Analytical evaluation of relativistic molecular integrals: III. Computation and results for molecular auxiliary functions

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Abstract
This work describes the fully analytical method for the calculation of the molecular integrals over Slater-type orbitals with non-integer principal quantum numbers. These integrals are expressed through relativistic molecular auxiliary functions derived in our previous paper (Bağcı and Hoggan in Phys Rev E 91(2):023303, 2015). The procedure for computation of the molecular auxiliary functions is detailed. It applies both in relativistic and non-relativistic electronic structure theory. It is capable of yielding highly accurate molecular integrals for all ranges of orbital parameters and quantum numbers.

Keywords Non-integer principal quantum numbers · Slater-type orbitals · Multi-center integrals

1 Introduction

Formulae for interpreting visible (Balmer) and all observed electronic spectra of hydrogen were first characterized by two integers \( n_1 \) (visible \( n_1 = 2 \)) and \( n_2 \). The idea of dropping the restriction to integer values of these numbers was first suggested by Rydberg (1890) in 1890. In the Bohr atom model (1913), the integers “\( n \)” became known as “quantum numbers” before full identification with the principle quantum number, with the solution of non-relativistic Schrödinger equation for the Coulomb interaction in atomic units. This was much earlier than any attempt to develop a stable method for electronic structure calculation of many-electron systems or to construct a more flexible basis orbital to be used in this method.

The solution of non-relativistic Schrödinger equation for the Coulomb interaction in atomic units (a.u.) leads to an expression for the wavelengths \( \lambda \) of spectral line emitted in a transition of the atom from quantum state \( n_2 \) to state \( n_1 \) Bethe and Salpeter (1957),
\[
\frac{1}{\lambda} = \frac{1}{2\pi} (E_{n_2} - E_{n_1}) = \frac{Z^2}{4\pi} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right). \tag{1}
\]

where \( Z \) is the nuclear charge, \( E_{n_1}, E_{n_2} \) are the lower and upper energy levels for hydrogen-like atoms. \((n_1, n_2)\) are the principal quantum numbers. According to Bohr theory, they have integer values. Rydberg through investigation of alkali metal spectra showed that for many-electron atoms, a similar empirical expression could be used:
\[
\frac{1}{\lambda} = \frac{1}{2\pi} (E_{n_2} - E_{n_1}) = \frac{Z^2}{4\pi} \left( \frac{1}{(n_1 - \delta_1)^2} - \frac{1}{(n_2 - \delta_2)^2} \right). \tag{2}
\]

Here, \( n^* = n - \delta \) is an effective quantum number with non-integer values. The quantity \( \delta \) is called the quantum defect Seaton (1983). For atomic orbitals, it depends on the angular momentum quantum number \( l \). Equation (2) was obtained assuming that the \( Z - 1 \) core electrons (a full shell for alkali metal cations) influence the energy of the outermost electron only by screening the pure Coulomb potential (Hertel and Schulz 2015; Kostelecký and Nieto 1985). This screened Coulomb potential is used to solve the Schrödinger-like equation for the outermost electron. An analytical wave function with a similar form to the hydrogen atom solution...
but with non-integer values of principal quantum numbers is obtained (Kostelecký and Nieto 1985). Note that quantum mechanical justification of the Ritz expansion (Ritz 1903) for the quantum defect was finally given by Hartree (1928). Such modification of Bohr’s theory thus guided work towards concepts used in the analytical Hartree–Fock SCF equations (Roothaan 1951) and derivation of basis orbitals with non-integer principal quantum numbers as basis sets.

Many-electron atoms are well described with each electron occupying an “atomic orbital” which corresponds physically to the hydrogen-like eigenfunction for that electron in the field of the “bare” nucleus screened by all the other electrons. This can be visualized easily for such electronic configurations as the alkali metals, Li, Na, K, etc., where the single electron in the highest “n” shell evolves in an effective charge of approximately $Z - 1$. In all cases, the idea is that a screening constant $\sigma$ can be ascribed to the other electrons on the basis of the “average time spent” by this electron between the nucleus and the electron of interest. The non-integer principal quantum number orbitals are hydrogen-like eigen functions in this model, such that the energy of a given electron is given (in a.u.) by $\frac{1}{2} - \frac{1}{n} + \frac{1}{n}^2$ as it is for hydrogen and its eigen functions (here, $\sigma$ is the sum of shielding constants for all other electrons). In the 1930s, variational studies for the atoms with $n = 2$ were carried out by Zener (1930). The hydrogen-like eigen functions are used but $n^+$ (as well as the exponent, giving values of $\sigma$) are variational parameters. The results show modest departure from $n = 2$ and give a set of shielded exponents.

Slater (1930a) realized that the use of arbitrary basis functions is possible in the variational or Hartree method for atomic structure of many-electron systems. The orbitals that carry his name were explicitly defined, just after Zener’s work in 1930 Slater (1930b). This paper extends Zener’s variational approach but with simplified radial functions using a single power $(n-1)$ of $r$ from the hydrogen-like eigen functions. The exponents and principal quantum numbers are replaced by shielded values known as “Slater screening constants” and non-integer values, obtained variationally. Tabulated screening constants and effective quantum numbers give reasonable ionization energies for the elements. It becomes necessary to modify the principal quantum number from $n = 4$, replaced by $n = 3.7$.

Application of the atomic Hamiltonian to these Slater-type functions yields approximate energies, as they are not eigen functions (so some $r$-dependence generally results); however, the approximation is very useful for properties of many-electron atoms.

Slater-type orbitals with non-integer principal quantum numbers (NSTOs).

$$\chi(\zeta, r) = \frac{(2\zeta)^{n+1/2}}{\sqrt{I(2n + 1)}} r^{n-1} e^{-\zeta r} \psi_{lm}(\theta, \varphi) \quad (3)$$

are obtained by simplification of Laguerre functions in hydrogen-like wave function (obtained from solution of Schrödinger-like equation) by keeping only the term of the highest power of $r$. Compared to integer $n$-STO, they provide extra flexibility for closer variational description of atoms and molecules since now in addition to orbital parameters $\zeta$, the principal quantum numbers are also variational parameters. This was already highlighted by Zener with a particular note that by allowing extra parameters in the basis orbitals to be flexible, better variational performance may be obtained without increased complexity. Moreover, it was also predicted that using such sophisticated basis orbitals in molecular Hartree–Fock SCF calculations makes evaluation of the molecular integrals laborious. Absence of mathematical difficulties in evaluation of integrals for atomic systems, on the other hand, allowed for research on using NSTOs (Saturno and Parr 1958; Synder 1960; Allouche 1974) from different points of view. Complexity of basis sets was increased, effectiveness of such approximations on physical representation of a quantum mechanical system was investigated. It should be noted that the work performed so far on electronic structure calculation of atoms and molecules with NSTOs, which are investigated in detail below, clearly takes inspiration from Zener (1930).

Years after Zener’s paper, Parr and Joy made the first attempt to calculate molecular electronic structure Parr and Joy (1957) in 1957. In their next work, they revealed the integral evaluation bottleneck that causes problems in solving molecular calculations Joy and Parr (1958). Four kinds of basic integral, the overlap, kinetic energy, nuclear attraction, electron–electron repulsion integrals were described. The prolate spheroidal coordinate method was used to evaluate these integrals from their expressions in terms of gamma functions, incomplete gamma functions, incomplete beta functions. The stability of results for the incomplete gamma functions varies according to domain of parameters (Gil et al. 2012). They have no explicit closed-form relations (Backeljauw et al. 2014; Nemes 2015, 2016; Nemes and Daalhuis 2019; Greengard and Rokhlin 2019).

Following Parr, the single-center approach to molecular calculations using coordinate space was developed, in particular by Bishop (1963a, b, 1965, 1967). This author is well known for chemical applications of group theory which seemingly guided his choice of molecule: $\text{H}_2\text{O}^+$, $\text{CH}_4$, $\text{NH}_3$ using Slater-type orbitals with non-integer principal quantum numbers. These studies suffer from a lack of mathematical and/or numerical tool box for accurate calculation of molecular integrals over NSTOs. Nevertheless,
researchers had a desire to explore the advantages of using of NSTOs in molecular calculations.

Shortly afterwards, an alternative approach, based on momentum space was broached by Prosser and Blanchard (1962) the convolution theorem for the Fourier transform method was suggested instead of auxiliary function methods. The latter method expresses the two-center integrals in ellipsoidal coordinates. The resulting basic integrals are called auxiliary functions.

All subsequent studies so far, in an effort to derive an individual palatable technique for the solution, have used either the auxiliary function method (Saturno and Parr 1960; Ludwig and Parr 1961; Geller 1962) or the Fourier transform convolution method (Prosser and Blanchard 1962). The former originated from Hobson (1931) and was suggested for use in quantum chemistry by Mulliken et al. (1949), the latter results in highly oscillatory integrands, involving spherical Bessel functions. The hydrogen molecule example has rightly been considered because it is the simplest possible molecule, with two protons \( R \) apart and two electrons (\( H_2^+ \) has one-electron). Mathematically expressing the problem of integral evaluation within this framework was done by Geller and Silverstone in series of papers (Geller 1963, 1966, 1967).

In another bold attempt made by Allouche (1976) to eliminate the problem of integral evaluation taking into account the accuracy for results, prolate spheroidal coordinates were used. The two-center one-electron integrals were again expressed in terms of auxiliary functions integrals involving the incomplete gamma functions. The two-center two-electron integrals were expressed in terms of auxiliary function integrals involving the product of Legendre polynomials with different centers and the incomplete gamma functions. This time for integration of the resulting molecular auxiliary functions the numerical Gaussian quadrature procedure was suggested. Both the numerical procedure and its computer code makes it challenging to get accurate results for the auxiliary function integrals given in Allouche (1976). This may be because practical multi-precision libraries and the symbolic programming languages were not available when Allouche’s paper was published. Even if they were available, in fact, it would still be laborious [please see Romanowski (2008a, b), Romanowski and Krukowski (2008), Romanowski and Jalbout (2009) where numerical three-dimensional adaptive integration procedure used for calculation of two-center integrals with Slater-type functions (STOs)]. The principal quantum numbers were restricted to be integers yet, even for the lowest values of quantum numbers the results are insufficient). A far-reaching transformation method suggested for radial parts of NSTOs in Allouche (1976) as

\[
\begin{align*}
  r_B^n e^{-\zeta r_B} \\
  = \sqrt{2\pi} \sum_{l=0}^{\infty} \frac{1}{r_A R_{AB}} V_{n+2l}(r_A, R_{AB}, \zeta) Y_{l0}(\theta_A, \varphi_A),
\end{align*}
\]

(4)

shows that if the accuracy problem for two- and three-center integrals is eliminated then, it is eliminated for four-center integrals as well. The last pre-90s study that needs to be highlighted in the context of this paper was performed by Taylor (1978). There a general manipulation for inverse Gauss transforms was derived. Formulas for inverse Gauss transforms of Slater-type orbitals obtained in a previous research Kikuchi (1954) were generalized to NSTOs. As far as we know, no detailed implementation of this method for molecular calculations has yet been devised. It is beyond the scope of the present paper but remains an interesting work to be noted for the future.

In the 90s, applications using NSTOs concentrated only on atomic implementations. It can be said that Koga et al. played a dominant role in this work (Koga et al. 1993, 1997, 1998; Koga and Kanayama 1997a, b; Miguel et al. 2000) through exclusively investigating the atoms for each individual modification to the basis sets. As stated above, the aim here was finding the optimal basis sets to be used in Hartree–Fock SCF calculations that represent the physical properties of the system as ideally as possible. For atoms with nuclear charge \( Z \), \( Z \leq 54 \) detailed calculations using Slater-type basis orbitals had been performed by Clementi and Roetti (1974). In this study, with single-, double-zeta basis set approximations, the ground, excited state energies and linear combination coefficients of the atomic wave function (in analytical solution of Hartree–Fock SCF equations the atomic wave function is represented by linear combination of primitive basis orbitals) were perfected. Reference STO basis sets can be obtained from these studies, as well as from the numerical Slater-DFT code ADF that was developed by Baerends et al. (1973).

Formally, studies on basis set construction methods (de la Vega and Miguel 1993, 1994, 1995; de la Vega et al. 1996; Ema et al. 1999) and re-optimization of orbital exponents (Koga et al. 1993, 1993, 1995) which are considered to improve the results given in Clementi and Roetti (1974) were performed using Slater-type orbitals. Thus, using the strategies developed in this work and dropping the restriction on principal quantum numbers provided further improvements. Note that, in early works of the 90s, it was believed that using NSTOs as basis orbitals in analytical solution of Hartree–Fock SCF equations may...
result in lower values for energy then numerical solutions (Bunge et al. 1992). In this class of computation, however, the main idea is testing basis set limits, in terms of energy.

Electron correlation and the relativistic effects are ignored. The best results for energy of atoms are found from numerical solution of Hartree–Fock SCF equations. When analytical and numerical solution coincide, the so-called Hartree–Fock limit is reached for a given basis set.

The following improvements for the results given in Clementi and Roetti (1974) were inspired from the work in Höjer (1979). New variational parameters, like $(\eta)$ in $(\rho^{n+1} e^{-\xi n})$ (Koga and Kanayama 1997) and from work in Szalewicz and Monkhorst (1981) new functions of $(\cosh(\beta r + \gamma))$, such as $r^{n+1} e^{-\xi n} \cosh(\beta r + \gamma)$ (Koga 1998a, b; Koga et al. 1999), embedded into the radial part of NSTOs. These new amendments also led to closer results to numerical solution for Hartree–Fock SCF. Besides, the quantity $\beta r$ in hyperbolic cosine was written as $\beta r^n$ (Guseinov and Erturk 2012). Then the final generalized of hyperbolic cosine functions was embedded as $\cos_{pq}(\beta r^n + \gamma)$ (Erturk 2015). Using this kind of basis set produced results which are so far the closest to numerical references because each basis orbital in the linear combination has at least four variational parameter and basis set approximations such as double-zeta have not yet been considered.

The improvements so far obtained for comprehensively investigating the physical properties of atoms via the Hartree–Fock SCF method have led to a decision about molecular applications of derived formulae and algorithms. A solution for the integral evaluation problem in molecular calculations even with pure NSTOs without any additional parameter or functions is still pending. In the late 90s, one more attempt was made by Mekelleche and Baba-Ahmed (1997, 2000). Due to lack of benchmark values for the integrals then, a tremendous number of papers were published [mostly by Guseinov and Mamedov (2002, 2004), Guseinov (2002, 2007, 2009a, b), Guseinov et al. (2002), Özdoğan and Orbay (2002), Özdoğan (2003, 2004) and Özdoğan et al. (2003)]. We only cite here, those that are noteworthy. We refer the interested readers for more information Weniger (2005, 2008, 2012). In almost all this work the ill-conditioned binomial series expansion,

$$\sum_{s=0}^{\infty} (-1)^s F_s(n) x^{n-s} y^s,$$

where $F_s(n)$ are the binomial coefficients indexed by $n$, and $s$ is usually written $\begin{pmatrix} n \end{pmatrix}$, with

$$\begin{pmatrix} n \end{pmatrix} = \frac{\Gamma(n+1)}{\Gamma(s+1) \Gamma(n-s+1)}.$$  

$\Gamma(n)$ is the gamma function or the single-center expansion approximation,

$$x_{nm}(\zeta, \rho) = \lim_{N \to \infty} \sum_{n=0}^{N} V_{nl}^{N} x_{n,m}(\zeta, \rho)$$

was used. Here, $V_{nl}^{N}$ are the expansion coefficients used to represent the Slater-type orbitals with non-integer principal quantum numbers in terms of Slater-type orbitals with integer principal quantum numbers Guseinov (2007). It has been assumed that the results of calculations obtained with any of these approximations are accurate. Accordingly, these approximations have been applied for solution of various problems (Guseinov and Mamedov 2002, 2003, 2004; Özdoğan 2004; Guseinov and Mamedov 2005a, b; Guseinov 2008, 2012a, b). Finally, the benchmark results for two-, three-center one- and two-electron molecular integrals which have been in demand for years to test the accuracy of any analytical method to be derived, obtained via numerical global-adaptive method through Gauss–Kronrod numerical integration extension (Davis and Rabinowitz 1975) by us (Bağcı and Hoggan 2014, 2015a, b) with 35 correct decimals. A new molecular auxiliary function was introduced (Bağcı and Hoggan 2015a). Note that, the analytical evaluation of these functions involve some challenges, namely power functions with non-integer exponents, incomplete gamma functions and their multiplications have no explicit closed-form relations. The stability of results for the incomplete gamma functions varies according to domain of parameters. Four domains for computation of incomplete gamma functions ratios were indicated in Gil et al. (2012) (please see also references therein) considering the methods available in the literature. Efficient and accurate approximation for computation of the incomplete gamma functions is still being studied in the literature (Backeljauw et al. 2014), Nemes (2015, 2016), Nemes and Daalhuis (2019) and Greengard and Rokhlin (2019).

In the following, the definition and the origin of these new molecular auxiliary functions are re-visited, and an analytical method based on a recurrence strategy which is based on the criterion defined in our previous papers of the series is developed for their computation (Bağcı and Hoggan 2018a, b). Necessity of computing the incomplete gamma functions is avoided.

The main scope of this paper is to show that neither in terms of accuracy nor CPU speed do disadvantages of using NSTOs in molecular calculations occur in comparison to Slater-type orbitals. The algorithm thereof for the molecular auxiliary functions computation is detailed. A computer code is written using Julia programming language (Bezanson et al. 2017). The results obtained for molecular auxiliary functions are compared with those obtained from a numerical global-adaptive method based on Gauss–Kronrod numerical
integration extension. This numerical method is known to derive benchmark values (Bağcı and Hoggan 2014, 2015a). Note that a possible choice would be just presenting the formulas and sharing the details of computations upon request. The problem of molecular integral evaluation with NSTOs has preoccupied researchers for decades. As stated above, plenty of research articles are available in the literature that produce suspicious approaches and results. We thus believe there should be sufficient information in this paper for both beginner and expert readers to re-compute the given formulas and reproduce the results. To conclude this section, we are convinced this work leads to an analytical solution of the molecular integrals problem with non-integer Slater-type orbitals. The rest of this paper demonstrates that highly accurate numerical values can then be obtained with suitable algorithms and controlled expansions.

2 Revisiting the molecular auxiliary function features

The molecular auxiliary functions defined in prolate spheroidal coordinates (\(\xi, \nu, \phi\)) where \(1 \leq \xi < \infty, -1 \leq \nu \leq 1, 0 \leq \phi \leq 2\pi\) have the following form:

\[
\begin{align*}
\mathcal{P}_{n_1,q}^{n_2,0}(p_{123}) &= 
\frac{p_{1}^{n_1}}{(n_4 - n_1)_n} \int_{1}^{\infty} \int_{-1}^{1} \frac{\Gamma(p_1(\xi + \nu))}{\Gamma(n_4 - n_1, p_1(\xi + \nu))} e^{p_2 \xi - p_3 \nu} \text{d}\xi \text{d}\nu, \quad (9)
\end{align*}
\]

where \(\{q, n_1\} \in \mathbb{Z}, \{n_2, n_3, n_4\} \in \mathbb{R}, p_{123} = \{p_1, p_2, p_3\}\) (and in subsequent notation), \(p_1 > 0, p_2 > 0, -p_1 \leq p_3 \leq p_2\).

\(P, Q\) are the normalized complementary incomplete gamma and the normalized incomplete gamma functions (Abramowitz and Stegun 1972; Temme 1994),

\[
P[a, z] = \frac{\gamma(a, z)}{\Gamma(a)}, \quad Q[a, z] = \frac{\Gamma(a, z)}{\Gamma(a)},
\]

where \(\gamma(a, z)\) and \(\Gamma(a, z)\) are incomplete gamma functions,

\[
\gamma(a, z) = \int_{0}^{z} t^{a-1} e^{-t} \text{d}t, \quad \Gamma(a, z) = \int_{z}^{\infty} t^{a-1} e^{-t} \text{d}t,
\]

\(\Gamma(a)\) is a complete gamma function,

\[
\Gamma(a) = \Gamma(a, z) + \gamma(a, z),
\]

and the Pochhammer’s symbol \((a)_n\) is defined,

\[
(a)_n = \frac{\Gamma(a + n)}{\Gamma(a)}.
\]

The incomplete gamma functions in Eq. (9) arise as a result of two-electron interactions. As stated in our previous work, the symmetry properties of two-center two-electron integrals allow us to take advantage of the sum \(P + Q = 1\) instead of immediate expansion of incomplete gamma functions or using the relations \(P = Q = 1, Q = P - 1\) with their conditional convergence (Temme 1994). This feature was formalized by a criterion given as

\[
\text{Criterion Let } P[n_4 - n_1, z] \text{ and } Q[n_4 - n_1, z] \text{ then } n_4 - n_1 = a \pm c, n_4 - n_1 = a \pm d, \text{ where } a \in \mathbb{R}, \{c, d\} \in \mathbb{Z} \text{ are true for any integrals that can be reduced to Eq. (9).}
\]

It is now legitimate to use up- and down-ward distant recurrence relations for normalized incomplete gamma functions Temme (1994) and reduce Eq. (9) to well-known overlap-like integrals defined in prolate spheroidal coordinates (Bağcı and Hoggan 2018b) which are independent from electron–electron interactions as follows:

\[
\mathcal{G}_{n_1,n_1}^{n_1,q}(p_{123}) = \frac{p_{1}^{n_1}}{\Gamma(n_1 + 1)} \times \int_{1}^{\infty} \int_{-1}^{1} (\xi \nu)^{q} (\xi + \nu)^{p_1 - p_2 - p_3} e^{-p_2 \xi - p_3 \nu} \text{d}\xi \text{d}\nu.
\]

Using the following relationship:

\[
(\xi \nu)^{q} = \frac{1}{2^{2q}} \sum_{s_1} (-1)^{s_1} F_{s_1}(q)(\xi + \nu)^{2q - 2s_1}(\xi - \nu)^{2s_1},
\]

for Eq. (14), we have,

\[
\mathcal{G}_{n_1,n_1}^{n_1,q}(p_{123}) = \frac{1}{2^{2q}} \sum_{s_1} (-1)^{s_1} F_{s_1}(q) \mathcal{G}_{n_1 + 2q - 2s_1, n_1 + 2s_1}^{n_1,0}(p_{123}),
\]

\(0 \leq s_1 \leq q\).

The vectorization procedure which runs faster than the corresponding code containing loops is used for computation of molecular auxiliary functions. It is, therefore, more advantageous to detail the computer program code to be written in two sections. In Sect. 3, formulas used for computation are given explicitly. In Sect. 4, their constituent sum-functions are expressed via recurrence relations that allow us to reduce the sum indices arising in the formulas and to take advantage of storage. Four sum indices which intrinsically appear in the equations are defined as follows:

- \(s_1\) is used for binomial expansion of \((\xi \nu)^{q}\),
- \(s_2\) is used for series expansion of \(e^{-p_2 \xi}\),
- \(s_3\) is used for binomial expansion of \((\xi \nu)^{2q}\),
- \(s_4\) is used for series expansion of incomplete beta functions.
These indices appear in Sect. 3 through explicitly writing Eq. (14) by including all the sub-functions in its content. On the other hand, storing the value of all terms in explicit form of Eq. (14) requires using two indices (instead of four) run over a finite sum and an infinite sum, respectively. This causes to define additional indices as \( s_5, s_6 \) (please see the Appendix 1).

### 3 Computation of the molecular auxiliary functions

The relationships derived in our previous papers (Bağcı and Hoggan 2018a, b) for molecular auxiliary functions can be recapitulated in the present paper. Equation (16) is still primary, but its reduced form \( G^{n,0}_{n_1,n_3}(p_{123}) \) on the right-hand side is as follows:

\[
G^{n,0}_{n_1,n_3}(p_{123}) = \begin{cases} 
G^{n,0}_{n_1,n_3}(p_{102}) & \text{if } p_3 = 0 \\
\frac{p_1^{n_1}}{\Gamma(n_1 + 1)} \sum_{t_2} (-1)^{t_2} G^{s_2,s_3}_{n_2,n_3}(p_{302}) & \text{if } p_3 \neq 0,
\end{cases}
\]

where

\[
G^{n,0}_{n_2,n_3}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} e^{-p_2} \times \int_1^\infty \int_0^1 \xi^{-q_3}(\xi v)^2(\xi + v)^{p_3} e^{-p_2 \xi} d\xi dv.
\]

(17)

The binomial expansion in Eq. (15) is also used for \( G^{n,q}_{n_2,n_3}(p_{123}) \):

\[
G^{n,q}_{n_2,n_3}(p_{123}) = \frac{1}{2^{2q_2}} \sum_{s_1,s_2,s_3} (-1)^{s_1+s_2+s_3} F_{s_2}(q_2) \ G^{n,q}_{n_2+n_1-2s_1-n_3,2s_1,2s_3}(p_{123}).
\]

(18)

A general analytical expression to be used while \( p_3 \neq 0 \), for the right-hand side of Eq. (19) was previously expressed in terms of incomplete beta functions (Bağcı and Hoggan 2018b). Here, we use a simplified form that is easier for coding:

\[
G^{n,q}_{n_2,n_3}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} e^{-p_2} \times \int_1^\infty \int_0^1 \xi^{-q_3}(\xi v)^2(\xi + v)^{p_3} e^{-p_2 \xi} d\xi dv \times F_{s_2}(q_2) \left\{ \frac{p_3^{n_2}}{\Gamma(s_2 + 1)} \right\} \left\{ \frac{1}{2^{s_2}} \right\} \left\{ B_{n_2+n_1-2s_1-n_3,2s_1+2s_2+1} \times E_{s_2}(n_2+n_1+2s_2+1)(p_2) \right\}
\]

(19)

4 Recurrence relations to be used for vectorization of sub-functions arising in Eq. (24)

One of the main difficulties of the formula given in the previous section is calculating the \( m^{n_1}_{n_2}(p) \) auxiliary functions. They contain all four summation indices. Moreover, two different \( m^{n_1}_{n_2}(p) \) functions arise in Eq. (24). Yet, symmetry relationships for these functions are found. The four sum

\[
G^{n,q}_{n_2,n_3}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} e^{-p_2} \times \int_1^\infty \int_0^1 \xi^{-q_3}(\xi v)^2(\xi + v)^{p_3} e^{-p_2 \xi} d\xi dv \times F_{s_2}(q_2) \left\{ \frac{p_3^{n_2}}{\Gamma(s_2 + 1)} \right\} \left\{ \frac{1}{2^{s_2}} \right\} \left\{ B_{n_2+n_1-2s_1-n_3,2s_1+2s_2+1} \times E_{s_2}(n_2+n_1+2s_2+1)(p_2) \right\}
\]

(20)

The analytical expression for \( _{n_1,n_3}(p_{123}) \) auxiliary functions was obtained previously as

\[
\begin{align*}
m^{n_1}_{n_2}(p) & = 2^m U(n_2 + 1, n_1 + 1 + 2, p) \Gamma(n_2 + 1) e^{-p}, \\
U(\alpha, \beta, z) & \text{ are confluent hypergeometric functions of the second kind Abramowitz and Stegun (1972).}
\end{align*}
\]

The following final and explicit expression for Eq. (16) is obtained in addition to our previous work, to collect and store all the terms as

\[
G^{n,q}_{n_2,n_3}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} e^{-p_2} \times \int_1^\infty \int_0^1 \xi^{-q_3}(\xi v)^2(\xi + v)^{p_3} e^{-p_2 \xi} d\xi dv \times F_{s_2}(q_2) \left\{ \frac{p_3^{n_2}}{\Gamma(s_2 + 1)} \right\} \left\{ \frac{1}{2^{s_2}} \right\} \left\{ B_{n_2+n_1-2s_1-n_3,2s_1+2s_2+1} \times E_{s_2}(n_2+n_1+2s_2+1)(p_2) \right\}
\]

(21)
indices are reduced to one while $p_3 = 0$ and to two while $p_3 \neq 0$. This allows to calculate only one $m_{n_1}^m(p)$ function and extract the data necessary for the other from disc memory. The following recurrence relationships are derived accordingly:

\[
m_{n_1+p+1}^{n_2+2q-s}(p) = \frac{1}{4} \left( \frac{1}{(n_1+s) + 2q-s+1} \right) m_{n_1+p+1}^{n_2+2q-(s-1)}(p) + \frac{1}{2} \left( \frac{1}{(n_2-n_1+2q-2s-p_2+1)} \right) \times m_{n_1+p+1}^{n_2+2q-(s-1)}(p),
\]

(25)

\[
m_{n_1+p+1}^{n_2+2q-s'}(p) = \frac{1}{4} \left( \frac{1}{(n_1+s) + 2q-s'+1} \right) m_{n_1+p+1}^{n_2+2q-(s'-2)}(p) + \frac{1}{2} \left( \frac{1}{(n_2+s) - n_3 + 2q-2s'-p_2+1} \right) \times m_{n_1+p+1}^{n_2+2q-(s'-1)}(p),
\]

(26)

\[
m_{n_1+p+1}^{n_2+2q-s'}(p) = \frac{1}{4} \left( \frac{1}{(n_1+s) + 2q+2p+1} \right) m_{n_1+p+1}^{n_2+2q-(s'+1)}(p) + \frac{1}{2} \left( \frac{1}{(n_2+s) - 2q+1} \right) \times m_{n_1+p+1}^{n_2+2q-(s'+2)}(p).
\]

(27)

For the sake of completeness, the recurrence relations for common special functions, i.e., beta functions, exponential integral function and Pochehammer symbols derived in accordance with the problem are given below. This provides sufficient information in the present text for the reader to reproduce the results.

The generalized exponential integral functions Abramowitz and Stegun (1972) are computed by

\[
E_{-a-s}(p) = \frac{1}{p} \left\{ e^{-p} + (a+s)E_{-a-s+1}(p) \right\},
\]

(28)

here $-(a+s) = -(n_2+2q+n_3) - s_2$, $p = p_2$.

The recurrence relationships derived for the beta function are given as

\[
B_{z-2s,2s+2}(p) = \frac{(z+2s-1)(z+2s-2)}{(z-2s)(z-2s+1)} \times B_{z-2s,2s+2}(p).
\]

(29)

The down-, up-ward recurrence relationships are used for Pochehammer’s symbols arising in $G_{n_1,n_2}(p_{123})$ auxiliary functions are derived as

\[
(z-2s)_{\nu} = \frac{(z-2s)(z-2s+1)}{(z-2s+s')(z-2s+s'+1)} \times (z-2s+2)_{\nu},
\]

(32)

\[
(z+2s)_{\nu} = \frac{(z+2s+s'-1)(z+2s+s'-2)}{(z+2s-1)(z+2s-2)} \times (z+2s-2)_{\nu},
\]

(33)

\[
(z-2s)_{s} = \frac{(-z-2s)}{(-z-s)}(-z-2s+1)(-z-2s+2)s_{s-1},
\]

(34)

\[
(z-2s+s')_{s'} = \frac{(-z-2s+s')}{(-z-2s+s')}(z-2s+s'-1)(-z-2s+s'-1)_{s'}.
\]

(35)

### 5 An alternative recurrence relation method

The following recurrence relations together with Eq. (16) in vectorized form may be used

\[
G_{n_1,n_2,n_3+1}(p_{123}) = \left( \frac{p_2 + p_3}{p_2 - p_3} \right) \left( \frac{n_3 + 1}{n_2} \right) G_{n_1,n_2}(p_{123})
\]

\[
+ \left( \frac{p_2}{p_2 - p_3} \right) \left( - \frac{n_1,0}{n_2} \right) (p_{123}) + \left( \frac{p_3}{p_2 - p_3} \right) \left( \frac{1}{n_2} \right) r_{n_1,n_2}(p_{123}).
\]

(36)

Thus, we have,
\[ G[s_1 + 1] = \left( \frac{p_2 + p_3}{p_2 - p_3} \right) \left( \frac{n_2 + s_1 + 1}{n_2 + 2q - s_1} \right) G[s_1] \]
\[ + \left( \frac{p_2}{p_2 - p_3} \right) \{ -l[s_1, s_1 + 1] + + l[s_1 + 1, s_1] \} \]
\[ + \left( \frac{p_3}{p_2 - p_3} \right) \left( \frac{1}{n_2 + 2q - s_1} \right) h[s_1, s_1 + 1]. \]  

Here, for vectorized form of \( -l \) and \( +l \), we have for \( -l \),
\[ -p_{n_2,n_3}^{p_0} (p_{123}) = e^{-p_2} \int_1^n (\mu + 1)^{n_2} (\mu - 1)^{n_3} e^{-p_3} d\mu, \]  
\[ -l[s_1 + 1, s_1 + 1] = \left( \frac{p_3}{n_2 - s_1 + 1} \right) -l[s_1, s_1 + 1] \]
\[ - \left( \frac{n_3 + s_1}{n_2 - s_1 + 1} \right) -l[s_1, s_1], \]  
\[ -l[s_1, s_1 + 1] = -l[s_1, s_1 + 1] - 2^{-l}[s_1 + 1, s_1 + 1], \]  
for \( +l \),
\[ +p_{n_2,n_3}^{p_0} (p_{123}) = \left( \frac{1}{e^{p_2}} \right) +p_{n_2,n_3}^{p_0} (p_{123}) \]
\[ +l[s_1 + 1, s_1 + 1] = \left( \frac{p_3}{n_2 - s_1 + 1} \right) +l[s_1 + 1, s_1] \]
\[ - \left( \frac{n_3 + s_1}{n_2 - s_1 + 1} \right) +l[s_1, s_1], \]  
\[ +l[s_1 + 1, s_1 + 1] = +l[s_1 + 1, s_1] + 2^{+l}[s_1 + 1, s_1 + 1]. \]  

For \( h \) auxiliary functions the relationships are obtained in a similar form:
\[ h_{n_2,n_3}^{p_0} (p_{123}) = e^{-p_2} \int_1^n (1 + v)^{n_2} (1 - v)^{n_3} e^{-p_3} dv, \]
\[ h[s_1 + 1, s_1 + 1] = \left( \frac{p_3}{n_2 - s_1 + 1} \right) h[s_1, s_1 + 1] \]
\[ + \left( \frac{n_3 + s_1}{n_2 - s_1 + 1} \right) h[s_1, s_1], \]  
\[ h[s_1 + 1, s_1 + 2] = -h[s_1, s_1 + 1] + 2h[s_1 + 1, s_1 + 1]. \]  

Note that explicit form for the \( -l \), \( +l \) and \( h \) auxiliary functions used for computation of the initial values are given in Bağcı and Hoggan (2018a).

### 6 Results and discussion

An efficient method for computation of the relativistic molecular auxiliary functions given in Eq. (9) is presented. They are reduced to Eq. (24) according to the criterion that represents the symmetry of two-electron interactions. This is also consistent with the idea that the overlap integrals are basic building block for molecular integrals since Eq. (24) is, in fact, the representation of two-center overlap integrals in prolate spheroidal coordinates. This simply provide the necessary and sufficient condition to prove the accuracy of proposed fully analytical method. The two-center overlap integrals of non-integer Slater-type orbitals in the lined-up coordinate systems are given as
\[ S_{\mu \nu \nu' \lambda} (\rho, \tau) = \int \chi_{\mu \lambda}^{*} (\zeta, \bar{r}_A) \chi_{\nu' \nu \lambda} (\zeta', \bar{r}_B) dV \]  
with
\[ \rho = \frac{R}{2} (\zeta + \zeta'), \quad \tau = \frac{\zeta - \zeta'}{\zeta + \zeta'} \]  
and \( \bar{R} = \bar{R}_{AB} = \bar{r}_A - \bar{r}_B, \zeta, \zeta' \) are orbital parameters. Please see Bağcı and Hoggan (2014) (and references therein) for the explicit form of Eq. (47). The following expression given for the two-center overlap integrals accordingly is used:
\[ S_{\mu \nu \nu' \lambda} (\rho, \tau) = N_{\mu \nu} (\rho, \tau) \sum_{l} \sum_{l'} g_{\nu \lambda} (l \lambda, l' \lambda) \]
\[ \times \delta_{\lambda, l + l' + \lambda} (0, \rho, \tau). \]  
The \( g_{\nu \lambda} \) coefficients arise from the product of two spherical harmonics with different centers Guseinov and Mamedov (2002). The results of calculations presented in Tables 1, 2 and 3 are obtained from Eq. (48). It is clear from this equation that the method’s accuracy should be tested by increasing the values of angular momentum coefficients \( l, l' \) and considering as high as possible values for principal quantum numbers \( n, n' \). In Tables 1 and 2 presented in this study, the fixed values for principal quantum numbers, \( n = 50.1, n' = 50.0 \) are used. The values of orbital parameters are chosen as \( \rho = 5.1, \tau = 0.0 \). These values are based on experience from previous calculations from which we know that methods hitherto developed to calculate the two-center overlap integrals with non-integer principal quantum numbers have failed.
Note that, the calculations are performed via Eq. (24). Even if the parameter \( \tau \) in the given tables is equal to zero (this is means \( p_3 = 0 \)), the calculations are performed by ignoring this simplicity. Instead, Eq. (24) is still used through Eq. (17) but when \( p_3 \neq 0 \). The values of angular momentum quantum numbers \( l, l' \) are increased from \( \{l, l'\} = 0 \) to \( \{l, l'\} = 20 \), respectively. Benchmark results are obtained via numerical global-adaptive method with Gauss–Kronrod numerical integration extension using Mathematica programming language [http://www.wolfram.com/mathematica]. The calculations are performed with 40-digit accuracy by setting the Working Precision option to 40. This causes all internal computations to be done to 40-digit precision.

The Julia programming language (Bezanson et al. 2017; Bağcı 2020) is used for computation of the fully analytical method. This programming language allows easy use of this existing code written in C or Fortran programming languages. It has a “no boilerplate”

### Table 1

| \( n \) | \( l \) | \( n' \) | \( l' \) | \( \lambda \) | \( \rho \) | Results |
|---|---|---|---|---|---|---|
| 50.1 | 0 | 50.0 | 0 | 5.1 | 0 | \( 9.5791465146381897790344169256655702E - 01(35) \) |
| 50.1 | 1 | 50.0 | 1 | 1 | 5.1 | 0 | \( 9.72384175441618264608189658316551E - 01(35) \) |
| 50.1 | 2 | 50.0 | 2 | 0 | 5.1 | 0 | \( 9.18991919336943171985439433090158E - 01(35) \) |
| 50.1 | 3 | 50.0 | 3 | 1 | 5.1 | 0 | \( 9.1319959325140880194794082370292E - 01(35) \) |
| 50.1 | 4 | 50.0 | 4 | 2 | 5.1 | 0 | \( 9.08402381840245997117432248291100064E - 01(40) \) |
| 50.1 | 5 | 50.0 | 5 | 1 | 5.1 | 0 | \( 8.6619574959325140880194794082370292E - 01(40) \) |
| 50.1 | 10 | 50.0 | 10 | 5 | 5.1 | 0 | \( 7.45778214778258538404367126054883314E - 01(40) \) |
| 50.1 | 20 | 50.0 | 20 | 10 | 5.1 | 0 | \( 7.45778214778258538404367126054883314E - 01(40) \) |

The numbers in parentheses represent the upper limit of summation \( N \).

### Table 2

| \( n \) | \( l \) | \( n' \) | \( l' \) | \( \lambda \) | \( \rho \) | Results |
|---|---|---|---|---|---|---|
| 50.1 | 5 | 50.0 | 5 | 1 | 5.1 | 0 | \( 1.32568 13525 90586 81329 51435 96242 73791 E+36 (10) \) |
| | | | | | | \( - 2.90971 87630 90363 23342 45215 08552 63018 E+34 (15) \) |
| | | | | | | \( 1.23299 50039 89889 33472 47029 50376 17086 E+32 (20) \) |
| | | | | | | \( - 8.07987 96650 25341 37309 26554 15979 78721 E+28 (25) \) |
| | | | | | | \( 1.93904 45950 34950 77981 80976 64495 06345 E+24 (30) \) |
| | | | | | | \( 1.64177 83542 71254 80306 89257 94945 30469 E+20 (35) \) |
| | | | | | | \( 2.24224 67720 72493 39894 23507 37260 10690 E+15 (40) \) |
| | | | | | | \( 8.10564 74767 07974 06257 20626 75989 83928 E+08 (45) \) |
| | | | | | | \( - 1.56878 26202 66460 85553 98231 88490 25729 E+01 (50) \) |
| 8.66195 75005 97684 59795 29121 58447 52427 E-01 (55) |
| 8.66195 74959 32514 00384 71911 22855 68889 E-01 (60) |
| 8.66195 74959 32514 08801 68929 31385 75004 E-01 (65) |
| 8.66195 74959 32514 08801 94793 64570 45165 E-01 (70) |
| 8.66195 74959 32514 08801 94794 08242 21380 E-01 (75) |
| 8.66195 74959 32514 08801 94794 08243 70283 E-01 (80) |
| 8.66195 74959 32514 08801 94794 08243 70292 E-01 (85) |
| 8.66195 74959 32514 08801 94794 08243 70292 E-01 (90) |

The numbers in parentheses represent the upper limit of summation \( N \).
Table 3 The comparative values for the two-center overlap integrals over non-integer Slater-type orbitals for \( \{n, n'\} = 10.3, 1 \leq \{l, l'\} \leq 9, \lambda = 0, p = 5.25, \tau = 0.042857\)

\[
\begin{align*}
\{l, l'\} = 1 & \quad 5.33254 \quad 16754 \quad 75150 \quad 35873 \quad 89692 \quad 95849 \quad 08406 \quad E=01^a \quad 5.33254 \quad 16754 \quad 75150 \quad 35873 \quad 89692 \quad 95849 \quad 08406 \quad E=01\quad (60) \\ & \quad 5.33254 \quad 16754 \quad 75150 \quad 35873 \quad 89692 \quad 95849 \quad 08409 \quad E=01\quad (60) \\
\{l, l'\} = 2 & \quad 4.02744 \quad 06611 \quad 00683 \quad 49171 \quad 98143 \quad 94069 \quad 35215 \quad E=01^a \quad 4.02744 \quad 06611 \quad 00683 \quad 49171 \quad 98143 \quad 94065 \quad 00268 \quad E=01\quad (60) \\ & \quad 4.02744 \quad 06611 \quad 00683 \quad 49171 \quad 98143 \quad 94069 \quad 35214 \quad E=01\quad (60) \\
\{l, l'\} = 3 & \quad 1.72854 \quad 78519 \quad 16793 \quad 16122 \quad 59760 \quad 98073 \quad 75256 \quad E=01^a \quad 1.72854 \quad 78519 \quad 16793 \quad 16122 \quad 59760 \quad 98073 \quad 75256 \quad E=01\quad (60) \\ & \quad 1.72854 \quad 78519 \quad 16793 \quad 16122 \quad 59760 \quad 98073 \quad 78465 \quad E=01\quad (60) \\
\{l, l'\} = 4 & \quad 3.58885 \quad 92067 \quad 44717 \quad 68659 \quad 73552 \quad 74552 \quad 35564 \quad E=02^a \quad 3.58885 \quad 92067 \quad 44717 \quad 68659 \quad 73552 \quad 74552 \quad 35527 \quad E=02\quad (60) \\ & \quad 3.58885 \quad 92067 \quad 44717 \quad 68659 \quad 73552 \quad 74550 \quad 11748 \quad E=02\quad (60) \\
\{l, l'\} = 5 & \quad 1.90254 \quad 40455 \quad 98846 \quad 89470 \quad 55411 \quad 39927 \quad 20322 \quad E=01^a \quad 1.90254 \quad 40455 \quad 98846 \quad 89470 \quad 55411 \quad 39927 \quad 20322 \quad E=01\quad (60) \\ & \quad 1.90254 \quad 40455 \quad 98846 \quad 89470 \quad 55411 \quad 39798 \quad 82949 \quad E=01\quad (60) \\
\{l, l'\} = 6 & \quad 2.69793 \quad 63811 \quad 55732 \quad 20371 \quad 99094 \quad 03039 \quad 03361 \quad E=01^a \quad 2.69793 \quad 63811 \quad 55732 \quad 20371 \quad 99094 \quad 03039 \quad 03704 \quad E=01\quad (60) \\ & \quad 2.69793 \quad 63811 \quad 55732 \quad 20371 \quad 99094 \quad 03360 \quad 03704 \quad E=01\quad (60) \\
\{l, l'\} = 7 & \quad 2.76169 \quad 52021 \quad 99871 \quad 31457 \quad 21080 \quad 48365 \quad 94045 \quad E=01^a \quad 2.76169 \quad 52021 \quad 99871 \quad 31457 \quad 21080 \quad 48365 \quad 94046 \quad E=01\quad (60) \\ & \quad 2.76169 \quad 52021 \quad 99871 \quad 31457 \quad 21064 \quad 98454 \quad 86591 \quad E=01\quad (60) \\
\{l, l'\} = 8 & \quad 2.26468 \quad 82907 \quad 84068 \quad 19993 \quad 72655 \quad 80216 \quad 11695 \quad E=01^a \quad 2.26468 \quad 82907 \quad 84068 \quad 19993 \quad 72655 \quad 80216 \quad 11695 \quad E=01\quad (60) \\ & \quad 2.26468 \quad 82907 \quad 84068 \quad 19993 \quad 72655 \quad 80216 \quad 11695 \quad E=01\quad (60) \\
\{l, l'\} = 9 & \quad 1.45363 \quad 09555 \quad 16561 \quad 23619 \quad 65147 \quad 45076 \quad 18588 \quad E=01^a \quad 1.45363 \quad 09555 \quad 16561 \quad 23619 \quad 65147 \quad 45076 \quad 18588 \quad E=01\quad (60) \\ & \quad 1.45363 \quad 09555 \quad 16561 \quad 23619 \quad 65147 \quad 45076 \quad 18588 \quad E=01\quad (60) \\
\end{align*}
\]

The numbers in parentheses represent the upper limit of summation \( N \)

\( ^a \)Benchmark result obtained via global-adaptive method with Gauss–Kronrod extension

\( ^b \)Results obtained via Eq. (24)

\( ^c \)Results obtained via Eqs. (36, 37)

philosophy: functions can be called directly from it without any “glue” code, code generation, or compilation even from the interactive prompt. This is accomplished by making an appropriate call with \( ecall \), which looks like an ordinary function call. The most common syntax for \( ecall \) is as follows:

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For accuracy, only an additional computer algebra package, called Nemo Fieker et al. (2017) is required. This package is based on C libraries such as FLINT, ANTIC, Arb, Pari and Singular. It has a module system which is used to provide access to Nemo. It is imported and used all exported functionality by simply type using Nemo.

In the light of the previous sections, for the fully analytical method, the upper limit of summation \( N \) that gives results equivalent to numerical ones is found to be \( N = 85 \). In addition, it has been among our goals to perform calculations for larger values of angular momentum quantum numbers such as \( \{ l, l' \} = 30 \) or \( \{ l, l' \} = 40 \). It is, however, observed that the methods presented in this study are unsuitable for practical evaluation of two-center overlap integrals for these values. Direct recurrence relationships for the two-center overlap integrals instead of their sub-auxiliary functions are needed.

In Table 3, the values for orbital parameters are chosen to be \( \rho = 5.25 \). The calculations are performed with the parameter \( \tau, \tau \neq 0 \) as \( \tau = 3/70 \). The fixed values for principal quantum numbers \( \{ n, n' \} \) are chosen to be \( \{ n, n' \} = 10.3 \). The values of angular momentum quantum numbers \( \{ l, l' \} \) are increased from \( \{ l, l' \} = 1 \) to \( \{ l, l' \} = 9 \). The second angular momentum quantum number \( \lambda \) arises due to definition of overlap integrals in the aligned-coordinate systems fixed to the minimum, \( \lambda = 0 \). As it is seen from Eq. (48), this leads to increasing the computation time to a maximum. The calculation results presented in the left-hand side of the table show that even if the parameter \( \tau \neq 0 \), the results from the fully analytical method via Eq. (24) agree with the benchmark results obtained from the Mathematica numerical global-adaptive method. The accuracy of the results obtained from the recurrence relation formulas, Eq. (36) is from 20 – 35 digits depending on angular momentum quantum numbers \( \{ l, l' \} \). The results presented in the right-hand side show that the convergence is not arbitrary. There is a direct relationship between the upper limit of summation and number of accurate digits. Setting up the upper limit of summation to \( N = 50 \), \( N = 40 \), give 30 and 25 accurate digits for the results, respectively.

The calculation times for the results given in Table 3 are presented in Fig. 1. Left- and right-hand sides of the figure represent the CPU time used to obtain the results given in the left- and right-hand sides of the table, respectively.

The convergence of the results obtained via Eq. (24) is dependent on the values of principal quantum numbers. Numerical results assembled in Tables 1 and 2 are obtained for extreme values of principal and angular momentum quantum numbers. The upper limit of summation \( N \) should be at least \( N = 70 \) to achieve a satisfactory precision.

Numerical results assembled in Table 3, on the other hand, in terms of applications indicate convergence for more reasonable value of the principal quantum number. The accuracy obtained for these values with \( N = 30 \) thus is sufficient for most applications, at 21–23 decimal digits.

Acknowledgements More details of the method of computation and the results presented are available in an electronic form upon request to AB at the e-mail address: ali.bagci@yahoo.com.tr. In this study, the author A. B. was supported by the Scientific Research Coordination Unit of Pamukkale University under the project number 2020BSP011.
Vectorized form for the \( m \) auxiliary functions given in Sects. 3 and IV

\( m_n^m(p) \) auxiliary function computation requires special attention. These functions contain hypergeometric functions. Reliable and fast computation with finite-precision for these functions is a subject studied in computer science. Here we avoid calculating the hypergeometric functions in every step of computation. The details for these functions are given in this section.

In vector forms for \( m_1 \) and \( m_2 \) auxiliary functions, we have for \( p_3 = 0 \),

\[
\begin{align*}
m_1[s_5 + 1] &= \frac{1}{3} c_{11} m_1[s_5] + \frac{1}{3} c_{12} m_2[s_5], \\
m_2[s_5 + 1] &= \frac{1}{4} c_{21} m_1[s_5] + \frac{1}{4} c_{22} m_2[s_5], \\
m_1[s_5] &= m_1[s_5], \\
m_2[s_5] &= m_2[s_5], \\
M_1[s_4, s_1] &= m_1[s_5] + 2f[s_4], \\
M_2[s_4, s_0] &= m_2[s_5] + 2f[s_4],
\end{align*}
\]

(49)

where \( f \) is used to represent the factorials in Eq. (22), \( 2s_1 \leq s_5 \leq N + 2s_1, s_p = q - s_1, N \) is the upper limit of summation, respectively. \( s_5 \) defines the size of the list that contain all the required values of \( m \) auxiliary functions.

For \( p_3 \neq 0 \),

\[
\begin{align*}
m_1[s_5, 1] &= 4r_{11}[s_4, 1]m_1[s_5 - 2, 1] \\
&\quad + r_{12}[s_4, 1]m_1[s_5 - 1, 1], \\
m_1[s_5, 2] &= 4r_{11}[s_4, 2]m_1[s_5 - 2, 2] \\
&\quad + r_{12}[s_4, 2]m_1[s_5 - 1, 2], \\
m_2[s_5, 1] &= 4r_{21}[s_4, 1]m_2[s_5 - 2, 1] \\
&\quad + r_{22}[s_4, 1]m_2[s_5 - 1, 1], \\
m_2[s_5, 2] &= 4r_{21}[s_4, 2]m_2[s_5 - 2, 2] \\
&\quad + r_{22}[s_4, 2]m_2[s_5 - 1, 2], \\
m_1[s_5, s_6] &= \frac{1}{4} c_{11}[s_5, s_6]m_1[s_5, s_6 - 2] + c_{12}[s_5, s_6]m_1[s_5, s_6 - 1] \\
m_2[s_5, s_6] &= \frac{1}{4} c_{21}[s_5, s_6]m_2[s_5, s_6 - 2] + c_{22}[s_5, s_6]m_2[s_5, s_6 - 1]
\end{align*}
\]

(50)-(55)

with \( r_{11}, r_{12}, r_{21}, r_{22} \) and \( c_{11}, c_{12}, c_{21}, c_{22} \), e.g., used to represent the coefficients for the recurrence relationships given in Eqs. (25–35), respectively. "r" and "c" letters indicate the row and column elements of the matrices. The numbers used together with these letters such as \( m_1, m_2 \) are for the first and second auxiliary functions \( f_{n_2m}^{p_1} (p_{12}) \) arising in Eq. (24).

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