Theor Chem Acc (2000) 103:463–468
DOI 10.1007/s002149900084

Theoretical
Chemistry Accounts

Regular article

Unified analytical treatment of one-electron two-center integrals with noninteger *n* Slater-type orbitals

Sidi Mohamed Mekelleche, Abdellatif Baba-Ahmed

Laboratoire de Chimie Théorique, Institut de Chimie, Université de Tlemcen, B.P. 119, Tlemcen 13000, Algeria

Received: 1 April 1999 / Accepted: 2 July 1999 /

Abstract. A unified treatment of one-electron two-center integrals over noninteger *n* Slater-type orbitals is described. Using an appropriate prolate spheroidal coordinate system with the two atomic centers as foci, all the molecular integrals are expressed by a single analytical formula which can be readily and compactly programmed. The analysis of the numerical performance of the computational algorithm is also presented.

Key words: One-electron integrals – Two-center integrals – Overlap integrals – Slater-type orbitals – Noninteger “quantum numbers”

1 Introduction

In molecular calculations based on the linear combination of atomic orbitals – molecular orbitals approximation [1], the estimation of energies and other properties of molecular systems requires the calculation of a great number of molecular integrals over atomic orbitals. The choice of reliable basis functions is of prime importance in accurate quantum chemistry calculations since the quality of several molecular properties may depend strongly on the nature of these functions [2]. Slater-type orbitals (STOs) would be desirable for basis sets in molecular calculations because they can satisfy two primordial mathematical conditions for atomic electronic distributions: namely, the cusp condition at the origin [3] and the exponential decay at long range [4–6]. Unfortunately, this kind of function has never been used extensively in accurate ab initio quantum chemistry calculations. Indeed, most ab initio calculations are carried out by employing Gaussian-type orbitals (GTOs) [7, 8] in spite of their poor representation of the electronic density near the nucleus and at large distances. The popularity of Gaussian functions is essentially due to the fact that numerous multicenter molecular integrals may be computed with great ease; however, a large number of GTOs have to be used in large-scale calculations, which leads to more computational cost. Therefore, interest in using STOs in ab initio packages has recently risen again, especially for investigations in which the behavior of the wave function at very short or long distances from a nucleus is essential, but also for cutting down the number of basis functions to be used in a calculation. We note that many researchers hope that the next generation of ab initio programs will be based on the usage of STOs [9, 10]; therefore, it does not seem impossible to envisage that STOs may compete with GTOs in accurate molecular calculations in the near future. Indeed, much effort is being made to develop efficient molecular algorithms for integrals over conventional STOs or other related basis functions [11–13].

Several approaches to the calculation of molecular integrals with STOs and other exponential-type orbitals can be found in the literature [14]. Although the extensive literature on the calculation of one-electron two-center integrals over STOs (Refs. [10–22], and references therein) contains a great number of explicit formulas, the large body of the formulas developed with integer *n* STOs does not generally apply to noninteger *n* STOs (NISTOs). Furthermore, most existing programs for the calculation of molecular integrals are limited to positive integer values of the principal quantum number and cannot be used in the case of noninteger values of *n*; however, it is well recognized that NISTOs provide a more flexible basis for molecular calculations than integer *n* STOs [23]. Although Slater’s rules [24] for determining n and ζ led to noninteger n for $n > 3$, it was Parr and Joy [25] who first advocated the use of STOs with variationally determined noninteger values of $n > 0$. Unfortunately, the idea of using NISTOs in quantum chemistry calculations seems to have been dormant for the last two decades. Some results on atomic and molecular calculations using STOs with noninteger *n* can be found in the literature [23–35]. Some recent results on overlap integrals over NISTOs are also available [36]. In the last few years, extensive work due to Koga and coworkers has proven that the extension of the STO principal quantum number from integer to

---

Correspondence to: A. Baba-Ahmed

noninteger values considerably improves the quality of the single-zeta [37–39] and the double-zeta [40] wave functions. The energies calculated over NISTOs and compared with numerical Hartree–Fock energies prove that NISTOs lead to better atomic energies than conventional integer n STOs [37–40]. Moreover, it has been demonstrated [38] that the advantages of NISTOs over conventional STOs increase for higher angular momentum quantum numbers. However, given the overwhelming dominance of GTOs, it is realistic to ask what, if any, niche NISTOs can occupy in contemporary computational quantum chemistry. Since the advantages of NISTOs will be greatest for minimal basis sets and for systems with occupied d- and f-type atomic orbitals, this convenient basis set can be useful for the study of the electronic structure of large molecules and clusters containing transition metals and other heavy atoms.

In a previous paper [36], we presented an efficient algorithm for the calculation of some one-electron two-center integrals over STOs with possible noninteger values of the principal "quantum numbers". Using a prolate spheroidal coordinate system, explicit formulas for overlap, kinetic energy and nuclear attraction integrals were developed in terms of the so-called "sigma" function, which depends on the quantum numbers and scaling parameters and on the internuclear distance. The analysis of the numerical aspects of this auxiliary function and several numerical tests confirmed that the convergence and the numerical stability of the algorithm is guaranteed for a sufficiently wide range of atomic orbital parameters (quantum numbers and scaling parameters) and internuclear distances. Furthermore, the algorithm seems to be able to provide accurate and rapid estimates of all these integrals.

In the present work, we present a unified analytical treatment of all one-electron two-center integrals of the form

$$\int \mathrm{d}^3\mathbf{r}\left[\chi_{nlm\zeta}(\mathbf{r})\right]^* \hat{M}\left[\chi'_{n'l'm'\zeta'}(\mathbf{r}-\mathbf{R})\right] \ , \tag{1}$$

where χ and χ' are two NISTOs centered on the nuclei A and B, respectively, and $\hat{M}$ is a general one-electron operator ($\hat{M} = 1,\ 1/r,\ -\Delta/2,\ z,\ z^2,\ x^2+y^2,\ x \pm iy, \ldots$). Only three types of one-electron integrals occur in the Hamiltonian matrix, according to the three different one-electron operators, i.e., the identity, the Laplacian, and the Coulomb operator for overlap, kinetic energy, and nuclear attraction integrals, respectively. The other one-electron operators are needed for the calculation of transition probabilities, coupling constants, and several electric and magnetic molecular quantities. It is of interest to note that the overlap integrals are needed in both semiempirical and ab initio quantum chemical calculations. They are also used to introduce new strategies for more complicated multicenter molecular integrals.

2 General definitions

The NISTOs are defined by

$$\chi_{nlm\zeta}(r) = R_{n\zeta}(r)Y_{l,m}(\theta,\varphi) \ , \tag{2a}$$

$$R_{n\zeta}(r) = N_{n\zeta}r^{n-1}\exp(-\zeta r) \ , \tag{2b}$$

$$N_{n\zeta} = \frac{(2\zeta)^{n+\frac{1}{2}}}{\left[\Gamma(2n+1)\right]^{1/2}} \ . \tag{2c}$$

In Eq. (2), $\Gamma(z)$ is the gamma function and ζ is the orbital exponent. $Y_{l,m}\ (\theta,\varphi)$ is a normalized complex spherical harmonic defined by the Condon-Shortley phase condition [41, 42]:

$$Y_{l,m}(\theta,\varphi) = i^{m+|m|}\left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}\right]^{1/2} \times P_l^{|m|}(\cos\theta)\phi_m(\varphi) \ , \tag{3}$$

where $P_l^m(x)$ are the associated Legendre functions and $\phi_m(\varphi)$ are the orthonormal functions defined as

$$\phi_m(\varphi) = (2\pi)^{-1/2}\exp(im\varphi) \ . \tag{4}$$

It is advantageous in our later developments to use the expanded form of the associated Legendre functions $P_l^m(x)$ which is given (for $m \geq 0$) by [43, 44]

$$P_l^m(x) = (1-x^2)^{m/2}\sum_{u=0}^{l-m} C_{lmu}x^u \ , \tag{5}$$

where the expansion coefficients C_{lmu} are defined as (Ref. [36], p. 845)

$$C_{lmu} = \frac{(-1)^{(l-m-u)/2}\left[1+(-1)^{l-m-u}\right](l+m+u)!}{2^{l+1}u!\,([l-m-u]/2)!\,([l+m+u]/2)!} \ . \tag{6}$$

We note that the representation (Eqs. 5–6) of associated Legendre functions and that given in Ref. [43] are essentially the same.

3 Evaluation of one-electron two-center integrals involving NISTOs

The two-center integrals defined by Eq. (1) can be, conveniently, evaluated by means of a prolate spheroidal coordinate system whose foci are the positions of the A and B nuclei. On the other hand, since most differential operators can be reduced to multiplicative operators, the one-electron operator $\hat{M}$ is therefore considered to be purely multiplicative and in prolate spheroidal coordinates can be written as [45]

$$\hat{M}(\xi,\eta,\varphi) = \hat{M}(\xi,\eta)\exp(i\tau\varphi) \ , \tag{7a}$$

where [45]

$$\hat{M}(\xi,\eta) = \sum_{k=0}^{k_{\max}} \Omega_k(R/2)^{\lambda}(\xi+\eta)^{a_k}(\xi-\eta)^{b_k}(1+\xi\eta)^{c_k} \times (1-\xi\eta)^{d_k}\left[(\xi^2-1)(1-\eta^2)\right]^{\frac{1}{2}e_k} \ , \tag{7b}$$

which is a simple sum with coefficients Ω_k and a common factor $(R/2)^{\lambda}$. The x_k (i.e., a_k, b_k, c_k, d_k, and e_k) are positive or negative integers. A brief listing of the parameters $\{\tau, \lambda, \Omega_k, x_k\}$ is given in Table 1. A more complete listing of these parameters can be found in Ref. [45].

Table 1. One-electron coefficients

$\hat{M}$	τ	λ	Ω_0	a_0	B_0	c_0	d_0	e_0	Ω_1	a_1	b_1	c_1	d_1	e_1
1	0	0	1	0	0	0	0	0						
r_A^{-n}	0	$-n$	1	$-n$	0	0	0	0						
r_B^{-n}	0	$-n$	1	0	$-n$	0	0	0						
z	0	1	1	0	0	0	0	0	-1	0	0	0	1	0
$x \pm iy$	± 1	1	1	0	0	0	0	1						
r_A^n	0	n	1	n	0	0	0	0						
r_B^n	0	n	1	0	n	0	0	0						
$\cos^n\theta_\mathrm{A}$	0	0	1	$-n$	0	n	0	0						
$\cos^\mathrm{n}\theta_\mathrm{B}$	0	0	1	0	$-n$	0	n	0						
$\sin^\mathrm{n}\theta_\mathrm{A}$	0	0	1	$-n$	0	0	0	n						
$\sin^\mathrm{n}\theta_\mathrm{B}$	0	0	1	0	$-n$	0	0	n						
z^2	0	2	1	0	0	0	0	0	-1	0	0	1	1	0
$x^2 + y^2$	0	2	1	0	0	0	0	2						
$z(x \pm iy)$	± 1	2	1	0	0	0	0	1	-1	-1	0	0	1	1
$(x \pm iy)^2$	± 2	2	1	0	0	0	0	2						

Using the definitions of χ and χ' given previously, and after converting spherical coordinates into prolate spheroidal coordinates and doing the φ integration, the one-electron two-center integral can be put in the following form:

$$\begin{aligned} M_{nlm\zeta}^{n'l'm'\zeta'}(R) &= \delta(m, m' + \tau) N_{n\zeta} N_{n'\zeta'} (R/2)^{n+n'+\lambda+1} \\ &\times D_{ll'}^{mm'} \sum_{k=0}^{k_{\max}} \sum_{u=0}^{l-m} \sum_{v=0}^{l'-m'} (-1)^{h_k} \\ &\times C_{lmu} C_{l'm'v} \int_1^\infty \mathrm{d}\xi \int_{-1}^{+1} \mathrm{d}\eta \\ &\times W(\xi, \eta) \exp(-\alpha\xi - \beta\eta) \ , \end{aligned} \tag{8a}$$

where

$$\alpha = (R/2)(\zeta + \zeta') \ , \tag{8b}$$

$$\beta = (R/2)(\zeta - \zeta') \ , \tag{8c}$$

$$D_{ll'}^{mm'} = \left[\frac{(2l+1)(2l'+1)}{4} \frac{(l-m)!\,(l'-m')!}{(l+m)!\,(l'+m')!} \right]^{1/2} \ , \tag{8d}$$

and

$$\begin{aligned} W(\xi, \eta) &= (\xi + \eta)^{n-m-u+a_k} (\xi - \eta)^{n'-m'-v+b_k} (1 + \xi\eta)^{u+c_k} \\ &\times (1 - \xi\eta)^{v+d_k} [(\xi^2 - 1)]^{m+\frac{1}{2}e_k} [(1 - \eta)^2]^{m'+\frac{1}{2}e_k} \ . \end{aligned} \tag{8e}$$

The factor $\delta(m, m' + \tau)$, which appears in Eq. (8a), is just the Kronecker symbol.

In Eq. (8e), the exponents $(n - m - u + a_k)$ and $(n' - m' - v + b_k)$ have noninteger values for noninteger principal "quantum numbers" n and n'. We also note that the elliptical coordinates ξ and η are limited by $1 \leq \xi \leq \infty$ and $-1 \leq \eta \leq 1$, respectively; hence, the condition $|\xi| \geq |\eta|$ is satisfied.

Using the well-known binomial relationships

$$(a + b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} b^k, \quad \text{(for an integer } n) \tag{9a}$$

and

$$(a + b)^x = \sum_{k=0}^{\infty} \binom{x}{k} a^{x-k} b^k$$

$$\text{(for an arbitrary real or complex } x \text{ and } |a| > |b|) \tag{9b}$$

with

$$\binom{x}{k} = (-1)^k \frac{(-x)_k}{k!} \ , \tag{9c}$$

where the Pochhammer symbols $(x)_k$ are defined by the following relationships

$$\begin{cases} (x)_0 = 1 \\ (x)_k = x(x-1)(x-2)\ldots(x+k-1) = \frac{\Gamma(x+k)}{\Gamma(x)} \end{cases} \ , \tag{9d}$$

and after some straightforward algebraic simplification, the one-electron two-center integral can be put in the following final form:

$$\begin{aligned} & M_{nlm\zeta}^{n'l'm'\zeta'}(R) \\ &= \delta(m, m' + \tau) N_{n\zeta} N_{n'\zeta'} (R/2)^{n+n'+\lambda+1} D_{ll'}^{mm'} \\ &\times \sum_{k=0}^{k_{\max}} \sum_{p=0}^{\infty} \sum_{p'=0}^{\infty} \sum_{u=0}^{l-m} \sum_{v=0}^{l'-m} \sum_{q=0}^{m+\frac{1}{2}e_k} \sum_{q'=0}^{m'+\frac{1}{2}e_k} \sum_{t=0}^{u+c_k} \sum_{t'=0}^{v+d_k} (-1)^{h_k} \\ &\times \Omega_k\ C_{lmu}\ C_{l'm'v} \binom{n - m - u + a_k}{p} \\ &\times \binom{n - m - v + b_k}{p'} \binom{m + \frac{1}{2}e_k}{q} \binom{m' + \frac{1}{2}e_k}{q'} \\ &\times \binom{u + c_k}{t} \binom{v + d_k}{t'}\ A_{i_k}(\alpha)\ B_{j_k}(\beta) \ , \end{aligned} \tag{11a}$$

where

$$\begin{aligned} i_k &= n + n' - m - m' - p - p' \\ &\quad + 2q - t - t' + a_k + b_k + c_k \ , \end{aligned} \tag{11b}$$

$$\begin{aligned} j_k &= p + p' + m + m' - 2q' + u - t \\ &\quad + v - t' + c_k + d_k + e_k \ , \end{aligned} \tag{11c}$$

$$h_k = p' - q - q' + m + m' + 2v - t' + d_k + e_k \ . \tag{11d}$$

$A_{i_k}(\alpha)$ and $B_{j_k}(\beta)$ are two additional functions defined by

$$A_{i_k}(\alpha) = \int_1^\infty d\xi \xi^{i_k} \exp(-\alpha\xi) \ , \tag{12}$$

$$B_{j_k}(\beta) = \int_{-1}^1 d\eta \eta^{j_k} \exp(-\beta\eta) \ , \tag{13}$$

where α (see Eq. 8b) is a positive real number. The parameter β is defined by Eq. (8c).
Since the numerical performance (accuracy, speed, numerical stability, etc) is the decisive criterion for practical applicability of any molecular integral algorithm, the study of the numerical aspects of the proposed algorithm is of prime importance.

4 Numerical discussion

The aim of this section is to discuss the efficiency of the computational algorithm based on Eq. (11a). Now, the question that arises concerns the convergence of this infinite series representation. The quantities which depend on p and/or p' are the auxiliary functions $A_{i_k}(\alpha)$ and $B_{j_k}(\beta)$, and the binomial coefficients $\binom{n-m-u+a_k}{p}$ and $\binom{n'-m'-v+b_k}{p'}$. If the existence of the functions $A_{i_k}(\alpha)$ (Eq.12) for arbitrary real i_k is a triviality, there is no difficulty to show the existence of the function $B_{j_k}(\beta)$ (Eq. 13) for all positive values of j_k. We note that the index j_k is limited by

$$0 \le j_k \le p_{\max} + p'_{\max} + m + m' + u + v + c_k + d_k + e_k \ . \tag{14}$$

On the other hand, the asymptotic estimate of $\binom{x}{p}$ when $p \to \infty$ (Ref. [36], p. 847) proves that the term (see Eq. 11a) depending on p can be bounded above, in absolute value, by a series of the Riemann type (i.e., $\frac{C_x}{p^{x+1}}$ with x > 0), which is obviously convergent. The $A_{i_k}(\alpha)$ and $B_{j_k}(\beta)$ integrals depending on p do not occur in the convergence since they can be bounded above by a constant independent of p. An analogous construction can be done for p'.

4.1 Evaluation of the integrals $A_{i_k}(\alpha)$

The integrals $A_{i_k}(\alpha)$ can be conveniently expressed, for noninteger values of the index i_k, with the aid of the incomplete gamma function, as follows:

$$A_{i_k}(\alpha) = \alpha^{-i_k-1}\Gamma(i_k+1,\alpha) \ , \tag{15}$$

where α (see Eq. 8a) is a positive real number. The index i_k (see Eq. 11b) depends on the nature of the sum $n+n'$ (i.e., i_k is noninteger if $n+n'$ is noninteger). The incomplete gamma function $\Gamma(a,x)$ is defined as [46]

$$\Gamma(a,x) = \int_x^\infty z^{a-1}e^{-z}\, dz, \quad a \in C \text{ and } x \in S_\pi \tag{16}$$

where $S_\pi = \{x \in C : |\arg x| < \pi\}$

Obviously the calculation of the function $A_{i_k}(\alpha)$ can be reduced to the calculation of the incomplete gamma function $\Gamma(a,x)$ or eventually its complementary incomplete gamma function $\gamma(a,x)$, which are related to each other by (Ref. [46], p. 942)

$$\Gamma(a,x) + \gamma(a,x) = \Gamma(a), \quad a \notin [0,-1,-2,\ldots],\ x \in S_\pi \tag{17}$$

where $\Gamma(a)$ denotes the complete gamma function.

In order to evaluate the special functions $\Gamma(a,x)$ and $\gamma(a,x)$ with an accurate and numerically stable algorithm, we implemented in our computational algorithm the routines GSER and GCF, which are available from the Fortran numerical recipes library [47]. These convenient routines are based on the usage of the following expressions:

$$\gamma(a,x) = e^{-x}x^a\Gamma(a)\sum_{n=0}^{\infty}\frac{x^n}{\Gamma(a+n+1)}, \qquad a \notin [0,-1,-2,\ldots], \quad x \in S_\pi \tag{18}$$

$$\Gamma(a,x) = e^{-x}x^a\Lambda(a,x), \quad a \notin [0,-1,-2,...], \quad x \in S_\pi \tag{19}$$

where $\Lambda(a,x)$ denotes the regular continued fraction in x^{-1}[48]:

$$\Lambda(a,x) = \frac{x^{-1}}{1+}\frac{(1-a)x^{-1}}{1+}\frac{1x^{-1}}{1+}\frac{(2-a)x^{-1}}{1+}\frac{2x^{-1}}{1+}\cdots, \qquad a \notin [0,-1,-2,\ldots], \quad x \in S_\pi \ . \tag{20}$$

For each a, the continued fraction (Eq. 20) converges uniformly, on every subset of S_π (see, e.g., Ref. [49], Sect. 9.6.17 and Ref. [50], Sect. 92). On the other hand – as we have already mentioned – since the parameter α cannot take zero or negative values, the continued fraction (Eq. 19) can be considered as a very useful numerical tool for all positive real values of x. On the other hand, it turns out that the infinite series representation (Eq. 18) converges rapidly for x less than about $a+1$, while the continued fraction representation (Eq. 19) converges rapidly for x greater than about $a+1$. Thus, by using either Eq. (18) or (19) the incomplete gamma function can be computed efficiently and accurately for all positive values of a and x.

For negative values of a, we used a recurrence formula (Ref. [48], Eq. 2.9) which is valid for all real or complex values of a and nonnegative integer values of k:

$$\frac{e^x}{x^a}\Gamma(a,x) = \frac{x^k}{(a)_k}\Lambda(a+k,x) - \sum_{i=0}^{k-1}\frac{x^i}{(a)_{i+1}} \ , \qquad a \notin [-k+1,-k+2,-k+3,\ldots] \text{ and } x \in S_\pi \ . \tag{21}$$

The notation $\Lambda(a,\ x)$ is defined by Eq. (20), and the Pochhammer symbol $(a)_k$ is defined by Eq. (9d).

4.2 Evaluation of the integrals $B_{j_k}\ (\beta)$

Since the index j_k (Eq. 11c) takes only positive and integer values, the simplest way of calculating the

►

Table 2. Convergence of the expression (Eq. 11a) for the overlap integral with $n = 5.7$, $n' = 3.8$, $l = m = l' = m' = 1$, $\zeta = 2.1$, $\zeta' = 1.3$, and $R = 1.4$ a.u

p_{max}	Eq. (11a)[a]	Eq. (11a)[b]
0	0.93580729	0.9358077680226358
1	0.71719515	0.7171956850867207
2	0.88627970	0.8862803023791527
3	0.86400998	0.8640105620763281
4	0.86700732	0.8670079659493909
5	0.86689150	0.8668923730510802
6	0.86688894	0.8668897405520058
7	0.86688870	0.8668895238595778
8	0.86688852	0.8668894882666365
9	0.86688840	0.8668894809586378
10	0.86688834	0.8668894786207930
11	0.86688834	0.8668894777123034
12		0.8668894773178845
13		0.8668894771401665
14		0.8668894770520387
15		0.8668894770059326
16		0.8668894769802845
17		0.8668894769654508
18		0.8668894769564992
19		0.8668894769509344
20		0.8668894769473651
21		0.8668894769450214
22		0.8668894769434466
23		0.8668894769423660
24		0.8668894769416112
25		0.8668894769410755
26		0.8668894769406896
27		0.8668894769404071
28		0.8668894769401985
29		0.8668894769400428
30		0.8668894769399250
31		0.8668894769398346
32		0.8668894769397657
33		0.8668894769397117
34		0.8668894769396697
35		0.8668894769396365
36		0.8668894769396100
37		0.8668894769395890
38		0.8668894769395724
39		0.8668894769395591
40		0.8668894769395481
41		0.8668894769395384
42		0.8668894769395304
43		0.8668894769395239
44		0.8668894769395186
45		0.8668894769395145
46		0.8668894769395113
47		0.8668894769395077
48		0.8668894769395052
49		0.8668894769395026
50		0.8668894769395015
51		0.8668894769394991
52		0.8668894769394975
53		0.8668894769394961
54		0.8668894769394948
55		0.8668894769394934
56		0.8668894769394924
57		0.8668894769394917
58		0.8668894769394913
59		0.8668894769394906
60		0.8668894769394899
61		0.8668894769394890
62		0.8668894769394884
63		0.8668894769394884

[a] Results obtained with Fortran single precision

[b] Results obtained with Fortran double precision

function B_{j_k} (β) (Eq. 13) is through its recurrence formula:

$$B_{j_k}(\beta) = \left[j_k B_{j_k^{-1}}(\beta) + (-1)^{j_k} \mathrm{e}^{\beta} - \mathrm{e}^{-\beta} \right] / \beta \tag{22a}$$

with

$$B_0(\beta) = \left[\mathrm{e}^{\beta} - \mathrm{e}^{-\beta} \right] / \beta \ . \tag{22b}$$

Unfortunately, the recurrence formula (Eq. 22a) is not able to provide an accurate estimate of the function $B_{j_k}(\beta)$ for large values of β and j_k; therefore, it is more convenient to use the following infinite-series representation:

$$B_{j_k}(\beta) = \sum_{k=0}^{\infty} \frac{(-\beta)^k [1 - (-1)^{k+j_k+1}]}{[k!(k + j_k + 1)]} \ . \tag{23}$$

The programs were written in the Fortran programming language and were implemented using a personal computer (Pentium processor, 166 MHz, 16 MB RAM). To have a fairly good idea about the convergence of the infinite-series representation given by Eq. (11a), we have reported in Table 2 some test values for the overlap integral ($\hat{M} = 1$) involving the parameters $n = 5.7$, $n' = 3.8$, $l = m = l' = m' = 1$, $\zeta = 2.1$, $\zeta' = 1.3$, and $R = 1.4$ a.u. From the values presented in this table, it might be observed that only six decimal digits are correct (with $p_{\text{max}} = p'_{\text{max}} = 11$) if the calculations are done in single precision, while an accuracy of 16 decimal places is reached (with $p_{\text{max}} = p'_{\text{max}} = 63$) with a program written in double precision.

The computations were performed for a wide range of physically significant atomic parameters (n, l, m, ζ, n', l', m', and ζ') and internuclear distances. The principal "quantum numbers" n and n' are considered to be nonintegers. Several other one-electron two-center integrals could be calculated using Eq. (11a). For this purpose, a set of parameters has to be defined for each one-electron operator (see, e.g., Ref. [45], p. 2585).

We have listed some test values for the two-center overlap integral ($\hat{M} = 1$) with different quantum numbers, scaling parameters, and internuclear distances in Table 3. In the tenth column we list the number of terms of the infinite-series representation (Eq. 11a) which is required to obtain an accuracy of 12 decimal places. In the 12th column we list the computation time required for the calculations. Unfortunately, because of the unavailability of literature values of overlap integrals with NISTOs, it was not possible for us to compare our values and to comment on how well literature values are reproduced.

5 Conclusion

A unified analytical treatment of one-electron two-center integrals over STOs was presented. A single analytical

Table 3. Overlap integrals between orbital $\chi'(n'l'm'\zeta')$ located at the origin (0, 0, 0) and $\chi(n\ l\ m\ \zeta)$ located at (0, 0, R). *Numbers* in *parantheses* denote powers of 10

R	n	l	m	ζ	n'	l'	m'	ζ'	$P_{\max}$	Eq. (11a)[a]	Time[b]
1.0	7.3	4	4	3.0	7.3	4	4	1.0	8	0.101734314960	9
1.4	3.8	0	0	2.2	5.5	0	0	1.1	37	0.290802069369	22
1.4	5.7	1	1	2.1	3.8	1	1	1.3	24	0.866889476942	15
3.0	6.4	1	0	0.9	6.4	0	0	2.5	41	0.312095409105	36
3.0	10.3	0	0	2.5	10.3	9	0	1.0	23	0.152926483369 (−4)	72
5.0	4.1	2	2	2.3	3.7	2	2	1.8	24	0.293217486171 (−1)	25
5.0	7.7	4	4	0.9	6.6	4	4	1.5	17	0.234831448531	31

[a] Normalization factors of the Slater-type orbitals have been included
[b] Computation time in milliseconds

formula (Eq. 11a) for carrying out the computation of all these interesting molecular integrals was derived, and an analysis of the numerical aspects of this formula reveals its stability for a wide range of quantum numbers, scaling parameters, and internuclear distances. The algorithm proposed in this work can be useful for the calculation of one-electron integrals occurring in the construction of the Hamiltonian matrix needed in ab initio and semiempirical methods. It could also be useful for the calculation of several electric and magnetic quantities which can be represented by one-electron operators.

Acknowledgements. The authors wish to thank Hassan Dib (Institute of Mathematics, University of Tlemcen) for helpful discussions and the Algerian "Ministere de l'Enseignement Superieur et de la Recherche Scientifique" for financial support.

References

1. Roothaan CCJ (1951) Rev Mod Phys 23: 69
2. Davidson ER, Feller D (1986) Chem Rev 86: 681
3. Kato T (1957) Commun Pure Appl Math 10: 151
4. Agmon S (1988) Anal Math Appl 1: 1
5. Agmon S (1982) *Lectures on exponential decay of solutions of second-order elliptic equations: bounds on eigenfunctions of N-body Schrödinger operators* Princeton University, Princeton
6. (a) Ahlrichs R (1972) Chem Phys Lett 15: 609; (b) Ahlrichs R (1973) Chem Phys Lett 18: 521
7. Boys SF (1950) Proc R Soc A Lond Ser 200: 542
8. Hehre WH, Radom L, Schleyer PR, Pople JA (1986) *Ab initio molecular orbital theory* Wiley, New York
9. Kutzelnigg W (1988) J Mol Struct (Theochem) 50: 33
10. Bouferguene A, Fares M, Hoggan PE (1996) Int J Quantum Chem 57: 801
11. Fernandez Rico J, Lopez R, Aguado R, Ema I, Ramirez G (1998) J Comput Chem 19: 1284
12. Safouhi H, Hoggan PE (1998) J Phys A 31: 8941–8951
13. Safouhi H, Pinchon D, Hoggan PE (1998) Int J Quantum Chem 70: 181–188
14. Weatherford CA, Jones HW (eds) (1982) *1981 International Conference on ETO Multicenter Molecular Integrals, Tallahassee*, Reidel, Dordrecht
15. Fernandez Rico J, Lopez R, Ramirez G (1988) J Comput Chem 9: 790
16. Fernandez Rico J, Lopez R, Ramirez G (1989) J Chem Phys 91: 4204
17. Bouferguene A, Rinaldi D (1994) Int J Quantum Chem 50: 21
18. Jones HW (1997) Int J Quantum Chem 61: 881
19. Guseinov II, Yassen RF (1995) Int J Quantum Chem 54: 197
20. (a) Grotendorst J, Weniger EJ, Steinborn EO (1986) Phys Rev A 33: 3706; (b) Weniger EJ, Grotendorst J, Steinborn EO (1986) Phys Rev A 33: 3688; (c) Steinborn EO, Homeier HHH (1990) Int J Quantum Chem Symp 24: 349; (d) Homeier HHH, Steinborn EO (1990) J Comput Phys 87: 61; (e) Homeier HHH, Steinborn EO (1991) Int J Quantum Chem 39: 625; (f) Homeier HHH, Steinborn EO (1992) Int J Quantum Chem 42: 761
21. Hierse HW, Oppeneer PM (1994) Int J Quantum Chem 52: 1249
22. (a) Bhattacharya AK, Dhabal SC (1986) J Chem Phys 84: 1598; (b) Weniger EJ, Steinborn EO (1987) J Chem Phys 87: 3709
23. Silverstone HJ (1966) J Chem Phys 45: 4337
24. Slater JC (1930) Phys Rev 36: 57
25. (a) Parr RG, Joy HW (1957) J Chem Phys 26: 424; (b) Joy HW, Parr RG (1958) J Chem Phys 28: 448
26. Snyder LG (1960) J Chem Phys 33: 1711
27. (a) Saturno AF, Parr RG (1958) J Chem Phys 29: 490; (b) Saturno AF, Parr RG (1960) J Chem Phys 33: 22
28. Snyder LG (1960) J Chem Phys 33: 1711
29. Bishop DM (1967) Adv Quantum Chem 3: 25
30. (a) Geller M (1962) J Chem Phys 36: 2424; (b) Geller M (1963) J Chem Phys 39: 84; (c) Geller M (1964) J Chem Phys 41: 4006
31. Allouche A (1976) Theor Chim Acta 42: 325
32. Taylor WJ (1978) J Math Phys 19: 52
33. Baba-Ahmed A, Gayoso J (1983) Theor Chim Acta 62: 507
34. Baba-Ahmed A, Gayoso J, Maouche B, Ouamerali O (1984), QCPE Bull, 4 program QCPE 474
35. Mekelleche SM, Baba-Ahmed A (1991), QCPE Bull, 11 program QCMP 099
36. Mekelleche SM, Baba-Ahmed A (1997) Int J Quantum Chem 63: 843
37. Koga T, Kanayama K (1997) Chem Phys Lett 266: 123
38. Koga T, Kanayama K, Thakkar AJ (1997) Int J Quantum Chem 62: 1
39. Koga T, Kanayama K (1997) J Phys B At Mol Opt Phys 30: 1623
40. Koga T, Garcia de la Vega JM, Miguel B (1998) Chem Phys Lett 283: 97
41. Steinborn EO, Ruedenberg K (1973) Adv Quantum Chem 7: 1
42. Condon EU, Shortley GH (1970) *The theory of atomic spectra*. Cambridge University Press, Cambridge, p 48
43. Magnus W, Oberhettinger F, Soni RP (1966) *Formulas and theorems for the special functions of mathematical physics*. Springer, Berlin, Heidelberg New York, p 167
44. Jahnke E, Emde E (1945) *Tables of functions with formulae and curves*. Dover, New York
45. Wahl AC, Cade PE, Roothaan CC (1964) J Chem Phys 41: 2578
46. Gradshteyn IS, Ryzhik IM (1980) *Tables of integrals, series, and products, 4th edn*. Academic Press, New York, Eq 8.350, p 940
47. Press WH, Flannery BP, Teukosky SA, Vatterling WT (1989) *Numerical recipes* (*Fortran version*). Cambridge University Press, Cambridge, pp. 160–163
48. Jones WB, Thron WJ (1985) J Comput Appl Math 12–13: 401
49. Jones WB, Thron WJ (1980) *Continued fractions: analytic theory and applications, encyclopedia of mathematics and its applications* 11. Addisson-Wesley, Reading, Mass
50. Wall HS (1948) *Analytic theory of continued fractions*. Van Nostrand, New York