Numerical evaluation of molecular one- and two-electron multicenter integrals with exponential-type orbitals via the Fourier-transform method

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The method of Bonham, Peacher, and Cox for computing molecular multicenter integrals for 1*s* Slater-type orbitals is generalized to include all states. This was possible by using *B* functions as basis functions which have the simplest structure under Fourier transformation, compared with other commonly used exponential-type orbitals (ETO's). Those ETO's which differ from *B* functions, like Slater-type orbitals (STO's), can be expressed by finite linear combinations of *B* functions. Therefore multicenter integrals occurring in molecular calculations with any of the commonly used ETO basis sets can be represented by integrals with *B* functions. In the present paper the three-center nuclear attraction integrals and the two-electron multicenter integrals with *B* functions are evaluated in a unified way via the Fourier-transform method and Feynman's identity. The resulting expressions require a two- or three-dimensional numerical integration, respectively. The numerical and computational properties of the resulting formulas are discussed and various test values are given. Comparison is made with some values of integrals with STO's which exist in the literature.

I. INTRODUCTION

Currently, molecular *ab initio* calculations are carried out mostly by employing Gaussian-type orbitals (GTO's) as basis sets. The popularity of GTO's is largely due to the fact that with GTO's the numerous molecular integrals can be evaluated rather easily. However, it is well recognized that exponential-type orbitals (ETO's) are better suited than GTO's to represent electron wave functions near the nucleus and in long distances. This implies that a lesser number of ETO's than GTO's is needed for comparable accuracy. In spite of the well-known difficulties associated with the evaluation of multicenter ETO molecular integrals, these features of ETO's may become beneficial in the long run, particularly if one goes beyond the Hartree-Fock level either by employing the configuration-interaction method or by employing methods of many-body perturbation theory. Thus the problem of calculating molecular multicenter integrals for ETO's remains of considerable interest. Some recent reviews were given at the 1981 conference on ETO multicenter molecular integrals.[1] A survey of the older literature on evaluation techniques for multicenter integrals can be found in several review papers.[2–4]

One of the most successful methods for the evaluation of multicenter integrals appears to be the 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 simplicity of its Fourier transform. It was shown that *B* functions[5] have the simplest Fourier transforms of all commonly occurring ETO's.[6,7] Consequently, it is not surprising that the Fourier integral representations of overlap, two-center nuclear attraction and Coulomb integrals of *B* functions, and certainly the simpler molecular integrals, could be evaluated analytically in a simple unified way.[8] Furthermore, efficient algorithms for a rapid and accurate calculation of the resulting closed-form expressions could be developed.[9–12] Hence the aforementioned types of molecular integrals with *B* functions can be evaluated in a computationally satisfying way, whereas the evaluation of other one-electron and two-electron integrals with *B* functions, also needed in molecular calculations, was not yet possible. The numerical evaluation of these missing integrals, which is necessary for full-scale molecular calculations, is investigated in the present paper.

In this paper we use the Fourier-transform method and Feynman's identity to evaluate the more complicated multicenter integrals of *B* functions, the three-center nuclear attraction integral, and the four-center exchange integral. The resulting expressions are systematic generalizations of the results which were given by Bonham, Peacher, and Cox[13] for *s*-type orbitals only. The formulas resulting from the analytic manipulations require a two- or three-dimensional numerical integration, respectively. The numerical and computational properties of the resulting representations are discussed extensively and various test values are given.

It should be emphasized that all commonly used ETO's can be expressed by finite linear combinations of *B* functions. Therefore, integrals with such ETO's different from *B* functions, for instance, Slater-type orbitals, can be expressed by a finite number of integrals over *B* functions. Thus, as the more-complicated one- and two-electron multicenter integrals with *B* functions can be evaluated analytically and numerically, as shown in the present paper, the respective integrals with ETO's different from *B* functions can also be evaluated equivalently.

Slater-type orbitals (STO's), the most widely used ETO's, have a very simple structure in the coordinate representation, but less attractive properties under Fourier transformation, whereas *B* functions, being rath-

er complicated in the coordinate representation, have a simple Fourier transform. The integrals with B functions are evaluated by exploiting the advantageous properties of B functions under Fourier transformation. Therefore, it turns out that by going this bypass over the Fourier transformation of B functions, it is possible to arrive at results which are also valuable for the use of other ETO's than B functions with a more cumbersome behavior under Fourier transformation, and which could not be derived by working in coordinate space despite of the fact that such ETO's, like STO's, have a much simpler structure in the coordinate representation than B functions. But this is a by-product of our investigations on the evaluation of multicenter ETO molecular integrals. The main reason for developing economical procedures for multicenter integrals with B functions is to use B functions as basis functions in molecular calculations.

II. DEFINITIONS AND BASIC PROPERTIES

The ETO's used in this paper are the B functions of Filter and Steinborn which are defined as follows:[5]

$$B^m_{n,l}(\alpha,\mathbf{r})=[2^{n+l}(n+l)!]^{-1}\mathcal{Y}^m_l(\alpha\mathbf{r})\hat{k}_{n-1/2}(\alpha r)\ , \tag{2.1}$$

where $n\in\mathbb{Z}$ and $-l\le n<\infty$. The radial part of the B function is described by a reduced Bessel function[14,15] (RBF) which is defined by

$$\hat{k}_\nu(z)=(2/\pi)^{1/2}z^\nu K_\nu(z)\ , \tag{2.2}$$

where $K_\nu(z)$ is the modified Bessel function of the second kind.[16]

The RBF's satisfy the following three-term recurrence relation[17]

$$\hat{k}_{\nu+1}(z)=2\nu\hat{k}_\nu(z)+z^2\hat{k}_{\nu-1}(z)\ . \tag{2.3}$$

Since the RBF's are the dominant solution of this difference equation, the recurrence formula, Eq. (2.3), may safely be used in the upward direction. In the case of half-integral orders, $\nu=n+\frac{1}{2}$, $n\in\mathbb{N}_0$, the RBF's can be represented by an exponential multiplied by a terminating confluent hypergeometric function ${}_1F_1$,[18]

$$\hat{k}_{n+1/2}(z)=2^n(\tfrac{1}{2})_n e^{-z}\,{}_1F_1(-n;-2n;2z)\ . \tag{2.4}$$

Here, $(a)_n$ stands for the Pochhammer symbol[19] which may be defined in terms of the Gamma function $\Gamma(z)$ according to

$$(a)_n=\Gamma(a+n)/\Gamma(a)=a(a+1)\cdots(a+n-1)\ ,$$
$$\text{with } (a)_0=1\ . \tag{2.5}$$

The regular solid harmonic is given by

$$\mathcal{Y}^m_l(\mathbf{r})=r^l Y^m_l(\theta,\phi)\ , \tag{2.6}$$

and the spherical harmonic $Y^m_l(\theta,\phi)$ is defined with the use of the phase convention of Condon and Shortley,[20] i.e.,

$$Y^m_l(\theta,\phi)=i^{m+|m|}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2}\times P_l^{|m|}(\cos\theta)e^{im\phi}\ . \tag{2.7}$$

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

$$P^m_l(x)=(1-x^2)\frac{d^{l+m}}{dx^{l+m}}\left[\frac{(x^2-1)^l}{2^l l!}\right]$$
$$=(1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x)\ . \tag{2.8}$$

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

$$\langle l_3m_3\,|\,l_2m_2\,|\,l_1m_1\rangle=\int[Y^{m_3}_{l_3}(\Omega)]^*Y^{m_2}_{l_2}(\Omega)Y^{m_1}_{l_1}(\Omega)d\Omega\ . \tag{2.9}$$

The Gaunt coefficients linearize the product of two spherical harmonics,

$$[Y^{m_1}_{l_1}(\Omega)]^*Y^{m_2}_{l_2}(\Omega)=\sum_{l=l_{\min}}^{l_{\max}{}^{(2)}}\langle l_2m_2\,|\,l_1m_1\,|\,lm_2-m_1\rangle Y^{m_2-m_1}_l(\Omega)\ . \tag{2.10}$$

The symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two. The summation limits $l_{\min}$ and $l_{\max}$ follow directly from the selection rules for the Gaunt coefficients.[21]

It is important to note that the regular solid harmonic, Eq. (2.6), is a homogeneous polynomial of degree l in the Cartesian components x, y, and z of $\mathbf{r}$;[22]

$$\mathcal{Y}^m_l(\mathbf{r})=\left[\frac{2l+1}{4\pi}(l+m)!\,(l-m)!\right]^{1/2}\times\sum_{k\ge0}\frac{(-x-iy)^{m+k}(x-iy)^k z^{l-m-2k}}{2^{m+2k}(m+k)!\,k!\,(l-m-2k)!}\ . \tag{2.11}$$

If we replace these components of $\mathbf{r}$ by the corresponding Cartesian components of the gradient $\nabla=(\partial/\partial x,\partial/\partial y,\partial/\partial z)$ we obtain the differential operator $\mathcal{Y}^m_l(\nabla)$. With the help of this "spherical tensor gradient" [$\mathcal{Y}^m_l(\nabla)$ is an irreducible spherical tensor of rank l] it is extremely easy to generate nonscalar B functions by differentiating scalar B functions according to[23]

$$B^m_{n,l}(\alpha,\mathbf{r})=(-\alpha)^{-l}(4\pi)^{1/2}\mathcal{Y}^m_l(\nabla)B^0_{n+l,0}(\alpha,\mathbf{r})\ . \tag{2.12}$$

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

$$\bar{f}(\mathbf{p})=(2\pi)^{-3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}}f(\mathbf{r})d^3\mathbf{r} \tag{2.13}$$

and

$$f(\mathbf{r})=(2\pi)^{-3/2}\int e^{i\mathbf{r}\cdot\mathbf{p}}\bar{f}(\mathbf{p})d^3\mathbf{p}\ . \tag{2.14}$$

The Fourier transformation is not only defined for functions that are absolutely integrable but also for functions which belong to the space of tempered distributions.[24] This fact makes it possible to define the Fourier trans-

form of the Coulomb potential,[25]

$$(2\pi)^{-3/2}\int \frac{1}{r}e^{-i\mathbf{p}\cdot\mathbf{r}}d^3\mathbf{r}=\frac{(2/\pi)^{1/2}}{p^2}\ . \tag{2.15}$$

The Fourier transform of a B function is given by[26]

$$\overline{B^m_{n,l}}(\alpha,\mathbf{p})=(2/\pi)^{1/2}\frac{\alpha^{2n+l-1}}{(\alpha^2+p^2)^{n+l+1}}\mathcal{Y}^m_l(-i\mathbf{p})\ . \tag{2.16}$$

The Fourier transforms of all other commonly occurring exponentially decreasing functions, such as the well-known Slater-type functions (STO's), given in normalized form by

$$\chi^m_{n,l}(\alpha,\mathbf{r})=N(n,\alpha)(\alpha r)^{n-1}e^{-\alpha r}Y^m_l(\theta,\phi),\quad n\in\mathbb{N} \tag{2.17}$$

$$N(n,\alpha)=\alpha^{-n+1}[(2\alpha)^{2n+1}/(2n)!]^{1/2}\ , \tag{2.18}$$

can be expressed as linear combinations of Fourier transforms of B functions.[7,27,28]

For the three-center nuclear attraction integral and the two-electron multicenter integral of B functions we write

$$D^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta,\mathbf{R}_1,\mathbf{R}_2)=\int [B^{m_1}_{n_1,l_1}(\alpha,\mathbf{r})]^*\frac{1}{|\mathbf{r}-\mathbf{R}_1|}B^{m_2}_{n_2,l_2}(\beta,\mathbf{r}-\mathbf{R}_2)d^3\mathbf{r}\ , \tag{2.19}$$

$$V^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)=\int\int [B^{m_1}_{n_1l_1}(\rho_1,\mathbf{r}-\mathbf{R}_1)]^*[B^{m_3}_{n_3l_3}(\rho_3,\mathbf{r}'-\mathbf{R}_3)]^*\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$
$$\times B^{m_2}_{n_2l_2}(\rho_2,\mathbf{r}-\mathbf{R}_2)B^{m_4}_{n_4l_4}(\rho_4,\mathbf{r}'-\mathbf{R}_4)d^3\mathbf{r}\,d^3\mathbf{r}'\ . \tag{2.20}$$

We shall also consider the Fourier transform of a two-center product of B functions

$$\tilde{S}^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R};\mathbf{p})=\int e^{-i\mathbf{r}\cdot\mathbf{p}}P^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R};\mathbf{r})d^3\mathbf{r}\ , \tag{2.21}$$

where

$$P^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R};\mathbf{r})=[B^{m_1}_{n_1l_1}(\alpha,\mathbf{r})]^*B^{m_2}_{n_2l_2}(\beta,\mathbf{r}-\mathbf{R}) \tag{2.22}$$

is a two-center charge distribution described by the product of two B functions. It is important to note that the lower indices and the first parameter in the argument list of the symbol P for the two-center charge distribution on the left-hand side of Eq. (2.22) correspond to the quantum numbers, and the exponential parameter of that complex-conjugated B function in the product of two B functions on the right-hand side of Eq. (2.22) which is centered at 0. For short we often write B^m_{nl} for $B^m_{n,l}$ if there is no ambiguity possible.

For overlap integrals of B functions we write

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R})=\int P^{n_2,l_2,m_2}_{n_1,l_1,m_1}(\alpha,\beta;\mathbf{R};\mathbf{r})d^3\mathbf{r}$$
$$=\int [B^{m_1}_{n_1,l_1}(\alpha,\mathbf{r})]^*$$
$$\times B^{m_2}_{n_2,l_2}(\beta,\mathbf{r}-\mathbf{R})d^3\mathbf{r}\ . \tag{2.23}$$

Obviously, the two-center overlap integral, Eq. (2.23), follows as a special case of the Fourier transform of a two-center charge distribution, Eq. (2.22), with the zero transformation vector $\mathbf{p}$, i.e., we have

$$S^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R})=\tilde{S}^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R};0)\ . \tag{2.24}$$

III. FOURIER TRANSFORMATION AND MULTICENTER INTEGRALS

In this section we shall discuss the advantageous properties of the Fourier-transform method for the evaluation of the one- and two-electron multicenter integrals of B functions, Eqs. (2.19)–(2.22). With the help of Eqs. (2.13) and (2.14) it is easy to see that the two-center integrals in coordinate space

$$S(f,g;\mathbf{R})=\int f^*(\mathbf{r})g(\mathbf{r}-\mathbf{R})d^3\mathbf{r} \tag{3.1}$$

and

$$C(f,g,h;\mathbf{R})=\int\int f^*(\mathbf{r})g(\mathbf{r}-\mathbf{r}'-\mathbf{R})h(\mathbf{r}')d^3\mathbf{r}\,d^3\mathbf{r}' \tag{3.2}$$

can be transformed into the following one-center integrals in momentum space:[29,30]

$$S(f,g;\mathbf{R})=\int e^{-i\mathbf{R}\cdot\mathbf{p}}\bar{f}^*(\mathbf{p})\bar{g}(\mathbf{p})d^3\mathbf{p} \tag{3.3}$$

and

$$C(f,g,h;\mathbf{R})=(2\pi)^{3/2}\int e^{-\mathbf{R}\cdot\mathbf{p}}\bar{f}^*(\mathbf{p})\bar{g}(\mathbf{p})\bar{h}(\mathbf{p})d^3\mathbf{p}\ . \tag{3.4}$$

The main advantage of the representations of the two-center integrals (3.1) and (3.2) as inverse Fourier integrals according to Eqs. (3.3) and (3.4) is that a separation of the integration variables can be achieved if f, g, and h are irreducible spherical tensors. This can easily be seen by inserting the well-known Rayleigh expansion of the plane wave in terms of spherical Bessel functions and spherical harmonics,

$$e^{\pm i\mathbf{x}\cdot\mathbf{y}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(\pm i)^l j_l(xy)[Y^m_l(\mathbf{x}/x)]^*$$
$$\times Y^m_l(\mathbf{y}/y)\ , \tag{3.5}$$

into the integrals in Eqs. (3.3) and (3.4), respectively. Obviously, the possibility of evaluating the momentum-space integrals in Eqs. (3.3) and (3.4) in closed form depends crucially upon the functional form of the Fourier transform of the functions involved. It seems that B functions, which have the simplest Fourier transforms of

all commonly occurring ETO's, are the most convenient class of ETO's for the evaluation of multicenter integrals via the Fourier-transform method.

Now, we consider the three-center nuclear attraction integrals

$$D(\Phi_1,\Phi_2;\mathbf{R}_1,\mathbf{R}_2)=\int[\Phi_1(\mathbf{r})]^*\frac{1}{|\mathbf{r}-\mathbf{R}_1|}\Phi_2(\mathbf{r}-\mathbf{R}_2)d^3\mathbf{r} \tag{3.6}$$

$$=\int\frac{1}{|\mathbf{r}-\mathbf{R}_1|}P_{\Phi_1,\Phi_2,\mathbf{R}_2}(\mathbf{r})d^3\mathbf{r}\ , \tag{3.7}$$

where we have introduced the two-center charge distribution

$$P_{\Phi_1,\Phi_2,\mathbf{R}_2}(\mathbf{r})=[\Phi_1(\mathbf{r})]^*\Phi_2(\mathbf{r}-\mathbf{R}_2)\ , \tag{3.8}$$

of so far unspecified one-electron basis functions Φ_1 and Φ_2. If Φ_1 and Φ_2 are B functions, P will be denoted according to Eq. (2.22).

If we combine Eqs. (3.7), (3.3), and (2.15) we obtain

$$D(\Phi_1,\Phi_2;\mathbf{R}_1,\mathbf{R}_2)=(2/\pi)^{1/2}\int\frac{e^{i\mathbf{p}\cdot\mathbf{R}_1}}{p^2}\overline{P_{\Phi_1,\Phi_2,\mathbf{R}_2}}(\mathbf{p})d^3\mathbf{p}\ . \tag{3.9}$$

Whether the Fourier integral representation (3.9) is advantageous for the evaluation of the three-center nuclear attraction integral (3.6) depends essentially upon the possibility of evaluating the Fourier transform of a two-center product $\overline{P_{\Phi_1,\Phi_2,\mathbf{R}_2}}(\mathbf{p})$ efficiently.

The two-electron multicenter integral can be written as

$$V(\Phi_1,\Phi_2,\Phi_3,\Phi_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)=\int\int[\Phi_1(\mathbf{r}-\mathbf{R}_1)]^*\Phi_2(\mathbf{r}-\mathbf{R}_2)\frac{1}{|\mathbf{r}'-\mathbf{r}|}[\Phi_3(\mathbf{r}'-\mathbf{R}_3)]^*\Phi_4(\mathbf{r}'-\mathbf{R}_4)d^3\mathbf{r}\,d^3\mathbf{r}'\ . \tag{3.10}$$

Under the transformations $\mathbf{r}\rightarrow\mathbf{r}+\mathbf{R}_1$ and $\mathbf{r}'\rightarrow\mathbf{r}'+\mathbf{R}_4$ we get

$$V(\Phi_1,\Phi_2,\Phi_3,\Phi_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)=\int\int P_{\Phi_1,\Phi_2,\mathbf{R}_{21}}(\mathbf{r})\frac{1}{|\mathbf{r}'-\mathbf{r}-\mathbf{R}_{14}|}[P_{\Phi_4,\Phi_3,\mathbf{R}_{34}}(\mathbf{r}')]^*d^3\mathbf{r}\,d^3\mathbf{r}' \tag{3.11}$$

using the notation for two-center charge distributions, Eq. (3.8), and $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$. Combining Eqs. (3.11), (3.4), and (2.15) we obtain

$$V(\Phi_1,\Phi_2,\Phi_3,\Phi_4,;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)=4\pi\int e^{-i\mathbf{R}_{14}\cdot\mathbf{p}}\overline{P_{\Phi_1,\Phi_2,\mathbf{R}_{21}}}(\mathbf{p})\frac{1}{p^2}[\overline{P_{\Phi_4,\Phi_3,\mathbf{R}_{34}}}(\mathbf{p})]^*d^3\mathbf{p}\ . \tag{3.12}$$

As in the case of the three-center nuclear attraction integral, the Fourier transform of a two-center product of basis functions forms the basic building block in the Fourier integral representation of the two-electron multicenter integral. Currently, the most promising approach for the evaluation of two-center integrals representing the Fourier transform of a product of two basis functions with centers separated by a distance $\mathbf{R}$,

$$\tilde{S}(\Phi_1,\Phi_2;\mathbf{R};\mathbf{p})=\int e^{-i\mathbf{r}\cdot\mathbf{p}}[\Phi_1(\mathbf{r})]^*\Phi_2(\mathbf{r}-\mathbf{R})d^3\mathbf{r}$$

$$=(2\pi)^{3/2}\overline{P_{\Phi_1,\Phi_2,\mathbf{R}}}(\mathbf{p})\ , \tag{3.13}$$

is the application of the Fourier integral transformation, Eq. (3.3). Identifying $f(\mathbf{r})$ in Eq. (3.1) with $e^{i\mathbf{r}\cdot\mathbf{p}}\Phi_1(\mathbf{r})$ and $g(\mathbf{r})$ with $\Phi_2(\mathbf{r})$ we obtain from Eq. (3.3) that

$$\tilde{S}(\Phi_1,\Phi_2;\mathbf{R};\mathbf{p})=\int e^{-i(\mathbf{p}+\mathbf{p}')\cdot\mathbf{R}}[\overline{\Phi_1}(\mathbf{p}')]^*$$

$$\times\overline{\Phi_2}(\mathbf{p}'+\mathbf{p})d^3\mathbf{p}'\ . \tag{3.14}$$

For $\mathbf{p}=0$ we obtain Eq. (3.3), the Fourier integral representation of overlap integrals, from Eq. (3.14). In this approach it is not the analytical simplicity of a basis function that matters but the analytical simplicity of its Fourier transform. If the basis functions Φ are chosen to be B functions, we get with the help of Eqs. (2.16), (2.21), (2.22), and (3.14)

$$\tilde{S}^{n_2l_2m_2}_{n_1l_1m_1}(\alpha,\beta;\mathbf{R};\mathbf{p})=(2/\pi)\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}\int\frac{[\mathcal{Y}^{m_1}_{l_1}(-i\mathbf{p}')]^*\mathcal{Y}^{m_2}_{l_2}(-i(\mathbf{p}+\mathbf{p}'))e^{-i(\mathbf{p}'+\mathbf{p})\cdot\mathbf{R}}}{(\alpha^2+p'^2)^{n_1+l_1+1}[\beta^2+(\mathbf{p}+\mathbf{p}')^2]^{n_2+l_2+1}}d^3\mathbf{p}'\ . \tag{3.15}$$

Using the so-called Feynman identity[31]

$$\frac{1}{ab}=\int_0^1\frac{1}{[bt+(1-t)a]^2}dt\ , \tag{3.16}$$

Trivedi and Steinborn[32] derived the following relatively compact expression for the Fourier transform of a two-center charge distribution described by the product of B functions,

$$\tilde{S}^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta;\mathbf{R};\mathbf{p})=(4\pi)^3(2l_1+1)!!\,(2l_2+1)!!\frac{(n_1+n_2+l_1+l_2+1)!}{(n_1+l_1)!(n_2+l_2)!}\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}$$
$$\times\sum_{l_1'=0}^{l_1}\sum_{m_1'}\frac{\langle l_1 m_1 \mid l_1' m_1' \mid l_1-l_1' m_1-m_1'\rangle}{(2l_1'+1)!!\,[2(l_1-l_1')+1]!!}[\mathcal{Y}^{m_1-m_1'}_{l_1-l_1'}(\mathbf{p})]^*$$
$$\times\sum_{l_2'=0}^{l_2}\sum_{m_2'}\frac{\langle l_2 m_2 \mid l_2' m_2' \mid l_2-l_2' m_2-m_2'\rangle}{(2l_2'+1)!!\,[2(l_2-l_2')+1]!!}\mathcal{Y}^{m_2-m_2'}_{l_2-l_2'}(\mathbf{p})$$
$$\times\sum_{l=l_{\min}}^{l_1'+l_2'}{}^{(2)}\langle l_2' m_2' \mid l_1' m_1' \mid l m_2'-m_1'\rangle i^{l_1+l_2+l_1'+l_2'}(-1)^{l_1+l_2+l_2'}$$
$$\times\int_0^1 e^{-i(1-t)\mathbf{p}\cdot\mathbf{r}}\frac{t^{n_2+l_2+l_1-l_1'}(1-t)^{n_1+l_1+l_2-l_2'}}{[\gamma(\alpha,\beta;p,t)]^{2(n_1+n_2+l_1+l_2)-(l_1'+l_2')+1}}$$
$$\times\left[\sum_{j=0}^{\Delta l}(-1)^j\binom{\Delta l}{j}B^{m_2'-m_1'}_{n_1+n_2+2\Delta l_0-j+1,\,l}(\gamma(\alpha,\beta;p,t),\mathbf{R})\right]dt\ , \tag{3.17}$$

where

$$\gamma(\alpha,\beta;p,t)=[p^2t(1-t)+\alpha^2(1-t)+\beta^2t]^{1/2}\ , \tag{3.18}$$

$$\Delta l=(l_1'+l_2'-l)/2\ , \tag{3.19}$$

and

$$\Delta l_0=(l_1+l_2-l)/2\ . \tag{3.20}$$

The summation limits of $l_{\min}$, m_1', and m_2' follow directly from the selection rules for the Gaunt coefficient. Another consequence of these selection rules is that Δl as well as Δl_0 are always positive integers or zero. Formula (3.17) is valid for all quantum numbers and orbital scaling parameters of the participating orbitals. It is also independent of the orientation of the coordinate axes and allows an angular momentum decomposition, a fact which is important for an application in the evaluation of the Fourier integral representations of the three-center nuclear attraction integral, Eq. (3.9), and the two-electron multicenter integral, Eq. (3.12). The usefulness of the Fourier integral transformation, Eq. (3.14), in connection with Feynman's identity, Eq. (3.16), for evaluating integrals representing the Fourier transform of a two-center product of ETO's was first noticed by Bonham, Peacher, and Cox.[13] Later, on the basis of the formula of Bonham *et al.* (for *s*-type orbitals only), Guidotti *et al.*[33] derived expressions which are applicable to states of higher angular momentum. They gave one special formula for each combination of two specific STO's. Because of the fact that Slater-type orbitals are given by a linear combination of B functions,[34] Trivedi and Steinborn's result is a systematic generalization of the formulas discussed so far. Several other expressions have been given in the literature for the Fourier transform of a two-center product of ETO's, usually STO's, which were derived using nonspherical coordinates such as elliptical or prolate spheroidal coordinates.[35–38] But these representations in general depend on the orientation of the coordinate axes and do not allow a useful expansion into spherical harmonics. Consequently, these expressions are not suited for an application in the evaluation of the one- and two-electron multicenter integrals, Eqs. (3.6) and (3.10), with the help of their Fourier integral representations, Eqs. (3.9) and (3.12). Recently, the derivation of Eq. (3.17) was simplified considerably by a systematic exploitation of the properties of the spherical tensor gradient $\mathcal{Y}_l^m(\nabla)$ in connection with B functions, and an efficient procedure to compute the resulting one-dimensional integral representation was presented.[39]

Specializing the basis functions Φ_1 and Φ_2 in Eq. (3.6) to B functions we get, from Eqs. (3.6)–(3.9), (2.19), (2.21), (2.22), and (3.13), that

$$D^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta;\mathbf{R}_1,\mathbf{R}_2)=\int\frac{1}{|\mathbf{r}-\mathbf{R}_1|}P^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta;\mathbf{R}_2;\mathbf{r})d^3\mathbf{r} \tag{3.21}$$

$$=(2/\pi)^{1/2}\int\frac{e^{i\mathbf{p}\cdot\mathbf{R}_1}}{p^2}\overline{P^{n_2 l_2 m_2}_{n_1 l_1 m_1}}(\alpha,\beta;\mathbf{R}_2;\mathbf{p})d^3\mathbf{p} \tag{3.22}$$

$$=\frac{1}{2\pi^2}\int\frac{e^{i\mathbf{p}\cdot\mathbf{R}_1}}{p^2}\tilde{S}^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta;\mathbf{R}_2;\mathbf{p})d^3\mathbf{p}\ . \tag{3.23}$$

Now, we insert the one-dimensional integral representation for the Fourier transform of a two-center product of B functions, Eq. (3.17), into Eq. (3.23), and interchange the order of the $\mathbf{p}$ and t integration. The angular integration can readily be done if we use the Rayleigh expansion, Eq. (3.5), for the resulting plane wave and couple the spherical harmonics according to Eq. (2.10). Finally, we eventually arrive at the following result for the three-center nuclear attraction integral with B functions,[32]

$$
\begin{aligned}
&D_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta;\mathbf{R}_1,\mathbf{R}_2) \\
&\quad = 8(4\pi)^2 \frac{(n_1+l_1+n_2+l_2+1)!}{(n_1+l_1)!\,(n_2+l_2)!}(2l_1+1)!!\,(2l_2+1)!!\,\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1} \\
&\qquad \times \sum_{l_1'=0}^{l_1}\sum_{m_1'} \frac{\langle l_1 m_1 \mid l_1' m_1' \mid l_1-l_1' m_1-m_2' \rangle}{(2l_1'+1)!!\,[2(l_1-l_1')+1]!!} \\
&\qquad\quad \times \sum_{l_2'=0}^{l_2}\sum_{m_2'} \frac{\langle l_2 m_2 \mid l_2' m_2' \mid l_2-l_2' m_2-m_2' \rangle}{(2l_2'+1)!!\,[2(l_2-l_2')+1]!!} \\
&\qquad\quad\quad \times \sum_{l=l_{\min}}^{(2)\,l_1'+l_2'} i^{l_1+l_2+l_1'+l_2'}(-1)^{l_1+l_2+l_2'}\langle l_2' m_2' \mid l_1' m_1' \mid l m_2'-m_1' \rangle \\
&\qquad\quad\quad\quad \times \sum_{l'=l'_{\min}}^{(2)\,l_1+l_2-l_1'-l_2'} (-i)^{l'}\langle l_2-l_2' m_2-m_2' \mid l_1-l_1' m_1-m_1' \mid l' m_2-m_2'-m_1+m_1' \rangle \\
&\qquad\quad\quad\quad\quad \times \int_0^1 t^{n_2+l_2+l_1-l_1'}(1-t)^{n_1+l_1-l_2-l_2'} Y_{l'}^{m_2-m_2'-m_1+m_1'}\left[\frac{(1-t)\mathbf{R}_2-\mathbf{R}_1}{|(1-t)\mathbf{R}_2-\mathbf{R}_1|}\right] \\
&\qquad\quad\quad\quad\quad\quad \times \int_0^\infty \frac{p^{l_1-l_1'+l_2-l_2'} j_{l'}(p\,|\,(1-t)\mathbf{R}_2-\mathbf{R}_1\,|)}{[\gamma(\alpha,\beta;p,t)]^{2(n_1+l_1+n_2+l_2)-(l_1'+l_2')+1}} \\
&\qquad\quad\quad\quad\quad\quad\quad \times \left[\sum_{j=0}^{\Delta l}(-1)^j\binom{\Delta l}{j} B_{n_1+n_2+l_1+l_2-l-j+1,\,l}^{m_2'-m_1'}(\gamma(\alpha,\beta;p,t)\mathbf{R}_2)\right] dp\,dt ,
\end{aligned}
\tag{3.24}
$$

where $\gamma(\alpha,\beta;p,t)$ and Δl are defined according to Eq. (3.18) and Eq. (3.19), respectively.

Now, we want to treat two-electron multicenter integrals with B functions. Using the notations in Eqs. (2.20)–(2.22), we obtain from Eqs. (3.10)–(3.13)

$$
\begin{aligned}
&V_{n_1 l_1 m_1, n_3 l_3 m_3}^{n_2 l_2 m_2, n_4 l_4 m_4}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4) \\
&\qquad = \int\int P_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\rho_1,\rho_2;\mathbf{R}_{21};\mathbf{r})\frac{1}{|\mathbf{r}'-\mathbf{r}-\mathbf{R}_{14}|}[P_{n_4 l_4 m_4}^{n_3 l_3 m_3}(\rho_4,\rho_3;\mathbf{R}_{34};\mathbf{r}')]^* d^3\mathbf{r}'\,d^3\mathbf{r} \qquad (3.25) \\
&\qquad = 4\pi\int \frac{e^{-i\mathbf{R}_{14}\cdot\mathbf{p}}}{p^2}\overline{P_{n_1 l_1 m_1}^{n_2 l_2 m_2}}(\rho_1,\rho_2;\mathbf{R}_{21};\mathbf{p})[\overline{P_{n_4 l_4 m_4}^{n_3 l_3 m_3}}(\rho_4,\rho_3;\mathbf{R}_{34};\mathbf{p})]^* d^3\mathbf{p} \qquad (3.26) \\
&\qquad = \frac{1}{2\pi^2}\int \frac{e^{-i\mathbf{R}_{14}\cdot\mathbf{p}}}{p^2}\tilde{S}_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\rho_1,\rho_2;\mathbf{R}_{21};\mathbf{p})[\tilde{S}_{n_4 l_4 m_4}^{n_3 l_3 m_3}(\rho_4,\rho_3;\mathbf{R}_{34};\mathbf{p})]^* d^3\mathbf{p} . \qquad (3.27)
\end{aligned}
$$

As in the case of the three-center nuclear attraction integral, we evaluate the Fourier integral, Eq. (3.27), by substituting the one-dimensional integral representation for the Fourier transform of a two-center product of B functions.

If we collect the plane waves and apply successively the Rayleigh expansion, Eq. (3.5), for the resulting plane wave, and the coupling rule for the spherical harmonics, Eq. (2.10), we obtain, after integrating the angular part of $\mathbf{p}$,

$$
\begin{aligned}
&V^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4) \\
&\quad = 8(4\pi)^3(2l_1+1)!!\,(2l_2+1)!!\,(2l_3+1)!!\,(2l_4+1)!! \\
&\quad\times \frac{(n_1+l_1+n_2+l_2+1)!\,(n_3+l_3+n_4+l_4+1)!}{(n_1+l_1)!\,(n_2+l_2)!\,(n_3+l_3)!\,(n_4+l_4)!}\rho_1^{2n_1+l_1-1}\rho_2^{2n_2+l_2-1}\rho_3^{2n_3+l_3-1}\rho_4^{2n_4+l_4-1} \\
&\quad\times \sum_{l_1'=0}^{l_1}\sum_{m_1'}\frac{\langle l_1 m_1 \mid l_1' m_1' \mid l_1-l_1' m_1-m_1'\rangle}{(2l_1'+1)!!\,[2(l_1-l_1')+1]!!}\sum_{l_2'=0}^{l_2}\sum_{m_2'}\frac{\langle l_2 m_2 \mid l_2' m_2' \mid l_2-l_2' m_2-m_2'\rangle}{(2l_2'+1)!!\,[2(l_2-l_2')+1)]!!} \\
&\quad\times \sum_{l_3'=0}^{l_3}\sum_{m_3'}\frac{\langle l_3 m_3 \mid l_3' m_3' \mid l_3-l_3' m_3-m_3'\rangle}{(2l_3'+1)!!\,[2(l_3-l_3')+1]!!}\sum_{l_4'=0}^{l_4}\sum_{m_4'}\frac{\langle l_4 m_4 \mid l_4' m_4' \mid l_4-l_4' m_4-m_4'\rangle}{(2l_4'+1)!!\,[2(l_4-l_4')+1]!!} \\
&\quad\times i^{l_1+l_2+l_1'+l_2'}(-1)^{l_1+l_2}\sum_{l_{12}=l_{12}^{\min}}^{(2)\ l_1-l_1'+l_2-l_2'}\langle l_2-l_2' m_2-m_2' \mid l_1-l_1' m_1-m_1' \mid l_{12} m_2-m_2'-m_1+m_1'\rangle \\
&\quad\times (-i)^{l_3+l_4+l_3'+l_4'}(-1)^{l_3+l_4}\sum_{l_{34}=l_{34}^{\min}}^{(2)\ l_3-l_3'+l_4-l_4'}\langle l_3-l_3' m_3-m_3' \mid l_4-l_4' m_4-m_4' \mid l_{34} m_3-m_3'-m_4+m_4'\rangle \\
&\quad\times \sum_{l'=l'_{\min}}^{(2)\ l_{12}+l_{34}}\langle l_{12} m_2-m_2'-(m_1-m_1') \mid l_{34} m_3-m_3'-(m_4-m_4') \mid l' m_2-m_2'-(m_1-m_1')-[m_3-m_3'-(m_4-m_4')]\rangle \\
&\quad\times (-i)^{l'}\int_0^1 s^{n_2+l_2+l_1-l_1'}(1-s)^{n_1+l_1+l_2-l_2'}\int_0^1 t^{n_3+l_3+l_4-l_4'}(1-t)^{n_4+l_4+l_3-l_3'} \\
&\quad\times Y_{l'}^{m_2-m_2'-(m_1-m_1')-[m_3-m_3'-(m_4-m_4')]}\left(\frac{(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{34}+\mathbf{R}_{14}}{|(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{34}+\mathbf{R}_{14}|}\right) \\
&\quad\times \int_0^\infty \frac{p^{l_1-l_1'+l_2-l_2'+l_3-l_3'+l_4-l_4'} j_{l'}(p\,|\,(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{34}+R_{14}\,|)}{[\gamma_{12}(\rho_1,\rho_2;p,s)]^{2(n_1+l_1+n_2+l_2)-(l_1'+l_2')+1}[\gamma_{43}(\rho_3,\rho_4;p,t)]^{2(n_3+l_3+n_4+l_4)-(l_3'+l_4')+1}} \\
&\quad\times S^{n_2+l_2-l_2', l_2', m_2'}_{n_1+l_1-l_1', l_1', m_1'}(\gamma_{12}(\rho_1,\rho_2;p,s);\gamma_{12}(\rho_1,\rho_2;p,s);\mathbf{R}_{21}) \\
&\quad\times [S^{n_3+l_3-l_3', l_3', m_3'}_{n_4+l_4-l_4', l_4', m_4'}(\gamma_{43}(\rho_3,\rho_4;p,t),\gamma_{43}(\rho_3,\rho_4;p,t);\mathbf{R}_{34})]^* dp\,dt\,ds\ ,
\end{aligned}
\tag{3.28}
$$

where

$$
\gamma_{12}(\rho_1,\rho_2;p,s)=[p^2 s(1-s)+(1-s)\rho_1^2+s\rho_2^2]^{1/2} \tag{3.29}
$$

and

$$
\gamma_{43}(\rho_3,\rho_4;p,t)=[p^2 t(1-t)+(1-t)\rho_4^2+t\rho_3^2]^{1/2}\ . \tag{3.30}
$$

The overlap integrals with equal scaling parameters in Eq. (3.28) have the following simple representation:[40]

$$
S^{n'l'm'}_{nlm}(\alpha,\alpha;\mathbf{R})=(-1)^{l'}\frac{4\pi}{\alpha^3}\sum_{l''=0}^{(2)\ l+l'}\langle l'm' \mid lm \mid l''m'-m\rangle\sum_{j=0}^{\Delta l}(-1)^j\binom{\Delta l}{j}B^{m'-m}_{n+n'+l+l'-l''-j+1,\,l''}(\alpha,\mathbf{R})\ , \tag{3.31}
$$

with now $\Delta l=(l+l'-l'')/2$.

In the special cases $\mathbf{R}_{21}=0$, or $\mathbf{R}_{34}=0$, or $\mathbf{R}_{21}=\mathbf{R}_{34}=0$ we obtain the simpler three-center hybrid or two-center Coulomb integrals. The Fourier transform of a one-center product of B functions can be evaluated in closed analytic form.[41] Hence, the three-dimensional integral representation in Eq. (3.28) reduces to a two- or one-dimensional integral representation in these cases. In the case of two-center Coulomb integrals the remaining radial p integration can also be done analytically, as is well known. The resulting expression can be represented as a linear combination of B functions.[42]

Bonham, Peacher, and Cox[13] were first to use the Fourier-transform method in connection with Feynman's identity to evaluate the two-electron multicenter integral with 1s Slater-type orbitals. The formula of Bonham *et al.* was the starting point for several analytical and numerical investigations to tackle the general two-electron multicenter integral with ETO's (usually STO's).[43–46] Quite independently Shavitt and Karplus[47,48] obtained an expression which is equivalent to the formula of Bonham *et al.* using the Gaussian-transform method. This method is based on the following integral transformation of a 1s STO, suggested by Kikuchi:[49]

$$e^{-\alpha r}=(\alpha/2)\pi^{-1/2}\int_0^\infty s^{-3/2}e^{-\alpha^2(4s)^{-1}-sr^2}\,ds\ . \tag{3.32}$$

If this is introduced into the multicenter integral, after several transformations of variables and manipulations, one obtains integrals between Gaussians which can be performed analytically and integrals over dummy variables which have to be evaluated numerically. Recently, Tai[50] used an expression of Shakeshaft,[51] a one-dimensional integral representation for a two-center exchange integral associated with the proton-hydrogen collision problem, for the evaluation of molecular multicenter integrals with STO's. He also could reproduce the expression of Bonham *et al.* if all four orbitals are of 1*s* type. Many authors mentioned above were able to generalize the expression of Bonham *et al.* to states with higher quantum numbers by the application of differential operators (with respect to scaling parameters and/or internuclear distances) to the basic 1*s* formula. This method to generate formulas for multicenter integrals involving orbitals with higher quantum numbers by applying differential operators to the starting formula which holds for *s*-type orbitals only was first suggested by Boys.[52] However, no general formula for the four-center integral with STO's was found so far. The results obtained are special formulas for special combinations of STO's only. This is certainly a drawback if one tries to program these formulas. For *B* functions the situation is much simpler. Using Eq. (2.12) we have the following simple relationship between multicenter integrals with nonscalar *B* functions and multicenter integrals with scalar *B* functions:

$$\begin{aligned}V^{n_2l_2m_2,n_4l_4m_4}_{n_1l_1m_1,n_3l_3m_3}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)&=(4\pi)^2(-1)^{l_1+l_2+l_3+l_4}\rho_1^{-l_1}\rho_2^{-l_2}\rho_3^{-l_3}\rho_4^{-l_4}\\&\times[\mathcal{Y}^{m_1}_{l_1}(\nabla_{\mathbf{R}_1})]^*\mathcal{Y}^{m_2}_{l_2}(\nabla_{\mathbf{R}_2})[\mathcal{Y}^{m_3}_{l_3}(\nabla_{\mathbf{R}_3})]^*\mathcal{Y}^{m_4}_{l_4}(\nabla_{\mathbf{R}_4})\\&\times\int\int B^0_{n_1+l_1,0}(\rho_1,\mathbf{r}-\mathbf{R}_1)B^0_{n_3+l_3,0}(\rho_3,\mathbf{r}'-\mathbf{R}_3)\frac{1}{|\mathbf{r}-\mathbf{r}'|}\\&\times B^0_{n_2+l_2,0}(\rho_3,\mathbf{r}-\mathbf{R}_2)\\&\times B^0_{n_4+l_4,0}(\rho_4,\mathbf{r}'-\mathbf{R}_4)d^3\mathbf{r}\,d^3\mathbf{r}'\ .\end{aligned} \tag{3.33}$$

Therefore the general expression for the four-center integral with nonscalar *B* functions, Eq. (3.28), can be obtained by applying four spherical tensor gradients to the simpler expression for the four-center integral with scalar *B* functions which contains no sums. The Fourier transform of STO's can be expressed as linear combinations of Fourier transforms of *B* functions.[6,7] Thus an analogous evaluation of the four-center exchange integral with STO's via the Fourier-transform method, as described above, would yield an expression with the same structure as Eq. (3.28) but containing four additional sums. Hence *B* functions are more convenient for the evaluation of multicenter integrals via the Fourier-transform method than STO's.

It should be noted here that the Fourier-transform method was also used in connection with addition theorems to evaluate molecular multicenter integrals with ETO's (usually STO's).[53–59] However, the resulting representations contain many slowly converging infinite series which lead to nontrivial numerical problems. In some cases, the necessary differentiations, which would lead to very complicated expressions, were not yet carried out.

IV. THREE-CENTER NUCLEAR ATTRACTION INTEGRAL

In this section we want to analyze the numerical properties of the two-dimensional integral representation for the three-center nuclear attraction integral with *B* functions, Eq. (3.24). First we shall consider expression (3.24) for the simpler nuclear attraction integrals with scalar *B* functions. If $l_1=l_2=m_1=m_2=0$ holds and if we replace the integration variable t by $1-s$, we obtain

$$\begin{aligned}D^{n_200}_{n_100}(\alpha,\beta;\mathbf{R}_1,\mathbf{R}_2)=\frac{\alpha^{2n_1-1}\beta^{2n_2-1}}{\pi n_1!\,n_2!\,2^{n_1+n_2}}\int_0^1 s^{n_1}(1-s)^{n_2}\int_0^\infty&\frac{j_0(p\,|\,s\mathbf{R}_2-\mathbf{R}_1\,|\,)}{[\gamma(\alpha,\beta;p,s]^{2n_1+2n_2+1}}\\&\times\hat{k}_{n_1+n_2+1/2}(\gamma(\alpha,\beta;p,s)R_2)dp\,ds\ ,\end{aligned} \tag{4.1}$$

with

$$\gamma(\alpha,\beta;p,s)=[p^2s(1-s)+\alpha^2s+(1-s)\beta^2]^{1/2}\ . \tag{4.2}$$

It is of interest to note that the angular dependence of the geometry of the three centers is contained in the argument of the zeroth-order spherical Bessel function in Eq. (4.1). In order to obtain a reliable and economical procedure for the numerical integration of the two-dimensional integral (4.1) we have to examine the integrand. Although the geometrical parameters $\mathbf{R}_1$ and $\mathbf{R}_2$ and the scaling parameters α and β are connected in quite a complicated fashion, the integrand consists of two

parts in general, one oscillatory part through j_0 and one part which is exponentially decreasing through the $\hat{k}$ function. The behavior of the inner p integrand

$$w_s(p)=\frac{\sin(p\,|\,s\mathbf{R}_2-\mathbf{R}_1\,|\,)}{p\,|\,s\mathbf{R}_2-\mathbf{R}_1\,|\,[\gamma(\alpha,\beta;p,s)]^{2n_1+2n_2+1}} \times\hat{k}_{n_1+n_2+1/2}(\gamma(\alpha,\beta;p,s)R_2) \tag{4.3}$$

is dominated by the exponentially decreasing $\hat{k}$ function as is shown in Fig. 1. The oscillations of j_0 are strongly damped and almost completely suppressed by the $\hat{k}$ function. This implies that a low point quadrature in the vicinity of 0 should yield a good approximation for the inner p integral in Eq. (4.1). Figure 2 shows the integrand of the outer s integral

$$v(s)=s^{n_2}(1-s)^{n_1}\int_0^\infty w_s(p)dp \tag{4.4}$$

for $\alpha=1.0$ and different values of β. With increasing β ($\geq\alpha$) the main contribution to the s integral is shifted from the central part of the integration interval ($\alpha=\beta$) to the upper endpoint of it. A corresponding behavior for $v(s)$ in the vicinity of 0, the lower endpoint of the integration interval, occurs, if β is constant and α ($\geq\beta$) becomes larger. Therefore it is advisable to replace the s integral by a sum of integrals over suitable subintervals by concentrating the integration points around the peaks of the integrands. For the numerical integration of the two-dimensional integral in Eq. (4.1) we used Gauss product rules. The inner semi-infinite p integral was approximated by Gauss-Laguerre formulas and the outer s integral by composite Gauss-Legendre formulas.[60] The weights and abscissas for both Gauss-Laguerre and Gauss-Legendre quadratures were computed with the help of the subroutine D01BCF from the NAG library.[61] The calculation was performed with an accuracy of 11 decimal digits. Since the inner p integrand $w(p)$ is exponentially decreasing the inner p quadrature summation is truncated as soon as a relative accuracy of 10^{-11} is achieved. In Table I we study the convergence behavior of the quadrature method used for the approximation of integral (4.1) having different quantum numbers n_1 and n_2, scaling parameters α and β, and geometries $\mathbf{R}_1$ and $\mathbf{R}_2$. The numbers N_L, N_M, and N_U correspond to the orders of the Gauss-Legendre formulas for the chosen subintervals [0,0.1], [0.1,0.9], and [0.9,1]. The order of the Gauss-Laguerre quadrature used is 80. N_G, the number of evaluations of the inner p integrand, indicates that approximately half of these function evaluations can be saved if the truncation condition for the summation of the inner Gauss-Laguerre quadrature sum mentioned above is used. Therefore, depending upon the precision required, the "tail" of the semi-infinite p integral can be ignored in a practical computation. A comparison of the numerical results in rows 1 and 2 with 3 and 4 of Table I shows that N_G becomes smaller if the radial part of $\mathbf{R}_2$ is

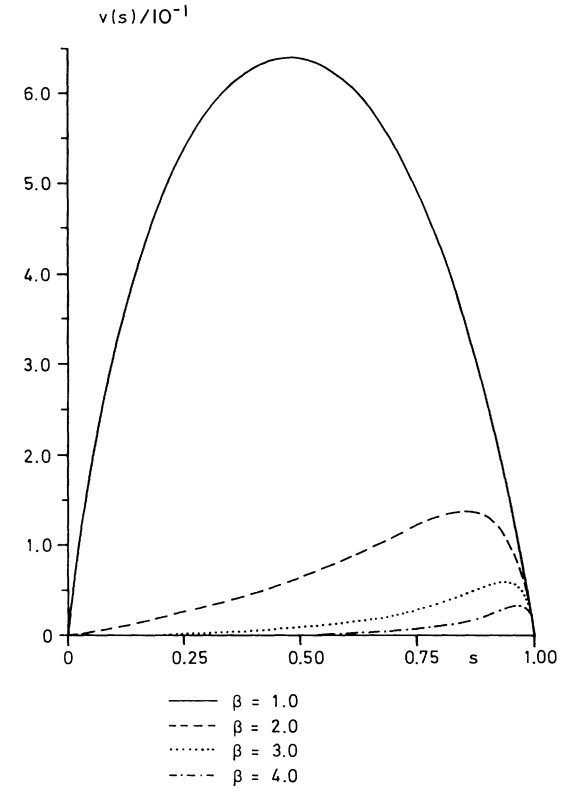

FIG. 2. s integrand $v(s)$, Eq. (4.4), in units 10^{-1}, with parameters as in Fig. 1 but different values of β.

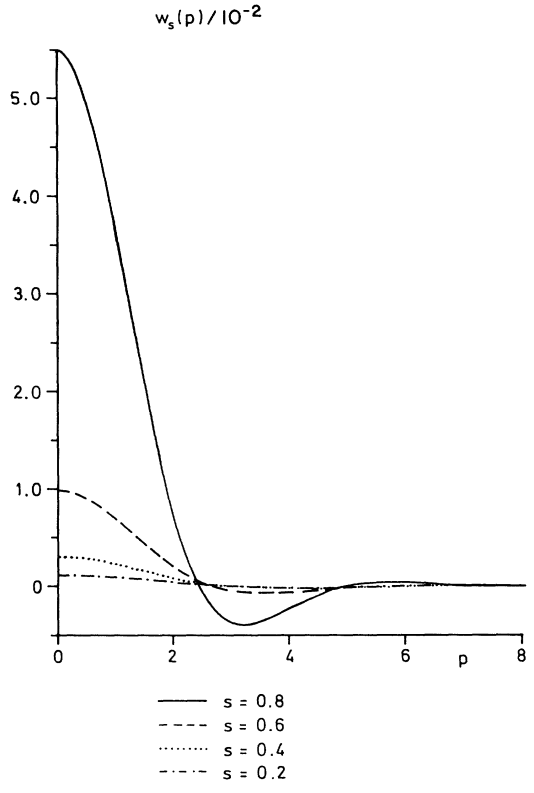

FIG. 1. p integrand $w_s(p)$, Eq. (4.3), in units 10^{-2}, with parameters $n_1=n_2=1$, $\mathbf{R}_1=(1,0,0)$, $\mathbf{R}_2=(0,1,0)$, $\alpha=1.0$, $\beta=4.0$, and different values of s. Lengths are in a.u.

TABLE I. Three-center nuclear attraction integrals with scalar B functions, Eq. (4.1). Numbers in square brackets denote powers of 10 by which the preceding figure is to be multiplied.

n_1	α	n_2	β	(R_1,θ_1,Φ_1)	(R_2,θ_2,Φ_2)	N_L	N_M	N_U	Integral (4.1)	N_G
1.	1.0	1	1.0	(2.0,90.0,0.0)	(1.5,90.0,0.0)	8	20	8	0.292 220 015 9[−01]	1269
1	1.0	1	1.0	(2.0,90.0,0.0)	(1.5,90.0,0.0)	10	30	10	0.292 220 008 7[−01]	1745
1	1.0	1	1.0	(2.0,90.0,0.0)	(10.0,90.0,0.0)	8	20	8	0.419 894 684 7[−04]	700
1	1.0	1	1.0	(2.0,90.0,0.0)	(10.0,90.0,0.0)	10	30	10	0.419 894 695 6[−04]	963
5	1.0	1	1.0	(1.5,90.0,90.0)	(2.0,90.0,90.0)	5	15	10	0.824 710 845 8[−02]	749
5	1.0	1	1.0	(1.5,90.0,90.0)	(2.0,90.0,90.0)	10	25	15	0.824 711 555 5[−02]	1281
5	1.0	1	1.0	(10.0,90.0,90.0)	(2.0,90.0,90.0)	5	15	10	0.158 690 106 3[−02]	735
5	1.0	1	1.0	(10.0,90.0,90.0)	(2.0,90.0,90.0)	10	25	15	0.158 690 139 4[−02]	1255

increased. This is a direct consequence of the fact that $|\mathbf{R}_2|$ is a parameter of the exponential in the $\hat{k}$ function [see Eq. (4.1)] of the p-dependent integrand. However, a variation of the radial part of $\mathbf{R}_1$ leads to no remarkable variation of N_G, as can be seen by a comparison of the results in rows 5 and 6 with 7 and 8 of Table I.

In all applications in which integrals are to be approximated via Gauss quadrature, one has the problem of controlling the produced error. Since theoretical error estimates of Gauss quadrature formulas are not applicable in realistic problems, the error analysis has to be done numerically. An internal error check by comparing an M-point Gauss rule with an N-point Gauss rule $(N>M)$ is uneconomical since Gauss abscissas are in general different for different orders, which implies that such convergence checks require additional function evaluations. Therefore we investigated whether the application of an automatic, adaptive integration method to integral (4.1) which takes into account the special nature of the integrand is an advantageous alternative to Gauss formulas. A quadrature routine is automatic if it provides an approximation of specified tolerance. It is called adaptive if for calculating a sequence of integral approximations the location of the integration points of the nth iterate depends on information gathered from iterates $1,\ldots,n-1$. This is usually achieved by a successive partitioning of the integration interval in such a way that many points are located in the neighborhood of a difficult region of the integrand, causing a high density of quadrature points there. Our integration was performed by using successively the IMSL (Ref. 62) routine DCADRE due to de Boor[63] for the s integration and D01AMF, a QUADPACK (Ref. 64) routine from the NAG library, for the p integration in Eq. (4.1). In Table II we compare the results of the automatic integration method with the results obtained by the Gauss quadrature method mentioned above for various quantum numbers n_1 and n_2, and scaling parameters α and β. N_L, N_M, N_U, and N_G have the same meaning as in Table I, N_A denotes the number of function evaluations of the inner p integrand in integral (4.1) in the case of automatic integration, and "ACCREL" denotes the required relative accuracy. A comparison of the integral approximations with the corresponding numbers of function evaluations of the p integrand shows that the application of suitable composite Gauss product formulas is far superior to a successive performance of automatic integrators, particularly in the case of larger differences of α and β. The numerical problems associated with nested one-dimensional automatic quadrature routines have been discussed by Fritsch *et al.*[65] and Lyness.[66] Lyness estimated that an automatic integration routine in general requires three times as many function evaluations as would be needed by a routine which computes the results with a fixed number of function evaluations on the basis of a properly chosen quadrature rule. Furthermore, an automatic integration routine has a jagged performance profile, whereas a routine implementing a quadrature rule performs much more smoothly. For integrating a jagged integrand function one has to pay an additional surcharge. Consequently, automatic integration is useful only if a few integrals are to be evaluated with a certain guaranteed accuracy and if efficiency is a factor of minor importance. However, if efficiency rather than reliability

TABLE II. Three-center nuclear attraction integrals with scalar B functions, Eq. (4.1). We always have $\mathbf{R}_1=(R_1,\theta_1,\Phi_1)=(0.5,90°,0°)$ and $\mathbf{R}_2=(R_2,\theta_2,\Phi_2)=(2.0,90°,0°)$. Lengths are in a.u. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

n_1	α	n_2	β	N_L	N_M	N_U	"ACCREL"	Adaptive quadrature	N_A	Gaussian quadrature	N_G
1	1.0	1	1.0	4	15	4	1.0[−03]	0.281 224 778 1[−01]	2145	0.281 218 428 4[−01]	708
1	1.0	1	1.0	8	25	8	1.0[−04]	0.281 222 091 2[−01]	6435	0.281 222 151 6[−01]	1322
1	1.0	1	1.0	12	35	12	1.0[−05]	0.281 222 027 6[−01]	8025	0.281 222 111 7[−01]	1907
1	1.0	1	5.0	4	8	10	1.0[−03]	0.401 000 288 8[−03]	11 010	0.401 000 210 1[−03]	859
1	1.0	1	5.0	6	12	15	1.0[−04]	0.400 999 773 6[−03]	12 660	0.400 999 369 7[−03]	1301
1	1.0	1	5.0	8	18	25	1.0[−05]	0.400 999 431 3[−03]	17 685	0.400 999 119 5[−03]	2018

becomes the decisive issue, nested automatic integrators are no longer computationally attractive. In all applications in which a somewhat broader class of integrals are to be evaluated via Gauss quadrature, the error analysis has to be done experimentally. First one has to determine how many integration points are needed to obtain a prescribed accuracy even in the most unfavorable case. Then all integrals in this class will be evaluated with this fixed integration grid.

Apart from a numerical factor, a $1s$ STO is equal to the B function $B^0_{1,0}$. We have explicitly, with Eqs. (2.1) and (2.17),

$$\chi^0_{1,0}(\alpha,\mathbf{r})=4\alpha^{3/2}B^0_{1,0}(\alpha,\mathbf{r}) \ . \tag{4.5}$$

Hence we can compare six integral approximations given in Table II with values in the literature. If we multiply our values by $16(\alpha\beta)^{3/2}$ we obtain an excellent agreement between our results for the B function $B^0_{1,0}$ and the corresponding values 0.449 956 and 0.717 329 from Hirschfelder and Weygandt,[67] and Trivedi and Steinborn,[68] respectively.

Now, we want to analyze numerical and computational aspects of the two-dimensional integral representation (3.24) for the three-center nuclear attraction integral with nonscalar B functions. First we rewrite formula (3.24) in a way which is advantageous for computational purposes. We introduce the new integration variable $s=1-t$, rearrange the order of the m'_1 and l'_2 summations and shift the s and p integral signs in front of the finite sums over the angular momentum and magnetic quantum numbers. This yields the following expression which is quite convenient for computational purposes:

$$\begin{aligned}
&D^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha,\beta;\mathbf{R}_1,\mathbf{R}_2) \\
&=8(4\pi)^2\frac{(2l_1+1)!!\,(2l_2+1)!!\,\alpha^{2n_1+l_1-1}\beta^{2n_2+l_2-1}}{(n_1+l_1)!\,(n_2+l_2)!\,2^{n_1+n_2+l_1+l_2+1}} \\
&\times\int_0^1\int_0^\infty[\gamma(\alpha,\beta;p,s)]^{-2(n_1+l_1+n_2+l_2)-1}\sum_{l'_1=0}^{l_1}\frac{(1-s)^{n_2+l_2+l_1-l'_1}p^{l_1-l'_1}[\gamma(\alpha,\beta;p,s)]^{l'_1}}{(2l'_1+1)!!\,[2(l_1-l'_1)+1]!!} \\
&\times\sum_{l'_2=0}^{l_2}\frac{s^{n_1+l_1+l_2-l'_2}p^{l_2-l'_2}[\gamma(\alpha,\beta;p,s)]^{l'_2}(-1)^{l'_2}}{(2l'_2+1)!!\,[2(l_2-l'_2)+1]!!} \\
&\times\sum_{m'_1=\max(-l'_1,\,m_1-l_1+l'_1)}^{\min(l'_1,\,m_1+l_1-l'_1)}\langle l_1m_1\,|\,l'_1m'_1\,|\,l_1-l'_1m_1-m'_1\rangle \\
&\times\sum_{m'_2=\max(-l'_2,\,m_2-l_2+l'_2)}^{\min(l'_2,\,m_2+l_2-l'_2)}\langle l_2m_2\,|\,l'_2m'_2\,|\,l_2-l'_2m_2-m'_2\rangle \\
&\times\left[\sum_{l=l_{\min}}^{l'_1+l'_2\,(2)}\langle l'_2m'_2\,|\,l'_1m'_1\,|\,lm'_2-m'_1\rangle[R_2\gamma(\alpha,\beta;p,s)]^l Y_l^{m'_2-m'_1}(\mathbf{R}_2/|\,\mathbf{R}_2\,|)\right. \\
&\quad\left.\times\sum_{j=0}^{\Delta l}\frac{(\Delta l-j+1)_j}{j!}(-2)^j(n_1+n_2+l_1+l_2-j+2)_j\hat{k}_{n_1+n_2+l_1+l_2-l-j+1/2}(\gamma(\alpha,\beta;p,s)R_2)\right] \\
&\times\left[\sum_{l'=l'_{\min}}^{l_1+l_2-l'_1-l'_2\,(2)}(-1)^{(l_1-l'_1+l_2-l'_2+l')/2}\langle l_2-l'_2m_2-m'_2\,|\,l_1-l'_1m_1-m'_1\,|\,l'm_2-m'_2-m_1+m'_1\rangle\right. \\
&\quad\left.\times j_{l'}(p\,|\,s\mathbf{R}_2-\mathbf{R}_1\,|\,)Y_{l'}^{m_2-m'_2-m_1+m'_1}\left(\frac{s\mathbf{R}_2-\mathbf{R}_1}{|\,s\mathbf{R}_2-\mathbf{R}_1\,|}\right)\right]dp\,ds \ .
\end{aligned} \tag{4.6}$$

The behavior of the s and p integrand in integral (4.6) is essentially the same as in the case of scalar B functions. The p integrand decreases exponentially and the s integrand may have peaks in the vicinity of 0 or 1, the endpoints of the integration interval. The sharpness of these peaks depends upon the magnitude of the quantum numbers n_1, n_2, l_1, and l_2 and the scaling parameters α and β, as well as on the ratio α/β. This may be seen easily from the factor in front of the first sum of the integrand in Eq. (4.6).

We have written a computer program based on Eq. (4.6). We used the same Gauss quadrature technique as in the case of scalar B functions. Since the integration procedure requires repeated evaluation of the integrand

function of the various abscissas, we precomputed all s- and p-independent coefficients of the integrand, such as the Gaunt coefficients, spherical harmonics, etc., and stored them in appropriate arrays in order to save CPU time. The computation of Gaunt coefficients and spherical harmonics was performed recursively with the help of subroutines GAUNT and RECYLM of Weniger and Steinborn.[69] For the evaluation of the spherical Bessel functions we used the well-known homogeneous three-term recurrence relation[70]

$$j_{n+1}(x)=\frac{(2n+1)}{x}j_n(x)-j_{n-1}(x)\ . \tag{4.7}$$

For $x>N$ (=maximal order to be computed) the recurrence formula (4.7) can safely be used in the upward direction. For $x<N$ this recurrence relation becomes numerically unstable. In this case we used the Miller algorithm.[71] At some value $M>N$ we assume tentatively as starting values $F_{M+1}=0$ and $F_M=1.0$ and use Eq. (4.7) in the backward direction to obtain the sequence $F_N,F_{N-1},\ldots,F_0$. If M was chosen large enough, each term of this sequence up to F_N is proportional, to a certain relative accuracy, to the corresponding term in the sequence $j_N(x),j_{N-1}(x),\ldots,j_0(x)$ of true values. The factor of proportionality may be obtained by comparing F_0 with the true value $j_0(x)=\sin x/x$. The RBF's occurring in Eq. (4.6) were computed with the help of the three-term recurrence relation, Eq. (2.3), which is stable in the upward direction.

In Table III we have listed some test values for the three-center nuclear attraction integral (4.6) with different quantum numbers n_1, l_1, m_1, n_2, l_2, and m_2 and scaling parameters α and β. The values of the spherical coordinates of $\mathbf{R}_1$ and $\mathbf{R}_2$, the scaling parameters α and β, the orders N_L, N_M, and N_U of the composite Gauss-Legendre quadrature used, and the order of the Gauss-Laguerre quadrature used are chosen to be equal for the integrals in Tables II and III. A comparison of N_G in Tables II and III shows that in the case of nonscalar B functions considerably fewer evaluations of the p integrand are needed in order to obtain the same or an even better accuracy. This can immediately be understood by the factor

$$1/[\gamma(\alpha,\beta;p,s)]^q,\quad q=2(n_1+l_1+n_2+l_2)+1$$

in front of the first sum of the integrand in Eq. (4.6). The larger the values of the quantum numbers n_1, l_1, n_2, and l_2 become, the steeper the integrand decreases and the sooner the Gauss-Laguerre quadrature sum is truncated by the convergence truncation condition. A second point is that the absolute values of the nuclear attraction integrals tend to become smaller if the quantum numbers become larger.

Before leaving the topic of three-center nuclear attraction integrals with nonscalar B functions it is legitimate to turn to the question of their correctness and accuracy. We computed the following integral for STO's by using our numerical procedure for B functions and compared the result with values published in the literature:

$$\int \chi^0_{2,1}(1.0,\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{R}_1|}\chi^0_{1,0}(1.0,\mathbf{r}-\mathbf{R}_2)d^3\mathbf{r}\ , \tag{4.8}$$

with $\mathbf{R}=(2.0,120°,0°)$ and $\mathbf{R}_2=(2.0,60°,0°)$. Using Eq. (4.5) and

$$\chi^0_{2,1}(\alpha,\mathbf{r})=16(\alpha^3/3)^{1/2}B^0_{1,1}(\alpha,\mathbf{r})\ , \tag{4.9}$$

which is readily obtained with Eqs. (2.1), (2.4), (2.17), and (2.18), we see that apart from the numerical factor $64/\sqrt{3}$ integral (4.8) is equal to the following three-center nuclear attraction integral with B functions

$$\int B^0_{1,1}(1.0,\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{R}_1|}B^0_{1,0}(1.0,\mathbf{r}-\mathbf{R}_2)d^3\mathbf{r}\ . \tag{4.10}$$

Applying the same quadrature method as in Table III, with $N_L=15$, $N_M=30$, and $N_U=15$ for the composite Gauss-Legendre rules and 80 for the order of the Gauss-Laguerre rule, we obtain 0.001 569 067 4 for integral (4.10).

The published results for integral (4.8) were obtained with quite different mathematical and numerical methods. Trivedi and Steinborn[72] used addition theorems of Λ functions[73] and obtained 0.057 976 (with an uncertainty of 1 in the last figure), whereas Talman[74] gave 0.057 977 3 using Fourier transformation in connec-

TABLE III. Three-center nuclear attraction integrals with nonscalar B functions, Eq. (4.6). Same geometry as in Table II. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

n_1	l_1	m_1	α	n_2	l_2	m_2	β	N_L	N_M	N_U	Integral (4.6)	N_G
5	5	5	1.0	5	5	5	1.0	4	15	4	0.397 767 383 3[−07]	423
5	5	5	1.0	5	5	5	1.0	8	25	8	0.397 767 383 5[−07]	792
5	5	5	1.0	5	5	5	1.0	12	35	12	0.397 767 383 5[−07]	1167
5	5	5	1.0	1	0	0	1.0	4	15	4	−0.696 294 308 7[−07]	565
5	5	5	1.0	1	0	0	1.0	8	25	8	−0.696 224 070 8[−07]	1047
5	5	5	1.0	1	0	0	1.0	12	35	12	−0.696 224 086 5[−07]	1539
3	3	2	1.0	3	3	2	5.0	4	8	10	0.262 083 333 4[−08]	765
3	3	2	1.0	3	3	2	5.0	6	12	15	0.261 740 359 7[−08]	1163
3	3	2	1.0	3	3	2	5.0	8	18	25	0.261 739 808 5[−08]	1803
1	0	0	1.0	5	4	4	5.0	4	8	10	0.621 912 961 4[−05]	754
1	0	0	1.0	5	4	4	5.0	6	12	15	0.621 916 059 0[−05]	1144
1	0	0	1.0	5	4	4	5.0	8	18	25	0.621 916 063 6[−05]	1774

tion with addition theorems for Slater-type orbitals. If we multiply our value by the normalization factor $64/\sqrt{3}$ we obtain 0.057 977 7, which agrees well with the published results.

V. TWO-ELECTRON MULTICENTER INTEGRALS

In this section we shall discuss the properties of the three-dimensional integral representation for the two-electron multicenter integral with B functions, Eq. (3.28), and a numerical-integration technique for its evaluation. As in the case of the three-center nuclear attraction integrals, we first consider expression (3.28) for the simpler integrals with scalar B functions. Setting $l_1=l_2=l_3=l_4=0$ and replacing the integration variable t by $1-t$, we obtain

$$V_{n_1 00,n_3 00}^{n_2 00,n_4 00}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4) = \frac{\rho_1^{2n_1-1}\rho_2^{2n_2-1}\rho_3^{2n_3-1}\rho_4^{2n_4-1}}{n_1!n_2!n_3!n_4!2^{n_1+n_2+n_3+n_4}\pi} \times \int_0^1 (1-s)^{n_1}s^{n_2} \times \int_0^1 (1-t)^{n_3}t^{n_4} \times \int_0^\infty j_0(p\,|\,(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}\,|) \times \frac{\hat{k}_{n_1+n_2+1/2}(\gamma_{12}(\rho_1,\rho_2;p,s)R_{21})\hat{k}_{n_3+n_4+1/2}(\gamma_{34}(\rho_3,\rho_4;p,t)R_{43})}{[\gamma_{12}(\rho_1,\rho_2;p,s)]^{2n_1+2n_2+1}[\gamma_{34}(\rho_3,\rho_4;p,t)]^{2n_3+2n_4+1}}dp\,dt\,ds\ , \tag{5.1}$$

where

$$\gamma_{12}(\rho_1,\rho_2;p,s)=[p^2s(1-s)+(1-s)\rho_1^2+s\rho_2^2]^{1/2} \tag{5.2}$$

and

$$\gamma_{34}(\rho_3,\rho_4;p,t)=[p^2t(1-t)+(1-t)\rho_3^2+t\rho_4^2]^{1/2}\ . \tag{5.3}$$

We note that the angular dependence of the geometry of the four centers as well as the coupling between the one-electron two-center charge distributions $P_{n_1 00}^{n_2 00}(\rho_1,\rho_2;\mathbf{R}_{21};\mathbf{r}_1)$ and $P_{n_4 00}^{n_3 00}(\rho_4,\rho_3;\mathbf{R}_{34};\mathbf{r}_2)$ in the two-electron multicenter integral (3.25) is represented in expression (5.1) by the distance function

$$D_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4}(s,t)=|\,(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}\,| \tag{5.4}$$

in the argument of the zeroth-order spherical Bessel function. Integrating over s and t ($s\in[0,1]$ and $t\in[0,1]$) means that the distance function $D_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4}(s,t)$ runs over all distances between a point $\mathbf{R}$ on the line segment joining $\mathbf{R}_1$ to $\mathbf{R}_2$ and a point $\mathbf{Q}$ on the line segment joining $\mathbf{R}_3$ to $\mathbf{R}_4$ (Fig. 3). Now, we have to study the integrand of the three-dimensional integral in Eq. (5.1). The inner p integrand

$$w_{s,t}(p)=j_0(p\,|\,(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}\,|) \times \frac{\hat{k}_{n_1+n_2+1/2}(\gamma_{12}(\rho_1,\rho_2;p,s)R_{21})\hat{k}_{n_3+n_4+1/2}(\gamma_{34}(\rho_3,\rho_4;p,t)R_{43})}{[\gamma_{12}(\rho_1,\rho_2;p,s)]^{2n_1+2n_2+1}[\gamma_{34}(\rho_3,\rho_4;p,t)]^{2n_3+2n_4+1}} \tag{5.5}$$

consists of three parts in general; the oscillatory Bessel function j_0 and the two exponentially declining reduced Bessel functions $\hat{k}$. The behavior of the p integrand is dominated by the exponentially decreasing $\hat{k}$ functions (Fig. 4). The s and t integrands given by

$$v_s(t)=(1-t)^{n_3}t^{n_4}\int_0^\infty w_{s,t}(p)dp\ , \tag{5.6}$$

$$u(s)=(1-s)^{n_1}s^{n_2}\int_0^1 v_s(t)dt\ , \tag{5.7}$$

may have peaks in the vicinity of 0 or 1, the endpoints of the integration intervals (Figs. 5 and 6). As a result of this special behavior of the s, t, and p integrand in integral (5.1) we choose an integration technique similar to the one we used in the case of the two-dimensional integral representation for the three-center nuclear attraction integral, Eq. (4.1). We applied Gauss product rules composed of Gauss-Laguerre formulas for the inner semi-infinite p integral and composite Gauss-Legendre formulas for the outer s and t integral. For the Gauss-

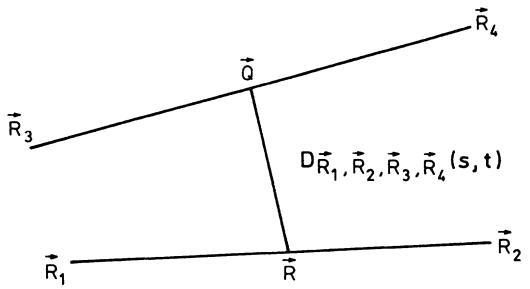

FIG. 3. Points in space used in calculating a four-center integral.

Laguerre quadrature sum we choose the convergence truncation condition 10^{-11}. In Table IV we demonstrate the convergence of the Gauss quadrature for evaluating two-electron multicenter integrals with $\rho_1=\rho_2=\rho_3=\rho_4=1.0$, $n_1=n_2=n_3=n_4=1$, and different nuclear centers $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, and $\mathbf{R}_4$ using representation (5.1). Because in this case the s and t integrand is symmetric with respect to the central point of the integration interval [0,1], the orders N_L, N_M, and N_U of the used composite Gauss-Legendre formulas corresponding to the interval subdivision [0,0.1], [0.1,0.9], and [0.9,1.0] are chosen equal for both the s and t integration. The order of the

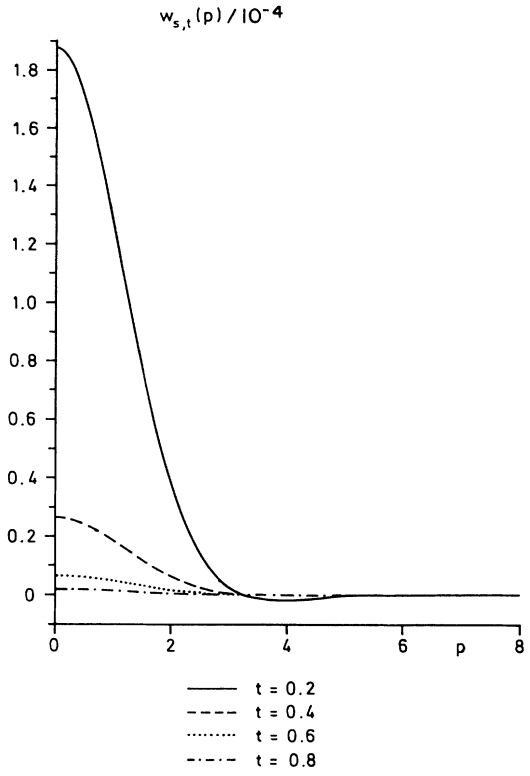

FIG. 4. p integrand $w_{s,t}(p)$, Eq. (5.5), in units 10^{-4}, with parameters $n_1=n_2=n_3=n_4=1$, $\mathbf{R}_1=(0,0,0)$, $\mathbf{R}_2=(1,0,0)$, $\mathbf{R}_3=(0,1,0)$, $\mathbf{R}_4=(0,0,1)$, $\rho_1=\rho_3=1.0$, $\rho_2=\rho_4=4.0$, $s=0.5$, and different values of t. Lengths are in a.u.

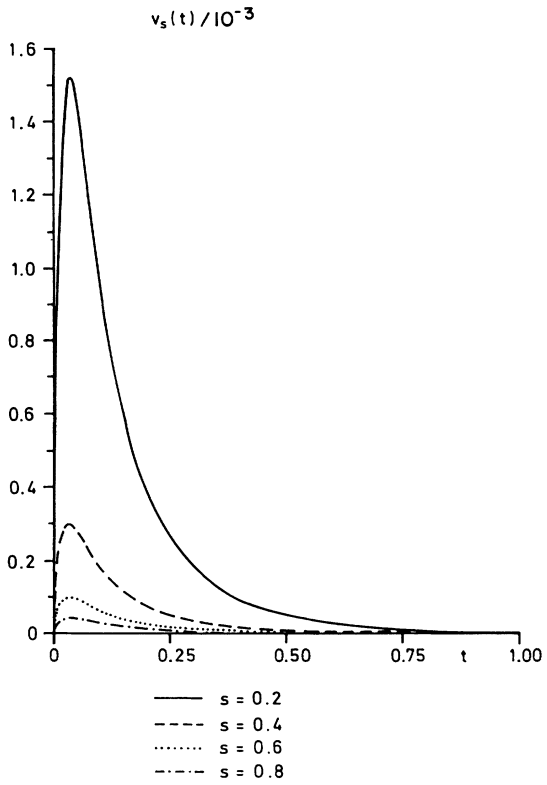

FIG. 5. t integrand $v_s(t)$, Eq. (5.6), in units 10^{-3}, with parameters as in Fig. 4 but different values of s.

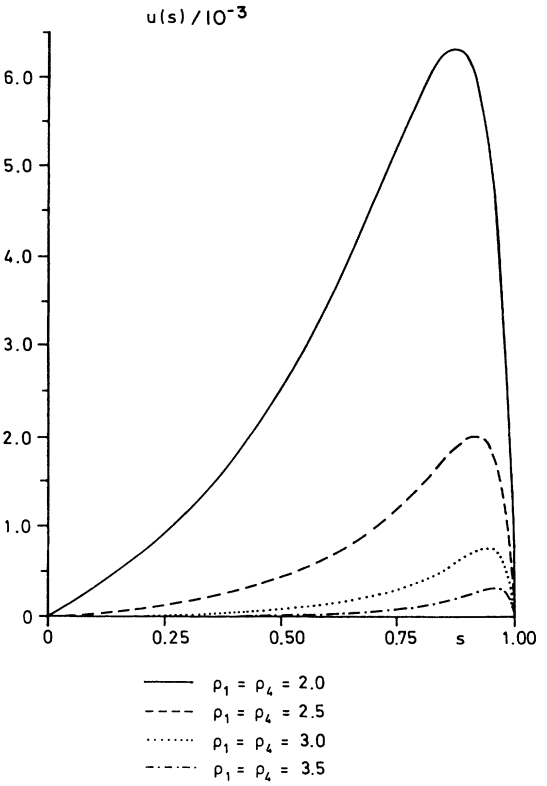

FIG. 6. s integrand $u(s)$, Eq. (5.7), in units 10^{-3}, with parameters as in Fig. 4 but $\rho_2=\rho_3=1.0$ and different values of $\rho_1=\rho_4$.

TABLE IV. Two-electron multicenter integrals with scalar B functions, Eq. (5.1). We always have $n_1=n_2=n_3=n_4=1$ and $\rho_1=\rho_2=\rho_3=\rho_4=1.0$; $\mathbf{R}_i=(X_i,Y_i,Z_i)$, $i=1,2,3,4$. Lengths are in a.u. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

(X_1,Y_1,Z_1)	(X_2,Y_2,Z_2)	(X_3,Y_3,Z_3)	(X_4,Y_4,Z_4)	N_L	N_M	N_U	Integral (5.1)	N_G
(0.0,0.0,0.0)	(0.0,0.0,0.0)	(1.5,0.0,0.0)	(1.5,0.0,0.0)	5	12	5	0.191 538 073 1[−02]	13 900
(0.0,0.0,0.0)	(0.0,0.0,0.0)	(1.5,0.0,0.0)	(1.5,0.0,0.0)	8	20	8	0.191 538 072 4[−02]	37 476
(0.0,0.0,0.0)	(1.0,0.0,0.0)	(1.5,0.0,0.0)	(1.5,0.0,0.0)	5	12	5	0.182 915 804 2[−02]	11 778
(0.0,0.0,0.0)	(1.0,0.0,0.0)	(1.5,0.0,0.0)	(1.5,0.0,0.0)	8	20	8	0.182 915 805 6[−02]	31 684
(−5.0,0.0,0.0)	(5.0,0.0,0.0)	(0.0,5.0,0.0)	(0.0,−5.0,0.0)	5	12	5	0.419 964 122 5[−08]	6000
(−5.0,0.0,0.0)	(5.0,0.0,0.0)	(0.0,5.0,0.0)	(0.0,−5.0,0.0)	8	20	8	0.419 964 121 7[−08]	16 096

Gauss-Laguerre quadrature which we used is 60. A comparison of the numerical results in Table IV shows that N_G, the number of evaluations of the inner p integrand, becomes smaller if the distances R_{21} and/or R_{43} become larger. This is a direct consequence of the fact that R_{21} and R_{43} are parameters of the exponentials in the $\hat{k}$ functions occurring in Eq. (5.1). In Table V we study the approximation behavior of the Gauss quadrature method used in the case of fixed nuclear centers $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, and $\mathbf{R}_4$, various scaling parameters ρ_1, ρ_2, ρ_3, and ρ_4, and quantum numbers n_1, n_2, n_3, and n_4. N_{Ls}, N_{Ms}, and N_{Us} and N_{Lt}, N_{Mt}, and N_{Ut} denote the orders of the composite Gauss-Legendre quadrature used for the s and t integration, respectively. As may be expected, the convergence of the integration procedure becomes slower if the s and/or t integrand possesses a peak in the vicinity of the lower or upper endpoint of the integration interval [0.1]. In these cases (depending on the values of the scaling parameters and quantum numbers), the main contributions to the value of the integral (5.1) come from the first or last subinterval. One has to investigate whether the integration procedure has converged by varying in a suitable way either the width of the subintervals chosen or the number of integration points used there.

Using the relationship (4.5) between a $1s$ STO and the special B Function $B^0_{1,0}$ we can compare the first three integral approximations in Table IV with values in the literature. If we multiply our values by $256(\rho_1\rho_2\rho_3\rho_4)^{3/2}$ we obtain an excellent agreement between our results for the basis functions $B^0_{1,0}$ and the corresponding value 0.296 835 in Table II of Gravac *et al.*[75]

Now, we shall analyze the numerical properties of the three-dimensional integral representation (3.28) for the two-electron multicenter integral with nonscalar B functions. Again, we rewrite formula (3.28) in a way which is advantageous for computational purposes. We replace the integration variable t by $1-t$, rearrange the order of the m'_1 and l'_2, and m'_3 and l'_4 summations and shift the s, t, and p integral sign in front of the finite sums over the angular momentum and magnetic quantum numbers. Using the property

$$[S^{n'l'm'}_{nlm}(\alpha,\beta,\mathbf{R})]^*=S^{n'l'm'}_{nlm}(\alpha,\beta,-\mathbf{R}) \tag{5.8}$$

and replacing the occurring overlap integrals with equal scaling parameters in Eq. (3.28) by their simple analytic representations, Eq. (3.31), we obtain the following expression which is quite convenient for computational purposes and which is the basis of our algorithm:

TABLE V. Two-electron multicenter integrals with scalar B functions, Eq. (5.1). We always have $\mathbf{R}_1=(1.0,0,0)$, $\mathbf{R}_2=(0,0,1.0)$, $\mathbf{R}_3=(0,0,0)$, and $\mathbf{R}_4=(0,0,-1.0)$. Lengths are in a.u. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

n_1	n_2	n_3	n_4	ρ_1	ρ_2	ρ_3	ρ_4	N_{Ls}	N_{Ms}	N_{Us}	N_{Lt}	N_{Mt}	N_{Ut}	Integral (4.1)	N_G
1	1	1	1	1.2	1.2	1.2	1.2	3	6	3	3	6	3	0.409 903 041 6[−03]	3205
1	1	1	1	1.2	1.2	1.2	1.2	4	8	4	4	8	4	0.409 903 072 2[−03]	5716
1	1	1	1	1.2	1.2	1.2	1.2	5	12	5	5	12	5	0.409 903 079 5[−03]	10 698
2	2	2	2	1.2	5.0	1.2	5.0	9	5	3	9	5	3	0.145 474 336 0[−06]	7162
2	2	2	2	1.2	5.0	1.2	5.0	12	7	4	12	7	4	0.145 423 531 1[−06]	13 155
2	2	2	2	1.2	5.0	1.2	5.0	18	9	5	18	9	5	0.145 396 781 4[−06]	25 582
3	1	2	2	1.2	2.0	1.2	6.0	8	10	4	9	5	3	0.739 463 586 3[−06]	8501
3	1	2	2	1.2	2.0	1.2	6.0	11	13	6	13	7	4	0.740 397 237 2[−06]	16 532
3	1	2	2	1.2	2.0	1.2	6.0	15	16	7	17	10	5	0.740 384 772 6[−06]	27 932
4	4	4	4	1.2	3.0	1.2	3.0	9	8	4	9	8	4	0.376 949 720 4[−06]	7823
4	4	4	4	1.2	3.0	1.2	3.0	13	10	5	13	10	5	0.376 976 973 7[−06]	13 987
4	4	4	4	1.2	3.0	1.2	3.0	15	10	6	15	10	6	0.376 976 973 9[−06]	17 360
2	2	2	2	1.2	8.0	1.2	1.2	12	7	4	3	7	3	0.906 168 908 3[−06]	6576
2	2	2	2	1.2	8.0	1.2	1.2	16	9	4	5	11	5	0.906 318 031 8[−06]	13 457

$$
\begin{aligned}
&V^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3}(\rho_1,\rho_2,\rho_3,\rho_4;\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4) \\
&\quad = 8(4\pi)^5 (2l_1+1)!!\,(2l_2+1)!!\,(2l_3+1)!!\,(2l_4+1)!! \\
&\quad\times \frac{\rho_1^{2n_1+l_1-1}\rho_2^{2n_2+l_2-1}\rho_3^{2n_3+l_3-1}\rho_4^{2n_4+l_4-1}(-1)^{l_1+l_2}}{(n_1+l_1)!\,(n_2+l_2)!\,(n_3+l_3)!\,(n_4+l_4)!\,2^{n_1+l_1+n_2+l_2+n_3+l_3+n_4+l_4+2}} \\
&\quad\times \int_0^1 s^{n_2+l_2}(1-s)^{n_1+l_1}\int_0^1 t^{n_4+l_4}(1-t)^{n_3+l_3}\int_0^\infty [\gamma_{12}(\rho_1,\rho_2;p,s)]^{-(2n_1+2n_2+l_1+l_2+1)} \\
&\quad\times [\gamma_{34}(\rho_3,\rho_4;p,t)]^{-(2n_3+2n_4+l_3+l_4+1)} \\
&\quad\times \sum_{l_1'=0}^{l_1} \frac{(-1)^{l_1'}[ps/\gamma_{12}(\rho_1,\rho_2;p,s)]^{l_1-l_1'}}{(2l_1'+1)!!\,[2(l_1-l_1')+1]!!} \sum_{l_2'=0}^{l_2} \frac{[p(1-s)/\gamma_{12}(\rho_1,\rho_2;p,s)]^{l_2-l_2'}}{(2l_2'+1)!!\,[2(l_2-l_2')+1]!!} \\
&\quad\times \sum_{m_1'=\max(-l_1',\,m_1+l_1-l_1')}^{\min(l_1',\,m_1+l_1-l_1')} \langle l_1 m_1 \mid l_1' m_1' \mid l_1-l_1' m_1-m_1'\rangle \sum_{m_2'=\max(-l_2',\,m_2-l_2+l_2')}^{\min(l_2',\,m_2+l_2-l_2')} \langle l_2 m_2 \mid l_2' m_2' \mid l_2-l_2' m_2-m_2'\rangle \\
&\quad\times \Bigg[\sum_{l_{12}=l_{12}^{\min}}^{l_1'+l_2'\,(2)} \langle l_2' m_2' \mid l_1' m_1' \mid l_{12} m_2'-m_1'\rangle [R_{21}\gamma_{12}(\rho_1,\rho_2;p,s)]^{l_{12}} Y_{l_{12}}^{m_2'-m_1'}(\mathbf{R}_{21}/R_{21}) \\
&\qquad\times \sum_{j_{12}=0}^{\Delta l_{12}} \frac{(\Delta l_{12}-j_{12}+1)_{j_{12}}}{j_{12}!}(-2)^{j_{12}}(n_1+n_2+l_1+l_2-j_{12}+2)_{j_{12}}\,\hat{k}_{n_1+n_2+l_1+l_2-l_{12}-j_{12}+1/2}(R_{21}\gamma_{12}(\rho_1,\rho_2;p,s)) \Bigg] \\
&\quad\times \sum_{l_3'=0}^{l_3} \frac{(-1)^{l_3'}[pt/\gamma_{34}(\rho_3,\rho_4;p,t)]^{l_3-l_3'}}{(2l_3'+1)!!\,[2(l_3-l_3')+1]!!} \sum_{l_4'=0}^{l_4} \frac{[p(1-t)/\gamma_{34}(\rho_3,\rho_4;p,t)]^{l_4-l_4'}}{[2l_4'+1)!!\,[2(l_4-l_4')+1]!!} \\
&\quad\times \sum_{m_3'=\max(-l_3',\,m_3+l_3-l_3')}^{\min(l_3',\,m_3+l_3-l_3')} \langle l_3 m_3 \mid l_3' m_3' \mid l_3-l_3' m_3-m_3'\rangle \sum_{m_4'=\max(-l_4',\,m_4-l_4+l_4')}^{\min(l_4',\,m_4+l_4-l_4')} \langle l_4 m_4 \mid l_4' m_4' \mid l_4-l_4' m_4-m_4'\rangle \\
&\quad\times \Bigg[\sum_{l_{34}=l_{34}^{\min}}^{l_3'+l_4'\,(2)} \langle l_4' m_4' \mid l_3' m_3' \mid l_{34} m_4'-m_3'\rangle [R_{43}\gamma_{34}(\rho_3,\rho_4;p,t)]^{l_{34}} Y_{l_{34}}^{m_4'-m_3'}(\mathbf{R}_{43}/R_{43}) \\
&\qquad\times \sum_{j_{34}=0}^{\Delta l_{34}} \frac{(\Delta l_{34}-j_{34}+1)_{j_{34}}}{j_{34}!}(-2)^{j_{34}}(n_3+n_4+l_3+l_4-j_{34}+2)_{j_{34}}\,\hat{k}_{n_3+n_4+l_3+l_4-l_{34}-j_{34}+1/2}(R_{43}\gamma_{34}(\rho_3,\rho_4;p,t)) \Bigg] \\
&\quad\times \Bigg[\sum_{l_{12}'=l_{12}'^{\min}}^{l_1-l_1'+l_2-l_2'\,(2)} \langle l_2-l_2' m_2-m_2' \mid l_1-l_1' m_1-m_1' \mid l_{12}' m_2-m_2'-(m_1-m_1')\rangle \\
&\qquad\times \sum_{l_{34}'=l_{34}'^{\min}}^{l_3-l_3'+l_4-l_4'\,(2)} \langle l_3-l_3' m_3-m_3' \mid l_4-l_4' m_4-m_4' \mid l_{34}' m_3-m_3'-(m_4-m_4')\rangle \\
&\qquad\times \sum_{l'=l'^{\min}}^{l_{12}'+l_{34}'\,(2)} \langle l_{12}' m_2-m_2'-(m_1-m_1') \mid l_{34}' m_3-m_3'-(m_4-m_4') \mid l' m_2-m_2'-(m_1-m_1') \\
&\qquad\qquad -[m_3-m_3'-(m_4-m_4')]\rangle \\
&\qquad\times Y_{l'}^{m_2-m_2'-(m_1-m_1')-[m_3-m_3'-(m_4-m_4')]}\left(\frac{(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}}{|(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}|}\right) \\
&\qquad\times (-1)^{(l_1-l_1'+l_2-l_2'+l_3-l_3'+l_4-l_4'-l')/2} j_{l'}(p\,|(1-s)\mathbf{R}_{21}-(1-t)\mathbf{R}_{43}-\mathbf{R}_{31}|) \Bigg] dp\,dt\,ds\ , \qquad (5.9)
\end{aligned}
$$

where

$$\Delta l_{12}=(l_1'+l_2'-l_{12})/2 , \tag{5.10}$$

$$\Delta l_{34}=(l_3'+l_4'-l_{34})/2 , \tag{5.11}$$

and $\gamma_{12}(\rho_1,\rho_2;p,s)$ and $\gamma_{34}(\rho_3,\rho_4;p,t)$ are defined according to Eqs. (5.2) and (5.3), respectively. For the numerical integration of the three-dimensional integral in Eq. (5.9) it is important to note that the behavior of the s, t, and p integrand is essentially the same as in the case of scalar B functions. The p integrand decreases exponentially and the s and t integrand may have peaks in the vicinity of 0 or 1, the endpoints of their integration intervals [0,1]. The sharpness of these peaks depends essentially upon (i) the magnitude of the orbital parameters n_i, l_i, m_i, and ρ_i, $i=1,2,3,4$, (ii) the asymmetry of the two-center charge distributions (occurring if the ratios ρ_1/ρ_2 and/or ρ_3/ρ_4 differ greatly from unity), and (iii) the disparity of the two distributions with respect to their exponential parameters [as measured by the ratio $(\rho_1+\rho_2)/(\rho_3+\rho_4)$]. This may be deduced easily from the two factors in front of the first sum of the integrand in Eq. (5.9).

We have written a program based on Eq. (5.9) using the same Gauss quadrature technique for the numerical integration as in the case of scalar B functions. In order to save CPU time we precomputed all coefficients of the integrand which are independent of s, t, and p, such as Gaunt coefficients, spherical harmonics, etc., and stored them in appropriate arrays. The algorithms we applied for the evaluation of the Gaunt coefficients, spherical harmonics, spherical Bessel functions, and $\hat{k}$ functions are already described in Sec. IV. In Tables VI and VII we summarize some typical test values for two-electron multicenter integrals over nonscalar B functions with various quantum numbers n_i, l_i, and m_i, $i=1,2,3,4$, and exponential parameters ρ_i, $i=1,2,3,4$. Varying the orders N_{Ls}, N_{Ms}, and N_{Us} and N_{Lt}, N_{Mt}, and N_{Ut} of the composite Gauss-Legendre quadrature formulas used on the subintervals [0,0.1], [0.1,0.9], and [0.9,1.0] for the s and t integration, we demonstrate the convergence of the integration procedure in the case of four-center exchange (Table VI) and two-center Coulomb integrals (Table VII). The order of the Gauss-Laguerre quadrature used, with truncation condition 10^{-11} for the quadrature sum, is 50. A comparison of the numerical results in Tables VI and VII shows that N_G, the number of evaluations of the inner p integrand, becomes larger if the distances R_{21} and R_{43} become smaller. As in the case of scalar B functions, this can be explained by the fact that R_{21} and R_{43} are parameters of the exponentials in the $\hat{k}$ functions occurring in Eq. (5.9) and therefore determine how rapidly the p integrand decreases. A second point, easily seen from the results in Tables VI and VII, is that integrals in which the exponential parameters ρ_i of the four B functions are of similar magnitude converge much better than integrals with highly asymmetric charge distributions, i.e., when there are large differences between the exponential parameters. This may be explained by the occurrence of sharp peaks in the vicinity of 0 or 1, the endpoints of the integration intervals [0,1] for the s and t integration.

In order to support the reliability of our numerical procedure for calculating molecular multicenter integrals with exponential-type orbitals, especially for the case that nonscalar orbitals are used, we give some integral values with Slater-type orbitals (STO's) and compare these with some previously published results. This may be helpful because STO's are widely used ETO's.

Normalized STO's, Eqs. (2.17) and (2.18), can be expressed as linear combinations of B functions in the following way:[5]

$$\chi_{n,l}^{m}(\alpha,\mathbf{r})=\alpha^{-n+1}[(2\alpha)^{2n+1}/(2n)!]^{1/2} \times\sum_{p=p_{\min}}^{n-l}\frac{(-1)^{n-l-p}(n-l)!\,2^{l+p}(l+p)!}{(2p-n+l)!\,(2n-2l-2p)!!} \times B_{p,l}^{m}(\alpha,\mathbf{r}) , \tag{5.12}$$

where

$$p_{\min}=\begin{cases}(n-l)/2 & \text{if } n-l \text{ is even}\\ (n-l+1)/2 & \text{if } n-l \text{ is odd} .\end{cases} \tag{5.13}$$

Many authors[14,48,50,59] have used the configurations of the C and H atoms in CH_4 with C-H distances of 2 a.u. to calculate test values for molecular multicenter integrals. The H and C orbitals are given by

$$(1s)_{\mathrm{H}_i}(1.0,\mathbf{r})=\pi^{-1/2}e^{-r},\quad i=1,2,3,4 , \tag{5.14}$$

$$(1s)_{\mathrm{C}}(5.7,\mathbf{r})=(5.7^3/\pi)^{1/2}e^{-5.7r} , \tag{5.15}$$

$$(2p)_{\mathrm{C}}(1.625,\mathbf{r})=[(1.625)^5/\pi]^{1/2}re^{-1.625r}\tilde{Y}_1^{m}(\theta,\phi) , \tag{5.16}$$

with

$$\tilde{Y}_1^{m}(\theta,\phi)=\begin{cases}\cos\theta & \text{if } m=0\\ \sin\theta\cos\phi & \text{if } m=1\\ \sin\theta\sin\phi & \text{if } m=-1 .\end{cases} \tag{5.17}$$

In Table VIII we compare some integral values with STO's for the methane molecule which are obtained by using our integral evaluation procedure for B functions, with results previously published in the literature. The applied quadrature method is the same as the method applied in Tables VI and VII except that we use the truncation condition 10^{-8} for the Gauss-Laguerre quadrature sum. In Table VIII, it is seen that our method indeed generates accurate values for the multicenter integrals with STO's. Furthermore, a comparison of columns 8, 10, and 11 in Table VIII shows that our method yields results of the same level of accuracy as the method of Shavitt and Karplus,[48] even with fewer quadrature points.

TABLE VI. Four-center exchange integrals with nonscalar B functions, Eq. (5.9). Same geometry as in Table V and $\rho_1=\rho_3=1.2$. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

n_1	l_1	m_1	n_2	l_2	m_2	n_3	l_3	m_3	n_4	l_4	m_4	ρ_2	ρ_4	N_{Ls}	N_{Ms}	N_{Us}	N_{Lt}	N_{Mt}	N_{Ut}	Integral (5.9)	N_G
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	3	6	3	3	6	3	0.499 200 613 4[−04]	2994
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	4	8	4	4	8	4	0.499 200 627 7[−04]	5359
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	5	12	5	5	12	5	0.499 200 601 9[−04]	10 009
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	9	5	3	9	5	3	0.360 943 559 0[−09]	6876
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	12	7	4	12	7	4	0.360 261 790 2[−09]	12 594
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	18	9	5	18	9	5	0.360 181 111 6[−09]	24 472
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	8	10	4	9	5	3	0.341 662 297 7[−10]	8167
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	11	13	6	13	7	4	0.341 361 307 1[−10]	15 867
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	15	16	7	17	10	5	0.341 297 873 8[−10]	26 843
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	9	8	4	9	8	4	0.452 596 461 6[−19]	8121
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	13	10	5	13	10	5	0.452 591 300 8[−19]	14 515
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	15	10	6	15	10	6	0.452 591 300 8[−19]	18 014
2	2	2	2	2	2	2	2	2	2	2	2	8.0	1.2	12	7	4	3	7	3	0.534 761 979 7[−10]	5517
2	2	2	2	2	2	2	2	2	2	2	2	8.0	1.2	16	9	4	5	11	5	0.534 869 360 8[−10]	11 272

TABLE VII. Two-center Coulomb integrals with nonscalar B functions, Eq. (5.9). We always have $\mathbf{R}_1=(1.0,0,0)$, $\mathbf{R}_2=(1.0,0,0)$, $\mathbf{R}_3=(0,0,0)$, $\mathbf{R}_4=(0,0,0)$, and $\rho_1=\rho_3=1.2$. Numbers in square brackets denote powers of 10 by which the preceding number is to be multiplied.

n_1	l_1	m_1	n_2	l_2	m_2	n_3	l_3	m_3	n_4	l_4	m_4	ρ_2	ρ_4	N_{Ls}	N_{Ms}	N_{Us}	N_{Lt}	N_{Mt}	N_{Ut}	Integral (5.9)	N_G
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	3	6	3	3	6	3	0.116 475 172 8[−03]	3380
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	4	8	4	4	8	4	0.116 475 536 6[−03]	6100
1	1	0	1	1	0	1	0	0	1	0	0	1.2	1.2	5	12	5	5	12	5	0.116 475 544 6[−03]	11 516
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	9	5	3	9	5	3	0.187 659 823 9[−10]	7722
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	12	7	4	12	7	4	0.187 151 485 8[−10]	14 222
2	2	2	2	1	0	2	1	0	2	0	0	5.0	5.0	18	9	5	18	9	5	0.187 106 266 0[−10]	27 523
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	8	10	4	9	5	3	0.456 758 111 7[−09]	9759
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	11	13	6	13	7	4	0.456 411 622 9[−09]	18 951
3	0	0	1	1	−1	2	2	−2	2	0	0	2.0	6.0	15	16	7	17	10	5	0.456 334 856 5[−09]	32 030
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	9	8	4	9	8	4	0.127 202 933 0[−17]	8816
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	13	10	5	13	10	5	0.127 218 615 0[−17]	15 782
4	4	4	4	0	0	4	4	4	4	0	0	3.0	3.0	15	10	6	15	10	6	0.127 218 615 0[−17]	19 573
2	2	2	2	2	2	2	2	2	2	2	2	8.0	1.2	12	7	4	3	7	3	0.182 062 557 1[−09]	5883
2	2	2	2	2	2	2	2	2	2	2	2	8.0	1.2	16	9	4	5	11	5	0.182 062 490 8[−09]	12 050

TABLE VIII. Multicenter integrals with nonscalar STO's for the methane molecule. We have $R_C=(0,0,0)$, $\mathbf{R}_{H(1)}=(0,0,-2)$, $\mathbf{R}_{H(2)}=\frac{1}{3}(4\sqrt{2},0,2)$ $\mathbf{R}_{H(3)}=\frac{1}{3}(-2\sqrt{2},2\sqrt{6},2)$, and $\mathbf{R}_{H(4)}=\frac{1}{3}(-2\sqrt{2},-2\sqrt{6},2)$.

Integral[a]	N_{Ls}	N_{Ms}	N_{Us}	N_{Lt}	N_{Mt}	N_{Ut}	Result	N_G	Comparison value[b]	Comparison value[c]
$[(1s)_C(1s)_{H(1)};(2p_z)_C(1s)_{H(2)}]$	5	10	10	5	15	5	0.005 885 28	11 265	0.005 884 57	0.005 885 22
$[(2p_z)_C(1s)_{H(1)};(2p_z)_C(1s)_{H(2)}]$	5	15	5	5	15	5	0.008 548 58	10 124	0.008 548 64	0.008 548 49
$[(2p_z)_C(1s)_C;(1s)_{H(1)}(1s)_{H(2)}]$	10	10	5	5	15	5	−0.001 675 88	11 158	−0.001 675 84	−0.001 675 81
$[(2p_z)_C(2p_z)_C;(1s)_{H(1)}(1s)_{H(2)}]$	5	15	5	5	15	5	0.140 912 33	9361	0.140 912 36	0.140 912
$[(2p_z)_C(2p_z)_C;(2p_z)_C(1s)_{H(1)}]$	5	15	5	5	15	5	−0.255 022 61	11 252	−0.255 020 24	
$[(1s)_C(1s)_{H(1)};(2p_x)_C(1s)_{H(2)}]$	5	10	10	5	15	5	0.019 809 02	10 981	0.019 807 04	0.019 809 03
$[(2p_z)_C(1s)_{H(1)};(2p_x)_C(1s)_{H(2)}]$	5	15	5	5	15	5	−0.077 914 78	9880	−0.077 914 35	−0.077 914 52
$[2p_x)_C(1s)_C;(1s)_{H(1)}(1s)_{H(2)}]$	10	10	5	5	15	5	0.002 370 04	11 158	0.002 369 99	0.002 370 04
$[(2p_x)_C(2p_z)_C;(1s)_{H(1)}(1s)_{H(2)}]$	5	15	5	5	15	5	−0.001 435 98	10 371	−0.001 435 99	−0.001 435 79

[a]The first two symbols refer to the orbitals of the first electron, the last two symbols refer to the orbitals of the second electron.
[b]See Ref. 48, Table I, column 5; $24\times24\times28=16\,128$ quadrature points.
[c]Pitzer (see Ref. 48, Table I, footnote d), using the Barnett and Coulson (Ref. 76) method.

VI. SUMMARY

In this paper we present analytical and numerical methods for the evaluation of three-center nuclear attraction integrals and two-electron multicenter integrals with B functions. B functions, which are a special class of exponentially decreasing functions, have a relatively complicated analytical structure in coordinate space. However, the Fourier transform of a B function is of exceptional simplicity. The Fourier transforms of all other commonly used exponential-type orbitals, like Slater-type orbitals, can be expressed as linear combinations of Fourier transforms of B functions.[7,27,28] Consequently, B functions are the most convenient class of exponential-type orbitals for the evaluation of multicenter integrals via the Fourier-transform method. In Sec. III we apply the Fourier-transform theory in a unified way to three-center nuclear attraction integrals and two-electron multicenter integrals of B functions. It turns out that the Fourier-transform of a two-center product of B functions forms the basic building block in the Fourier integral representations of these multicenter integrals. Using our compact expression for the Fourier transform of a two-center charge distribution described by a product of B functions[32] (involving a one-dimensional numerical integration) the evaluation of the Fourier integral representations of the multicenter integrals mentioned above is readily accomplished. The resulting expressions are systematic generalizations of the results which Bonham, Peacher, and Cox[13] derived for s-type orbitals only.

In Sec. IV we analyze the numerical performance of the two-dimensional integral representation for the three-center nuclear attraction integral of B functions, Eq. (4.5). It turns out that Gauss product rules composed of Gauss-Laguerre formulas and special composite Gauss-Legendre formulas are best suited for the numerical quadrature of the remaining double integral. As is demonstrated by the convergence of the applied integration technique, we had no difficulty obtaining integral values with an accuracy of 6–8 decimal places for a sufficiently wide range of values of the orbital parameters n, l, m, and ρ and the geometrical parameters $\mathbf{R}_i$.

In Sec. V we analyze the numerical performance of the three-dimensional integral representation for the two-electron multicenter integral of B functions, Eq. (5.9). Since the integrand of representation (5.9) shows a similar behavior as the integrand of representation (4.5) for the three-center nuclear attraction integral, we again apply Gauss product rules composed of Gauss-Laguerre formulas and two special composite Gauss-Legendre formulas to the remaining triple integral in representation (5.9). The numerical results show that this integration procedure converges satisfactorily for exponential parameters of similar magnitude and a broad range of quantum numbers and geometrical parameters. For integrals with highly asymmetric charge distributions, i.e., when there are large differences between the exponential parameters, problems with the convergence of the Gauss-Legendre quadrature sums soon arise. However, we think that with a quadrature rule which would be better adapted to these numerical problems, this difficulty can be overcome.

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[1]*International Conference on ETO Multicenter Molecular Integrals, Tallahassee, 1981,* edited by C. A. Weatherford and H. W. Jones (Reidel, Dordrecht, 1982).
[2]S. Huzinaga, Prog. Theor. Phys. Suppl. **40**, 52 (1967).

[3]F. E. Harris and H. H. Michels, Adv. Chem. Phys. **8**, 205 (1967).
[4]J. C. Browne, Adv. At. Mol. Phys. **7**, 47 (1971).
[5]E. Filter and E. O. Steinborn, Phys. Rev. A **18**, 1 (1978), Eq. (2.14).
[6]E. J. Weniger and E. O. Steinborn, J. Chem. Phys. **78**, 6121 (1983).
[7]A. W. Niukkanen, Int. J. Quantum Chem. **25**, 941 (1984).
[8]E. J. Weniger, J. Grotendorst, and E. O. Steinborn, Phys. Rev. A **33**, 3688 (1986).
[9]D. Antolović and J. Delhalle, Phys. Rev. A **21**, 1815 (1980).
[10]E. J. Weniger and E. O. Steinborn, Phys. Rev. A **28**, 2026 (1983).
[11]A. K. Bhattacharya and S. C. Dhabal, J. Chem. Phys. **84**, 1598 (1986).
[12]J. Grotendorst, E. J. Weniger, and E. O. Steinborn, Phys. Rev. A **33**, 3706 (1986).
[13]R. A. Bonham, J. L. Peacher, and H. L. Cox, Jr., J. Chem. Phys. **40**, 3083 (1964).
[14]I. Shavitt, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2, p. 15, Eq. (55).
[15]E. O. Steinborn and E. Filter, Theor. Chim. Acta **38**, 273 (1975), Eq. (3.1).
[16]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, New York, 1966), p. 66.
[17]See Ref. 14, Eq. (2.12).
[18]See Ref. 6, Eq. (3.7).
[19]See Ref. 16, p. 2.
[20]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1970), p. 48.
[21]E. J. Weniger and E. O. Steinborn, Comput. Phys. Commun. **25**, 149 (1982), Eq. (3.1).
[22]L. C. Biedenharn and J. D. Louck, *Angular Momentum Theory in Quantum Physics* (Addison-Wesley, Reading, MA., 1981), p. 71, Eq. (3.153).
[23]See Ref. 6, Eq. (4.12).
[24]M. Reed and B. Simon, *Methods of Modern Mathematical Physics II, Fourier Analysis, Self-Adjointness* (Academic, New York, 1975), p. 5, Theorem IX.2.
[25]I. M. Gel'fand and G. E. Shilov, *Generalized Functions I, Properties and Operations* (Academic, New York, 1964), p. 194, Eq. (2).
[26]See Ref. 6, Eq. (3.7).
[27]E. J. Weniger and E. O. Steinborn, Phys. Rev. A **29**, 2268 (1984).
[28]E. J. Weniger, J. Math. Phys. **26**, 276 (1985), Sec. IV.
[29]F. P. Prosser and C. H. Blanchard, J. Chem. Phys. **36**, 1116 (1962).
[30]M. Geller, J. Chem. Phys. **39**, 853 (1963).
[31]R. P. Feynman, Phys. Rev. **76**, 769 (1949), Eq. (14.a).
[32]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **27**, 670 (1983).
[33]G. Guidotti, G. P. Arrighini, and F. Marinelli, Theor. Chim. Acta **53**, 165 (1979).
[34]See Ref. 5, Eqs. (3.3) and (3.4).
[35]J. Bentley and F. Stuart, J. Comput. Phys. **11**, 127 (1973).
[36]R. McCarroll, Proc. R. Soc. London **264**, 547 (1961).
[37]R. B. Junker, J. Phys. B **13**, 1049 (1980).
[38]R. B. Junker, Comput. Phys. Commun. **23**, 377 (1981).
[39]J. Grotendorst and E. O. Steinborn, J. Comput. Phys. **61**, 195 (1985).
[40]E. Filter and E. O. Steinborn, J. Math. Phys. **19**, 79 (1978), Eq. (4.1).
[41]J. Grotendorst, Ph.D. thesis, Universität Regensburg, 1985, p. 177, Eq. (7.1-7).
[42]See Ref. 12, Sec. VII.
[43]P. J. Roberts, Proc. Phys. Soc. London **89**, 63 (1966).
[44]H. Partridge III, Ph.D. thesis, Indiana University, Bloomington, 1978.
[45]A. Graovac, H. J. Monkhorst, and T. Zivkovic, Int. J. Quantum Chem. **7**, 233 (1973).
[46]A. Graovac, K. Kovačević, Z. B. Maksić, and A. Veseli, Int. J. Quantum Chem. **17**, 747 (1980).
[47]I. Shavitt and M. Karplus, J. Chem. Phys. **36**, 550 (1962).
[48]I. Shavitt and M. Karplus, J. Chem. Phys. **43**, 398 (1965).
[49]R. Kikuchi, J. Chem. Phys. **22**, 148 (1954).
[50]H. Tai, J. Phys. B **12**, 177 (1979).
[51]R. Shakeshaft, J. Phys. B **8**, L134 (1975).
[52]S. F. Boys, Proc. R. Soc. London **200**, 542 (1950).
[53]H. J. Silverstone, J. Chem. Phys. **48**, 4098 (1968); **48**, 4106 (1968).
[54]H. J. Silverstone and K. G. Kay, J. Chem. Phys. **48**, 4108 (1968).
[55]H. D. Todd, K. C. Daiker, R. D. Cloney, S. J., R. K. Moats, and H. J. Silverstone, Ref. 1, p. 73.
[56]R. K. Moats, Ph.D. thesis, Johns Hopkins University, Baltimore, 1981.
[57]D. Antolović, Ph.D. thesis, Johns Hopkins University, Baltimore, 1983.
[58]B. K. Novosadov, Int. J. Quantum Chem. **24**, 1 (1983).
[59]J. D. Talman, J. Chem. Phys. **80**, 2000 (1984).
[60]P. J. Davis and P. Rabinowitz, *Methods of Numerical Integration* (Academic, New York, 1984). See Sec. 2.7, pp. 95–132.
[61]The NAG FORTRAN Library, Mark 8, Numerical Analysis Group, NAG Central Office, Oxford, U.K., 1981.
[62]International Mathematical and Statistical Library, Inc., Houston, Texas.
[63]C. de Boor, in *Mathematical Software*, edited by J. R. Rice (Academic, New York, 1971).
[64]R. Piessens, E. de Doncker-Kapenga, C. W. Überhuber, and D. K. Kahaner, *QUADPACK, a Subroutine Package for Automatic Integration* (Springer, New York, 1983), pp. 64–65.
[65]F. N. Fritsch, D. K. Kahaner and J. N. Lyness, ACM Trans. Math. Software **7**, 46 (1981).
[66]J. N. Lyness, SIAM Rev. **25**, 63 (1983).
[67]J. O. Hirschfelder and C. N. Weygandt, J. Chem. Phys. **6**, 806 (1938).
[68]See Ref. 32, Table II.
[69]See Ref. 21.
[70]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), p. 439, Eq. 10.1.21.
[71]J. C. P. Miller, *Bessel Functions II, Mathematics Tables*, Vol. 10 of *British Association Advances in Science* (Cambridge University Press, Cambridge, England, 1952).
[72]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **25**, 113 (1982).
[73]E. Filter and E. O. Steinborn, J. Math. Phys. **21**, 2725 (1980).
[74]J. D. Talman, J. Chem. Phys. **84**, 6879 (1986).
[75]See Ref. 45, Table II.
[76]M. P. Barnett and C. A. Coulson, Philos. Trans. R. Soc. **243**, 221 (1951).