Benchmark values for molecular two-electron integrals arising from the Dirac equation

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The two-center two-electron Coulomb and hybrid integrals arising in relativistic and nonrelativistic *ab initio* calculations on molecules are evaluated. Compact, arbitrarily accurate expressions are obtained. They are expressed through molecular auxiliary functions and evaluated with the numerical Global-adaptive method for arbitrary values of parameters in the noninteger Slater-type orbitals. Highly accurate benchmark values are presented for these integrals. The convergence properties of new molecular auxiliary functions are investigated. The comparison for two-center two-electron integrals is made with results obtained from single center expansions by translation of the wave function to a single center with integer principal quantum numbers and results obtained from the Cuba numerical integration algorithm, respectively. The procedures discussed in this work are capable of yielding highly accurate two-center two-electron integrals for all ranges of orbital parameters.

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I. INTRODUCTION

The idea of atomic basis functions with the principal quantum numbers, n, in the set of positive real numbers (rather than just the integers) was first introduced by Parr and Joy [1] and performed for the He atom and single-center calculations on the H_2 molecule using noninteger Slater-type orbitals (NSTOs) to demonstrate that improved accuracy can be achieved in Hartree-Fock-Roothaan (HFR) calculations. The NSTOs satisfy Kato's conditions [2–4] and they are essential for use in solving the Dirac equation, hence the importance of the formalism. The NSTOs are written as

$$\chi(\zeta,\vec{r}) = R_n(\zeta,r)Y_{lm}(\theta,\phi), \tag{1}$$

$$R_n(\zeta,r) = N_n(\zeta)r^{n-1}e^{-\zeta r}, \tag{2}$$

where Y_{lm} are complex or real spherical harmonics ($Y^*_{lm} = Y_{l-m}; Y_{lm} \equiv S_{lm}$) [5–7],

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

are normalization factors, and $\Gamma(z)$ are gamma functions. The complexity of molecular integrals over NSTOs has been a major barrier to the implementation of this idea for many years. Pioneering attempts to derive analytical relations of molecular integrals over NSTOs were made by Silverstone [8,9], Geller [10], and Bishop and LeClerc [11] independently. The remarkable results obtained in atomic properties [12–18] have generated increased popularity for the use of NSTOs over the past decade. Unfortunately, no detailed investigation of molecular electronic structure calculations over NSTOs has been made yet because of major difficulties in the evaluation of multicenter molecular integrals and their lack of precision. The approaches used hitherto for evaluation of molecular integrals over NSTOs are based on the single-center expansion which is an expansion of NSTOs with noninteger principal quantum number in terms of Slater-type orbitals (STOs) with integer n [19–21] as follows:

$$\chi_{nlm}(\zeta,\vec{r}) = \lim_{N_e\to\infty}\sum_{\mu=l+1}^{N_e} V^{N_e}_{nl,\mu l}\chi_{\mu lm}(\zeta,\vec{r}), \tag{4}$$

where $n \in \mathbb{R}^+, \mu \in \mathbb{N}^+$ (please see Ref. [21] for definitions of expansion coefficients denoted $V^{N_e}_{nl,\mu l}$), or binomial expansions [22,23],

$$(x+a)^{N_1}(x-a)^{N_2} = \lim_{N_b\to\infty}\sum_{s=0}^{N_1'+N_b} F^{N_b}_s(N_1,N_2)x^{N_1+N_2-s}a^s, \tag{5}$$

where N_1' is the integer part of N_1 and $F^{N_b}_s(N_1,N_2)$ are generalized binomial coefficients. Detailed investigations of both methods have been made recently for two-center overlap integrals (see Ref. [24]). The results of Ref. [24] show that it is impossible to calculate molecular integrals over NSTOs accurately by use of single-center methods. This reference gives benchmark values for the first time, using an approach similar to that extended here. Conversely, evaluation of two-center overlap integrals over NSTOs via ellipsoidal coordinates through Eq. (5) with an infinite series is ill conditioned, making it necessary to take into consideration thousands of terms. In addition, the results given in Ref. [24] using the single-center expansion method determine the upper limit of summation to be $N_e = 250$ and constitute numerical proof of the nonexistence of the single-center expansion method made in Refs. [25,26] as the total number of terms used in these calculations is $\approx 4 \times 10^4$, which are overlap integrals over STOs and still show no satisfactory convergence.

The NSTOs provide a more flexible basis for molecular calculation than STOs. Nevertheless, it may not be said they have vital importance in nonrelativistic electronic structure theory. Many calculations [27–31] show that obtaining an adequate level of accuracy is possible by using appropriate basis sets of STOs. In fact, the NSTOs start to play a major role in relativistic electronic structure theory, hence the importance of accurate calculation of molecular integrals over NSTOs.

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The Dirac spectrum can be altered by negative-energy contributions. In relativistic electronic structure calculations the whole spectrum is needed for mathematical completeness as the contribution of the negative-energy states can significantly improve accuracy [32]. Variational instability, which is referred to as variational collapse [33–35], may arise throughout the solution of the Dirac equation to find the lowest eigenvalues of positive-energy states, due to the Dirac Hamiltonian being unbounded from below. The choice of relativistic basis function should satisfy the kinetic balance condition [36–38], which is the transformation between large and small components in the nonrelativistic limit ($c \to \infty$) and guarantees separation of positive and negative energy states. The kinetic balance condition is expressed through:

$$f^{\beta}_{n_r\kappa}(\zeta,\vec{r}) = \left(\beta\frac{d}{dr} + \frac{\kappa}{r}\right) f^{-\beta}_{n_r\kappa}(\zeta,\vec{r}); \quad c \to 0, \tag{6}$$

where c is the speed of light, $\beta = \mp 1$ represent the large and small components of the wave function, $-|\kappa| + \frac{1}{2} \leqslant \mu \leqslant |\kappa| - \frac{1}{2}$, n_r are radial quantum numbers [39], and ζ are orbital parameters.

As basis functions, the complete square integrable L spinors [40–42] are related analogously to the Dirac hydrogenic solutions and they smoothly reduce to Sturmian orbitals in the nonrelativistic limit. They are most useful for hydrogenic problems, either for isolated atoms or for atoms in static electromagnetic fields [43]. However, they should not be used as a basis to construct molecular electronic wave functions in the linear combination of the atomic orbital (LCAO-MO) method [44] directly. Relativistic exponential-type basis functions, obtained from the limit (or reduced cases) of L spinors, are available to be used in the LCAO-MO method. These basis functions, satisfying the kinetic balance condition, can be represented by the finite summation of NSTOs with following relation of generalized Laguerre polynomials L^p_q [45] as follows:

$$L^p_q(x) = \sum_{s=0}^{q} w^p_q(s) x^s. \tag{7}$$

The accurate evaluation of two-center electron repulsion integrals over NSTOs constitutes the basic building block in the study of relativistic molecular systems and they arise not only in their own right for the calculation of diatomic molecules but they are also central to the calculation of the multicenter multielectron integrals.

In this paper, molecular auxiliary functions, obtained by generalizing the solution of the Poisson equation as a partial differential equation in spherical coordinates by expanding the potential the set of functions referred to as spectral forms (SFs) [46,47], are introduced. The spectral forms were named analogously with a spectrum of functions. In this case, all the Coulomb potentials can be expressed as a sum of such functions.

Compact expressions for the two-center two-electron Coulomb and hybrid integrals over NSTOs are obtained in a simple way for the first time. Afterwards, the highly accurate evaluation of Coulomb and hybrid integrals over STOs and NSTOs using the numerical global-adaptive method, specifically using the Gauss-Kronrod rule (please see Ref. [24] for details), is performed. A computer program is constructed in the MATHEMATICA programming language [48] with the numerical methods therein. The calculations are performed for arbitrary values of quantum numbers and orbital parameters. The results obtained are compared with those found in the literature in the case of STOs. Comparison for NSTOs with results obtained from the single-center expansion method [19–21] and Cuba numerical integration library with Cuhre algorithm [49,50] is clearly in favor of the latter. The present benchmarks in the tables referred to under Results in this paper (Sec. III) are quoted with 25 correct decimals. Obtaining compact relations for many electron molecular integrals over exponential basis functions and accurate evaluation thereof has been a major difficulty prior to their use in relativistic electronic structure calculations. By the use of the methods suggested in this study this problem is solved regarding accuracy.

II. TWO-CENTER COULOMB AND HYBRID INTEGRALS

The expressions for two-center two-electron Coulomb energy enable the potential to be evaluated from spectral forms of Poisson's equation [46], a new set of functions. The Coulomb energy in terms of associated charge density is written as

$$\begin{aligned} E &= -\frac{1}{4\pi}\int V_a(\vec{r}_{a_2})\, \nabla^2_{\vec{r}_{b_2}}\, V^*_b(\vec{r}_{b_2}) dV_2 \\ &= \int V_a(\vec{r}_{a_2})\rho_b(\vec{r}_{b_2}) dV_2, \end{aligned} \tag{8}$$

where $dV = r^2 \sin(\theta) d\theta d\phi$ and the integration domain is $[0,\infty) \times [0,\pi] \times [0,2\pi]$. Note that these expressions are symmetric with respect to exchange in subscripts a,b.

The radial functions, obtained by expanding the single-center potential,

$$V_a(r_{a_2}) = \int \frac{\rho_a(\vec{r}_{a_1})}{r_{12}} dV_1, \tag{9}$$

taking into consideration

$$\frac{1}{r_{12}} = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\left(\frac{4\pi}{2L+1}\right)\frac{r^L_<}{r^{L+1}_>} Y_{LM}(\theta_1,\phi_1) Y^*_{LM}(\theta_2,\phi_2) \tag{10}$$

in the new set of functions, for normalized NSTOs, can be determined as

$$V(\vec{r}_{a_2}) = \sum_{L_1M_1} F^{L_1}_{N_1}(\vec{r}_{a_2}) \mathcal{C}_{L_1M_1}, \tag{11}$$

where

$$F^{L_1}_{N_1}(\vec{r}_{a_2}) = R^{L1}_{N1}(r_{a_2}) Y^*_{L_1M_1}(\theta_{a_2}\phi_{a_2}) \tag{12}$$

and

$$R^{L1}_{N1}(r_{a_2}) = \int_0^{\infty} R_{n_1}(\zeta_1, r_{a_1}) R_{n'_1}(\zeta'_1, r_{a_1}) \frac{r^{L1}_<}{r^{L1+1}_>} r^2_{a_1} dr_{a_1}. \tag{13}$$

By making use of Eq. (13), Eq. (12) is therefore obtained as follows:

$$F_{N_1}^{L_1}(\vec{r}_{a_2}) = \mathcal{N}_{n_1 n_1'}(1,t_1)(2\bar{\zeta}_1) f_{N_1}^{L_1}(2\bar{\zeta}_1 r_{a_2}) Y_{L_1 M_1}^{*}(\theta_{a_2}\phi_{a_2}), \quad (14)$$

$$f_{N_1}^{L_1}(x) = \Gamma(N_1+L_1+1)\frac{1}{x^{L_1+1}}\left\{P[N_1+L_1+1,x] + \frac{x^{2L_1+1}}{(N_1-L_1)_{2L_1+1}} Q[N_1-L_1,x]\right\}, \quad (15)$$

where P,Q are the normalized incomplete gamma and the normalized complementary incomplete gamma functions, respectively. The normalization term of P and Q is present to satisfy $P+Q=1$.

The coefficients

$$\mathcal{C}_{L_1 M_1} = \left(\frac{4\pi}{2L_1+1}\right)^{1/2} C^{L_1|M_1|}(l_1 m_1; l_1' m_1') A_{m_1 m_1'}^{M_1}, \quad (16)$$

$$\mathcal{N}_{n_i n_i'}(p_i,t_i) = \frac{[p_i+t_i]^{n_i+1/2}[p_i-t_i]^{n_i'+1/2}}{\sqrt{\Gamma[2n_i+1]\Gamma[2n_i'+1]}}, \quad (17)$$

with $\bar{\zeta}_i = \frac{1}{2}(\zeta_i+\zeta_i'), p_i = \frac{R}{2}(\zeta_i+\zeta_i'), t_i = \frac{\zeta_i-\zeta_1'}{\zeta_i+\zeta_i'}, N_i = n_i+n_i', C^{L|M|}$ are the generalized Gaunt coefficients; please see Refs. [51,52] for the definitions of generalized Gaunt coefficients and A^M coefficients.

Taking into account the single-center (ρ_{aa}) and the two-center (ρ_{ab}) radial charge densities of NSTOs and product of spherical harmonics in the same center,

$$Y_{lm}(\theta_a,\phi_a) Y_{l'm'}^{*}(\theta_a,\phi_a) = \sum_{LM}\left(\frac{2L+1}{4\pi}\right)^{1/2} C^{L|M|}(lm,l'm') \times A_{mm'}^{M} Y_{LM}^{*}(\theta_a,\phi_a), \quad (18)$$

where $|l-l'| \leqslant L \leqslant l+l', M = |m \pm m'|$, and, making use of of ellipsoidal coordinates (μ,ν,ϕ),

$$r_{a_i} = \frac{R}{2}(\mu+\nu); \quad r_{b_i} = \frac{R}{2}(\mu-\nu),$$

$$\cos\theta_{a_i} = \frac{1+\mu\nu}{\mu+\nu}; \quad \cos\theta_{b_i} = \frac{1-\mu\nu}{\mu-\nu},$$

$$dV = \left(\frac{R}{2}\right)^3 (\mu^2-\nu^2) d\mu d\nu d\phi,$$

the two-center two-electron Coulomb integrals

$$\mathcal{J}_{n_1 l_1 m_1, n_1' l_1' m_1'; n_2 l_2 m_2, n_2' l_2' m_2'}^{aa,bb}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = \int \chi_{n_1 l_1 m_1}^{*}(\zeta_1,\vec{r}_{a_1}) \chi_{n_1' l_1' m_1'}(\zeta_1',\vec{r}_{a_1}) \frac{1}{r_{12}} \chi_{n_2 l_2 m_2}(\zeta_2,\vec{r}_{b_2}) \chi_{n_2' l_2' m_2'}^{*}(\zeta_2',\vec{r}_{b_2}) dV_1 dV_2 \quad (19)$$

and hybrid integrals

$$\mathcal{H}_{n_1 l_1 m_1, n_1' l_1' m_1'; n_2 l_2 m_2, n_2' l_2' m_2'}^{aa,ab}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = \int \chi_{n_1 l_1 m_1}^{*}(\zeta_1,\vec{r}_{a_1}) \chi_{n_1' l_1' m_1'}(\zeta_1',\vec{r}_{a_1}) \frac{1}{r_{12}} \chi_{n_2 l_2 m_2}(\zeta_2,\vec{r}_{a_2}) \chi_{n_2' l_2' m_2'}^{*}(\zeta_2'\vec{r}_{b_2}) dV_1 dV_2 \quad (20)$$

in the lined-up coordinate system ($|m_i| = |m_i'| = \lambda; \phi_{a_i} = \phi_{b_i} = \phi$) considering Eq. (9) with Eqs. (10)–(18) can be obtained as

Coulomb integrals,

$$\mathcal{J}_{n_1 l_1 m_1, n_1' l_1' m_1'; n_2 l_2 m_2, n_2' l_2' m_2'}^{aa,bb}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = \int \sum_{L_1 L_2 M}\left(\frac{2L_2+1}{2L_1+1}\right)^{1/2} A_{m_1 m_1'}^{M} A_{m_2 m_2'}^{M} C^{L_1|M|}(l_1 m_1; l_1' m_1') C^{L_2|M|}(l_2 m_2; l_2' m_2') \times f_{N_1}^{L_1}(x_1,r_{a_2}) R_{n_2}(\zeta_2,r_{b_2}) R_{n_2'}(\zeta_2',r_{b_2}) P_{L_1\lambda}(\cos\theta_{a_2}) P_{L_2\lambda}(\cos\theta_{b_2}) dV_1 dV_2, \quad (21)$$

and hybrid integrals,

$$\mathcal{H}_{n_1 l_1 m_1, n_1' l_1' m_1'; n_2 l_2 m_2, n_2' l_2' m_2'}^{aa,ab}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = \int \sum_{L_1 M_1 L_2}\left(\frac{2L_2+1}{2L_1+1}\right)^{1/2} A_{m_1 m_1'}^{M_1} A_{M_1 m_2}^{m_2'} C^{L_1|M_1|}(l_1 m_1; l_1' m_1') C^{L_2|m_2'|}(L_1 M_1; l_2 m_2) \times f_{N_1}^{L_1}(x_1,r_{a_2}) R_{n_2}(\zeta_2,r_{a_2}) R_{n_2'}(\zeta_2',r_{b_2}) P_{L_2\lambda}(\cos\theta_{a_2}) P_{l_2'\lambda}(\cos\theta_{b_2}) dV_1 dV_2. \quad (22)$$

Finally, the two-center two-electron Coulomb and hybrid integrals using the product of two associated Legendre functions [53] with different centers in ellipsoidal coordinates [51,54] as follows:

$$P_{l\lambda}(\cos\theta_a) P_{l'\lambda}(\cos\theta_b) = \sum_{\alpha=-\lambda}^{l}\sum_{\beta=\lambda}^{l'}\sum_{q=0}^{\alpha+\beta} g_{\alpha\beta}^{q}(l\lambda,l'\lambda)\left[\frac{(\mu\nu)^q}{(\mu+\nu)^\alpha(\mu-\nu)^\beta}\right], \quad (23)$$

are written as

$$\mathcal{J}_{n_1 l_1 m_1, n_1' l_1' m_1'; n_1 l_2 m_2, n_2' l_2' m_2'}^{aa,bb}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = \frac{2}{R}\mathcal{N}_{n_1 n_1'}(1,t_1)\mathcal{N}_{n_2 n_2'}(p_2,t_2) \times \sum_{L_1 L_2 M}\left(\frac{2L_2+1}{2L_1+1}\right) A_{m_1 m_1'}^{M} A_{m_2 m_2'}^{M} C^{L_1|M|}(l_1 m_1; l_1' m_1') \times C^{L_2|M|}(l_2 m_2; l_2' m_2') \Gamma(n_1+n_1'+L_1+1) \frac{1}{p_1^{L_1}} \sum_{\alpha\beta q} g_{\alpha\beta}^{q}(L_1|M|,L_2|M|) \times \{\mathcal{P}_{L_1+\alpha, n_2+n_2'-\beta-1, n_1+n_1'+L_1+1}^{0,q}(p_1,p_2,-p_2) + \mathcal{Q}_{\alpha-(L_1+1), n_2+n_2'-\beta-1, n_1+n_1'+L_1+1}^{2L_1+1,q}(p_1,p_2,-p_2)\}, \quad (24)$$

TABLE I. The values of two-center Coulomb integrals over STO in lined-up coordinate systems.

n_1/n_1'	l_1/l_1'	m_1/m_1'	ζ_1/ζ_1'	n_2/n_2'	l_2/l_2'	m_2/m_2'	ζ_2/ζ_2'	R	Results
1; 1	0; 0	0; 0	5.2; 5.2	2; 2	0; 0	0; 0	4.1; 4.1	0.2	1.82289 25537 50662 68097 06249 99472 18105[a,b,c] 1.82289 2554[d,e]
1/2	0/1	0/0	5.2/3.1	2/3	0/2	0/0	4.1/2.5	0.2	$-2.36064\ 30209\ 20063\ 71569\ 41492\ 47834\ 51963 \times 10^{-2}$ [a,b] $-2.36064\ 3021 \times 10^{-2}$ [d,e]
2/1	1/0	1/0	4.0/5.2	2/2	1/0	1/0	3.1/4.1	0.2	$2.03568\ 85382\ 24252\ 94658\ 39569\ 97218\ 82382 \times 10^{-1}$ [a,b] $2.03568\ 8538 \times 10^{-1}$ [d,e]
1/1	0/0	0/0	5.2/5.2	2/2	1/1	$-1/-1$	3.1/3.1	8.5	$1.17392\ 89654\ 55745\ 79366\ 72606\ 57106\ 36806 \times 10^{-1}$ [a,b,c] $1.17392\ 8965 \times 10^{-1}$ [d,e]
2/2	1/1	0/0	3.1/3.1	4/4	2/2	2/2	0.5/0.5	8.5	$8.75284\ 77629\ 56292\ 02391\ 86570\ 66188\ 70938 \times 10^{-2}$ [a,b] $8.75284\ 7763 \times 10^{-2}$ [d,e]
3/3	2/2	$-2/-2$	1.8/1.8	2/2	0/0	0/0	4.1/4.1	8.5	$1.15668\ 97493\ 85519\ 57315\ 49276\ 08453\ 94326 \times 10^{-1}$ [a,b,c] $1.15668\ 9749 \times 10^{-1}$ [d,e]
4/2	3/1	0/0	3.5/3.1	4/4	2/3	2/2	0.5/3.0	2.5	$-7.36773\ 13766\ 53888\ 45151\ 51235\ 09992\ 20224 \times 10^{-5}$ [a,b,c] $-7.36773\ 1337 \times 10^{-5}$ [d] $-7.36773\ 13344\ 146751 \times 10^{-5}$ [f]
1/1	0/0	0/0	0.99/0.99	1/1	0/0	0/0	1.01/1.01	0.01	$6.24916\ 67058\ 30088\ 14983\ 45518\ 38351\ 29936 \times 10^{-1}$ [a,b,c] $6.24916\ 67102\ 7413 \times 10^{-1}$ [g] $6.24916\ 67058\ 30088\ 14983\ 45518\ 384 \times 10^{-1}$ [h]
1/1	0/0	0/0	5.2/5.2	2/2	0/0	0/0	4.1/4.1	100	$1.00000\ 00000\ 00000\ 00000\ 00000\ 00000\ 00000 \times 10^{-2}$ [a,b,c] $1.00000\ 00000\ 00000\ 00000\ 00000\ 000 \times 10^{-2}$ [h] $9.99999\ 99999\ 9997 \times 10^{-3}$ [i]
4/1	3/0	0/0	0.8/0.9	3/1	2/0	0/0	1.1/1.2	100	$1.32578\ 24709\ 36295\ 45612\ 88059\ 75651\ 53922 \times 10^{-10}$ [a,b] $1.71159\ 918548 \times 10^{-10}$ [h] $1.32578\ 24709\ 36295\ 45613 \times 10^{-10}$ [i]

[a]Global-adaptive method with Gauss-Kronrod extension.
[b]Recurrence relations.
[c]Series representation.
[d]Reference [67].
[e]Reference [60].
[f]Reference [68].
[g]Reference [69].
[h]Reference [70].
[i]These results obtained in Ref. [67] using the algorithm given in Ref. [71].

$$\max[|-L_1,-L_2|] \leqslant M \leqslant \min[L_1+L_2],\ |l_1-l_1'| \leqslant L_1 \leqslant l_1+l_1',\ |l_2-l_2'| \leqslant L_2 \leqslant l_2+l_2',$$

$$\begin{aligned}\mathcal{H}^{aa,ab}_{n_1l_1m_1,n_1'l_1'm_1';n_1l_2m_2,n_2'l_2'm_2'}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') = {} & \frac{2}{R}\mathcal{N}_{n_1n_1'}(1,t_1)\mathcal{N}_{n_2n_2'}(p_2,t_2)\times \sum_{L_1M_1L_2}\left(\frac{2L_2+1}{2L_1+1}\right)A^{M_1}_{m_1m_1'}A^{m_2'}_{M_1m_2'}C^{L_1|M_1|}(l_1m_1;l_1'm_1') \\ & \times C^{L_2|m_2'|}(L_1M_1;l_2m_2)\Gamma(n_1+n_1'+L_1+1)\frac{1}{p_1^{L_1}}\sum_{\alpha\beta q} g^q_{\alpha\beta}(L_1|m_2'|,l_2'|m_2'|) \\ & \times\left\{\mathcal{P}^{0,q}_{L_1+\alpha+1-n_2,n_2'-\beta,n_1+n_1'+L_1+1}(p_1,p_2,p_2t_2)+\mathcal{Q}^{2L_1+1,q}_{\alpha-L_1-n_2,n_2'-\beta-1,n_1+n_1'+L_1+1}(p_1,p_2,p_2t_2)\right\},\end{aligned} \tag{25}$$

$|l_1-l_1'| \leqslant L_1 \leqslant l_1+l_1'$ $-L_1 \leqslant M_1 \leqslant L_1$, $|L_1-l_2| \leqslant L_2 \leqslant L_1+l_2$.

Thus, the auxiliary functions occurring in compact form expressions given in Eqs. (24) and (25) are written as follows:

$$\begin{bmatrix}\mathcal{P}^{N_1,q}_{N_2N_3N_4}(p_1,p_2,p_3)\\ \mathcal{Q}^{N_1,q}_{N_2N_3N_4}(p_1,p_2,p_3)\end{bmatrix} = \frac{p_1^{N_1}}{(N_4-N_1)_{N_1}}\int_1^{\infty}\int_{-1}^{1}(\mu\nu)^q(\mu+\nu)^{N_2}(\mu-\nu)^{N_3}\begin{bmatrix}P[N_4-N_1,p_1(\mu+\nu)]\\ Q[N_4-N_1,p_1(\mu+\nu)]\end{bmatrix}e^{-p_2\mu-p_3\nu}d\mu d\nu, \tag{26}$$

where $(a)_n$ is the Pochhammer symbol and $N_1 \geqslant 0$, $-\infty < N_2 < \infty$, $[N_3,N_4] > 0, N_1 \in \mathbb{N}; \{N_2,N_3,N_4\} \in \mathbb{R}$. The potential operator can be generalized, analogously to the representation of the wave function in the integrand of Eq. (26) to the whole set of physical potential operators, through the argument f^k_{ij} as follows:

$$f^k_{ij}(\mu,\nu) = (\mu\nu)^k(\mu+\nu)^i(\mu-\nu)^j, \tag{27}$$

TABLE II. The values of two-center hybrid integrals over STO in lined-up coordinate systems.

n_1/n_1'	l_1/l_1'	m_1/m_1'	ζ_1/ζ_1'	n_2/n_2'	l_2/l_2'	m_2/m_2'	ζ_2/ζ_2'	R	Results
1/1	0/0	0/0	5.2/5.2	1/2	0/0	0/0	5.2/4.1	0.2	1.82283 32730 08003 82547 87867 31094 97571[a,b,c] 1.82283 3273[d,e]
1/2	0/1	0/0	5.2/3.1	2/3	1/2	1/1	4.0/3.0	0.2	$-6.86828\ 29183\ 60912\ 21475\ 49388\ 55052\ 76624 \times 10^{-2}$ [a,b] $-6.86828\ 2918 \times 10^{-2}$ [d,e]
2/1	0/0	0/0	1.0/1.5	1/2	0/0	0/0	1.0/1.5	0.5	$3.52830\ 59069\ 42601\ 45585\ 21523\ 21676\ 29343 \times 10^{-1}$ [a,b,c] $3.52830\ 59069\ 426004 \times 10^{-1}$ [f]
2/2	1/1	0/1	3.1/4.0	2/3	1/1	0/1	3.1/1.5	2.5	$5.09491\ 95301\ 70106\ 78339\ 51218\ 85823\ 60340 \times 10^{-2}$ [a,b] $5.09491\ 9530 \times 10^{-2}$ [d,e]
4/2	3/1	0/0	3.5/3.1	1/2	0/0	0/0	5.2/4.1	2.5	$1.45527\ 74805\ 70430\ 59391\ 69198\ 03337\ 30776 \times 10^{-4}$ [a,b] $1.45527\ 74805\ 70430\ 59398\ 10389\ 43559\ 98442 \times 10^{-4}$ [c] $1.45527\ 7481 \times 10^{-4}$ [d,e]
2/2	1/1	1/1	4.0/4.0	1/3	0/2	0/0	5.2/5.2	8.5	$6.52569\ 93988\ 77690\ 25939\ 54456\ 64202\ 47822 \times 10^{-7}$ [a,b] $6.52569\ 9424 \times 10^{-7}$ [d,e]
2/2	1/1	0/0	3.1/3.1	4/3	3/2	0/0	3.5/2.5	8.5	$1.08708\ 58144\ 55211\ 74102\ 89705\ 11940\ 46919 \times 10^{-5}$ [a,b] $1.08708\ 5814 \times 10^{-5}$ [d,e]
2/2	1/1	0/0	5.2/5.2	2/2	0/1	0/0	5.2/4.1	0.3	$8.99999\ 85103\ 06214\ 17316\ 79580\ 94484\ 15397 \times 10^{-1}$ [a,b] $8.99999\ 85102\ 379665 \times 10^{-1}$ [f]
10/1	2/0	0/0	0.2/5.2	4/3	3/2	1/1	2.6/3.0	8.5	$2.36533\ 58321\ 44220\ 60856\ 72486\ 90851\ 06350 \times 10^{-20}$ [a,b] $2.36533\ 5832 \times 10^{-20}$ [d] $2.36533\ 61038\ 280399 \times 10^{-20}$ [f]

[a]Global-adaptive method with Gauss-Kronrod extension.
[b]Recurrence relations.
[c]Series representation.
[d]Reference [67].
[e]Reference [60].
[f]Reference [68].

which are irreducible representation of elements required to generate the potential and possess that for the Coulomb potential as the special case when $i = 1, j = k = 0$ ($f_{10}^0(\mu,\nu) = \mu + \nu$), where $\{i,j,k\} \in \mathbb{N}$. Note that the sum of auxiliary functions $\mathcal{P}_{N_2N_3N_4}^{N_1,q}$ and $\mathcal{Q}_{N_2N_3N_4}^{N_1,q}$ is invariant to a change of f_{ij}^k.

III. RESULTS AND DISCUSSIONS

The derived compact expressions of two-center two-electron Coulomb and hybrid integrals in terms of auxiliary functions $\mathcal{P}_{N_2N_3N_4}^{N_1,q}$ and $\mathcal{Q}_{N_2N_3N_4}^{N_1,q}$ via ellipsoidal coordinates can be evaluated efficiently and accurately for arbitrary values of quantum numbers and orbital parameters using the numerical global-adaptive method with Gauss-Kronrod extension. The analytical relations can be obtained using upward and downward consecutive neighbor recurrence relations, first derivatives of the normalized complete gamma functions, the normalized complementary incomplete gamma functions, and integration by parts over μ and ν. In order to investigate the accuracy of two-electron integrals through numerical approximation to $\mathcal{P}_{N_2N_3N_4}^{N_1,q}$ and $\mathcal{Q}_{N_2N_3N_4}^{N_1,q}$, we use the quadrature rule of subdomain r, a sequence of n_r points in quadrature for approximation to integrals of $\mathcal{P}_{N_2N_3N_4}^{N_1,q;p_1,p_2,p_3}, \mathcal{Q}_{N_2N_3N_4}^{N_1,q;p_1,p_2,p_3}$, where

$$\begin{bmatrix} \mathcal{P}_{N_2N_3N_4}^{N_1,q:p_1,p_2,p_3}(\mu,\nu) \\ \mathcal{Q}_{N_2N_3N_4}^{N_1,q:p_1,p_2,p_3}(\mu,\nu) \end{bmatrix} = (\mu\nu)^q(\mu+\nu)^{N_2}(\mu-\nu)^{N_3} \times \begin{bmatrix} P[N_4-N_1,p_1(\mu+\nu)] \\ Q[N_4-N_1,p_1(\mu+\nu)] \end{bmatrix} e^{-p_2\mu-p_3\nu} \tag{28}$$

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

$$\begin{bmatrix} I_{\mathcal{P}} \\ I_{\mathcal{Q}} \end{bmatrix} = \sum_{s_1=1}^{n_{r1}} \sum_{s_2=1}^{n_{r2}} \omega_{r_1s_1}\omega_{r_2s_2} \begin{bmatrix} \mathcal{P}_{N_2N_3N_4}^{N_1,q:p_1,p_2,p_3}(\mu_{r_1s_1},\nu_{r_2s_2}) \\ \mathcal{Q}_{N_2N_3N_4}^{N_1,q:p_1,p_2,p_3}(\mu_{r_1s_1},\nu_{r_2s_2}) \end{bmatrix}. \tag{29}$$

Here ω_{rs} are weights, $\{\mu_{rs},\nu_{rs}\}$ are roots and their choice so

$$\begin{bmatrix} I_{\mathcal{P}} \\ I_{\mathcal{Q}} \end{bmatrix} \approx \begin{bmatrix} \mathcal{P}_{N_2N_3N_4}^{N_1,q}(p_1,p_2,p_3) \\ \mathcal{Q}_{N_2N_3N_4}^{N_1,q}(p_1,p_2,p_3) \end{bmatrix} \tag{30}$$

define the rule and provide both an integral estimate and an error (ϵ_r) estimate as a measure of the integral estimate accuracy (please see Refs. [24,55–58] for the details on the implementation of the procedure and information on the roots and singularities).

The algorithm described in Eq. (29) has been incorporated into a computer program written in the MATHEMATICA programming language with the included numerical computation packages. The MATHEMATICA program language can handle approximate real numbers with any number of digits and it is suitable only for benchmark evaluation in the view of the calculation times. It gives 25 correct decimals in minutes and more than 10 correct decimals in seconds. It is designed to provide benchmark integral values.

The results of calculation in atomic units are given in Tables I–V and Figs. 1 and 2 for arbitrary values of integer and noninteger quantum numbers with different values of orbital parameters. The benchmark results are obtained by implementing the numerical global-adaptive method based on the Gauss-Kronrod extension. Its maximum recursion and

TABLE III. The comparison of methods of computing two-center Coulomb integrals over NSTO in lined-up coordinate systems.

n_1/n_1'	l_1/l_1'	m_1/m_1'	ζ_1/ζ_1'	n_2/n_2'	l_2/l_2'	m_2/m_2'	ζ_2/ζ_2'	R	Results
1.1/1.1	0/0	0/0	5.2/5.2	2.1/2.1	0/0	0/0	4.1/4.1	2.0	4.99960 44305 09269 74512 47068 $\times 10^{-1}$ [a]
									4.99961 06137 47474 92577 78874 $\times 10^{-1}$(30)[b]
									4.99962 31580 95475 98094 12185 $\times 10^{-1}$(20)[b]
									4.99964 58052 30194 78329 92300 $\times 10^{-1}$(15)[b]
									4.99965 43225 14863 58247 50368 $\times 10^{-1}$(14)[b]
									4.99966 53763 19254 96182 61413 $\times 10^{-1}$(13)[b]
									4.99968 04424 50836 84467 82256 $\times 10^{-1}$(12)[b]
									4.99960 42903 49048 $\times 10^{-1}$ [c]
1.1/1.1	0/0	0/0	5.2/5.2	2.1/2.1	0/0	0/0	4.1/4.1	0.2	1.74489 32510 67943 65295 27064[a]
									1.74489 45172 69239 32119 36369 (30)[b]
									1.74489 70834 71446 60289 72755 (20)[b]
									1.74490 20112 52630 59570 82609 (15)[b]
									1.74490 42617 31309 91262 90263 (14)[b]
									1.74490 74806 43795 04387 74798 (13)[b]
									1.74491 20562 80159 01409 20517 (12)[b]
									1.74489 32510 679391[c]

[a]Global-adaptive method with Gauss-Kronrod extension.
[b]Single-center expansion method. The values in parentheses are upper limits of summation N_e.
[c]Cuba numerical integration algorithm.

working precision are 35 and 25 for Tables I and II and III–V, respectively. In these tables, the values entered in the first line are always the benchmark results given with 35 and 25 decimal accuracy for Tables I and II and III–V, respectively. Further contents are the results found in the literature or results obtained from alternative methods which are comparable. The underlines in the tables indicate the digits that match the exact results listed in the first line of each calculation.

Some values of the two-center Coulomb and hybrid integrals over STOs obtained from Eqs. (24) and (25) are presented in Tables I and II in order to support the reliability of the procedure. As can be seen from these tables the results obtained are in good agreement with values obtained from relations given in Refs. [51,59,60] and other values found in the literature.

In Tables III–V the results are given for the two-center Coulomb and hybrid integrals over NSTOs, respectively. In Table III, convergence of the single-center expansion method is tested. In this table, the upper limit of summation N_e used for the single-center expansion method is chosen as 12, 13, 14, 15, 20, and 30, respectively. Notice that the lowest upper limit of summation includes $\approx 10^4$ terms, which are the two-center electron repulsion integrals with STOs so the computing time drastically increases with the upper limit of summation. The results are obtained for the highest limit in days on a PC (Intel core i5, 3.2 GHz) running the MATHEMATICA platform. The digits in bold-face are approximate to show convergence to exact values. It can be seen from this table that using the single-center expansion method for evaluation of these integrals gives very few correct digits. Its convergence is rather slow to the numerical values even in prohibitive CPU times.

The single-center expansion method is also performed for the two-center Coulomb and hybrid integrals with the given values of quantum numbers and orbital parameters in Tables IV and V. It is observed that the same number of accurate digits (4–6) are obtained with Table III for low values of quantum numbers. Moreover, the number of accurate digits decreases on increasing the values of quantum numbers and orbital parameters. Therefore, the results obtained from the single-center expansion method are not presented in Tables IV and V. The benchmark results obtained from the numerical global-adaptive method with Gauss-Kronrod extension for NSTOs are presented in these tables. Comparison is made with the Cuba-Cuhre numerical integration algorithm on the MATHEMATICA platform. The input parameters are determined as follows: the accuracy goal, maximum points, precision goal, 50, 10^5, and 10^3, respectively. It can be seen from these tables that the Cuba-Cuhre algorithm gives much more accurate results than the single-center expansion and it gives up to about 10- to 12-digit accuracy for low values of orbital parameters in seconds.

The major problem in the evaluation of auxiliary functions based on the recurrence relation for NSTOs is that the resulting formulas reduced to lowest values of quantum numbers and orbital parameters should be described by infinite series representation [61] as follows:

$$P[a,bz] = e^{-bz}\sum_{s=0}^{\infty}\frac{bz+s}{\Gamma[a+s+1]}. \tag{31}$$

Thus the analytical relations for these auxiliary functions with $f_{10}^{0}(\mu,\nu)$ (i.e., for the Coulomb potential, see also the Supplementary Material [62]) can be obtained as follows:

$$\mathcal{P}_{N_2N_3N_4}^{N_1,q}(p_1,p_2,p_3) = \frac{p_1^{N_1}}{(N_4-N_1)_{N_1}}\sum_{s=0}^{\infty}\frac{p_1^{s}}{\Gamma[N_4-N_1+s+1]} \times\mathcal{G}_{N_2+sN_30}^{0,q}(0,p_2+p_1,p_3+p_1), \tag{32}$$

$$\mathcal{Q}_{N_2N_3N_4}^{N_1,q}(p_1,p_2,p_3) = \frac{p_1^{N_1}}{(N_4-N_1)_{N_1}}\left\{\mathcal{G}_{N_2N_30}^{0,q}(0,p_2,p_3) \times\sum_{s=0}^{\infty}\frac{p_1^{s}}{\Gamma[N_4-N_1+s+1]} \times\mathcal{G}_{N_2+sN_30}^{0,q}(0,p_2+p_1,p_3+p_1)\right\}, \tag{33}$$

TABLE IV. The values of two-center Coulomb integrals over NSTO in lined-up coordinate systems.

n_1/n_1'	l_1/l_1'	m_1/m_1'	ζ_1/ζ_1'	n_2/n_2'	l_2/l_2'	m_2/m_2'	ζ_2/ζ_2'	R	Results
1.1/1.1	0/0	0/0	3.3/7.5	2.1/2.1	0/0	0/0	5.2/4.1	2.0	3.70777 93430 04351 88597 41401 $\times 10^{-1}$ [a]
									3.70777 91146 97699 $\times 10^{-1}$ [b]
1.1/1.1	0/0	0/0	3.3/7.5	2.1/2.1	0/0	0/0	5.2/4.1	0.2	1.43116 03370 07045 41502 21987[a]
									1.43116 03370 070363[b]
1.5/2.5	0/0	0/0	5.2/5.2	2.2/1.3	0/0	0/0	4.1/4.1	2.0	4.03973 39319 31391 43106 54998 $\times 10^{-1}$ [a]
									4.03973 39029 016377 $\times 10^{-1}$ [b]
1.5/2.5	0/0	0/0	5.2/5.2	2.2/1.3	0/0	0/0	4.1/4.1	0.2	1.37950 96732 83485 29390 58534[a]
									1.37950 96732 834748[b]
3.3/1.2	0/0	0/0	3.5/4.5	1.3/3.5	0/0	0/0	5.3/5.2	2.0	1.43069 98608 06165 34609 69226 $\times 10^{-1}$ [a]
									1.43069 97832 695897 $\times 10^{-1}$ [b]
1.3/2.2	0/1	0/0	5.2/3.1	2.1/3.3	0/2	0/0	4.1/2.5	0.2	-2.20621 95808 46121 42004 26870 $\times 10^{-2}$ [a]
									-2.20621 95808 461294 $\times 10^{-2}$ [b]
2.3/2.5	0/1	0/0	5.2/3.1	2.5/3.5	0/2	0/0	4.1/2.5	0.2	-2.43223 06409 75118 67189 49036 $\times 10^{-2}$ [a]
									-2.43223 06409 75117 $\times 10^{-2}$ [b]
2.2/1.4	1/0	1/0	4.0/5.2	2.4/2.2	1/0	1/0	3.1/4.1	0.2	2.02231 33338 48645 17745 17104 $\times 10^{-1}$ [a]
									2.02231 33338 486546 $\times 10^{-1}$ [b]
1.7/1.7	0/0	0/0	5.2/5.2	2.5/2.5	1/1	$-1/-1$	3.1/3.1	8.5	1.17291 23163 43926 46406 72110 $\times 10^{-1}$ [a]
									1.17290 70005 783289 $\times 10^{-1}$ [b]
2.6/2.4	1/0	1/0	4.0/5.2	1.4/1.2	1/0	1/0	3.1/4.1	0.2	2.73167 34925 29429 58648 30570 $\times 10^{-1}$ [a]
									2.73167 34925 296465 $\times 10^{-1}$ [b]
3.1/3.1	2/2	$-2/-2$	1.8/1.8	2.3/2.5	0/0	0/0	4.1/4.1	8.5	1.15128 95407 69354 45822 45832 $\times 10^{-1}$ [a]
									1.15128 19943 95839 $\times 10^{-1}$ [b]

[a]Global-adaptive method with Gauss-Kronrod extension.
[b]Cuba numerical integration algorithm.

TABLE V. The values of two-center hybrid integrals over NSTO in lined-up coordinate systems.

n_1/n_1'	l_1/l_1'	m_1/m_1'	ζ_1/ζ_1'	n_2/n_2'	l_2/l_2'	m_2/m_2'	ζ_2/ζ_2'	R	Results
1.1/1.1	0/0	0/0	3.3/7.5	2.1/2.1	0/0	0/0	5.2/4.1	2.0	3.34570 65033 29520 49016 78182 $\times 10^{-2}$ [a]
									3.34570 49544 71777 $\times 10^{-2}$ [b]
1.1/1.1	0/0	0/0	3.3/7.5	2.1/2.1	0/0	0/0	5.2/4.1	0.2	1.42056 86050 09755 96650 10503[a]
									1.42056 86050 097461[b]
1.5/2.5	0/0	0/0	5.2/5.2	2.2/1.3	0/0	0/0	4.1/4.1	2.5	5.82088 47419 91349 23796 94930 $\times 10^{-3}$ [a]
									5.82087 59642 53641 $\times 10^{-3}$ [b]
1.5/2.5	0/0	0/0	5.2/5.2	2.2/1.3	0/0	0/0	4.1/4.1	0.25	1.31612 20582 17586 69403 48337[a]
									1.31612 20582 17552[b]
2.3/2.3	1/1	0/0	3.1/4.0	2.1/3.5	0/1	0/0	3.1/1.5	2.5	3.98086 07407 55049 65876 23549 $\times 10^{-1}$ [a]
									3.98086 07472 57121 $\times 10^{-1}$ [b]
2.3/2.3	1/1	0/0	3.1/4.0	2.1/3.5	0/1	0/0	3.1/1.5	0.25	9.62984 79396 02364 97003 91963 $\times 10^{-2}$ [a]
									9.62984 79396 0241 $\times 10^{-2}$ [b]
2.3/2.3	1/1	0/1	3.1/4.0	2.1/3.5	1/1	0/1	3.1/1.5	2.5	5.46328 06938 93362 73357 23212 $\times 10^{-3}$ [a]
									5.46329 74885 12861 $\times 10^{-3}$ [b]
2.3/2.3	1/1	0/1	3.1/4.0	2.1/3.54	1/1	0/1	3.1/1.5	0.25	1.16785 23072 08658 28310 17007 $\times 10^{-2}$ [a]
									1.16785 23072 089619 $\times 10^{-2}$ [b]
2.1/2.2	1/1	0/1	3.1/4.0	2.3/3.4	1/1	0/1	3.1/1.5	0.85	1.19610 29417 94992 00041 70305 $\times 10^{-2}$ [a]
									1.19610 29418 696619 $\times 10^{-2}$ [b]
2.1/2.2	1/1	0/1	3.1/4.0	2.3/3.4	1/1	0/1	3.1/1.5	8.5	6.21247 25221 86688 36073 21675 $\times 10^{-6}$ [a]
									6.17573 31239 59217 $\times 10^{-6}$ [b]

[a]Global-adaptive method with Gauss-Kronrod extension.
[b]Cuba numerical integration algorithm.

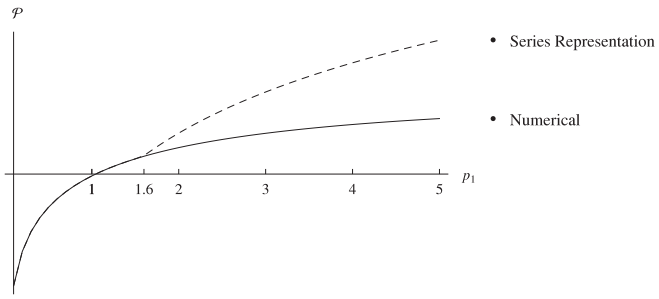

FIG. 1. The comparison of numerical and series representation calculations of $\mathcal{P}^{0,100}_{100\,100\,100}(p_1,12,9.6)$ auxiliary functions depending on p_1. The solid black line and the dashed black line is the numerical and series representation formulas, respectively.

with

$$\mathcal{G}^{0,q}_{N_2N_30}(0,p_2+p_1,p_3+p_1) = \lim_{s\to\infty}\sum_{k=0}^{N_2+s} F^s_k(N_2,N_3) \times A_{N_2+N_3+q-k}(p_2)B_{q+k}(p_3), \tag{34}$$

where

$$A_n(p) = \int_1^\infty \mu^n e^{-p\mu} d\mu \tag{35}$$

and

$$B_n(p) = \int_{-1}^1 \nu^n e^{-p\nu} d\nu \tag{36}$$

are the Mulliken auxiliary functions. The $F^s_k(n,m)$ are the generalized binomial coefficients, which are obtain from binomial theorem for parameters with noninteger values,

$$F^s_k(n,m) = \sum_{\sigma=0}^{s}(-1)^\sigma F_{k-\sigma}(n)F_\sigma(m), \tag{37}$$

where the coefficients $F_n(m)$ are the binomial coefficients.

The incomplete gamma functions in the region $0 \leqslant a < 1$ are unstable [61,63,64]. Generation of the incomplete gamma functions by means of recurrence relations for $0 \leqslant a < 1$ in an efficient approach and computing the gamma functions without erroneous last digits is still being studied in the literature [65,66].

The convergence properties of series representation formulas of $\mathcal{P}^{N_1,q}_{N_2N_3N_4}$ and $\mathcal{Q}^{N_1,q}_{N_2N_3N_4}$ auxiliary functions for $N_i \in \mathbb{N}$ are examined in Figs. 1 and 2 depending on p_1 and the upper limit of summation occurring in series representation formulas, respectively. In Fig. 1 the upper limit of summation is chosen to be 100. In Fig. 2 vertical lines show the critical values for the upper limit of summations which damp the oscillation.

Figures 1 and 2 show that values obtained from formulas of auxiliary functions diverge from accurate numerical values when increasing the parameter p_1 and for large values of parameters require a maximal increase in upper limits of summation.

Finally, we point out that the formulas and algorithm presented in this paper give highly accurate results for the two-center Coulomb and hybrid integrals and they can be useful in both relativistic and nonrelativistic electronic structure calculations for determination of various properties of molecules when HFR and Dirac-Hartree-Fock-Roothaan theories and explicitly correlated approximations are used. Calculation for these integrals is performed without assuming Hermiticity, which can then be used to check symmetry in the

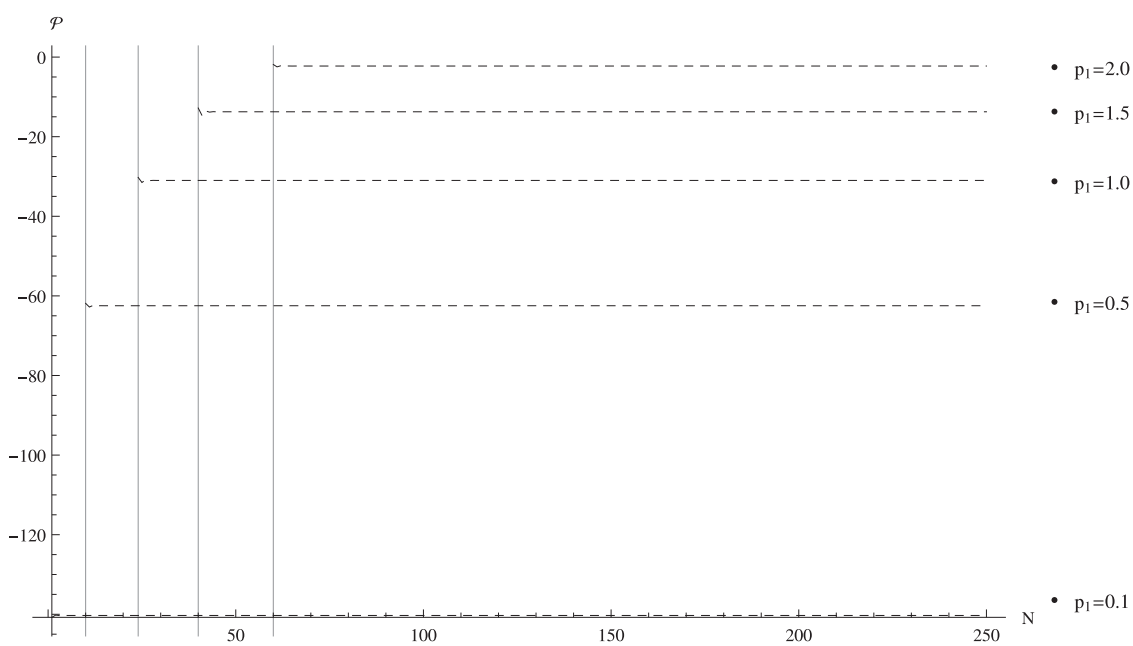

FIG. 2. The comparison of numerical and series representation calculations of $\mathcal{P}^{0,50}_{50\,50\,50}(p_1,12,9.6)$ auxiliary functions depending on upper limits of summation of series representation formulas with different values of p_1.

basis (but would have improved the accuracy). The method suggested in this study on solving one of the basic problems in theoretical atomic and molecular physics should find a broad readership.

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