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Extremely compact formulas for molecular two-center one-electron integrals and Coulomb integrals over Slater-type atomic orbitals

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Extremely compact analytical formulas are derived for molecular two-center one-electron integrals and Coulomb integrals, which occur in linear-combination-of-atomic-orbitals calculations with Slater-type orbitals (STO's). The derivation is based on the connection of the STO's with the reduced Bessel functions (RBF's) and makes use of the convolution theorems of RBF's. The final results are of a surprisingly simple structure and are, therefore, especially useful for practical applications.

I. INTRODUCTION

Slater-type atomic orbitals (STO's) constitute an important basis set for all calculations of physical properties of molecules and solids, which use the linear-combination-of-atomic-orbitals (LCAO) theory. Unfortunately, STO's lead to complicated molecular integrals which occur in great numbers in calculations of the electronic structure of molecules and solids. In order to circumvent this difficulty, Gaussian-type orbitals (GTO's) were introduced and successfully used in such calculations.[1,2] However, for problems in which the long-range part of the wave function and/or its behavior in the neighborhood of a nucleus is important, it is necessary to use basis sets which describe the physical situation better than the GTO's can do. As is well known, STO's are most suitable for this purpose, because they can fulfill the cusp condition and decline exponentially at long distances like the exact solution of the Schrödinger equation.[3-5] This fact is the reason why one needs many fewer STO's than GTO's in order to describe a wave function, especially for larger systems. Therefore, the use of STO's instead of GTO's can reduce considerably the number of molecular integrals that occur in an LCAO calculation, and this fact may be a substantial contribution to the efficiency of such a calculation. The advantages of the STO's motivated strong efforts to evaluate the molecular integrals over these functions despite the great difficulties involved. Until the early sixties, however, multicenter integrals over STO's could be evaluated only for certain cases. Even for the simplest multicenter integrals, namely, overlap integrals, explicit formulas were only given for the lowest quantum numbers, and although these formulas were not valid for the general case, they were very involved and complicated.[6-8] Later, a more systematic investigation of molecular integrals over STO's led to general and explicit formulas for all integrals which occur.[9-11] However, most of them are highly complicated and represent "formal solutions" only, which rather often cannot be used efficiently in numerical calculations.

One also can consider numerical evaluations of the necessary molecular integrals. However, even with modern computers, multidimensional integration procedures are too time consuming and inaccurate. There are indications that only one-dimensional numerical quadratures may be sufficiently reliable.[12,13] This means that one is forced to evaluate the integrals over non-Gaussian basis functions analytically.

In this paper we present new analytical expressions for all two-center one-electron integrals and the (two-electron) Coulomb integrals over STO's. These formulas are obtained by purely analytical methods and do not require any numerical integrations. They are very compact and surprisingly simple also for arbitrarily high quantum numbers. Therefore they are well suited for practical applications.

All rather old expressions for two-center one-electron integrals and Coulomb integrals over STO's, which are given in the literature, are much more complicated than the new formulas derived in the present article. Especially for higher quantum numbers the use of the older formulas is very difficult. Because they usually hold for special cases only, a special computer program is required for each case.[14] Furthermore, these old formulas, which are scattered over the literature and sometimes hard to find, are often not at all in a form which can easily be programmed. Therefore we feel that the new formulas presented in this article meet a real demand and offer a satisfying solution of the problem. Because of their simplicity, the formulas given here can be used and coded easily also by the nonspecialist.

In the present article we apply a new method for attacking the molecular multicenter-integral

problem which occurs in LCAO calculations with an STO basis set. The derivations given here are based on the fact that STO's can be represented by linear combinations of reduced Bessel functions (RBF's), as we have shown recently.[15,16] However, the representation of a given integral over STO's by a linear combination of integrals (of the same type) over RBF's is of great advantage, because multicenter integrals over RBF's can be evaluated more easily than those over STO's. This is due to the fact that for the treatment of the integrals over RBF's the convolution theorems of RBF's can be utilized. In this article, these convolution theorems, which we derived recently,[16] are used for the evaluation of the two-center one-electron integrals and Coulomb integrals over STO's. The convolution theorems are applicable also for the evaluation of the other types of molecular integrals, which are not yet considered in this article. Therefore the treatment discussed here establishes the basis of a new method, which, in fact, is rather promising, because it does not only provide a systematic approach to the integral problem, but also seems to furnish very compact results.

II. DEFINITIONS

The unnormalized Slater-type atomic orbital is written as

$$\chi^M_{N,L}(\alpha\vec{r}) = (\alpha r)^{N-1} e^{-\alpha r} Y^M_L(\Omega_{\vec{r}}), \tag{2.1}$$

with integer N, L, M. The surface spherical harmonics $Y^M_L(\Omega_{\vec{r}})$ are defined in Condon-Shortley phases.[17,18] For the regular solid spherical harmonics, the symbol

$$\mathcal{Y}^M_L(\vec{r}) = r^L Y^M_L(\Omega_{\vec{r}}) \tag{2.2}$$

is used, whereas the irregular solid spherical harmonics are written as

$$\mathcal{J}^M_L(\vec{r}) = r^{-L-1} Y^M_L(\Omega_{\vec{r}}). \tag{2.3}$$

The integral over the product of three spherical harmonics, i.e., the Gaunt coefficient, may be expressed by Clebsch-Gordan coefficients[19] as follows:

$$\begin{aligned}\langle L_1 M_1 | L_2 M_2 | lm\rangle &= \int d\Omega\, Y^{M_1 *}_{L_1}(\Omega) Y^{M_2}_{L_2}(\Omega) Y^m_l(\Omega) \\ &= [(2l+1)(2L_2+1)]^{1/2}[4\pi(2L_1+1)]^{-1/2} \\ &\quad \times C(l, L_2, L_1; 0, 0) C(l, L_2, L_1; m, M_2).\end{aligned} \tag{2.4a}$$

The Gaunt coefficient vanishes if the triangular conditions are not satisfied. They are given by

$$|L_1 - L_2| \le l \le L_1 + L_2, \quad m = M_2 - M_1, \quad L_1 + L_2 + l, \text{ even}. \tag{2.4b}$$

The angular momentum quantum numbers L_1, L_2, and l often appear in certain combinations for which we introduce the following abbreviations, where Δ should remind us of the triangular condition:

$$\Delta l = \tfrac{1}{2}(L_1 + L_2 - l), \quad \Delta L_1 = \tfrac{1}{2}(L_2 + l - L_1),$$
$$\Delta L_2 = \tfrac{1}{2}(l + L_1 - L_2); \tag{2.5}$$

$$\sigma(L_1) = \sigma(L_2) = \sigma(l) = \tfrac{1}{2}(L_1 + L_2 + l) = \sigma. \tag{2.6}$$

We define some functions which are related to Bessel functions. If $K_\nu(\alpha r)$ stands for the modified Bessel function of the second kind,[20] the product of $(\alpha r)^\nu$ with $K_\nu(\alpha r)$ has no singularity for $r \to 0$ if $\nu \ge 0$. Therefore the function

$$\hat{k}_\nu(\alpha r) = (2/\pi)^{1/2} (\alpha r)^\nu K_\nu(\alpha r) \tag{2.7}$$

is called a "reduced Bessel function."[21] It is related to STO's because for $r \to \infty$ it decreases exponentially for any real ν. It may be mentioned that $\hat{k}_\nu(\alpha r)$ decreases like $r^{-2\nu}$ for $r \to 0$ if $\nu < 0$. For half-integer order ν, one has

$$\hat{k}_{-1/2}(r) = r^{-1} e^{-r}, \tag{2.8}$$

$$\hat{k}_{N-1/2}(r) = r^{-1} e^{-r} \sum_{p=1}^{N} \frac{(2N-p-1)!}{(p-1)!(N-p)!} 2^{p-N} r^p \tag{2.9}$$

for natural numbers $N = 1, 2, \ldots$. The reduced Bessel function obeys the relationship[22]

$$D^N_x \hat{k}_\nu(x) = (-1)^N \hat{k}_{\nu-N}(x), \tag{2.10}$$

where the "Bessel operator" is defined by

$$D^N_x = \left(\frac{d}{x\,dx}\right)^N. \tag{2.11}$$

The following recursion formula[22] holds for all ν:

$$x^2 \hat{k}_{\nu-1/2}(x) = \hat{k}_{\nu+3/2}(x) - (2\nu+1)\hat{k}_{\nu+1/2}(x). \tag{2.12}$$

It is practical for numerical purposes. The $\hat{k}_\nu$ should not be confused with the spherical Bessel function, which for integer l is defined by $k_l(\alpha r) = (2/\pi)^{1/2}(\alpha r)^{-1/2} K_{l+1/2}(\alpha r)$.

We need nonscalar functions whose angular dependencies are given by spherical harmonics, and whose radial dependencies are related to the reduced Bessel functions. Therefore we introduce functions $\hat{B}^M_{\nu,L}(\alpha\vec{r})$ defined by

$$\begin{aligned}\hat{B}^M_{\nu,L}(\alpha\vec{r}) &= (\alpha r)^L \hat{k}_\nu(\alpha r) Y^M_L(\Omega_{\vec{r}}) \\ &= \hat{k}_\nu(\alpha r) \mathcal{Y}^M_L(\alpha\vec{r}).\end{aligned} \tag{2.13}$$

The order ν is arbitrary. However, in this paper we restrict ourselves to (positive or negative) half-integer order ν. For half-integer order $\nu = N - \frac{1}{2}$, it is advantageous to define

$$B^M_{N,L}(\alpha\vec{r}) = [2^{N+L}(N+L)!]^{-1} (\alpha r)^L \hat{k}_{N-1/2}(\alpha r) Y^M_L(\Omega_{\vec{r}}). \tag{2.14}$$

The definitions Eqs. (2.13) and (2.14) differ from definitions which we used in previous work. The relationships between the different definitions are discussed in Appendix B.

Furthermore, the following symbols and abbreviations will be applied. The double factorial function is defined by

$$(2n)!! = 2\times 4\times 6\times\cdots\times(2n) = 2^n n!\,, \tag{2.15}$$

$$(2n+1)!! = 1\times 3\times 5\times\cdots\times(2n+1) = (2^n n!)^{-1}(2n+1)!\,, \tag{2.16}$$

$$0!! = (-1)!! = 1!! = 1\,. \tag{2.17}$$

With the help of the Γ function the Pochhammer symbol[23] is defined by

$$(a)_N = a(a+1)\cdots(a+N-1) = \Gamma(a+N)/\Gamma(a),\quad (a)_0 = 1\,. \tag{2.18}$$

III. SLATER-TYPE ORBITALS AND REDUCED BESSEL FUNCTIONS

As we have shown previously,[15] an s-type STO can be represented by a (finite) linear combination of reduced Bessel functions according to

$$x^{n-1}e^{-x} = \sum_q \frac{(-1)^{n-q}n!}{(2q-n)!(2n-2q)!!}\hat{k}_{q-1/2}(x)\,. \tag{3.1}$$

The summation index q runs from min$q$ to max$q$ $=n$ with

$$\min q = \begin{cases} \frac{1}{2}n & \text{for } n \text{ even},\\ \frac{1}{2}(n+1) & \text{for } n \text{ odd}. \end{cases} \tag{3.2}$$

If both sides of Eq. (3.1) are multiplied by a solid spherical harmonic and the substitution $N=n+L$ is made, we obtain for STO's with integer $N\geq L+1$

$$\chi^m_{N,l}(\alpha\vec{r}) = \sum_{p=\min p}^{N-l}\frac{(-1)^{N-l-p}(N-l)!\,2^{l+p}(l+p)!}{(2p-N+l)!\,(2N-2l-2p)!!}\times B^m_{p,l}(\alpha\vec{r})\,, \tag{3.3}$$

$$\min p = \begin{cases} \frac{1}{2}(N-l), & \text{for } N-l \text{ even},\\ \frac{1}{2}(N-l+1), & \text{for } N-l \text{ odd}. \end{cases} \tag{3.4}$$

It is clear that with the help of Eq. (3.3) all molecular integrals over STO's can readily be obtained as simple sums of the corresponding integrals over B functions. If the formulas for the integrals over B functions are known, it is easy to write down the corresponding integrals over STO's. Therefore it is sufficient to consider molecular integrals over B functions only. The reduction of molecular integrals over STO's to the corresponding integrals over B functions is advantageous, because a lot of integrals over B functions have a very clear and simple structure as will be shown in the following sections.

IV. OVERLAP INTEGRALS

A. General aspects

Due to Eq. (3.3), the overlap integral of two STO's with scaling parameters α and β, respectively,

$$\int d\vec{r}\,\chi^{M_1*}_{N_1,L_1}(\alpha\vec{r})\chi^{M_2}_{N_2,L_2}(\beta(\vec{r}-\vec{R}))\,, \tag{4.1}$$

can be represented by a finite sum of corresponding overlap integrals S over B functions which are defined by

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\beta,\vec{R}) = \int d\vec{r}\,B^{M_1*}_{N_1,L_1}(\alpha\vec{r})\times B^{M_2}_{N_2,L_2}(\beta(\vec{r}-\vec{R}))\,. \tag{4.2}$$

This overlap integral should be distinguished from the convolution integral, which differs from the overlap integral by a parity factor $(-1)^{L_2}$. In a previous paper,[16] we already gave closed-form expressions for these convolution integrals, to which we must refer for details of the derivation. In the present paper, we do not denote the convolution integral, but the overlap integral Eq. (4.2) by S, because the latter is more important in quantum mechanics. The details are clarified in Appendix B.

B. Equal scaling parameters

For equal scaling parameters $\alpha=\beta$, the overlap integral Eq. (4.2) is given by the following surprisingly simple linear combination of B functions:

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;\vec{R}) = 4\pi\alpha^{-3}(-1)^{L_2}\sum_l\langle L_2M_2|L_1M_1|lm\rangle\sum_t(-1)^t\binom{\Delta l}{t}B^m_{N_1+N_2+L_1+L_2-l-t+1,\,l}(\alpha\vec{R})\,. \tag{4.3}$$

The overlap integral of two B functions which are centered at the same origin, i.e., for the case $\vec{R}=0$, may easily be obtained from the general formula Eq. (4.3) by using the orthogonality relation of the spherical harmonics[17] and the identity

$$B^M_{N,L}(0) = \delta_{L,0}\delta_{M,0}(4\pi)^{-1/2}(2N-3)!!/(2N)!!\,. \tag{4.4}$$

The resulting summation over t can then be performed with the help of Vandermonde's theorem.[40]

We obtain

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;0)=\alpha^{-3}\,\frac{(2L_1+1)!!(2N_1+2N_2+2L_1-1)!!}{(2N_1+2N_2+4L_1+2)!!}\times\delta_{L_1,L_2}\delta_{M_1,M_2}\,. \tag{4.5}$$

C. Unequal scaling parameters

For unequal scaling parameters $\alpha\neq\beta$, the overlap integral Eq. (4.2) is also given by a rather simple linear combination of B functions according to

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R})=\sum_l\langle L_2M_2|L_1M_1|lm\rangle(-1)^{L_2}\times\Bigg(\sum_{t=0}^{N_1+L_1}C^{N_2N_1t}_{L_2L_1l}(\beta,\alpha)B^m_{t-l,l}(\alpha\vec{R})+\sum_{t=0}^{N_2+L_2}C^{N_1N_2t}_{L_1L_2l}(\alpha,\beta)B^m_{t-l,l}(\beta\vec{R})\Bigg). \tag{4.6}$$

The coefficients

$$C^{\nu_1\nu_2t}_{\lambda_1\lambda_2l}(\alpha,\beta)=(-1)^{\nu_2+\lambda_2+t}\,4\pi\alpha^{-3}(\beta/\alpha)^{\lambda_1}\times[1-(\beta/\alpha)^2]^{-\nu_1-\lambda_1-1}\times P^{(-\nu_2-\Delta\lambda_1+t,\,\nu_1+\Delta\lambda_2)}_{\nu_2+\lambda_2-t}\left(\frac{(\alpha/\beta)^2+1}{(\alpha/\beta)^2-1}\right) \tag{4.7}$$

are closely related to the Jacobi polynomials $P^{(\gamma,\delta)}_N$.[24] This formula for the overlap integral should contain the formulas Eqs. (4.3) and (4.5) as special cases. However, this cannot be seen because for $\alpha\to\beta$, as well as for $R\to 0$, it contains undeterminate expressions like $\infty-\infty$ or $0/0$. For the same reason, the last formula Eq. (4.6) becomes numerically unstable if α and β become nearly equal. For practical applications it is, therefore, advantageous to have another representation for the overlap integral which is numerically stable in the case $\alpha\approx\beta$ as well as $R\approx 0$. Such a formula will be derived in Sec. IV D.

D. Nearly equal scaling parameters

The following equation, which can easily be obtained from standard literature,[25] makes it possible to expand a function $B^M_{q,L}(\alpha\vec{r})$ as an infinite series of functions $B^M_{p,L}(\beta\vec{r})$ times powers of $[1-(\alpha/\beta)^2]$:

$$B^M_{q,L}(\alpha\vec{r})=(\alpha/\beta)^{2q-1+L}\sum_{p=0}^{\infty}\binom{p+q+L}{p}[1-(\alpha/\beta)^2]^p\times B^M_{p+q,L}(\beta\vec{r})\quad\text{for }\beta\geq\alpha. \tag{4.8}$$

This provides the possibility of representing all overlap integrals over B functions with different scaling parameters by a series of overlap integrals over B functions with equal scaling parameters. We obtain

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R})=(\alpha/\beta)^{2N_1+L_1-1}\times\sum_{p=0}^{\infty}\binom{p+N_1+L_1}{p}[1-(\alpha/\beta)^2]^p\times S^{L_1,L_2}_{N_1+p,N_2}(\beta,\beta;\vec{R})\quad\text{for }\beta\geq\alpha. \tag{4.9}$$

This series converges very rapidly for $\alpha\approx\beta$. Therefore one needs only a few terms, i.e., integrals of the type $S^{l_1,l_2}_{n_1,n_2}(\beta,\beta;\vec{R})$. However, it is even possible to use this series expansion not only if $\alpha\approx\beta$, but for larger differences of the parameters, because the overlap integrals, which constitute the terms of the expansion, can be evaluated very easily with the help of the simple formula Eq. (4.3).

The formula for the "one-center limit" $\vec{R}=0$ for the case of unequal scaling parameters can be obtained from Eq. (4.9) by inserting Eq. (4.4). The resulting series may be written as a hypergeometric function[41]:

$$S^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;0)=(\alpha/\beta)^{2N_1+L_1+2}S^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;0)\;{}_2F_1(N_1+L_1+1,N_1+N_2+L_1+\tfrac{1}{2},N_1+N_2+2L_1+2;[1-(\alpha/\beta)^2]),\quad\beta\geq\alpha. \tag{4.10}$$

Obviously, the formula for the case $\beta\leq\alpha$ can be obtained from Eq. (4.9) by interchanging $N_1,N_2,L_1,L_2,\alpha,\vec{R}$ with $N_2,N_1,L_2,L_1,\beta,-\vec{R}$ on the right-hand side (rhs) of Eqs. (4.9) and (4.10) and by taking the complex conjugate of the result.

V. KINETIC-ENERGY INTEGRALS

Also with the help of Eq. (3.3) the kinetic-energy integrals over STO's can easily be expressed as linear combinations of integrals of the type

$$T^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R})=\int d\vec{r}\,B^{M_1*}_{N_1,L_1}(\alpha\vec{r})(-\tfrac{1}{2}\Delta)\times B^{M_2}_{N_2,L_2}(\beta(\vec{r}-\vec{R}))\,. \tag{5.1}$$

The latter integral Eq. (5.1) can be reduced to a sum of two overlap integrals by means of the relation

$$\left(\frac{\partial}{\partial\vec{r}}\right)^2 B^M_{N,L}(\alpha\vec{r}) = \alpha^2[B^M_{N,L}(\alpha\vec{r}) - B^M_{N-1,L}(\alpha\vec{r})]. \tag{5.2}$$

Therefore one obtains

$$T^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) = -(\tfrac{1}{2}\beta^2)[S^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) - S^{L_1,L_2}_{N_1,N_2-1}(\alpha,\beta;\vec{R})]. \tag{5.3}$$

The identity Eq. (5.2) is immediately obtained if the radial part Δ_r of the Laplacian Δ is expressed by the Bessel operator according to

$$\Delta_r = r^2 D_r^2 + 3D_r. \tag{5.4}$$

VI. NUCLEAR-ATTRACTION INTEGRALS

The two-center nuclear-attraction integral over STO's with a one-center charge distribution is given by

$$\int d\vec{r}\,\chi^{\mu}_{\nu,\lambda}(\alpha\vec{r})\frac{1}{|\vec{r}-\vec{R}|}\chi^{\mu'}_{\nu',\lambda'}(\beta\vec{r}). \tag{6.1}$$

This, of course, is also the potential at the point $\vec{R}$ which is generated by a charge distribution $\chi^{\mu}_{\nu,\lambda}(\alpha\vec{r})\chi^{\mu'}_{\nu',\lambda'}(\beta\vec{r})$. The product of two STO's can be written as a linear combination of STO's according to

$$\chi^{\mu}_{\nu,\lambda}(\alpha\vec{r})\chi^{\mu'}_{\nu',\lambda'}(\beta\vec{r}) = \frac{\alpha^{\nu-1}\beta^{\nu'-1}}{(\alpha+\beta)^{\nu+\nu'-2}} \times \sum_l \langle lm|\lambda\mu|\lambda'\mu'\rangle \times \chi^m_{\nu+\nu'-1,l}((\alpha+\beta)\vec{r}), \tag{6.2}$$

with the $\chi^{\mu}_{\nu,\lambda}(\alpha\vec{r})$ being defined by Eq. (2.1). Here, the coupling rule for spherical harmonics[26] has been applied. If, as with Eq. (3.3), each STO of Eq. (6.2) is represented by B functions, the integral Eq. (6.1) is reduced to a linear combination of integrals of the type

$$A^M_{N,L}(\alpha,\vec{R}) = \int d\vec{r}\,(|\vec{r}-\vec{R}|)^{-1}B^M_{N,L}(\alpha\vec{r}). \tag{6.3}$$

For this integral we can give two equivalent representations. The first one is a simple linear combination of irregular solid spherical harmonics $\mathfrak{I}^M_L$ and B functions, which is given by

$$A^M_{N,L}(\alpha,\vec{R}) = 4\pi\alpha^{-2}[(2L-1)!!\,\mathfrak{I}^M_L(\alpha\vec{R}) - \sum_{q=0}^{N+L} B^M_{q-L,L}(\alpha\vec{R})]. \tag{6.4}$$

This finite expansion has numerical advantages for medium-sized and large R, whereas for $R\to 0$ the following second relationship is more suited for numerical purposes:

$$A^M_{N,L}(\alpha,\vec{R}) = 4\pi\alpha^{-2}\sum_{q=0}^{\infty} B^M_{q+N+1,L}(\alpha\vec{R}). \tag{6.5}$$

This is easy to obtain from Eq. (6.4) if one uses the relationship

$$\mathfrak{I}^M_L(\alpha\vec{r}) = [(2L-1)!!]^{-1}(\beta/\alpha)^{L+1}\sum_{p=0}^{\infty} B^M_{p-L,L}(\beta\vec{r}), \tag{6.6}$$

which we derived in Ref. 16.

If $\vec{R}=0$, the nuclear attraction integral becomes

$$A^M_{N,L}(\alpha,0) = 2\pi^{1/2}\alpha^{-2}\delta_{L,0}\delta_{M,0}(2N-1)!!/(2N)!!. \tag{6.7}$$

This follows from Eq. (6.5) if the expression Eq. (4.4) for the B function with vanishing argument is inserted into Eq. (6.5). By doing so, one realizes that the remaining series represents the following hypergeometric function[42] ${}_2F_1(N+\frac{1}{2},1,N+2;1)$ which immediately leads to the expression Eq. (6.7) for the one-center nuclear attraction integral.

The two-center nuclear attraction integral over STO's with a two-center charge distribution is given by

$$\int d\vec{r}\,\chi^{\mu}_{\nu,\lambda}{}^*(\alpha\vec{r})\frac{1}{|\vec{r}-\vec{R}|}\chi^{\mu'}_{\nu',\lambda'}(\beta(\vec{r}-\vec{R})) = \beta\int d\vec{r}\,\chi^{\mu}_{\nu,\lambda}{}^*(\alpha\vec{r})\chi^{\mu'}_{\nu'-1,\lambda'}(\beta(\vec{r}-\vec{R})), \tag{6.8}$$

and, therefore, represents an overlap integral which has been treated in Sec. IV.

VII. COULOMB INTEGRALS

A. General aspects

Molecular Coulomb integrals are two-electron integrals

$$\int d\vec{r}_1\int d\vec{r}_2\,\Omega^{L_1,L_1'}_{N_1,N_1'}(\vec{r}_1)(|\vec{R}+\vec{r}_2-\vec{r}_1|)^{-1}\Omega^{L_2,L_2'}_{N_2,N_2'}(\vec{r}_2), \tag{7.1}$$

which contain only one-center charge distributions

$$\Omega^{L_i,L_i'}_{N_i,N_i'}(\vec{r}_i) = \chi^{M_i}_{N_i,L_i}{}^*(\alpha\vec{r}_i)\chi^{M_i'}_{N_i',L_i'}(\alpha'\vec{r}_i), \quad i=1,2. \tag{7.2}$$

With the help of Eq. (3.3) they can be reduced to the "basic Coulomb integral"

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) = \int d\vec{r}_1\int d\vec{r}_2 B^{M_1}_{N_1,L_1}{}^*(\alpha\vec{r}_1) \times(|\vec{R}+\vec{r}_2-\vec{r}_1|)^{-1} \times B^{M_2}_{N_2,L_2}(\beta\vec{r}_2). \tag{7.3}$$

If in Eq. (7.3) we perform the integration over $\vec{r}_1$, this basic Coulomb integral may be written

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) = \int d\vec{r}_2 A^{M_1 *}_{N_1,L_1}(\alpha,\vec{R}+\vec{r}_2) B^{M_2}_{N_2,L_2}(\beta\vec{r}_2), \tag{7.4}$$

which is a convolution product of a B function and a nuclear attraction integral as defined by Eq. (6.3). We shall show that this integral can be reduced to the convolution integrals of B functions, which we evaluated recently,[16] making any further integration superfluous. Again, the results are very compact.

B. Equal scaling parameters

The integrand of the Coulomb integral in Eq. (7.4) contains the nuclear attraction integral A. We now substitute this nuclear attraction integral by the series expansion in terms of B functions as given in Eq. (6.5). Then, with the help of Eq. (4.2), this leads to the following expression which gives the basic Coulomb integral Eq. (7.3) as a series of overlap integrals:

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) = \alpha^{-2} 4\pi \sum_{p=0}^{\infty} S^{L_1,L_2}_{N_1+p+1,N_2}(\alpha,\beta;\vec{R}). \tag{7.5}$$

For the case $\alpha=\beta$ this infinite series can be further simplified, if we express the overlap integral S in Eq. (7.5) by the formula Eq. (4.3). A rearrangement of the summations yields

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;\vec{R}) = (4\pi)^2\alpha^{-5}(-1)^{L_2}\sum_l \langle L_2M_2|L_1M_1|lm\rangle \sum_t (-1)^t \binom{\Delta l}{t} \sum_{q=0}^{\infty} B^m_{N_1+N_2+q+L_1+L_2-l-t+2,l}(\alpha\vec{R}). \tag{7.6}$$

Now, if we consider Eq. (6.6), it turns out that the infinite series over q represents an irregular solid spherical harmonic $\mathfrak{Z}^m_l(\alpha\vec{R})$, from which a linear combination of B functions is to be subtracted. Therefore we obtain

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;\vec{R}) = (4\pi)^2\alpha^{-5}(-1)^{L_2}\sum_l \langle L_2M_2|L_1M_1|lm\rangle \sum_t (-1)^t \binom{\Delta l}{t} [(2l-1)!!\mathfrak{Z}^m_l(\alpha\vec{R}) - \sum_q B^m_{q-l,l}(\alpha\vec{R})];$$

$$0 \le t \le \Delta l, \quad 0 \le q \le N_1+N_2+L_1+L_2+1-t. \tag{7.7}$$

This is a simple linear combination of nuclear attraction integrals as given by Eq. (6.4). A further simplification is possible if we use[27]

$$\sum_{t=0}^{m} \binom{\Delta l}{t} (-1)^t = (-1)^m \binom{\Delta l - 1}{m}. \tag{7.8}$$

With this identity, it follows that

$$\sum_t (-1)^t \binom{\Delta l}{t} \sum_{q=0}^{N_1+N_2+L_1+L_2+1-t} B^m_{q-l,l}(\alpha\vec{R}) = \sum_{q=0}^{\Delta l-1} (-1)^q \binom{\Delta l-1}{q} B^m_{N_1+N_2+L_1+L_2-q-l+1,l}(\alpha\vec{R}). \tag{7.9}$$

Hence, the basic Coulomb integral containing B functions with equal scaling parameters $\alpha=\beta$ finally becomes

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\alpha;\vec{R}) = 4\pi\alpha^{-3}\langle L_2M_2|L_1M_1|L_1+L_2,m\rangle A^m_{N_1+N_2+1,L_1+L_2}(\alpha,\vec{R}) - (4\pi)^2\alpha^{-5} \sum_{l=|L_1-L_2|}^{L_1+L_2-2} \sum_{q=0}^{\Delta l-1} \langle L_2M_2|L_1M_1|lm\rangle (-1)^q \binom{\Delta l-1}{q} B^m_{N_1+N_2+L_1+L_2-q-l+1,l}(\alpha\vec{R}). \tag{7.10}$$

We obtained this result by simplifying the series expansion of Eq. (7.5) with the help of Eqs. (4.2) and (6.5). However, this method does not work in the case $\alpha \neq \beta$, which will be treated in a different manner in Sec. VII C.

C. Unequal scaling parameters

Again we start from Eq. (7.4) and substitute the nuclear attraction integral A by an appropriate series expansion. But now we use the finite expansion given by Eq. (6.4). This yields

$$C^{L_1,L_2}_{N_1,N_2}(\alpha,\beta;\vec{R}) = 4\pi\alpha^{-2}(2L_1-1)!! \int d\vec{r}_2 \mathfrak{Z}^{M_1 *}_{L_1}(\alpha(\vec{R}+\vec{r}_2)) B^{M_2}_{N_2,L_2}(\beta\vec{r}_2) - 4\pi\alpha^{-2} \sum_{q=0}^{N_1+L_1} \int d\vec{r}_2 B^{M_1 *}_{q-L_1,L_1}(\alpha(\vec{R}+\vec{r}_2)) B^{M_2}_{N_2,L_2}(\beta\vec{r}_2). \tag{7.11}$$

In this form, the Coulomb integral is given by the difference of two integrals which are divergent in the ordinary sense. If each of these two integrals is considered as a distribution, they may be evaluated individually. Then by subtracting the two results from each other, it is possible to obtain the correct value of the original Coulomb integral.

This method of using the theory of distributions has the great advantage that it makes it possible to derive the simple finite expansion for the Coulomb integral, given in Eq. (7.13). However, for the sake of shortness, the procedure of applying the theory of distributions to the molecular integral problem cannot be elaborated here but must be discussed elsewhere.[28] Although, therefore, some details of the *derivation* will be omitted here, an independent *proof of the results*, which does not use the theory of distributions, will be given in Appendix A.

The formulas for the overlap integrals Eqs. (4.3), (4.5), (4.6), and (4.9) remain formally correct if N_1 assumes the values $N_1 = q - L_1$ for $q = 0, 1, 2, \ldots$. For $q - L_1 < -1$, these relationships are to be interpreted as formulas for distributions. This makes it possible to evaluate the second "integral" of Eq. (7.11).

The first "integral" of Eq. (7.11), which contains an irregular solid spherical harmonic and a B function, represents also a distribution. Its evaluation yields[28]

$$(2L_1-1)!!\int d\vec{r}_2 \mathfrak{Z}_{L_1}^{M_1*}(\alpha(\vec{R}+\vec{r}_2))B_{N_2,L_2}^{M_2}(\beta\vec{r}_2)$$
$$= (\beta/\alpha)^{L_1+1}4\pi\beta^{-3}(-1)^{L_2}\sum_l\sum_t \langle L_2M_2|L_1M_1|lm\rangle(-1)^t\binom{\Delta l}{t}\left((2l-1)!!\mathfrak{Z}_l^m(\beta\vec{R})-\sum_{p=0}^{N_2+L_2-t}B_{p-1,l}^m(\beta\vec{R})\right). \tag{7.12}$$

Inserting the two formulas Eq. (7.12) and Eq. (4.2) into Eq. (7.11), we find immediately the following finite series for the Coulomb integral:

$$C_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R}) = \left[\frac{(4\pi)^2}{\alpha^2\beta^3}\left(\frac{\beta}{\alpha}\right)^{L_1+1}\sum_l\sum_t\langle L_2M_2|L_1M_1|lm\rangle(-1)^t\binom{\Delta l}{t}(-1)^{L_2}\left((2l-1)!!\mathfrak{Z}_l^m(\beta\vec{R})-\sum_{q=0}^{N_2+L_2-t}B_{q-1,l}^m(\beta\vec{R})\right)\right]$$
$$-\frac{4\pi}{\alpha^2}\sum_{q=0}^{N_1+L_1}S_{q-L_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R}). \tag{7.13}$$

For the case $\alpha=\beta$ this relationship reduces to Eq. (7.7) which we already derived by another method.

D. Nearly equal scaling parameters

In Eq. (7.13), the Coulomb integral is given as a sum of nuclear attraction integrals A and overlap integrals S, which are defined by Eqs. (6.3) and (6.4) and Eq. (4.2), respectively. Although this formula Eq. (7.13) is true for all values of α and β, it is advisable to insert those formulas for A and S which are most appropriate for certain ranges of α and β, as it was discussed in the foregoing. Especially for the case $\alpha\approx\beta$, i.e., if α and β are different but nearly equal, the overlap integrals $S_{n_1^1,n_2^2}^{l_1,l_2}(\alpha,\beta;\vec{R})$, which are contained in Eq. (7.13), should be calculated with the numerically stable formula Eq. (4.9). This formula remains also correct if N_1 becomes negative and S is considered as a distribution.

However, if the overlap integrals S, given by Eq. (4.9), are inserted into Eq. (7.13), one can even achieve a further analytical simplification. Then, we can rearrange the resulting double series and obtain

$$\sum_{q=0}^{N_1+L_1}S_{q-L_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})$$
$$= (-1)^{L_2}\sum_{s=0}^{N_1+L_1}B_{s+N_2+L_2-l-t+1,l}^m(\beta\vec{R})$$
$$+\sum_{s=N_1+L_1+1}^{\infty}\left[\sum_{p=0}^{N_1+L_1}\binom{s}{p}\left(\frac{(\alpha/\beta)^2}{1-(\alpha/\beta)^2}\right)^p\right]$$
$$\times[1-(\alpha/\beta)^2]^s B_{s+N_2+L_2-l-t+1,l}^m(\beta\vec{R})$$
$$\text{for } \beta\geq\alpha. \tag{7.14}$$

If this expression is used to replace the last sum on the rhs of Eq. (7.13), we obtain the following formula for the Coulomb integral:

$$C_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})$$
$$= \left(\frac{\beta}{\alpha}\right)^{L_1+3}C_{N_1,N_2}^{L_1,L_2}(\beta,\beta;\vec{R})-\left(\frac{\beta}{\alpha}\right)^{L_1+1}\frac{4\pi}{\alpha^2}$$
$$\times\sum_{q=N_1+L_1+1}^{\infty}\left[\sum_{p=0}^{N_1+L_1}\binom{q}{p}\left(\frac{(\alpha/\beta)^2}{1-(\alpha/\beta)^2}\right)^p\right]$$
$$\times[1-(\alpha/\beta)^2]^q S_{q-L_1,N_2}^{L_1,L_2}(\beta,\beta;\vec{R})$$
$$\text{for } \beta\geq\alpha. \tag{7.15}$$

Hence, the Coulomb integral with different scaling parameters α and β is represented by a corresponding Coulomb integral with equal scaling parameters, from which a series of overlap integrals S is to be subtracted.

If the series expansion of Eq. (7.5) is inserted into Eq. (7.15), we obtain after a few manipulations the following formula for the Coulomb integral:

$$C_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R}) = 4\pi\alpha^{-2}(\beta/\alpha)^{L_1+1}\sum_{q=N_1+L_1+1}^{\infty}\left[\sum_{p=N_1+L_1+1}^{q}\binom{q}{p}\left(\frac{(\alpha/\beta)^2}{(1-(\alpha/\beta)^2}\right)^p\right]$$
$$\times[1-(\alpha/\beta)^2]^q S_{q-L_1,N_2}^{L_1,L_2}(\beta,\beta;\vec{R}) \quad \text{for } \beta\geq\alpha. \tag{7.16}$$

The above given formulas hold for all $\beta\geq\alpha$. Of course, the formulas for the case $\alpha\geq\beta$ can easily be obtained if one uses the symmetry relation

$$C_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R}) = C_{N_2,N_1}^{L_2,L_1*}(\beta,\alpha;-\vec{R}). \tag{7.17}$$

The convergence of the infinite series contained in Eqs. (7.15) and (7.16) is determined by the powers $[1-(\alpha/\beta)^2]^t$, where $t=q-p\geq 0$. Therefore the convergence is very good for nearly equal scaling parameters, and in this case ($\alpha\approx\beta$) the formulas are especially useful for numerical calculations.

VIII. SUMMARY

For the benefit of the user who is not interested in details of the derivations but only in the application of the final formulas, we summarize a few aspects of practical interest.

For each type of integral considered in this paper we have found several representations, each of which has numerical advantages for certain ranges of the scaling parameters α and β. For the overlap, kinetic energy, and Coulomb integrals, the equation numbers which locate the appropriate representation for each case are listed in Table I.

The two-center nuclear attraction integral is expressed by the finite sum of $\mathfrak{Z}$ and B functions given in Eq. (6.4), which becomes numerically instable for $\alpha\vec{R}\to 0$. In this case, i.e., if R is very small, Eq. (6.5) should be used.

The formulas given in this paper contain only well-known special functions and coefficients, namely, only Jacobi polynomials,[24] spherical harmonics,[18] reduced Bessel functions (RBF's), cf. Eq. (2.7), and Clebsch-Gordan coefficients.[19] Except for the RBF's, there exist standard computer programs[29-31] which make it possible to calculate these functions quickly and easily. The RBF's can easily be calculated by an upward recursion using Eq. (2.12). Functions $B_{N,L}^{M}$ with negative indices N can be obtained by using the property $K_\nu = K_{-\nu}$ of the modified Bessel functions of the second kind.

IX. CONCLUSION

In the present article we give analytical evaluations of molecular two-center one-electron integrals and Coulomb integrals over STO's as well as B functions. The results are extremely compact and simple, and they are remarkably well suited for practical applications. This fact is even more astonishing if one considers the formulas given so far in literature. Especially Coulomb integrals were investigated by various authors.[32-39] However, most of the published formulas are extremely complicated and utterly unhandy for numerical as well as for analytical applications. This is true not only for the Coulomb integrals, but even more so for the molecular exchange integrals. Because of this reason repeated efforts by various investigators have been made in the past in order to evaluate improved analytical expressions for these molecular integrals over STO's. Parallel to this development, partly be-

TABLE I. Equation numbers for the definitions and for the numerically stable results of different types of integrals with various scaling parameters α and β of the STO's.

	Integral		
	Overlap	Kinetic energy	Coulomb
Def.	Eq. (4.2)	Eq. (5.1)	Eq. (7.3)
$\alpha=\beta$	Eq. (4.3)	Eqs. (5.3), (4.3)	Eqs. (7.6), (7.10)
$\alpha\neq\beta$	Eqs. (4.6), (4.9)	Eqs. (5.3), (4.6), (4.9)	Eqs. (7.13), (7.15)
$\alpha\approx\beta$	Eq. (4.9)	Eqs. (5.3), (4.9)	Eqs. (7.15), (7.16)

cause of the same reasons, the use of Gaussian-type orbitals was favored. We feel that the hitherto published formulas for molecular integrals over STO's became so unsatisfactorily complicated because the relationship of STO's to B functions was not recognized and, therefore, a certain regular structure of the formulas based on properties of the B functions was not discovered.

As given by Eq. (3.3), an STO can be represented by a linear combination of B functions. Therefore, an integral over STO's is given by a linear combination of integrals over B functions. However, the B functions have some extraordinary properties like, for instance, their behavior under convolution[16] and translation.[15,49] In the present article, the convolution theorems are used for the evaluation of the two-center one-electron integrals and Coulomb integrals. These integrals can again be used for an analytical treatment of the more complicated exchange integrals.[49] Therefore, the systematic use of the B functions establishes a new approach to the molecular integral problem which, in our opinion, may contribute to an essential improvement of the utility and applicability of STO's in molecular LCAO-MO calculations.

STO's form a complete basis of the space $L^2(\mathfrak{R}^3)$.[50] The B functions are related to the STO's by the linear combination Eq. (3.3). Therefore, the basis of B functions can be obtained from the STO basis by a linear transformation which is represented by a triangular matrix. This means, because the B functions are also linearly independent, that the B basis is also complete in $L^2(\mathfrak{R}^3)$.[51] Therefore it is possible to use B functions in an LCAO calculation from the very beginning without relying on STO's.[43] Furthermore, the completeness of the B functions makes it possible to represent two-center charge densities by a linear combination of one-center charge densities. This offers the possibility to represent all multicenter integrals, which occur in a nonrelativistic LCAO calculation, in terms of the integrals which are treated in the present article.[28]

APPENDIX A: AN INDEPENDENT PROOF FOR THE COULOMB INTEGRAL

Two essential results for the Coulomb integral, defined by Eq. (7.3), are Eq. (7.13), which we call (a), and Eq. (7.16), which be call (b) now.

Both (a) and (b) can be obtained from Eq. (7.11). Formula (a) follows from Eq. (7.11) with the help of the theory of distributions as discussed in Sec. VII C. Formula (b) follows from Eq. (7.11) by classical methods as will be shown in this Appendix. The equivalence of (a) and (b) was shown in Sec. VII D. Hence, if we derive (b) from Eq. (7.11), this consideration also verifies (a) and, therefore, adds to our discussion another proof for (a). This is desirable because we could not discuss in all details the derivation of (a) which was given by using the theory of distributions. On the other hand, the application of the theory of distributions for the derivation of (a) was necessary because (a) could not be obtained otherwise; it is rather hopeless to derive (a) from (b), whereas (b) can be obtained from (a).

In order to derive (a) from Eq. (7.11) we must remove the "cancelling singularities" in the integrand of Eq. (7.11) before we can perform the integration over $\vec{r}_2$. This is possible with the help of Eqs. (4.8) and (6.6). Then, in Eq. (7.11), the singular parts of the integrands may be written

$$(2L_1-1)!!\,\mathfrak{Z}^{M_1*}_{L_1}(\alpha(\vec{R}+\vec{r}_2))-\sum_{q=0}^{N_1+L_1} B^{M_1*}_{q-L_1,\,L_1}(\alpha(\vec{R}+\vec{r}_2))$$

$$=\sum_{q=N_1+L_1+1}^{\infty}(\beta/\alpha)^{L_1+1}\left[\,[1-(\alpha/\beta)^2]^q-\sum_{p=0}^{N_1+L_1}\binom{q}{p}\left(\frac{(\alpha/\beta)^2}{1-(\alpha/\beta)^2}\right)^p\right][1-(\alpha/\beta)^2]^q B^{M_1*}_{q-L_1,\,L_1}(\beta(\vec{R}+\vec{r}_2)) \quad \text{for } \beta\geq\alpha\,. \tag{A1}$$

This expression does not contain any singularities. However, the removal of the singularities was only possible by representing the integrand as an infinite series, which also produces an infinite series in the result. If we introduce Eq. (A1) into the integrand of Eq. (7.11), the integration over $\vec{r}_2$ can be performed with the help of the convolution theorem Eq. (4.3). After a rearrangement of the resulting terms we obtain the same result as given by Eq. (7.16).

APPENDIX B: LIST OF SOME NOTATIONS

For the evaluation of the molecular integrals discussed in this article, the reduced Bessel functions (RBF's), which play the role of basis functions, as well as their overlap integrals, are of central importance. For a future extension of the method discussed in this article, it is advisable to use a notation for the RBF's and their overlap integrals which is particularly suitable for a

concise representation of molecular multicenter integrals.

In previous work, the RBF's and their overlap integrals were used in another context and denoted in a way which differs slightly from the notation used in the present paper. Because, however, some of the results given in our previous article[16] are the basis for the derivations given in the present paper, it seems necessary to clarify the situation in order to avoid confusion.

In the present article, the *nonscalar reduced Bessel function*

$$[2^{N+L}(N+L)!]^{-1}(\alpha r)^L \hat{k}_{N-1/2}(\alpha r) Y_L^M(\Omega_{\vec{r}}) \tag{B1}$$

is denoted by

$$B_{N,L}^M(\alpha\vec{r}) \tag{B2}$$

as stated in Eq. (2.14), whereas in our foregoing paper[44] the same function Eq. (B1) is denoted by

$$\mathfrak{B}_{N-1/2,L}^M(\alpha\vec{r}). \tag{B3}$$

The definition Eq. (2.14) is only used for integer N, because only in this case the factorial function, which is contained in the factor of the nonscalar reduced Bessel function Eq. (B1), is well defined.

In the present article, the function

$$(\alpha r)^L \hat{k}_\nu(\alpha r) Y_L^M(\Omega_{\vec{r}}) = \hat{k}_\nu(\alpha r)\mathcal{Y}_L^M(\alpha\vec{r}) \tag{B4}$$

is denoted by

$$\hat{B}_{\nu,L}^M(\alpha\vec{r}) \tag{B5}$$

as stated in Eq. (2.13), whereas in our previous work[45] the same function Eq. (B4) is denoted by

$$B_{\nu,L}^M(\alpha\vec{r}). \tag{B6}$$

The index ν describes the order of the RBF as given in Eq. (2.7).

For integer N, the first index N of the $B_{N,L}^M$ function defined by Eq. (2.14) differs from the order $(N-\frac{1}{2})$ of the $\hat{k}_{N-1/2}$ function by $-\frac{1}{2}$. The omission of this quantity simplifies the formulas.

For noninteger ν, the first index ν of the $\hat{B}_{\nu,L}^M$ function defined by Eq. (2.13) equals the order ν of the $\hat{k}_\nu$ function. This notation has advantages if the functions $\hat{k}_\nu(\alpha r)\mathcal{Y}_L^M(\alpha\vec{r})$ with arbitrary ν are used as LCAO basis functions in molecular calculations.

It may be noted that in this article as well as in previous papers[10,18] the *regular solid spherical harmonic* without modifying factor[46] is denoted by $\mathcal{Y}_L^M$, whereas the *irregular solid spherical harmonic* without modifying factor is denoted by $\mathfrak{Z}_L^M$, according to Eqs. (2.2) and (2.3).

In the present article, the *overlap integral*

$$\int d\vec{r}\, B_{N_1,L_1}^{M_1 *}(\alpha\vec{r}) B_{N_2,L_2}^{M_2}(\beta(\vec{r}-\vec{R})) \tag{B7}$$

is denoted by

$$S_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R}), \tag{B8}$$

whereas in the foregoing article[47] the *convolution integral*

$$\int d\vec{r}\, B_{N_1,L_1}^{M_1 *}(\alpha\vec{r}) B_{N_2,L_2}^{M_2}(\beta(\vec{R}-\vec{r})) \tag{B9}$$

was denoted by the same symbol as given above in Eq. (B8).

If relationships among *convolution integrals* are investigated, an abbreviation for the quantity Eq. (B9) is advantageous, because for the convolution integral one has

$$S_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})_{\text{convol}} = S_{N_2,N_1}^{L_2,L_1 *}(\alpha,\beta;\vec{R})_{\text{convol}}. \tag{B10}$$

Of course, the formula which is obtained by the analytical evaluation of the integral Eq. (B9) exhibits the same symmetry.[48]

For *overlap integrals* one has the less symmetric relationship

$$S_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})_{\text{overlap}} = S_{N_2,N_1}^{L_2,L_1 *}(\alpha,\beta;-\vec{R})_{\text{overlap}}. \tag{B11}$$

It is clear that

$$S_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})_{\text{overlap}} = (-1)^{L_2} S_{N_1,N_2}^{L_1,L_2}(\alpha,\beta;\vec{R})_{\text{convol}}. \tag{B12}$$

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[50]B. Klahn, Ph.D. dissertation (Göttingen, 1975), p. 79. See also, B. Klahn and W. A. Bingel, Theor. Chim. Acta (Berlin) 44, 9 (1977); 44, 27 (1977).
[51]See Ref. 50, p. 73.