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Analytical evaluation of relativistic molecular integrals. I. Auxiliary functions

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Abstract

The auxiliary functions provide efficient computation of integrals arising at the self-consistent field level for molecules using Slater-type bases. This applies both in relativistic and non-relativistic electronic structure theory. The relativistic molecular auxiliary functions derived in our previous paper (Bağcı and Hoggan, Phys Rev E 91:023303, 2015) are discussed here in detail. Two solution methods are proposed in the present study. The ill-conditioned binomial series representation formulae are first replaced by a convergent series representation for incomplete beta functions. They are then improved by inserting an extra parameter used to extend the domain of convergence. Highly accurate results can be achieved for integrals by the procedures discussed in the present study which place no restrictions on quantum numbers in all ranges of orbital parameters. The difficulty of obtaining analytical relations associated with using non-integer Slater-type orbitals which are non-analytic in the sense of complex analysis at $r = 0$ is, therefore, eliminated.

1 Introduction

When calculating molecular electronic structure at the Self-Consistent Field level (SCF), use of auxiliary functions in multi-center integral evaluation over Slater-type orbitals is one of the most efficient methods since it leads to fast and accurate calculations. It has a long history, beginning with Barnett and Coulson (Coulson 1942; Barnett and Coulson 1951; Mulliken et al. 1949; Roothaan 1951, 1956; Rüdenberg 1951; Löwdin 1956; Kotani et al. 1963; Harris and Michels 1965, 1966, 1967; Guseinov 1970). It is still being studied in the literature. In particular, the relationships obtained are constantly updated using developments

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in mathematical physics, chemistry and computer sciences (Guseinov et al. 2001; Harris 2002, 2003, 2004; Guseinov and Mamedov 2002a, 2009; Guseinov and Mamedov 2005; Fernández et al. 1997; Ema et al. 2008; Lesiuk and Moszynski 2014a, b; Bağcı and Hoggan 2014, 2015a, b).

Slater-type orbitals (STOs) (Slater 1930; Parr and Hubert 1957) are defined as follows:

$$\chi_{nlm}(\zeta, \boldsymbol{r}) = \frac{(2\zeta)^{n+1/2}}{\sqrt{\Gamma(2n+1)}} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \vartheta), \tag{1}$$

where Y_l^m are complex or real spherical harmonics. Phase $(Y_l^{m*} = Y_l^{-m}; Y_l^m \equiv S_l^m)$ differs from the Condon–Shortley phase, by a sign factor $(-1)^m$ (Condon and Shortley 1935; Steinborn and Rüedenberg 1973), $\{n, l, m\}$ are the principal, orbital, magnetic quantum numbers with, $n \in \mathbb{R}^+$, $0 \le l \le \lfloor n \rfloor - 1$, $-l \le m \le l$; $\lfloor n \rfloor$ stands for the integer part of n and ζ are orbital parameters. They are obtained by simplification of Laguerre polynomials in hydrogen-like one-electron eigen-functions (Willock 2009) by keeping only the terms of the highest power of r.

Other exponentially decaying bases, e.g. the hydrogen-like functions may be written as linear combinations of STOs (Weniger 2002). Such eigenfunctions satisfy Kato's cusp conditions for asymptotic behavior of the wave

function near the nucleus (Kato 1957). At long range all these orbitals decrease exponentially (Agmon 1982). They are, therefore, the natural choice of basis orbital in algebraic solution of the Schrödinger equation for many electron systems. They play a key role in the understanding of quantum theory problems. They often arise from testing limits of the methods obtained approximately to represent the physical systems, where reliable description of electron density is important, e.g. study of molecules in strong magnetic fields (Bouferguene et al. 1999). Second order perturbation energy corrections are related (Hoggan 2011).

So far, auxiliary functions for evaluation of molecular integrals over the STOs have been derived only for the integer values of principal quantum numbers. In that case, $n \in \mathbb{Z}^+$, $0 \le l \le n-1$ and $\Gamma(2n+1) = n!$. The use of non-integer principal quantum numbers in STOs, however, promises better results because they provide extra flexibility for closer variational description of molecules (Parr and Hubert 1957). The vital importance of generalising auxiliary function methods is then clear when extending the domain of applications that were previously limited to atoms (Koga et al. 1997; Koga and Kanayama 1997; Koga et al. 2000; Guseinov and Ertürk 2012) is considered. A basis spinor to be used in relativistic electronic structure calculation is obtained from the hydrogen atom Dirac–Hamiltonian eigenfunctions and it can be written in terms of Slater-type orbitals since its radial part has the following form (Grant 2007; Bağcı and Hoggan 2016):

$$f(\zeta, r) = \left\{ Ar^n + \zeta Br^{n+1} \right\} e^{-\zeta r}. \tag{2}$$

Deriving such mathematical tools, therefore, directly helps to evaluate the integrals arising from algebraic solution of the molecular Dirac equation since they in turn reduce to integrals over STOs.

The authors recent study (Bağcı and Hoggan 2015a) used the Laplace expansion of the Coulomb operator and prolate spheroidal coordinates to express the two-center molecular integrals in terms of the so-called relativistic molecular auxiliary functions. These auxiliary functions were evaluated numerically via the Global-adaptive method with Gauss–Kronrod numerical integration extension. Note that highly accurate values from the suggested numerical method are available only in the Mathematica programming language. Since the Mathematica programming language is suitable for bench-marking but requires prohibitive calculation time, extended-precision Fortran is being investigated for applications. Numerical calculations for the hydrogen molecule ion have recently been done to 96-decimal-digit accuacy in Koborov et al. (2013). The source code for fast multi-precision arithmetic used was also applied to calculate the recurrence relations for the generic Hylleraas three-electron integral (Pachucki et al. 2004).

One of us obtains analytical relations investigated in the reference, (Bağcı 2017). The relativistic auxiliary functions are expressed through series representation of incomplete beta functions and in terms of integrals involving Appell functions.

The double series of Appell's functions (Appell 1925)

$$F_1\left(\alpha; \beta_1, \beta_2; \gamma; x, y\right) = \sum_{s_1, s_2 = 0}^{\infty} \frac{(\alpha)_{s_1+s_2} (\beta_1)_{s_1} (\beta_2)_{s_2}}{(\gamma)_{s_1 s_2} s_1! s_2!} x^{s_1} y^{s_2}, \tag{3}$$

where $(\alpha)_n$ is the Pochhammer symbol, is mathematically convergent when the variables (x, y), $|x| < 1$ and $|y| < 1$. Since the variables (x, y) arising in relativistic auxiliary functions have values outside the convergence region, it is necessary to make use of recurrence relation formulae (Wang 2012) or numerical integration of a third order ordinary differential equation that represents the system of partial differential equations of Appell functions given for a set of analytic continuations (Colavecchia 2001). These methods are, however, computationally inefficient and may not give correct results for a particular set of parameters $\{\alpha, \beta_1, \beta_2, \gamma\}$. Besides, computing Appell's functions without erroneous last digits is still being studied in the literature (Colavecchia and Gasaneo 2004).

In the present study, we refer to the introductory remarks given in previous work. Certain concepts and the results therein are also used. Here, the relationships given in terms of integrals involving Appell's functions are also reduced to series representation formulae for incomplete beta functions. Computing Appell's functions is, therefore, avoided. Furthermore, a new binomial expansion method is developed through that given in Liao (2004), Liu (2010) where an extra parameter is used to extend the domain of convergence of the well-known Newton binomial expansion approximation. The ill-conditioned binomial series representation used for evaluation of the molecular integrals in the literature (Guseinov 2009; Mekelleche and Baba-Ahmed 2000; Guseinov and Mamedov 2002b, c) is thus improved. Therefore, reliable methods to analytically evaluate the molecular integrals over non-integer Slater-type orbitals are finally obtained in the present work.

2 Evaluation of relativistic molecular auxiliary functions

The compact expressions we previously derived for two-center, one- and two-electron relativistic molecular integrals in a lined-up coordinate system through Laplace expansion of Coulomb interaction and prolate spheroidal coordinates (ξ, ν, ϕ), where $1 \le \xi < \infty$, $-1 \le \nu \le 1$, $0 \le \phi \le 2\pi$, are obtained using the following auxiliary function integrals (Bağcı and Hoggan 2015a):

$$
\left\{ \begin{array}{c} \mathcal{P}_{n_2 n_3 n_4}^{n_1, q}(p_{123}) \\ \mathcal{Q}_{n_2 n_3 n_4}^{n_1, q}(p_{123}) \end{array} \right\}
$$

$$
= \frac{p_1^{n_1}}{(n_4 - n_1)_{n_1}} \int_1^\infty \int_{-1}^1 (\xi\nu)^q (\xi + \nu)^{n_2} (\xi - \nu)^{n_3}
$$

$$
\times \left\{ \begin{array}{c} P\left[n_4 - n_1, p_1(\xi + \nu)\right] \\ Q\left[n_4 - n_1, p_1(\xi + \nu)\right] \end{array} \right\} e^{p_2 \xi - p_3 \nu} \mathrm{d}\xi \mathrm{d}\nu, \tag{4}
$$

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), $p_1 > 0$, $p_2 > 0$, $-p_2 \leq p_3 \leq p_2$.

P, Q are the normalized complementary incomplete gamma and the normalized incomplete gamma functions

$$
P[\alpha, z] = \frac{\gamma(\alpha, z)}{\Gamma(\alpha)}, Q[\alpha, z] = \frac{\Gamma(\alpha, z)}{\Gamma(\alpha)}, \tag{5}
$$

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

$$
\gamma(\alpha, z) = \int_0^z t^{\alpha-1} e^{-t} \mathrm{d}t, \Gamma(\alpha, z) = \int_z^\infty t^{\alpha-1} e^{-t} \mathrm{d}t, \tag{6}
$$

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

$$
\Gamma(\alpha) = \Gamma(\alpha, z) + \gamma(\alpha, z), \tag{7}
$$

and the Pochhammer symbol $(\alpha)_n$ is defined as:

$$
(\alpha)_n = \frac{\Gamma(\alpha + n)}{\Gamma(\alpha)}, \tag{8}
$$

see, Abramowitz and Stegun (1972), Temme (1994). Evaluation of these auxiliary functions involves some challenges including power functions with non-integer exponents. Also, incomplete gamma functions and their products have no explicit closed-form relations. On the other hand, symmetry properties of two-center two-electron integrals allow us to take advantage of the sum $P + Q = 1$. This allows use of Eq. (4) via up- and down-ward distant recurrence relations of normalized incomplete gamma functions

$$
\left\{ \begin{array}{c} P[a, bz] \\ Q[a, bz] \end{array} \right\} = \left\{ \begin{array}{c} P[a+n, bz] + e^{-bz} \sum_{s=1}^n \frac{(bz)^{a+s-1}}{\Gamma(a+s)} \\ Q[a+n, bz] - e^{-bz} \sum_{s=1}^n \frac{(bz)^{a+s-1}}{\Gamma(a+s)} \end{array} \right\}, \tag{9}
$$

$$
\left\{ \begin{array}{c} P[a, bz] \\ Q[a, bz] \end{array} \right\} = \left\{ \begin{array}{c} P[a-n, bz] - e^{-bz} \sum_{s=1}^{n-1} \frac{(bz)^{a-s-1}}{\Gamma(a-s)} \\ Q[a-n, bz] + e^{-bz} \sum_{s=1}^{n-1} \frac{(bz)^{a-s-1}}{\Gamma(a-s)} \end{array} \right\}, \tag{10}
$$

in terms of the following form (please see Bağcı 2017):

$$
\mathcal{G}_{n_2 n_3}^{n_1, q}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)}
$$

$$
\times \int_1^\infty \int_{-1}^1 (\xi\nu)^q (\xi + \nu)^{n_2} (\xi - \nu)^{n_3} e^{-p_2 \xi - p_3 \nu} \mathrm{d}\xi \mathrm{d}\nu. \tag{11}
$$

The feature given above can, therefore, generally be defined as follows:

Criterion Let $P\left[n_4 - n_1, z\right]$ and $Q\left[n_4' - n_1', z\right]$, then $n_4 - n_1 = a \pm c$, $n_4' - n_1' = a \pm d$, where $a \in \mathbb{R}$, $\{c, d\} \in \mathbb{Z}$ are true for any integrals that can be reduced to Eq. (4).

Case 1 The parameter $p_3 = 0$.

Starting by lowering the indices q using

$$
(\xi\nu) = \frac{1}{4}\{(\xi + \nu)^2 - (\xi - \nu)^2\}, \tag{12}
$$

the auxiliary functions $\mathcal{G}^{n_1, q}$ are obtained as follows Bağcı (2017):

$$
\mathcal{G}_{n_2 n_3}^{n_1, q}(p_{120}) = \frac{1}{4}\left\{ \mathcal{G}_{n_2+2 n_3}^{n_1, q-1}(p_{120}) - \mathcal{G}_{n_2 n_3+2}^{n_1, q-1}(p_{120}) \right\}, \tag{13}
$$

here,

$$
\mathcal{G}_{n_2 n_3}^{n_1, 0}(p_{120}) = h_{n_2 n_3}^{n_1, 0}(p_{12}) + h_{n_3 n_2}^{n_1, 0}(p_{12}) - k_{n_2 n_3}^{n_1, 0}(p_{12}) - k_{n_3 n_2}^{n_1, 0}(p_{12}), \tag{14}
$$

$$
h_{n_2 n_3}^{n_1, q'}(p_{12}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} 2^{n_2+n_3+q'+1} B(n_2 + 1, n_3 + 1)
$$

$$
\times E_{-(n_2+n_3+q'+1)}(p_2) - l_{n_2 n_3}^{n_1, q'}(p_{12}), \tag{15}
$$

$$
l_{n_2 n_3}^{n_1, q'}(p_{12})
$$

$$
= \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} \sum_{s=0}^\infty \frac{(-n_2)_s}{(n_3 + s + 1)^* s!} m_{n_3+s+1}^{n_2+q'-s}(p_2), \tag{16}
$$

$$
m_{n_2}^{n_1}(p) = 2^{n_1} U(n_2 + 1, n_1 + n_2 + 2, p) \Gamma(n_2 + 1) e^{-p}, \tag{17}
$$

and

$$
k_{n_2, n_3}^{n_1, q'}(p_{12}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} 2^{n_2+n_3+q'+1} B\left(n_2 + 1, n_3 + 1, \frac{1}{2}\right)
$$

$$
\times E_{-(n_2+n_3+q'+1)}(p_2), \tag{18}
$$

with

$$U(\alpha, \beta; z) = \frac{\Gamma(\beta - 1)}{\Gamma(\alpha)} {}_1F_1(\alpha - \beta + 1, 2 - \beta; z)$$
$$+ \frac{\Gamma(1 - \beta)}{\Gamma(\alpha - \beta + 1)} {}_1F_1(\alpha; \beta; z), \tag{19}$$

where $U(\alpha, \beta; z)$ are confluent hypergeometric functions of second kind with

$${}_1F_1(\alpha, \beta; z)$$
$$= \frac{\Gamma(\beta)}{\Gamma(\beta - \alpha)\Gamma(\alpha)} \int_0^1 t^{\alpha - 1}(1 - t)^{\beta - \alpha - 1} e^{zt} \mathrm{d}t, \tag{20}$$

confluent hypergeometric functions of first kind and $B(\alpha, \beta, z)$ incomplete beta functions

$$B(\alpha, \beta, z) = \int_0^z t^{\alpha - 1}(1 - t)^{\beta - 1} \mathrm{d}t, \tag{21}$$

where $B(\alpha, \beta) = B(\alpha, \beta, 1)$ are beta functions, respectively (Abramowitz and Stegun 1972).

Case 2 The parameter $p_3 \neq 0$.

By lowering the indices q and using the series expansion of exponential functions e^z, where $z = -p_3 \nu$, the following relation is obtained (Bağcı 2017):

$$\mathcal{G}_{n_2 n_3}^{n_1, 0}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1 + 1)} \sum_{s=0}^{\infty} \frac{(-p_3^s)}{\Gamma(s + 1)} \left(\frac{1}{s + 1} \right)$$
$$\times \left\{ J_{n_2 n_3}^{s+1, s+2; 0}(p_2) + (-1)^s J_{n_3 n_2}^{s+1, s+2; 0}(p_2) \right\}, \tag{22}$$

The $J^{s,q}$ functions involve Appell's hypergeometric functions (Appell 1925):

$$F_1(\alpha; \beta_1, \beta_2; \gamma; x, y) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\alpha - \gamma)}$$
$$\times \int_0^1 u^{\alpha - 1}(1 - u)^{\gamma - \alpha - 1}(1 - ux)^{-\beta_1}(1 - uy)^{-\beta_2} du, \tag{23}$$

and their explicit forms are given as:

$$J_{n_2 n_3}^{s, s'; q}(p) = \int_1^{\infty} F_1\left(s; -n_2, -n_3; s'; \frac{1}{\xi}, -\frac{1}{\xi} \right)$$
$$\times \xi^{n_2 + n_3 + q} e^{-p\xi} \mathrm{d}\xi. \tag{24}$$

The sum of two $J_{n_2 n_3}^{s, s'; q}$ functions arising in the right-hand side of Eq. (22) is an integral in the form, written as:

$$\left(\frac{1}{s + 1} \right) \left\{ J_{n_2 n_3}^{s+1, s+2; 0}(p_2) + (-1)^s J_{n_3 n_2}^{s+1, s+2; 0}(p_2) \right\}$$
$$= \int_1^{\infty} \int_{-1}^1 (\xi + \nu)^{n_2}(\xi - \nu)^{n_3} \nu^s e^{-p_2 \xi} \mathrm{d}\xi \mathrm{d}\nu. \tag{25}$$

Dividing and multiplying the expression with $\xi^{s'}$ gives:

$$\mathcal{J}_{n_2 n_3}^{s, s'}(p_2)$$
$$= \int_1^{\infty} \int_{-1}^1 (\xi + \nu)^{n_2}(\xi - \nu)^{n_3} \left(\xi^{s'} \nu^s \right) \xi^{-s'} e^{-p_2 \xi} \mathrm{d}\xi \mathrm{d}\nu. \tag{26}$$

By again making use of Eq. (12), finally the following relation is obtained for $(s' = s)$:

$$\mathcal{J}_{n_2 n_3}^{s, s}(p_2) = \frac{1}{4} \left\{ \mathcal{J}_{n_2 + 2n_3}^{s-1, s}(p_2) - \mathcal{J}_{n_2 n_3 + 2}^{s-1, s}(p_2) \right\}, \tag{27}$$

$$\mathcal{J}_{n_2 n_3}^{0, s}(p_2) = \frac{1}{2^{-s}} \left\{ h_{n_2 n_3}^{1, -s}(p_{02}) + h_{n_3 n_2}^{1, -s}(p_{02}) \right.$$
$$\left. - k_{n_2 n_3}^{1, -s}(p_{02}) - k_{n_3 n_2}^{1, -s}(p_{02}) \right\} \tag{28}$$

with $p_{02} = \{1, p_2\}$. It should be noted that Eqs. (14 and 28) imply convergence properties of incomplete beta function expansions; $B_z(n_1, n_2)$ at $z = 0$, where the absolute value of z must be $|z| < 1$. Considering the domain given for auxiliary functions $\mathcal{G}^{n_1, q}$, it is easy to see that the convergence condition is satisfied, where $z = \frac{\xi - 1}{2\xi}$. Equation (22) gives the convergence properties for series representation of exponential functions e^z which are uniformly convergent for the entire complex plane for any z with $|z| < \infty$.

2.1 On the use of Newton's binomial theorem

Newton's binomial theorem is generalized by Liao, within the frame of the homotopic analysis (Liao 2004). An extra parameter h, the so-called auxiliary parameter, is used to extend the domain of convergence. The auxiliary parameter is generally used in homotopic analysis to construct the so-called zero-order deformation equation. A set of expressions is thus obtained in terms of the auxiliary parameter h as solutions.

Series with the mean convergence domain show rate of solution increased by choosing a proper value for h (Liao 2004; Liu 2010).

A power function such as $(\xi \pm \nu)^n$ with real number n ($n \neq 0, 1, 2, 3, \ldots$), can be written in the form:

$$(\xi \pm \nu)^n = \xi^n \left(1 \pm \frac{\nu_0}{\xi_0} \right)^n \left(1 \pm \frac{\frac{\nu}{\xi} - \frac{\nu_0}{\xi_0}}{1 \pm \frac{\nu_0}{\xi_0}} \right)^n, \tag{29}$$

where $\left| \frac{\frac{\nu}{\xi} - \frac{\nu_0}{\xi_0}}{1 \pm \frac{\nu_0}{\xi_0}} \right| < 1$, $\frac{\nu_0}{\xi_0} = \mp 1 \mp \frac{1}{h}$ with $|\frac{\nu_0}{\xi_0}| < 1$, respectively.

The auxiliary parameter h is then adjusted accordingly. By applying now the usual Newton's binomial expansion, the following relations are obtained:

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$$(\xi \pm v)^n = \lim_{N \to \infty} \sum_{s=0}^{N} (\pm 1)^s \mu_n^{N,s}(h) F_s(n) \xi^{n-s} v^s, \tag{30}$$

$$\mu_n^{N,s}(h) = \sum_{s'=0}^{N-s} (\pm 1)^{s'} F_{s'}(n-s)(-h)^{s-n}(h+1)^{s'}. \tag{31}$$

The terms arising in Eq. (4) can thus be re-written as:

$$(\xi + v)^{n_2}(\xi - v)^{n_2} = \lim_{N \to \infty} \sum_{s,s'=0}^{N} \mu_{n_2}^{N,s}(h) \mu_{n_3}^{N,s'}(h') \times F_s(n_2) F_{s'}(n_3) \xi^{n_2+n_3-s-s'} v^{s+s'}, \tag{32}$$

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

$$\binom{n}{s} = \frac{\Gamma(n+1)}{\Gamma(s+1)\Gamma(n-s+1)}. \tag{33}$$

According to the formulae given above the auxiliary functions, $\mathcal{G}^{n_1,q}$ are obtained as follows:

$$\mathcal{G}_{n_2 n_3}^{n_1,q}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1+1)} \lim_{N \to \infty} \sum_{s,s'=0}^{N} \mu_{n_2}^{N,s}(h) \mu_{n_3}^{N,s'}(h')$$
$$\times F_s(n_2) F_{s'}(n_3) \int_1^{\infty} \xi^{n_1+n_2+q-s-s'} e^{-p_2 \xi} d\xi$$
$$\times \int_{-1}^{1} v^{q+s+s'} e^{-p_3 v} dv, \tag{34}$$

$$\mathcal{G}_{n_2 n_3}^{n_1,q}(p_{123}) = \frac{p_1^{n_1}}{\Gamma(n_1+1)} \lim_{N \to \infty} \sum_{s,s'=0}^{N} \mu_{n_2}^{N,s}(h) \mu_{n_3}^{N,s'}(h')$$
$$\times F_s(n_2) F_{s'}(n_3) \left\{ \frac{E_{-(n_2+n_3)-q+k}(p_2)}{p_3^{q+k+1}} \right.$$
$$\left. \times \left(\gamma(q+k+1, p_3) - \gamma(q+k+1, -p_3) \right) \right\}, \tag{35}$$

where $k = s + s'$ and

$$E_n(p) = \int_1^{\infty} \frac{e^{-p\xi}}{\xi^n} d\xi, \tag{36}$$

are the exponential integral functions.

3 Conclusion

The renewed interest in molecular integrals over Slater-type orbitals with non-integer principal quantum numbers is increasing. Recent studies show that they are used in both relativistic and non-relativistic electronic structure calculations. These integrals are expressed in terms of molecular auxiliary functions. They involve power functions such as $f(z) = z^n = e^{n \log z}$ with non-integer exponents $n \in \mathbb{R}$ which cannot be represented by a power series because they are not analytic about $z = 0$ (Weniger 2008). This constitutes the underlying reason why the Slater-type orbitals with non-integer principal quantum numbers could not be used in molecular electronic structure calculations so far. Availability of computation methods for molecular auxiliary functions, on the other hand, needs urgent implementation and is precious. Two methods based on this reasoning are proposed in this study. Firstly, through expansion of exponential functions, the molecular $\mathcal{G}^{n,q}$ auxiliary functions reduce to integrals involving Appell functions (Eq. 22). Instead of using recurrence relations of Appell's functions, they are represented through convergent series expansion of incomplete beta functions. Secondly, through an improved form of the binomial series expansion of power functions they reduce to easily integrable expressions in which the variables are separated (Eq. 35). These methods are derived according to a criterion given below the Eq. (11). Compact form expressions obtained for multi-center integrals via Laplace expansion of the Coulomb interaction involve a sum of $\mathcal{P}_{n_2 n_3 n_4}^{n_1,q}(p_{123})$ and $\mathcal{Q}_{n_2' n_3' n_4'}^{n_1',q}(p_{123})$ auxiliary functions, where

$$n_1 = 0, n_4 = n + n' + L + 1 \quad \text{for } \mathcal{P}$$
$$n_1' = 2L + 1, n_4' = n + n' + L + 1 \quad \text{for } \mathcal{Q}$$

and

$$n_4 - n_1 = n + n' + L + 1 \quad \text{for } \mathcal{P}$$
$$n_4' - n_1' = n + n' - L \quad \text{for } \mathcal{Q}$$

where $\{n, n'\}$, L are principal and total angular momentum quantum numbers, respectively (Bağcı 2017). This is, therefore, the foundation for construction of the criterion.

The relationships given in the presented work are reliable and convergent. Benchmark results in our previous papers (Bağcı and Hoggan 2014, 2015a) can, therefore, be obtained with the formalism given in the present study.

The homotopy analysis method which is used to extend the domain of convergence of Newton's binomial series representation formulae may also be used to obtain non-analytic

solutions, which by their nature cannot be expressed through power series (Gorder 2017). The single-center expansion method i.e., expansion of Slater-type orbitals with non-integer principal quantum numbers in terms of an infinite series of Slater-type orbitals with integer principal quantum numbers (Guseinov et al. 2002; Guseinov 2007),

$$\chi_{nlm}(\zeta, \mathbf{r}) = \sum_{\mu=l+1}^{\infty} V_{nl,\mu'l} \chi_{\mu'lm}(\zeta, \mathbf{r}), \tag{37}$$

where, V are the expansion coefficients and $\mu \in \mathbb{Z}^+$, may thus also become useable.

The computational aspect of the formulae given here for molecular auxiliary functions and their applications will be the subject of future research.

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