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Formulas and numerical table for the radial part of overlap integrals with the same screening parameters of Slater-type orbitals

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Abstract. The numerical properties of the radial part of overlap integrals with the same screening parameters in the form of polynomials in $p = \xi R$ over Slater-type orbitals have been studied and obtained by using three different methods. For that purpose, the characteristics of auxiliary functions were used first, then Fourier transform convolution theorem, and recurrence relations for the basic coefficients of $A^s_{nl\lambda,n'l'\lambda}$ were used. The calculations of the radial part of overlap integrals with the same screening parameters were made in the range $1 \le n \le 75$, $1 \le n' \le 75$, and $10^{-6} \le p$.

Key words: The radial parts of overlap integrals with the same screening parameters – Gegenbauer coefficients – Recursion relations

1 Introduction

As is well known, the quantity known as the overlap integral is of considerable importance in the theory of molecular structure. An extensive collection of formulas for the evaluation of these integrals has been provided by Coulson [1] and Roothaan [2], who derived them by employing elliptical coordinates. Computer programs exist [3] that successfully implement this approach. Numerical tables and auxiliary functions for these integrals have been calculated by Mulliken et al. [4] and Kotani et al. [5], and Todd and et al. [6] gave a general overlap formula based on the technique of the Fourier transform and the theory of residues.

In order to evaluate overlap integrals, it is necessary first the specify the forms of the atomic orbitals (AOs). In quantum mechanical calculations of the electronic structure of molecules one has to evaluate overlap integrals over exponential-type orbitals (ETOs) accurately and efficiently. These integrals arise not only for Hartree–Fock–Roothaan equations for molecules, but are also central to the calculation of arbitrary multicenter integrals based on the series expansion formulas for ETOs about a new center. Some kind of ETOs, called B functions, in which radial parts are reduced to Bessel functions have been studied in Refs. [7, 8, 9, 10, 11, 12, 13] for the evaluation of overlap integrals.

One of the well-known ETOs are Slater-type orbitals (STOs), which are of fundamental importance in the study of various properties for molecules. STOs model the radial part of exact hydrogen-like AOs quite accurately but lead to difficulties in the evaluation of many-center integrals. To overcome this problem, Boys [14] introduced Gaussian-type orbitals (GTOs). GTOs suffer from their unphysical behavior close to and far from the nucleus. STOs are still used in most semiempirical methods, usually as minimal valence sets, sometimes including d functions [15]. In ab initio theory, GTOs are now widely established, except for atomic ab initio calculations, which often employ STO bases [16, 17, 18] and some benchmark STO calculations on small molecules [19, 20, 21, 22]. A comparison of STO and GTO bases needs about twice the size of a STO basis to obtain comparable accuracy [20, 21]; thus, STOs bases are still very attractive.

Some classical work on one-electron integrals (overlap, kinetic energy, nuclear attraction, and electron repulsion) over STOs can be found in Refs. [23, 24, 25, 26]. A variety of approaches for the evaluation of molecular two-electron multicenter integrals in STO bases also exists, for example, one-center expansions [27, 28, 29], recurrence schemes [30], integral transformation methods [31, 32], and other methods [22, 33].

It is known that in the Hartree–Fock–Roothaan approximation all the one- and two-center integrals (overlap, kinetic energy, and nuclear attraction) are expressed in terms of overlap integrals [24]. These integrals are in the form of infinite series of which limitations depend on quantum numbers. Although there is no limitation for one-center integrals in quantum numbers, in two-center integrals there is a limit in the values of the quantum numbers and in these integrals the accuracy is slightly lower than in the one-center integrals [30].

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It is well known that the existing literature [27, 30, 33, 34, 35, 36] contains a number of formulas for overlap integrals over STOs which are not satisfactory for large quantum numbers. Dealing with large quantum numbers of overlap integrals with the same screening parameters is unavoidable, especially in the approach based on the expansion of STOs in terms of STOs at a displaced center and on the relations for the expansions of one- and two-center charge densities over STOs at a new origin [33].

In Ref. [37], the general formula for overlap integrals with the same screening parameters of STOs was obtained by using Fourier transform convolution theorem. In Ref. [38], this formula was used to calculate overlap integrals on a computer in the range of $1 \le n \le 30$ and $1 \le n' \le 30$. In the case of quantum numbers above 30, it has been observed that precision fails owing to numerical errors in the coefficients $G^{NLM}_{nlm,n'l'm'}$ employed in the calculation of the overlap integrals with the same screening parameters.

It should be mentioned that overlap integrals between STOs with equal screening constants play an important role for evaluating multicenter integrals based on the expansion of STOs about a new center. The overlap integrals with the same screening parameters in the molecular coordinate system (non-lined-up coordinate systems) have the form

$$S_{nlm,n'l'm'}(\vec{p}) = \int \chi^*_{nlm}(\zeta, \vec{r}_a)\chi_{n'l'm'}(\zeta, \vec{r}_b)\mathrm{d}v \ . \tag{1}$$

Performing the angular part of the overlap integral leads to only one term, because of the orthogonality of the spherical harmonics. By carrying out the radial integration with the same screening parameters, Eq. (1) becomes [39]

$$S_{nlm,n'l'm'}(p, \theta = 0, \phi = 0) = \delta_{mm'} S_{nl\lambda,n'l'\lambda}(p) = \mathrm{e}^{-p} \sum_{s=0}^{n+n'} A^s_{nl\lambda,n'l'\lambda} p^s \ , \tag{2}$$

where $\lambda = |m| = |m'|$ and

$$A^s_{nl\lambda,n'l'\lambda} = \frac{a^s_{nl\lambda,n'l'\lambda}}{\sqrt{(2n)!(2n')!}} \ .$$

This integral corresponds to normalized real STOs.

In this study, we are dealing with the radial part of overlap integrals with the same screening parameters in the form of polynomials in $p = \xi R$. In Ref. [39], using the characteristics of auxiliary functions, general formulas were established for the coefficients $a^s_{nl\lambda,n'l'\lambda}$ by using nonnormalized real STOs. In the first sections of this article we introduce these expressions and for the calculations of $A^s_{nl\lambda,n'l'\lambda}$ some modifications were used. In Sect. 2.2, the coefficients $A^s_{nl\lambda,n'l'\lambda}$ are derived in terms of the Gaunt, the Gegenbauer, and the expansion coefficients by using equations given in Refs. [37, 38] for overlap integrals. Section 2.3. is devoted to a new homogeneous recurrence formula and analytical expressions for the coefficients of $A^s_{nl\lambda,n'l'\lambda}$ are derived. The new algorithm for the calculation of the radial part of overlap integrals with the same screening parameters over STOs is based on recurrence relations for the basic coefficients of $A^s_{nl\lambda,n'l'\lambda}$.

We therefore want to demonstrate in this article how the formulas for the $A^s_{nl\lambda,n'l'\lambda}$ coefficient can be used for the calculation of the radial part of overlap integrals. We shall show that the representations known so far for the Fourier-convolution transform techniques are indeed sufficient for a satisfactory calculation of these integrals. We shall do this by analyzing the merits and limitations of the computational algorithms we use and by comparing them critically with our algorithms that were for the following three cases.

2 Calculations the radial part of the overlap integrals between real STOs with the same screening parameters

2.1 The expression for $A^s_{nl\lambda,n'l'\lambda}$ in terms of auxiliary functions

In Ref. [39], the following explicit expression for the radial part of overlap integrals between real STOs with the same screening parameters is given in the form of polynomials in the parameters $p = \xi R$ by using the characteristics of the auxiliary functions:

$$S_{nl\lambda,n'l'\lambda}(p,0) = (-1)^{l'-\lambda} \bar{N}_{nn'}(p,0) \times \sum_{\alpha=-\lambda}^{l} \sum_{\beta=\lambda}^{l'} \sum_{q=0}^{\alpha+\beta} g^q_{\alpha\beta} Q^q_{n-\alpha,n'-\beta}(p,0) \ , \tag{3}$$

where

$$\bar{N}_{nn'}(p,0) = p^{n+n'+1} \ ,$$

$$Q^q_{nn'}(p,0) = \sum_{m=0}^{n+n'} F_m(n,n') A_{n+n'+q-m}(p) B_{q+m}(0) \ .$$

Here A_k and B_k are the well-known auxiliary functions:

$$B_k(0) = \frac{1 + (-1)^k}{k+1} \ ,$$

$$A_k(p) = \int_1^\infty \mu^k \mathrm{e}^{-p\mu} \mathrm{d}\mu \ .$$

In the same reference, the following formula for the coefficients $A^s_{nl\lambda,n'l'\lambda}$ is evaluated, for $s = 0$,

$$A^0_{nl\lambda,n'l'\lambda} = (-1)^{l'-\lambda} \frac{(n+n')!}{\sqrt{(2n)!(2n')!}} \delta_{ll'} \ , \tag{4}$$

and

$$A^s_{nl\lambda,\,n'l'\lambda} = (-1)^{l'-\lambda} \frac{(n+n'-s)!}{\sqrt{(2n)!(2n')!}} \sum_{\alpha=-\lambda}^{l} \sum_{\beta=\lambda}^{l'} \sum_{q=0}^{\alpha+\beta n} \sum_{k=0}^{-\alpha+n'-\beta} g^q_{\alpha\beta}(l\lambda, l'\lambda) \frac{1 + (-1)^{q+k}}{q+k+1} \times F_k(n-\alpha, n'-\beta) F_{s-(\alpha+\beta-q+k)}(n-\alpha+n'-\beta+q-k, 0), \quad \text{for } s \ge 1 \tag{5}$$

where

$$g^{q}_{\alpha\beta}(l\lambda, l'\lambda) = g^{0}_{\alpha\beta}(l\lambda, l'\lambda)F_q(\alpha+\lambda, \beta-\lambda) \ . \tag{6}$$

The exact definitions of the quantities $g^{0}_{\alpha\beta}(l\lambda,\ l'\lambda)$ and $F_k(n,\ m)$ appearing in Eq. (6) were defined in Ref. [40]. These quantities can be rewritten in terms of binomial coefficients, $F_s(n)$, in the following forms:

$$F_m(N, N') = \sum_{k=0}^{N'} (-1)^k F_{m-k}(N)F_k(N') \ , \tag{7}$$

where

$$E(n/2) = \frac{n}{2} - \frac{1-(-1)^n}{4},$$

$$k = E\left(\frac{n-l}{2}\right) + E\left(\frac{n'-l'}{2}\right) + E\left(\frac{N-L}{2}\right),$$

$$b_{i,j} = \sum_{m=0}^{j+1} (-1)^m 2^{2j+1-2m} F_m(j+1)F_{i+m}[2(i+m)-1] \ ,$$

$$g^{0}_{\alpha\beta}(l\lambda,\ l'\lambda) = \frac{(-1)^{\frac{1}{2}(l-\alpha)+\frac{1}{2}(l'-\beta)-\lambda}}{2^{l+l'+1}} \left((2l+1)(2l'+1)\frac{F_l(l+\lambda)F_{l'}(l'+\lambda)}{F_\lambda(l)F_\lambda(l')}\right)^{1/2}$$
$$\times F_{l'+\lambda}(l'+\beta)F_{\frac{1}{2}(l'-\beta)}(l') \sum_{i=0,2,4,\ldots}^{2\lambda} (-1)^{i/2} F_i(\lambda,\ \lambda)F_{\frac{1}{2}(l-\alpha)-\lambda+i/2}(l)F_{l+\lambda}(l+\alpha+2\lambda-i) \ . \tag{8}$$

2.2 The expression for $A^{s}_{nl\lambda,n'l'\lambda}$ by using the Fourier transform convolution theorem

In Ref. [38], using the Fourier transform convolution theorem, general formulas were established for the overlap integrals with the same screening parameters of STOs. We Insert $\theta = \phi = 0$ into Eq. (3) in Ref. [38] and then in order to illustrate the previous statements we compare two different representations (obtained equation from Ref. [38] and Eq. 2 in this study) for $A^{s}_{nl\lambda,n'l'\lambda}$:

$$A^{s}_{nl\lambda,n'l'\lambda} = \frac{2^{s+1}}{\sqrt{(2s+2)!}} \sum_{L=|l-l'|}^{l+l'} (-1)^{(l-l'-L)/2}(2L+1)C^{L}(l\lambda, l'\lambda)$$
$$\times \sum_{N=L+1}^{n+n'+1} \Omega^{L}_{s+1N}(n+n'+1)K^{NL}_{nl,n'l'} \ , \tag{9}$$

where $C_L(l\lambda,\ l'\lambda)$ is the Gaunt coefficients, and the expansion coefficients for the translation of STOs from one center to another are defined as follows from Ref. [41]:

$$\Omega^{L}_{nn'}(Z) = \sum_{k=\max(n,n')}^{Z} w^{L}_{kn} w^{L}_{kn'} \ ,$$

where

$$w^{L}_{nk} = (-1)^{k+L+1}\left[F_{k+L+1}(n+L+1)\right.$$
$$\left.\times F_{k-L-1}(n-L-1)F_{k-L-1}(2k)\right]^{1/2} \ .$$

The other coefficient in Eq. (9) has the following form [38]:

$$K^{NL}_{nl,n'l'} = \left(F_l(n)F_{l'}(n')F_L(N)\sqrt{F_n(2n)F_{n'}(2n')F_N(2N)}\right)^{-1}$$
$$\times \sum_{s=0}^{k} (-1)^s a_s(l+1, n-l; l'+1, n'-l'; L+1, N-L) b_{n+n'+N+1-g-s,g} \ , \tag{10}$$

$$a_s(\alpha, n; \alpha', n'; \alpha'', n'')$$
$$= \sum_{m=0}^{E(n/2)} \sum_{j=0}^{E(n'/2)} a_m(\alpha, n)a_j(\alpha', n')a_{s-m-j}(\alpha'', n'') \ , \tag{11}$$

where $a_{\mathrm{m}}(\alpha,n)$ are Gegenbauer coefficients [37] with

$$a_m(\alpha, n) = F_{\alpha-1}(\alpha-1+n-m)F_m(n-m) \ .$$

For special values of s and L, Eq. (9) gives the following properties:

$$\sum_{N'=1}^{n'} \left(\sqrt{\frac{n'}{2(2n'-1)}}\Omega^{0}_{NN'}(n')K^{N'0}_{00,n'-10} - \Omega^{0}_{NN'}(n'+1)K^{N'0}_{00,n'0}\right)$$
$$= \Omega^{0}_{Nn'+1}(n'+1)K^{n'+10}_{00,n'0}, \quad \text{for } n' \geq 1 \ , \tag{12}$$

$$\sum_{N'=1}^{n'+1} \Omega^{0}_{n'+1N'}(n'+1)K^{n'+10}_{00,n'0} = \sqrt{\frac{2n'+1}{2n'+2}} \ . \tag{13}$$

We use the recurrence relations for the Gegenbauer polynomials [42],

$$2\alpha\left(x^2-1\right)C^{\alpha+1}_{n-1}(x) = nxC^{\alpha}_{n}(x) - (2\alpha+n-1)C^{\alpha}_{n-1}(x) \ ,$$

and the relation

$$C^{\alpha}_{n}(x) = \sum_{s=0}^{E\left(\frac{n}{2}\right)} (-1)^s a_s(\alpha, n)(2x)^{n-2s} \ .$$

Then we obtain the following relation properties satisfied by Gegenbauer coefficients:

$$\sum_{s=0}^{E\left(\frac{n-1}{2}\right)}(-1)^s 2^{n-2s}\left(a_s(\alpha,n-1)-\frac{2n}{2\alpha+n-1}a_s(\alpha,n)\right)$$
$$=(-1)^{E\left(\frac{n}{2}\right)}\frac{2n}{2\alpha+n-1}2^{n-2E\left(\frac{n}{2}\right)}\left[E\left(\frac{n}{2}\right)-E\left(\frac{n-1}{2}\right)\right]$$
$$\times a_{E\left(\frac{n}{2}\right)}(\alpha,n)\ . \quad (14)$$

The symmetry properties satisfied by Gegenbauer coefficients are given in Ref. [38] in the following forms:

$$a_s(\alpha,n;\alpha',n')=a_s(\alpha',n';\alpha,n)=\sum_{j=0}^{E\left(\frac{n}{2}\right)}a_j(\alpha,n)a_{s-j}(\alpha',n'),$$
$$a_s(\alpha,n;\alpha',n';\alpha'',n'')=a_s(\alpha',n';\alpha,n;\alpha'',n'')=a_s(\alpha,n;\alpha'',n'';\alpha',n')$$
$$=a_s(\alpha'',n'';\alpha',n';\alpha,n)=\sum_{m=0}^{E\left(\frac{n}{2}\right)}a_m(\alpha,n)a_{s-m}(\alpha',n';\alpha'',n'')\ . \quad (15)$$

2.3 Recurrence relations for $A^s_{nl\lambda,n'l'\lambda}$

In order to derive the expression for Eq. (1) in terms of the basic coefficient $A^s_{nl\lambda,n'l'\lambda}$ we use Eqs. (1), (14), and (15) of Ref. [43] for the translation of spherical harmonics centered on the nucleus a. Then using the expansion formula for the product of two spherical harmonics both with the same center [40], it is easy to show that the overlap integrals with respect to lined-up coordinate systems are expressed through the basic coefficient $A^s_{nl\lambda,n'l'\lambda}$. If the analytical structures of the overlap integrals are analyzed, it becomes obvious that $A^s_{nl\lambda,n'l'\lambda}$ are best expressed in terms of Gaunt coefficients and $A^s_{n-l00,n'+l'L0}$:

$$A^s_{nl\lambda,n'l'\lambda}=\left(\frac{F_{2n'}(2n'+2l)}{F_{2n-2l}(2n)}\right)^{1/2}$$
$$\times\sum_{L=|l'-l|}^{l'+l}\sqrt{2L+1}C^L(l'\lambda,l\lambda)A^s_{n-l00,n'+lL0}\ . \quad (16)$$

For lowering the indices l' of the basic coefficients $A^s_{nl\lambda,n'l'\lambda}$ we use in Eq. (1) the recurrence relations for the normalized associated Legendre functions [42] and the relations $R=z_a-z_b$ in the lined-up coordinate systems. Then we obtain

$$A^s_{n,n'l'}=-\frac{a_{l'-1}}{4}\left[\frac{4}{\sqrt{2n'(2n'-1)}}A^{s-1}_{n,n'-1l'-1}+\sqrt{(2n'+1)(2n'+2)}A^{s+1}_{n,n'+1l'-1}\right.$$
$$\left.-\left(\frac{(2n+1)(2n+2)(2n+3)(n+2)}{n'(2n'-1)}\right)^{1/2}A^{s+1}_{n+2,n'-1l'-1}\right]-b_{l'-1}A^s_{n,n'L'-2}\ , \quad (17)$$

where $n\geq l$, $n'\geq l'+1$, $l'\geq 1$, $t=0$ and the coefficients a_l and b_l are determined by following equations:

$$a_l=\left(\frac{(l+1)^2}{(2l+1)(2l+3)}\right)^{1/2},\quad b_l=\left(\frac{l^2}{(2l-1)(2l+1)}\right)^{1/2}$$

Equation (17) allow us to express $A^s_{n,n'l'}\equiv A^s_{n00,n'l'0}$ in terms of the coefficients $A^s_{nn'}\equiv A^s_{n00,n'00}$ for the calculations of which can use the following recurrence relations.

$$A^s_{nn'}=\frac{(n+n'-s)!}{\sqrt{(2n)!(2n')!}}\sum_{k=0,2,4,\ldots}^{n+n'}\frac{F_k(n,n')F_{s-k}(n+n'-k,0)}{k+1}$$
$$=\frac{2^{s+1}}{\sqrt{(2s+2)!}}\sum_{N=1}^{n+n'}\Omega^0_{s+1N}(n+n'+1)K^{N0}_{n0,n'0}$$
$$=\left(\frac{n(2n'+1)}{(2n-1)(n'+1)}\right)^{1/2}A^s_{n-1,N2+1}$$
$$-\left(\frac{n(n-1)(2n'+1)}{2(2n-1)(2n-3)(n'+1)}\right)^{1/2}A^s_{n-2,n'+1}$$
$$+\left(\frac{n'}{2(2n'-1)}\right)^{1/2}A^s_{n,n'-1},\quad \text{for}\quad s\neq n+n'$$
$$=\left(\frac{n(2n'+1)}{(2n-1)(n'+1)}\right)^{1/2}A^{n+n'}_{n-1,n'+1},\ \text{for}\ s=n+n'\ , \quad (18)$$

$$A^{n'}_{0,n'}=0\ , \quad (19)$$

$$A^0_{nn'}=\frac{(n+n')!}{\sqrt{(2n)!(2n')!}}=\delta_{nn'}\ , \quad (20)$$

$$A^{n'-1}_{0,n'}=\left(\frac{2(2n'+1)}{(2n')!(n'+1)}\right)^{1/2}2^{n'-1}\quad \text{for}\ s=n'-1\ , \quad (21)$$

$$A^s_{0,n'}=\left(\frac{n'}{2(2n'-1)}\right)^{1/2}A^s_{0,n'-1}\quad \text{for}\ s\neq n'-1\ , \quad (22)$$

$$A^0_{n+2,n'-1l'-1}=\left(\frac{n'(2n'+1)(2n'+2)(2n'-1)}{(2n+1)(2n+2)(2n+3)(n+2)}\right)^{1/2}$$
$$\times A^0_{n,n'+1l'-1}\ . \quad (23)$$

The symmetry property is

$$A^s_{nl\lambda,n'l'\lambda'}=A^s_{n'l'\lambda',nl\lambda}\ . \quad (24)$$

3 Numerical results and discussion

3.1 The calculation method of the case in Sect. 2.1

To calculate the coefficient $A^s_{nl\lambda,n'l'\lambda}$ by using Eq. (5), it is necessary to know the values of the quantities $g^q_{\alpha\beta}(l\lambda,l'\lambda)$, which are given by Eq. (8) in terms of binomial coefficients. The quantities $g^q_{\alpha\beta}(l\lambda,l'\lambda)$ calculated from Eq. (8) are checked for their accuracy using Table 1 in Ref. [40]. In this comparison, perfect matching is obtained.

Table 1. The radial part of overlap integrals with the same screening parameters over Slater-type orbitals by using the characteristics of auxiliary functions (case 2.1), Fourier transform convolution theorem (case 2.2), and recurrence relations (case 2.3)

n	l	n'	l'	λ	p	$S_{nl\lambda,n'l'\lambda}(p)$ (case 2.1)	Computation time (ms)	$S_{nl\lambda,n'l'\lambda}(p)$ (case 2.2)	Computation time (ms)	$S_{nl\lambda,n'l'\lambda}(p)$ (case 2.3)	Computation time (ms)
4	2	3	2	1	25	$-5.65554471492814 \times 10^{-6}$	0.05	$-5.65554471492814 \times 10^{-6}$	0.05	$-5.65554471492814 \times 10^{-6}$	0.06
15	4	8	4	4	25	$2.5432413255908 \times 10^{-3}$	2.14	$2.5432413255908 \times 10^{-3}$	17.2	$2.5432413255908 \times 10^{-3}$	3.37
18	10	18	17	9	20	$-1.14908693234024 \times 10^{-2}$	7.75	$-1.14908693234024 \times 10^{-2}$	23.1	$-1.14908693234024 \times 10^{-2}$	7.19
25	12	20	17	11	30	$4.88129714016814 \times 10^{-2}$	35.45	$4.88129714016814 \times 10^{-2}$	51.23	$4.88129714016814 \times 10^{-2}$	22.10
30	15	29	10	8	50	$7.36659173237904 \times 10^{-2}$	35.01	$7.36659173237928 \times 10^{-2}$	130.18	$7.36659173237904 \times 10^{-2}$	21.45
34	14	34	12	10	75	$1.30016393590254 \times 10^{-4}$	38.49	$1.30016393591412 \times 10^{-4}$	178.49	$1.30016393590254 \times 10^{-4}$	24.32
40	29	40	15	15	15	$-6.64155436544458 \times 10^{-8}$	55.32	$-6.64155436545368 \times 10^{-8}$	215.34	$-6.64155436544458 \times 10^{-8}$	44.13
45	29	44	19	17	0.05	$-2.43613669445413 \times 10^{-9}$	302.5	$-5.10576631624786 \times 10^{-4}$	489.5	$-5.10576631675415 \times 10^{-4}$	122.18
48	8	15	3	3	100	$1.79326013046144 \times 10^{-7}$	14.8	$1.79326045879356 \times 10^{-7}$	156.47	$1.79326013046145 \times 10^{-7}$	16.25
50	15	15	13	11	10	$2.90100707205548 \times 10^{-4}$	333.3	$2.90100718467305 \times 10^{-4}$	658.6	$2.90100707205215 \times 10^{-4}$	137.4
50	17	25	15	13	10	$2.67465650120479 \times 10^{-2}$	443	$2.67465651798350 \times 10^{-2}$	840.51	$2.67465650120232 \times 10^{-2}$	214.2
50	17	35	17	16	25	$-1.22862346230359 \times 10^{-1}$	321.7	$-1.22862344027641 \times 10^{-1}$	872.2	$-1.22862346230312 \times 10^{-1}$	158.3
50	17	50	17	15	5	$7.91990104680712 \times 10^{-1}$	206.5	$7.91990100458219 \times 10^{-1}$	896.4	$7.91990104687359 \times 10^{-1}$	112.5
55	20	52	23	20	35	$-1.78167728016801 \times 10^{-2}$	28.3	$-1.78167465716549 \times 10^{-2}$	914.1	$-1.78167728016314 \times 10^{-2}$	15.4
60	14	52	17	12	35	$-7.50777781140254 \times 10^{-2}$	345.5	$-7.50777458731568 \times 10^{-2}$	957	$-7.50777781146405 \times 10^{-2}$	218.4
62	19	52	17	15	10	$3.16515414847652 \times 10^{-1}$	81.7	$3.16515589021751 \times 10^{-1}$	964.3	$3.16515414845183 \times 10^{-1}$	68.4
65	24	65	20	18	0.01	$-1.26130790350518 \times 10^{-10}$	539.1	$-1.26131576901648 \times 10^{-10}$	1012.1	$-1.26130790353512 \times 10^{-10}$	452.1
70	15	65	13	10	1×10^{-4}	$3.35027788145732 \times 10^{-11}$	133.4	$3.35024215760394 \times 10^{-11}$	996	$3.35027788179863 \times 10^{-11}$	109.7
70	25	70	15	14	25	$3.65666732448195 \times 10^{-3}$	100.4	$3.65666345057935 \times 10^{-3}$	1214	$3.65666732448635 \times 10^{-3}$	87.1
75	30	75	20	18	1×10^{-6}	$-4.92600264607682 \times 10^{-8}$	142.4	$-4.92601654027154 \times 10^{-8}$	1302.4	$-4.92600264607547 \times 10^{-8}$	105.3

3.2 The calculation method of the case in Sect. 2.2

The values of the Gaunt coefficients and the Gegenbauer coefficients should be known to calculate the radial part of overlap integrals with the same screening parameters, by using Eq. (9). Gegenbauer coefficients were calculated from Eq. (11) and stored in the memory and then they were used in the calculation of Eq. (9). The symmetry properties of the Gegenbauer coefficients given by Eq. (15) were also used to minimize the memory requirement. In order to put it into, or get it back from, the memory the position of a certain Gegenbauer coefficient is determined by the relation

$$G_{ns\alpha} = \sum_{t=0}^{n-1} \sum_{k=0}^{E\left(\frac{t}{2}\right)} \sum_{m=0}^{t+1-k} (1) + \sum_{i=0}^{s-1} \sum_{j=0}^{n+1-i} (1) + \alpha + 1$$
$$= \frac{n\left(6n^2+30n+39\right)}{48} + \frac{7(1-(-1)^n)}{32} + \frac{(-1)^{n-1}}{8} E\left(\frac{n}{2}\right) + s(n+2) - \frac{s(s-1)}{2} + \alpha + 1 \quad . \tag{25}$$

The second term in the left-hand side of Eq. (14) is put into the right-hand side and then the accuracy of the Gegenbauer coefficients is checked by using this equation for various α and n parameters. Each form that was constructed was found to be consistent with each other.

The Gaunt coefficients and their symmetries are calculated from Eqs. (6) and (8) in Ref. [44] through the binomial coefficients and from Eq. (7) in Ref. [44] through the Clebsch–Gordan coefficients for some selected quantum numbers.

3.3 The calculation method of the case in Sect. 2.3

As seen previously, the calculation of the radial part of overlap integrals with the same screening parameters can be reduced to the calculation of basic coefficients $A^s_{n,n'l'}$ followed by the application of several recurrence relations. The radial part of overlap integrals with the same screening parameters can be obtained by repeated application of recurrence relations (Eqs. 16, 17, 18, 19, 20, 21, 22, 23) and an analytical formula (Eq. 2). In this calculation the coefficient of $A^0_{0,0}$ was taken as the starting point.

For the three previously mentioned cases, the results of the radial part of overlap integrals with the same screening parameters and the computation times in milliseconds are shown in Table 1. As can be seen from Table 1, all the calculations were made in the range $1 \le n \le 75$, $1 \le n' \le 75$, and $10^{-6} \le p$.

For $\theta = \phi = 0$ in Eq. (12) of Ref. [38], one can obtain the following recurrence relation:

$$S_{nl\lambda,n'l'\lambda}(p) = \frac{\sqrt{(2n+1)(2n+2)}}{2p}\left[A_{l\lambda}S_{n+1l+1\lambda,n'l'\lambda}(p) + B_{l\lambda}S_{n+1l-1\lambda,n'l'\lambda}(p)\right]$$
$$- \frac{\sqrt{(2n'+1)(2n'+2)}}{2p}\left[A_{l'\lambda}S_{nl\lambda,n'+1l'+1\lambda}(p) + B_{l'\lambda}S_{nl\lambda,n'+1l'-1\lambda}(p)\right] \quad . \tag{26}$$

This relation determines the accuracy of the computer results of the radial part of overlap integrals with the same screening parameters. This relation also conforms all the methods used to calculate the radial part of overlap integrals with the same screening parameters. However, the method used in case 2.2 gives the accuracy up to eight decimal digits for n, $n' > 50$, whereas the other cases are much more sensitive (at least 12 decimal digits) to n, $n' \le 75$.

The symmetry property of the coefficients $A^s_{nl\lambda,n'l'\lambda}$ given by Eq. (24) are taken into account from the stored coefficients $A^s_{nl\lambda,n'l'\lambda}$, recalling relations of a certain coefficient $A^s_{nl\lambda,n'l'\lambda}$ are determined by Eqs. (17), (18), and (19) of Ref. [38].

The methods used in cases 2.1 and 2.3 are especially useful for computation using computers for large quantum numbers of the overlap integrals with the same screening parameters contained in the series expansion formulas of the multicenter molecular integrals. The methods also have the remarkable property that their computational complexity does not increase with n and n'.

The algorithms which were described in this article are more efficient and should be sufficient for the practical application of the given formulas in molecular calculations. It can be shown that our computational algorithms allow a reliable and fast evaluation of these integrals even for extremely high values of the orders n and n'.

The computer program was written in Turbo PASCAL 7.0 on an IBM PC 340. In all parts of the program double-precision arithmetic was used.

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References

1. Coulson CA (1941) Proc Camb Philos Soc 38: 210
2. Roothaan CCJ (1951) J Chem Phys 19: 1450

3. McLean AD (1971) In: Lester WA Jr (ed) Proceeding of the conference on potential energy surfaces in chemistry. IBM, San Jose, Calif, pp 108–113
4. Mulliken R, Rieke C, Orloff D, Orloff H (1949) J Chem Phys 17: 1278
5. Kotani M, Ameniya A, Ishigura E, Kimura T (1963) Tables of molecular integrals. Maruzen, Tokyo
6. (a) Todd HD, Kay KG, Silverstone HJ (1970) J Chem Phys 53: 3951; (b) Silverstone HJ (1975) In: Eyring H, Henderson D, Jost W (eds) Physical chemistry: an advanced treatise, vol XIA. Academic, New York, pp 59–65
7. Filter E, Steinborn EO (1978) Phys Rev A 18: 1
8. Trivedi HP, Steinborn EO (1983) Phys Rev A 27: 670
9. Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 42: 761
10. Shavitt I (1963) In: Alder B, Fernbach S, Rotenberg M (eds) Methods in computational physics. Academic, New York, pp 1–45
11. Todd HD, Kay KG, Silverstone HJ (1970) J Chem Phys 53: 395
12. Antolovic D, Delhalle J (1980) Phys Rev A 21: 1815
13. (a) Jones HW (1980) Int J Quantum Chem 41: 749; (b) Jones HW (1997) Int J Quantum Chem 61: 881
14. Boys SF (1950) Proc R Soc Lond Ser A 201: 125
15. Malagoli M, Thiel W (1995) Chem Phys 206: 73
16. Doggett G (1984) J Chem Soc Faraday Trans 2 80: 1413
17. Francisco E, Pueyo L (1988) Phys Rev B 37: 5278
18. Garcia de la Vega JM, Miguel B (1988) J Comput Chem 12: 1172
19. Weatherford CA, Jain BL (1980) Int J Quantum Chem Symp 14: 493
20. Etemadi B, Jones HW (1993) Int J Quantum Chem Symp 27: 755
21. Bolotin AB, Kuzmenko VV, Rossikhin VV, Vonronkov EO (1994) J Mol Struct (THEOCHEM) 117: 233
22. Op de Beek SS, Driessen JPJ, Beijerinck HCV, Verhaar BJ (1997) J Chem Phys 106: 182
23. Mulliken RS, Rieke CA, Orloff D, Orloff H (1949) J Chem Phys 17: 1248
24. Roothaan CCJ (1951) J Chem Phys 19: 1445
25. Ruedenberg K (1951) J Chem Phys 19: 1459
26. Ruedenberg K, Roothaan CCJ, Jauzemis W (1954) J Chem Phys 24: 201
27. (a) Jones HW (1981) Int J Quantum Chem 20: 1217; (b) Jones HW (1982) Int J Quantum Chem 21: 1079; (c) Jones HW (1983) Int J Quantum Chem 23: 953; (d) Jones HW (1984) Phys Rev A 30: 1; (e) Jones HW (1984) Int J Quantum Chem Symp 18: 61; (f) Jones HW (1986) Int J Quantum Chem Symp 19: 157; (g) Jones HW (1997) Int J Quantum Chem 61: 881
28. Bouferguene A, Rinaldi D (1994) Int J Quantum Chem 50: 21
29. Bouferguene A, Fares M (1994) Int J Quantum Chem 51: 345
30. (a) Fernández Rico J, López R, Ramirez G (1988) J Comput Chem 9: 790; (b) Fernández Rico J, López R, Ramirez G (1989) J Comput Chem 10: 869; (c) Fernández Rico J, López R, Ramirez G (1989) J Chem Phys 91: 4202; (d) Fernández Rico J, López R, Ramirez G (1989) J Chem Phys 91: 4213; (e) Fernández Rico J, López R, Ramirez G (1990) Int J Quantum Chem 37: 69; (f) Fernández Rico J, López R, Paniagua M, Ramirez G (1991) Comput Phys Commun 64: 329; (g) Fernández Rico J, López R, Ramirez G (1991) J Chem Phys 94: 5032; (h) Fernández Rico J, López R, Ramirez G (1992) J Chem Phys 97: 7613; (i) Fernández Rico J, López R, Ramirez G (1992) Stud Phys Theor Chem 77: 241; (j) Fernández Rico J, López R, Ramirez G, Tablero C (1994) J Chem Phys 101: 9807; (k) Fernández Rico J, López R, Ema I, Ramirez G (1997) Comput Phys Commun 105: 216; (l) Fernández Rico J, Fernández JJ, Ema I, López R, Ramirez G (2000) Int J Quantum Chem 78: 83; (m) Fernández Rico J, Fernández JJ, López R, Ramirez G (2000) Int J Quantum Chem 78: 137
31. (a) Filter E, Steinborn EO (1980) J Math Phys 21: 2725; (b) Weniger EJ, Steinborn EO (1983) Phys Rev A 28: 2026; (c) Trivedi HP, Steinborn EO (1983) Phys Rev A 27: 670; (d) Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 41: 399; (e) Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 42: 761; (f) Steinborn EO, Homeier HHH, Ema I, Lopez R, Ramirez G (2000) Int J Quantum Chem 76: 244
32. (a) Magnasco V, Rapallo A, Casanova M (1999) Int J Quantum Chem 73: 333; (b) Magnasco V, Rapallo A (2000) Int J Quantum Chem 79: 91
33. (a) Guseinov II (1985) Phys Rev A 31: 2851; (b) Guseinov II (1986) Int J Quantum Chem Symp 19: 149; (c) Guseinov II (1987) Int J Quantum Chem 31: 565
34. Tai H (1992) Phys Rev A 45: 1454
35. Talman JD (1993) Phys Rev A 48: 243
36. Hierse W, Oppeneer PM (1994) Int J Quantum Chem 52: 1249
37. Guseinov II, Ilik A, Allahverdiyev SI (1996) Int J Quantum Chem 60: 637
38. Guseinov II, Öztekin E, Hüseyin S (2001) J Mol Struct (THEOCHEM) 536: 59
39. Guseinov II (1985) Phys Rev A 32: 1864
40. Guseinov II (1970) J Phys B 3: 1399
41. Guseinov II (1995) J Mol Struct (THEOCHEM) 336: 17
42. Gradshteyn IS, Ryzhik IM (1965) Tables of integrals, sums, series and products. Academic, New York
43. Guseinov II (1996) J Mol Struct (THEOCHEM) 83: 367
44. Guseinov II, Özmen A, Atav Ü, Yüksel H (1995) J Comput Phys 122: 343