Analytical evaluation of relativistic molecular integrals. I. Auxiliary functions

Ali Bağcı · Philip E. Hoggan

Received: date / Accepted: date

Abstract The auxiliary functions provide efficient computation level for integrals arising at the self-consistent field (SCF) 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 [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 first, are replaced by convergent series representation for incomplete beta functions then, they are 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 also places 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.

Keywords Slater-type orbitals · Multi-center integrals · Auxiliary functions

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 [1,2], Mulliken et al. [3], Roothaan [4,5], Rüdenberg [6], Löwdin [7], Kotani et al. [8], Harris and Mitchell [9–11], Guseinov [12]. It is still being studied in the literature. In particular, the relationships obtained are constantly updated using developments in mathematical physics, chemistry and computer sciences [13–26]. Slater-type orbitals (STOs) [27, 28] are defined as follows:

\[
Y_{nlm}^m(\zeta, r) = \frac{(2\zeta)^{n+1/2}}{\sqrt{\Gamma(2n+1)}} \psi^m_{nlm} e^{-\zeta r} Y^m_l(l, \theta),
\]

here, \( Y^m_l \) are complex or real spherical harmonics \((Y^m_l \equiv Y^m_{l\pm m}, Y^m_{l\pm m} \equiv \text{S}_l^m)\) differs from the Condon–Shortley phases by sign factor \((-1)^m\) [29–31]. \( n, l, m \) are the principal, orbital, magnetic quantum numbers with, \( n \in \mathbb{R}^+, 0 \leq l < |n| - 1, -l \leq m \leq l; |n| \) stands for the integer part of \( n \) and \( \zeta \) are orbital parameters. They are obtained by simplification of Laguerre polynomial in hydrogen-like one-electron eigen-functions [31] by keeping only the term of the highest power of \( r \). Other exponentially decaying bases, including the hydrogen-like functions may be written as linear combinations of STOs [32]. The related eigenfunctions satisfy Kato’s cusp conditions for asymptotic behavior of the wave function near the nucleus [33] at long range all these orbitals decrease exponentially [34]. 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 mechanical theoretical problems; arising from testing limits of the methods obtained approximately to represent the physical systems, where reliable description of electron density is important e.g., investigation the molecules under strong magnetic field [35], second order perturbation energy corrections [36].

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, \( n \in \mathbb{Z}^+, 0 \leq l \leq n - 1 \) and \( \Gamma(2n+1) = n! \). The use of non-integer...
principal quantum numbers in STOs however, promise better results because they provide extra flexibility for closer variational description of molecules [28]. The vital importance of generalising auxiliary function methods is then clear when extending the domain of applications that were previously limited to atoms [37–40], 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 [41, 42]:

\[ f(\zeta, r) = \left\{ A r^\alpha + \zeta B r^{\alpha+1} \right\} e^{-\zeta r}. \]  

(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 in their recent study [25] through Laplace expansion of Coulomb interaction and prolate spheroidal coordinates, expressed the two-center molecular integrals in terms of so called relativistic molecular auxiliary functions. These auxiliary functions were evaluated numerically via Global-adaptive method with Gauss-Kronrod numerical integration extension. Note that highly accurate values from the suggested numerical method are available only in Mathematica programming language. Extended-precision Fortran is being investigated for applications, since the Mathematica programming language is suitable for bench-marking but requires prohibitive calculation time. One of us obtains analytical relations investigated in the reference [43]. The relativistic auxiliary functions are expressed through series representation of incomplete beta functions and in terms of integrals involving Appell’s functions. Double series of Appell’s functions [44],

\[ F_1(\alpha; b_1, b_2; c; x, y) = \sum_{s_1 s_2 = 0}^{\infty} \frac{(a)_{s_1 + s_2}(b_1)_{s_1}(b_2)_{s_2}}{(c)_{s_1 s_2} s_1! s_2!} x^{s_1} y^{s_2}, \]  

(3)

with \( (\alpha) \) is 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 of convergence region it is necessary to make use of recurrence relations formulæ [45] or a 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 [46]. These methods are, however, computationally inefficient and may not give correct results for a particular set of parameters \(\{a, b_1, b_2, c\} \). Besides, computing the Appell’s functions without erroneous last digits is still being studied in the literature [47].

In the present study, we refer to the introductory remarks given in previous studies. Certain concepts and the results of previous work are also used. Here, the relationships given in terms of integrals involving Appell’s functions are also reduced to series representation formulæ for incomplete beta functions. Computing Appell’s functions is therefore avoided. Furthermore, a new binomial expansion method is developed through that given in [48 49], 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 [21, 50–52] 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 \((\xi, \nu, \phi) \) where, \(1 \leq \xi < \infty, -1 \leq \nu \leq 1, 0 \leq \phi \leq 2\pi \), are obtained using the following auxiliary functions integrals [25]:

\[
\begin{align*}
\left\{ \frac{P_{n_2 n_3}}{P_{n_1 n_4}}(p_{123}) \right\} \\
\left\{ \frac{Q_{n_2 n_3}}{Q_{n_1 n_4}}(p_{123}) \right\}
\end{align*}
\]

\[
= \frac{p_{11}^{n_1}}{(n_4 - n_1)_{n_1}} \int_{1}^{\infty} (\xi \nu)^{s_1} (\xi + \nu)^{s_2} (\xi - \nu)^{s_3} \left\{ P[n_4 - n_1, p_1(\xi + \nu)] \right\} \left\{ Q[n_4 - n_1, p_1(\xi + \nu)] \right\} e^{p_{12}^{n_4} - p_{11}^{n_4}} d\xi d\nu, \]

(4)

here, \(\{q, n_1\} \in \mathbb{Z}, \{n_2, n_3, n_4\} \in \mathbb{R}, p_{123} = \{p_1, p_2, p_3\} \) (and in subsequent notations). \(P, Q\) are the normalized complementary incomplete gamma and the normalized incomplete gamma functions,

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

(5)

with \(\gamma(\alpha, z)\) and \(\Gamma(\alpha, z)\) are incomplete gamma functions,

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

(6)

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

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

(7)

and the Pochhammer symbol \((\alpha)\),

\[
(\alpha)_n = \frac{\Gamma(\alpha + n)}{\Gamma(\alpha)}, \]

(8)

respectively [53, 54]. Evaluation of these auxiliary functions involve 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 sum \( P + Q = 1 \) and so, represent the Eq. (4) through upward and downward distant recurrence relations of normalized incomplete gamma functions

\[
\begin{align*}
\{ P[a, b, f] \} & = \left\{ P[a + n, b, f] + e^{-b} \Gamma \sum_{i=1}^{n} \left( \frac{(b)^{a+i-1}}{(a+i)} \right) \right\}, \\
\{ Q[a, b, f] \} & = \left\{ Q[a + n, b, f] - e^{-b} \Gamma \sum_{i=1}^{n} \left( \frac{(b)^{a+i-1}}{(a+i)} \right) \right\},
\end{align*}
\]

(9)

\[
\begin{align*}
\{ P[a, b, f] \} & = \left\{ P[a - n, b, f] - e^{-b} \Gamma \sum_{i=1}^{n} \left( \frac{(b)^{a+i-1}}{(a+i)} \right) \right\}, \\
\{ Q[a, b, f] \} & = \left\{ Q[a - n, b, f] + e^{-b} \Gamma \sum_{i=1}^{n} \left( \frac{(b)^{a+i-1}}{(a+i)} \right) \right\},
\end{align*}
\]

(10)
in terms of the following form (please see [43]):

\[
\begin{align*}
g^{n_{1}, q}_{n_{3}}(p_{123}) & = \frac{p_{1}^{n_{1}}}{\Gamma(n_{1} + 1)} \\
& \times \int_{1}^{z} \int_{1}^{\xi} (\xi + v)^{q_{3}} \left( \xi - v \right)^{n_{3}} e^{-p_{2} z - p_{3} v} d\xi dv.
\end{align*}
\]

(11)
The feature given above can therefore generally be defined as follows:

**Criterion.** Let \( P[n_{4} - n_{1}, 1] \) and \( Q[n_{4}' - n_{1}', 1] \) then \( n_{4} - n_{1} = a + c, n_{4}' - n_{1}' = a + d \), 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,

\[
(\xi v) = \frac{1}{4} \left( (\xi + v)^{2} - (\xi - v)^{2} \right),
\]

(12)

the auxiliary functions \( g^{n_{1}, q}_{n_{3}} \) are obtained as follows [43],

\[
\begin{align*}
g^{n_{1}, q}_{n_{3}}(p_{12}) & = \frac{1}{4} \left( g^{n_{1}, q-1}_{n_{3}+2}\left(p_{123}\right) - g^{n_{1}, q-1}_{n_{3}+2}\left(p_{12}\right) \right),
\end{align*}
\]

(13)

here,

\[
\begin{align*}
g^{n_{1}, 0}_{n_{3}}(p_{12}) & = \frac{\Gamma(n_{1} + 1)}{\Gamma(n_{1} + 1)} \sum_{j=0}^{n_{3}} \frac{b^{j}}{(n_{3} + s + 1)} \left( \frac{1}{s + 1} \right) \\
& \times \left\{ g^{n_{1}, 0}_{n_{3}+2}\left(p_{12}\right) \right\},
\end{align*}
\]

(14)

\[
\begin{align*}
h^{n_{1}, q}_{n_{3}}(p_{12}) & = \frac{p_{1}^{n_{1}}}{\Gamma(n_{1} + 1)} 2^{n_{2} + n_{3} + q + 1} B(n_{2} + 1, n_{3} + 1) \\
& \times E_{-(n_{2} + n_{3} + q + 1)}(p_{2}) - g^{n_{1}, q}_{n_{3}}(p_{12}),
\end{align*}
\]

(15)

\[
\begin{align*}
p^{n_{1}, q}_{n_{3}}(p_{12}) & = \frac{p_{1}^{n_{1}}}{\Gamma(n_{1} + 1)} \sum_{s=0}^{n_{3}} \frac{(-n_{2})_{s}}{(n_{3} + s + 1)!} \left( n_{2} + q + s \right)_{s} \left( p_{2} \right),
\end{align*}
\]

(16)

\[
m^{n_{1}}_{n_{3}}(p) = 2^{n_{1}} U(n_{2} + 1, n_{1} + n_{2} + 2, p) \Gamma(n_{2} + 1) e^{-p},
\]

(17)

and,

\[
k^{n_{1}, q}_{n_{3}}(p_{12}) = \frac{p_{1}^{n_{1}}}{\Gamma(n_{1} + 1)} 2^{n_{2} + n_{3} + q + 1} B(n_{2} + 1, n_{3} + 1) \left( \frac{1}{2} \right) \\
\times E_{-(n_{2} + n_{3} + q + 1)}(p_{2}),
\]

(18)

with,

\[
U(a, b; z) = \frac{\Gamma(b - 1)}{\Gamma(a)} F_{1}(a - b + 1, 2 - b; z) \\
+ \frac{\Gamma(1 - b)}{\Gamma(a - b + 1)} F_{1}(a; b; z),
\]

(19)

here, \( U(a, b; z) \) are confluent hypergeometric functions of second kind with,

\[
F_{1}(a; b; z) = \frac{\Gamma(b)}{\Gamma(b - a) \Gamma(a)} \int_{0}^{1} t^{a-1} (1 - t)^{b-1} e^{a z} dt,
\]

(20)

confluent hypergeometric functions of first kind and \( B(a, b, z) \) incomplete beta functions,

\[
B(a, b, z) = \int_{0}^{z} t^{a-1} (1 - t)^{b-1} dt,
\]

(21)

\( B(a, b) = B(a, b, 1) \) are beta functions, respectively [43].

**Case 2.** The parameter \( p_{3} \neq 0 \).

By lowering the indices \( q \) and using the series expansion of exponential functions \( e^{c} \), where \( z = -p_{3} v \), the following relation is obtained [43],

\[
\begin{align*}
g^{n_{1}, 0}_{n_{3}}(p_{123}) & = \frac{p_{1}^{n_{1}}}{\Gamma(n_{1} + 1)} \sum_{j=0}^{n_{3}} \frac{p_{3}^{j}}{\Gamma(s + 1)} \left( \frac{1}{s + 1} \right) \\
& \times \left\{ J^{n_{1}, r+2}(p_{2}) + (-1)^{r} J^{n_{1}, r+2}(p_{2}) \right\},
\end{align*}
\]

(22)

The \( J^{n, q} \) functions involve Appell’s hypergeometric functions [44].

\[
F_{1}(a; b_{1}, b_{2}; c; x, y) = \frac{\Gamma(c)}{\Gamma(a - c)} \\
\times \int_{0}^{1} (1 - u)^{c-a-1} (1 - u)^{-b_{1}} (1 - u)^{-b_{2}} du,
\]

(23)

and their explicit forms are given as,

\[
\begin{align*}
J^{n, q}_{n_{3}}(p) & = \int_{1}^{\infty} F_{1}\left( s - n_{2}, -n_{3}; 1 \right) \\
& \times \left( \frac{1}{\xi} - \frac{1}{\xi} \right) \\
& \times \xi^{n_{2} + n_{3} + q} e^{-p_{2} \xi} d\xi.
\end{align*}
\]

(24)
The sum of two $\phi_{n,s}(\xi)$ functions arising in the right-hand-side of Eq. (22) is an integral in the form written as:

$$
\left(1 + \underbrace{\Phi_{n,1,s,2+0}}_{ \left( s + 1 \right)} \right) \left( J_{n,1,s,2+0} (p_2) + (-1)^s J_{n,1,s,2+0} (p_2) \right) = \int_1^\infty \int_1 \left( \xi + v \right)^{n_1} \left( \xi - v \right)^{n_2} \nu^v e^{-\nu^v} d\xi d\nu.
$$

By dividing and multiplying the expression with $\xi^2$ we obtain:

$$
\phi_{n,s}^{s',s} (p_2) = \int_1^\infty \int_1 \left( \xi + v \right)^{n_1} \left( \xi - v \right)^{n_2} \nu^v e^{-\nu^v} d\xi d\nu.
$$

By again making use of Eq. (22), finally the following relation is obtained for $(s' = s)$:

$$
\phi_{n,s}^{s,s} (p_2) = \frac{1}{4} \left\{ \phi_{n,s+2,s} (p_2) - \phi_{n,s-2,s} (p_2) \right\},
$$

$$
\phi_{n,s}^{0,s} (p_2) = \frac{1}{2} \left\{ h_{n,s}^{0} (p_0) + h_{n,s}^{0} (p_2) - k_{n,s}^{1,1} (p_0) - k_{n,s}^{1,1} (p_2) \right\}
$$

with, $p_0 = \{ 1, p_2 \}$. It should be note that Eqs. (24) imply convergence properties of incomplete beta function expansions; $B (n_1, n_2)$ at $z = 0$, where absolute value of $z$ must be $|z| < 1$. Considering the domain given for auxiliary functions $\phi_{n,s}^{s,s}$, it is easy to see that the convergence condition is satisfied, where, $z = \frac{x - y}{\theta}$. The Eq. (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 [48]. 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 $h$ [48, 49].

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

$$
(\xi \pm v)^n = \xi^n \left( 1 + \frac{v}{\xi^2} \right)^n \left( 1 \pm \frac{v}{\nu} \right)^n,
$$

where, $\left| \frac{x - y}{\theta} \right| < 1$, $\frac{v}{\xi^2} = \frac{v}{\nu}$ with $\frac{v}{\nu} < 1$, respectively.

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

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

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

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

$$
(\xi + v)^n = \lim_{N \to \infty} \sum_{s = 0}^N (\pm 1)^s \mu_n^{s,n} (h) \mu_n^{s',n} (h') \times F_s (n_2) \mu_n^{s',n-s'} (h')
$$

where, $F_s (n)$, are the binomial coefficients indexed by $n$, $s$ is usually written $\left( \begin{array}{c} n \\ s \end{array} \right)$, with,

$$
\left( \begin{array}{c} n \\ s \end{array} \right) = \frac{\Gamma (n+1)}{\Gamma (s+1) \Gamma (n-s+1)}.
$$

According to formuale given above the auxiliary functions $\phi_{n,s}^{s,s}$ are obtained as follows:

$$
\phi_{n,s}^{s,s} (p_{123}) = \frac{p_1^{n_1}}{\Gamma (n_1 + 1)} \lim_{N \to \infty} \sum_{s' = 0}^N \mu_n^{s,n} (h) \mu_n^{s',n} (h') \times F_s (n_2) \mu_n^{s',n-s'} (h')
$$

$$
\phi_{n,s}^{s,s} (p_{123}) = \frac{p_1^{n_1}}{\Gamma (n_1 + 1)} \lim_{N \to \infty} \sum_{s' = 0}^N \mu_n^{s,n} (h) \mu_n^{s',n} (h') \times F_s (n_2) \mu_n^{s',n-s'} (h')
$$

$$
\phi_{n,s}^{s,s} (p_{123}) = \frac{p_1^{n_1}}{\Gamma (n_1 + 1)} \lim_{N \to \infty} \sum_{s' = 0}^N \mu_n^{s,n} (h) \mu_n^{s',n} (h')
$$

$$
\times F_s (n_2) \mu_n^{s',n-s'} (h') \left\{ E_{(n_2-n_3)} (p_2) \frac{p_3^{q+k+1}}{p_3^{q+k+1}} \right\} \times \left( \Gamma (q+k+1, p_3) - \gamma (q+k+1, -p_3) \right),
$$

where, $k = s + s'$, and

$$
E_n (p) = \int_1^\infty \frac{e^{-p^2}}{\xi^n} d\xi,
$$

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 $f(z) = e^{x \log z}$ with non-integer exponents $n \in \mathbb{R}$ which cannot be represented by a power series because they are not analytic about $z = 0$. 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, need urgent implementation and are precious. Two methods based on this reasoning are proposed in this study. Firstly, through expansion of exponential functions the molecular $\varphi^{\mu\nu\alpha\beta\gamma\epsilon}$ 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). This criterion is correct, from using the Laplace expansion of the Coulomb interaction to evaluate multicenter integrals (please see [43] for more detail). The relationships given in the presented work are reliable and convergent. Benchmark results in our previous papers [24, 25] 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 the power series [56]. 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 (integer principal quantum number) Slater-type orbitals [57, 58],

$$
\chi_{\text{nlm}}(\xi, \sigma) = \sum_{\mu=1}^{\infty} V_{\mu}(\xi) \chi_{\text{nlm}}^{\mu}(\xi, \sigma),
$$

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

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

Acknowledgement

A.B. would like to thank to Department of Physics, Faculty of Arts and Sciences, Pamukkale University for providing working facilities. He would like also give a special thank to Prof. Dr. Muzaffer Adak and Prof. Dr. Mestan Kalay for their fruitful discussions.

References

1. Coulson, C A (1942) Two-centre integrals occurring in the theory of molecular structure. Mathematical Proceedings of the Cambridge Philosophical Society 38(2):210-223. doi:10.1017/S0305004100021873
2. Barnett MP, Coulson CA (1951) The evaluation of integrals occurring in the theory of molecular structure. Parts I&II. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 243(864):221-249 doi:10.1098/rsta.1951.0003
3. Mulliken RS, Rieke CA, Orloff D, Orloff H (1949) Formulas and Numerical Tables for Overlap Integrals. The Journal of Chemical Physics 17(12):1248-1267. doi:10.1063/1.1747150
4. Roothaan CCJ (1951) A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. I. The Journal of Chemical Physics 19(12):1445-1458. doi:10.1063/1.1748100
5. Roothaan CCJ (1956) Study of Two-Center Integrals Useful in Calculations on Molecular Structure. IV. The Auxiliary Functions $\alpha\beta\gamma\epsilon(\rho, \phi, \psi)$ for $\alpha \geq 0$. The Journal of Chemical Physics 24(5):947-960. doi:10.1063/1.1742721
6. Rüdenberg K (1951) A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. II. The Two-Center Exchange Integrals. The Journal of Chemical Physics 19(12):1459-1477. doi:10.1063/1.1748101
7. Löwdin PO (1956) Quantum theory of cohesive properties of solids. Advances in Physics 5(17):1-171. doi:10.1080/00018735600101155
8. Kotani M, Amemiya A, Ishiguro E, Kimura T (1963) Table of Molecular Integrals. Maruzen Company Ltd., Tokyo, Japan.
9. Harris FE, Michels HH (1965) Multicenter Integrals in Quantum Mechanics. I. Expansion of Slater-Type Orbitals about a New Origin. The Journal of Chemical Physics 43(10):S165-S169. doi:10.1063/1.1701480
10. Harris FE, Michels HH (1966) Multicenter Integrals in Quantum Mechanics. II. Evaluation of Electron-Repulsion Integrals for Slater-Type Orbitals. The Journal of Chemical Physics 45(1):116-123. doi:10.1063/1.1727293
11. Harris FE, Michels HH (1967) The Evaluation of Molecular Integrals for Slater-Type Orbitals. In: Prigogine I (ed) Advances in Chemical Physics Volume 13, John Wiley&Sons, Inc., Hoboken, NJ, USA, pp 205-266. doi:10.1002/9780470140154.ch8
12. Guseinov II (1970) Analytical evaluation of two-centre Coulomb, hybrid and one-electron integrals for
Slater-type orbitals. Journal of Physics B: Atomic and Molecular Physics 3(11):1399-1412. doi:10.1088/0022-3700/3/11/001

13. Guseinov II, Mamedov BA, Kara M, Orbay M (2001) On the computation of molecular auxiliary functions $A_n$ and $B_n$. Pramana 56(5):691-696. doi:10.1007/s12043-001-0093-x

14. Harris FE (2002) Analytical evaluation of two-center STO electron repulsion integrals via ellipsoidal expansion. International Journal of Quantum Chemistry 88(6):701-734. doi:10.1002/qua.10184

15. Guseinov II, Mamedov BA (2002) On the calculation of arbitrary multielectron molecular integrals over Slater-type orbitals using recurrence relations for overlap integrals. III. Auxiliary functions $Q_{nl}$ and $G_{nl}$. International Journal of Quantum Chemistry 86(5):440-449. doi:10.1002/qua.10045

16. Harris FE (2003) Comment: "On the computation of molecular auxiliary functions $A_n$ and $B_n". Pramana 61(4):C779-C80. doi:10.1007/BF02706128

17. Harris FE (2004) Efficient evaluation of the molecular auxiliary function $B_n$ by downward recursion. International Journal of Quantum Chemistry 100(2):142-145. doi:10.1002/qua.10812

18. Guseinov II, Mamedov BA (2005) Fast evaluation of molecular auxiliary functions $A_n$ and $B_n$ by analytical relations. Journal of Mathematical Chemistry 38(1):21-26. doi:10.1007/s10910-005-4527-4

19. Fernández JJ, López R, Ema I, Ramírez G, Fernández RJ (2006) Auxiliary functions for molecular integrals with Slater-type orbitals. I. Translation methods. International Journal of Quantum Chemistry (106)9:1986-1997. doi:10.1002/qua.21002

20. Ema I, López R, Fernández JJ, Ramírez, G, Rico, JF (2008) Auxiliary functions for molecular integrals with Slater-type orbitals. II. Gauss transform methods. International Journal of Quantum Chemistry 108(1):25-39. doi:10.1002/qua.21409

21. Guseinov II (2009) Use of auxiliary functions $Q_{nl}$ and $G_{nl}$ in evaluation of multiecenter integrals over integer and noninteger n-Slater type orbitals arising in Hartree-Fock-Roothaan equations for molecules. Journal of Mathematical Chemistry 45(4):974-980. doi:10.1007/s10910-008-9431-2

22. Lesiuk M, Moszynski R (2014) Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. I. Coulomb and hybrid integrals. Physical Review E 90(6):063318. doi:10.1103/PhysRevE.90.063318

23. Lesiuk M, Moszynski R (2014) Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. II. Neumann expansion of the exchange integrals. Physical Review E 90(6):063319. doi:10.1103/PhysRevE.90.063319

24. Bağcı A, Hoggan PE (2014) Performance of numerical approximation on the calculation of overlap integrals with noninteger Slater-type orbitals. Physical Review E (89)7:053307. doi:10.1103/PhysRevE.89.053307

25. Bağcı A, Hoggan PE (2015) Benchmark values for molecular two-electron integrals arising from the Dirac equation. Physical Review E 91(2):023303. doi:10.1103/PhysRevE.91.023303

26. Bağcı A, Hoggan PE (2015) Benchmark values for molecular three-center integrals arising in the Dirac equation. Physical Review E (92)4:043301. doi:10.1103/PhysRevE.92.043301

27. Slater JC (1930) Atomic Shielding Constants. Physical Review 36(1):57-64. doi:10.1103/PhysRev.36.57

28. Parr RG, Hubert WJ (1957) Why Not Use Slater Orbitals of Nonintegral Principal Quantum Number? The Journal of Chemical Physics 26(2):424-424. doi:10.1063/1.1743314

29. Condon EU, Shortley GH (1935) The Theory of Atomic Spectra. Cambridge University Press, Cambridge, UK.

30. Steinborn EO, Rüdenberg K (1973) Rotation and Translation of Regular and Irregular Solid Spherical Harmonics. Advances in Quantum Chemistry 7(1):1-81. doi:10.1016/S0065-3276(08)60558-4

31. Willock DJ (2009) Appendix 9: The Atomic Orbitals of Hydrogen. In: Molecular Symmetry, John Wiley & Sons Ltd, Chichester, UK. doi:10.1002/9780470747414.app9

32. Weniger EJ (2002) Addition theorems as three-dimensional Taylor expansions. II. B functions and other exponentially decaying functions. International Journal of Quantum Chemistry 90(1):92-104. doi:10.1002/qua.948

33. Kato T (1957) On the eigenfunctions of many-particle systems in quantum mechanics. Communications on Pure and Applied Mathematics 10(2):151-177. doi:10.1002/cpa.3160100201

34. Agmon S (1982) Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operations. Princeton University Press, Princeton, NJ.

35. Bougergue A, Weatherford CA, Jones HW (1999) Addition theorem of Slater-type orbitals: Application to $H_2$ in a strong magnetic field. Physical Review E 59(2):2412-2423. doi:10.1103/PhysRevE.59.2412

36. Hoggan PE (2011) Slater-Type Orbital Basis Sets: Reliable and Rapid Solution of the Schrödinger Equation for Accurate Molecular Properties. In: Popelier P (ed) Solving the Schrödinger Equation, Imperial College Press, Covent Garden, London, UK. doi: 10.1142/9781848167254_0007

37. Koga T, Kanayama K, Thakkar AJ (1997) Noninteger principal quantum numbers increase the efficiency of Slater-type basis sets. International Journal of Quantum Chemistry 62(1):1-11. doi:10.1002/(SICI)1097-
Analytical evaluation of relativistic molecular integrals. I. Auxiliary functions

37. Koga T, Kanayama K (1997) Noninteger principal quantum numbers increase the efficiency of Slater-type basis sets: singly charged cations and anions. Journal of Physics B: Atomic, Molecular and Optical Physics 30(7):1623-1631. doi:10.1088/0953-4075/30/7/004

38. Koga T, Shimazaki T, Satoh T (2000) Noninteger principal quantum numbers increase the efficiency of Slater-type basis sets: double-zeta approximation. Journal of Molecular Structure: THEOCHEM 496(1):95-100. doi:10.1016/S0166-1280(99)00176-1

39. Guseinov II, Ertőrök M (2012) Use of noninteger n-generalized exponential type orbitals with hyperbolic cosine in atomic calculations. International Journal of Quantum Chemistry 112(6):1559-1565. doi:10.1002/qua.23133

40. Grant IP (2007) Relativistic Quantum Theory of Atoms and Molecules. Springer, New York.

41. Bağcı A, Hoggan PE (2016) Solution of the Dirac equation using the Rayleigh-Ritz method: Flexible basis coupling large and small components. Results for one-electron systems. Physical Review E 94(1):013302.

42. Bağcı A (2017) Notes on mathematical difficulties arising in relativistic SCF approximation. [arXiv:1603.02307 [physics.chem-ph].]

43. Appell P. (1925) Sur les fonctions hypergéométriques de plusieurs variables, les polynômes d’Hermite et autres fonctions sphériques dans l’hyperespace. Mémoire des sciences mathématiques. Gauthier-Villars, Paris, France.

44. Wang X (2012) Recursion formulas for Appell functions. Integral Transforms and Special Functions 23(6):421-433. doi:10.1080/10652469.2011.596483

45. Colavecchia FD, Gasaneo G, Miraglia JE (2001) Numerical evaluation of Appell’s F1 hypergeometric function. Computer Physics Communications 138(1):29-43. doi:10.1016/S0010-4655(01)00186-2

46. Colavecchia FD, Gasaneo G (2004) F1: a code to compute Appell’s F1 hypergeometric function. Computer Physics Communications 157(1):32-38. doi:10.1016/S0010-4655(03)00490-9

47. Liao SJ (2004) Beyond perturbation: introduction to the homotopy analysis method. Chapman&Hall/CRC, Boca Raton, Florida, USA.

48. Liu CS (2010) The essence of the generalized Newton binomial theorem. Communications in Nonlinear Science and Numerical Simulation 15(10):2766-2768. doi:10.1016/j.cnsns.2009.11.004

49. Mekelleche SM, Baba-Ahmed A (2000) Unified analytical treatment of one-electron two-center integrals with noninteger n Slater-type orbitals. Theoretical Chemistry Accounts 103(6):63-468. doi:10.1007/s002149900084

50. Guseinov II, Mamedov BA (2002) Computation of multicenter nuclear-attraction integrals of integer and noninteger n Slater orbitals using auxiliary functions. Journal of Theoretical and Computational Chemistry 1(1):17-24. doi:10.1142/S021963660200130

51. Guseinov II, Mamedov BA (2002) Computation of multicenter nuclear-attraction integrals of integer and noninteger n Slater orbitals using auxiliary functions. Journal of Theoretical and Computational Chemistry 1(1):17-24. doi:10.1142/S021963660200130

52. Guseinov II, Mamedov BA (2002) Computation of multicenter nuclear-attraction integrals of integer and noninteger n Slater orbitals using auxiliary functions. Journal of Theoretical and Computational Chemistry 1(1):17-24. doi:10.1142/S021963660200130

53. Guseinov II (2007) Expansion formulae for two-center integer and noninteger n STO charge densities and their use in evaluation of multi-center integrals. Journal of Mathematical Chemistry 42(3):415-422. doi:10.1007/s10910-006-9111-z