Performance of numerical approximation on the calculation of overlap integrals with noninteger Slater-type orbitals

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(Received 12 December 2013; revised manuscript received 6 March 2014; published 13 May 2014)

Computing two-center overlap integrals arising in Hartree-Fock-Roothaan equations is considered by using the numerical Global-adaptive method. These integrals are expressed through auxiliary functions in ellipsoidal coordinates. They involve Slater-type basis sets with noninteger principal quantum numbers. A computationally simple, efficient, and reliable program procedure is presented. Comparison is made with the results of numerical three-dimensional adaptive integration procedure presented by Ramanowski, with methods used for analytical solution via auxiliary functions and series expansions by translation to a single center. Highly accurate results can be achieved for overlap integrals by numerical approximations both for integer and noninteger principal quantum numbers also, these extended calculations are efficient with no restriction and over a wide range of orbital parameters.

DOI: 10.1103/PhysRevE.89.053307 PACS number(s): 02.60.−x, 31.10.+z

I. INTRODUCTION

Hydrogen-like functions generalized as exponential-type orbitals (ETOs) are eigen-functions for the single electron atom Hamiltonian, which makes them a natural basis to construct molecular electronic wave functions in the linear combination of atomic orbital (LCAO-MO) method [1], and they satisfy Kato's cusp conditions for behavior of the wave function at the nuclei and at long distances from them [2,3]. Calculation of electronic structure of molecules using ETOs begins with the solution of two-center overlap integrals. Particularly, the overlap integrals constitute the basic building block of more complicated multicenter integrals. Besides, these integrals arise in Hartree-Fock-Roothaan equations (HFR) both for *ab initio* and semiempirical methods [4]. Computing such integrals, defined in a nonaligned molecular coordinate system by

$$S_{nlm,n'l'm'}(\boldsymbol{p},\tau) = \int \Psi^*_{nlm}(\zeta,\boldsymbol{r}_a)\Psi_{n'l'm'}(\zeta',\boldsymbol{r}_b)dV, \qquad (1)$$

is very longstanding and extensively studied in the literature [5–10] (see also reference therein), where, n, n', are principal quantum numbers, l,m; l',m' are the angular momentum quantum numbers, ζ, ζ' are screening constants, $\boldsymbol{p} = \frac{1}{2}(\zeta+\zeta')\boldsymbol{R}$, $\tau = \frac{\zeta-\zeta'}{\zeta+\zeta'}$ and $\boldsymbol{R} = \boldsymbol{R}_{ab} = \boldsymbol{r}_a - \boldsymbol{r}_b$ is the internuclear distance vector. The vectors $\boldsymbol{r}_a$, $\boldsymbol{r}_b$ are radius vectors of electrons with respect to nuclear labels a, b. The Ψ_{nlm} functions, considering the simplest form of ETOs, are referred to as noninteger Slater-type orbitals (NSTOs) for $n \in \mathbb{R}^+$. These functions provide extra flexibility for closer variational description of molecules. They are obtained by simplification of Laguerre functions in hydrogen-like orbitals by keeping only the term of the highest power of r, for integer n. Then, n is treated as a parameter. They can be written as

$$\Psi_{nlm}(\zeta,\boldsymbol{r}) = N_n(\zeta)r^{n-1}e^{-\zeta r}S_{lm}(\theta,\varphi), \qquad (2)$$

here,

$$N_n(\zeta) = \frac{(2\zeta)^{n+1/2}}{\Gamma(2n+1)} \qquad (3)$$

are normalization factors, $\Gamma(z)$ are gamma functions, and S_{lm} are complex ($S_{lm} = Y_{lm}$) or real spherical harmonics [11]. It should be noted that the definition of phases used in this work for the complex spherical harmonics ($Y_{lm} = Y_{l-m}$) differs from the Condon-Shortley phases [12] by a sign factor $(-1)^m$.

The first analytical derivations for two-center overlap integrals over NSTOs were made by Silverstone in Ref. [13], using the Fourier-transform convolution theorem to reduce NSTOs overlap integrals to a one-dimensional integration. Then the same author obtained the final expression from a previous paper by defining it as a series in the internuclear distance [14]. The remarkable results obtained for atomic properties [15–19] have caused increased popularity for the use of NSTOs over the last decade. No detailed investigation of molecular electronic structure calculations over NSTOs has been made because of difficulties in the evaluation of multicenter molecular integrals and its lack of the precision to date. The most fundamental two-center overlap integrals hitherto had these precision problems even for integer principal quantum numbers (see Refs. [8,20]). The NSTOs situation is much more complicated. Outstanding work on obtaining analytical relations for the two-center overlap integrals over NSTOs has been made possible after [13,14] in [4,7,21,22] via the ellipsoidal coordinate system using auxiliary functions and the single-center expansion procedure [23], respectively. It should be noted that the auxiliary functions used in analytical derivation of overlap integrals over NSTOs need to be convergent and numerically stable. On the other hand, single-center expansion of NSTOs in terms of Slater-type orbitals with integer principal quantum numbers (ISTOs) at the same center must have as high as possible an upper limit of summation. These two methods are internally consistent, but they provide different results with correct digits varying according to the quantum numbers. It has been uncertain which reference gives the more accurate values [21]. This work gives benchmark values that can be used to remove such uncertainty.

Alternatively, the numerical algorithm based on the ADAPT-like adaptive integration procedure was recently used to calculate two-center integrals over ISTOs in Ref. [24]. The results compared well with analytical solution. It seems from the results presented in Tables I and II here that the accuracy

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TABLE I. The comparative values of two-center overlap integrals over ISTOs.

n	l	m	n'	l'	m'	p	τ	Θ	Φ	Results
1	0	0	1	0	0	0.1	0	0	0	**9.98337 28456 63420 62391 22146 22559 01738** E-01[a] **9.98337 28456 63420 62391 22146 22559 01738** E-01[b] **9.98337 2**913 E-01[c] **9.98337 28456 6342**5 E-01[e]
8	0	0	8	0	0	51/20	49/51	0	0	**7.15537 44350 12757 24983 22690 59617 20779** E-10[a] **7.15537 44350 12757 24983 22690 59617 20779** E-10[b] **7.15**224 4882 E-10[c] **7.15537 44350 127**68 E-10[e]
3	2	1	3	2	1	25.0	0.6	0	0	**−4.42287 76698 82608 80679 54150 24354 52085** E-04[a] **−4.42287 76698 82608 80679 54150 2435**7 E-04[d] **−4.4**0796 15156 10623 E-04 E-04[e]
6	5	4	5	4	3	100.0	0.9	30	120	**3.22601 93043 96471 01300 54876 30236 40989** E-09[a] **3.22601 93043 96471 01300 54876 30236** E-09[d]
6	5	4	5	4	3	125.0	0.09	30	120	**8.37290 47190 38628 26960 63231 72822 20235** E-40[a] **8.37290 47190 38628 26960 63231 72822 2023**9 E-40[b]
13	12	12	13	12	12	25.0	0.01	0	0	**1.35310 57870 24712 38186 18677 70288 53421** E-04[a] **1.35310 57870 24712 38186 18677 70288** E-04[d]
13	12	12	13	12	12	250.0	0.001	0	0	**7.09059 49024 39344 74525 33028 03956 05290** E-90[a] **7.09059 49024 39344 74525 33028 03956 05290** E-90[b]
21	10	6	9	8	6	45.0	0	0	0	**5.38980 68533 81437 73017 27203 24019 14298** E-05[a] **5.38980 68533 81437 73017 27203 24019** E-05[d]
25	11	6	12	8	3	45.0	0.001	45	135	**−7.23339 14676 87606 82677 55821 58140 80371** E-03[a] **−7.23339 14676 87606 82677 55821 58140 80371** E-03[b]
40	4	3	12	4	3	15.0	0.6	0	0	**9.48379 22083 22556 78538 44190 07653 62745** E-02[a] **9.48379 22083 22556 78538 44190 0765**4 E-02[d]
40	4	3	12	4	3	15.0	0.6	125	35	**1.09293 91789 07866 13706 54526 97582 19446** E-01[a] **1.09293 91789 07866 13706 54526 97582 19446** E-01[d]

[a][Numerical].
[b][Analytic].
[c]Reference [24].
[d]Reference [10].
[e][Cuba].

of given results for overlap integrals over ISTOs even with lowest values quantum numbers is insufficient.

In this paper, we use the adaptive integration method on the two-center overlap integrals over NSTOs, which are expressed with two-dimensional auxiliary functions $\mathrm{Q}^{q}_{NN'}$ in ellipsoidal coordinates [21]. This method gives benchmark values for overlap integrals. The Global-adaptive strategy is used to reach the required precision and accuracy goals of the integral estimate. The computer program is constructed in the Mathematica programming language [25] with the included numerical methods; the calculations were performed with $n, n' \in \mathbb{R}^{+}$ for arbitrary values of quantum numbers and orbital parameters.

II. DEFINITION AND BASIC FORMULAS

The overlap integrals over NSTOs are defined by following formula [10,21,22,26]:

$$S_{nlm,n'l'm'}(\boldsymbol{p},\tau) = \sum_{\lambda=0}^{min(l.l')} T^{\lambda *}_{lm,l'm'}(\Theta,\Phi) S_{nl\lambda,n'l'\lambda}(p,\tau), \quad (4)$$

$$S_{nl\lambda,n'l'\lambda}(p,\tau) = N_{nn'}(p,\tau) \sum_{\alpha=0}^{l} \sum_{\beta=\lambda}^{l'} \sum_{q=0}^{\alpha+\beta} g^{q}_{\alpha\beta}(l\lambda,l'\lambda) \times \mathrm{Q}^{q}_{n-\alpha,n'-\beta}(p,\tau), \quad (5)$$

where, $N_{nn'}$ is a normalization constant,

$$N_{nn'}(p,\tau) = \frac{[p(1+\tau)]^{n+1/2}[p(1-\tau)]^{n'+1/2}}{[\Gamma(2n+1)\Gamma(2n'+1)]^{1/2}}, \quad (6)$$

and the auxiliary functions $\mathrm{Q}^{q}_{NN'}$ in ellipsoidal coordinates are defined as

$$\mathrm{Q}^{q}_{NN'}(p,\tau) = \int_{1}^{\infty} \int_{-1}^{1} Q^{q;p,\tau}_{NN'}(\mu,\nu) d\mu d\nu, \quad (7)$$

$$Q^{q;p,\tau}_{NN'}(\mu,\nu) = (\mu\nu)^{q}(\mu+\nu)^{N}(\mu-\nu)^{N'} e^{-p\mu-p\tau\nu}. \quad (8)$$

Here, $\mu = \frac{r_a+r_a}{R}$, $\nu = \frac{r_a-r_a}{R}$. The relationships for rotated-angular functions $T^{\lambda}_{lm,l'm'}$ and auxiliary functions $g^{q}_{\alpha\beta}$ occurring in Eqs. (4) and (5) in terms of binomial coefficients given as [21,27,28].

TABLE II. The convergence behavior of the analytical solution of two-center overlap integrals with Eq. (21).

n	l	m	n'	l'	m'	p	τ	Θ	Φ	Results
5	4	4	5	4	4	5.0	0	0	0	**3.56825 98684 57483 60689 04872 31073 68139** E-01[a]
										3.56825 98684 57483 60689 04872 31073 68139 E-01[b]
										3.56825 9972 E-01[c]
										3.56825 98618 92429 E-01[n]
5.1	4	4	5.1	4	4	5.0	0	0	0	**3.68837 33855 08336 58641 31918 22868 35839** E-01[a]
										3.68837 33855 05726 37942 01568 75075 77285 E-01[d]
										3.68837 33855 02829 31225 21439 34449 97437 E-01[e]
										3.68837 33854 94605 78092 61548 46231 82180 E-01[f]
										3.68837 33854 94605 78092 61548 46231 82180 E-01[f]
										3.68837 33854 63771 70501 74331 34118 31567 E-01[g]
										3.68837 33852 74417 43376 93079 44890 38419 E-01[h]
										3.68837 33815 49121 07703 85081 75542 56719 E-01[k]
										3.68837 32224 55592 65438 31561 52778 02193 E-01[l]
										3.68837 07606 36279 99583 24709 21920 68306 E-01[m]

[a][Numerical].
[b][Analytic].
[c]Reference [24].
[d][$N_a = 1500$].
[e][$N_a = 1250$].
[f][$N_a = 1000$].
[g][$N_a = 750$].
[h][$N_a = 500$].
[k][$N_a = 250$].
[l][$N_a = 100$].
[m][$N_a = 50$].
[n][Cuba].

The rotated-angular functions,

$$T^{\lambda}_{lm,l'm'}(\Theta,\Phi) = \sum_{L=|l-l'|}^{l+l'} \mathrm{T}^{\lambda,L}_{lm,l'm'} Y_{LM}(\Theta,\Phi), \tag{9}$$

where

$$\mathrm{T}^{\lambda,L}_{lm,l'm'} = \frac{(i)^{\delta_{m,-|m|}}(-i)^{\delta_{m',-|m'|}}}{2[(1+\delta_{m0})(1+\delta_{m'0})]^{1/2}}\left(\mathrm{T}^{\lambda,L}_{l|m|,l'|m'|} + \varepsilon_m \mathrm{T}^{\lambda,L}_{l-|m|,l'|m'|} + \varepsilon_{m'} \mathrm{T}^{\lambda,L}_{l|m|,l'-|m'|} + \varepsilon_m \varepsilon_{m'} \mathrm{T}^{\lambda,L}_{l-|m|,l'-|m'|}\right), \tag{10}$$

$$\mathrm{T}^{\lambda,L}_{lm,l'm'} = \frac{2}{1+\delta_{\lambda 0}} C^{ll'L}_{-mm'M} C^{ll'L}_{-\lambda\lambda 0}\left(\frac{4\pi}{2L+1}\right)^{1/2}. \tag{11}$$

Here, the quantities C are the Clebsch-Gordan coefficients and $M = -m + m'$,

$$\varepsilon_m = \begin{cases} +1 & \text{for} \quad m \geqslant 0 \\ -1 & \text{for} \quad m < 0 \end{cases}. \tag{12}$$

The auxiliary functions $g^q_{\alpha\beta}$,

$$g^q_{\alpha\beta}(l\lambda,l'\lambda) = g^0_{\alpha\beta}(l\lambda,l'\lambda) F_q(\alpha+\lambda,\beta-\lambda), \tag{13}$$

$$g^0_{\alpha\beta}(l\lambda,l'\lambda) = \left[\sum_{i=0}^{\lambda} (-1)^i F_i(\lambda) g^{l\lambda}_{\alpha+2\lambda-2i}\right] g^{l'\lambda}_{\beta}, \tag{14}$$

$$g^{l'\lambda}_{\beta} = \frac{(-1)^{(l-\beta)/2}}{2^l}\left[\frac{2l+1}{2}\frac{F_l(l+\lambda)}{F_\lambda(l)}\right]^{1/2} \times F_{(l-\beta)/2}(l) F_{\beta-\lambda}(l+\beta). \tag{15}$$

Here, $F_k(n)$, $F_k(n,n')$ are the binomial and generalized binomial coefficients, respectively.

Note that the essential problem in the calculation of overlap integrals is based on the accurate calculation of Eq. (7). All other components occurring in overlap integrals are coefficients and no computational problem emerges except "tragic cancellation", and here, computing a sum of positive and negative terms may be obtained with less precision than the sum of computed positive and negative terms. Mathematica, by making use of numerical precision, evaluates any expression to n-digit precision. The number of digits of input parameters is set equal to the requested numbers of digits for overlap integrals to prevent the occurrence of tragic cancellation. Therefore, we can say that the results of overlap integrals become as precise as $\mathrm{Q}^q_{NN'}$ function evaluation.

When the single-center expansion methods or series representation formulas are used in the evaluation of integrals, hermiticity cannot be assumed. If it is imposed as a constraint, the accuracy is reduced. In the present work, it is not assumed. The hermiticity properties of overlap integrals [10] can be used to control the digital accuracy,

$$S_{n'l'm',nlm}(\boldsymbol{p'},\tau') = S^*_{nlm,n'l'm'}(\boldsymbol{p},\tau), \tag{16}$$

where $\tau' = \frac{\zeta'-\zeta}{\zeta'+\zeta}$, $\boldsymbol{p'} = \frac{\boldsymbol{R'}}{2}(\zeta'+\zeta)$, and $\boldsymbol{R'} = -\boldsymbol{R}$.

In order to investigate the accuracy of overlap integrals through numerical calculation of $\mathrm{Q}^q_{NN'}$ functions, the quadrature rule of subdomain r in a sequence of n_r point quadrature for approximation to integrals of $Q^{q;p,\tau}_{NN'}(\mu,\nu)$ given in Eq. (8)

on intervals $[1,\ \infty) \times [-1,\ 1]$, determined by

$$I = \sum_{s_1}^{n_{r_1}} \sum_{s_2}^{n_{r_2}} \omega_{r_1 s_1} \omega_{r_2 s_2} Q_{NN'}^{q;p,\tau}(\mu_{r_1 s_1}, \nu_{r_2 s_2}). \tag{17}$$

Here, ω_{rs} are the weights, $\{\mu_{rs}, \nu_{rs}\}$ are roots and their choice so that $I \approx Q_{NN'}^{q}$ define the rule and provide both an integral estimate and an error (ε_r) estimate as a measure of the integral estimate accuracy.

Most numerical integration rules consist of approximating the integrand by a polynomial and then integrating the polynomial exactly. To ensure higher accuracy for a wide range of integrals requires treatment of the roots as additional degrees of freedom and is referred to as Gauss-quadrature. This differs from Newton-Cotes quadrature as the roots are not equally spaced and they are not fixed. If a specified degree of accuracy is needed, new roots, which are called for re-computation of all roots at each iteration and a number of roots (unknown in advance), can be added via Kronrod extension (Please see Ref. [25b] for weights and information on the singularities depending on input criteria in Gauss-quadrature with Kronrod extension).

An adaptive algorithm is used commonly over a wide range of integrands to compute an approximation as $\varepsilon_r \to 0$ recursively by partition of the integration interval into disjoint sub-intervals to increase the number of roots until the required accuracy is achieved. The procedure recursively subdivides the integration subregion (with the largest error estimate) into two halves and computes integral and error estimates for each half. It is referred to as global strategy and it can be used in an adaptive algorithm to obtain results for multidimensional integrals of a given accuracy in a more reasonable time since the algorithm in each subinterval provides an error estimate [25a,29,30].

III. RESULTS AND DISCUSSIONS

The Mathematica programming language can handle approximate real numbers with any number of digits, and it is used with the included numerical computation packages to perform the calculations using the Global-adaptive strategy. However, Mathematica is suitable only for benchmarking in the view of the calculation times. The Gauss-Kronrod rule is used since it is suitable for benchmarking highly accurate values for the integral. The input criteria given by precision and accuracy goals are used to stop the algorithm via a Global-adaptive strategy by a specific Gauss-Kronrod rule. Note that, if the precision goal is increased, a narrow spike in the integrand is not missed. In the present paper the precision goal is determined as 50 and other input criteria can be determined depending on orbital parameters and quantum numbers. The calculations for $Q_{NN'}^{q}$ auxiliary functions are also performed with the Cuba integration algorithm [31] and analytical solution via infinite series representations [21]. The results obtained by calculating Eq. (5) are presented for two-center overlap integrals over NSTOs with integer and noninteger principal quantum numbers. The single-center expansion method proposed in Ref. [32] in order to calculate molecular integrals over NSTOs is also investigated for overlap integrals. Note that in this study all results are given in atomic units (a.u.).

The results obtained are presented in Tables I, II, and III for arbitrary values of integer and noninteger quantum numbers with different values of orbital parameters. This is always the first line in table entries, which provides benchmark accuracy to 35 decimal digits. Further content is given with decreasing accuracy for comparison. The second line is generally the analytical evaluation given in Eq (5). Some entries from the Cuba integration algorithm are also included.

In Table I the results obtained for two-center overlap integrals are presented with $n, n' \in \mathbb{N}^+$. It can be seen from Table I, the applied strategy in this paper for numerical calculation overlap integrals gives exactly the same results as analytical calculation, which is the solution of Eq. (5) by using Mulliken auxiliary functions [33], where

$$A_s(p) = \int_1^\infty \mu^s e^{-p\mu} d\mu, \tag{18}$$

$$B_s(p,\tau) = \int_{-1}^1 \nu^s e^{-p\tau\nu}, \tag{19}$$

and

$$Q_{NN'}^{q}(p,\tau) = \sum_{k=0}^{N+N'} F_k(N,N') A_{N+N'+q-k}(p) B_{q+k}(p,\tau). \tag{20}$$

Some results obtained are also compared with results of the Cuba numerical integration algorithm via a Cuhre globally adaptive scheme using the Mathematica platform. Here, the accuracy goal, maximum points, and precision goal have been chosen as 50, E+5, E+3, respectively. Note that the Cuba algorithm gives up to about 10–12 digit accuracy for the low values of orbitals parameters (see Fig. 1). The details on the algorithm and on the quadrature rules used by Cuba can be found in Ref. [34].

In Table II the convergence properties for analytical solution of overlap integrals with $n, n' \in \mathbb{R}^+$ are investigated, where $Q_{NN'}^{q}$ are now expressed with infinite series,

$$Q_{NN'}^{q}(p,\tau) = \lim_{N_a \to \infty} \sum_{k=0}^{N+N_a} F_k^{N_a}(N,N') A_{N+N'+q-k}(p) B_{q+k}(p,\tau), \tag{21}$$

$$F_k^{N_a}(N,N') = \sum_{\sigma=0}^{N_a} (-1)^\sigma F_{k-\sigma}(N) F_\sigma(N'). \tag{22}$$

The results are presented depending on the upper limit of summation N_a. As can be seen from this table, the computer program constructed to evaluate Eqs. (5) through (21) is consistent, and results obtained by increasing the upper limit of summation are getting closer to the results obtained by solution of Eq. (5) using numerical Global-adaptive method with Gauss-Kronrod extension. However, the convergence of results is bad, it is worse after the upper limit of summation 250 and only a few more exact digits are obtained by increasing the

TABLE III. The comparative values of two-center overlap integrals over NSTOs.

n	l	m	n'	l'	m'	p	τ	Θ	Φ	N_e	Results
7.3	4	4	7.3	4	4	2.0	0.5	0	0	50	**1.01734 31495 95668 84009 52107 36427 25565** E-02[a] **1.01734 31495 95668 8400**7 86947 52077 34718 E-02[b] **1.01734 31495 95668** 36968 25958 39497 31859 E-02[c] **1.01734 31495 9**344 E-02[d] **1.01734 3149**6 0 E-01[e] **1.01734 31495 95668** E-01[f]
6.4	1	0	6.4	0	0	5.1	–8/17	0	0	75	**3.12099 12216 53204 22891 71991 67638 91165** E-01[a] **3.12099 12216 53204 22**768 13000 53889 56350 E-01[b] **3.12099 12216 53204** 48179 50345 40070 48609 E-01[c] **3.12099 12216 5**129 E–01[d] **3.1209**5 40910 5 E–01[e] **3.12099 12216 5**2738 E-10[f]
3.8	0	0	5.5	0	0	2.31	11/33	0	0	50	**2.90802 04650 66341 47700 88166 91317 05703** E-01[a] **2.90802 04650 6634**0 76485 08364 06364 42126 E-01[b] **2.90802 04650 663**22 65270 93348 40769 12961 E-01[c] **2.90802 04650** 5438 E-01[d] **2.90802 0**6936 9 E-01[e] **2.90802 04650 66341** E-01[f]
5.7	1	1	3.8	1	1	2.38	4/17	0	0	50	**8.66889 50632 72588 09962 28315 86072 66015** E-01[a] **8.66889 50632 72588 0**1466 19441 06578 54985 E-01[b] **8.66889 50632 72**426 54151 02360 41307 43577 E-01[c] **8.66889 5063**3 1727 E-01[d] **8.66889** 476942 E-01[e] **8.66889 50632 72**6 E-01[f]
3.6	2	1	2	1	1	0.8	0.3	72	180	50	**6.49621 73637 32212 98813 20684 64320 73379** E-02[a] **6.49621 73637 3**1904 68474 20731 82929 20005 E-02[b] **6.49621 7363**3 59793 04074 14262 99135 25490 E-02[c] **6.49621 736**44 9485 E-02[d] **6.49621 73637 32**153 E-02[f]
6.3	5	4	5.5	4	4	15.0	0.1	120	240	40	**1.85058 95468 20783 59133 54756 23091 64154** E-02[a] **1.85058 954**03 14289 92881 34756 78487 22549 E-02[c] **1.85058 9**4705 91934 44517 09029 45209 52352 E-02[b] **1.85**610 75335 3492 E-02[d] **1**.75344 05078 04364 E-02[f]
4.1	2	2	3.7	2	2	10.25	5/41	0	0	40	**2.93541 97236 64768 15362 90672 35811 14085** E-02[a] **2.93541 9723**4 26640 97329 01022 58524 91729 E-02[c] **2.93541 9723**5 73426 91638 11859 94834 42774 E-02[b] **2.93541 9**6688 0792 E-02[d] **2.93**217 48617 1 E-02[e] **2.935**39 60891 94248 E-02[f]
10.3	0	0	10.3	9	0	5.25	3/7	0	0	50	**1.52896 89539 18532 09475 62114 33969 06544** E-05[a] **1.52896 89539** 37703 62033 75440 99497 83633 E-05[c] **1.52896 89**418 36941 49796 69264 42398 82275 E-05[b] **1.52**927 43006 2972 E-05[d] **1.52**926 48336 9 E-05[e] **1.52896 89**931 28066 E-05[f]

[a][Numerical].
[b][Analytic].
[c][Single-centre expansion method based on Ref. [32]].
[d]Reference [21].
[e]Reference [7].
[f][Cuba].

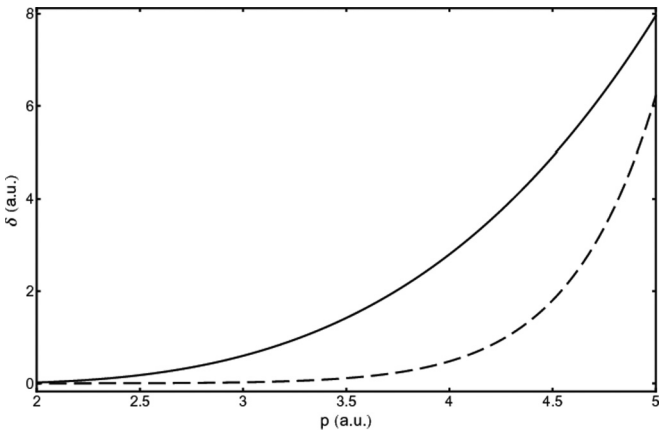

FIG. 1. The comparison of methods of computing $Q^{q}_{NN'}$ auxiliary functions depending on orbital parameters p with $q = 1, N = 3.1, N' = 2.2$, and $\tau = 0.5$. The solid black line and the dashed black line is the δ_{MA} and δ_{MC}, respectively. The results multiplied by 10^6 for δ_{MA} and by 10^8 for δ_{MC}.

upper limit of summation up to 1500. Note that the expression Eq. (21) with an infinite series, which requires recalculation of every term in the sum, is ill-conditioned, and it is necessary to take into consideration thousands of terms. Further, Eqs. (18) and (19) are expressed with incomplete Gamma functions, which may have erroneous last digits (many papers on that issue exist [35,36]).

The results in Table III, to be used for NSTOs, are presented with $n, n' \in \mathbb{R}^+$ and compared with results obtained from the solution of Eq. (5) analytically. The upper limit of summation in Eq. (5) is determined as 250 in this table. It should be noted that the results obtained for overlap integrals with Eq. (21) are closer to numerical methods than the results presented in Ref. [21] using the same method. Availability of the single-center expansion method, which uses expansion of NSTOs in terms of an infinite series of ISTOs at a displaced center, applied to a single-center

$$\Psi_{nlm}(\zeta,\boldsymbol{r}) = \lim_{N_e\to\infty} \sum_{n'=l+1}^{N_e} V^{*N_e}_{nl,n'l}\, \Psi_{n'lm}(\zeta,\boldsymbol{r}). \qquad (23)$$

Here, $n \in \mathbb{R}^+, n' \in \mathbb{N}^+$ (please see Ref. [32] for definition of $V^{N_e}_{nl,n'l}$ expansion coefficients) is investigated and the results are presented in Table III. In this table, the results found in the literature and Cuba performance for overlap integrals with noninteger principal quantum number are also included.

Dependence of numerical and analytical solutions of $Q^2_{3,1,2,2}(p,0.5)$ on the orbital parameters are given in Fig. 1. In this figure, the difference between the logarithm of values obtained with Mathematica-Nintegrate, analytical solution (δ_{MA}), and results obtained from Cuba integration algorithm (δ_{MC}), respectively, are plotted. It can be seen from this figure that the correct number of the digits decreases upon increasing the values of orbital parameters (p), and the effect of orbital parameters on the number of correct digits is becoming less with two digits when the Cuba integration algorithm is implemented, where $N_a = 25$ and default Cuba-Cuhre inputs are used (accuracy goal 3 and maximum points 50 E+3).

The computing time depends intensively on the angular momentum quantum numbers due to the number of $Q^{q}_{NN'}$ auxiliary functions in the sum determined by upper limits of summations in Eq. (5). The seventh lines of Table I and the first line of Table III are some of lines have high values of angular momentum quantum numbers. The results are obtained for overlap integrals with these values using numerical Global-adaptive method in 76.5 minutes and 57.3 minutes on a PC (Intel core i5-3.2 Ghz) running the Mathematica platform, respectively. The results for overlap integrals through Eq. (21) with the same values are obtained in 0.006 minutes and 2.44 minutes.

On the other hand, accurate calculation of overlap integrals via Eq. (21) depends on orbital parameters. In the case of large values of orbital parameters (p if $\tau = 0$ else $p\tau$) getting more accurate number of decimals is required, taking into consideration the upper limit of summation N_a, which must be as high as possible. In the second line of Table II the value obtained for overlap integrals through Eq. (21) with most accurate decimals, where $N_a = 1500$ is computed in 894.3 minutes. The given benchmark value for the same quantum numbers and orbital parameters is computed in 93.8 minutes.

Finally, it can be said that highly accurate results can be obtained using Eq. (20) for overlap integrals with integer principal quantum number values and it is the fastest method among the methods investigated in this paper. The calculations for the overlap integrals with noninteger values of quantum numbers can be performed via the single-center expansion method or molecular auxiliary functions only for small values of parameters (in nonrelativistic molecular electronic structure calculations usually 10 accurate decimals is considered sufficient). Some results presented in the tables, obtained from Cuba numerical integration algorithm in less than a few seconds with any values of quantum numbers and orbital parameters, are more accurate than either methods for $p\tau \leqslant 1$.

ACKNOWLEDGMENTS

A.B. acknowledges funding for a postdoctoral research fellowship from innov@pole: the Auvergne Region and FEDER. The authors thank Dr. Didier Pinchon for his very helpful advice. The authors thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of paper.

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