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APPLICATION OF LAGUERRE POLYNOMIALS TO EVALUATION OF TWO-CENTER, TWO- AND THREE-ELECTRON INTEGRALS IN THE BASIS OF SLATER-TYPE ORBITALS — ALGORITHM AND NUMERICAL RESULTS

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Numerical verification of the algorithm for evaluation of the two-center, two- and three-electron integrals with the correlation factors of the type r_{12}^k, elaborated by us previously is presented. The influence of different parameters on the accuracy of the expressions for evaluating the integrals is discussed on the basis of the numerical results obtained.

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1. Introduction

The allowance for the correlation factors in the form of non-negative powers of the interelectron-distance function in a variation wave function leads to the expressions for the Hamiltonian matrix elements which take the form of a combination of the multi-electron integrals. In the case of the formulation presented in [1–3], at most the eight-center and four-electron integrals have to be taken into account.

The knowledge of algorithms for computing appropriate integrals is necessary to perform calculations in the frame of that model. A remarkable progress [4–10] has been achieved in this field by creating a series of interesting methods for evaluating two-electron integrals with the operator r_{12}^{-1}, involving multicenter integrals — up to four-center ones. At present, however, there are no methods for evaluation of the above-mentioned integrals with the operators involving correlation factors of the type r_{ij}^k for arbitrary molecule.

The problem discussed in this paper is limited to two-atom molecules, therefore in this case the problem is reduced to two-center integrals only. Evaluation of some two-center integrals with the correlation factors of the type r_{ij}^k has been discussed by Rothstein [11], and applied (with some modifications) by Clary [12], where, at a particular stage of calculation, one has to introduce a numerical integration. The problem, but limited to the two-electron integrals, has been also discussed by Guseinov et al. [13].

Analytical formulas for evaluating the two-center, two- and three-electron integrals in prolate spherical coordinates [14, 15] as well as the two- and three-electron integrals with the one-electron operator [16] have been obtained. The numerical tests performed [16] give positive results justifying the usefulness of that method in practical applications.

Another method, defined in spherical coordinates and utilizing the expansion of the function r_{12}^k by means of the generalized Laguerre polynomials, has been also elaborated [17, 18]. The analytical expressions for evaluating the two-center, one-, two-, three- and four-electron integrals defined in [3] as well as the integrals with one-electron operator have been obtained as a result of that method.

In this paper, the numerical verification of the algorithm given in [18] was performed for the case of the two- and three-electron integrals of the type

$$I_2 = \left\langle \phi_{\alpha_1}\phi_{\alpha_2} \left| r_{12}^u \right| \phi_{\alpha_1'}\phi_{\alpha_2'} \right\rangle , \tag{1}$$

$$I_3 = \left\langle \phi_{\alpha_1}\phi_{\alpha_2}\phi_{\alpha_3} \left| r_{12}^u r_{23}^v \right| \phi_{\alpha_1'}\phi_{\alpha_2'}\phi_{\alpha_3'} \right\rangle . \tag{2}$$

In the above expressions r_{ij} are the interelectron-distance functions, and u and v are integers taking the values -1, 0, 1, 2, ... The functions ϕ_α are the Slater-type orbitals [19] expressed by the coordinates of the local system with the origin in the center (atom) A or B. The quantum numbers and exponent defining the Slater orbital are represented by the index $\alpha = (n, l, m, \zeta)$.

2. The algorithm for evaluating two-center, two- and three-electron integrals

As it is shown in [18], simplification of calculations requires the Slater orbitals to be grouped into the pairs relating to the coordinates of the same electron $\phi_\alpha^* \phi_{\alpha'}$, where $\alpha = (n, l, m, \zeta)$ and $\alpha' = (n', l', m', \zeta')$. As a result of the use of the Perkins formula [20] for the function r_{ij}^u, where the radial part is expanded into the double series of the generalized Laguerre polynomials, the following expression for the two-electron integrals I_2 was obtained:

$$I_2 = (-1)^{M_1}\delta_{M_1,-M_2} \sum_{s=|M_1|}^{\min(L_1^u, L_1, L_2)} \tilde{\boldsymbol{U}}_s(1) \boldsymbol{S}_{u,s} \boldsymbol{U}_s(2), \tag{3}$$

where $M_i = m_i' - m_i$. The upper limit of the summation in (3) should be a minimum value among the three quantities: L_1^u which takes the value $u/2$ if u is even, and infinity if u is odd; L_i ($i = 1, 2$) — in dependence whether the orbitals in an i-th pair belong to the center A or B: if both the orbitals belong to the center A (the case $[AA]$) then $L_i = l_i + l_i'$, and in other cases ($[AB]$, $[BA]$ and $[BB]$) $L_i = \infty$.

Therefore, except the particular cases, the summation over the index s in Eq. (3) runs up to infinity.

The quantity $\boldsymbol{S}_{u,s}$ in Eq. (3) is a matrix with the elements being the coefficients of the above-mentioned expansion of the radial parts of the Perkins formula into the double series of the Laguerre polynomials. The values of those coefficients can be calculated by means of Eq. (31) in [18]. For a given u, the set of matrices with respect to the index s should be determined. For even u, the range of these matrices is equal to u; for other cases — infinity, but in practice it is approximated by a finite value assuming the computing accuracy desired. Moreover, the quantity $\boldsymbol{U}_s(i)$ in Eq. (3) is a vector with the following components:

$$U^{\nu}_{s\mu}(i) = N_i N'_i \int_0^{\infty} F_s(\alpha_i, \alpha'_i; r, R) L^{\nu}_{\mu}(r) \mathrm{d}r, \tag{4}$$

where $F_s(\alpha_i, \alpha'_i; r, R)$ is a function of the form dependent on the distribution of the Slater orbitals in the i-th pair with respect to the centers A and B (detailed expressions are given by Eqs. (23)–(26) in [18]); $L^{\nu}_{\mu}(r)$ are the generalized Laguerre polynomials of the range μ [21] with respect to the variable r, where ν is a constant, $\nu > -1$, and it may be treated as the parameter of the expansion; N_i and N'_i are the normalization factors for the radial part of the Slater orbitals in a given pair.

The numerical calculations based on Eq. (3) lead to the conclusion that the choice of the generalized Laguerre polynomials $L^{\nu}_{\mu}(ar)$ as the base functions, where a is a positive parameter, instead of $L^{\nu}_{\mu}(r)$ improves the numerical computations. In this case, we get the following expansion for the function r^k_{12}:

$$r^k_{12} = 4\pi \sum_{s=0}^{L^k_1} \sum_{m=-s}^{s} Y^{m^*}_s(\hat{r}_1) Y^m_s(\hat{r}_2) \sum_{\mu_1,\mu_2=0}^{L^k_3} s^{ks\nu}_{\mu_1\mu_2}(a,b) L^{\nu}_{\mu_1}(ar_1) L^{\nu}_{\mu_2}(br_2), \tag{5}$$

where $Y^m_s(\hat{r})$ are spherical harmonics [19]; L^k_1 and L^k_3 take infinite values for odd k, and values equal to $k/2$ and k, respectively, for even k. Moreover,

$$S^{ks\nu}_{\mu_1\mu_2}(a,b) = \frac{(ab)^{\nu+1}\mu_1!\mu_2!}{(\mu_1+\nu)!(\mu_2+\nu)!} \sum_{p_1=0}^{\min(\mu_1,k+\nu+1)} b^{\mu_1-p_1} \binom{k+\nu+1}{p_1}$$

$$\times \sum_{p_2=0}^{\min(\mu_2,k+\nu+1)} a^{\mu_2-p_2} \binom{k+\nu+1}{p_2} \frac{(-1)^{p_1+p_2}(q-1)!}{(\mu_1-p_1)!(\mu_2-p_2)!} \sum_{t=0}^{L^k_2} C_{kst}$$

$$\times \left[B(s+2t+\nu+\mu_1-p_1, q; a, b) + B(s+2t+\nu+\mu_2-p_2, q; b, a)\right]. \tag{6}$$

In the above expression, L^k_2 takes the values $(k+1)/2$ and $k/2-s$ for odd and even k, respectively, $q = k+2\nu+2+\mu_1-p_1+\mu_2-p_2$,

$$C_{kst} = \frac{1}{k+2}\binom{k+2}{2t+1} \prod_{j=0}^{\min(s-1,(k+1)/2)} \frac{2t-k-2j}{2t+1+2s-2j}, \tag{7}$$

and

$$B(n,m;a,b) = \int_0^1 \frac{x^n \mathrm{d}x}{(a+bx)^m} \tag{8}$$

is the integral computable by means of the following formula:

$$B(n,m;a,b) = \frac{n!}{(m-1)!}\sum_{i=0}^{\infty}\frac{(m-1+i)!b^i}{(n+1+i)!(a+b)^{m+i}}. \tag{9}$$

Because of the slow convergence of Eq. (9) for $a < b$, the integrals $B(n,m;a,b)$ can be evaluated by means of the following recurrences:

$$B(n,m;a,b) = \frac{1}{(m-1)a}\left[\frac{1}{(a+b)^{m-1}} + (m-n-2)B(n,m-1;a,b)\right], \tag{10}$$

$$B(n,m;a,b) = \frac{1}{(n+1)a}\left[\frac{1}{(a+b)^{m-1}} + b(m-n-2)B(n+1,m;a,b)\right], \tag{11}$$

$$B(n,m;a,b) = aB(n,m+1;a,b) + bB(n+1,m+1;a,b), \tag{12}$$

if the integrals of fixed initial values m and n are previously computed.

Taking into account the above expansion of the function r_{12}^k, we get the modified expression for the integral I_2:

$$I_2 = \delta_{M_1,-M_2}(-1)^{M_1}\sum_{s=|M_1|}^{\min(L_1^u,L_1,L_2)}\tilde{\boldsymbol{V}}_s(1,a)\boldsymbol{S}_{u,s}(a,b)\,\boldsymbol{V}_s(2,b), \tag{13}$$

where $\boldsymbol{S}_{u,s}(a,b)$ is the matrix with elements given by Eq. (6), and $\boldsymbol{V}_s(i,a)$ is a vector with the following components:

$$V_{s\mu}^{\nu}(i,a) = N_iN_i'\int_0^{\infty}F_s(\alpha_i,\alpha_i';r,R)L_{\mu}^{\nu}(ar)\mathrm{d}r. \tag{14}$$

In the case $[AA]$, the integration existing in Eq. (14) leads to the following results:

$$V_{s\mu}^{\nu}(i,a) = N_iN_i'\frac{q_i!}{d_i^{q_i+1}} \times\sum_{j=0}^{\min(\mu,q_i-\nu)}(-1)^j\binom{q_i-\nu}{j}\binom{q_i+\mu-\nu}{\mu-j}\left[\frac{d_i-a}{d_i}\right]^{\mu-j}, \tag{15}$$

if $\nu \le q_i$, and

$$V_{s\mu}^{\nu}(i,a) = N_iN_i'\frac{q_i!}{d_i^{q_i+1}} \times\sum_{j=0}^{\mu}(-1)^j\binom{\nu-q_i+j-1}{j}\binom{q_i+\mu-j}{q_i}\left[\frac{d_i-a}{d_i}\right]^{\mu-j}, \tag{16}$$

if $\nu > q_i$, where $q_i = n_i + n_i'$ and $d_i = \zeta_i + \zeta_i'$.

In the other cases ($[AB]$, $[BA]$ and $[BB]$), the integration domain should be divided into two ones: $0 \le r \le R$ and $R \le r \le \infty$, where R is the distance between the centers A and B. As it results from the explicit form of the function $F_s(\alpha_i,\alpha_i';r,R)$, the component $V_{s\mu}^{\nu}(i,a)$ of the vector $\boldsymbol{V}_s(i,a)$ is a linear combination of the integrals of the following type in the domain $0 \le r \le R$:

$$A(n,\rho,R) = \int_0^R r^n\mathrm{e}^{-\rho r}\mathrm{d}r, \tag{17}$$

where $\rho \geq 0$ and $n \geq 0$. In the interval $R \leq r \leq \infty$, it is a linear combination of the integrals of the type

$$E(n, \omega, R) = \int_R^\infty r^n \mathrm{e}^{-\omega r} \mathrm{d}r, \tag{18}$$

where $\omega > 0$, and n is an integer.

In order to illustrate the above discussion, the explicit expressions for the case $[AB]$ are given below. Using Eq. (24) in [18], we get

$$V_{s\mu}^{\nu}(i,a) = N_i N_i' (2s+1)^{1/2} \sum_{\lambda=|s-l|}^{s+l} C^s(\lambda, m'; l, m)$$

$$\times \sum_{p=0}^{n'} I(n, \lambda, p, \mu, \nu; \zeta, \zeta', R) g_{\lambda p}(n', l', m'; r, R), \tag{19}$$

where $C^s(\lambda, m'; l, m)$ are the Condon–Shortley parameters [19, 22], and

$$I(n, \lambda, p, \mu, \nu; \zeta, \zeta', R)$$

$$= \begin{cases} \displaystyle\sum_{f=0}^{\infty} c_{\lambda+p,f} \zeta'^{\lambda+2p+2f} \\ \times \displaystyle\sum_{k=0}^{\mu} t_{\mu k}^{\nu}(a) A(n+1+k+\lambda+2p+2f, \zeta, R) & \text{for } r \leq R, \\ (-1)^p \displaystyle\sum_{f=0}^{\lambda+p} s_{\lambda+p,f} \zeta'^{-\lambda-1+p} \\ \times \displaystyle\sum_{k=0}^{\mu} t_{\mu k}^{\nu}(a) E(n+1+k-\lambda-1, \zeta+\zeta', R) & \text{for } r \geq R, \end{cases} \tag{20}$$

$$c_{lf} = \frac{2^l (f+l)!}{(2f+2l+1)! f!}, \qquad s_{lf} = \frac{(2l-f)!}{2^{l-f}(l-f)! f!}, \tag{21}$$

and

$$t_{\mu k}^{\nu}(a) = \frac{(-a)^k}{k!} \binom{\mu+\nu}{\mu-k}. \tag{22}$$

The functions $g_{\lambda p}(n', l', m'; r, R)$, existing in Eq. (19), are defined by Eqs. (16)–(21) in [18]. For the cases $[BA]$ and $[BB]$, we get similar expressions using Eq. (25) and (26) in [18], respectively.

Taking into account the expansion (5) of the interelectron distance, we get the following form for the integral I_3:

$$I_3 = \delta_{M_1,-M_2-M_3}(-1)^{M_1}$$

$$\times \sum_{s_1=|M_1|}^{\min(L_1^u,L_1)} \sum_{s_3=|M_3|}^{\min(L_1^v,L_3)} \sum_{s_2=|s_1-s_3|}^{\min(s_1+s_3,L_2)} (2s_2+1)^{1/2} C^{s_2}(s_1,M_1;s_3,-M_3)$$

$$\times \tilde{\boldsymbol{V}}_{s_1}(1,a)\boldsymbol{S}_{u,s_1}(a,b)\boldsymbol{M}_{s_2}(2,b)\boldsymbol{S}_{v,s_3}(b,c)\boldsymbol{V}_{s_3}(3,c), \tag{23}$$

where — in comparison with the expression for I_2 — new quantities $\boldsymbol{M}_s(i,a)$ exist. $\boldsymbol{M}_s(i,a)$ are the matrices with the components defined by

$$M^{\nu}_{s\mu_1\mu_2}(i,a) = N_i N_i' \int_0^{\infty} F_s(\alpha_i,\alpha_i';r,R) L^{\nu}_{\mu_1}(ar) L^{\nu}_{\mu_2}(ar)\mathrm{d}r. \tag{24}$$

In the case $[AA]$, these components, for $q_i \leq \nu$, can be calculated as follows:

$$M^{\nu}_{s\mu_1\mu_2}(i,a) = N_i N_i' \frac{q_i!}{d_i^{q_i+1}} \sum_{j=0}^{\min(\mu_1,q_i-\nu)} (-1)^j \binom{q_i-\nu}{j} \binom{q_i+\mu_1-j}{q_i}$$

$$\times \sum_{l=0}^{\min(\mu_2,q_i-\nu)} (-1)^l \binom{q_i-\nu}{l} \sum_{k=0}^{\min(\mu_1-j,\mu_2-l)} \binom{\mu_1-j}{k}$$

$$\times \binom{q_i+\mu_1+\mu_2-j-l-k}{\mu_2-l-k} \left[\frac{2a-d_i}{d_i}\right]^k \left[\frac{d_i-a}{d_i}\right]^{\mu_1+\mu_2-j-l-2k}. \tag{25}$$

In the case $[AB]$, these components, similarly as those of the vector $V_s(i,a)$, are linear combinations of the integrals of the types $A(n,\rho,R)$ and $E(n,\omega,R)$. Computations of the integrals given by Eq. (24) are based on expressions being similar to Eqs. (19) and (20) with the difference consisting in existence of two Laguerre polynomials in Eq. (24) — in comparison with Eq. (14) where only one polynomial exists.

In final expressions for the integrals I_2 given by Eq. (13) and I_3 given by Eq. (23), the summation over indices s and s_1, s_3, respectively, runs, in general, up to infinity.

3. Numerical results and conclusions

Using Eqs. (13) and (23), a series of numerical calculations was performed. The results of those calculations are collected in Tabs. I–V. All the results were obtained under assumptions that all Slater orbitals are of the type $\phi_\alpha = 1s(\zeta)$ and the distance R between the centers A and B is equal to 2 a.u. The following convention of the integral notation is introduced here:

$$\left\langle \phi_{\alpha_1}\phi_{\alpha_2} \left| r_{12}^u \right| \phi_{\alpha_1'}\phi_{\alpha_2'} \right\rangle = \left(\phi_{\alpha_1}\phi_{\alpha_1'} \left| \phi_{\alpha_2}\phi_{\alpha_2'} \right| u\right), \tag{26}$$

$$\left\langle \phi_{\alpha_1}\phi_{\alpha_2}\phi_{\alpha_3} \left| r_{12}^u r_{23}^v \right| \phi_{\alpha_1'}\phi_{\alpha_2'}\phi_{\alpha_3'} \right\rangle = \left(\phi_{\alpha_1}\phi_{\alpha_1'} \left| \phi_{\alpha_2}\phi_{\alpha_2'} \right| \phi_{\alpha_3}\phi_{\alpha_3'} \right| u, v\right). \tag{27}$$

This convention makes it legible to refer the Slater orbitals in a pair to the centers A and/or B.

TABLE I

The convergence test for the integrals I_2 and I_3 with respect to the values of summation limits s in Eq. (13), and s_1, s_3 in Eq. (23), for fixed parameters: $\nu = 0$, $\mu_{\max} = 40$ and $a = b = 2.0$.

[a]	$(AB\|AB\|u)$		$(AB\|AA\|AB\|u,v)$	$(AB\|AB\|AB\|u,v)$
	$u=-1$		$u=-1,$	$v=-1$
$s=0$	0.1597872183	$s_1=s_3=0$	0.0991905375	0.0527307638
$s=1$	0.1804344442	$s_1=s_3=1$	0.1012922237	0.0603246175
$s=2$	0.1834601259	$s_1=s_3=2$	0.1014053984	0.0615301846
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$s=10$	0.1841562597	$s_1=s_3=10$	0.1014172123	0.0618254225
$s=11$	0.1841563819	$s_1=s_3=11$	0.1014172132	0.0618254753
$s=12$	0.1841564457	$s_1=s_3=12$	0.1014172133	0.0618255028
$s=13$	0.1841564905	$s_1=s_3=13$	0.1014172134	0.0618255176
$s=14$	0.1841565003	$s_1=s_3=14$	0.1014172134	0.0618255259
$s=15$	0.1841565120	$s_1=s_3=15$	0.1014172135	0.0618255303
Comparison values[b]	0.1841564571		0.1014171959	0.0618254269
	$u=1$		$u=1,$	$v=1$
$s=0$	0.9656207784	$s_1=s_3=0$	2.2922041292	1.4773595778
$s=1$	0.8565092404	$s_1=s_3=1$	2.3295279872	1.3275115772
$s=2$	0.8520000162	$s_1=s_3=2$	2.3296972670	1.3217790593
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$s=10$	0.8515400477	$s_1=s_3=10$	2.3297015417	1.3212239297
$s=11$	0.8515400406	$s_1=s_3=11$	2.3297015417	1.3212239215
$s=12$	0.8515400375	$s_1=s_3=12$	2.3297015417	1.3212239180
$s=13$	0.8515400369	$s_1=s_3=13$	2.3297015417	1.3212239163
$s=14$	0.8515400354	$s_1=s_3=14$	2.3297015417	1.3212239155
$s=15$	0.8515400351	$s_1=s_3=15$	2.3297015417	1.3212239150
Comparison values[b]	0.8515400349		2.3297015417	1.3212239146

[a] All the Slater orbitals are of the type $1s$ with $\zeta = 1.0$.

[b] The integral values obtained on the basis of the algorithm defined in [15, 16].

In general, the expressions for evaluating the integrals I_2 and I_3 depend on some parameters regarding the expansion of the function r_{12}^k. They are the summation limits of s, μ_1 and μ_2 in Eq. (5), running to infinity for odd k, the order ν of the Laguerre polynomials, as well as the expansion constants a and b. In practice, the upper limit for values μ_1 and μ_2 is fixed as a value $\mu_{\max}$ determining the range of the matrix $\boldsymbol{S}_{k,s}(a,b)$ with elements given by Eq. (6).

TABLE II

The values of the two-center integrals I_2 for different values of the expansion parameter ν, and fixed parameters: $\mu_{\max} = 40$, $s_{\max} = 15$, and $a = b = 2.0$.

[a]	$(AA\|AB\|u)$	$(AA\|BB\|u)$	$(AB\|AB\|u)$
	$u = -1$		
$\nu = 0$	0.3080364658	0.425974292	0.184156
$\nu = 1$	0.308036465	0.425974292	0.184156
$\nu = 2$	0.308036465	0.42597429	0.18415
$\nu = 3$	0.308036	0.4259	0.18415
$\nu = 5$	0.308	0.425	0.184
Comparison values[b]	0.3080364658	0.4259742928	0.1841564571
	$u = 1$		
$\nu = 0$	1.4776890110	2.919487504	0.85154003
$\nu = 1$	1.477689011	2.919487504	0.8515400
$\nu = 2$	1.477689011	2.91948750	0.8515400
$\nu = 3$	1.477689	2.91948	0.85154
$\nu = 5$	1.4776	2.9194	0.8515
Comparison values[b]	1.4776890110	2.9194875040	0.8515400349

[a], [b] See footnotes at Tab. I.

Assuming some fixed values for the parameters other than s, s_1 and s_3, we get numerical results for the integrals I_2 and I_3, as it is shown in Tab. I with respect to increasing values of the summation index s in Eq. (13), and s_1, s_3 in Eq. (23). The so-called comparison values are the computation results obtained by means of the method presented in [15, 16], based on the Neumann expansion. In our opinion, they are rather accurate. As it is seen, the convergence is rather slow and the obtained results have only 5–7 exact significant digits for some integrals.

To investigate the influence of the parameter ν on the convergence of the expression (13), the computation for its different values were performed. The results are presented in Tab. II. As it can be seen, the best results are obtained for $\nu = 0$; the increase in that parameter over the value 2 leads to essential worsening of the convergence of Eq. (13).

TABLE III

The influence of parameters a and b on the computing accuracy for the integrals I_2 with fixed parameters: $\gamma_1 = 1.3$, $\gamma_2 = 0.8$, $\nu = 0$, $\mu_{\max} = 40$ and $s_{\max} = 15$.

[a]	$(AA\|AB\|u)$	$(AA\|BB\|u)$	$(AB\|AB\|u)$
$u = -1$			
$a = 0.2,\ b = 0.1$	0.26	0.27	0.205
$a = 1.0,\ b = 0.6$	0.2616447405	0.271926791	0.205031
$a = 1.3,\ b = 0.8$	0.2616447405	0.2719267917	0.2050318
$a = 1.5,\ b = 1.0$	0.2616447405	0.2719267917	0.205031
$a = 2.2,\ b = 1.5$	0.261	0.271	0.205
$a = 3.0,\ b = 2.0$	not convergent		
Comparison values[b]	0.2616447405	0.2719267917	0.2050318
$u = 1$			
$a = 0.2,\ b = 0.1$	4.2575	4.9099	3.311
$a = 1.0,\ b = 0.6$	4.2575101498	4.9099900977	3.3115325
$a = 1.3,\ b = 0.8$	4.2575101498	4.9099900977	3.3115325
$a = 1.5,\ b = 1.0$	4.2575101498	4.9099900977	3.3115325
$a = 2.2,\ b = 1.5$	4.2575101	4.90999009	3.311532
$a = 3.0,\ b = 2.0$	not convergent		
Comparison values[b]	4.2575101498	4.9099900977	3.31153255

[a] All the Slater orbitals are of the type $1s$ with $\zeta_1 = \zeta_1' = 0.65$ and $\zeta_2 = \zeta_2' = 0.4$.
[b] See footnote at Tab. I.

There is a strong influence of the parameters a and b on the convergence of Eq. (13) with regard to values of the Slater-orbital exponents ζ and the distance R. A convenient measure of the influence is the parameter γ defined as follows:

$$\gamma_i = R(\zeta_i + \zeta_i')/2, \tag{28}$$

where ζ_i and ζ_i' are the Slater-orbital exponents in the i-th pair. The computation results for the integrals I_2 for the fixed value $\gamma_1 = 1.3, \gamma_2 = 0.8$ and variable values of a and b, are presented in Tab. III. As it is seen, the computing accuracy increases according to the decrease in the difference between values of the parameters γ_1 and a; γ_2 and b. The optimum case takes place for $\gamma_1 \approx a$ and $\gamma_2 \approx b$, but expression (13) is divergent for $a \gg \gamma_1$ or/and $b \gg \gamma_2$. Similar conclusions concern Eq. (23) for the integrals I_3.

TABLE IV

The values of the two-center integrals I_2 for different values of $\mu_{\max}$, and fixed parameters $\nu = 0$, $\gamma_1 = \gamma_2 = 2.0$, $s_{\max} = 15$ and $a = b = 2.0$.

[a]	$(AA\|AB\|u)$	$(AA\|BB\|u)$	$(AB\|AB\|u)$
	$u = -1$		
$\mu_{\max} = 10$	0.308036	0.4259	0.184
$\mu_{\max} = 20$	0.30803646	0.425974	0.1841
$\mu_{\max} = 30$	0.3080364658	0.425974292	0.184156
$\mu_{\max} = 40$	0.3080364658	0.4259742928	0.184156
Comparison values[b]	0.3080364658	0.4259742928	0.1841564571
	$u = 1$		
$\mu_{\max} = 10$	1.4776890	2.91948	0.8515
$\mu_{\max} = 20$	1.477689011	2.91948750	0.85154
$\mu_{\max} = 30$	1.4776890110	2.9194875040	0.85154003
$\mu_{\max} = 40$	1.4776890110	2.9194875040	0.851540034
Comparison values[b]	1.4776890110	2.9194875040	0.8515400349

[a], [b] See footnotes at Tab. I.

The influence of the range μ of the matrices $\boldsymbol{S}_{k,s}(a,b)$ on the integral values is illustrated in Tabs. IV and V for the integrals I_2 and I_3, respectively. In general, there is a strong influence of the parameter $\mu_{\max}$ on the computation accuracy which increases as the $\mu_{\max}$-value increases.

Numerical algorithm of computing two-center two- and three-electron integrals, defined in [18] and modified in this paper by taking into account the correction resulting from introducing the scaling factors a and b in the expansion of the radial part of the Perkins expression for the interelectron distance function r_{12}^k into double series of Laguerre polynomials, was tested. This algorithm is a new proposition in relation to that defined in [15, 16] and based on the Neumann expansion for r_{12}^k. The comparison of the numerical results obtained in this work with those obtained previously [15, 16] allows to verify numerical values of the integrals discussed. The comparison of the results obtained by both methods confirms the correctness of the algorithm verified in the present paper.

TABLE V

The values of the two-center integrals I_3 for different values of μ_{max} and fixed parameters: $\nu = 0$, $\gamma_1 = \gamma_2 = \gamma_3 = 2.0$, $s_{max} = 15$ and $a = b = c = 2.0$.

[a]	$(AA\|AA\|AA\|u,v)$	$(AA\|AA\|AB\|u,v)$	$(AA\|AB\|AB\|u,v)$	$(AB\|AB\|AB\|u,v)$
	$u=-1,\ v=-1$			
$\mu_{max}=10$	0.4259	0.2046	0.10	0.06
$\mu_{max}=20$	0.4259259259	0.204649	0.10303	0.061
$\mu_{max}=30$	0.4259259259	0.204649682	0.103030	0.0618
$\mu_{max}=40$	0.4259259259	0.2046496820	0.1030305	0.061825
Comparison values[b]	0.4259259259	0.2046496820	0.1030305895	0.0618254269
	$u=-1,\ v=1$			
$\mu_{max}=10$	1.25810	0.868534	0.41994	0.250
$\mu_{max}=20$	1.2581018518	0.868534469	0.4199423	0.2502
$\mu_{max}=30$	1.2581018518	0.8685344697	0.41994235	0.250209
$\mu_{max}=40$	1.2581018518	0.8685344697	0.419942357	0.2502097
Comparison values[b]	1.2581018518	0.8685344697	0.4199423573	0.2502097521
	$u=1,\ v=1$			
$\mu_{max}=10$	5.193287	3.442778	2.28740	1.32122
$\mu_{max}=20$	5.1932870370	3.4427785	2.287406	1.321223
$\mu_{max}=30$	5.1932870370	3.4427785891	2.28740687	1.3212239
$\mu_{max}=40$	5.1932870370	3.4427785891	2.287406876	1.321223914
Comparison values[b]	5.1932870370	3.4427785891	2.2874068760	1.3212239146

[a], [b] See footnotes at Tab. I.

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