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Nuclear attraction and electron interaction integrals of exponentially decaying functions and the Poisson equation*

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Summary. The technique proposed by O-Ohata and Ruedenberg (J Math Phys 7:547 (1966)) and by Silver and Ruedenberg (J Chem Phys 49:4306 (1968)) of computing nuclear attraction and electron interaction integrals by solving an inhomogeneous Laplace equation can also be applied if *B* functions (Filter E, Steinborn EO (1978) Phys Rev A 18:1) are used as basis functions in atomic and molecular calculations. It is shown that because of the remarkable mathematical properties of *B* functions the derivation of compact explicit expressions for the multicenter integrals mentioned above is particularly simple. These results are also of interest in the context of other exponentially decaying functions, since all the other commonly occurring exponentially decaying functions as, for instance, Slater functions or bound state hydrogen eigenfunctions can be expressed as simple linear combinations of *B* functions. Consequently, their multicenter integrals can also be expressed in terms of multicenter integrals of *B* functions.

Key words: Nuclear attraction – Electron interaction integrals – Exponentially decaying functions

1. Introduction

Exponentially decaying functions as, for instance, Slater functions are able to satisfy the cusp condition [1] at the nuclei, and for large distances they behave as exact eigenstates of atomic and molecular Hamiltonians do [2]. Consequently, it is generally accepted that the use of exponentially decaying basis functions in molecular electronic structure calculations would be highly desirable. Unfortunately, their notoriously complicated multicenter integrals have so far prevented a routine application of exponentially decaying functions in molecular calculations. A survey of the older literature on molecular multicenter integrals of exponentially decaying functions and a description of the various methods for their evaluation can be found in review articles by Huzinaga [3], Harris and Michels [4], and Browne [5]. More recent references on multicenter integrals can

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* Dedicated to Prof. Klaus Ruedenberg on the occasion of his 70th birthday

be found in the proceedings of a conference on molecular multicenter integrals [6], or in review articles by Steinborn [7, 8]. We would also like to mention that recently some progress has been made concerning the evaluation of the notorious four-center interelectronic repulsion integrals of exponentially decaying functions using integral transform techniques and numerical quadratures [9–15].

In this article, we want to discuss a method for the evaluation of nuclear attraction and electron interaction integrals, which was first proposed by O-Ohata and Ruedenberg [16] and by Silver and Ruedenberg [17] in connection with Coulomb integrals of Slater functions. In this approach, an inhomogeneous Laplace or Poisson equation for the multicenter integral is constructed,

$$\vec{\nabla}^2 \Phi(\vec{x}) = -4\pi \varrho(\vec{x}), \tag{1.1}$$

where

$$\Phi(\vec{x}) = \int \frac{\varrho(\vec{y})}{|\vec{x} - \vec{y}|} \, d^3\vec{y}. \tag{1.2}$$

Unless explicitly stated we shall always tacitly assume in this article that the Laplace operator $\vec{\nabla}^2$ acts on the coordinates of $\vec{x}$.

The approach introduced by O-Ohata and Ruedenberg [16] and by Silver and Ruedenberg [17] is best understood by considering a simple example. Therefore, let us consider the following two-center nuclear attraction integral:

$$\mathscr{A}(f; \vec{x}) = \int \frac{1}{|\vec{x} - \vec{y}|} f(\vec{y}) \, d^3\vec{y}. \tag{1.3}$$

Obviously, the integral $\mathscr{A}(f; \vec{x})$ is of the type of Eq. (1.2). Consequently, it follows from Eqs. (1.1) and (1.2) that it can be evaluated by solving the Poisson equation:

$$\vec{\nabla}^2 \mathscr{A}(f; \vec{x}) = -4\pi f(\vec{x}). \tag{1.4}$$

The same technique works also in the case of multicenter integrals which describe the interelectronic repulsion of two charge densities f and g that are located at different centers separated by a vector $\vec{x}$,

$$\mathscr{C}(f, g; \vec{x}) = \int\int f^*(\vec{y}) \frac{1}{|\vec{x} - \vec{y} + \vec{z}|} g(\vec{z}) \, d^3\vec{y} \, d^3\vec{z}. \tag{1.5}$$

If we now use in this integral the relationship:

$$\vec{\nabla}^2 \frac{1}{|\vec{x} - \vec{y}|} = -4\pi \delta(\vec{x} - \vec{y}), \tag{1.6}$$

we obtain:

$$\begin{aligned}\vec{\nabla}^2 \mathscr{C}(f, g; \vec{x}) &= -4\pi \int\int f^*(\vec{y}) \delta(\vec{x} - \vec{y} + \vec{z}) g(\vec{z}) \, d^3\vec{y} \, d^3\vec{z} \\ &= -4\pi \int f^*(\vec{y}) g(\vec{y} - \vec{x}) \, d^3\vec{y}.\end{aligned} \tag{1.7}$$

If we introduce for the overlap integral in Eq. (1.7) the notation

$$\mathscr{S}(f, g; \vec{x}) = \int f^*(\vec{y}) g(\vec{y} - \vec{x}) \, d^3\vec{y}, \tag{1.8}$$

we see that the interelectronic repulsion integral $\mathscr{C}(f, g; \vec{x})$ can be computed by solving the following Poisson equation, where the inhomogeneity is an overlap integral:

$$\vec{\nabla}^2 \mathscr{C}(f, g; \vec{x}) = -4\pi \mathscr{S}(f, g; \vec{x}). \tag{1.9}$$

This relationship was used by O-Ohata and Ruedenberg [16] and by Silver and Ruedenberg [17] to derive explicit expressions and recurrence relationships for Coulomb integrals of Slater functions.

In this article, we also want to derive explicit expressions for nuclear attraction and Coulomb integrals by solving the Poisson equations (1.4) and (1.9). However, instead of Slater functions we shall consider another class of exponentially decaying functions, the so-called B functions [18]. We shall show that because of the remarkable mathematical properties of these functions, which give them a unique position among exponentially decaying functions, it is in many cases surprisingly easy to derive compact explicit expressions for nuclear attraction and Coulomb integrals of B functions with the help of the technique originally proposed by O-Ohata and Ruedenberg [16] and by Silver and Ruedenberg [17].

2. Definitions and basic properties of B functions

The spherical harmoncis $Y_l^m(\vartheta, \varphi)$ are defined using the phase convention of Condon and Shortley [19]:

$$Y_l^m(\vartheta, \varphi) = i^{m+|m|} \left\{ \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right\}^{1/2} P_l^{|m|}(\cos \vartheta)\, e^{im\varphi}. \tag{2.1}$$

Here, $P_l^{|m|}(\cos \vartheta)$ is an associated Legendre polynomial:

$$\begin{aligned} P_l^m(z) &= (1-z^2)^{m/2} \frac{d^{l+m}}{dz^{l+m}} \left\{ \frac{(z^2-1)^l}{2^l l!} \right\} \\ &= (1-z^2)^{m/2} \frac{d^m}{dz^m} P_l(z), \qquad m \geqslant 0. \end{aligned} \tag{2.2}$$

For the regular and irregular solid harmonic we write:

$$\mathscr{Y}_l^m(\vec{x}) = x^l Y_l^m(\vec{x}/x), \tag{2.3}$$

$$\mathscr{Z}_l^m(\vec{x}) = x^{-l-1} Y_l^m(\vec{x}/x). \tag{2.4}$$

It is important to note that the regular solid harmonic $\mathscr{Y}_l^m(\vec{x})$ is a homogeneous polynomial of degree l in the Cartesian components of $\vec{x}$ (see, for instance, Eq. (3.153) of [20]). If we replace in the explicit expression for $\mathscr{Y}_l^m(\vec{x})$ the Cartesian components of $\vec{x}$ by the Cartesian components of $\vec{\nabla}$, we obtain a differential operator $\mathscr{Y}_l^m(\vec{\nabla})$ which is also a spherical tensor of rank l and which we call spherical tensor gradient. A discussion of the properties of this differential operator and a survey of the relevant literature can be found in articles by Niukkanen [21], Rashid [22], and the authors [23, 24].

For the integral of the product of three spherical harmonics over the surface of the unit sphere in $\mathbb{R}^3$, the so-called Gaunt coefficient, we write:

$$\langle l_3 m_3 | l_2 m_2 | l_1 m_1 \rangle = \int [Y_{l_3}^{m_3}(\Omega)]^* Y_{l_2}^{m_2}(\Omega) Y_{l_1}^{m_1}(\Omega)\, d\Omega. \tag{2.5}$$

Gaunt coefficients linearize the product of two spherical harmonics:

$$[Y_{l_1}^{m_1}(\Omega)]^{*} Y_{l_2}^{m_2}(\Omega) = \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle Y_l^{m_2 - m_1}(\Omega). \tag{2.6}$$

The symbol $\sum^{(2)}$ indicates that the summation proceeds in steps of two. The summation limits in Eq. (2.6), which follow from the selection rules satisfied by the Gaunt coefficient, are [25]:

$$l_{\max} = l_1 + l_2, \tag{2.7a}$$

$$l_{\min} = \begin{cases} \max(|l_1 - l_2|, |m_2 - m_1|) & \text{if } \max(|l_1 - l_2|, |m_2 - m_1|) + l_{\max} \text{ is even,} \\ \max(|l_1 - l_2|, |m_2 - m_1|) + 1 & \text{if } \max(|l_1 - l_2|, |m_2 - m_1|) + l_{\max} \text{ is odd.} \end{cases} \tag{2.7b}$$

The so-called B functions, which were introduced by Filter and Steinborn [18], are defined as follows:

$$B_{n,l}^{m}(\alpha, \vec{x}) = [2^{n+l}(n+l)!]^{-1} \hat{k}_{n-1/2}(\alpha x) \mathcal{Y}_l^m(\alpha \vec{x}). \tag{2.8}$$

The radial part of a B function is a so-called reduced Bessel function [26],

$$\hat{k}_\nu(z) = (2/\pi)^{1/2} z^\nu K_\nu(z), \tag{2.9}$$

where $K_\nu(z)$ is a modified Bessel function of the second kind [27].

If the order n of a B function is a positive integer, $n \geqslant 1$, then the radial part of a B function is an exponential in x multiplied by a polynomial in x [18]. If, however, the order n is a negative integer or zero satisfying $-l \leqslant n \leqslant 0$, then the B function may become singular at the origin. Consequently, only B functions with orders $n \geqslant 1$ can be used as basis functions in atomic and molecular calculations.

It follows from its definition, Eq. (2.8), that a B function is in general a relatively complicated mathematical object. However, it could be shown by the authors [28] and shortly afterwards also by Niukkanen [29] that the Fourier transform of a B function is of exceptional simplicity:

$$\begin{aligned} \bar{B}_{n,l}^{m}(\alpha, \vec{p}) &= (2\pi)^{-3/2} \int e^{-i\vec{p}\cdot\vec{x}} B_{n,l}^{m}(\alpha, \vec{x})\, d^3\vec{x} \\ &= (2/\pi)^{1/2} \frac{\alpha^{2n+l-1}}{[\alpha^2 + p^2]^{n+l+1}} \mathcal{Y}_l^m(-i\vec{p}). \end{aligned} \tag{2.10}$$

This remarkably compact Fourier transform explains why B functions have comparatively simple addition theorems [24, 26, 30, 31] and why it was possible to obtain relatively simple expressions for molecular multicenter integrals of B functions [9–15, 18, 28, 32–36].

In articles by Niukkanen [29] and by the authors [28, 37] it was shown that the Fourier transforms of all the commonly occurring exponentially decaying functions as, for instance, Slater functions or bound-state hydrogen eigenfunctions can be expressed as simple finite sums of Fourier transforms of B functions. Consequently, the commonly occurring exponentially decaying functions can all be expressed as simple finite sums of B functions [11, 18, 28, 29, 37]. This property of B functions is quite consequential from a practical point of view because it makes it possible to express the molecular multicenter integrals of all the commonly occurring exponentially decaying functions as simple finite sums of the corresponding integrals of B functions. Actually, in many cases the simplest way of computing multicenter integrals of other exponentially decaying functions consists in expressing these integrals in terms of integrals of B functions.

It follows immediately from the Fourier integral representation of a B function [35],

$$B^m_{n,l}(\alpha, \vec{x}) = \frac{\alpha^{2n+l-1}}{2\pi^2} \int e^{i\vec{x}\cdot\vec{p}} \frac{\mathcal{Y}^m_l(-i\vec{p})}{[\alpha^2+p^2]^{n+l+1}}\, d^3\vec{p}, \tag{2.11}$$

that the differential operator of the modified Helmholtz equation is a shift operator for B functions [23]:

$$[1-\alpha^{-2}\vec{\nabla}^2] B^m_{n,l}(\alpha, \vec{x}) = B^m_{n-1,l}(\alpha, \vec{x}). \tag{2.12}$$

This relationship remains meaningful in the sense of classical analysis for all integers $n > -l$. If the order n is a negative integer satisfying $n = -l$, this relationship holds in the sense of generalized functions because a B function of order $n = -l-k$ with $k \geqslant 1$ can be identified with a derivative of the three-dimensional delta function [23],

$$B^m_{-l-k,l}(\alpha, \vec{x}) = (2l-1)!!(4\pi/\alpha^{l+3})[1-\alpha^{-2}\nabla^2]^{k-1}\delta^m_l(\vec{x}), \tag{2.13}$$

where the spherical delta function $\delta^m_l(\vec{x})$ is defined by:

$$\delta^m_l(\vec{x}) = \frac{(-1)^l}{(2l-1)!!}\mathcal{Y}^m_l(\vec{\nabla})\delta(\vec{x}). \tag{2.14}$$

The multiplication theorem of B functions [18],

$$B^m_{n,l}(\alpha, \vec{x}) = (\alpha/\beta)^{2n+l-1} \sum_{\nu=0}^{\infty} \frac{(n+l+1)_\nu}{\nu!} \left\{\frac{\beta^2-\alpha^2}{\beta^2}\right\}^{\nu} B^m_{n+\nu,l}(\beta, \vec{x}), \tag{2.15}$$

which converges provided that $|1-(\alpha/\beta)^2| < 1$, can be used to express a molecular multicenter integral of B functions with different scaling parameters as an infinite series of integrals of B functions with equal scaling parameters.

3. Nuclear attraction integrals

Let us now consider the following nuclear attraction integral involving a B function:

$$A^m_{n,l}(\alpha, \vec{x}) = \int \frac{1}{|\vec{x}-\vec{y}|} B^m_{n,l}(\alpha, \vec{y})\, d^3\vec{y}. \tag{3.1}$$

It follows from Eq. (1.4) that this integral can be evaluated by solving the following Poisson equation:

$$\vec{\nabla}^2 A^m_{n,l}(\alpha, \vec{x}) = -4\pi B^m_{n,l}(\alpha, \vec{x}). \tag{3.2}$$

It is relatively easy to obtain the following factor-free series expansion for the integral (3.1) in terms of B functions by inspection:

$$A^m_{n,l}(\alpha, \vec{x}) = \frac{4\pi}{\alpha^2} \sum_{\nu=0}^{\infty} B^m_{n+\nu+1,l}(\alpha, \vec{x}). \tag{3.3}$$

The correctness of Eq. (3.3) can be shown by differentiation. To simplify the application of the Laplacian $\vec{\nabla}^2$ to the right-hand side of Eq. (3.3), we rewrite Eq. (2.12) in the following way:

$$\vec{\nabla}^2 B_{n,l}^m(\alpha, \vec{x}) = \alpha^2 [B_{n,l}^m(\alpha, \vec{x}) - B_{n-1,l}^m(\alpha, \vec{x})]. \tag{3.4}$$

If we apply the Laplacian to Eq. (3.3), it follows from Eq. (3.4) that only a single term of the infinite series on the right-hand side of Eq. (3.3) survives, and we finally obtain Eq. (3.2). Hence, formally we can write:

$$\begin{aligned} [\vec{\nabla}^2]^{-1} B_{n,l}^m(\alpha, \vec{x}) &= -(4\pi)^{-1} A_{n,l}^m(\alpha, \vec{x}) \\ &= -\alpha^{-2} \sum_{\nu=0}^{\infty} B_{n+\nu+1,l}^m(\alpha, \vec{x}). \end{aligned} \tag{3.5}$$

This formal notation can be made rigorous with the help of the theory of pseudodifferential operators [38–40].

Unfortunately, the convergence of the infinite series in Eq. (3.3) is extremely bad. It can be shown that if this series is truncated after the first $N + 1$ terms, then the truncation error behaves like $N^{-l-1/2}$ as $N \to \infty$ [36]. Particularly for small values of l, such an asymptotic behavior of the truncation error seems to indicate that the series expansion (3.3) is practically useless. This conclusion is certainly true if one tries to evaluate the integral (3.1) in a straightforward way by adding up one term of the infinite series (3.3) after the other. Fortunately, the convergence of the infinite series (3.3) can be improved significantly by applying suitable nonlinear convergence accelerators to the sequence of partial sums of this series. Only a relatively small number of terms of the infinite series (3.3) are needed to produce remarkably accurate approximations to the nuclear attraction integral (3.1) with the help of nonlinear sequence transformations [36, 41–44].

Moreover, the use of nonlinear sequence transformations is not the only possibility to overcome the prohibitively slow convergence of the infinite series (3.3). As an alternative, we can also use the following expansion of an irregular solid harmonic in terms of B functions [18],

$$\mathscr{Z}_l^m(\alpha\vec{x}) = [(2l-1)!!]^{-1} (\beta/\alpha)^{l+1} \sum_{\nu=0}^{\infty} B_{\nu-l,l}^m(\beta, \vec{x}), \tag{3.6}$$

which yields for $\alpha = \beta$

$$\sum_{\nu=0}^{\infty} B_{n+\nu+1,l}^m(\alpha, \vec{x}) = (2l-1)!! \mathscr{Z}_l^m(\alpha\vec{x}) - \sum_{\nu=0}^{n+l} B_{\nu-l,l}^m(\alpha, \vec{x}) \tag{3.7}$$

for the infinite series in Eq. (3.3). Hence, formally we can write:

$$[\vec{\nabla}^2]^{-1} B_{n,l}^m(\alpha, \vec{x}) = -\alpha^{-2} \left\{ (2l-1)!! \mathscr{Z}_l^m(\alpha\vec{x}) - \sum_{\nu=0}^{n+l} B_{\nu-l,l}^m(\alpha, \vec{x}) \right\}. \tag{3.8}$$

Combination of Eqs. (3.3) and (3.7) yields a very compact expression for the nuclear attraction integral (3.1):

$$A_{n,l}^m(\alpha, \vec{x}) = \frac{4\pi}{\alpha^2} \left\{ (2l-1)!! \mathscr{Z}_l^m(\alpha\vec{x}) - \sum_{\nu=0}^{n+l} B_{\nu-l,l}^m(\alpha, \vec{x}) \right\}. \tag{3.9}$$

This representation permits a very convenient computation of the nuclear attraction integral (3.1). However, it should be taken into account that Eq. (3.9) cannot be used if x is close to zero because both the irregular spherical harmonic and the finite sum on the right-hand side become singular at the origin. If x is small, it is necessary to use the infinite series representation (3.3) in connection with suitable nonlinear sequence transformations [36, 41–44].

Both Eq. (3.3) as well as Eq. (3.9) were derived originally as limiting cases of overlap integrals of B functions [18], and later also via the Fourier transform method [35]. However, the previous derivations of these representations were considerably more involved than our simple derivation which is based upon the Poisson equation.

4. Coulomb integrals

In the last section, we showed that the construction of an explicit solution of a Poisson equation becomes virtually trivial if the inhomogeneity is a B function. Since the Poisson equation is a linear differential equation, the principle of superposition holds. Thus, if the inhomogeneity of the Poisson equation can be expressed as a sum or series of B functions, then the solution of this Poisson equation can be expressed as the same sum or series of nuclear attraction integrals.

In this section, we want to exploit this fact for the derivation of explicit expressions for Coulomb integrals of B functions. For the sake of simplicity, we shall only consider *reduced* Coulomb integrals with one-center densities that are given by a single B function. For these integrals we use the notation:

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) = \int\int [B_{n_1, l_1}^{m_1}(\alpha, \vec{y})]^* \frac{1}{|\vec{x} - \vec{y} + \vec{z}|} B_{n_2, l_2}^{m_2}(\beta, \vec{z})\, d^3\vec{y}\, d^3\vec{z}. \quad (4.1)$$

The Coulomb integrals, which occur in molecular calculations, have densities that are products of two basis functions located at the same center. If B functions are used as basis functions, then the product of two B functions has to be expressed as a finite sum of B functions [11, 32] in order to express the pertaining Coulomb integral as a finite sum of reduced Coulomb integrals of the type of Eq. (4.1).

It follows from Eq. (1.9) that in the case of a Coulomb integral we are confronted with a Poisson equation where the inhomogeneity is an overlap integral. For the overlap integral of two B functions with scaling parameters α and β, respectively, we use the following notation:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) = \int [B_{n_1, l_1}^{m_1}(\alpha, \vec{y})]^* B_{n_2, l_2}^{m_2}(\beta, \vec{y} - \vec{x})\, d^3\vec{y}. \quad (4.2)$$

We first want to consider Coulomb integrals with equal scaling parameters. In this case, we have to solve the following Poisson equation:

$$\vec{\nabla}^2 C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha, \vec{x}) = -4\pi S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha, \vec{x}). \quad (4.3)$$

The overlap integral of two B functions with equal scaling parameters is essentially a finite sum of B functions [18]:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \alpha, \vec{x}) = (-1)^{l_2} \frac{4\pi}{\alpha^3} \sum_{l = l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$
$$\times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} B_{n_1 + n_2 + 2\Delta l - t + 1, l}^{m_2 - m_1}(\alpha, \vec{x}). \quad (4.4)$$

The summation limits $l_{\min}$ and $l_{\max}$ of the outer sum in Eq. (4.4) are given by Eq. (2.7). It is a direct consequence of these summation limits that the summation limit

$$\Delta l = (l_1 + l_2 - l)/2 \tag{4.5}$$

of the inner sum in Eq. (4.4) is either a positive integer or zero for all admissible angular momentum quantum numbers l_1 and l_2.

If we combine Eqs. (4.3) and (4.4) and formally divide by the Laplacian, we obtain the following formal expression for the Coulomb integral with equal scaling parameters:

$$\begin{aligned} C^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \vec{x}) &= (-1)^{l_2+1} \frac{(4\pi)^2}{\alpha^3} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\ &\times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} [\vec{\nabla}^2]^{-1} B^{m_2 - m_1}_{n_1 + n_2 + 2\Delta l - t + 1, l}(\alpha, \vec{x}). \end{aligned} \tag{4.6}$$

If we now take into account that according to Eq. (3.2)

$$[\vec{\nabla}^2]^{-1} B^{m_2 - m_1}_{n_1 + n_2 + 2\Delta l - t + 1, l}(\alpha, \vec{x}) = -(4\pi)^{-1} A^{m_2 - m_1}_{n_1 + n_2 + 2\Delta l - t + 1, l}(\alpha, \vec{x}), \tag{4.7}$$

we see that we can formally write:

$$\begin{aligned} [\vec{\nabla}^2]^{-1} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \vec{x}) &= \frac{(-1)^{l_2+1}}{\alpha^3} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\ &\times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} A^{m_2 - m_1}_{n_1 + n_2 + 2\Delta l - t + 1, l}(\alpha, \vec{x}). \end{aligned} \tag{4.8}$$

Hence, we obtain a representation of the Coulomb integral with equal scaling parameters in terms of nuclear attraction integrals, which is formally identical with the simple expression for the overlap integral of two B functions with equal scaling parameters, Eq. (4.4):

$$\begin{aligned} C^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \vec{x}) &= (-1)^{l_2} \frac{4\pi}{\alpha^3} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\ &\times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} A^{m_2 - m_1}_{n_1 + n_2 + 2\Delta l - t + 1, l}(\alpha, \vec{x}). \end{aligned} \tag{4.9}$$

Next, we want to construct infinite series representations for Coulomb integrals with different scaling parameters α and β. In this case, we have to solve the following Poisson equation:

$$\vec{\nabla}^2 C^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) = -4\pi S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}). \tag{4.10}$$

First, let us use the following two infinite series representations for the overlap integral of two B functions [18, 35], which were derived with the help of the multiplication theorem (2.15):

$$\begin{aligned} &S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) \\ &= (\alpha/\beta)^{2n_1 + l_1 - 1} \sum_{\nu=0}^{\infty} \frac{(n_1 + l_1 + 1)_\nu}{\nu!} \left\{ \frac{\beta^2 - \alpha^2}{\beta^2} \right\}^\nu S^{n_2 l_2 m_2}_{n_1 + \nu l_1 m_1}(\beta, \beta, \vec{x}) \end{aligned} \tag{4.11}$$

$$S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) = (\beta/\alpha)^{2n_2 + l_2 - 1} \sum_{\nu=0}^{\infty} \frac{(n_2 + l_2 + 1)_\nu}{\nu!} \left\{ \frac{\alpha^2 - \beta^2}{\alpha^2} \right\}^\nu S^{n_2 + \nu l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \vec{x}). \tag{4.12}$$

The infinite series in Eq. (4.11) converges for $|1 - (\alpha/\beta)^2| < 1$, and the infinite series in Eq. (4.12) converges for $|1 - (\beta/\alpha)^2| < 1$. Hence, the two infinite series are analytic continuations [35]. If we now proceed as in the case of the Coulomb integral with equal scaling parameters, Eq. (4.9), we immediately obtain the following two series expansions:

$$C^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) = (\alpha/\beta)^{2n_1 + l_1 - 1} \sum_{\nu=0}^{\infty} \frac{(n_1 + l_1 + 1)_\nu}{\nu!} \left\{ \frac{\beta^2 - \alpha^2}{\beta^2} \right\}^\nu C^{n_2 l_2 m_2}_{n_1 + \nu l_1 m_1}(\beta, \beta, \vec{x}) \tag{4.13}$$

$$= (\beta/\alpha)^{2n_2 + l_2 - 1} \sum_{\nu=0}^{\infty} \frac{(n_2 + l_2 + 1)_\nu}{\nu!} \left\{ \frac{\alpha^2 - \beta^2}{\alpha^2} \right\}^\nu C^{n_2 + \nu l_2 m_2}_{n_1 l_1 m_1}(\alpha, \alpha, \vec{x}). \tag{4.14}$$

The infinite series in Eq. (4.13) converges for $|1 - (\alpha/\beta)^2| < 1$, and the infinite series in Eq. (4.14) converges for $|1 - (\beta/\alpha)^2| < 1$. Hence, as in the case of Eqs. (4.11) and (4.12), these two infinite series are analytic continuations.

These two infinite series representations can be used for the computation of the Coulomb integral (4.1) if the two scaling parameters α and β differ only slightly. For larger differences of the two scaling parameters, the convergence of the infinite series will become quite slow. However, it can be expected that the convergence of these series expansions (4.13) and (4.14) can be improved considerably by applying suitable convergence accelerators to the partial sums of these series [36, 45].

The following infinite series representation [35] for the overlap integral with different scaling parameters,

$$\begin{aligned} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) = {} & \frac{\alpha^{2n_1 + l_1 - 1} \beta^{2n_2 + l_2 - 1}}{[(\alpha^2 + \beta^2)/2]^{n_1 + n_2 + (l_1 + l_2)/2 - 1}} \\ & \times \sum_{\nu=0}^{\infty} {}_2F_1(-\nu, n_1 + l_1 + 1; n_1 + n_2 + l_1 + l_2 + 2; 2) \\ & \times \frac{(n_1 + n_2 + l_1 + l_2 + 2)_\nu}{\nu!} \left\{ \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} \right\}^\nu \\ & \times S^{n_2 l_2 m_2}_{n_1 + \nu l_1 m_1}([(\alpha^2 + \beta^2)/2]^{1/2}, [(\alpha^2 + \beta^2)/2]^{1/2}, \vec{x}), \end{aligned} \tag{4.15}$$

which converges for all $\alpha, \beta > 0$, looks significantly more complicated than the infinite series representations (4.11) and (4.12). However, the terminating hypergeometric series ${}_2F_1$ in Eq. (4.15) can be computed recursively [35]. In addition, it can be shown that the infinite series in Eq. (4.15) converges normally faster than the series in Eqs. (4.11) and (4.12) [36].

If we now proceed as in the case of the Coulomb integral with equal scaling parameters, we immediately obtain the following infinite series representation for the Coulomb integral with different scaling parameters, which is formally identical with the infinite series representation (4.15) for the overlap integral:

$$
\begin{aligned}
C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) = {} & \frac{\alpha^{2n_1 + l_1 - 1} \beta^{2n_2 + l_2 - 1}}{[(\alpha^2 + \beta^2)/2]^{n_1 + n_2 + (l_1 + l_2)/2 - 1}} \\
& \times \sum_{v=0}^{\infty} {}_2F_1(-v, n_1 + l_1 + 1; n_1 + n_2 + l_1 + l_2 + 2; 2) \\
& \times \frac{(n_1 + n_2 + l_1 + l_2 + 2)_v}{v!} \left\{ \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} \right\}^v \\
& \times C_{n_1 + v l_1 m_1}^{n_2 l_2 m_2}([(\alpha^2 + \beta^2)/2]^{1/2}, [(\alpha^2 + \beta^2)/2]^{1/2}, \vec{x}).
\end{aligned}
\tag{4.16}
$$

The infinite series representations (4.13), (4.14), and (4.16) were first derived with the help of the Fourier transform method [35]. However, the original derivations were much more involved than the derivation with the help of the Poisson equation which in fact is very simple.

5. Integrals with delta function contributions

In addition to the infinite series representations (4.11), (4.12), and (4.15) for the overlap integral of two B functions with different scaling parameters, which were used in the last section to construct the infinite series representations (4.13), (4.14), and (4.16), respectively, for the Coulomb integral, there is also a representation for the overlap integral which contains only a finite number of terms [18]:

$$
\begin{aligned}
S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) = {} & (-1)^{l_2} 4\pi \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\
& \times \Bigg[\frac{(-1)^{n_1 + l_1} (\alpha/\beta)^{l_2}}{\beta^3 [1 - (\alpha/\beta)^2]^{n_2 + l_2 + 1}} \\
& \times \sum_{s=0}^{n_1 + l_1} (-1)^s P_{n_1 + l_1 - s}^{(s - n_1 - \Delta l_2, n_2 + \Delta l_1)} \left(\frac{\beta^2 + \alpha^2}{\beta^2 - \alpha^2} \right) B_{s - l, l}^{m_2 - m_1}(\alpha, \vec{x}) \\
& + \frac{(-1)^{n_2 + l_2} (\beta/\alpha)^{l_1}}{\alpha^3 [1 - (\beta/\alpha)^2]^{n_1 + l_1 + 1}} \\
& \times \sum_{s=0}^{n_2 + l_2} (-1)^s P_{n_2 + l_2 - s}^{(s - n_2 - \Delta l_1, n_1 + \Delta l_2)} \left(\frac{\alpha^2 + \beta^2}{\alpha^2 - \beta^2} \right) B_{s - l, l}^{m_2 - m_1}(\beta, \vec{x}) \Bigg].
\end{aligned}
\tag{5.1}
$$

Here, $P_n^{(\alpha, \beta)}(x)$ is a Jacobi polynomial [27]. It follows from the summation limits (2.7) that

$$
\Delta l_1 = (l - l_1 + l_2)/2 \tag{5.2}
$$

and

$$
\Delta l_2 = (l + l_1 - l_2)/2 \tag{5.3}
$$

are similarly as Δl, which is defined by Eq. (4.5), always either positive integers or zero for all admissible angular momentum quantum numbers l_1 and l_2.

This Jacobi polynomial representation of the overlap integral cannot be used if the two scaling parameters α and β differ only slightly, because there are terms that become singular as $\alpha \to \beta$. In addition, it can also not be used if x is small because B functions with negative orders $n = -l$ are singular at the origin. If, however, x is not close to zero, and if the scaling parameters α and β are sufficiently different, then the Jacobi polynomial representation (5.1) permits a very convenient and extremely fast evaluation of the overlap integral [36].

Consequently, it is evident to try to derive an analogous Jacobi polynomial representation for the Coulomb integral with different scaling parameters that has the same advantages and disadvantages as the Jacobi polynomial representation (5.1) for the overlap integral.

If we would apply the Poisson equation technique as we did in the case of Eq. (4.9) for the Coulomb integral with equal scaling parameters, then we would only have to replace the B functions in Eq. (5.1) by analogous nuclear attraction integrals. However, in the case of the Jacobi polynomial representation (5.1) this approach would in general lead to a wrong result.

The reason is that in the derivation of the Jacobi polynomial representation (5.1) B functions with orders $n < -l$, which are derivatives of the spherical delta functions according to Eq. (2.13), were neglected (see p. 3696 of [35]). Hence, Eq. (5.1) is only correct for nonvanishing arguments $\vec{x}$.

This neglect of delta functions is irrelevant if the Jacobi polynomial representation (5.1) is only used for the evaluation of the overlap integral of two B functions with different scaling parameters, because it cannot be used if x is close to zero due to numerical instabilities. If, however, we want to use Eq. (5.1) as the inhomogeneity of a Poisson equation, we need the delta function contributions.

The delta function contributions of the overlap integral of two B functions with different scaling parameters can be constructed most easily with the help of the Fourier transform method. Consequently, our starting point is the following Fourier integral representation for the overlap integral of two B functions [35]:

$$\begin{aligned} S^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta, \vec{x}) = {} & \frac{2}{\pi}\, \alpha^{2n_1 + l_1 - 1} \beta^{2n_2 + l_2 - 1} i^{l_1 - l_2} \\ & \times \sum_{l = l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\ & \times \int e^{-i\vec{x}\cdot\vec{p}} \frac{p^{l_1 + l_2 - l} \mathcal{Y}_l^m(\vec{p})}{[\alpha^2 + p^2]^{n_1 + l_1 + 1} [\beta^2 + p^2]^{n_2 + l_2 + 1}}\, d^3\vec{p}. \end{aligned} \tag{5.4}$$

If we use in the Fourier integral (5.4) the partial fraction decomposition [28]

$$\begin{aligned} & [\alpha^2 + p^2]^{-n_1 - l_1 - 1} [\beta^2 + p^2]^{-n_2 - l_2 - 1} \\ & = \frac{(-1)^{n_2 + l_2 + 1}}{(n_2 + l_2)!} \\ & \quad \times \sum_{\nu = 0}^{n_1 + l_1} \frac{(n_1 + n_2 + l_1 + l_2 - \nu)!}{(n_1 + l_1 - \nu)!} \frac{(\alpha^2 - \beta^2)^{\nu - n_1 - n_2 - l_1 - l_2 - 1}}{(\alpha^2 + p^2)^{\nu + 1}} \\ & \quad + \frac{(-1)^{n_1 + l_1 + 1}}{(n_1 + l_1)!} \\ & \quad \times \sum_{\nu = 0}^{n_2 + l_2} \frac{(n_1 + n_2 + l_1 + l_2 - \nu)!}{(n_2 + l_2 - \nu)!} \frac{(\beta^2 - \alpha^2)^{\nu - n_1 - n_2 - l_1 - l_2 - 1}}{(\beta^2 + p^2)^{\nu + 1}} \end{aligned} \tag{5.5}$$

together with [35]

$$p^{2\Delta l} = (-\alpha^2)^{\Delta l} \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} [(\alpha^2 + p^2)/\alpha^2]^t, \tag{5.6}$$

we obtain with the help of the Fourier integral representation (2.11) for a B function the following expression (see Eq. (5.5) on p. 3696 of [35]) which contains B functions with orders $n \geqslant -l$, which are ordinary functions according to Eq. (2.8), and B functions with orders $n < -l$, which are derivatives of the delta function according to Eq. (2.13):

$$\begin{aligned}
S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) &= (-1)^{l_2} 4\pi \alpha^{2n_1 + l_1 - 1} \beta^{2n_2 + l_2 - 1} \sum_{l = l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\
&\times \left\{ \frac{(-1)^{n_2 + l_2 + 1}}{(n_2 + l_2)!} \frac{\alpha^{l_1 + l_2 + 1}}{[\alpha^2 - \beta^2]^{n_1 + n_2 + l_1 + l_2 + 1}} \sum_{v=0}^{n_1 + l_1} \frac{(n_1 + n_2 + l_1 + l_2 - v)!}{(n_1 + l_1 - v)!} \left\{ \frac{\alpha^2 - \beta^2}{\alpha^2} \right\}^v \right. \\
&\times \left[\sum_{t=0}^{\min(v, \Delta l)} (-1)^t \binom{\Delta l}{t} B_{v-t-l,l}^{m_2 - m_1}(\alpha, \vec{x}) + \sum_{t=v+1}^{\Delta l} (-1)^t \binom{\Delta l}{t} B_{v-t-l,l}^{m_2 - m_1}(\alpha, \vec{x}) \right] \\
&+ \frac{(-1)^{n_1 + l_1 + 1}}{(n_1 + l_1)!} \frac{\beta^{l_1 + l_2 + 1}}{[\beta^2 - \alpha^2]^{n_1 + n_2 + l_1 + l_2 + 1}} \sum_{v=0}^{n_2 + l_2} \frac{(n_1 + n_2 + l_1 + l_2 - v)!}{(n_2 + l_2 - v)!} \left\{ \frac{\beta^2 - \alpha^2}{\beta^2} \right\}^v \\
&\times \left. \left[\sum_{t=0}^{\min(v, \Delta l)} (-1)^t \binom{\Delta l}{t} B_{v-t-l,l}^{m_2 - m_1}(\beta, \vec{x}) + \sum_{t=v+1}^{\Delta l} (-1)^t \binom{\Delta l}{t} B_{v-t-l,l}^{m_2 - m_1}(\beta, \vec{x}) \right] \right\}.
\end{aligned} \tag{5.7}$$

By changing the order of the inner summations, we obtain a generalization of the Jacobi polynomial representation (5.1), which contains the required delta function contributions:

$$\begin{aligned}
S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \vec{x}) &= (-1)^{l_2} 4\pi \sum_{l = l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\
&\times \left\{ \frac{(-1)^{n_1 + l_1} (\alpha/\beta)^{l_2}}{\beta^3 [1 - (\alpha/\beta)^2]^{n_2 + l_2 + 1}} \right. \\
&\times \left[\sum_{s=0}^{n_1 + l_1} (-1)^s P_{n_1 + l_1 - s}^{(s - n_1 - \Delta l_2, n_2 + \Delta l_1)} \left(\frac{\beta^2 + \alpha^2}{\beta^2 - \alpha^2} \right) B_{s-l,l}^{m_2 - m_1}(\alpha, \vec{x}) \right. \\
&+ \frac{(\alpha/\beta)^{2(n_1 + l_1)}}{[1 - (\alpha/\beta)^2]^{n_1 + l_1}} \frac{(n_1 + n_2 + l_1 + l_2)!}{(n_1 + l_1)!(n_2 + l_2)!} \sum_{q=0}^{\Delta l - 1} (-1)^{q+1} \binom{\Delta l}{q+1} B_{-q-l-1,l}^{m_2 - m_1}(\alpha, \vec{x}) \\
&\times \left. {}_3F_2 \left(q - \Delta l + 1, -n_1 - l_1, 1; q + 2, -n_1 - n_2 - l_1 - l_2; \frac{\alpha^2 - \beta^2}{\alpha^2} \right) \right] \\
&+ \frac{(-1)^{n_2 + l_2} (\beta/\alpha)^{l_1}}{\alpha^3 [1 - (\beta/\alpha)^2]^{n_1 + l_1 + 1}} \\
&\times \left[\sum_{s=0}^{n_2 + l_2} (-1)^s P_{n_2 + l_2 - s}^{(s - n_2 - \Delta l_1, n_1 + \Delta l_2)} \left(\frac{\alpha^2 + \beta^2}{\alpha^2 - \beta^2} \right) B_{s-l,l}^{m_2 - m_1}(\beta, \vec{x}) \right.
\end{aligned}$$

$$+\frac{(\beta/\alpha)^{2(n_2+l_2)}}{[1-(\beta/\alpha)^2]^{n_2+l_2}}\frac{(n_1+n_2+l_1+l_2)!}{(n_1+l_1)!(n_2+l_2)!}\sum_{q=0}^{\Delta l-1}(-1)^{q+1}\binom{\Delta l}{q+1}B^{m_2-m_1}_{-q-l-1,l}(\beta,\vec{x})$$

$$\left.\left.\times\,{}_3F_2\left(q-\Delta l+1,\,-n_2-l_2,\,1;\,q+2,\,-n_1-n_2-l_1-l_2;\,\frac{\beta^2-\alpha^2}{\beta^2}\right)\right]\right\}. \quad (5.8)$$

It should be noted that the delta function contributions in Eq. (5.8) vanish for $\Delta l = 0$ because the sums from $q = 0$ to $q = \Delta l - 1$ are then empty sums which are zero. Since $l_1 = l_2 = 0$ implies also $\Delta l = 0$, we see that the Jacobi polynomial representation for the overlap integral of scalar B functions with orders $n_1, n_2 \geqslant 1$ cannot contain delta function contributions. In the case of nonscalar B functions, however, there are in general delta function contributions which cannot be neglected if the Jacobi polynomial representation (5.8) is to be used in integrals or as the inhomogeneity of a Poisson equation. If we proceed as described in the last section, we obtain the following Jacobi polynomial representation for the Coulomb integral of two B functions with different scaling parameters:

$$C^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,\vec{x}) = (-1)^{l_2}4\pi\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\,\langle l_2m_2|l_1m_1|lm_2-m_1\rangle$$

$$\times\left\{\frac{(-1)^{n_1+l_1}(\alpha/\beta)^{l_2}}{\beta^3[1-(\alpha/\beta)^2]^{n_2+l_2+1}}\right.$$

$$\times\left[\sum_{s=0}^{n_1+l_1}(-1)^sP^{(s-n_1-\Delta l_2,n_2+\Delta l_1)}_{n_1+l_1-s}\left(\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2}\right)A^{m_2-m_1}_{s-l,l}(\alpha,\vec{x})\right.$$

$$+\frac{(\alpha/\beta)^{2(n_1+l_1)}}{[1-(\alpha/\beta)^2]^{n_1+l_1}}\frac{(n_1+n_2+l_1+l_2)!}{(n_1+l_1)!(n_2+l_2)!}\sum_{q=0}^{\Delta l-1}(-1)^{q+1}\binom{\Delta l}{q+1}A^{m_2-m_1}_{-q-l-1,l}(\alpha,\vec{x})$$

$$\left.\times\,{}_3F_2\left(q-\Delta l+1,\,-n_1-l_1,\,1;\,q+2,\,-n_1-n_2-l_1-l_2;\,\frac{\alpha^2-\beta^2}{\alpha^2}\right)\right]$$

$$+\frac{(-1)^{n_2+l_2}(\beta/\alpha)^{l_1}}{\alpha^3[1-(\beta/\alpha)^2]^{n_1+l_1+1}}$$

$$\times\left[\sum_{s=0}^{n_2+l_2}(-1)^sP^{(s-n_2-\Delta l_1,n_1+\Delta l_2)}_{n_2+l_2-s}\left(\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2}\right)A^{m_2-m_1}_{s-l,l}(\beta,\vec{x})\right.$$

$$+\frac{(\beta/\alpha)^{2(n_2+l_2)}}{[1-(\beta/\alpha)^2]^{n_2+l_2}}\frac{(n_1+n_2+l_1+l_2)!}{(n_1+l_1)!(n_2+l_2)!}\sum_{q=0}^{\Delta l-1}(-1)^{q+1}\binom{\Delta l}{q+1}A^{m_2-m_1}_{-q-l-1,l}(\beta,\vec{x})$$

$$\left.\left.\times\,{}_3F_2\left(q-\Delta l+1,\,-n_2-l_2,\,1;\,q+2,\,-n_1-n_2-l_1-l_2;\,\frac{\beta^2-\alpha^2}{\beta^2}\right)\right]\right\}. \quad (5.9)$$

Formally, Eqs. (5.8) and (5.9) are identical since we only have to replace the B functions in Eq. (5.8) by the corresponding nuclear attraction integrals to obtain Eq. (5.9). However, we still have to analyze the nuclear attraction integrals in Eq. (5.9) with orders $n < -l$. These integrals are convolutions of the Coulomb potential with a B function that is a derivative of the delta function according to Eq. (2.13), and we have to find out whether such a convolution produces again delta functions or whether also nondistributional contributions occur.

It follows from the Fourier integral representation [35]

$$A_{n,l}^{m}(\alpha, \vec{x}) = \frac{2}{\pi} \alpha^{2n+l-1} \int e^{-i\vec{x}\cdot\vec{p}} \frac{\mathcal{Y}_{l}^{m}(i\vec{p})}{p^{2}[\alpha^{2}+p^{2}]^{n+l+1}} d^{3}\vec{p}, \tag{5.10}$$

that the differential operator of the modified Helmholtz equation is similarly as in the case of *B* functions a shift operator for the order *n* of a nuclear attraction integral:

$$[1 - \alpha^{-2}\vec{\nabla}^{2}]^{k} A_{n,l}^{m}(\alpha, \vec{x}) = A_{n-k,l}^{m}(\alpha, \vec{x}). \tag{5.11}$$

If we apply this relationship with $k = n + l + q + 1$ to Eq. (3.3), we obtain with the help of Eq. (2.12):

$$A^{m}_{-q-l-1,l}(\alpha, \vec{x}) = \frac{4\pi}{\alpha^{2}} \sum_{\nu=0}^{\infty} B_{\nu-q-l,l}^{m}(\alpha, \vec{x}). \tag{5.12}$$

Next, we use Eq. (3.6) with $\alpha = \beta$ to extract an irregular solid harmonic in Eq. (5.12). Hence, we obtain for the distributional nuclear attraction integrals in Eq. (5.9):

$$A^{m}_{-q-l-1,l}(\alpha, \vec{x}) = \frac{4\pi}{\alpha^{2}} \left\{ (2l-1)!!\mathcal{Z}_{l}^{m}(\alpha\vec{x}) + \sum_{\sigma=0}^{q-1} B_{\sigma-q-l,l}^{m}(\alpha, \vec{x}) \right\}. \tag{5.13}$$

The *B* functions with orders $\sigma - q - l$ are all derivatives of the delta function according to Eq. (2.13) and can be neglected if the Jacobi polynomial representation (5.9) is to be used for the evaluation of the Coulomb integral (4.1). However, we would have missed the irregular solid harmonic in Eq. (5.13) if we had used Eq. (5.1) instead of Eq. (5.8) as the inhomogeneity in the Poisson equation (4.10).

6. Discussion

The nuclear attraction integral (1.3) represents the potential energy of an electron charge distribution *f* attracted by an atomic nucleus, whereas the Coulomb integral (1.5) represents the potential energy of two electron charge distributions *f* and *g* located at different centers. These physical pictures suggest that it should be a good idea to try to evaluate these integrals with the help of the Poisson equation. Indeed, it could be shown in this article that compact explicit expressions for the nuclear attraction and Coulomb integral can be derived quite easily, if the charge distributions *f* and *g* are *B* functions [18].

The most serious obstacle for a routine application of exponentially decaying basis functions in molecular electronic structure calculations are the notorious four-center interelectronic repulsion integrals which have no classical counterpart. Although these integrals cannot be interpreted like Coulomb integrals in terms of the electrostatic interaction of two quasiclassical charge densities of the type $\varrho(\vec{x}) = |\psi(\vec{x})|^{2}$, one could nevertheless try to evaluate them with the help of the Poisson equation. However, since more than a single internuclear distance occurs in the case of a four-center integral, such an integral satisfies more than a single Poisson equation. In addition, the inhomogeneity of the Poisson equation for a four-center interelectronic repulsion integral would be a four-center overlap-type integral, for which no manageable expressions are currently known. Thus, it seems that the Poisson equation technique is confined to two-center nuclear attraction and Coulomb integrals.

It turns out that B functions have some specific advantages among exponentially decaying functions. They possess an exceptionally simple Fourier transform [28, 29], repeated derivatives can often be expressed quite compactly [15, 21, 23, 24, 28], and they can also be extended into the domain of generalized functions [23]. In view of these advantageous properties it is not surprising that B functions possess simple addition theorems [24, 26, 30, 31], and that many relatively simple explicit expressions for their multicenter integrals could be derived [9–15, 23, 32–36]. In addition, it could be shown that all the commonly occurring exponentially decaying functions such as Slater functions or bound-state hydrogen eigenfunctions can be represented in terms of simple linear combinations of B functions [11, 18, 28, 29, 37]. Consequently, the molecular multicenter integrals of all the commonly occurring exponentially decaying functions can also be represented as simple finite sums of the corresponding integrals of B functions. In view of the unique properties of B functions, this may often constitute the most simple way of computing molecular multicenter integrals of other exponentially decaying functions, although one would have to compute a larger number of integrals.

Since B functions are also of the type of an exponential multiplied by a polynomial, in variational calculations they span the same function space as Slater functions. Consequently, B functions can be used as basis functions from the very beginning of an electronic structure calculation, making the argument obsolete that the use of B functions instead of Slater functions would inevitably lead to a larger number of molecular integrals.

Now, the Poisson equation method, which is based on physical intuition, makes it possible to transform the problem of evaluating a molecular integral into the problem of solving an inhomogeneous partial differential equation. As shown in this article, this technique is especially successful if mathematical properties of B functions can be employed. This enables us to produce compact closed-form expressions for the nuclear attraction integrals (3.1) and the *reduced* Coulomb integrals (4.1). Since linearization theorems for B functions are known [11, 32], the Coulomb integrals, which occur in actual molecular calculations and which have densities consisting of two functions located at the same center, can be expressed as finite linear combinations of *reduced* Coulomb integrals.

This discussion should suffice to show that old concepts like the concept of using the Poisson equation as suggested by Ruedenberg and coworkers [16, 17], can still be helpful for the derivation of new results for molecular integrals. It also shows that the complete solution of the molecular integral problem, i.e., the evaluation of all the integrals occurring in a molecular calculation, needs to be attacked from different sides as it was already done by Ruedenberg and colleagues in the fifties and sixties.

The pioneering work of the Chicago group in Mulliken's laboratory [46] on the foundations of large scale atomic and molecular *ab initio* calculations was based on investigations on atomic and molecular integrals with Slater functions, leading to some early land-mark papers by Ruedenberg [47] and Roothaan [48, 49]. The original choice of Slater functions as basis set in atomic and molecular calculations is based upon a compromise between the demand of using physically meaningful functions which can describe the cusp and the behavior of the exact wavefunction in long distances from the origin, and the demand that the functions are computationally manageable. The difficulties encountered with the multicenter molecular integrals for Slater functions led to the use of Gaussian-type basis functions. Their use was also substantially facilitated by

Ruedenberg and coworkers [50]. The use of Gaussian-type basis functions made it less urgent to pursue the research on the original problem of evaluating the molecular integrals with exponentially decaying functions. However, the growing demand for higher accuracies and the need to use an excessively large number of Gaussian-type functions in some calculations led to a revival of the interest in using exponentially decaying basis functions. Obviously, it is of interest not only to pursue research in new directions but also to have another look at older approaches.

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