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Analytical evaluation of three-center nuclear-attraction integrals over s-Slater orbitals for asymmetrical conformations of the centers

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Analytical formulas for three-center nuclear-attraction integrals over Slater orbitals are given for any location of the three atomic centers. In the mathematical derivations the Neumann expansion has been used and new general auxiliary integrals which depend on the elliptical coordinates of one of the centers are defined. The orbital exponents within the integrals may be different.

KEY WORDS: nuclear-attraction integrals, Slater orbitals, different exponents

1. Introduction

The analytical evaluation of integrals over Slater orbitals is of great importance in molecular calculations to be able to perform sufficiently accurate calculations with a reasonable computational effort. In a previous paper [1] we have derived compact analytical expressions for the nuclear-attraction integral in the case of different orbital exponents and a linear symmetrical molecular conformation. In figure 1 the used coordinates are defined. In this paper, we release the last restriction and derive the expressions in the case of triangular conformations, as well as linear asymmetrical ones, which are the cases of most heterogeneous three-center molecules.

The three-center nuclear-attraction integrals were usually solved for the case of equal orbital exponents and symmetrical linear conformations of the atoms [2, 3]. Our method of calculation differs from the existing ones, see References in [1], principally in that we are not using expansions for the orbitals. These integrals are necessary for Configuration Interaction (CI) and Hylleraas-Configuration Interaction (Hy-CI) [4] calculations of three-center molecules. This study has been done with the help of the algebraic program package Maple [5].

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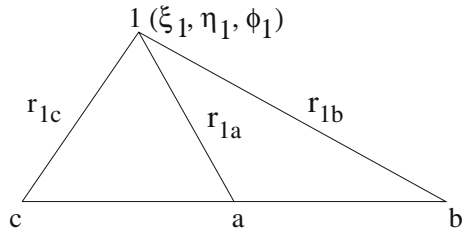

Figure 1. Definition of the atomic centers and the radial coordinates of one electron with respect to every center.

2. Theory

A CI wave function of a molecule can be written:

$$\Psi = \sum_{k=1}^{N} C_k \Phi_k, \quad \Phi_k = \hat{O}(L^2)\hat{\mathcal{A}}\phi_k\chi, \tag{1}$$

where Φ_k are symmetry adapted configurations, N is the number of configurations, and the constants C_k are determined variationally. The operator $\hat{O}(L^2)$ projects over the proper spatial space, so that every configuration is an eigenfunction of the square of the angular momentum operator $\hat{L}^2$. $\hat{\mathcal{A}}$ is the antisymmetrization operator, and χ is a spin eigenfunction. The configurations ϕ_k, are products of one-electron molecular orbitals of the required symmetry. As in this work, we treat only s-orbitals, every basis function is a configuration of Σ-symmetry. The atomic orbitals are defined with respect to the centers a, b, and c shown in figure 1:

$$n_{i\nu}s_\nu(i) = r_{i\nu}^{n_{i\nu}-1}e^{-p_{i\nu}r_{i\nu}}, \quad \nu = a, b, c, \tag{2}$$

where $n_{i\nu}$ are the principal quantum numbers, the parameters $p_{i\nu}$ are positive real, and these last may be optimized. In addition, $n'_{i\nu}$, $p'_{i\nu}$ are the corresponding parameters for the spin antisymmetrized basis functions of the left side of the matrix elements to be solved.

The effective Hamiltonian for an n-electron σ-configuration of a three-center molecule with centers $\nu, \mu = a, b, c$ in radial coordinates is [6]:

$$\begin{aligned}\hat{H} = &-\sum_{\nu=1}^{3}\sum_{i=1}^{n}\left(\frac{1}{2}\frac{\partial^2}{\partial r_{i\nu}^2} + \frac{1}{r_{i\nu}}\frac{\partial}{\partial r_{i\nu}}\right) - \sum_{\nu=1}^{3}\sum_{i=1}^{n}\frac{Z_\nu}{r_{i\nu}} + \sum_{i<j}^{n}\frac{1}{r_{ij}} \\ &-\frac{1}{2}\sum_{i=1}^{n}\sum_{\nu<\mu}^{3}\frac{r_{i\nu}^2 + r_{i\mu}^2 - R_{\nu\mu}^2}{r_{i\nu}r_{i\mu}}\frac{\partial^2}{\partial r_{i\nu}\partial r_{i\mu}} + \sum_{\nu<\mu}^{3}\frac{Z_\nu Z_\mu}{R_{\nu\mu}}.\end{aligned} \tag{3}$$

After applying the Hamiltonian to the wave function, the first challenge comes through the calculation of the potential nuclear-attraction part of the energy which leads to integrals of the form, i.e.:

$$K_{a,n'_{ib}s_b n_{ic}s_c} = \int \frac{n'_{ib}s'_b(i)n_{ic}s_c(i)}{r_{ia}}\mathrm{d}\tau_i = \int \frac{r_{ib}^{n'_{ib}-1}e^{-p'_{ib}r_{ib}}r_{ic}^{n_{ic}-1}e^{-p_{ic}r_{ic}}}{r_{ia}}\mathrm{d}\tau_i, \quad (4)$$

$$K_{c,n'_{ia}s_a n_{ib}s_b} = \int \frac{n'_{ia}s'_a(i)n_{ib}s_b(i)}{r_{ic}}\mathrm{d}\tau_i = \int \frac{r_{ia}^{n'_{ia}-1}e^{-p'_{ia}r_{ia}}r_{ib}^{n_{ib}-1}e^{-p_{ib}r_{ib}}}{r_{ic}}\mathrm{d}\tau_i \quad (5)$$

with $d\tau_i$ as volume element. By exchanging the centers attending the symmetry of the molecule, the appearing three-center nuclear-attraction integrals can be reduced to the types given here.

To calculate these three-center nuclear-attraction integrals the coordinates are transformed from radial to elliptical ones and the Neumann expansion between two points in elliptical coordinates is used [7]:

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{k=0}^{\infty}(2k+1)Q\begin{pmatrix}\xi_1\\ \xi_2\end{pmatrix}P\begin{pmatrix}\xi_2\\ \xi_1\end{pmatrix}P(\eta_1)P(\eta_2), \quad \begin{cases}\xi_1 > \xi_2,\\ \xi_1 < \xi_2\end{cases} \quad (6)$$

with

$$\xi_i = \frac{1}{R_{\nu\mu}}(r_{i\nu} + r_{i\mu}), \qquad \eta_i = \frac{1}{R_{\nu\mu}}(r_{i\nu} - r_{i\mu}), \quad i = 1, 2, \quad (7)$$

where the point 2 will be replaced by one fixed center a, b, or c. For comparison see also [2].

The integrals of equations (4) and (5) differ on the location of the charge distribution of the electron and the third center. Those centers which are involved in the charge distribution are the focii of the elliptic coordinate system and the third atom is external to the elliptical coordinates. This distinction has consequences for the calculation.

Let us first discuss the symmetrical and asymmetrical cases of the integral of equation (4). In the symmetrical case, we set $r_{12} = r_{1a}$ and use elliptical coordinates with the atoms b and c as centers. We calculate $\xi_a = \frac{1}{R_{bc}}(R_{ab} + R_{ac}) = 1$ and $\eta_a = 0$. This simplifies the Neumann expansion since $\xi_1 \in [1, \infty[$ is never smaller than ξ_a. Therefore the integral can be calculated by the methods of the bibliography. In addition, in the asymmetrical case, we get the same coordinate for $\xi_a = 1$ given its central position and a different one for η_a, a value in the interval $[-1, 1]$. Therefore, integral equation (4) can be calculated in both cases, symmetrical and asymmetrical, by the formula which we give here

for completeness:

$$K_{a,n'_{ib}s_b n_{ic}s_c} = \left(\frac{R_{ab}}{2}\right)^{n'_{ib}+n_{ic}} \pi \sum_{k=0}^{\infty}(2k+1)$$
$$\times P_k(\eta_a) \sum_{i=0}^{n'_{ib}} \sum_{j=0}^{n_{ic}} \binom{n'_{ib}}{i}\binom{n_{ic}}{j}(-1)^{n_{ic}-j} F^k_{i+j}(\alpha) G_k^{n'_{ib}+n_{ic}-i-j}(\beta). \tag{8}$$

The auxiliary integrals F_n^k, G_k^n are defined as in [1]:

$$F_n^k(\alpha) = \int_1^{\infty} Q_k(\xi)\xi^n e^{-\alpha\xi}\ \mathrm{d}\xi, \tag{9}$$

$$G_k^n(\beta) = \int_{-1}^{+1} P_k(\eta)\eta^n e^{-\beta\eta}\ \mathrm{d}\eta. \tag{10}$$

The triangular conformation of equation (4) can be calculated as the triangular conformation of equation (5) which will be discussed in the next paragraphs.

Now let us study the integral equation (5). In this integral the electronic charge distribution is located between the centers a, b. We get for center c the coordinates $\xi_c = 3$ and $\eta_c = 1$ in the linear symmetrical case. We have to split the integration over ξ_1 into the two region integrals $\int_1^3$ and $\int_3^{\infty}$ as shown in [1]. For all cases, linear symmetrical and asymmetrical, and triangular conformations, the three-center nuclear-attraction integral is an infinite sum, which we write here in a more general form than equation (44) of Ref. [1]:

$$K_{c,n'_{ia}s_a n_{ib}s_b} = \left(\frac{R_{ab}}{2}\right)^{n'_{ia}+n_{ib}} \pi \sum_{k=0}^{\infty}(2k+1)$$
$$\times \Bigg[Q_k(\xi_c) P_k(\eta_c) \sum_{i=0}^{n'_{ia}} \sum_{j=0}^{n_{ib}} \binom{n'_{ia}}{i}\binom{n_{ib}}{j}(-1)^{n_{ib}-j} D^k_{i+j}(\xi_c,\alpha)$$
$$\times G_k^{n'_{ia}+n_{ib}-i-j}(\beta) + P_k(\xi_c) P_k(\eta_c) \sum_{i=0}^{n'_{ia}} \sum_{j=0}^{n_{ib}} \binom{n'_{ia}}{i}\binom{n_{ib}}{j}(-1)^{n_{ib}-j}$$
$$\times C^k_{i+j}(\xi_c,\alpha) G_k^{n'_{ia}+n_{ib}-i-j}(\beta) \Bigg] \tag{11}$$

with $\alpha = \frac{R_{ab}}{2}(p'_{1a} + p_{1b})$ and $\beta = \frac{R_{ab}}{2}(p'_{1a} - p_{1b})$, $\xi_c = \frac{R_{ac}+R_{bc}}{R_{ab}}$ and $\eta_c = \frac{R_{ac}-R_{bc}}{R_{ab}}$.

Test calculations of this integral equation (11) for the linear symmetrical conformation are shown in Table 1 using quadruple precision (QP), i.e., real*16 arithmetic. The computer program is written in Fortran90. The integral

Table 1
Convergence pattern of the nuclear-attraction integral $K_{c,2s_a1s_b}$ of a linear symmetrical conformation of the centers for $p_{1b} = 1.0$, $p_{2a} = 1.5$, and $R = 2.54$ a.u.

l	S_l	$K_{c,2s_a1s_b} = \frac{R^3\pi}{4}\sum_{k=0}^{l} S_k$
0	$0.2448\ 0595\ 5187\ 2905 \times 10^{-01}$	0.3150 7432 1389 3577
1	$-0.4494\ 0284\ 5582\ 8546 \times 10^{-02}$	0.2572 3451 2511 2870
2	$0.5491\ 2065\ 1747\ 9520 \times 10^{-04}$	0.2579 4125 1105 8526
3	$0.5904\ 0442\ 4136\ 5134 \times 10^{-04}$	0.2587 0112 3442 8543
4	$-0.7907\ 9969\ 0441\ 3127 \times 10^{-05}$	0.2585 9934 4596 9802
5	$0.6335\ 8937\ 5886\ 0911 \times 10^{-06}$	0.2586 0749 9126 6563
6	$-0.3884\ 0554\ 6497\ 6918 \times 10^{-07}$	0.2586 0699 9234 3482
7	$0.1980\ 6688\ 7632\ 0404 \times 10^{-08}$	0.2586 0702 4726 2894
8	$-0.8737\ 3990\ 1217\ 7856 \times 10^{-10}$	0.2586 0702 3601 7538
9	$0.3408\ 6081\ 8839\ 3515 \times 10^{-11}$	0.2586 0702 3645 6239
10	$-0.1192\ 9843\ 9504\ 5258 \times 10^{-12}$	0.2586 0702 3644 0884
11	$0.3783\ 3417\ 0355\ 4061 \times 10^{-14}$	0.2586 0702 3644 1371
12	$-0.1069\ 4714\ 0407\ 6448 \times 10^{-15}$	0.2586 0702 3644 1358
13	$-0.2005\ 2054\ 5981\ 2743 \times 10^{-17}$	0.2586 0702 3644 1357

of Table 1 with different exponents has converged to 15 decimal digits. The integral has been also calculated using Maple [5], confirming these results. We have compared our results with the ones of Fernández Rico et al [8] by the ellipsoidal coordinate method, reproducing the integral value (Table 3.) of Ref. [8] with full accuracy (our value has to be multiplied by their normalization constants). In this example, with $R_{ab} = R_{ac} = 3.0$ a.u. and $p'_{1a} = p_{1b} = 1.6$ our method leads to $0.741\ 579\ 466\ 622\ 132\ 337\ 84 \times 10^{-1}$ compared with $0.741\ 579\ 466\ 622\ 133 \times 10^{-1}$ of Ref. [8]. Our integral converges to more than 20 decimal digits because in the case of equal exponents the Neumann expansion breaks down after some terms.

In figure 2, one can see that although the conformations of the centers are free, one can still express the elliptical coordinates of one of the centers focused in the others. Let us call the coordinate $\xi = x$ in general, where x is a variable from $[1, \infty)$ which can be calculated for a given case, using the definition of an elliptic coordinate which depends on the atomic distances equation (7):

$$x = \xi_a = \frac{R_{ab} + R_{ac}}{R_{bc}}, \qquad x = \xi_b = \frac{R_{ab} + R_{bc}}{R_{ac}}, \qquad x = \xi_c = \frac{R_{ac} + R_{bc}}{R_{ab}}. \quad (12)$$

Then the auxiliary integrals $D_n^k(\xi_c, \alpha)$ and $C_n^k(\xi_c, \alpha)$ from equation (11) are redefined as:

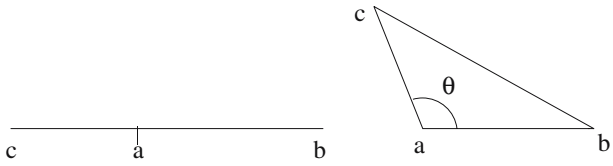

Figure 2. The two cases of conformations of the atomic centers: linear asymmetrical and triangular conformations.

$$D_n^k(x,\alpha) = \int_1^x P_k(\xi)\xi^n e^{-\alpha\xi}\ \mathrm{d}\xi, \tag{13}$$

$$C_n^k(x,\alpha) = \int_x^\infty Q_k(\xi)\xi^n e^{-\alpha\xi}\ \mathrm{d}\xi. \tag{14}$$

Now the problem is reduced to solve the auxiliary integrals of equations (13) and (14).

The first integral $D_n^k(x,\alpha)$ is solvable by using the recurrence relations:

$$\begin{aligned} D_0^0(x,\alpha) &= \frac{1}{\alpha}\left(e^{-\alpha} - e^{-\alpha x}\right), \\ D_n^0(x,\alpha) &= \frac{1}{\alpha}\left(n D_{n-1}^0(x,\alpha) + e^{-\alpha} - x^n e^{-\alpha x}\right), \\ D_n^k(x,\alpha) &= \frac{1}{k}\left((2k-1)D_{n+1}^{k-1}(x,\alpha) - (k-1)D_n^{k-2}(x,\alpha)\right). \end{aligned} \tag{15}$$

To obtain equation (15) the recurrence relation of the Legendre polynomials P_k has been used. To find a common solution for $C_n^k(x,\alpha)$ one has to look first at $k = 0$.

$$\begin{aligned} C_0^0(x,\alpha) &= \frac{1}{(2\alpha)}\left[e^{-x\alpha}\ln\left(\frac{x+1}{x-1}\right) - e^{\alpha}\mathrm{Ei}(-\alpha(x+1)) + e^{-\alpha}\mathrm{Ei}(-\alpha(x-1))\right], \\ C_1^0(x,\alpha) &= \frac{1}{\alpha}C_0^0(x,\alpha) + \frac{1}{(2\alpha)}\left[e^{-x\alpha}\ln\left(\frac{x+1}{x-1}\right) + e^{\alpha}\mathrm{Ei}(-\alpha(x+1))\right. \\ &\quad \left. + e^{-\alpha}\mathrm{Ei}(-\alpha(x-1))\right], \end{aligned} \tag{16}$$

where $\mathrm{Ei}(-x)$ is the exponential Integral:

$$\mathrm{Ei}(-x) = -\int_x^\infty \frac{e^{-t}}{t}\ \mathrm{d}t. \tag{17}$$

For higher n the following formula has been found:

$$C_n^0(x,\alpha) = \frac{n}{\alpha} C_{n-1}^0(x,\alpha) + \frac{1}{2\alpha} x^n e^{-x\alpha} \ln\frac{x+1}{x-1} - \frac{(-1)^n}{2\alpha} e^{\alpha}\,\mathrm{Ei}(-\alpha(x+1)) + \frac{1}{2\alpha} e^{-\alpha}\,\mathrm{Ei}(-\alpha(x-1)) + \frac{e^{-x\alpha}}{2} \sum_{i=0}^{n-1} \sum_{j=0}^{i} \sum_{l=0}^{i-j} \left((-1)^{n-1-i} - (-1)^{i-j-l}\right) \frac{n!}{(i+1)l!(i-j-l)!} \frac{x^l}{\alpha^{j+2}}. \tag{18}$$

A proof of equation (18) is given in the Appendix A.

We redefine also the auxiliary integral $A_n(x,\alpha) = \int_x^\infty \xi^n e^{-\alpha\xi}\,\mathrm{d}\xi$ and get

$$A_n(x,\alpha) = \frac{x^n e^{-x\alpha}}{\alpha} + \frac{n}{\alpha} A_{n-1}(x,\alpha) = \frac{e^{-x\alpha}}{\alpha} \sum_{l=0}^{n} \frac{n!}{(n-l)!} \frac{x^{n-l}}{\alpha^l} \tag{19}$$

then, finally

$$C_n^1 = C_{n+1}^0(x,\alpha) - A_n(x,\alpha),$$
$$C_n^k(x,\alpha) = \frac{1}{k}\left((2k-1)C_{n+1}^{k-1}(x,\alpha) - (k-1)C_n^{k-2}(x,\alpha)\right). \tag{20}$$

The above derived formulas hold for any triangular conformation.

We have performed test calculations of the three-center nuclear-attraction integrals type $K_{c,ab}$ for the two cases of figure 2 using QP, the results are shown in Tables 2 and 3. The integrals converge to 15 and 16 decimal digits. All the values have been also reproduced with the Maple program using higher precision. We have also checked our computer program comparing our results with the integral values obtained by Fernádez Rico et al. [8]. We obtain for the linear asymmetrical conformation $p'_{1a} = p_{1b} = 2.0$, $R_{ab} = 6$, and $R_{ac} = 7$ a.u. (taking into account normalization constants) the value $0.453\ 377\ 500\ 111\ 513\ 8130 \times 10^{-3}$ compared with their value of Table 1 $0.453\ 377\ 500\ 115\ 482 \times 10^{-3}$. The agreement is of 11 decimal digits. The triangular integral of Ref. [8] has been also reproduced. For different exponents $p_{1a} = 3.6$, $p_{1b} = 1.6$, $R_{ab} = 3$, $R_{ac} = \sqrt{18}$ a.u., and $\theta = 45°$, the integral value of $0.270\ 272\ 901\ 902 \times 10^{-1}$ has been obtained by this method, compared with $0.270\ 272\ 901\ 898 \times 10^{-1}$ of Table 4 of Ref. [8], showing a good agreement.

We have studied the stability of the calculations of the three-center nuclear attraction integral by using very large exponents and distances. For very large distances of one of the atoms the three-center nuclear attraction integral looks like a two-center nuclear attraction one. If the far atom is not involved into the charge distribution, the integral always converges. In Table 4, several calculations are shown and the number of decimal digits for which the integral converges.

Table 2
Convergence pattern of the nuclear-attraction integral $K_{c,2s_a1s_b}$ for the linear asymmetrical conformation of figure 2. $p_{1b} = 1.0$, $p_{2a} = 1.5$, $R_{ac} = 3.048$, and $R_{ab} = 2.54$ a.u.

1	S_l	$K_{c,2s_a1s_b} = \frac{R_{ab}^3\pi}{4} \sum_{k=0}^{l} S_k$
0	$0.2145\ 2512\ 6898\ 2430 \times 10^{-01}$	0.2761 0177 5084 3460
1	$-0.3474\ 8580\ 0642\ 5477 \times 10^{-02}$	0.2313 7906 6951 6427
2	$0.4239\ 6135\ 1035\ 6816 \times 10^{-04}$	0.2319 2472 0895 6845
3	$0.3458\ 7145\ 8176\ 6502 \times 10^{-04}$	0.2323 6987 0258 5323
4	$-0.4154\ 4288\ 5701\ 5536 \times 10^{-05}$	0.2323 1640 1222 1323
5	$0.3009\ 0857\ 9341\ 6172 \times 10^{-06}$	0.2323 2027 4026 8753
6	$-0.1690\ 2365\ 0402\ 0294 \times 10^{-07}$	0.2323 2005 6487 1839
7	$0.8011\ 7101\ 7327\ 1902 \times 10^{-09}$	0.2323 2006 6798 5513
8	$-0.3329\ 1157\ 7665\ 9257 \times 10^{-10}$	0.2323 2006 6370 0817
9	$0.1237\ 4887\ 5147\ 6220 \times 10^{-11}$	0.2323 2006 6386 0087
10	$-0.4166\ 1336\ 3975\ 2084 \times 10^{-13}$	0.2323 2006 6385 4725
11	$0.1283\ 3945\ 6457\ 4284 \times 10^{-14}$	0.2323 2006 6385 4890
12	$-0.4036\ 0274\ 9979\ 2993 \times 10^{-16}$	0.2323 2006 6385 4885
13	$0.7735\ 0494\ 3630\ 9634 \times 10^{-17}$	0.2323 2006 6385 4886

The integral is very stable. On the other hand, if the charge distribution is very asymmetrical, i.e., one of the involved atoms is very far from the others, the integral does not converge. For example, the integral $K_{a,bc}$ with $p_{1c} = 1$, $p_{1b} = 35$, $R_{ab} = 2.54$, and $R_{ac} = 25.4$ a.u. does not converge, and the integral $K_{c,ab}$, for the same parameters converges to 15 decimal digits.

The mathematical derivations to prove the formulas used for the auxilary integrals are given in the Appendix A. In Appendix B we correct the values of an exchange integral of Ref. [1].

Acknowledgments

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Appendix A

To prove the formula which has been obtained with the help of Ref. [5]:

Table 3
Convergence pattern of the nuclear-attraction integral $K_{c,2s_a1s_b}$ for the triangular conformation of figure 2. $p_{1b} = 1.0$, $p_{2a} = 1.5$, $R_{ab} = R_{ac} = 2.54$ a.u., and $\theta = 60°$.

l	S_l	$K_{c,2s_a1s_b} = \frac{R_{ab}^3\pi}{4} \sum_{k=0}^{l} S_k$
0	0.3725 7608 2588 8746 $\times 10^{-01}$	0.4795 1920 2454 7996
1	0.0	0.4795 1920 2454 7996
2	0.2075 5775 4082 4595 $\times 10^{-04}$	0.4797 8633 6963 2987
3	0.0	0.4797 8633 6963 2987
4	−0.2099 0281 9515 5143 $\times 10^{-04}$	0.4795 1618 4268 8271
5	0.0	0.4795 1618 4268 8271
6	0.1285 2924 3996 4367 $\times 10^{-06}$	0.4795 1783 8487 7491
7	0.0	0.4795 1783 8487 7491
8	−0.3266 0605 4877 2975 $\times 10^{-09}$	0.4795 1783 4284 2084
9	0.0	0.4795 1783 4284 2084
10	0.4780 7758 8940 2651 $\times 10^{-12}$	0.4795 1783 4290 3614
11	0.0	0.4795 1783 4290 3614
12	−0.7578 9596 9356 1865 $\times 10^{-14}$	0.4795 1783 4290 2639
13	0.0	0.4795 1783 4290 2639

$$C_n^0(x,\alpha) = \frac{n}{\alpha} C_{n-1}^0(x,\alpha) + \frac{1}{2\alpha} x^n e^{-x\alpha} \ln\frac{x+1}{x-1} - \frac{(-1)^n}{2\alpha} e^{\alpha}\,\mathrm{Ei}(-\alpha(x+1)) + \frac{1}{2\alpha} e^{-\alpha}\,\mathrm{Ei}(-\alpha(x-1)) + \frac{e^{-x\alpha}}{2} \sum_{i=0}^{n-1} \sum_{j=0}^{i} \sum_{l=0}^{i-j} \left((-1)^{n-1-i} - (-1)^{i-j-l}\right) \frac{n!}{(i+1)l!(i-j-l)!} \frac{x^l}{\alpha^{j+2}} \tag{A.1}$$

we use an induction from $(n-1)$ to n. First writing explicitly the second-order Legendre Polynomial in equation (14), we have:

$$C_n^0(x,\alpha) = \int_x^{\infty} \frac{1}{2} \ln\frac{\xi+1}{\xi-1} \xi^n e^{-\alpha\xi}\, \mathrm{d}\xi. \tag{A.2}$$

Performing partial integration and using the variable t instead of ξ, one gets:

$$C_n^0(x,\alpha) = \int_x^{\infty} \frac{1}{2} \ln\frac{t+1}{t-1} t^n e^{-\alpha t}\, \mathrm{d}t = \frac{n}{\alpha} \int_x^{\infty} \frac{1}{2} \ln\frac{t+1}{t-1} t^{n-1} e^{-\alpha t}\, \mathrm{d}t + \frac{1}{2\alpha} x^n e^{-\alpha x} \ln\frac{x+1}{x-1} + \frac{1}{2\alpha} \int_x^{\infty} t^n e^{-\alpha t} \left(\frac{1}{t+1} - \frac{1}{t-1}\right) \mathrm{d}t. \tag{A.3}$$

Looking at equation (2), one can see that the first term of equation (3) is just $\frac{n}{\alpha} C_{n-1}^0(x,\alpha)$, and the second term is the second term of equation (1). Therefore

Table 4
Study of the convergence of the integral $\left\langle \frac{e^{-p'r_{1a}}e^{-pr_{1b}}}{r_{1c}} \right\rangle$ for increasing orbital exponents and distances to atom c given in the last column as the number of significant decimal figures*.

p'_{1a}	p_{1b}	R_{ab}	R_{ac}	Conv.
1.0	1.0	2.54	2.54	20
5.0	1.0	2.54	2.54	10
15.0	1.0	2.54	2.54	9
30.0	1.0	2.54	2.54	8
1.0	1.0	2.54	5.08	20
5.0	1.0	2.54	5.08	13
15.0	1.0	2.54	5.08	13
30.0	1.0	2.54	5.08	13
1.0	1.0	2.54	12.70	20
5.0	1.0	2.54	12.70	17
15.0	1.0	2.54	12.70	14
30.0	1.0	2.54	12.70	15

* Digits different from zero.

the first two terms of equation (1) have been already obtained. To integrate the remaining term of equation (3), let us use the substitution

$$s = t + 1 \quad \text{and } s = t - 1, \text{ respectively} \tag{A.4}$$

and we get

$$\frac{1}{2\alpha}\int_x^\infty t^n e^{-\alpha t}\frac{1}{t+1}\,\mathrm{d}t - \frac{1}{2\alpha}\int_x^\infty t^n e^{-\alpha t}\frac{1}{t-1} = \frac{1}{2\alpha}\int_{x+1}^\infty \frac{(s-1)^n e^{-\alpha(s-1)}}{s}\,\mathrm{d}s - \frac{1}{2\alpha}\int_{x-1}^\infty \frac{(s+1)^n e^{-\alpha(s+1)}}{s}\,\mathrm{d}s. \tag{A.5}$$

Using the binomial Theorem for $(s+1)^n$ and $(s-1)^n$ and including s^{-1} into the respective sum, equation (5) can be rewritten as:

$$\frac{1}{2\alpha}\int_{x+1}^\infty \sum_{i=-1}^{n-1}(-1)^{n-1-i}\binom{n}{i+1}s^i e^{-\alpha(s-1)}\,\mathrm{d}s - \frac{1}{2\alpha}\int_{x-1}^\infty \sum_{i=-1}^{n-1}\binom{n}{i+1}s^i e^{-\alpha(s+1)}\,\mathrm{d}s. \tag{A.6}$$

Now let us change the order of the summation and integration, and write the first sum of $i = -1$ separately. Then one gets:

$$\frac{1}{2\alpha}\sum_{i=0}^{n-1}\binom{n}{i+1}\left[(-1)^{n-1-i}e^{\alpha}\int_{x+1}^\infty s^i e^{-\alpha s}\,\mathrm{d}s - e^{-\alpha}\int_{x-1}^\infty s^i e^{-\alpha s}\,\mathrm{d}s\right] - \frac{1}{2\alpha}((-1)^n e^{\alpha}\mathrm{Ei}(x+1) - e^{-\alpha}\mathrm{Ei}(x-1)). \tag{A.7}$$

Table 5
Erratum of the exchange integral of Table 4 in [1]: The first nine terms of $[1s_a 1s_b|2s_a 1s_b]$ for $R = 2.54$, $p_{1b} = 1.0$, $p_{2a} = 1.5$, and $p_{1a} = 3.6$.

l	S_l	$[1s_a 1s_b\|2s_a 1s_b] = \frac{R^6\pi^2}{16}\sum_{k=0}^{l} S_k$
0	$1.477\ 8128\ 5582\ 7748 \times 10^{-4}$	0.024 4794 4136 3951
1	$-3.772\ 0461\ 3334\ 3192 \times 10^{-6}$	0.023 8546 1541 4040
2	$-2.897\ 6310\ 8624\ 3925 \times 10^{-6}$	0.023 3746 3318 9022
3	$-3.212\ 3152\ 9143\ 9111 \times 10^{-8}$	0.023 3693 1210 3641
4	$-2.886\ 5727\ 7154\ 5733 \times 10^{-8}$	0.023 3645 3059 9094
5	$-2.534\ 1892\ 2097\ 8061 \times 10^{-9}$	0.023 3641 1081 9714
6	$-9.290\ 8342\ 3901\ 9034 \times 10^{-11}$	0.023 3640 9542 9779
7	$-1.974\ 5730\ 0184\ 3228 \times 10^{-12}$	0.023 3640 9510 2698
8	$-2.798\ 5616\ 7167\ 5973 \times 10^{-14}$	0.023 3640 9509 8063
9	$-2.862\ 0597\ 5247\ 4726 \times 10^{-16}$	0.023 3640 9509 8015

The last term of the equation (A.7) is the exponential integral which appears as the third term of equation (1). The remaining integrals can be rewritten as A-auxiliary integrals using the definition formula $A_i(x+1,\alpha) = \int_{x+1}^{\infty} s^i e^{-\alpha s}\,\mathrm{d}s$, leading to:

$$\frac{1}{2\alpha}\sum_{i=0}^{n-1}\binom{n}{i+1}\left[(-1)^{n-1-i}e^{\alpha}A_i(x+1,\alpha) - e^{-\alpha}A_i(x-1,\alpha)\right]. \tag{A.8}$$

Using the definition of the A-integrals, see equation (19):

$$A_n(x,\alpha) = \frac{e^{-x\alpha}}{\alpha}\sum_{l=0}^{n}\frac{n!}{(n-l)!}\frac{x^{n-l}}{\alpha^l} \tag{A.9}$$

substituting equation (A.9) into equation (A.8):

$$\sum_{i=0}^{n-1}\binom{n}{i+1}\left[(-1)^{n-1-i}\frac{e^{\alpha}}{2\alpha}\frac{e^{-(x+1)\alpha}}{\alpha}\sum_{j=0}^{i}\frac{i!}{(i-j)!}\frac{(x+1)^{i-j}}{\alpha^j} - \frac{e^{-\alpha}}{2\alpha}\frac{e^{-(x-1)\alpha}}{\alpha}\sum_{j=0}^{i}\frac{i!}{(i-j)!}\frac{(x-1)^{i-j}}{\alpha^j}\right] \tag{A.10}$$

combining the exponential functions and the αs, and grouping together the two summations, one gets:

$$\frac{e^{-x\alpha}}{2}\sum_{i=0}^{n-1}\sum_{j=0}^{i}\binom{n}{i+1}\left[(-1)^{n-1-i}\frac{i!}{(i-j)!}\frac{(x+1)^{i-j}}{\alpha^{j+2}} - \frac{i!}{(i-j)!}\frac{(x-1)^{i-j}}{\alpha^{j+2}}\right]. \tag{A.11}$$

Let us use again the binomial Theorem, this time on $(x+1)^{i-j}$ and $(x-1)^{i-j}$, we obtain:

$$\frac{e^{-x\alpha}}{2}\sum_{i=0}^{n-1}\sum_{j=0}^{i}\binom{n}{i+1}\frac{i!}{(i-j)!} \times\left[(-1)^{n-1-i}\sum_{l=0}^{i-j}\binom{i-j}{l}\frac{x^l}{\alpha^{j+2}}-\sum_{l=0}^{i-j}\binom{i-j}{l}(-1)^{i-j-l}\frac{x^l}{\alpha^{j+2}}\right] \tag{A.12}$$

expanding the binomial coefficients and simplifying the summations, the final result is:

$$\frac{e^{-x\alpha}}{2}\sum_{i=0}^{n-1}\sum_{j=0}^{i}\sum_{l=0}^{i-j}\left((-1)^{n-1-i}-(-1)^{i-j-l}\right)\frac{n!}{(i+1)l!(i-j-l)!}\frac{x^l}{\alpha^{j+2}} \tag{A.13}$$

as we wanted to demonstrate.

Appendix B

In the Table 4 of the previous authors' paper [1] is listed an erroneous integral. We correct that integral for the one given here. The first ten terms of $[2s_a1s_b|1s_a1s_b]$ for $R = 2.54$, $\alpha_1 = 3.175$, $\alpha_2 = 5.842$, $\beta_1 = 0.635$, and $\beta_2 = 3.302$ are given here in Table 5 calculated with a Fortran90 program using QP and confirmed by Maple [5] calculations using higher precision.

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