.37	4.641	1.912	$0.24841\,23824\,87268\,99465\,09023\,95570 \times 10^{-9}$
$(3d_{-2}3f_0, 4f_14d_{-1}, 4d_14d_{-1}", 4f_{-2}"4f_0")$	7.37	7.37	4.641	1.912	$0.30542\,46695\,37834\,64692\,44178\,10476 \times 10^{-9}$

The orbital exponents are $\alpha_i = 0.956$ for orbitals with ", otherwise $\alpha_i = 3.685$

where the Condon-Shortley [28, Eqs. 6–11] coefficients are defined by:

$$C^L(l', m', l, m) = \frac{(4\pi)^{1/2}}{(2L+1)^{1/2}} \int Y_L^{m'-m}(\theta, \phi) Y_{l'}^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) \sin\theta d\theta d\phi, \tag{6}$$

L_i satisfy the triangular condition $|l_i - l_i'| \le L \le l_i + l_i'$ and the restriction $L_i \ge |M_i|$.

The four-electron integrals which appear in the Hy-CI method are of the type:

$$\begin{aligned} &L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)_{L_1, L_2, L_3, L_4}^{M_1, M_2, M_3, M_4} \\ &= \int \Omega_1(\mathbf{r}_1)\Omega_2(\mathbf{r}_2)\Omega_3(\mathbf{r}_3)\Omega_4(\mathbf{r}_4) \frac{r_{12} r_{13}}{r_{14}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \end{aligned} \tag{7}$$

where the powers of the interelectronic distances ν, μ and λ have been set to 1, 1, −1, corresponding to the integral cases which actually appear in the Hy-CI method. The other two kinds of four-electron integrals are:

$$\begin{aligned} &K_1(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)_{L_1, L_2, L_3, L_4}^{M_1, M_2, M_3, M_4} \\ &= \int \Omega_1(\mathbf{r}_1)\Omega_2(\mathbf{r}_2)\Omega_3(\mathbf{r}_3)\Omega_4(\mathbf{r}_4) \frac{r_{12} r_{13}}{r_{34}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \end{aligned} \tag{8}$$

and

$$\begin{aligned} &K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)_{L_1, L_2, L_3, L_4}^{M_1, M_2, M_3, M_4} \\ &= \int \Omega_1(\mathbf{r}_1)\Omega_2(\mathbf{r}_2)\Omega_3(\mathbf{r}_3)\Omega_4(\mathbf{r}_4) \frac{r_{12} r_{34}}{r_{23}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \tag{9}$$

Graphically the L integrals are represented by a three-vertex and K integrals by an open square [2]. Substituting for the charge distributions, the integrals to be evaluated become:

$$\begin{aligned} &L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)_{L_1, L_2, L_3, L_4}^{M_1, M_2, M_3, M_4} \\ &= \frac{1}{(4\pi)^2} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \\ &\quad \times \prod_{i=1}^{4} (2L_i+1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\ &\quad \times \int r_1^{N_1-1} r_2^{N_2-1} r_3^{N_3-1} r_4^{N_4-1} e^{-\omega_1 r_1} e^{-\omega_2 r_2} e^{-\omega_3 r_3} e^{-\omega_4 r_4} \\ &\quad \times Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_2, \phi_2) Y_{L_3}^{M_3}(\theta_3, \phi_3) Y_{L_4}^{M_4}(\theta_4, \phi_4) \frac{r_{12} r_{13}}{r_{14}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \tag{10}$$

The K integrals are defined similarly:

$$
\begin{aligned}
&K_1(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)^{M_1,M_2,M_3,M_4}_{L_1,L_2,L_3,L_4} \\
&= \frac{1}{(4\pi)^2} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \\
&\quad \times \prod_{i=1}^{4} (2L_i+1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\
&\quad \times \int r_1^{N_1-1} r_2^{N_2-1} r_3^{N_3-1} r_4^{N_4-1} e^{-\omega_1 r_1} e^{-\omega_2 r_2} e^{-\omega_3 r_3} e^{-\omega_4 r_4} \\
&\quad \times Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_2, \phi_2) Y_{L_3}^{M_3}(\theta_3, \phi_3) Y_{L_4}^{M_4}(\theta_4, \phi_4) \frac{r_{12} r_{13}}{r_{34}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4,
\end{aligned}
\tag{11}
$$

and

$$
\begin{aligned}
&K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)^{M_1,M_2,M_3,M_4}_{L_1,L_2,L_3,L_4} \\
&= \frac{1}{(4\pi)^2} \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \\
&\quad \times \prod_{i=1}^{4} (2L_i+1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\
&\quad \times \int r_1^{N_1-1} r_2^{N_2-1} r_3^{N_3-1} r_4^{N_4-1} e^{-\omega_1 r_1} e^{-\omega_2 r_2} e^{-\omega_3 r_3} e^{-\omega_4 r_4} \\
&\quad \times Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_2, \phi_2) Y_{L_3}^{M_3}(\theta_3, \phi_3) Y_{L_4}^{M_4}(\theta_4, \phi_4) \frac{r_{12} r_{34}}{r_{23}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4.
\end{aligned}
\tag{12}
$$

First the angular integration will be carried out, then the radial one.

2.1 L integrals

The four-electron integrals Eqs. 10–12, are functions of the quantum numbers, exponents of the charge distributions of the four electrons and the powers of the inter-electronic coordinates. The method employed here consists of the direct integration over the r_{ij} coordinates after a rotation of an axis and a change in the variables of integration.

Let us consider the triangle formed by r_1, r_2 and r_{12} in Fig. 1, and pass the z-axis along r_1 which is taken as a constant. A rotation has taken place. As r_1 coincides with the z-axis, the angles have been transformed as $\theta_2 \to \theta_{12}$ and $\phi_2 \to \phi_{12}$. The same

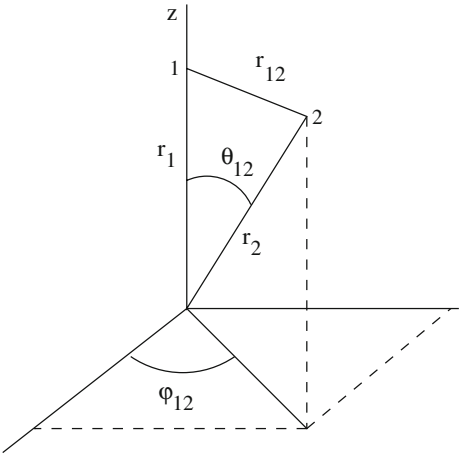

Fig. 1 Definition of the coordinates of two electrons in an atomic center

rotation can be successively done for electrons 3 and 4. The angular functions of these electrons are transformed according to the equation [6]:

$$Y_{L_j}^{M_j}(\theta_j, \phi_j) = \sum_{M_j'} Y_{L_j}^{M_j}(\theta_j, \phi_j) P_{L_j}^{M_j'}(\cos\theta_{1j}) e^{iM_j'\phi_{1j}}, \tag{13}$$

Here i is the imaginary number and the index $j = 2, 3, 4$ represents the electrons. These rotations can be expressed as, e.g.in the case $j = 2$:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \sum_{m_2'=-l_2}^{l_2} Y_{l_2}^{m_2}(\theta_1, \phi_1) \left(\frac{4\pi}{2l_2+1}\right)^{1/2} Y_{l_2}^{m_2'}(\theta_{12}, \phi_{12}), \tag{14}$$

and have the same effect as those by Calais and Löwdin [22, Eq. 14], and those of Drake [25, Eq. 6]. The details of the angular transformation and the proof of Eqs. 13,14 are given in the Appendix A of paper I [6] of this series.

ϕ_{12}, ϕ_{13}, and ϕ_{14} are independent variables of integration (see in Fig. 1 how ϕ_{12} is allowed to vary for a fixed r_{12}), so substituting Eq. 13 into the integral Eq. 10 and integrating over ϕ_{12}, ϕ_{13}, and ϕ_{14} yields a factor of 2π for $m_2' = m_3' = m_4' = 0$, otherwise the integral vanishes. For convenience we will use factors 4π and $\frac{1}{2}$.

Because of the axis rotation, the variables are transformed according to $\theta_2 \to \theta_{12}$, $\theta_3 \to \theta_{13}$, $\theta_4 \to \theta_{14}$, see Fig. 1. After these steps we have:

$$L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)_{L_1, L_2, L_3, L_4}^{M_1, M_2, M_3, M_4}$$
$$= 4\pi \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} (2) \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} (2) \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} (2) \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} (2)$$

$$
\begin{aligned}
&\times \prod_{i=1}^{4} (2L_i+1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\
&\times \int_0^\infty r_1^{N_1+1} dr_1 \int_0^\infty r_2^{N_2+1} dr_2 \int_0^\pi \frac{1}{2} r_{12} P_{L_2}(\cos\theta_{12}) \sin\theta_{12} d\theta_{12} \\
&\times \int_0^\infty r_3^{N_3+1} dr_3 \int_0^\pi \frac{1}{2} r_{13} P_{L_3}(\cos\theta_{13}) \sin\theta_{13} d\theta_{13} \\
&\times \int_0^\infty r_4^{N_4+1} dr_4 \int_0^\pi \frac{1}{2} \frac{1}{r_{14}} P_{L_4}(\cos\theta_{14}) \sin\theta_{14} d\theta_{14} \\
&\times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \varphi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_4}^{M_4}(\theta_1, \phi_1) \sin\theta_1 d\theta_1 d\phi_1.
\end{aligned}
\tag{15}
$$

The variables of integration, θ_{12}, θ_{13} and θ_{14} can be exchanged by the Hylleraas variables r_{12}, r_{13} and r_{14} because both sets of variables are closely related by the cosine theorem:

$$
\cos\theta_{1j} = \frac{(r_1^2 + r_j^2 - r_{1j}^2)}{2 r_1 r_j}. \tag{16}
$$

As the respective volume elements of electrons 2, 3, 4 are $d\tau_j = r_j^2 dr_j \sin\theta_{1j} d\theta_{1j}$ $d\phi_{1j}$, the differentiation on both sides of the this expression yields the equation which expresses the change of variables:

$$
\sin\theta_{1j} d\theta_{1j} = \frac{r_{1j}}{r_1 r_j} dr_{1j}. \tag{17}
$$

The integration domains should be appropriately rewritten for r_{1j} variables. The minimal value of r_{1j} is the absolute value of the difference between r_1 and r_j, and r_{1j} takes its maximal value when r_1 and r_j are on the same line in opposite directions, $r_1 + r_j$. With these considerations, the radial part of the L integral can be defined as:

$$
\begin{aligned}
&L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1; L_2, L_3, L_4) \\
&= \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
&\quad \times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^2}{r_1 r_2} P_{L_2}(\cos\theta_{12}) dr_{12} \\
&\quad \times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2} \frac{r_{13}^2}{r_1 r_3} P_{L_3}(\cos\theta_{13}) dr_{13} \\
&\quad \times \int_0^\infty r_4^{N_4+1} e^{-\omega_4 r_4} dr_4 \int_{|r_1-r_4|}^{r_1+r_4} \frac{1}{2} \frac{1}{r_1 r_4} P_{L_4}(\cos\theta_{14}) dr_{14},
\end{aligned}
\tag{18}
$$

where $\cos\theta_{1j}$ has the radial form given in Eq. 16. The integration over θ_1 is independent of the integrations over r_{1j} (or θ_{12} and θ_{13} in Eq. 15), therefore we can solve first

the four-fold integral over spherical harmonics:

$$I = \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_4}^{M_4}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \quad (19)$$

Using the property of the spherical harmonics:

$$Y_{L_3}^{M_3}(\theta_1, \phi_1) = (-1)^{M_3} Y_{L_3}^{-M_3 *}(\theta_1, \phi_1) \quad (20)$$

and linearizing their product using Eq. 5 we get:

$$\begin{aligned} & Y_{L_3}^{-M_3 *}(\theta_1, \phi_1) Y_{L_4}^{M_4}(\theta_1, \phi_1) \\ & = \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \frac{(2L+1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) Y_L^{M_3+M_4}(\theta_1, \phi_1). \end{aligned} \quad (21)$$

The integral Eq. 19 is then

$$\begin{aligned} I = (-1)^{M_3} & \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \frac{(2L+1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) \\ & \times \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{M_3+M_4}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1. \end{aligned} \quad (22)$$

Using again

$$Y_{L_1}^{M_1}(\theta_1, \phi_1) = (-1)^{M_1} Y_{L_1}^{-M_1 *}(\theta_1, \phi_1), \quad (23)$$

we obtain an equation which can be evaluated using the definition of Eq. 6 of the Condon and Shortley coefficients. Since $M_1+M_2+M_3+M_4 = 0$ we have $M_3+M_4 = -M_1 - M_2$:

$$\begin{aligned} & \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{M_3+M_4}(\theta_1, \phi_1) \sin\theta_1 d\theta_1 d\phi_1 \\ & = (-1)^{M_1} \int_0^{\pi} \int_0^{2\pi} Y_{L_1}^{-M_1 *}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{-M_1-M_2}(\theta_1, \phi_1) \sin\theta_1 d\theta_1 d\phi_1 \\ & = (-1)^{M_1} \delta(M_1 + M_2 + M_3 + M_4, 0) C^L(L_1, -M_1; L_2, M_2) \frac{(2L+1)^{1/2}}{(4\pi)^{1/2}}. \end{aligned} \quad (24)$$

Finally substituting Eq. 24 into Eq. 22:

$$\begin{aligned} I = (-1)^{M_1+M_3} & \delta(M_1 + M_2 + M_3 + M_4, 0) \\ & \times \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \frac{(2L+1)}{4\pi} C^L(L_4, M_4; L_3, -M_3) C^L(L_1, -M_1; L_2, M_2) \end{aligned} \quad (25)$$

and substituting this expression into the four-electron integral L yields:

$$
\begin{aligned}
&L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)^{M_1,M_2,M_3,M_4}_{L_1,L_2,L_3,L_4} \\
&= (-1)^{M_1+M_3}\delta(M_1 + M_2 + M_3 + M_4, 0) \\
&\times \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \prod_{i=1}^{4} \\
&\times (2L_i + 1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\
&\sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} (2L + 1) C^L(L_1, -M_1; L_2, M_2) C^L(L_4, M_4; L_3, -M_3) \\
&\qquad L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; L_2, L_3, L_4)
\end{aligned} \tag{26}
$$

The integration of the angular part leads to angular coefficients and radial four-electron integrals. Due to the Kronecker δ and the Condon and Shortley coefficients many terms of the summation vanish.

The radial four-electron integrals are defined in Eq. 18. We integrate over the coordinates of only one electron, i.e. electron 2, in order to obtain a three-electron radial integral of electrons 1, 3 and 4. During the following integration steps the coordinates of electrons 3 and 4 are not affected.

The Legendre Polynomials $P_{L_2}(\cos\theta_{12})$ are expanded according to the Rodrigues formula [29]:

$$
P_L(x) = \frac{1}{2^L} \sum_{k=0}^{\lfloor L/2 \rfloor} (-1)^k \binom{L}{K} \binom{2L-2k}{L} x^{L-2k}, \tag{27}
$$

where $\lfloor L_2/2 \rfloor$ is the floor function and means the integer part of $L_2/2$. After using the Binomial Theorem twice and collecting powers in Eq. 18 we obtain:

$$
\begin{aligned}
&L(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1; L_2, L_3, L_4) \\
&= \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \\
&\times \binom{L_2-2k-q}{p} \frac{(-1)^{k+q}}{2^{2L_2-2k}} \int_0^\infty r_1^{N_1+L_2-2k-2p-2q} e^{-\omega_1 r_1} dr_1 \\
&\times \int_0^\infty dr_3 r_3^{N_3+1} e^{-\omega_3 r_3} \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2} \frac{r_{13}^2}{r_1 r_3} P_{L_3}(\cos\theta_{13}) dr_{13} \\
&\times \int_0^\infty dr_4 r_4^{N_4+1} e^{-\omega_4 r_4} \int_{|r_1-r_4|}^{r_1+r_4} \frac{1}{2} \frac{1}{r_1 r_4} P_{L_4}(\cos\theta_{14}) dr_{14} \\
&\times \int_0^\infty r_2^{N_2-L_2+2k+2p} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} r_{12}^{2q+2} dr_{12}.
\end{aligned} \tag{28}
$$

Now it is possible to integrate directly over the r_{12} variable, for which the domain of integration following Perkins [7] is divided in two parts:

$$D_1 \to \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} + \int_{r_1}^{\infty} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} \to \int_0^{\infty} dr_2 \int_{r_1-r_2}^{r_2+r_1} dr_{12}, \quad (29)$$

$$D_2 \to \int_{r_1}^{\infty} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} - \int_{r_1}^{\infty} dr_2 \int_{r_2-r_1}^{r_1+r_2} dr_{12}. \quad (30)$$

The L integral is the difference:

$$L = D_1 - D_2. \quad (31)$$

In the first part D_1 the integral over r_{12} is:

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{2q+2} = \frac{1}{(2q+3)} \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} r_1^{2q+4-2i} r_2^{2i-1}, \quad (32)$$

as a result the variable r_{12} has been expanded in powers of r_1 and r_2. In the integral part D_1 the variable r_2 is not linked to any other variable, therefore it is possible to integrate over r_2 leading to a one-electron auxiliary $A(n, \alpha)$ integral, defined in Appendix A:

$$\begin{aligned} D_1 = & \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\ & \times \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \binom{L_2-2k-q}{p} \\ & \times \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2+2k+2p+2i-L_2-1, \omega_2) \\ & \times \int_0^{\infty} r_1^{N_1+L_2+4-2k-2p-2i} e^{-\omega_1 r_1} dr_1 \\ & \times \int_0^{\infty} dr_3 r_3^{N_3+1} e^{-\omega_3 r_3} \\ & \times \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2} \frac{r_{13}^2}{r_1 r_3} P_{L_3}(\cos\theta_{13}) dr_{13} \\ & \times \int_0^{\infty} dr_4 r_4^{N_4+1} e^{-\omega_4 r_4} \int_{|r_1-r_4|}^{r_1+r_4} \frac{1}{2} \frac{1}{r_1 r_4} P_{L_4}(\cos\theta_{14}) dr_{14}. \end{aligned} \quad (33)$$

The remaining integral over r_1, r_3, r_4, r_{13} and r_{14} can be written as a three-electron integral [6, Eq. 21]. Altogether:

$$
\begin{aligned}
D_1 = & \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\
& \times \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \binom{L_2-2k-q}{p} \\
& \times \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2+2k+2p+2i-L_2-1, \beta) \\
& \times J(N_1+L_2+3-2k-2p-2i, N_3, N_4; \omega_1, \omega_3, \omega_4; 1, -1; L_3, L_4), \quad (34)
\end{aligned}
$$

where the integral $A(N_2-1+2k+2p+2i-L, \omega_2)$ does not take negative powers because by definition $N_2 - 1 \geqslant L$. $J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3)$ is the radial three-electron integral defined and evaluated in part I of this series of papers. These integrals and the basic two-electron ones will be given in the next Section.

The integration steps in the case of the D_2 integral part are the same as for D_1, except for the domain of integration Eq. 30:

$$
\begin{aligned}
D_2 = & \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\
& \times \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \binom{L_2-2k-q}{p} \\
& \times \int_0^{\infty} r_1^{N_1+L_2-2k-2q-2p} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} dr_3 r_3^{N_3+1} e^{-\omega_3 r_3} \\
& \times \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2} \frac{r_{13}^2}{r_1 r_3} P_{L_3}(\cos\theta_{13}) dr_{13} \\
& \times \int_0^{\infty} dr_4 r_4^{N_4+1} e^{-\omega_4 r_4} \int_{|r_1-r_4|}^{r_1+r_4} \frac{1}{2} \frac{1}{r_1 r_4} P_{L_4}(\cos\theta_{14}) dr_{14} \\
& \times \int_{r_1}^{\infty} r_2^{N_2+2k+2p-L_2} e^{-\omega_2 r_2} dr_2 \left\{ \int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{2q+2} - \int_{r_2-r_1}^{r_1+r_2} \frac{1}{2} r_{12}^{2q+2} \right\}. \quad (35)
\end{aligned}
$$

The direct integration over r_{12} leads to:

$$
\frac{1}{(2q+3)} \frac{1}{2} [(r_2 - r_1)^{2q+3} - (r_1 - r_2)^{2q+3}]. \quad (36)
$$

$2q+3$ is in this case always odd, therefore the difference never vanishes and can be simplified as:

$$
\frac{1}{(2q+3)} (r_2 - r_1)^{2q+3}. \quad (37)
$$

Due to the integration limits over r_2 in Eq. 35, we change the variables using $r_2 - r_1 = y$ and the Binomial Theorem:

$$(r_1+y)^{N_2+2k+2p-L_2}=\sum_{j=1}^{N_2+2k+2p+1-L_2}\binom{N_2+2k+2p-L_2}{j-1}r_1^{N_2+2k+2p-L_2-j}y^{j-1}. \quad (38)$$

The integral over y also leads to an one-electron $A(n,\beta)$ auxiliary integral. Substituting these expressions in Eq. 35:

$$\begin{aligned}D_2=&\sum_{k=0}^{\lfloor L_2/2\rfloor}\sum_{q=0}^{L_2-2k}\sum_{p=0}^{L_2-2k-q}\frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)}\\&\times\binom{L_2}{k}\binom{2L_2-2k}{L_2}\binom{L_2-2k}{q}\binom{L_2-2k-q}{p}\\&\times\frac{1}{(2q+3)}\sum_{j=1}^{N_2+2k+2p+1-L_2}\\&\times\binom{N_2+2k+2p-L_2}{j-1}A(2q+2+j;\omega_2)\\&\times\int_0^\infty r_1^{N_1+N_2-2q-j}e^{-(\omega_1+\omega_2)r_1}dr_1\\&\times\int_0^\infty dr_3 r_3^{N_3+1}e^{-\omega_3 r_2}\int_{|r_1-r_3|}^{r_1+r_3}\frac{1}{2}\frac{r_{13}^2}{r_1 r_3}P_{L_3}(\cos\theta_{13})dr_{13}\\&\times\int_0^\infty dr_4 r_4^{N_4+1}e^{-\omega_4 r_4}\int_{|r_1-r_4|}^{r_1+r_4}\frac{1}{2}\frac{1}{r_1 r_4}P_{L_4}(\cos\theta_{14})dr_{14}. \quad (39)\end{aligned}$$

The remaining integrals over r_1, r_3, r_4, r_{13} and r_{14} can be rewritten as a three- electron integral:

$$\begin{aligned}D_2=&\sum_{k=0}^{\lfloor L_2/2\rfloor}\sum_{q=0}^{L_2-2k}\sum_{p=0}^{L_2-2k-q}\frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)}\\&\times\binom{L_2}{k}\binom{2L_2-2k}{L_2}\binom{L_2-2k}{q}\binom{L_2-2k-q}{p}\\&\times\frac{1}{(2q+3)}\sum_{j=1}^{N_2+2k+2p+1-L_2}\\&\times\binom{N_2+2k+2p-L_2}{j-1}A(2q+2+j;\beta)\\&\times J(N_1+N_2-2q-j-1,N_3,N_4;\omega_1+\omega_2,\omega_3,\omega_4;1,-1;L_3,L_4). \quad (40)\end{aligned}$$

Altogether:

$$L(N_1,N_2,N_3,N_4;\omega_1,\omega_2,\omega_3,\omega_4;1,1,-1;L_2,L_3,L_4)$$

$$
\begin{aligned}
= & \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\
& \times \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \binom{L_2-2k-q}{p} \\
& \times \left\{ \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2-1+2k+2p+2i-L_2, \omega_2) \right. \\
& \quad \times J(N_1+L_2+2-2k-2p-2i, N_3, N_4; \omega_1, \omega_3, \omega_4; 1, -1; L_3, L_4) \\
& \quad - \sum_{j=1}^{N_2+2k+2p+1-L_2} \binom{N_2+2k+2p-L_2}{j-1} A(2q+2+j; \beta) \\
& \quad \left. \times J(N_1+N_2-2q-j-1, N_3, N_4; \omega_1+\omega_2, \omega_3, \omega_4; 1, -1; L_3, L_4) \right\}.
\end{aligned}
\tag{41}
$$

The total four-electron integral L is calculated with Eqs. 26, 41 and it consists of a linear combination of three-electron ones of the type $\langle r_{12}/r_{13} \rangle$. In part I of this series of papers we have demonstrated that the three-electron integrals are expanded as a linear combination of two-electron ones.

For $L_3, L_4 = 0$, the integral reduces to a radial one and agrees with the result of Perkins [7, Eq. 20]. The auxiliary A integrals occurring in the expression of L have no negative powers as $N_2 - 1 \geq L_2$ is by definition fulfilled. As the electron 1 is linked to the other three, some cases of L four-electron integrals using this method[2] present a difficulty. If the arguments of the J integrals are $N_1 + L_2 + 2 - 2k - 2p - 2i + L_4 \leq 2$ or $N_1 + N_2 - 2q - j - 1 + L_4 \leq 2$, the J integrals are evaluated in a different way, namely expanding them in auxiliary A integrals and combining these A integrals appropriately. We show this in Appendix B. In Table 1 most of the integrals given are examples of this special case of angular integrals with low quantum numbers. For higher quantum numbers this problem does not appear.

In Table 1 the calculated values for a number of four-electron integrals are listed. They have been calculated with quadruple precision (30 digits on our computer). Using our method we have been able to reproduce all integrals of Tables 1 and 2 of Sims and Hagstrom [19], with 30 decimal digits accuracy except for the 13th and 17th integral of Table 1 of this paper, which have been reproduced with 26–28 decimal digits. To improve the number of digits our program would need higher precision than quadruple, as test calculations using Maple with 100 digits have shown.

[2] If the evaluation of four-electron integrals is made in terms of A integrals, A with negative powers appear even for radial four-electron integrals with low quantum numbers of r_1 (for example, integrals 1 and 2 of Table 1). The use of the non-trivial V auxiliary integrals given by Eq. 33 of Ref. [30] avoids most of them.

2.2 K_1 integrals

We distinguish here two types of K integrals, K_1 and K_2. K_1 arises from $\langle r_{12}r_{13}/r_{34}\rangle$ (or the equivalent $\langle r_{12}r_{23}/r_{34}\rangle$ obtained by exchanging the indices 1 by 2). The integral K_1 is defined in Eqs. 8, 11. In order to perform the angular integration, a rotation is made first:

$$Y_{L_2}^{M_2}(\theta_2,\phi_2) = \sum_{M_2'} Y_{L_2}^{M_2}(\theta_1,\phi_1) P_{L_2}^{M_2'}(\cos\theta_{12}) e^{iM_2'\phi_{12}}. \tag{42}$$

Considering the interelectronic coordinates which appear in the integral K_1, we start by performing the rotation $\theta_4 \to \theta_{34}$ and $\phi_4 \to \phi_{34}$ which transforms $Y_{L_4}^{M_4}(\theta_4,\phi_4)$. This is accomplished by a rotation of the z-axis to coincide with r_3:

$$Y_{L_4}^{M_4}(\theta_4,\phi_4) = \sum_{M_4'} Y_{L_4}^{M_4}(\theta_3,\phi_3) P_{L_4}^{M_4'}(\cos\theta_{34}) e^{iM_4'\phi_{34}}, \tag{43}$$

integrating over ϕ_{34} the integral does not vanish for $M_4' = 0$, which leads to a factor 2π:

$$\begin{aligned} &4\pi \int_0^{\pi}\int_0^{2\pi} Y_{L_3}^{M_3}(\theta_3,\phi_3) Y_{L_4}^{M_4}(\theta_3,\phi_3)\sin(\theta_3) d\theta_3 d\phi_3 \\ &\quad\times \int_{|r_3-r_4|}^{r_3+r_4} \frac{1}{2}\frac{1}{r_3 r_4} P_{L_4}(\cos\theta_{34}) dr_{34}. \end{aligned} \tag{44}$$

Writing $Y_{L_3}^{M_3}(\theta_3,\phi_3)$ as $Y_{L_3}^{-M_3*}(\theta_3,\phi_3)$ we can expand the product of spherical harmonics with the same argument:

$$\begin{aligned} &Y_{L_3}^{-M_3*}(\theta_3,\phi_3) Y_{L_4}^{M_4}(\theta_3,\phi_3) \\ &\quad= \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \frac{(2L+1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) Y_L^{M_3+M_4}(\theta_3,\phi_3). \end{aligned} \tag{45}$$

Considering now the interelectronic distance r_{13} in K_1 we rotate $Y_L^{M_3+M_4}(\theta_3,\phi_3)$ as follows:

$$Y_L^{M_3+M_4}(\theta_3,\phi_3) = \sum_{M'} Y_L^{M_3+M_4}(\theta_1,\phi_1) P_L^{M'}(\cos\theta_{13}) e^{iM'\phi_{13}}. \tag{46}$$

Integrating over ϕ_{13} we obtain:

$$\begin{aligned} &K_1(N_1,N_2,N_3,N_4;\omega_1,\omega_2,\omega_3,\omega_4;\nu,\mu,\kappa)_{L_1,L_2,L_3,L_4}^{M_1,M_2,M_3,M_4} \\ &\quad= \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \end{aligned}$$

$$\times \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)}(4\pi)^{1/2}(-1)^{M_3}$$
$$\times \prod_{i=1}^{4}(2L_i+1)^{1/2}(2L+1)^{1/2}C^{L_i}(l_i', m_i'; l_i, m_i)C^{L}(L_4, M_4; L_3, -M_3)$$
$$\times \int_0^\infty r_1^{N_1-1}e^{-\omega_1 r_1}dr_1 \int_0^\infty r_2^{N_2-1}e^{-\omega_2 r_2}dr_2 \int_0^\pi \frac{1}{2}r_{12}P_{L_2}(\cos\theta_{12})\sin\theta_{12}d\theta_{12}$$
$$\times \int_0^\infty r_3^{N_3-1}e^{-\omega_3 r_3}dr_3 \int_0^\pi \frac{1}{2}r_{13}P_{L}(\cos\theta_{13})\sin\theta_{13}d\theta_{13}$$
$$\times \int_0^\infty r_4^{N_4-1}e^{-\omega_4 r_4}dr_4 \int_0^\pi \frac{1}{2}\frac{1}{r_{34}}P_{L_4}(\cos\theta_{34})\sin\theta_{34}d\theta_{34}$$
$$\times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1,\phi_1)Y_{L_2}^{M_2}(\theta_1,\phi_1)Y_{L}^{M_3+M_4}(\theta_1,\phi_1)\sin\theta_1 d\theta_1 d\phi_1. \quad (47)$$

The three-fold integration over spherical harmonics can be done by using the Condon and Shortley coefficients equation (Eq. 6) since $M_3 + M_4 = -M_1 - M_2$ due to $\delta(M_1 + M_2 + M_3 + M_4, 0)$:

$$(-1)^{M_2}\int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1,\phi_1)Y_{L_2}^{-M_2*}(\theta_1,\phi_1)Y_{L}^{M_3+M_4}(\theta_1,\phi_1)\sin\theta_1 d\theta_1 d\phi_1$$
$$= (-1)^{M_2}\delta(M_1+M_2+M_3+M_4,0)\frac{(2L+1)^{1/2}}{(4\pi)^{1/2}}C^{L}(L_2,-M_2;L_1,M_1). \quad (48)$$

Finally after angular integration we have the equation:

$$K_1(N_1,N_2,N_3,N_4;\omega_1,\omega_2,\omega_3,\omega_4;1,1,-1)_{L_1,L_2,L_3,L_4}^{M_1,M_2,M_3,M_4}$$
$$= (-1)^{M_2+M_3}\delta(M_1+M_2+M_3+M_4,0)$$
$$\times \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)}$$
$$\times \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \prod_{i=1}^{4}(2L_i+1)^{1/2}(2L+1)$$
$$\times C^{L_i}(l_i', m_i'; l_i, m_i)C^{L}(L_2,-M_2;L_1,M_1)C^{L}(L_4,M_4;L_3,-M_3)$$
$$\times K_1(N_1,N_2,N_3,N_4;\omega_1,\omega_2,\omega_3,\omega_4;L_2,L,L_4), \quad (49)$$

which is written in terms of the four-electron radial integral K_1 defined as:

$$K_1(N_1,N_2,N_3,N_4;\omega_1,\omega_2,\omega_3,\omega_4;1,1,-1;L_2,L_3,L_4)$$
$$= \int_0^\infty r_1^{N_1+1}e^{-\omega_1 r_1}dr_1 \int_0^\infty r_2^{N_2+1}e^{-\omega_2 r_2}dr_2$$

$$\times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2}\frac{r_{12}^2}{r_1 r_2} P_{L_2}(\cos\theta_{12}) dr_{12}$$
$$\times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_{|r_1-r_3|}^{r_1+r_3} \frac{1}{2}\frac{r_{13}^2}{r_1 r_3} P_{L_3}(\cos\theta_{13}) dr_{13}$$
$$\times \int_0^\infty r_4^{N_4+1} e^{-\omega_4 r_4} dr_4 \int_{|r_3-r_4|}^{r_3+r_4} \frac{1}{2}\frac{1}{r_3 r_4} P_{L_4}(\cos\theta_{34}) dr_{34}. \quad (50)$$

The following steps of radial integration are the same as in the case of the L four-electron integral. Integrating over r_2 the resulting integrals are in this case linear combinations of integrals of the type $\langle r_{13}/r_{34}\rangle$. Note that these resulting three-electron integrals can be rewritten by exchanging 3 by 1 and 1 by 2 and 4 by 3 in the form $\langle r_{12}/r_{13}\rangle$:

$$\begin{aligned}
&K_1(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1; L_2, L_3, L_4) \\
&= \sum_{k=0}^{\lfloor L_2/2\rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \\
&\quad \times \binom{L_2}{k}\binom{2L_2-2k}{L_2}\binom{L_2-2k}{q}\binom{L_2-2k-q}{p} \\
&\quad \times \Bigg\{ \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_1-1+2k+2p+2i-L_2, \omega_2) \\
&\qquad \times J_2(N_3, N_1+L_2+2-2k-2p-2i, N_4; \omega_3, \omega_1, \omega_4; 1, -1; L_3, L_4) \\
&\qquad - \sum_{j=1}^{N_2+2k+2p+1-L_2} \binom{N_2+2k+2p-L_2}{j-1} A(2q+2+j; \beta) \\
&\qquad \times J_2(N_3, N_1+N_2-2q-j-1, N_4; \omega_3, \omega_1+\omega_2, \omega_4; 1, -1; L_3, L_4) \Bigg\}.
\end{aligned} \quad (51)$$

Mathematically, this expression is the same as L but in J the positions of the variables of electrons 1 and 3 are interchanged. The auxiliary integrals A do not have any negative powers. Although one of the arguments of J may be negative, this fact leads to the non-trivial auxiliary integrals V defined in Sect. 4. In this integral there is no need to expand it into one-electron A integrals. Note that to achieve this goal an additional J_2 integral is introduced. The J_2 three-electron integral is calculated by integrating over electron 3, and it is given in Sect. 3. As we see there are several possibilities for evaluating an integral by this method. In Table 2 a number of K_1 integral values are shown. We have been able to reproduce all integrals of Tables 5 and 6 of Sims and Hagstrom [19] to full accuracy.

2.3 K_2 integrals

The four-electron integral K_2 is usually known as $\langle r_{12}r_{34}/r_{23}\rangle$. The integration steps are similar to the evaluation of L and K_1. The integral is defined in Eqs. 9, 12. In K_2 one has to pay attention to the details of the angular integration and to make the radial integration this time over electron 4, in order to break the integral into a three-electron one $\langle r_{12}/r_{23}\rangle$ which (by exchanging the electrons) has the same form as $\langle r_{12}/r_{13}\rangle$. Similar to the case of K_1 we make the rotation $\theta_4 \to \theta_{34}$ and $\phi_4 \to \phi_{34}$:

$$Y_{L_4}^{M_4}(\theta_4,\phi_4) = \sum_{M_4'} Y_{L_4}^{M_4}(\theta_3,\phi_3) P_{L_4}^{M_4'}(\cos\theta_{34}) e^{iM_4'\phi_{34}}, \tag{52}$$

and expanding the product of spherical harmonics:

$$\begin{aligned} &Y_{l_3}^{-M_3*}(\theta_3,\phi_3) Y_{L_4}^{M_4}(\theta_3,\phi_3) \\ &\quad = \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)}\frac{(2L+1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) Y_L^{M_3+M_4}(\theta_3,\phi_3). \end{aligned} \tag{53}$$

Because of the interelectronic distance r_{23} we have to rotate $Y_L^{M_3+M_4}(\theta_3,\phi_3)$:

$$Y_L^{M_3+M_4}(\theta_3,\phi_3) = \sum_{M'} Y_L^{M_3+M_4}(\theta_2,\phi_2) P_L^{M'}(\cos\theta_{23}) e^{iM'\phi_{23}}, \tag{54}$$

and to integrate over ϕ_{23}. The integral does not vanish for $M' = 0$. After the rotation, the product of spherical harmonics with the same argument is again linearized:

$$\begin{aligned} &Y_{L_2}^{-M_2*}(\theta_2,\phi_2) Y_L^{M_3+M_4}(\theta_2,\phi_2) \\ &\quad = \sum_{L'=|L_2-L|}^{L_2+L} {}^{(2)}\frac{(2L'+1)^{1/2}}{(4\pi)^{1/2}} C^{L'}(L, M_3+M_4; L_2, -M_2) Y_{L'}^{M_2+M_3+M_4}(\theta_2,\phi_2), \end{aligned} \tag{55}$$

still a rotation $\theta_2 \to \theta_{12}$ takes place:

$$Y_{L'}^{M_2+M_3+M_4}(\theta_2,\phi_2) = \sum_{M'} Y_{L'}^{M_2+M_3+M_4}(\theta_1,\phi_1) P_{L'}^{M'}(\cos\theta_{12}) e^{iM'\phi_{12}}. \tag{56}$$

Integrating over ϕ_{12}, we are left with an integral which can be solved by the orthogonality property of the spherical harmonics:

$$\begin{aligned} &(-1)^{M_1+M_2+M_3} \int_0^{\pi}\int_0^{2\pi} Y_{L_1}^{-M_1*}(\theta_1,\phi_1) Y_{L'}^{M_2+M_3+M_4}(\theta_1,\phi_1) \sin\theta_1 d\theta_1 d\phi_1 \\ &\quad = \delta(L_1, L')\delta(M_1+M_2+M_3+M_4, 0). \end{aligned} \tag{57}$$

Finally we have:

$$
\begin{aligned}
&K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1)^{M_1,M_2,M_3,M_4}_{L_1,L_2,L_3,L_4} \\
&= (-1)^{M_1+M_2+M_3}\delta(M_1 + M_2 + M_3 + M_4, 0) \\
&\times \sum_{L_1=|l_1-l_1'|}^{l_1+l_1'} {}^{(2)} \sum_{L_2=|l_2-l_2'|}^{l_2+l_2'} {}^{(2)} \sum_{L_3=|l_3-l_3'|}^{l_3+l_3'} {}^{(2)} \sum_{L_4=|l_4-l_4'|}^{l_4+l_4'} {}^{(2)} \prod_{i=1}^{4} \\
&\times (2L_i + 1)^{1/2} C^{L_i}(l_i', m_i'; l_i, m_i) \\
&\times \sum_{L=|L_3-L_4|}^{L_3+L_4} {}^{(2)} \sum_{L_1=|L_2-L|}^{L_2+L} {}^{(2)} \delta(L_1, L')(2L + 1)^{1/2}(2L' + 1)^{1/2} \\
&\times C^{L}(L_4, M_4; L_3, -M_3) C^{L'}(L, M_3 + M_4; L_2, -M_2) \\
&\times K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; L', L, L_4). \qquad (58)
\end{aligned}
$$

Note that the quantum numbers are in this case L' and L. The radial K_2 integral is defined as:

$$
\begin{aligned}
&K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1; L_2, L_3, L_4) \\
&= \int_0^\infty r_1^{N_1+1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2+1} e^{-\omega_2 r_2} dr_2 \\
&\times \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} \frac{r_{12}^2}{r_1 r_2} P_{L_2}(\cos\theta_{12}) dr_{12} \\
&\times \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} dr_3 \int_{|r_2-r_3|}^{r_2+r_3} \frac{1}{2} \frac{1}{r_2 r_3} P_{L_3}(\cos\theta_{23}) dr_{23} \\
&\times \int_0^\infty r_4^{N_4+1} e^{-\omega_4 r_4} dr_4 \int_{|r_3-r_4|}^{r_3+r_4} \frac{1}{2} \frac{r_{34}^2}{r_3 r_4} P_{L_4}(\cos\theta_{34}) dr_{34}. \qquad (59)
\end{aligned}
$$

Again the integration steps are the same as for the L and K_2 four-electron integrals. Integrating over r_4, the resulting integrals are linear combinations of $\langle r_{13}/r_{23}\rangle$ integrals. These three-electron integrals can be rewritten by exchanging 3 by 1 and 2 by 3 in the $\langle r_{12}/r_{13}\rangle$ form:

$$
\begin{aligned}
&K_2(N_1, N_2, N_3, N_4; \omega_1, \omega_2, \omega_3, \omega_4; 1, 1, -1; L_2, L_3, L_4) \\
&= \sum_{k=0}^{[L_4/2]} \sum_{q=0}^{L_4-2k} \sum_{p=0}^{L_4-2k-q} \frac{(-1)^{k+q}}{2^{2L_4-2k}(2q+2)} \binom{L_4}{k} \binom{2L_4-2k}{L_4} \binom{L_4-2k}{q} \\
&\times \binom{L_4-2k-q}{p} \\
&\times \left\{ \sum_{i=1}^{2q+2} \binom{2q+3}{2i-1} A(N_4 - 1 + 2k + 2p + 2i - L_4, \omega_4) \right.
\end{aligned}
$$

Table 4 Radial three-electron integrals $J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; \nu, \mu; L_2, L_3)$ calculated with logarithms for fixed values of the charge distributions $\omega_1, \omega_2, \omega_3$

N_1	N_2	N_3	ω_1	ω_2	ω_3	L_2	L_3	J
0	5	5	6.0	4.0	2.0	2	0	$-0.14266\ 50857\ 19476\ 12083\ 50450\ 68127\times10^{-4}$
3	5	5	6.0	4.0	2.0	4	0	$-0.49331\ 13373\ 76615\ 31682\ 76534\ 87812\times10^{-6}$
0	5	5	6.0	4.0	2.0	4	2	$-0.17528\ 95633\ 06438\ 99538\ 76513\ 41964\times10^{-7}$
4	7	7	6.0	4.0	2.0	6	0	$0.35428\ 55073\ 38306\ 66730\ 68130\ 45224\times10^{-5}$
0	7	7	6.0	4.0	2.0	6	0	$-0.19235\ 56509\ 54578\ 54425\ 91799\ 81494\times10^{-5}$
0	7	7	6.0	4.0	2.0	6	2	$-0.39543\ 96770\ 93723\ 45277\ 40630\ 83331\times10^{-7}$
0	7	7	6.0	4.0	2.0	6	4	$-0.54334\ 04155\ 61880\ 05793\ 04685\ 06906\times10^{-8}$
1	3	0	4.0	6.0	6.0	2	2	$-0.35281\ 77181\ 63470\ 39310\ 53392\ 42635\times10^{-8}$
1	3	−2	4.0	6.0	4.0	2	2	$-0.74083\ 86745\ 43215\ 15568\ 43293\ 09478\times10^{-7}$
1	4	0	4.0	6.0	6.0	3	3	$-0.34057\ 37116\ 33261\ 99831\ 61174\ 62451\times10^{-9}$
1	4	−1	4.0	6.0	6.0	3	3	$-0.81443\ 71430\ 70749\ 51970\ 23684\ 04683\times10^{-9}$
1	4	−2	4.0	6.0	6.0	3	3	$-0.25239\ 92946\ 27632\ 92289\ 45554\ 52185\times10^{-8}$
1	4	−3	4.0	6.0	6.0	3	3	$-0.11251\ 17498\ 58478\ 27242\ 70051\ 11489\times10^{-7}$
1	5	−4	6.0	6.0	4.0	4	4	$-0.30727\ 91301\ 67632\ 47356\ 86814\ 26286\times10^{-8}$
1	6	−5	6.0	6.0	4.0	5	5	$-0.15002\ 99442\ 10105\ 40434\ 19894\ 34622\times10^{-8}$

$\nu = 1$ and $\mu = -1$

$$\times J(N_2, N_1, N_3 + l_4 + 2 - 2k - 2q - 2p - 2i; \omega_2, \omega_1, \omega_3; 1, -1; L_2, L_3)$$
$$- \sum_{j=1}^{N_4+2k+2p+1-L_4} \binom{N_4 + 2k + 2p - L_4}{j - 1} A(2q + 2 + j; \omega_4)$$
$$\times J(N_2, N_1, N_3 + N_4 - 2q - j - 1; \omega_2, \omega_1, \omega_3 + \omega_4; 1, -1; L_2, L_3)\Big\}. \quad (60)$$

Equations 58, 60 define this class of four-electron integrals. The A integrals which occur always have positive powers. There is only one case of this integral that has to be treated especially, see Appendix B. In Table 3 some K_2 integral values are given. We have reproduced all integrals of Tables 3 and 4 of Sims and Hagstrom [19] with full accuracy.

3 Radial three- and two-electron integrals

The radial three-electron integrals have been derived in the first paper of this series [6]. Two kinds of three-electron radial three-electron integrals J are used here. The first J is obtained by integration over electron 2 and it is used in the four-electron integrals L and K_2:

$$
\begin{aligned}
&J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
&= \sum_{k=0}^{\lfloor L_2/2 \rfloor} \sum_{q=0}^{L_2-2k} \sum_{p=0}^{L_2-2k-q} \frac{(-1)^{k+q}}{2^{2L_2-2k}(2q+3)} \binom{L_2}{k} \binom{2L_2-2k}{L_2} \binom{L_2-2k}{q} \\
&\quad \times \binom{L_2-2k-q}{p} \\
&\quad \times \Bigg\{ \sum_{i=1}^{q+2} \binom{2q+3}{2i-1} A(N_2 - 1 + 2k + 2p + 2i - L_2, \omega_2) \\
&\qquad \times I(N_1 + L_2 + 2 - 2k - 2q - 2p - 2i, N_3; \omega_1, \omega_3; -1; L_3) \\
&\qquad - \sum_{j=1}^{N_2+2k+2p+1-L_2} \binom{N_2 + 2k + 2p - L_2}{j-1} A(2q + 2 + j; \omega_2) \\
&\qquad \times I(N_1 + N_2 - 2q - j - 1, N_3; \omega_1 + \omega_2, \omega_3; -1; L_3) \Bigg\}. \qquad (61)
\end{aligned}
$$

The radial three-electron integrals J are then linear combinations of basic radial two-electron integrals:[3]

$$
\begin{aligned}
I(N_1, N_2; \omega_1, \omega_2; -1; L) = \frac{1}{(2L+1)} &[V(N_1 + L + 1, N_2 - L; \omega_1, \omega_2) \\
&+ V(N_2 + L + 1, N_1 - L; \omega_2, \omega_1)]. \qquad (62)
\end{aligned}
$$

with the conditions $N_1 + L \geq -1$, $N_2 + L \geq -1$ and $N_1 + N_2 \geq -2$ in I so that the first argument k of $V(k, l; \alpha, \beta)$ is positive and $k + l \geq -1$.

The second J is J_2 and it is used in K_1. In J_2 the integration is done over electron 3. The final expression is:

$$
\begin{aligned}
&J_2(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3) \\
&= \sum_{k=0}^{\lfloor L_3/2 \rfloor} \sum_{q=0}^{L_3-2k} \sum_{p=0}^{L_3-2k-q} \frac{(-1)^{k+q}}{2^{2L_3-2k}(2q+1)} \binom{L_3}{k} \binom{2L_3-2k}{L_3} \binom{L_3-2k}{q}
\end{aligned}
$$

[3] Unfortunately there is a typo in Eqs. 41, 44 of the paper I of this series. The correct expressions are given in this paper in Eqs. 62, 64. Also Eq. 46 of paper I should read:

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

$$\times \binom{L_3 - 2k - q}{p}$$
$$\times \left\{ \sum_{i=1}^{q+1} \binom{2q+1}{2i-1} A(N_3 - 1 + 2k + 2p + 2i - L_3, \omega_3) \right.$$
$$\times I(N_1 + L_2 - 2k - 2p - 2i, N_2; \omega_1, \omega_2; 1; L_2)$$
$$- \sum_{j=1}^{N_3+2k+2p+1-L_3} \binom{N_3 + 2k + 2p - L_3}{j-1} A(2q + j; \omega_3)$$
$$\left. \times I(N_1 + N_3 - 2q - j - 1, N_3; \omega_1 + \omega_3, \omega_2; 1; L_2) \right\}. \quad (63)$$

The J_2 are expanded in integrals of the type $I(N_1, N_2; \omega_1, \omega_2; 1; L)$:

$$I(N_1, N_2; \omega_1, \omega_2; 1; L) = \frac{1}{(2L+1)}$$
$$\times \left[-\frac{1}{(2L-1)} (V(N_1 + L + 1, N_2 - L + 2; \omega_1, \omega_2) \right.$$
$$+ V(N_2 + L + 1, N_1 - L + 2; \omega_2, \omega_1))$$
$$\times \frac{1}{(2L+3)} (V(N_1 + L + 3, N_2 - L; \omega_1, \omega_2)$$
$$\left. + V(N_2 + L + 3, N_1 - L; \omega_2, \omega_1)) \right] \quad (64)$$

The conditions are the same as before: $N_1 + L \geq -1$, $N_2 + L \geq -1$ and $N_1 + N_2 \geq -2$.

4 Auxiliary integrals

We have expanded the $I(N_1, N_2; \omega_1, \omega_2; \nu; L)$ integrals in two-electron auxiliary integrals $V(k, l; \alpha, \beta)$. In the calculation of four-electron integrals three kinds of auxiliary V integrals can occur. The first kind with $k, l \leq 0$ is the trivial one. The second kind is the V integral with $k + l \geq -1$ and $k > 0$, which is non-trivial and computationally more demanding. The non-trivial two-electron auxiliary integrals V have been accurately evaluated by Sims and Hagstrom Eq. 33 of Ref. [30] using the so-called Larsson sum [31]:

$$V(k, l; \alpha, \beta) = \sum_{q=1} \frac{\alpha^{q-1} k!}{(k+q)!} A(k + l + q; \alpha + \beta). \quad (65)$$

Fast and stable techniques of calculation of V are given in Ref. [30].

The results using the Larsson sum have been compared with direct Maple calculations using the definition of the $V(k,l;\alpha,\beta)$ integrals and reversing the order of integration. The power l is negative, we write it here explicitly as $-l$:

$$V(k,-l;\alpha,\beta) = \int_0^\infty r_1^k e^{-\alpha r_1} dr_1 \int_{r_1}^\infty \frac{1}{r_2^l} e^{-\beta r_2} dr_2 = \int_0^\infty \frac{1}{r_2^l} e^{-\beta r_2} dr_2 \int_0^{r_2} r_1^k e^{-\alpha r_1} dr_1. \quad (66)$$

For a pair of given powers k, l the Maple results of Eq. 66 agree completely with the ones of Eq. 65. For instance, numerical checks up to $k = 300$ and $l = -10$, for exponents $s = 0.0001$ ($s = \alpha/(\alpha+\beta)$) have shown full agreement on one hand side using more than 500 digits precision of Maple and on the other hand side using Eq. 65 in a Fortran program with quadruple precision.

When k, l are both positive, these integrals are trivial and well-known. We have used the Frolov and Smith expansion in terms of A auxiliary integrals [16] which is very stable since it consists of a summation:

$$V(k,l;\alpha,\beta) = \sum_{l'=0}^{l} \binom{l}{l'} A(l',\alpha) A(k+l-l',\alpha+\beta), \qquad k,l \geq 0 \quad (67)$$

and again there is no loss of precision.

The third kind of V integrals are a new kind of integrals with arguments $k+l \leq -2$, which do not converge alone but certain combinations of them converge to a solution. They will be treated in Appendix B.

5 Discussion

The Hy-CI method represents a true alternative to CI atomic calculations. The research on integral evaluation methods, which is of mathematical nature, is important to facilitate the application of the Hy-CI method to atoms with number of electrons $N \geq 5$, in order to be able to determine with high accuracy the energy levels of ground and excited states, and properties of atoms with a large number of electrons.

Independent methods of integral evaluation are useful in the practice for checking the computer program codes. Also efficiency and computation time can be compared.

In this work a new alternative method of evaluating all four-electron integrals appearing in the Hy-CI method has been developed. This method has the advantage that it requires only the calculation of two-electron auxiliary integrals. These two-electron auxiliary integrals are an element of the classical method which has been incorporated in this method to avoid its disadvantages. These disadvantages were due to successive reduction to integrals of lower order, which led finally to one-electron integrals containing negative powers. Integrations over variables with negative powers were early known as "difficult integrals in Quantum Chemistry". We have formulated this method avoiding most of them.

The two-electron auxiliary integrals are easy to compute and stable algorithms are reported. The calculated four-electron integrals using quadruple precision have been thoroughly checked with the ones of Sims and Hagstrom [19] showing a complete agreement to more than 30 decimal digits, except the cases discussed in the Appendix B where we have obtained an agreement of 26-28 decimal digits. This accuracy could be improved in our program by using higher precision arithmetic for those cases. The integrals have also been checked using the algebraic package Maple with 100 digits precision. The binomials and factorials of the formulas in the program have been defined as real variables and have been calculated with quadruple precision.

By studying some cases of four-electron integrals which lead to lower order integrals with negative arguments, new mathematical relations among one- and two-electron auxiliary integrals and their solutions have been found. These auxiliary integrals with negative powers of the coordinates maybe of importance for the solution of integrals in other methods, e.g. relativistic integrals and many-electron integrals.

Our method is conceptually messier than the traditional method of expanding the integrals in four-electron auxiliary ones, which looks more straightforward. But once the algorithms are established, this method provides an easy way of computing four-electron integrals using a minimum of computer memory. A computer program has been written in Fortran 90 in the form of a tree: a subroutine for a four-electron integral calls a subroutine or function for a three-electron integral which in turn calls a subroutine or function for a two-electron integral. This structure is very appropriate for computer programs, since modern computers prefer direct calculation to large amounts of storage. We plan to use our integral codes to perform the first Hy-CI calculation on the boron atom.

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Appendix A: the auxiliary integrals A, V, W and X

The so-called auxiliary integrals A, V, W, and X are the basic integrals used in the calculation of atomic integrals. Although in this work only one- and two-electron auxiliary integrals are used, for completeness the definitions of the remaining ones are given. The one-electron integrals for $n \geq 0$ are:

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

The auxiliary two-electron integrals are defined to be:

$$V(k,l;\alpha,\beta) = \int\int_{0<r_1<r_2<\infty} r_1^k r_2^l e^{-\alpha r_1} e^{-\beta r_2} dr_1 dr_2$$
$$= \int_0^\infty r_1^k e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^l e^{-\beta r_2} dr_2. \quad \text{(A.2)}$$

They can be calculated directly for positive powers $k, l \geq 0$ [26], and for a negative power $l < 0$ and $k + l \geq -1$ [30]. Traditionally they were calculated using recursion relations [11,32]. As the domain of integration is partitioned into two regions: $r_1 < r_2$ and $r_2 < r_1$, a two-electron integral is a sum of 2 V integrals.

In the domain of integration of the three-electron integrals there are $3! = 6$ regions given by permutations of r_1, r_2 and r_3. These regions are: $r_1 < r_2 < r_3$, $r_1 < r_3 < r_2$, $r_2 < r_1 < r_3$, $r_2 < r_3 < r_1$, $r_3 < r_1 < r_2$, and $r_3 < r_2 < r_1$. Integration leads to a sum of 6 auxiliary integrals W defined as [11]:

$$W(f,g,h;\alpha,\beta,\gamma) = \int\int\int_{0<r_1<r_2<r_3} r_1^f r_2^g r_3^h e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} dr_1 dr_2 dr_3$$
$$= \int_0^\infty r_1^f e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^g e^{-\beta r_2} dr_2 \int_{r_2}^\infty r_3^h e^{-\gamma r_3} dr_3. \quad \text{(A.3)}$$

Recurrence relations for $f, g, h \geq 0$ are given in Refs. [11,30,32]. Analytic expressions are given in Refs. [16,17,26,33], [30, Eq. 32].

The auxiliary four-electron integrals are defined to be [2]:

$$X(f,g,h,i;\alpha,\beta,\gamma,\delta)$$
$$= \int\int\int\int_{0<r_1<r_2<r_3<r_4} r_1^f r_2^g r_3^h r_4^i e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} e^{-\delta r_4} dr_1 dr_2 dr_3 dr_4$$
$$= \int_0^\infty r_1^f e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^g e^{-\beta r_2} dr_2 \int_{r_2}^\infty r_3^h e^{-\gamma r_3} dr_3 \int_{r_3}^\infty r_4^i e^{-\delta r_4} dr_4 \quad \text{(A.4)}$$

The domain of integration contains 4! regions given by permutations of r_1, r_2, r_3 and r_4. Recurrence relations of X for $f, g, h, i \geq 0$ are given in [2,12,19]. A four-electron integral is a sum of 12 X integrals.

Appendix B: the basic integrals I with negative power

In this Appendix two algorithms for evaluating some difficult cases of four-electron integrals are given in detail. The algorithms allow for the calculation of these cases without the need for the W auxiliary three-electron integrals. As mentioned previously, some cases of L four-electron integrals, e.g. $\langle s(1)p(2)p(3)p(4)r_{12}r_{13}/r_{14}s(1)p(2)p(3)p(4)\rangle$, lead to $A(-n,\alpha)$ with negative argument which have no solution by themselves but they do have a solution when combined. Also there is one case of a $K2$ four-electron integral, $\langle p(1)p(2)s(3)s(4)r_{12}r_{34}/r_{23}p(1)p(2)s(3)s(4)\rangle$, which leads to $I(N_1, N_2; \omega_1, \omega_2; -1; L)$ with both $N_1, N_2 < 0$. These integrals also do not have a solution by themselves but they do when combined.

Case 1: I containing $A(-n, \alpha)$.

As mentioned in Sect. 2, the calculation of the L radial four-electron integrals leads to negative N_1 in $J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, -1; L_2, L_3)$ integrals which lead to negative N_1 in $I(N_1, N_2; \omega_1, \omega_2; -1; L)$ with $N_1 + L < -1$ and $N_2 + L < -1$, and therefore to $V(k, l; \alpha, \beta)$ integrals with $k < 0$ which are not defined. This happens when n_1, n_1' ($N_1 = n_1 + n_1' - 1$) are the lowest quantum numbers for a given symmetry s, p, or d ($N_1 = 1, 2, 3$) of the linked electron 1 and there are high angular momentum coupling numbers L_2, L_3, L_4.

In the computer program the resulting three-electron integrals J are first checked to predict which ones will lead to some integrals $V(k, l; \alpha, \beta)$, (e.g. $k, l < 0$) which are not defined. The idea is to use the Larsson sum for $V(k, l; \alpha, \beta)$ wherever possible, otherwise the computation will become very computationally intensive. The computer program contains two subroutines for the two-electron integrals $I(N_1, N_2; \omega_1, \omega_2; -1; L)$. Those I which do not lead to $k, l < 0$ in $V(k, l; \alpha, \beta)$ are computed as usual. The ones that lead to $k, l < 0$ are expanded as a linear combination of auxiliary integrals $A(n, \alpha)$. This last kind of I integrals is separated into two parts. In one part the sums including positive $A(n, \alpha)$ are calculated, setting the undefined $A(-n, \alpha)$ to zero, and in the other part are the sums of I containing negative $A(-n, \alpha)$. These two parts are added. This can be programmed in different ways. Here we give the formulas for the integration of negative one-electron integrals.

First the four-electron integrals should be expanded into one-electron integrals $A(n, \alpha)$.[4] The basic two-electron integral for any value of $\nu \geq -1$ can be written as [6, Eq. 39]:

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

Expanding the Legendre polynomials $P_{L_2}(\cos\theta_{12})$ according to Eq. 28, using the Binomial theorem twice, with indices q, p and collecting powers:

$$\begin{aligned} &I(N_1, N_2; \omega_1, \omega_2; \nu; L) \\ &= \sum_{k=0}^{\lfloor L/2 \rfloor} \sum_{q=0}^{L-2k} \sum_{p=0}^{L-2k-q} \frac{(-1)^{k+q}}{2^{2L-2k}} \binom{L}{K} \binom{2L-2k}{L} \binom{L-2k}{q} \\ &\quad \times \binom{L-2k-q}{p} \end{aligned}$$

[4] The following formulation is valid in general for any four-electron integral but would lead to many more cases of integrals $A(n, \alpha)$ with negative powers n than in the case of using $V(k, l; \alpha, \beta)$. See Ref. [7].

$$\times \int_0^\infty r_1^{N_1+L-2k-2q-2p} e^{-\omega_1 r_1} dr_1$$
$$\times \int_0^\infty r_2^{N_2-L+2k+2p} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu+2q+1} dr_{12}, \tag{B.2}$$

Integrating over the r_{12} variable and taking into account the two domains of integration Eqs. 30, 31 we finally have:

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

with $O(\nu)$ as 1 for odd ν, and 0 for even ν. In the evaluation of four-electron integrals only the case $\nu = -1$ occurs. These equations are general and they could have been also been used to evaluate all the four-, three- and two-electron integrals, but the use of $V(k, l; \alpha, \beta)$ wherever possible is better computationally.

In Eq. (B.3) $A(N_2 - L - 1 + 2k + 2p + 2i, \omega_2)$ and $A(\nu + 2q + 1 + j, \omega_2)$ never have a negative argument. But the integrals: $A(N_1 + \nu + 3 - 2k - 2p - 2i, \omega_1)$ and $A(N_1 + N_2 + 1 - 2q - j, \omega_1 + \omega_2)$ may take negative arguments n.

The $A(n, \alpha)$ integrals with negative power n do not have a solution by themselves but they do have a solution when they are combined. For example, consider the well known relation:[5]

$$A(-1, \alpha) - A(-1, \alpha + \gamma) = \ln\left(\frac{\alpha+\gamma}{\alpha}\right) \tag{B.4}$$

[5] We use the notation α, β, γ for the exponents in the integrals.

In general, we have obtained the form of the combinations of A integrals and their value with the help of Maple [27]:

$$A_g(n,\alpha,\gamma) = A(-n,\alpha) - A(-n,\alpha+\gamma) - \sum_{l=1}^{n-1} \frac{\gamma^l}{l!} A(-n+l,\alpha+\gamma)$$
$$= \frac{1}{(n-1)!}\left[(-\alpha)^{n-1}\ln\left(\frac{\alpha+\gamma}{\alpha}\right) + \sum_{k=1}^{n-1}\frac{\gamma^k(-\alpha)^{n-1-k}}{k}\right] \quad \text{(B.5)}$$

Due to the minus sign in Eq. B.5, some loss of precision is inevitable. The values of these expressions can be calculated with high accuracy using Maple. Using Fortran 90 and quadruple precision, about 26 decimal digit precision is achieved.

The combination of A integrals in Eq. B.5 are a difference of terms. The $A(n,\alpha)$ with positive sign originate from the first sum of Eq. B.3 and the $A(n,\alpha)$ integrals with negative sign from the second one. As the integrals I come from the J integrals, in the practice, we have to deal with sums of three exponents: $\omega_1, \omega_2, \omega_3$.

Similar to the negative one-electron auxiliary integrals, the basic negative two-electron integrals do not usually have a solution by themselves for $N_1 + L \le -1$ but they do have a solution when they are combined. These combinations are of the kind:

$$I(N_1,N_2;\omega_1,\omega_3;-1;l) - \sum_{k=0}^{N_1+L+3}\frac{\omega_2^k}{k!} I(N_1+k,N_2,\omega_1+\omega_2,\omega_3;-1;L),$$
$$N_1 \le -L-2, \qquad N_2 \ge L \quad \text{(B.6)}$$

We consider here only the case $\nu = -1$, the generalization for $\nu > -1$ is straightforward.

The evaluation of these groups of integrals leads to the groups of negative one-electron integrals Eq. B.4. Using the symbol $\to$ for the negative part of an integral we have:

$$I(N_1,N_2;\omega_1,\omega_3;-1;L) - \sum_{k=0}^{-N_1-L-2}\frac{\omega_2^k}{k!} I(N_1+k,N_2,\omega_1+\omega_2,\omega_3;-1;L)$$
$$\to \frac{A(N_2+L+1,\omega_3)}{2L+1}\Big[A_g(-N_1+L,\omega_1,\omega_3)$$
$$- \sum_{k=0}^{-N_1-L-2}\frac{\omega_2^k}{k!} A_g(-N_1-k+L,\omega_1+\omega_3,\omega_2)$$
$$+ \sum_{k=0}^{-N_1-L-2}\omega_3^k A_g(-N_1-L-k-1;\omega_1+\omega_2,\omega_3)$$
$$\times \begin{cases} \frac{1}{(2L+k+1)!} & \text{if } m < 2L+k+1 \\ \frac{[m-(2L+1)]!}{k!m!} & \text{if } m \ge 2L+k+1 \end{cases}\Bigg] \quad \text{(B.7)}$$

with $m = N_2 + L + 1$. In Table 1 values of L integrals have been calculated considering up to powers of -14. Integrals over several g-, h- orbitals are perhaps too computationally intensive to be used in practice, i.e., in actual calculations using the Hy-CI the order for using angular orbitals will be used s-, p-, d-, f-,.. together with one interelectronic distance per configuration. We give integrals over several g-, h- orbitals here to show that the method is working for them.

Case 2: I containing $V(k, -l; \alpha, \beta)$ with $k - l \leq -2$

.

In the evaluation of the K_2 integrals, one case $\langle p(1)p(4)r_{12}r_{34}/r_{23}p(1)p(4)\rangle$ appears (the same is true for d-, f-,$\cdots$ orbitals), which leads to integrals of the kind $V(k, -l; \alpha, \beta)$ with $k-l \leq -2$ which can not be solved used the Larsson sum. In discussing this case, consider the following integrals ($N_1, N_2 < 0$ and $N_1 + N_2 < -2$):

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_3; -1, L) - \sum_{q=0}^{-N_1-N_2-3} \frac{\omega_2^q}{q!} I(N_1 + 1 + q, N_2; \omega_1 + \omega_2, \omega_3; -1, L) \\ = \frac{1}{2L+1} V_g(N_1 + L + 1, N_2 - L; \omega_1, \omega_3, \omega_2) \\ + \frac{A(L + N_2 + 1, \omega_3)}{2l + 1} \Bigg[A_g(L - N_1, \omega_1, \omega_3) \\ - \sum_{q=0}^{-N_1-N_2-3} \frac{\omega_2^q}{q!} A_g(L - N_1 - q, \omega_1 + \omega_2, \omega_3) \Bigg] \\ + \sum_{q=0}^{-N_1-N_2-3} \frac{\omega_3^{L+N_2+2+q}}{(L + N_2 + 2 + q)!} \\ \times A_g(-N_1 - N_2 - 3 + q, \omega_1 + \omega_3, \omega_2) \end{aligned} \tag{B.8}$$

Analogous to the relations among $A(n, \alpha)$ integrals, there are relations among the $V(k, -l; \alpha, \gamma)$ integrals for $k - l \leq -2$. Some examples of these relations are:

$$\begin{aligned} &V(1, -3; \alpha, \gamma) - V(1, -3; \alpha + \beta, \gamma) \\ &V(1, -4; \alpha, \gamma) - \beta V(2, -4; \alpha + \beta, \gamma) - V(1, -4; \alpha + \beta, \gamma) \end{aligned} \tag{B.9}$$

These can be evaluated using the V definition of Eq. A.2. Changing the domain of integration:

$$\int_0^\infty dr_1 \int_{r_1}^\infty dr_2 = \int_0^\infty dr_2 \int_0^{r_2} dr_1 = \int_0^\infty dr_2 \left(\int_0^\infty dr_1 - \int_{r_2}^\infty dr_1 \right) \tag{B.10}$$

using

$$\int_{r_2}^{\infty} r_1^n e^{-\beta r_1} dr_1 = \frac{n!}{\beta^{n+1}} e^{-\beta r_2} \sum_{q=0}^{n} \frac{(\beta r_2)^q}{q!} \tag{B.11}$$

and adding and substracting some terms one gets in general:

$$\begin{aligned} V_g(k,-l;\alpha,\gamma,\beta) = V(k,-l;\alpha,\gamma) \\ - \sum_{q=0}^{l-k-2} \frac{\beta^q}{q!} V(k+q,-l;\alpha+\beta,\gamma) = A(k,\alpha) A_g(l,\gamma,\alpha) \\ - \sum_{q=0}^{l-k-2} \frac{\beta^q}{q!} A(k+q,\alpha+\beta) A_g(l,\gamma,\alpha+\beta) \\ + \sum_{s=0}^{l-k-2} \frac{\alpha^s k!}{(k+s+1)!} A_g(l-k-s-1,\gamma+\alpha,\beta) \end{aligned} \tag{B.12}$$

The groups of integrals $A_g(l,\gamma,\alpha)$ are given by Eq. B.5.

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