PHYSICAL REVIEW A VOLUME 33, NUMBER 6 JUNE 1986

Unified analytical treatment of overlap, two-center nuclear attraction, and Coulomb integrals of B functions via the Fourier-transform method

E. Joachim Weniger, Johannes Grotendorst, and E. Otto Steinborn
Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany
(Received 19 March 1985; revised manuscript received 17 October 1985)

In this paper a unified analytical treatment of overlap, two-center nuclear attraction, and Coulomb integrals of B functions [E. Filter and E. O. Steinborn, Phys. Rev. A **18**, 1 (1978)] via the Fourier-transform method is presented. B functions, which are a special class of exponentially decreasing functions (for large arguments), have a relatively complicated analytical structure. However, the Fourier transform of a B function is of exceptional simplicity. Consequently, it is relatively easy to express the Fourier integral representations of the two-center integrals mentioned above as finite sums or infinite series of Fourier integral representations for B functions and irregular solid harmonics which may be considered to be limiting cases of special B functions. The only advanced mathematical concepts which we need are the connection between B functions, classically divergent Fourier integrals, and derivatives of the three-dimensional δ functions. The other mathematical tools—partial-fraction decompositions and Taylor expansions of rational functions—are fairly elementary. Our approach leads not only to a considerable simplification of the derivation of the previously known analytical representations for the two-center integrals but also to a large number of hitherto unknown representations.

I. INTRODUCTION

It is well known that exact eigenstates of atomic and molecular Hamiltonians satisfy the cusp condition[1] and decrease exponentially at large distances.[2] Consequently, it is not surprising that exponentially decreasing functions (for large arguments), in particular Slater-type functions, could be used successfully as basis functions in atomic calculations. However, an equally successful application of these functions in molecular calculations has so far been prevented by the fact that despite enormous efforts no completely satisfactory method for the evaluation of the notorious multicenter integrals of Slater-type or other exponentially decreasing functions has been found yet. A survey of the older literature on multicenter integrals was given in review papers by Huzinaga,[3] Harris and Michels,[4] and Browne.[5] More recent references can be found in Ref. 6 and in a review paper by Steinborn.[7]

Slater-type functions have the simplest analytical structure of all exponentially decreasing functions. Other commonly occurring functions of that class, for instance, hydrogen eigenfunctions, can normally be expressed quite easily as linear combinations of Slater-type functions. This implies that multicenter integrals of other exponentially decreasing functions can be expressed in terms of the basic multicenter integrals over Slater-type functions. Probably, this was the reason why only multicenter integrals of Slater-type functions have been examined thoroughly in the literature whereas the integrals of other exponentially decreasing functions have largely been neglected. It did not seem to make much sense to investigate the multicenter integrals of the more complicated functions as long as the multicenter integrals of the simplest representative of that class could not be computed in a reasonable way. In view of the extreme complexity of multicenter integrals of exponentially decreasing functions a restriction to Slater-type functions looks very natural and also very economical. Unfortunately, this line of reasoning is probably superficial and based upon false premises. Currently, the most promising approach for the evaluation of multicenter integrals appears to be the so-called Fourier-transform method where multicenter integrals are transformed into inverse Fourier integrals. In this approach it is not the analytical simplicity of a basis function that matters but the analytical simplicity of its Fourier transform.

In numerous papers it was demonstrated that the Fourier transform of a Slater-type function is a fairly complicated mathematical object.[8–11] Therefore, in this paper we prefer to use a different class of exponentially decreasing functions, the so-called B functions.[12] These functions have a relatively complicated mathematical structure. However, the Fourier transform of such a B function is of exceptional simplicity.[13] Consequently, these functions may be considered to be some fundamental entities in momentum space just as Slater-type functions are in coordinate space. This fact was also emphasized by Niukkanen[14] who investigated mathematical properties of Fourier transforms of exponentially decreasing functions.

Because of the simplicity of the Fourier transform of a B function it is an obvious idea to evaluate multicenter integrals of B functions via the Fourier-transform method. In Sec. III we shall discuss the relevant properties of B functions. Particular emphasis will be given to the relationship between B functions, irregular solid harmonics, and derivatives of the delta function.[15] We shall need some distribution theory for the derivation of analytical expressions for overlap integrals

$$S(f,g;\mathbf{R})=\int f^*(r)g(\mathbf{r}-\mathbf{R})d^3r \ , \tag{1.1}$$

two-center nuclear attraction integrals

$$A(f;\mathbf{R})=\int \frac{1}{|\mathbf{r}-\mathbf{R}|}f(\mathbf{r})d^3r \ , \tag{1.2}$$

and Coulomb integrals

$$C(f,g;\mathbf{R})=\int\int f^*(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}|}g(\mathbf{r}_2)d^3r_1\,d^3r_2 \ , \tag{1.3}$$

via the Fourier-transform method. In the remaining sections we shall develop all mathematical tools which we need for the derivation of closed-form expressions for the integrals (1.1)—(1.3) if f and g are B functions. With the help of these tools a large number of analytical representations for these integrals will be derived which are mostly new.

The Fourier-transform method can also be used for the evaluation of more complicated multicenter integrals as, for instance, the notorious four-center exchange integral. Then, it is no longer possible to obtain manageable closed-form expressions, and numerical quadratures can no longer be avoided.[16–18] However, even in this case some of the analytical methods which are described here can be employed quite profitably.[19]

It is not a new idea to do a unified treatment of overlap, two-center nuclear attraction, and Coulomb integrals. This was already done in papers by Silverstone,[9] Harris and Michels,[4] and Todd, Kay, and Silverstone[20] where integrals of Slater-type functions were treated. However, we think that the problems associated with these integrals are now much better understood and that considerable progress could be achieved. In our opinion, this is mainly a consequence of the investigation and exploitation of properties of B functions.

Finally, we would like to emphasize that this paper is devoted to the derivation of analytical expressions for overlap, two-center nuclear attraction, and Coulomb integrals of B functions. The numerical properties of the formulas presented here, their merits as well as their shortcomings, will be discussed extensively in the following paper.[21]

II. DEFINITIONS AND BASIC PROPERTIES

For the commonly occurring special functions of mathematical physics we shall use the notations and conventions of Magnus, Oberhettinger, and Soni[22] unless explicitly stated (hereafter, this reference will be denoted as MOS in the text).

The spherical harmonics $Y_l^m(\theta,\phi)$ are defined with use of the phase convention of Condon and Shortley,[23] i.e.,

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

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

$$P_l^m(x)=(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}\left[\frac{(x^2-1)^l}{2^l l!}\right] =(1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x) \ . \tag{2.2}$$

For the regular and irregular solid harmonics we write

$$\mathcal{Y}_l^m(\mathbf{r})=r^lY_l^m(\theta,\phi) \ , \tag{2.3}$$

$$\mathcal{Z}_l^m(\mathbf{r})=r^{-l-1}Y_l^m(\theta,\phi) \ . \tag{2.4}$$

It is important to note that the regular solid harmonic is a homogeneous polynomial of degree l in the Cartesian components x, y, and z of $\mathbf{r}$:[24]

$$\mathcal{Y}_l^m(\mathbf{r})=\left[\frac{2l+1}{4\pi}(l+m)!(l-m)!\right]^{1/2} \times\sum_{k\geq 0}\frac{(-x-iy)^{m+k}(x-iy)^kz^{l-m-2k}}{2^{m+2k}(m+k)!k!(l-m-2k)!} \ . \tag{2.5}$$

Hence, in Eq. (2.5) the Cartesian components of $\mathbf{r}=(x,y,z)$ can be replaced by the Cartesian components of $\nabla=(\partial/\partial x,\partial/\partial y,\partial/\partial z)$ to yield the differential operator $\mathcal{Y}_l^m(\nabla)$ which is also a spherical tensor of rank l. This $\mathcal{Y}_l^m(\nabla)$ which we call spherical tensor gradient was treated in papers by Santos,[25] Rowe,[26] Bayman,[27] Fieck,[28] Stuart,[29] and more recently by Niukkanen[30,31] and ourselves.[11,15,18,32]

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

$$\langle l_3,m_3|l_2,m_2|l_1,m_1\rangle =\int [Y_{l_3}^{m_3}(\Omega)]^*Y_{l_2}^{m_2}(\Omega)Y_{l_1}^{m_1}(\Omega)d\Omega \ . \tag{2.6}$$

These Gaunt coefficients linearize the product of two spherical harmonics,

$$[Y_{l_1}^{m_1}(\Omega)]^*Y_{l_2}^{m_2}(\Omega) =\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle Y_l^{m_2-m_1}(\Omega) \ . \tag{2.7}$$

The symbol $\sum^{(2)}$ indicates that the summation proceeds in steps of 2. The summation limits in Eq. (2.7), which follow from the selection rules satisfied by the Gaunt coefficients, are[33]

$$l_{\max}=l_1+l_2 \ , \tag{2.8a}$$

$$l_{\min}=\begin{cases}\max(|l_1-l_2|,|m_2-m_1|) & \text{if } l_{\max}+\max(|l_1-l_2|,|m_2-m_1|) \text{ is even}\\ \max(|l_1-l_2|,|m_2-m_1|)+1 & \text{if } l_{\max}+\max(|l_1-l_2|,|m_2-m_1|) \text{ is odd} \ .\end{cases} \tag{2.8b}$$

In the following text we shall frequently use the following combinations of the angular momentum quantum numbers l_1, l_2, and l which occur in Eq. (2.7):

$$\Delta l = (l_1 + l_2 - l)/2 , \quad (2.9a)$$

$$\Delta l_1 = (l - l_1 + l_2)/2 , \quad (2.9b)$$

$$\Delta l_2 = (l + l_1 - l_2)/2 . \quad (2.9c)$$

Due to the summation limits (2.8) these quantities are either positive integers or zero.

If $K_\nu(z)$ stands for the modified Bessel function of the second kind (MOS, p. 66), the reduced Bessel function $\hat{k}_\nu(z)$ is defined by[34]

$$\hat{k}_\nu(z) = (2/\pi)^{1/2} z^\nu K_\nu(z) . \quad (2.10)$$

As a nonscalar generalization of the reduced Bessel functions with half-integral orders $\nu = n - \frac{1}{2}$, $n \in \mathbb{Z}$, the so-called B function was introduced:[12]

$$B_{n,l}^m(\alpha, \mathbf{r}) = [2^{n+l}(n+l)!]^{-1} \hat{k}_{n-1/2}(\alpha r) \mathcal{Y}_l^m(\alpha \mathbf{r}) . \quad (2.11)$$

For the overlap, two-center nuclear attraction, and Coulomb integrals of B functions we write

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \mathbf{R}) = \int [B_{n_1, l_1}^{m_1}(\alpha, \mathbf{r})]^* B_{n_2, l_2}^{m_2}(\beta, \mathbf{r} - \mathbf{R}) d^3 r , \quad (2.12)$$

$$A_{n,l}^m(\alpha, \mathbf{R}) = \int \frac{1}{|\mathbf{r} - \mathbf{R}|} B_{n,l}^m(\alpha, \mathbf{r}) d^3 r , \quad (2.13)$$

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \mathbf{R}) = \int \int [B_{n_1, l_1}^{m_1}(\alpha, \mathbf{r}_1)]^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}|} \times B_{n_2, l_2}^{m_2}(\beta, \mathbf{r}_2) d^3 r_1 \, d^3 r_2 . \quad (2.14)$$

We shall also consider the overlap integral of an irregular solid harmonic and a B function for which we write

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta, \mathbf{R}) = \int [\mathcal{Z}_{l_1}^{m_1}(\alpha \mathbf{r})]^* B_{n_2, l_2}^{m_2}(\beta, \mathbf{r} - \mathbf{R}) d^3 r . \quad (2.15)$$

In this paper we shall use the symmetric version of the Fourier transformation, i.e., a given function $f(\mathbf{r})$ and its Fourier transform $\bar{f}(\mathbf{p})$ are connected by the relationships

$$\bar{f}(\mathbf{p}) = (2\pi)^{-3/2} \int e^{-i\mathbf{p}\cdot\mathbf{r}} f(\mathbf{r}) d^3 r , \quad (2.16)$$

$$f(\mathbf{r}) = (2\pi)^{-3/2} \int e^{i\mathbf{r}\cdot\mathbf{p}} \bar{f}(\mathbf{p}) d^3 p . \quad (2.17)$$

Classically, Fourier transformation is only defined for functions that are absolutely integrable, i.e., which belong to the space $L^1(\mathbb{R}^3)$. However, if one uses the theory of generalized functions Fourier transformation can be extended to the space of tempered distributions.[35] This fact is very important for our purposes since it makes it possible to define the Fourier transform of the Coulomb potential,[36]

$$(2\pi)^{-3/2} \int \frac{1}{r} e^{-i\mathbf{p}\cdot\mathbf{r}} d^3 r = \frac{(2/\pi)^{1/2}}{p^2} . \quad (2.18)$$

This relationship which holds in the sense of distributions can be used to derive representations as inverse Fourier integrals for the two-center nuclear attraction integral (1.2) and the Coulomb integral (1.3). If we combine Eq. (2.18) with either[37]

$$S(f, g; \mathbf{R}) = \int e^{-i\mathbf{R}\cdot\mathbf{p}} \bar{f}^*(\mathbf{p}) \bar{g}(\mathbf{p}) d^3 p \quad (2.19)$$

or[38]

$$\int \int f^*(\mathbf{r}_1) g(\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}) h(\mathbf{r}_2) d^3 r_1 \, d^3 r_2 = (2\pi)^{3/2} \int e^{-i\mathbf{R}\cdot\mathbf{p}} \bar{f}^*(\mathbf{p}) \bar{g}(\mathbf{p}) \bar{h}(\mathbf{p}) d^3 p \quad (2.20)$$

we obtain

$$A(f; \mathbf{R}) = (2\pi)^{1/2} \int \frac{e^{-i\mathbf{R}\cdot\mathbf{p}}}{p^2} \bar{f}(\mathbf{p}) d^3 p , \quad (2.21)$$

$$C(f, g; \mathbf{R}) = 4\pi \int \frac{e^{-i\mathbf{R}\cdot\mathbf{p}}}{p^2} \bar{f}^*(\mathbf{p}) \bar{g}(\mathbf{p}) d^3 p . \quad (2.22)$$

The main advantage of the representation of the two-center integrals (1.1)–(1.3) as inverse Fourier integrals according to Eqs. (2.19), (2.21), and (2.22) is that a separation of integration variables can be achieved quite easily if f and g are irreducible spherical tensors. To show this we only have to insert the well-known Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics,

$$e^{\pm i\mathbf{x}\cdot\mathbf{y}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (\pm i)^l j_l(xy) [Y_l^m(\mathbf{x}/x)]^* Y_l^m(\mathbf{y}/y) , \quad (2.23)$$

into the integrals in Eqs. (2.19), (2.21), and (2.22).

Another advantage of this Fourier-transform method is that it makes it possible to decide whether a given multicenter integral exists or not, and if it does, in what sense. Following Triebel[39] we shall say that a multicenter integral exists whenever the corresponding Fourier integral makes sense. This is a very general and flexible definition because it encompasses not only Fourier integrals which converge absolutely, but also integrals which do not converge in the sense of classical analysis and which have to be regularized,[40] and even integrals which represent derivatives of the three-dimensional delta function. We shall return to these questions in the later sections of this paper and discuss them more extensively.

III. PROPERTIES OF B FUNCTIONS

In this section we shall discuss only those properties of B functions which will be required for the derivation of closed-form expressions for the two-center integrals (2.12)–(2.15). More complete treatments of the mathematical properties of B functions were given elsewhere.[11,15,41,42]

If the order ν of a reduced Bessel function $\hat{k}_\nu(z)$, which was defined in Eq. (2.10), is negative we may use

$$\hat{k}_{-\nu}(z) = z^{-2\nu} \hat{k}_\nu(z) , \quad (3.1)$$

which follows from a symmetry relationship satisfied by the modified Bessel function of the second kind (MOS, p. 67),

$$K_{-\nu}(z)=K_{\nu}(z) \; . \tag{3.2}$$

If the order ν is half-integral and positive, $\nu=n+\frac{1}{2}$ and $n\in\mathbb{N}$, a reduced Bessel function may be represented as an exponential multiplied by a terminating hypergeometric series,[43]

$$\hat{k}_{n+1/2}(z)=2^n(\tfrac{1}{2})_n e^{-z}\,{}_1F_1(-n;-2n;2z), \quad n\geq 0 \; , \tag{3.3}$$

where $(a)_n\equiv\Gamma(a+n)/\Gamma(a)$, for $n\in\mathbb{N}$ with $(a)_0=1$, is a Pochhammer symbol.

If we combine the definition of a B function, Eq. (2.11), with Eq. (3.3) we see that a B function is a relatively complicated mathematical object and that it can be expressed as a linear combination of Slater-type functions[44] which are defined by

$$\chi_{n,l}^m(\alpha,\mathbf{r})=(\alpha r)^{n-1}e^{-\alpha r}Y_l^m(\theta,\phi), \quad n\in\mathbb{N} \; . \tag{3.4}$$

However, it could be shown that the Fourier transform of a B function is of exceptional simplicity:[45]

$$\bar{B}_{n,l}^{\,m}(\alpha,\mathbf{p})=(2\pi)^{-3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}}B_{n,l}^m(\alpha,\mathbf{r})d^3r = (2/\pi)^{1/2}\frac{\alpha^{2n+l-1}}{(\alpha^2+p^2)^{n+l+1}}\mathcal{Y}_l^m(-i\mathbf{p}) \; . \tag{3.5}$$

The Fourier transforms of other exponentially decreasing functions such as Slater-type functions or hydrogen eigenfunctions are significantly more complicated. In papers by Niukkanen,[14] Weniger and Steinborn,[11,46] and Weniger[47] it was shown that the Fourier transforms of all commonly occurring exponentially decreasing functions can be expressed as linear combination of Fourier transforms of B functions.

B functions have another property which seems to be unique among exponentially decreasing functions: It is extremely easy to generate anisotropic B functions by differentiating scalar B functions. One only has to apply the spherical tensor gradient $\mathcal{Y}_l^m(\nabla)$ to a scalar B function in order to obtain a nonscalar B function,[48] i.e., a spherical tensor of rank l:

$$B_{n,l}^m(\alpha,\mathbf{r})=(-\alpha)^{-l}(4\pi)^{1/2}\mathcal{Y}_l^m(\nabla)B_{n+l,0}^0(\alpha,\mathbf{r}) \; . \tag{3.6}$$

This remarkable property of B functions could be used quite profitably in connection with some multicenter integrals.[49] In these cases, only closed-form expressions for multicenter integrals over scalar B functions had to be derived which can be obtained more easily than the corresponding integrals over nonscalar functions. Then, a suitable application of spherical tensor gradients according to Eq. (3.6) yielded the desired expressions.

We can learn a lot about the properties of B functions if we study the representation of a B function as an inverse Fourier integral according to Eqs. (2.17) and (3.5),

$$B_{n,l}^m(\alpha,\mathbf{r})=\frac{\alpha^{2n+l-1}}{2\pi}\int e^{i\mathbf{r}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^m(-i\mathbf{p})}{(\alpha^2+p^2)^{n+l+1}}d^3p \; . \tag{3.7}$$

For $n\geq 1$ the Fourier integral converges absolutely. One can show that in this case B functions are absolutely integrable and square integrable, i.e., they belong to $L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)$.

For $-l\leq n\leq 0$ it follows from Eq. (3.1) that B functions may be singular at the origin. Hence, these functions are in general neither elements of $L^1(\mathbb{R}^3)$ nor of $L^2(\mathbb{R}^3)$. Also, the Fourier integral in Eq. (3.7) need no longer exist in the sense of classical analysis. However, even in the most extreme case of the so-called modified Helmholtz harmonic $B_{-l,l}^m$ the classically divergent integral can be regularized by applying a suitable cutoff function.[40]

For $n<-l$ it follows from Eq. (2.11) that a B function is zero everywhere except at the origin, where it is undefined. This is due to the occurrence of $(n+l)!=\Gamma(n+l+1)$ in the denominator in Eq. (2.11). However, the integral representation (3.7) remains meaningful even for $n<-l$. Of course, in this case the integral no longer represents a function but a derivative of the three-dimensional delta function,[50]

$$B_{-n-l,l}^m(\alpha,\mathbf{r})=(4\pi/\alpha^{l+3})[(2l-1)!!] \times(1-\alpha^{-2}\nabla^2)^{n-1}\delta_l^m(\mathbf{r}), \quad n\geq 1 \tag{3.8}$$

where the spherical delta function δ_l^m is defined by

$$\delta_l^m(\mathbf{r})=(-1)^l[(2l-1)!!]^{-1}\mathcal{Y}_l^m(\nabla)\delta(\mathbf{r}) \; . \tag{3.9}$$

Modified Helmholtz harmonics and irregular solid harmonics are closely related. If we combine Eqs. (2.11), (3.1), and (3.3) we find

$$\mathcal{Z}_l^m(\mathbf{r})=[(2l-1)!!]^{-1}\lim_{\epsilon\to 0}[\epsilon^{l+1}B_{-l,l}^m(\epsilon,\mathbf{r})] \; . \tag{3.10}$$

We can exploit this relationship to define the Fourier transform of an irregular solid harmonic which is not an element of $L^1(\mathbb{R}^3)$. Consequently, Fourier transformation as well as inverse Fourier transformation are in this case not defined in the sense of classical analysis. However, if we combine Eqs. (3.5) and (3.10) we find

$$\bar{\mathcal{Z}}_l^m(\mathbf{p})=(2\pi)^{-3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}}\mathcal{Z}_l^m(\mathbf{r})d^3r = \frac{(2/\pi)^{1/2}}{(2l-1)!!}\frac{1}{p^2}\mathcal{Y}_l^m(-i\mathbf{p}) \; . \tag{3.11}$$

Because of $1/r=(4\pi)^{1/2}\mathcal{Z}_0^0(\mathbf{r})$ we see that Eq. (3.11) contains Eq. (2.18) as a special case. If we combine Eqs. (3.7) and (3.10) we obtain a representation of the irregular solid harmonic as an inverse Fourier integral:

$$\mathcal{Z}_l^m(\mathbf{r})=\{2\pi[(2l-1)!!]\}^{-1}\int e^{i\mathbf{r}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^m(-i\mathbf{p})}{p^2}d^3p \; . \tag{3.12}$$

Finally, we are in a position to give explicit integral representations for the integrals (2.12)–(2.15) which will be treated in this paper. If we combine Eqs. (2.19) and (3.5) and if we couple the spherical harmonics according to Eq. (2.7) we obtain, for the overlap integral (2.12),

$$S_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=\frac{2}{\pi}\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}i^{l_1-l_2} \times\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{p^{l_1+l_2-l}\mathcal{Y}_l^{m_2-m_1}(\mathbf{p})}{(\alpha^2+p^2)^{n_1+l_1+1}(\beta^2+p^2)^{n_2+l_2+1}}d^3p \; . \tag{3.13}$$

In the case of the nuclear attraction integral (2.13) we combine Eqs. (2.21) and (3.7):

$$A_{n,l}^{m}(\alpha,\mathbf{R})=\frac{2}{\pi}\alpha^{2n+l-1}\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^m(i\mathbf{p})}{p^2(\alpha^2+p^2)^{n+l+1}}d^3p\ . \tag{3.14}$$

In the case of the Coulomb integral (2.14) we combine Eqs. (2.7), (2.22), and (3.5):

$$C_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=8\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}i^{l_1-l_2}\times\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{p^{l_1+l_2-l}\mathcal{Y}_l^{m_2-m_1}(\mathbf{p})}{p^2(\alpha^2+p^2)^{n_1+l_1+1}(\beta^2+p^2)^{n_2+l_2+1}}d^3p\ . \tag{3.15}$$

In the case of the integral (2.15) we combine Eqs. (2.7), (2.19), (3.5), and (3.11):

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=\frac{2/\pi}{(2l_1-1)!!}\frac{\beta^{2n_2+l_2-1}}{\alpha^{l_1+1}}i^{l_1-l_2}\times\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{p^{l_1+l_2-l}\mathcal{Y}_l^{m_2-m_1}(\mathbf{p})}{p^2(\beta^2+p^2)^{n_2+l_2+1}}d^3p\ . \tag{3.16}$$

IV. TRANSFORMATIONS OF THE DENOMINATORS

In this section we shall show how the denominators which occur in the integral representations (3.13)—(3.16) can be expressed in terms of simpler functions such as p^{-2} or $(\alpha^2+p^2)^{-n-l-1}$ using partial-fraction decomposition or Taylor expansion.

We start with the following partial-fraction decomposition:[51]

$$(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}=\frac{(-1)^{n_2+l_2+1}}{(n_2+l_2)!}\sum_{\nu=0}^{n_1+l_1}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_1+l_1-\nu)!}\frac{(\alpha^2-\beta^2)^{\nu-n_1-n_2-l_1-l_2-1}}{(\alpha^2+p^2)^{\nu+1}}+\frac{(-1)^{n_1+l_1+1}}{(n_1+l_1)!}\sum_{\nu=0}^{n_2+l_2}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_2+l_2-\nu)!}\frac{(\beta^2-\alpha^2)^{\nu-n_1-n_2-l_1-l_2-1}}{(\beta^2+p^2)^{\nu+1}}\ . \tag{4.1}$$

From Eq. (4.1) we immediately obtain, as a special case,

$$p^{-2}(\alpha^2+p^2)^{-n-l-1}=\alpha^{-2n-2l-4}\left[\alpha^2/p^2-\sum_{\nu=0}^{n+l}[\alpha^2/(\alpha^2+p^2)]^{\nu+1}\right]. \tag{4.2}$$

We can combine Eqs. (4.1) and (4.2) to obtain a partial fraction decomposition for the denominator which occurs in the integral representation (3.15) for the Coulomb integral:

$$\frac{1}{p^2(\alpha^2+p^2)^{n_1+l_1+1}(\beta^2+p^2)^{n_2+l_2+1}}=\frac{1}{p^2\alpha^{2n_1+2l_1+2}\beta^{2n_2+l_2+2}}+\frac{\alpha^{-2n_1-2l_1-4}}{(\beta^2-\alpha^2)^{n_2+l_2+1}}\sum_{\nu=0}^{n_1+l_1}\left[\frac{\alpha^2}{\alpha^2+p^2}\right]^{\nu+1}\sum_{\mu=0}^{n_1+l_1-\nu}\frac{(n_2+l_2+1)_\mu}{\mu!}\left[\frac{\alpha^2}{\alpha^2-\beta^2}\right]^{\mu}+\frac{\beta^{-2n_2-2l_2-4}}{(\alpha^2-\beta^2)^{n_1+l_1+1}}\sum_{\nu=0}^{n_2+l_2}\left[\frac{\beta^2}{\beta^2+p^2}\right]^{\nu+1}\sum_{\mu=0}^{n_2+l_2-\nu}\frac{(n_1+l_1+1)_\mu}{\mu!}\left[\frac{\beta^2}{\beta^2-\alpha^2}\right]^{\mu}\ . \tag{4.3}$$

In Eqs. (4.1)—(4.3) the constituents of the denominators are completely separated. Hence, if we use these partial fraction decompositions in the integral representations (3.13)—(3.16) we obtain, because of Eqs. (3.7) and (3.12), expressions which only involve B functions and irregular solid harmonics. However, in the case of the Coulomb integral (2.14) this need not be the most economical approach. Instead, it may be more convenient to use one of the following incomplete partial fraction decompositions:

$$\frac{1}{p^2(\alpha^2+p^2)^{n_1+l_1+1}(\beta^2+p^2)^{n_2+l_2+1}}=\frac{(-1)^{n_2+l_2+1}}{(n_2+l_2)!}\sum_{\nu=0}^{n_1+l_1}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_1+l_1-\nu)!}\frac{(\alpha^2-\beta^2)^{\nu-n_1-n_2-l_1-l_2-1}}{p^2(\alpha^2+p^2)^{\nu+1}}+\frac{(-1)^{n_1+l_1+1}}{(n_1+l_1)!}\sum_{\nu=0}^{n_2+l_2}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_2+l_2-\nu)!}\frac{(\beta^2-\alpha^2)^{\nu-n_1-n_2-l_1-l_2-1}}{p^2(\beta^2+p^2)^{\nu+1}} \tag{4.4}$$

$$=\frac{1}{\alpha^{2n_1+2l_1+2}}\left[\frac{1}{p^2(\beta^2+p^2)^{n_2+l_2+1}}-\sum_{\nu=0}^{n_1+l_1}\frac{\alpha^{2\nu}}{(\alpha^2+p^2)^{\nu+1}(\beta^2+p^2)^{n_2+l_2+1}}\right] \tag{4.5}$$

$$=\frac{1}{\beta^{2n_2+2l_2+2}}\left[\frac{1}{p^2(\alpha^2+p^2)^{n_1+l_1+1}}-\sum_{\nu=0}^{n_2+l_2}\frac{\beta^{2\nu}}{(\alpha^2+p^2)^{n_1+l_1+1}(\beta^2+p^2)^{\nu+1}}\right]. \tag{4.6}$$

Because of Eqs. (3.7) and (3.12) we shall obtain closed-form expressions for the two-center integrals (2.12)–(2.15) which contain only a finite number of B functions and irregular solid harmonics if we insert the partial fraction decompositions into the Fourier integrals (3.13)–(3.16). Therefore, we may expect that these representations will allow a very efficient evaluation of the two-center integrals (2.12)–(2.15). Unfortunately, we shall see later that none of these very compact expressions will be numerically stable for the whole range of distances, scaling parameters, and quantum numbers. Hence, we see that partial fraction decompositions alone are not sufficient for a reliable evaluation of the two-center integrals, and that they have to be supplemented by alternative transformations of the denominators in Eqs. (3.13)–(3.16) which do not lead to numerical instabilities.

This aim can be accomplished with the help of Taylor expansions. Our starting point is[52]

$$(\alpha^2+p^2)^{-n-l-1}=(\beta^2+p^2)^{-n-l-1}\times {}_1F_0(n+l+1;(\beta^2-\alpha^2)/(\beta^2+p^2)) . \tag{4.7}$$

The generalized hypergeometric series ${}_1F_0$ in Eq. (4.7) converges absolutely and uniformly for all $p\in\mathbb{R}$ provided that $\alpha\in(0,2^{1/2}\beta)$. If we use Eq. (4.7) in the integral representation (3.7) we obtain the multiplication theorem of B functions which can also be derived via a Taylor expansion:

$$B_{n,l}^m(\alpha,\mathbf{r})=(\alpha/\beta)^{2n+l-1}\sum_{\nu=0}^{\infty}\frac{(n+l+1)_\nu}{\nu!}\left[\frac{\beta^2-\alpha^2}{\beta^2}\right]^\nu \times B_{n+\nu,l}^m(\beta,\mathbf{r}) . \tag{4.8}$$

In Eq. (4.7) we set $n=l=0$ and perform the limit $\alpha\to0$. This yields

$$p^{-2}=\sum_{\nu=0}^{\infty}\beta^{2\nu}/(\beta^2+p^2)^{\nu+1} . \tag{4.9}$$

If we combine this expansion, which converges absolutely and uniformly for all $\beta\in\mathbb{R}$ and $p\in[\epsilon,\infty)$ with $\epsilon>0$, with Eqs. (3.7) and (3.12) we obtain the expansion of an irregular solid harmonic in terms of B functions[53] which can also be derived directly from Eq. (4.8):

$$\mathcal{Z}_l^m(\alpha,\mathbf{r})=\frac{(\beta/\alpha)^{l+1}}{(2l-1)!!}\sum_{\nu=0}^{\infty}B_{\nu-l,l}^m(\beta,\mathbf{r}) . \tag{4.10}$$

With the help of the Taylor expansion (4.7) the denominator in Eq. (3.13) can be brought into an integrable form:

$$(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}=(\beta^2+p^2)^{-n_1-n_2-l_1-l_2-2}\,{}_1F_0(n_1+l_1+1;(\beta^2-\alpha^2)/(\beta^2+p^2)) \tag{4.11}$$

$$=(\alpha^2+p^2)^{-n_1-n_2-l_1-l_2-2}\,{}_1F_0(n_2+l_2+1;(\alpha^2-\beta^2)/(\alpha^2+p^2)) . \tag{4.12}$$

The generalized hypergeometric series ${}_1F_0$ in Eq. (4.11) converges absolutely and uniformly for all $p\in\mathbb{R}$ provided that $\alpha\in(0,2^{1/2}\beta)$, whereas the infinite series in Eq. (4.12) requires $\beta\in(0,2^{1/2}\alpha)$. Since there is an overlapping region where both expansions are defined, Eqs. (4.11) and (4.12) may be considered to be analytic continuations.

Next, we consider the case $\beta=0$ and $n_2=l_2=0$ in Eq. (6.8). This yields

$$p^{-2}(\alpha^2+p^2)^{-n-l-1}=(\alpha^2+p^2)^{-n-l-2}\sum_{\nu=0}^{\infty}[\alpha^2/(\alpha^2+p^2)]^\nu . \tag{4.13}$$

This expansion converges absolutely and uniformly for all $\alpha\in\mathbb{R}$ and $p\in[\epsilon,\infty)$, $\epsilon>0$.

Finally, we multiply Eq. (4.9) by either Eq. (4.11) or (4.12). After some algebra we find

$$p^{-2}(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}=(\beta^2+p^2)^{-n_1-n_2-l_1-l_2-3}\sum_{\nu=0}^{\infty}\left[\frac{\beta^2}{\beta^2+p^2}\right]^\nu\sum_{\kappa=0}^{\nu}\frac{(n_1+l_1+1)_\kappa}{\kappa!}\left[\frac{\beta^2-\alpha^2}{\beta^2}\right]^\kappa \tag{4.14}$$

$$=(\alpha^2+p^2)^{-n_1-n_2-l_1-l_2-3}\sum_{\nu=0}^{\infty}\left[\frac{\alpha^2}{\alpha^2+p^2}\right]^\nu\sum_{\kappa=0}^{\nu}\frac{(n_2+l_2+1)_\kappa}{\kappa!}\left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\kappa . \tag{4.15}$$

The infinite series in Eq. (4.14) converges for $\alpha \in (0, 2^{1/2}\beta)$ and the infinite series in Eq. (4.15) converges for $\beta \in (0, 2^{1/2}\alpha)$.

For the inner sums in Eqs. (4.14) and (4.15) various alternative representations can be derived, for instance,

$$\sum_{\kappa=0}^{\nu} \frac{(n_2+l_2+1)_\kappa}{\kappa!} \left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\kappa = (\alpha/\beta)^{2(n_2+l_2+1)} - \sum_{\kappa=\nu+1}^{\infty} \frac{(n_2+l_2+1)_\kappa}{\kappa!} \left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\kappa . \tag{4.16}$$

However, these alternative representations do not seem to offer any computational advantage. Therefore, we shall not consider them explicitly.

In the next section we shall show that the use of either Eq. (4.11) or (4.12) in Eq. (3.13) leads to infinite-series expansions for the overlap integral with different scaling parameters in terms of overlap integrals with equal scaling parameters. The numerical properties of these expansions which were originally derived using the multiplication theorem of B functions, Eq. (4.8), were already studied quite extensively.[41] It turned out that these expansions converge fairly well if the two scaling parameters do not differ too much. However, their convergence may become prohibitively slow.

Hence, in view of these convergence problems and because of the inherent numerical instability of all expressions which are based upon partial fraction decompositions it would be desirable to have alternative representations which converge more rapidly than the hitherto known expansions and yet do not contain canceling singularities which cannot be avoided if partial fraction decompositions are used.

In the later sections of this paper as well as in the following paper[21] it will become clear that we can achieve our aim with the help of the following generating function for terminating hypergeometric functions ${}_2F_1$:[54]

$$(1-s)^{a-c}(1-s+sz)^{-a} = \sum_{n=0}^{\infty} {}_2F_1(-n,a;c;z)\frac{(c)_n}{n!}s^n . \tag{4.17}$$

If we set $z=2$, $a=n_1+l_1+1$, $c=n_1+n_2+l_1+l_2+2$, and $s=[(\alpha^2-\beta^2)/(\alpha^2+\beta^2+2p^2)]$ we obtain

$$(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1} = [(\alpha^2+\beta^2)/2+p^2]^{-n_1-n_2-l_1-l_2-2} \times \sum_{\nu=0}^{\infty} {}_2F_1(-\nu,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2)\frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2+2p^2}\right]^\nu . \tag{4.18}$$

In Eq. (4.18) there occur terminating hypergeometric series of the general type ${}_2F_1(-\nu,m+1;m+n+2;2)$ with $m,n\in\mathbb{N}$. If we use (MOS, p. 47)

$${}_2F_1(a,b;c;z) = (1-z)^{-a}\,{}_2F_1(a,c-b;c;z/(z-1)) , \tag{4.19}$$

we find that these functions satisfy the symmetry relationship

$${}_2F_1(-\nu,m+1;m+n+2;2) = (-1)^\nu\,{}_2F_1(-\nu,n+1;m+n+2;2) . \tag{4.20}$$

These functions can be computed recursively. We only have to use (MOS, p. 46)

$$(c-a)\,{}_2F_1(a-1,b;c;z) + [2a-c-(a-b)z]\,{}_2F_1(a,b;c;z) + a(z-1)\,{}_2F_1(a+1,b;c;z) = 0 \tag{4.21}$$

to obtain

$$(m+n+\nu+2)\,{}_2F_1(-\nu-1,m+1;m+n+2;2) = (n-m)\,{}_2F_1(-\nu,m+1;m+n+2;2) + \nu\,{}_2F_1(-\nu+1,m+1;m+n+2;2) . \tag{4.22}$$

For $m=n$ this three-term recurrence formula simplifies to a two-term recursion,

$${}_2F_1(-\nu-2,m+1;2m+2;2) = \frac{\nu+1}{2m+\nu+3}\,{}_2F_1(-\nu,m+1;2m+2;2) . \tag{4.23}$$

Repeated application of this recurrence formula yields

$${}_2F_1(-2\nu,m+1;2m+2;2) = \frac{(\frac{1}{2})_\nu}{(m+\frac{3}{2})_\nu} , \tag{4.24}$$

$${}_2F_1(-2\nu-1,m+1;2m+2;2) = 0, \quad \nu\in\mathbb{N} . \tag{4.25}$$

If we use Eqs. (4.24) and (4.25) in Eq. (4.18) we obtain, after some algebraic manipulation, if $n_1+l_1=n_2+l_2$ holds,

$$[(\alpha^2+p^2)(\beta^2+p^2)]^{-n_1-l_1-1} = [(\alpha^2+\beta^2)/2+p^2]^{-2(n_1+l_1+1)} \times \sum_{\nu=0}^{\infty} \frac{(n_1+l_1+1)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2+2p^2}\right]^{2\nu} . \tag{4.26}$$

In Eq. (4.18) we set $\beta=0$ and $n_2=l_2=0$. This yields

$$p^{-2}(\alpha^2+p^2)^{-n-l-1} = (\alpha^2/2+p^2)^{-n-l-2} \times \sum_{\nu=0}^{\infty} {}_2F_1(-\nu,n+l+1;n+l+2;2) \times \frac{(n+l+2)_\nu}{\nu!}\left[\frac{\alpha^2}{\alpha^2+2p^2}\right]^\nu . \tag{4.27}$$

If we combine Eq. (4.9) with Eq. (4.18) we find

$$p^{-2}(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}$$
$$=[(\alpha^2+p^2)/2+p^2]^{-n_1-n_2-l_1-l_2-3}$$
$$\times\sum_{\nu=0}^{\infty}\left[\frac{(\alpha^2-\beta^2)/2}{(\alpha^2+\beta^2)/2+p^2}\right]^{\nu}\sum_{\kappa=0}^{\nu}{}_2F_1(-\kappa,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2)\frac{(n_1+n_2+l_1+l_2+2)_\kappa}{\kappa!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^{\kappa}. \tag{4.28}$$

Just as in Eqs. (4.14) or (4.15) other representations for the inner sum in Eq. (4.28) can be derived. However, since these new representations do not seem to offer any computational advantage we shall not consider them explicitly.

V. OVERLAP INTEGRALS

In this section overlap integrals of B functions will be treated. First a new derivation for the convolution theorem of two B functions with equal scaling parameters will be presented which is much simpler than the original derivation by Filter and Steinborn.[55] If we set $\alpha=\beta$ in Eq. (3.13) and use the relationship

$$p^{2\Delta l}=(-1)^{\Delta l}\alpha^{2\Delta l}\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}[(\alpha^2+p^2)/\alpha^2]^t, \tag{5.1}$$

which is merely a special case of the binomial theorem, we obtain

$$S_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\alpha,\mathbf{R})=(-1)^{l_2}\frac{4\pi}{\alpha^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}(-1)^l\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}\frac{\alpha^{2n_1+2n_2+2l_1+2l_2-2t-l+1}}{2\pi^2}$$
$$\times\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^{m_2-m_1}(-i\mathbf{p})}{(\alpha^2+p^2)^{n_1+n_2+l_1+l_2-t+2}}d^3p\,. \tag{5.2}$$

Here, we made use of the fact that due to the summation limits (2.8) $l_1+l_2-l=2\,\Delta l$ is always an even positive integer or zero.

If we compare Eq. (5.2) with the Fourier integral representation of B functions, Eq. (3.7), we immediately find the well-known result[55]

$$S_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\alpha,\mathbf{R})=(-1)^{l_2}\frac{4\pi}{\alpha^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}B_{n_1+n_2+l_1+l_2-l-t+1,l}^{m_2-m_1}(\alpha,\mathbf{R})\,. \tag{5.3}$$

Hence, a systematic exploitation of the properties of B functions under Fourier transformation leads to an extremely simple derivation of Eq. (5.3). The original derivation given by Filter and Steinborn[55] was much more complicated since it involved some nontrivial manipulations of special functions.

A similar approach is also possible in the case of different scaling parameters. If we combine Eqs. (3.13), (4.1), and (5.1), we find

$$S_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})$$
$$=(-1)^{l_2}\frac{2}{\pi}\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}$$
$$\times\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}(-1)^l\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle$$
$$\times\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}\left[\frac{(-1)^{n_2+l_2+1}}{(n_2+l_2)!}\sum_{q=0}^{n_1+l_1}\frac{(n_1+n_2+l_1+l_2-q)!}{(n_1+l_1-q)!}\right.$$
$$\times\frac{\alpha^{l_1+l_2-l-2t}}{(\alpha^2-\beta^2)^{n_1+n_2+l_1+l_2-q+1}}\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^{m_2-m_1}(-i\mathbf{p})}{(\alpha^2+p^2)^{q-t+1}}d^3p$$
$$+\frac{(-1)^{n_1+l_1+1}}{(n_1+l_1)!}\sum_{q=0}^{n_2+l_2}\frac{(n_1+n_2+l_1+l_2-q)!}{(n_2+l_2-q)!}\frac{\beta^{l_1+l_2-l-2t}}{(\beta^2-\alpha^2)^{n_1+n_2+l_1+l_2-q+1}}$$
$$\left.\times\int e^{-i\mathbf{R}\cdot\mathbf{p}}\frac{\mathcal{Y}_l^{m_2-m_1}(-i\mathbf{p})}{(\beta^2+p^2)^{q-t+1}}d^3p\right]. \tag{5.4}$$

In principle, we can proceed as we did in our derivation of Eq. (5.3). However, we are confronted with the additional complication that those Fourier integrals in Eq. (5.4) with $q < t$ do not represent ordinary functions but derivatives of the three-dimensional delta function according to Eq. (3.8). Hence, we obtain

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (-1)^{l_2} 4\pi \alpha^{2n_1+l_1-1} \beta^{2n_2+l_2-1} \times \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2,m_2 | l_1,m_1 | l,m_2-m_1 \rangle \times \sum_{t=0}^{\Delta l} (-1)^t \binom{\Delta l}{t} \times \Bigg[\frac{(-1)^{n_2+l_2+1}}{(n_2+l_2)!} \frac{\alpha^{l_1+l_2+1}}{(\alpha^2-\beta^2)^{n_1+n_2+l_1+l_2+1}} \times \sum_{q=0}^{n_1+l_1} \frac{(n_1+n_2+l_1+l_2-q)!}{(n_1+l_1-q)!} \left[\frac{\alpha^2-\beta^2}{\alpha^2} \right]^q B_{q-t-l,l}^{m_2-m_1}(\alpha,\mathbf{R}) + \frac{(-1)^{n_1+l_1+1}}{(n_1+l_1)!} \frac{\beta^{l_1+l_2+1}}{(\beta^2-\alpha^2)^{n_1+n_2+l_1+l_2+1}} \times \sum_{q=0}^{n_2+l_2} \frac{(n_1+n_2+l_1+l_2-q)!}{(n_2+l_2-q)!} \left[\frac{\beta^2-\alpha^2}{\beta^2} \right]^q B_{q-t-l,l}^{m_2-m_1}(\beta,\mathbf{R}) \Bigg] . \tag{5.5}$$

If Eq. (5.5) is to be used only for a numerical evaluation of the overlap integral then the distributive B functions with $q < t$ can safely be neglected since for $R > 0$ they do not contribute to the numerical value of the overlap integral.

In Eq. (5.5) we now neglect the distributive B functions by changing the lower limit of the two q summations from $q=0$ to $q=t$ and introduce the new summation variable $s=q-t$. After a lengthy but in principle straightforward calculation we obtain the so-called Jacobi polynomial representation of the overlap integral with different scaling parameters,[55]

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (-1)^{l_2} 4\pi \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)}\langle l_2,m_2 | l_1,m_1 | l,m_2-m_1 \rangle \times \Bigg[\frac{(-1)^{n_1+l_1}(\alpha/\beta)^{l_2}}{\beta^3[1-(\alpha/\beta)^2]^{n_2+l_2+1}} \times \sum_{s=0}^{n_1+l_1} (-1)^s P_{n_1+l_1-s}^{(s-n_1-\Delta l_2, n_2+\Delta l_1)} \left[\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2} \right] B_{s-l,l}^{m_2-m_1}(\alpha,\mathbf{R}) + \frac{(-1)^{n_2+l_2}(\beta/\alpha)^{l_1}}{\alpha^3[1-(\beta/\alpha)^2]^{n_1+l_1+1}} \times \sum_{s=0}^{n_2+l_2} (-1)^s P_{n_2+l_2-s}^{(s-n_2-\Delta l_1, n_1+\Delta l_2)} \left[\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2} \right] B_{s-l,l}^{m_2-m_1}(\beta,\mathbf{R}) \Bigg] . \tag{5.6}$$

Here, $P_n^{(\alpha,\beta)}(x)$ is a Jacobi potential (MOS, pp. 209—217), and the abbreviations Δl_1 and Δl_2 were defined in Eq. (2.9).

Since no distributive B functions occur in the Jacobi polynomial representation (5.6) we have to conclude that this representation is only correct for numerical evaluations of overlap integrals. If Eq. (5.6) is to be used in integrals the distributive B functions of Eq. (5.5) have to be added explicitly.

Instead of the partial fraction decomposition (4.1) we can also use the Taylor expansions (4.11) or (4.12) in Eq. (3.13). Then we obtain series expansions in terms of overlap integrals with equal scaling parameters:

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (\alpha/\beta)^{2n_1+l_1-1} \sum_{\nu=0}^{\infty} \frac{(n_1+l_1+1)_\nu}{\nu!} \left[\frac{\beta^2-\alpha^2}{\beta^2} \right]^\nu S_{n_1+\nu l_1 m_1}^{n_2 l_2 m_2}(\beta,\beta,\mathbf{R}) \tag{5.7}$$

$$= (\beta/\alpha)^{2n_2+l_2-1} \sum_{\nu=0}^{\infty} \frac{(n_2+l_2+1)_\nu}{\nu!} \left[\frac{\alpha^2-\beta^2}{\alpha^2} \right]^\nu S_{n_1 l_1 m_1}^{n_2+\nu l_2 m_2}(\alpha,\alpha,\mathbf{R}) . \tag{5.8}$$

The infinite series in Eq. (5.7) converges for $|(\beta^2-\alpha^2)/\beta^2|<1$, and the infinite series in Eq. (5.8) converges for $|(\alpha^2-\beta^2)/\alpha^2|<1$. The numerical properties of the two infinite-series expansions (5.7) and (5.8) and the Jacobi polynomial representation (5.6) were already studied quite extensively.[41]

Finally, we want to use the Taylor expansion (4.18) in the integral representation (3.13). After some algebra we find

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2-1}} \times\sum_{\nu=0}^{\infty} {}_2F_1(-\nu,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2)\frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^\nu \times S_{n_1+\nu l_1 m_1}^{n_2 l_2 m_2}([(\alpha^2+\beta^2)/2]^{1/2},[(\alpha^2+\beta^2)/2]^{1/2},\mathbf{R})\ . \tag{5.9}$$

If $n_1+l_1=n_2+l_2$ holds then we use the Taylor expansion (4.26) in Eq. (3.13), and we obtain the simplified expansion

$$S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2-1}} \times\sum_{\nu=0}^{\infty}\frac{(n_1+l_1+1)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^{2\nu} S_{n_1+2\nu l_1 m_1}^{n_2 l_2 m_2}([(\alpha^2+\beta^2)/2]^{1/2},[(\alpha^2+\beta^2)/2]^{1/2},\mathbf{R})\ . \tag{5.10}$$

The new infinite-series expansion for overlap integrals, Eq. (5.9), looks significantly more complicated than the previous known series expansions (5.7) and (5.8). Nevertheless, we may expect that the infinite series in Eq. (5.9) will converge faster than the series in Eqs. (5.7) and (5.8). In Ref. 41, where the numerical properties of Eqs. (5.7) and (5.8) were investigated, it was demonstrated that the rates of convergence of these expansions depend most strongly upon the magnitudes of either $(\beta^2-\alpha^2)/\beta^2$ or $(\alpha^2-\beta^2)/\alpha^2$. If these quantities are close to zero, convergence will be good, and if they approach one, convergence will become very bad. Now, we observe that $(\alpha^2-\beta^2)/(\alpha^2+\beta^2)$ which determines the rate of convergence in Eq. (5.9) is always smaller than $(\beta^2-\alpha^2)/\beta^2$ or $(\alpha^2-\beta^2)/\alpha^2$ which determine the rates of convergence in Eqs. (5.7) and (5.8). Our optimism is also supported by the fact that the terminating hypergeometric series ${}_2F_1$ in Eq. (5.9) is bounded. This can be shown with the help of the integral representation (MOS, p. 54)

$${}_2F_1(a,b;c;z) =\frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)}\int_0^1 t^{b-1}(1-t)^{c-b-1}(1-zt)^{-a}dt\ , \tag{5.11}$$

from which we may deduce

$$|{}_2F_1(-\nu,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2)| \leq\frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\ . \tag{5.12}$$

In the following paper[21] we shall present a very detailed study of the different infinite-series expansions which were treated in this section. The main result will be that in all relevant cases the new infinite-series representation (5.9) will be computationally much more attractive than the previously known representations (5.7) and (5.8).

VI. NUCLEAR ATTRACTION AND RELATED INTEGRALS

In this section we shall derive closed-form expressions for the two-center nuclear attraction integral (2.13) and for the overlap integral (2.15).

If we insert the partial fraction decomposition (4.2) into the Fourier integral (3.14) and use the integral representations (3.7) and (3.12) we obtain

$$A_{n,l}^m(\alpha,\mathbf{R})=\frac{4\pi}{\alpha^2}\left[(2l-1)!!\mathscr{Z}_l^m(\alpha\mathbf{R})-\sum_{\nu=0}^{n+l}B_{\nu-l,l}^m(\alpha,\mathbf{R})\right]\ . \tag{6.1}$$

If we use the Taylor expansion (4.13) instead of the partial fraction decomposition (4.2) we obtain an infinite-series expansion:

$$A_{n,l}^m(\alpha,\mathbf{R})=\frac{4\pi}{\alpha^2}\sum_{\nu=0}^{\infty}B_{n+\nu+1,l}^m(\alpha,\mathbf{R})\ . \tag{6.2}$$

Equations (6.1) and (6.2) were already derived by Filter and Steinborn.[56] As a third alternative we may use Eq. (4.27) in the Fourier integral (3.14) which leads to

$$A_{n,l}^m(\alpha,\mathbf{R})=\frac{4\pi}{\alpha^2}2^{n+(l+1)/2} \times\sum_{\nu=0}^{\infty}{}_2F_1(-\nu,n+l+1;n+l+2;2) \times\frac{(n+l+2)_\nu}{\nu!}B_{n+\nu+1,l}^m(2^{-1/2}\alpha,\mathbf{R})\ . \tag{6.3}$$

There is an alternative approach for the derivation of Eqs. (6.1)–(6.3). We can exploit the fact that the Coulomb potential $1/r$ may be considered to be the limiting case of the Yukawa potential $e^{-\epsilon r}/r$ which is essentially the function $B_{0,0}^0(\epsilon,\mathbf{r})$. Hence, we can write

$$A_{n,l}^{m}(\alpha,\mathbf{R})=(4\pi)^{1/2}\lim_{\epsilon\to 0}[\epsilon S_{000}^{nlm}(\epsilon,\alpha,\mathbf{R})] . \qquad (6.4)$$

If we perform this limit in the Jacobi polynomial representation (5.6) we obtain Eq. (6.1), and if we do that in the infinite-series representations (5.7) and (5.9) we obtain Eqs. (6.2) and (6.3). Here, it must be emphasized that it is by no means guaranteed that the resulting expansions (6.2) and (6.3) converge. For every $\epsilon>0$ the infinite-series representations (5.7) and (5.9) for $S_{000}^{nlm}(\epsilon,\alpha,\mathbf{R})$ will converge since their circles of convergence are given by the relationships $|(\alpha^2-\epsilon^2)/\alpha^2|<1$ and $|(\alpha^2-\epsilon^2)/(\alpha^2+\epsilon^2)|<1$, respectively. However, if the limit $\epsilon\to 0$ is performed we are no longer in the interior of the circles of convergence, and it is in general not immediately obvious for which points on its circle of convergence a given series converges or diverges. A very detailed investigation of the infinite series in Eqs. (6.2) and (6.3) and of other series expansions will be given in the following paper.[21]

In the following part of this section we want to derive closed-form expressions for the integral (2.15). For that purpose we could proceed as we did in the case of the nuclear attraction integral (2.13) and insert either the partial fraction decomposition (4.2) or the Taylor expansions (4.13) and (4.27) into the Fourier integral (3.16). Another option would be the use of Eq. (3.10) which implies

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) =[(2l-1)!!]^{-1}\lim_{\epsilon\to 0}[(\epsilon/\alpha)^{l_1+1}S_{-l_1 l_1 m_1}^{n_2 l_2 m_2}(\epsilon,\beta,\mathbf{R})] . \qquad (6.5)$$

However, we prefer to present a third method which is based upon the fact that the application of the spherical tensor gradient $\mathcal{Y}_l^m(\nabla)$ to the Coulomb potential $1/r$ generates the irregular solid harmonic:

$$\mathcal{Z}_l^m(\mathbf{r})=\{(-1)^l/[(2l-1)!!]\}\mathcal{Y}_l^m(\nabla)\frac{1}{r} . \qquad (6.6)$$

This relationship which was in principle already known to Hobson[57] can be proved quite easily using known properties of the spherical tensor gradient. If we use Eq. (6.6) in the integral (2.15) and exploit the fact that a differential operator is invariant under translation, we obtain for the integral (2.15), with $\nabla=\nabla_{\mathbf{R}}$,

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=(-1)^{l_1+l_2}\{\alpha^{l_1+1}[(2l_1-1)!!]\}^{-1} \times[\mathcal{Y}_{l_1}^{m_1}(\nabla)]^* A_{n_2,l_2}^{m_2}(\beta,\mathbf{R}) . \qquad (6.7)$$

Hence, in order to obtain closed-form expressions for the integral (2.15) we only have to differentiate Eqs. (6.1)–(6.3). The remaining differentiations can be done quite easily. We only need[58]

$$[\mathcal{Y}_{l_1}^{m_1}(\nabla)]^* B_{n_2,l_2}^{m_2}(\alpha,\mathbf{R})=(-\alpha)^{l_1}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}B_{n_2+l_2-l-t,l}^{m_2-m_1}(\alpha,\mathbf{R}) \qquad (6.8)$$

$$=(-1)^{l_1+l_2}(\alpha^{l_1+3}/4\pi)S_{-l_1-1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\alpha,\mathbf{R}) \qquad (6.9)$$

and[59]

$$[\mathcal{Y}_{l_1}^{m_1}(\nabla)]^*\mathcal{Z}_{l_2}^{m_2}(\alpha\mathbf{R})=(-\alpha)^{l_1}\{[(2l_1+2l_2-1)!!]/[(2l_2-1)!!]\}\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\alpha,\mathbf{R}) . \qquad (6.10)$$

If we combine Eqs. (6.1) and (6.7) and use Eqs. (6.9) and (6.10) we find

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\{(\beta/\alpha)^{l_1+1}/[(2l_1-1)!!]\}\left[(-1)^{l_2}\frac{4\pi}{\beta^3}\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle[(2l_1+2l_2-1)!!]\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\beta\mathbf{R}) - \sum_{\sigma=0}^{n_2+l_2}S_{-l_1-1,l_1 m_1}^{\sigma-l_2,l_2 m_2}(\beta,\beta,\mathbf{R})\right] . \qquad (6.11)$$

If we insert Eq. (5.3) for the overlap integrals in Eq. (6.11) we find that in general many of the occurring B functions are derivatives of the three-dimensional delta function according to Eq. (3.8). For instance, if we set in Eq. (5.3) $n_1=-l_1-1$ and $n_2=-l_2$ we obtain

$$S_{-l_1-1 l_1 m_1}^{-l_2 l_2 m_2}(\beta,\beta,\mathbf{R})=(-1)^{l_2}\frac{4\pi}{\beta^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}B_{-l-t,l}^{m_2-m_1}(\beta,\mathbf{R}) . \qquad (6.12)$$

Here, only the functions with $t=0$ contribute to the numerical value of the integral. The other functions with $t>0$ are derivatives of the delta functions according to Eq. (3.8) and have to be included only if such an overlap integral is to be used in other integrals.

If we apply the spherical tensor gradient to Eqs. (6.2) and (6.3) we obtain, with the help of Eq. (6.9),

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=\frac{(\beta/\alpha)^{l_1+1}}{(2l_1-1)!!}\sum_{\nu=0}^{\infty}S_{\nu-l_1l_1m_1}^{n_2l_2m_2}(\beta,\beta,\mathbf{R}) \tag{6.13}$$

$$=2^{n_2+(l_2-l_1)/2+1}(\beta/\alpha)^{l_1+1}[(2l_1-1)!!]^{-1}$$
$$\times\sum_{\nu=0}^{\infty}{}_2F_1(-\nu,n_2+l_2+1;n_2+l_2+2;2)\frac{(n_2+l_2+2)_\nu}{\nu!}S_{\nu-l_1l_1m_1}^{n_2l_2m_2}(2^{-1/2}\beta,2^{-1/2}\beta,\mathbf{R})\ . \tag{6.14}$$

If we apply the spherical tensor gradient to the Fourier integral (3.14) and use successively Eqs. (2.7) and (5.1), we find, after some algebra,

$$[\mathcal{Y}_{l_1}^{m_1}(\nabla)]^*A_{n_2,l_2}^{m_2}(\beta,\mathbf{R})=(-\beta)^{l_1}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}A_{n_2+l_2-l-t,l}^{m_2-m_1}(\beta,\mathbf{R})\ . \tag{6.15}$$

This relationship is formally almost identical with Eq. (6.8). If we insert it into Eq. (6.7) we obtain

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=(-1)^{l_2}\beta^{l_1}\alpha^{-l_1-1}[(2l_1-1)!!]^{-1}$$
$$\times\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}A_{n_2+l_2-l-t,l}^{m_2-m_1}(\beta,\mathbf{R})\ . \tag{6.16}$$

Inserting Eq. (6.1) for the nuclear attraction integrals into Eq. (6.16) and discarding all distributive B functions leads after some algebra to another representation for the integral (2.15):

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=(-1)^{l_2}\frac{4\pi}{\beta^3}(\beta/\alpha)^{l_1+1}[(2l_1-1)!!]^{-1}$$
$$\times\Bigg\{(2l_1+2l_2-1)!!\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\beta,\mathbf{R})$$
$$-\sum_{t=0}^{n_2+l_2}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\frac{(1-\Delta l)_t}{t!}B_{n_2+l_2-l-t,l}^{m_2-m_1}(\beta,\mathbf{R})\Bigg\}\ . \tag{6.17}$$

Finally, we want to show how the integrals (2.13) and (2.15) can be computed recursively. From Eq. (6.2) we may deduce

$$A_{n,l}^m(\alpha,\mathbf{R})=A_{n+1,l}^m(\alpha,\mathbf{R})+\frac{4\pi}{\alpha^2}B_{n+1,l}^m(\alpha,\mathbf{R})\ . \tag{6.18}$$

In the same way we obtain from Eq. (6.13)

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=Z_{l_1m_1}^{n_2+1l_2m_2}(\alpha,\beta,\mathbf{R})+\frac{(\beta/\alpha)^{l_1+1}}{(2l_1-1)!!}S_{-l_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})\ . \tag{6.19}$$

VII. COULOMB INTEGRALS

In this section we want to treat Coulomb integrals of B functions. First, we want to consider the simpler case of equal scaling parameters. If we set $\alpha=\beta$ in Eq. (3.15) and compare the resulting expression with Eq. (3.16) we find

$$C_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\alpha,\mathbf{R})=\frac{4\pi}{\alpha^2}[(2l_1-1)!!]Z_{l_1m_1}^{n_1+n_2+l_1l_2m_2}(\alpha,\alpha,\mathbf{R})\ . \tag{7.1}$$

Hence, insertion of Eqs. (6.11), (6.13), (6.14), (6.17), and (6.18) into Eq. (7.1) gives us the following representations for the Coulomb integral with equal scaling parameters:

$$C_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\alpha,\mathbf{R})=(-1)^{l_2}\frac{(4\pi)^2}{\alpha^5}\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle[(2l_1+2l_2-1)!!]\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\alpha\mathbf{R})$$
$$-\frac{4\pi}{\alpha^2}\sum_{\sigma=0}^{n_1+n_2+l_1+l_2+1}S_{-l_1-1l_1m_1}^{\sigma-l_2l_2m_2}(\alpha,\alpha,\mathbf{R}) \tag{7.2}$$

$$=\frac{4\pi}{\alpha^2}\sum_{\nu=0}^{\infty}S_{n_1+\nu l_1m_1}^{n_2+1l_2m_2}(\alpha,\alpha,\mathbf{R}) \tag{7.3}$$

$$=\frac{4\pi}{\alpha^2}2^{n_1+n_2+(l_1+l_2)/2}\sum_{\nu=0}^{\infty}{}_2F_1(-\nu,n_1+n_2+l_1+l_2+2;n_1+n_2+l_1+l_2+3;2)$$

$$\times\frac{(n_1+n_2+l_1+l_2+3)_\nu}{\nu!}S_{n_1+\nu l_1 m_1}^{n_2+1 l_2 m_2}(2^{-1/2}\alpha,2^{-1/2}\alpha,\mathbf{R}) \tag{7.4}$$

$$=(-1)^{l_2}\frac{4\pi}{\alpha^3}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\sum_{t=0}^{\Delta l}(-1)^t\binom{\Delta l}{t}A_{n_1+n_2+l_1+l_2-l-t+1,l}^{m_2-m_1}(\alpha,\mathbf{R}) \tag{7.5}$$

$$=(-1)^{l_2}\frac{(4\pi)^2}{\alpha^5}\Bigg[(2l_1+2l_2-1)!!\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\alpha,\mathbf{R})$$

$$-\sum_{t=0}^{n_1+n_2+l_1+l_2+1}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle\frac{(1-\Delta l)_t}{t!}$$

$$\times B_{n_1+n_2+l_1+l_2-l-t+1,l}^{m_2-m_1}(\alpha,\mathbf{R})\Bigg]. \tag{7.6}$$

Only the infinite-series expansion (7.3) and, in a somewhat disguised form, also Eq. (7.6) are already known.[60] If we compare Eqs. (5.3) and (7.5) we find that there is a remarkable analogy between overlap integrals with equal scaling parameters and Coulomb integrals with equal scaling parameters. Replacement of the B functions in Eq. (5.3) by nuclear attraction integrals yields Eq. (7.5).

Finally, we want to treat the most complicated integral of this paper, the Coulomb integral with different scaling parameters. First, we shall derive representations in which this integral is expressed in terms of simpler integrals such as Coulomb integrals with equal scaling parameters, overlap integrals of B functions, and overlap integrals involving irregular solid harmonics.

Inserting either Eq. (4.5) or (4.6) into the Fourier integral (3.15) yields

$$C_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=\frac{4\pi}{\alpha^2}\left[(2l_1-1)!!Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})-\sum_{\nu=0}^{n_1+l_1}S_{\nu-l_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})\right] \tag{7.7}$$

$$=\frac{4\pi}{\alpha^2}\left[(\beta/\alpha)^{l_1-l_2}[(2l_1-1)!!]Z_{l_1m_1}^{n_1+l_1-l_2l_2m_2}(\beta,\alpha,\mathbf{R})-\sum_{\nu=0}^{n_2+l_2}S_{n_1l_1m_1}^{\nu-l_2l_2m_2}(\alpha,\beta,\mathbf{R})\right]. \tag{7.8}$$

In these two relationships we can set $\alpha=\beta$ and obtain two additional representations for the Coulomb integral with equal scaling parameters.

Inserting the partial fraction decomposition (4.4) into the integral representation (3.15) leads to

$$C_{n_1l_1m_1}^{n_2l_2m_2}(\alpha,\beta,\mathbf{R})=4\pi[(2l_1-1)!!]\Bigg[\frac{(-1)^{n_2+l_2+1}(\beta/\alpha)^{2n_2+l_2-1}}{\alpha^2(n_2+l_2)!}$$

$$\times\sum_{\nu=0}^{n_1+l_1}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_1+l_1-\nu)!}\left[\frac{\alpha^2}{\alpha^2-\beta^2}\right]^{n_1+n_2+l_1+l_2-\nu+1}Z_{l_1m_1}^{\nu-l_2l_2m_2}(\alpha,\alpha,\mathbf{R})$$

$$+\frac{(-1)^{n_1+l_1+1}(\alpha/\beta)^{2n_1+l_1-1}}{\beta^2(n_1+l_1)!}$$

$$\times\sum_{\nu=0}^{n_2+l_2}\frac{(n_1+n_2+l_1+l_2-\nu)!}{(n_2+l_2-\nu)!}$$

$$\times\left[\frac{\beta^2}{\beta^2-\alpha^2}\right]^{n_1+n_2+l_1+l_2-\nu+1}Z_{l_1m_1}^{\nu-l_2l_2m_2}(\beta,\beta,\mathbf{R})\Bigg]. \tag{7.9}$$

In the same way various infinite-series representations can be derived. For instance, from Eq. (4.13) we can derive

$$p^{-2}(\alpha^2+p^2)^{-n_1-l_1-1}(\beta^2+p^2)^{-n_2-l_2-1}=(\alpha^2+p^2)^{-n_1-l_1-1}\sum_{\nu=0}^{\infty}\beta^{2\nu}/(\beta^2+p^2)^{n_2+l_2+\nu+2} \tag{7.10}$$

$$=(\beta^2+p^2)^{-n_2-l_2-1}\sum_{\nu=0}^{\infty}\alpha^{2\nu}/(\alpha^2+p^2)^{n_1+l_1+\nu+2}. \tag{7.11}$$

If we use these expansions in Eq. (3.15) we obtain

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{4\pi}{\alpha^2}\sum_{\nu=0}^{\infty} S_{n_1+\nu+1\,l_1\,m_1}^{n_2\,l_2\,m_2}(\alpha,\beta,\mathbf{R}) \tag{7.12}$$

$$=\frac{4\pi}{\beta^2}\sum_{\nu=0}^{\infty} S_{n_1\,l_1\,m_1}^{n_2+\nu+1\,l_2\,m_2}(\alpha,\beta,\mathbf{R}) \ . \tag{7.13}$$

If we use the Taylor expansions (4.11) and (4.12) in Eq. (3.15) we obtain expansions in terms of Coulomb integrals with equal scaling parameters:

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=(\alpha/\beta)^{2n_1+l_1-1}\sum_{\nu=0}^{\infty}\frac{(n_1+l_1+1)_\nu}{\nu!}\left[\frac{\beta^2-\alpha^2}{\beta^2}\right]^\nu C_{n_1+\nu l_1 m_1}^{n_2 l_2 m_2}(\beta,\beta,\mathbf{R}) \tag{7.14}$$

$$=(\beta/\alpha)^{2n_2+l_2-1}\sum_{\nu=0}^{\infty}\frac{(n_2+l_2+1)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\nu C_{n_1 l_1 m_1}^{n_2+\nu l_2 m_2}(\alpha,\alpha,\mathbf{R}) \ . \tag{7.15}$$

The infinite series in Eqs. (7.14) and (7.15) converge for $\alpha\in(0,2^{1/2}\beta)$ and $\beta\in(0,2^{1/2}\alpha)$, respectively. Alternatively, we can also use the Taylor expansion (4.18) in Eq. (3.15) which yields

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2-1}}$$
$$\times\sum_{\nu=0}^{\infty}\frac{(n_1+n_2+l_1+l_2+2)_\nu}{\nu!}\,{}_2F_1(-\nu,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2)$$
$$\times\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^\nu C_{n_1+\nu l_1 m_1}^{n_2 l_2 m_2}([(\alpha^2+\beta^2)/2]^{1/2},[(\alpha^2+\beta^2)/2]^{1/2},\mathbf{R}) \ . \tag{7.16}$$

If $n_1+l_1=n_2+l_2$ holds then we can use Eq. (4.26) and obtain

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2-1}}$$
$$\times\sum_{\nu=0}^{\infty}\frac{(n_1+l_1+1)_\nu}{\nu!}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^{2\nu} C_{n_1+2\nu l_1 m_1}^{n_2 l_2 m_2}([(\alpha^2+\beta^2)/2]^{1/2},[(\alpha^2+\beta^2)/2]^{1/2},\mathbf{R}) \ . \tag{7.17}$$

We obtain expansions in terms of overlap integrals with equal scaling parameters by inserting either Eq. (4.14) or (4.15) into the integral representation (3.15):

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=\frac{4\pi}{\beta^2}(\alpha/\beta)^{2n_1+l_1-1}\sum_{\nu=0}^{\infty} S_{n_1+\nu l_1 m_1}^{n_2+1 l_2 m_2}(\beta,\beta,\mathbf{R})\sum_{\kappa=0}^{\nu}\frac{(n_1+l_1+1)_\kappa}{\kappa!}\left[\frac{\beta^2-\alpha^2}{\beta^2}\right]^\kappa \tag{7.18}$$

$$=\frac{4\pi}{\alpha^2}(\beta/\alpha)^{2n_2+l_2-1}\sum_{\nu=0}^{\infty} S_{n_1+\nu l_1 m_1}^{n_2+1 l_2 m_2}(\alpha,\alpha,\mathbf{R})\sum_{\kappa=0}^{\nu}\frac{(n_2+l_2+1)_\kappa}{\kappa!}\left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\kappa . \tag{7.19}$$

The infinite series in Eqs. (7.18) and (7.19) converge for $\alpha\in(0,2^{1/2}\beta)$ and $\beta\in(0,2^{1/2}\alpha)$, respectively.

Finally, we insert Eq. (4.28) into the integral representation (3.15) and obtain

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R})=4\pi\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{[(\alpha^2+\beta^2)/2]^{n_1+n_2+(l_1+l_2)/2}}$$
$$\times\sum_{\nu=0}^{\infty} S_{n_1+\nu l_1 m_1}^{n_2+1 l_2 m_2}([(\alpha^2+\beta^2)/2]^{1/2},[(\alpha^2+\beta^2)/2]^{1/2},\mathbf{R})$$
$$\times\sum_{\kappa=0}^{\nu}\left[\frac{\alpha^2-\beta^2}{\alpha^2+\beta^2}\right]^\kappa\frac{(n_1+n_2+l_1+l_2+2)_\kappa}{\kappa!}\,{}_2F_1(-\kappa,n_1+l_1+1;n_1+n_2+l_1+l_2+2;2) \ . \tag{7.20}$$

After these infinite-series expansions we shall derive other representations which contain only a finite number of terms. For that purpose we insert Eq. (6.18) into Eq. (7.9). After some algebra we then obtain

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (-1)^{l_2}(4\pi)^2 \times \Bigg\{ (2l_1+2l_2-1)!!\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle \alpha^{-l_1-3}\beta^{-l_2-3}\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\mathbf{R})$$
$$+(-1)^{n_1+l_1+1}\frac{\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}[(n_1+n_2+l_1+l_2)!]}{(\beta^2-\alpha^2)^{n_1+n_2+l_1+l_2+1}[(n_1+l_1)!][(n_2+l_2)!]} \times \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle$$
$$\times \Bigg[\alpha^{l_1+l_2-1}\sum_{\nu=0}^{n_1+l_1}\frac{(-n_1-l_1)_\nu}{(-n_1-n_2-l_1-l_2)_\nu}\left[\frac{\alpha^2-\beta^2}{\alpha^2}\right]^\nu \times \sum_{t=0}^{\nu}\frac{(1-\Delta l)_t}{t!}B_{\nu-t-l,l}^{m_2-m_1}(\alpha,\mathbf{R})$$
$$-\beta^{l_1+l_2-1}\sum_{\nu=0}^{n_2+l_2}\frac{(-n_2-l_2)_\nu}{(-n_1-n_2-l_1-l_2)_\nu}\left[\frac{\beta^2-\alpha^2}{\beta^2}\right]^\nu \times \sum_{t=0}^{\nu}\frac{(1-\Delta l)_t}{t!}B_{\nu-t-l,l}^{m_2-m_1}(\beta,\mathbf{R}) \Bigg] \Bigg\} . \tag{7.21}$$

Now we proceed as we did in our derivation of Eq. (5.6), i.e., we introduce a new summation variable $\sigma=\nu-t$ and discard all B functions which are derivatives of the delta function according to Eq. (3.8). After rearranging the order of summations we find that the resulting inner sums can be written as terminating hypergeometric series ${}_2F_1$. Since representations in terms of hypergeometric series are in general not unique we choose a representation where the summation variable σ occurs in only one of the three parameters of the ${}_2F_1$:

$$C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (-1)^{l_2}(4\pi)^2 \times \Bigg[(2l_1+2l_2-1)!!\langle l_2,m_2|l_1,m_1|l_1+l_2,m_2-m_1\rangle \alpha^{-l_1-3}\beta^{-l_2-3}\mathcal{Z}_{l_1+l_2}^{m_2-m_1}(\mathbf{R})$$
$$-\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2,m_2|l_1,m_1|l,m_2-m_1\rangle \times \Bigg[\frac{(\alpha/\beta)^{l_2-2}}{\beta^5[1-(\alpha/\beta)^2]^{n_2+l_2+1}} \times \sum_{\sigma=0}^{n_1+l_1}\frac{(n_2+\Delta l_1+2)_{n_1+l_1-\sigma}}{(n_1+l_1-\sigma)!}$$
$$\times {}_2F_1(\sigma-n_1-l_1,n_2+l_2+1;n_2+\Delta l_1+2;\beta^2/(\beta^2-\alpha^2))B_{\sigma-l,l}^{m_2-m_1}(\alpha,\mathbf{R})$$
$$+\frac{(\beta/\alpha)^{l_1-2}}{\alpha^5[1-(\beta/\alpha)^2]^{n_1+l_1+1}} \times \sum_{\sigma=0}^{n_2+l_2}\frac{(n_1+\Delta l_2+2)_{n_2+l_2-\sigma}}{(n_2+l_2-\sigma)!}$$
$$\times {}_2F_1(\sigma-n_2-l_2,n_1+l_1+1;n_1+\Delta l_2+2;\alpha^2/(\alpha^2-\beta^2))B_{\sigma-l,l}^{m_2-m_1}(\beta,\mathbf{R}) \Bigg] \Bigg] . \tag{7.22}$$

The terminating hypergeometric series ${}_2F_1$ in Eq. (7.22) can be computed recursively. If we use Eq. (4.21) we find

$$
\begin{aligned}
(m+n-\sigma+1)\,{}_2F_1(\sigma-n,k+1;m+2;x^2/(x^2-y^2))
&= \left[2n+m-2\sigma-(n+k-\sigma)\frac{x^2}{x^2-y^2}\right]{}_2F_1(\sigma-n+1,k+1;m+2;x^2/(x^2-y^2)) \\
&\quad +(n-\sigma+1)\frac{y^2}{x^2-y^2}\,{}_2F_1(\sigma-n+2,k+1;m+2;x^2/(x^2-y^2)) \, .
\end{aligned} \tag{7.23}
$$

It is well known that every terminating hypergeometric series ${}_2F_1$ can be expressed as a Jacobi polynomial $P_n^{(\alpha,\beta)}$ and vice versa (MOS, pp. 39 and 212). Consequently, we can derive a representation for the Coulomb integral with different scaling parameters which is formally almost identical with the Jacobi polynomial representation of the overlap integral, Eq. (5.6):

$$
\begin{aligned}
C_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta,\mathbf{R}) = (-1)^{l_2}(4\pi)^2 \Bigg\{ & (2l_1+2l_2-1)!!\langle l_2,m_2 | l_1,m_1 | l_1+l_2,m_2-m_1\rangle \alpha^{-l_1-3}\beta^{-l_2-3}\mathcal{Y}_{l_1+l_2}^{m_2-m_1}(\mathbf{R}) \\
& + \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2,m_2 | l_1,m_1 | l,m_2-m_1\rangle \\
& \times \Bigg[(-1)^{n_1+l_1+1}\frac{(\alpha/\beta)^{l_2-2}}{\beta^5[1-(\alpha/\beta)^2]^{n_2+l_2+1}} \\
& \times \sum_{\sigma=0}^{n_1+l_1} (-1)^{\sigma} P_{n_1+l_1-\sigma}^{(\sigma-n_1-\Delta l_2-1,n_2+\Delta l_1+1)}\left[\frac{\beta^2+\alpha^2}{\beta^2-\alpha^2}\right] B_{\sigma-l,l}^{m_2-m_1}(\alpha,\mathbf{R}) \\
& + (-1)^{n_2+l_2+1}\frac{(\beta/\alpha)^{l_1-2}}{\alpha^5[1-(\beta/\alpha)^2]^{n_1+l_1+1}} \\
& \times \sum_{\sigma=0}^{n_2+l_2} (-1)^{\sigma} P_{n_2+l_2-\sigma}^{(\sigma-n_2-\Delta l_1-1,n_1+\Delta l_2+1)}\left[\frac{\alpha^2+\beta^2}{\alpha^2-\beta^2}\right] B_{\sigma-l,l}^{m_2-m_1}(\beta,\mathbf{R}) \Bigg] \Bigg\} \, .
\end{aligned} \tag{7.24}
$$

In Eqs. (7.22) and (7.24) no distributive B functions occur. Consequently, Eq. (7.22) and (7.24) are only correct for numerical evaluations and cannot be used in integrals.

Only Eq. (7.7) and, in a somewhat disguised form, also Eq. (7.18) are already known.[61]

VIII. DISCUSSION

In this section we want to compare our results with the work done by other authors. One of the most important approaches for the evaluation of two-center integrals is based upon the use of confocal elliptical coordinates which possess the symmetry of a two-center problem. Consequently, these coordinates were used quite frequently, in particular in the older literature on multicenter integrals, as it can be seen in the review papers by Huzinaga,[3] Harris and Michels,[4] and Browne.[5] More recent applications of these coordinates can be found in papers by Eschrig,[62] Yasui and Saika,[63] Randic,[64] and Guseinov.[65] However, if we try to compare our results with expressions which were derived using elliptical coordinates we are confronted with the problem that the use of either elliptical or spherical coordinates leads in general to different mathematical structures. Usually, completely different special and auxiliary functions occur. Therefore, it is very hard to compare the efficiency and feasibility of formulas which are expressed in terms of different sets of coordinates. In our opinion, the only meaningful criterion for such a comparison would be the performance of programs. Since this cannot be done here we shall only consider papers in which spherical coordinates are used. In these cases the same mathematical structures as in this paper are bound to appear and comparisons can be made on the level of analytical expressions alone.

If we perform the angular integrations in the Fourier integrals in Eqs. (3.13)—(3.16) using the well-known Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics, we find that the resulting radial integrals are special cases of the following class of integrals:

$$
J_{mn}^{kl}(\alpha,\beta,R) = \int_0^{\infty} \frac{p^{2k+l} j_l(Rp)}{(\alpha^2+p^2)^m(\beta^2+p^2)^n}\,dp \, . \tag{8.1}
$$

Here, $j_l(Rp)$ is a spherical Bessel function and k, l, m, and n are either positive integers or zero.

Integrals which are closely related to the ones in Eq. (8.1) have been studied quite frequently in the literature.

For instance, Geller and Griffith[66] tabulated analytical expressions for the auxiliary functions

$$A(2m;p,q)=\int_0^\infty \frac{t^2 j_{2m}(Rt)}{(\alpha^2+t^2)^p(\beta^2+t^2)^q}dt \tag{8.2}$$

and

$$B(2m+1;p,q)=\int_0^\infty \frac{t^3 j_{2m+1}(Rt)}{(\alpha^2+t^2)^p(\beta^2+t^2)^q}dt\ . \tag{8.3}$$

Their expressions for these integrals are closely related to the Jacobi polynomial representations for overlap and Coulomb integrals, Eqs. (5.6) and (7.24), since they also contain inverse powers of $(\alpha^2-\beta^2)$. In addition, the tabulated expressions contain functions which are closely related to reduced Bessel functions. However, Geller and Griffith did not give any infinite-series representation which would be able to avoid canceling singularities for $\alpha\to\beta$ and $R\to 0$.

Harris and Michels[67] developed a multidimensional recursive scheme by means of which they could compute all integrals of the type of Eq. (8.1) which are required for overlap and Coulomb integrals of Slater-type functions. In the case of nearly equal scaling parameters Harris and Michels modified their recursive algorithm in such a way that it is equivalent to a suitably truncated infinite-series expansion.

Harris[68] also developed a recursive scheme for the evaluation of Coulomb integrals. In this scheme Coulomb integrals are expressed in terms of the simpler nuclear attraction and overlap integrals. Harris was also able to give closed-form expressions for Coulomb integrals. However, all these representations contain canceling singularities for $R\to 0$ and become numerically unstable in that case.

Shakeshaft,[69] who was apparently unaware of the earlier work by Harris and Michels,[67] also developed a recursive scheme for the evaluation of the integral (8.1) but did not devise any precautions for the troublesome case of nearly equal scaling parameters.

Silverstone[9,20,70] also published several papers on overlap and Coulomb integrals of Slater-type functions. However, the formulas given in these papers usually contain complicated differential operators. Consequently, it would be extremely difficult to compare our results with the expressions given by Silverstone and co-workers.

More recently, Jones[71–74] published several papers on overlap and Coulomb integrals of Slater-type functions. His starting point was Löwdin's[75] alpha-function expansion of a Slater-type function and the well-known Laplace expansion of the Coulomb potential. The resulting expressions are then simplified with the help of some computer algebra and all nonvanishing quantities are stored. Jones distinguished between integrals with equal and different scaling parameters. In the case of different scaling parameters Jones obtained expressions involving only a finite number of terms which are equivalent to the Jacobi polynomial representations (5.6) and (7.24), and also truncated Taylor expansions which are to be used for nearly equal scaling parameters. However, all formulas given by Jones for Coulomb integrals contain canceling singularities for $R\to 0$. The advantage of this computer-algebra-oriented approach is that for each individual integral the most compact representation can be derived. The disadvantage of this approach is that no closed-form expressions can be derived and that under unfavorable circumstances fairly long lists of nonvanishing coefficients have to be stored.

In the references mentioned above where overlap and Coulomb integrals of exponential functions were treated, rather complicated mathematical operations involving special functions had to be done and yet in many cases it was not possible to derive closed-form expressions. In the present paper we used B functions instead of Slater-type functions, which leads to considerable mathematical simplifications. The only advanced mathematical concept which we needed is the connection between B functions, classically divergent Fourier integrals, and derivatives of the three-dimensional delta functions. Consequently, we could define the Fourier integral representation for the irregular solid harmonic as a limiting case of the classically divergent Fourier integral representation for the modified Helmholtz harmonic $B^m_{-l,l}$. The other mathematical tools which we needed—partial fraction decompositions and Taylor expansions of rational functions—are fairly elementary.

All we had to do was to transform the denominators of the Fourier integrals (2.12)–(2.15) in such a way that we obtain sums and series of Fourier integral representations for irregular solid harmonics and B functions. Due to the simplicity of our approach we were not only able to simplify the derivation of already known formulas but could also obtain a large number of hitherto unknown representations. It is an interesting side aspect of our approach that we were able to derive numerous analytical expressions for the two-center integrals (2.12)–(2.15) without having to evaluate explicitly a single integral. We also hope that this paper demonstrates that B functions assume indeed an exceptional position among exponentially decreasing functions.

In this paper no attempt was made to analyze the numerical properties of the various representations for the two-center integrals (2.12)–(2.15). These aspects which are very important for practical applications will be discussed in the following paper.[21]

[1]T. Kato, Commun. Pure Appl. Math. **10**, 151 (1951).

[2]S. Agmon, *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operators* (Princeton University, Princeton, N.J., 1982), and references therein.

[3]S. Huzinaga, Prog. Theor. Phys. Suppl. **40**, 52 (1967).

[4]F. E. Harris and H. H. Michels, Adv. Chem. Phys. **8**, 205 (1967).

[5]J. C. Browne, Adv. At. Mol. Phys. **7**, 47 (1971).

[6]*International Conference on ETO Multicenter Molecular Integrals, Tallahassee, 1981*, edited by C. A. Weatherford and H. W. Jones (Reidel, Dordrecht, 1982).

[7]E. O. Steinborn, in *Methods of Computational Molecular Physics*, edited by G. H. F. Diercksen and S. Wilson (Reidel, Dor-

drecht, 1983), p. 37.
[8]M. Geller, J. Chem. Phys. **39**, 84 (1963), Eq. (17).
[9]H. J. Silverstone, J. Chem. Phys. **45**, 4337 (1966), Eq. (13).
[10]P. Kaijser and V. H. Smith, Jr., Adv. Quantum. Chem. **10**, 37 (1977), Eqs. (53), (56), and (57).
[11]E. J. Weniger and E. O. Steinborn, J. Chem. Phys. **78**, 6121 (1983), Eqs. (3.11), (3.15)—(3.17), (3.19), and (3.20).
[12]E. Filter and E. O. Steinborn, Phys. Rev. A **18**, 1 (1978), Eq. (2.14).
[13]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eq. (3.7).
[14]A. W. Niukkanen, Int. J. Quantum Chem. **25**, 941 (1984).
[15]E. J. Weniger and E. O. Steinborn, J. Math. Phys. **24**, 2553 (1983).
[16]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **27**, 670 (1983), and references therein.
[17]J. D. Talman, J. Chem. Phys. **80**, 2000 (1984).
[18]J. Grotendorst and E. O. Steinborn, J. Comput. Phys. **61**, 195 (1985).
[19]J. Grotendorst and E. O. Steinborn (unpublished).
[20]H. D. Todd, K. G. Kay, and H. J. Silverstone, J. Chem. Phys. **53**, 3951 (1970).
[21]J. Grotendorst, E. J. Weniger, and E. O. Steinborn, following paper, Phys. Rev. A **33**, 3706 (1986).
[22]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, New York, 1966). This reference will be denoted as MOS in the text.
[23]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, England, 1970), p. 48.
[24]L. C. Biedenharn and J. D. Louck, *Angular Momentum In Quantum Physics* (Addison-Wesley, Reading, Mass., 1981), p. 71, Eq. (3.153).
[25]F. D. Santos, Nucl. Phys. **A212**, 341 (1973).
[26]E. G. P. Rowe, J. Math. Phys. **19**, 1962 (1978).
[27]B. F. Bayman, J. Math. Phys. **19**, 2558 (1978).
[28]G. Fieck, Theor. Chim. Acta **54**, 323 (1980).
[29]S. N. Stuart, J. Aust. Math. Soc. Ser. B **22**, 368 (1981).
[30]A. W. Niukkanen, J. Math. Phys. **24**, 1989 (1983).
[31]A. W. Niukkanen, J. Math. Phys. **25**, 698 (1984).
[32]E. J. Weniger and E. O. Steinborn, J. Math. Phys. **26**, 644 (1985).
[33]E. J. Weniger and E. O. Steinborn, Comput. Phys. Commun. **25**, 149 (1982), Eq. (3.1).
[34]E. O. Steinborn and E. Filter, Theor. Chim. Acta **38**, 273 (1975), Eq. (3.1).
[35]M. Reed and B. Simon, *Methods of Modern Mathematical Physics II, Fourier Analysis, Self-Adjointness* (Academic, New York, 1975), p. 5, Theorem IX.2.
[36]I. M. Gel'fand and G. E. Shilov, *Generalized Functions I, Properties and Operations* (Academic, New York, 1964), p. 194, Eq. (2).
[37]F. P. Prosser and C. H. Blanchard, J. Chem. Phys. **36**, 1112 (1962).
[38]M. Geller, J. Chem. Phys. **39**, 853 (1963).
[39]H. Triebel, *Theory of Function Spaces* (Birkhäuser, Basel, 1983), p. 28.
[40]An example for such a regularization can be found in E. J. Weniger and E. O. Steinborn, Ref. 11, Appendix.
[41]E. J. Weniger and E. O. Steinborn, Phys. Rev. A **28**, 2026 (1983).
[42]E. J. Weniger, Ph.D. thesis, Universität Regensburg, 1982.
[43]See E. J. Weniger and E. O. Steinborn, Ref. 41, Eq. (3.7).
[44]E. Filter and E. O. Steinborn, J. Math. Phys. **21**, 2725 (1980), Eq. (3.8).
[45]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eq. (3.7).
[46]E. J. Weniger and E. O. Steinborn, Phys. Rev. A **29**, 2268 (1984).
[47]E. J. Weniger, J. Math. Phys. **26**, 276 (1985), Sec. IV.
[48]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eq. (4.12).
[49]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eqs. (4.21)—(4.28); J. Grotendorst and E. O. Steinborn, Ref. 18, Sec. III.
[50]See E. J. Weniger and E. O. Steinborn, Ref. 15, Eq. (6.20).
[51]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eq. (5.1).
[52]See E. J. Weniger and E. O. Steinborn, Ref. 11, Eq. (5.15).
[53]See E. Filter and E. O. Steinborn, Ref. 12, Eq. (5.2).
[54]A. Erdélyi, W. Magnus, F. Oberhettinger, and G. Tricomi, *Higher Transcendental Functions I* (McGraw-Hill, New York, 1953), p. 82.
[55]E. Filter and E. O. Steinborn, J. Math. Phys. **19**, 79 (1978).
[56]See E. Filter and E. O. Steinborn, Ref. 12, Eqs. (6.4) and (6.5).
[57]E. W. Hobson, Proc. London Math. Soc. **24**, 55 (1892). See also E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Chelsea, New York, 1965), p. 127, Eq. (9).
[58]See E. J. Weniger and E. O. Steinborn, Ref. 15, Eq. (6.25).
[59]See E. J. Weniger and E. O. Steinborn, Ref. 32, Eq. (4.7).
[60]See E. Filter and E. O. Steinborn, Ref. 12, Eqs. (7.5) and (7.10).
[61]See E. Filter and E. O. Steinborn, Ref. 12, Eqs. (7.13) and (7.16).
[62]H. Eschrig, Phys. Status Solidi B **96**, 329 (1979).
[63]J. Yaisui and A. Saika, J. Chem. Phys. **76**, 468 (1982).
[64]M. Randic, in Ref. 6, pp. 141—155.
[65]I. I. Guseinov, in Ref. 6, pp. 171—176.
[66]M. Geller and R. W. Griffith, J. Chem. Phys. **40**, 2309 (1964), Eqs. (16) and (17) and Table VIII.
[67]See F. E. Harris and H. H. Michels, Ref. 4, pp. 228—230.
[68]F. E. Harris, J. Chem. Phys. **51**, 4770 (1969).
[69]R. Shakeshaft, J. Comput. Phys. **5**, 345 (1970).
[70]H. J. Silverstone, J. Chem. Phys. **46**, 4368 (1967).
[71]H. W. Jones, Int. J. Quantum. Chem. **18**, 709 (1980).
[72]H. W. Jones, Int. J. Quantum. Chem. **20**, 1217 (1981).
[73]H. W. Jones, Int. J. Quantum. Chem. **19**, 567 (1981).
[74]H. W. Jones, Int. J. Quantum. Chem. **21**, 1079 (1982).
[75]P. O. Löwdin, Adv. Phys. **5**, 1 (1956).