Numerical properties of a new translation formula for exponential-type functions and its application to one-electron multicenter integrals

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Hitherto known formulas for the translation of exponential-type functions (ETF's) from one center to another (i.e., addition theorems) encounter serious difficulties of one kind or another in practical applications. In contrast, the recently derived new addition theorem of Λ functions appears to be free of many of those difficulties. The Λ functions are a special class of ETF's, defined by a product of an exponential, a Laguerre function, and a regular solid spherical harmonic:

$$\Lambda_{nl}^{m}(r,\theta,\phi)=2^{3/2}N(n,l)e^{-r}L_{n-l-1}^{(2l+2)}(2r)(2r)^{l}Y_{l}^{m}(\theta,\phi).$$

We have examined the new one-range addition theorem for its applicability to quantum-mechanical multicenter problems from the computational point of view and found it very useful. Test calculations on molecular multicenter one-electron integrals are reported. Under term-by-term integration, accuracy of 10^{-6} could be achieved for all these integrals with an acceptable number of expansion terms.

I. INTRODUCTION

In many problems of molecular physics, addition theorems which express an exponential-type function (ETF) in terms of ETF's shifted to a different center are often desired. Barnett and Coulson[1] were the first to develop a method for achieving this goal with Slater-type orbitals (STO's). Their success was limited in that they were unable to obtain the expansion coefficients in a closed form. Moreover, their method requires the introduction and evaluation of a multitude of special functions and becomes unwieldy very rapidly as the quantum numbers as well as the number of centers of the STO's increase.

Smeyers[2] and later Guseinov[3,4] developed another method to express an STO in terms of shifted STO's and have applied it to the calculation of multicenter integrals keeping only a small number of terms (8—10) in the expansion. We shall show in Sec. VI that many more terms (up to 80) may be required at times to compute two-center nuclear attraction and overlap integrals with a not unreasonable absolute accuracy of 10^{-6}. As we shall see in Sec. III, there are strong mathematical reasons to suspect that this method would be beset with intolerably large cancellation errors as more terms are kept in the expansion.

New addition theorems for ETF's were recently reported from this laboratory[5] (Ref. 5 is hereafter referred to as I). These offer intriguing, new possibilities. In particular, the addition theorem for the complete, orthonormal set of so-called Λ functions (defined in Sec. II) appears to be very economical. The expansion coefficients are themselves expressed in terms of Λ functions and appear in a closed form. Moreover, the Λ addition theorem does not divide space into different regions—an important factor in the evaluation of molecular multicenter integrals.

We define Λ functions and describe their relationships with other ETF's in Sec. II. The Λ addition theorem is itself described and discussed in Sec. III. In Sec. IV we consider some of its numerical aspects, in particular, its pointwise convergence. We apply the theorem to the problem of one-electron multicenter integrals in Sec. V. Results described in Sec. VI show its behavior under term-by-term integration. An overall assessment is presented in Sec. VII.

II. DEFINITIONS AND BASIC FORMULAS

We call a function of the form

$$\Phi_{n,l}^{m}(\vec{r})=e^{-r}p_{n}(r)\mathcal{Y}_{l}^{m}(\vec{r}) , \tag{2.1}$$

where $p_n(r)$ is an arbitrary polynomial of order n, an exponential-type function (ETF). The regular solid spherical harmonic $\mathscr{Y}_l^m(\vec{r})$ is given by the product $r^l Y_l^m(\hat{r})$, where $\hat{r}$ specifies the direction (θ,ϕ) of the local vector $\vec{r}$ defined by spherical coordinates r,θ,ϕ. For the surface spherical harmonics $Y_l^m(\theta,\phi)$ of order l with z projection m we use the definition of Condon and Shortley.[6]

Various ETF's can be obtained by different definitions of $p_n(r)$. In this paper, we restrict ourselves to the discussion of STO's and lambda functions. A well-established set of ETF's is given by the system of Slater-type functions (or orbitals, STO's). The unnormalized STO's are defined by

$$\chi_{n,l}^m(\alpha\vec{r})=(\alpha r)^{n-1}e^{-\alpha r}Y_l^m(\hat{r}) . \tag{2.2}$$

The STO's form a complete but nonorthogonal basis set.[7] By a simple linear transformation given in Eq. (2.7), the STO's are closely related to the so-called lambda functions, which were introduced in I. In these functions, defined by

$$\Lambda_{nl}^m(\alpha\vec{r})=(2\alpha)^{3/2}N(n,l)e^{-\alpha r}L_{n-l-1}^{(2l+2)}(2\alpha r)(2\alpha r)^l Y_l^m(\hat{r}) , \tag{2.3a}$$

with the normalization factor

$$N(n,l)=[(n-l-1)!/(n+l+1)!]^{1/2} , \tag{2.3b}$$

the polynomial $p_n(r)$ is essentially given by the associated Laguerre polynomial

$$L_n^{(\alpha)}(x)=\sum_{p=0}^{n}\begin{bmatrix}n+\alpha\\ n-p\end{bmatrix}\frac{(-1)^p}{p!}x^p . \tag{2.4}$$

The Λ functions so defined satisfy the orthonormality relation

$$\langle\Lambda_{n_b l_b}^{m_b}(\vec{r})\,|\,\Lambda_{n_k l_k}^{m_k}(\vec{r})\rangle=\langle n_b l_b m_b\,|\,n_k l_k m_k\rangle=\delta_{n_b n_k}\delta_{l_b l_k}\delta_{m_b m_k} . \tag{2.5}$$

Later on, as in Eq. (2.5), the subscripts b and k shall be used to denote the bra state and the ket state, respectively.

Now it can be shown that[5]

$$\Lambda_{nl}^m(\alpha\vec{r})=(2\alpha)^{3/2}N(n,l)\sum_{p=0}^{n-l-1}(-2)^p 2^l(p!)^{-1}\begin{bmatrix}n+l+1\\ n-l-1-p\end{bmatrix}\chi_{p+l+1,l}^m(\alpha\vec{r}) \tag{2.6}$$

and, conversely,

$$\chi_{nl}^m(\alpha\vec{r})=(n-l-1)!2^{-2l}(2\alpha)^{-3/2}\sum_{p=0}^{n-l-1}(-1)^p\begin{bmatrix}n+l+1\\ n-l-1-p\end{bmatrix}N^{-1}(p+l+1,l)\Lambda_{p+l+1,l}^m(\alpha\vec{r}) . \tag{2.7}$$

Hence, any STO is given by a simple linear combination of Λ functions and vice versa. A similar two-way relation also exists[5] between Λ's and reduced Bessel functions (RBF's) defined by

$$B_{n,l}^m(\alpha\vec{r})=\hat{k}_{n-1/2}(\alpha r)(\alpha r)^l Y_l^m(\hat{r})[(2n+2l)!!]^{-1} , \tag{2.8a}$$

$$\hat{k}_{n-1/2}(r)=r^{-1}e^{-r}\sum_{p=1}^{n}\frac{(2n-p-1)!}{(p-1)!(n-p)!}2^{p-n}r^p . \tag{2.8b}$$

They are

$$\Lambda_{n,l}^m(\alpha\vec{r})=\alpha^{3/2}\sum_{t=l+1}^{n}b_t^{n,l}B_{t-l,l}^m(\alpha\vec{r}) , \tag{2.9a}$$

$$b_t^{n,l}=(-1)^{t-l-1}2^{t+1/2}(n+t)![(t-l-1)!(n-t)!(2t+1)!!]^{-1}N(n,l)(2n+1) \tag{2.9b}$$

and, conversely,

$$B_{n+1,l}^m(\alpha\vec{r})=(2\alpha)^{-3/2}n![(2n+2l+2)!!]^{-1}\sum_{p=0}^{n}(-1)^p\begin{bmatrix}2n+2l+3\\ n-p\end{bmatrix}N^{-1}(p+l+1,l)\Lambda_{p+l+1,l}^m(\alpha\vec{r}) . \tag{2.10}$$

For the representation of *physical* orbitals any of these basis sets can be used because the transformation formulas [Eqs. (2.6)–(2.10)] are numerically safe for lower values of the principal quantum number n. However, it should be noted that in the case of high principal quantum numbers n—which occur in expansions—the transformation formulas [Eqs. (2.6)–(2.10)] are numerically no longer stable.

In this paper we shall only consider Λ functions and their addition theorem as a prototype of ETF's.

III. ADDITION THEOREMS FOR THE REDUCTION OF MULTICENTER INTEGRALS

The matrix elements which have to be calculated in the LCAO(-MO) scheme are in the general case multicenter one- and two-electron integrals. The most complicated one-electron integral which may occur is the three-center nuclear attraction integral

$$\int \chi_\alpha^*(\vec{r}-\vec{A})\frac{1}{|\vec{r}-\vec{C}|}\chi_\beta(\vec{r}-\vec{B})d\vec{r}\,. \tag{3.1}$$

Here χ stands for an atomic orbital (AO), α and β stand for the sets of quantum numbers required to specify the atomic orbitals. The vectors $\vec{A}$, $\vec{B}$, and $\vec{C}\in\mathscr{R}^3$ are position vectors of the centers under consideration. The most complicated two-electron integral is the general four-center exchange integral

$$\int\int \chi_\alpha^*(\vec{r}_1-\vec{A})\chi_\beta^*(\vec{r}_2-\vec{B})\frac{1}{|\vec{r}_1-\vec{r}_2|}\chi_\gamma(\vec{r}_1-\vec{C})\chi_\delta(\vec{r}_2-\vec{D})d\vec{r}_1 d\vec{r}_2\,. \tag{3.2}$$

The main difficulty associated with the evaluation of these multicenter integrals arises from the fact that the orbitals contain shifted vectors as arguments; i.e., the orbitals are defined with respect to different centers. This difficulty can be tackled with the help of so-called addition theorems which are analytical representations of shifted functions where one or more variables are separated. If an addition theorem is available and applied to a multicenter integral, the number of centers can possibly be reduced because an orbital (i.e., a function in three-dimensional space) which is defined with respect to a certain origin can be shifted to another origin. As some of the variables can also then be separated, the integral ususally becomes easier to evaluate.

The best known examples of addition theorems are the Laplace expansion of the Coulomb potential

$$\frac{1}{|\vec{r}-\vec{R}|}=4\pi\sum_{l=0}^{\infty}(2l+1)^{-1}\sum_{m=-l}^{l}r_<^l r_>^{-l-1}Y_l^{m*}(\hat{r})Y_l^m(\hat{R})\,, \tag{3.3}$$

and the Green's function expansion of the Yukawa potential

$$\frac{e^{-\alpha|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|}=-4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}j_l(i\alpha r_<)h_l^{(1)}(i\alpha r_>)Y_l^{m*}(\hat{r})Y_l^m(\hat{R})\,. \tag{3.4}$$

The equivalence of an addition theorem and a translation formula is obvious from the Laplace expansion [Eq. (3.3)] as it expresses the Coulomb potential field of a unit point charge *shifted by* $\vec{R}$ from the origin O by a superposition of functions (the potential fields of multipoles) centered on O.

A typical feature of these addition theorems is the fact that two different regions of space have to be distinguished between: $r\leq R$ and $r>R$. We shall, therefore, call this kind of addition theorem two-range addition theorem. Similar two-range addition theorems are also known for the RBF's and STO's.[8,9] However, the two-range structure of these addition theorems causes serious problems with the radial integration as it requires the knowledge of indefinte integrals of special functions. In the case of two-electron integrals where two nested radial integrations are to be performed, this problem is further exacerbated. Barnett and Coulson[1] tried to evaluate molecular integrals over STO's using such addition theorems in connection with numerical integration of the radial integrals and complicated (and possibly unstable) multidimensional recurrence schemes. This approach could not compete with integral packages using Gaussians as atomic orbitals.

For certain classes of functions, e.g., Gaussians and spherical Bessel functions, one-range addition theorems are known.[10] The one-range addition theorems are expansions where the variables $\vec{r}$ and

$\vec{R}$ are completely separated, i.e., space need no longer be divided into regions according as whether $r \leq R$ or $r > R$.

For all functions which can be used as atomic orbitals, i.e., elements of the Hilbert space $L_2(\mathscr{R}^3)$, such one-range addition theorems must exist.[5] Let us assume that $\{\phi_n(\vec{r})\}_{n=0}^{\infty}$ is a complete orthonormal basis in $L_2(\mathscr{R}^3)$. Then the following expansion exists for any function $\psi \in L_2(\mathscr{R}^3)$:

$$\psi(\vec{r}-\vec{R}) = \sum_n C_n \phi_n(\vec{r}) \ . \tag{3.5}$$

The coefficients C_n are given by the two-center overlap integral

$$C_n = \int \phi_n^*(\vec{r}) \psi(\vec{r}-\vec{R}) d\vec{r} \ . \tag{3.6}$$

From the last equation it can be seen that the dependence with respect to $\vec{R}$ is completly contained in the coefficients C_n, i.e., we have $C_n = C_n(\vec{R})$. It can be shown[5] that the coefficients $C_n(\vec{R})$ themselves are elements of the same Hilbert space $L_2(\mathscr{R}^3)$. Thus, for any functions $\psi \in L_2(\mathscr{R}^3)$ the following double expansion exists:

$$\psi(\vec{r}-\vec{R}) = \sum_{m,n} \gamma_{mn} \phi_m(\vec{R}) \phi_n(\vec{r}) \ . \tag{3.7}$$

No functional dependence upon $\vec{r}$ and $\vec{R}$ is contained in the coefficients γ_{mn}. The choice of the basis $\{\phi_n\}_{n=0}^{\infty}$ of the Hibert space $L_2(\mathscr{R}^3)$ is, in principle, arbitrary, but for the expansion of exponential-type atomic orbitals (ETO's) the use of the Λ functions which were introduced recently in I appears to be most advantageous. For RBF's and the Λ functions themselves the following one-range addition theorems were also derived in I (Ref. 11):

$$B_{n_1 l_1}^{m_1}(\alpha(\vec{r}-\vec{R})) = \alpha^{-3} \sum_{l_3} \sum_{l_2} \sum_{m_2} \langle l_1 m_1 \mid l_3 m_1 - m_2 \mid l_2 m_2 \rangle (-1)^{l_2} \sum_{n_2} \sum_{n_3} a_{n_3 l_3}^{n_2 l_2 n_1 + l_1, l} \Lambda_{n_3 l_3}^{m_1 - m_2}(\alpha \vec{r}) \Lambda_{n_2 l_2}^{m_2}(\alpha \vec{R}) \ , \tag{3.8}$$

$$\Lambda_{n_1 l_1}^{m_1}(\alpha(\vec{r}-\vec{R})) = \alpha^{-3/2} \sum_{l_3} \sum_{l_2} \sum_{m_2} \langle l_1 m_1 \mid l_3 m_1 - m_2 \mid l_2 m_2 \rangle (-1)^{l_2} \sum_{n_2} \sum_{n_3} T_{n_3 l_3}^{n_1 l_1, n_2 l_2} \Lambda_{n_3 l_3}^{m_1 - m_2}(\alpha \vec{r}) \Lambda_{n_2 l_2}^{m_2}(\alpha \vec{R}) \ , \tag{3.9a}$$

$$l_2 + 1 \leq n_2 < \infty \ , \tag{3.9b}$$

$$\max(l_3 + 1, |n_1 - n_2| - 1) \leq n_3 \leq n_1 + n_2 + 1 \ . \tag{3.9c}$$

Both these series expansions are convergent not only with respect to the norm of $L_2(\mathscr{R}^3)$ but also in a pointwise sense. Here, $\langle l_1 m_1 \mid l_3 m_3 \mid l_2 m_2 \rangle$ are the Gaunt coefficients

$$\langle Y_{l_1}^{m_1}(\hat{r}) \mid Y_{l_3}^{m_3}(\hat{r}) \mid Y_{l_2}^{m_2}(\hat{r}) \rangle \ .$$

The coefficients

$$T_{n_3 l_3}^{n_1 l_1, n_2 l_2}$$

of the series expansion [Eq. (3.9a)] were defined in I and will be discussed in more detail in Sec. IV. It is important to note that for each value of n_2, the n_3 summation is limited to at most $2n_1 + 3$ terms and does not increase with increasing summation index n_2. Since n_1 refers to a physical orbital, in practice it involves very few terms, e.g., 11 terms for $4f$ orbitals. This compact result is due to the fact that the two-center overlap integrals [Eq. (3.6)] were themselves expressed in terms of Λ functions.

The idea of deriving one-range addition theorems with the help of a complete orthonormal basis of $L_2(\mathscr{R}^3)$ is not new. Already in 1966 Smeyers[2] investigated the evaluation of two- and three-center integrals over STO's by shifting one orbital from its center to another center and by using an expansion of the shifted function in terms of Λ functions. The two-center integrals remaining in the formula for the reduction of a three-center integral, were then evaluated in elliptical coordinates. In 1978 and 1980 Guseinov[3,4] independently suggested making the same expansion and arrived at somewhat formidable expressions for the integrals.

The method proposed by Smeyers and Guseinov suffers from several drawbacks. A typical feature of this method is the evaluation of the expansion coefficients $C_n(\vec{R})$—which are themselves overlap integrals between Λ functions and STO's—as a linear combination of overlap integrals *over STO's*. However, the representation of a set of orthonormal functions as a linear combination of STO's leads to serious numerical difficulties. It is well

known that Eq. (2.6) cannot be used for the computation of Laguerre polynomials of higher orders because of unavoidable cancellation errors. This numerical problem persists after term-by-term integration. Another disadvantage of this approach is the fact that the number of pure STO-overlap integrals which are required for an expansion coefficient in the sense of Smeyers and Guseinov is proportional to the summation index. Therefore, when the infinite series representing the shifted STO is truncated after $n_2^{\max}$ terms, the number of STO-overlap integrals required is proportional to $(n_2^{\max})^2$, i.e., the evaluation becomes increasingly time consuming. However, in the case of the new addition theorems, Eqs. (3.8) and (3.9), the total number of Λ functions required increases only linearly with $n_2^{\max}$. Moreover, it is not demonstrated that the overlap integrals *over STO's* can be safely evaluated in the case of higher quantum numbers. As will be shown in Sec. VI, in some cases up to 80 terms of the $n_2^{\max}$ summation are required in order to obtain satisfactory accuracy. Such extended expansions are certainly not manageable if the overlap integrals between Λ functions and STO's are expressed as linear combinations of overlap integrals over STO's. We doubt that the accuracy of the numerical results presented in Table I of Guseinov[4] can readily be improved by increasing the number of terms. Due to the transformation formula, Eq. (2.9), between the Λ functions and the RBF's, it would be trivial to express overlap integrals over Λ functions in terms of overlap integrals over RBF's, which possess a much more compact structure[12] than overlap integrals over STO's. However, we discovered that this approach suffered from the same numerical inadequacies as that of Smeyers and Guseinov. In fact, this was one of the main reasons for the derivation of Eq. (3.9) which, as will be shown later, is numerically stable even for such high summation limits as $l_2^{\max}=20$ and $n_2^{\max}=150$.

The recently derived one-range addition theorems have certain advantages over the hitherto known two-range addition theorems, as the integration can be performed much more easily due to the complete separation of integration variables. However, a comparison of the one-range and two-range formulas shows that the one-range formulas contain one infinite summation for the radial part where the two-range formulas contain only a finite sum. This is the price one has to pay in order to be able to perform the radial integrations analytically.

Our aim in the rest of this paper is to investigate the usefulness of the recently derived one-range addition theorem [Eq. (3.9)] for computational purposes, e.g., the rate of convergence, the numerical stability, etc. To this end we have also investigated all molecular one-electron integrals with ETF's which can occur in an LCAO(-MO) calculation. Results of test calculations with various parameters are presented.

IV. NUMERICAL PROPERTIES OF THE Λ FUNCTION ADDITION THEOREM

Any application of the Λ functions addition theorem [Eq. (3.9)] (e.g., evaluation of multicenter integrals) typically involves a string (or strings) of T coefficients. Whether the theoretical advantages of using a one-range addition theorem can be realized, in practice, depends upon the relative sizes of the (T) coefficients in the string(s). Large variations in their relative sizes would inevitably lead to large cancellations and, hence, to unacceptably large round-off errors. We have computed T coefficients involved in the expansion of physical orbitals up to $4f$ and found them to be typically of the order 10^{-1} to 10^{+1} for all values of the expansion indices (as high as $n_2 \leq 150$ and $l_2 \leq 20$ were tried). Such a narrow spread in magnitude is unlikely to produce appreciable round-off errors.

We have used the formulas given in I for computing T coefficients. They are reproduced below for the sake of completeness. For $n_1, n_2 \leq n_3$,

$$T_{n_3 l_3}^{n_1 l_1, n_2 l_2} = \pi(-1)^{l_1+n_3-1} N^{-1}(n_3, l_3)^{-n_3+3/2} \times \sum_{t_1=\min(t_1)}^{\Delta n_3} \left[\sum_{t_1=\min(t_2)}^{t_1} b_{t_2-t_1+n_1}^{n_1 l_1} \frac{(t_2+n_3-l_3-1)!(2t_2+2n_3+1)!!}{(t_2+2n_3+1)!(2t_2)!!} \right] \times \left[\sum_{p=\min(p)}^{\max(p)} (-1)^p \begin{bmatrix} \Delta l_3 \\ p \end{bmatrix} b_{t_1-\Delta n_3+n_2+p}^{n_2 l_2} \right] . \tag{4.1a}$$

Here

$$\Delta n_3 = n_1 + n_2 + n_3 + 1 \,, \qquad \Delta l_3 = (l_1 + l_2 - l_3)/2 \,, \tag{4.1b}$$

and the summation limits are

$$\begin{aligned} \min(t_1) &= \max(0, \Delta n_3 - n_2 + l_2 + 1 - \Delta l_3) \,, \\ \min(t_2) &= \max(0, l_1 + 1 + t_1 - n_1) \,, \\ \min(p) &= \max(0, \Delta n_3 - n_2 + l_2 + 1 - t_1) \,, \\ \max(p) &= \min(\Delta l_3, \Delta n_3 - t_1) \,, \end{aligned} \tag{4.1c}$$

where the b coefficients (already encountered in Sec. II) are given by Eq. (2.9b). Using the symmetry relations

$$T^{n_1 l_1, n_2 l_2}_{n_3 l_3} = T^{n_1 l_1, n_3 l_3}_{n_2 l_2} \tag{4.2a}$$

$$= (-1)^{l_2} T^{n_3 l_3, n_2 l_2}_{n_1 l_1} \tag{4.2b}$$

$$= (-1)^{l_3} T^{n_2 l_2, n_1 l_1}_{n_3 l_3} \tag{4.2c}$$

in conjunction with Eq. (4.1), all required T coefficients were computed.

A. Accuracy of computed T coefficients

This is an appropriate stage to discuss the accuracy of the computed T coefficients. A partial test is furnished by setting $\vec{R}=0$ in Eq. (3.9). We then get

$$\Lambda^{m_1}_{n_1 l_1}(\alpha \vec{r}) = (4\pi\alpha^3)^{-1/2} \sum_{n_2} T^{n_1 l_1, n_2 0}_{n_3 l_1} \Lambda^0_{n_2 0}(0) \Lambda^{m_1}_{n_3 l_1}(\alpha \vec{r}) \,. \tag{4.3}$$

As the Λ functions form a complete orthonormal basis set, we may equate the coefficients of $\Lambda^{m_1}_{n_3 l_1}(\alpha \vec{r})$ on both sides to obtain

$$\delta_{n_3 n_1} = (4\pi\alpha^3)^{-1} \sum_{n_2} T^{n_1 l_1, n_2 0}_{n_3 l_1} \Lambda^0_{n_2 0}(0) \,. \tag{4.4}$$

The sum over n_2 is restricted by the condition

$$\max(1, |n_1 - n_3| - 1) \le n_2 \le n_1 + n_3 + 1 \,. \tag{4.5}$$

As at least one set of n's in the T's correspond to a physical orbital, it is convenient to choose $n_1 l_1$ to correspond to this physical state in view of the condition $n_1, n_2 \le n_3$ of Eq. (4.1). In Table I the results of inserting computed T's (obtained using 26 digit arithmetic) in the right-hand side of Eq. (4.4) are shown. While $n_1 l_1$ are confined to physical orbitals up to $4f$, n_3 is a summation index which was allowed to go up to 70. The deviation of test results from $\delta_{n_1 n_3}$ shows a uniform trend with respect to both n_1 and n_3, and remains acceptably small ($\le 10^{-13}$) throughout the range of expansion.

TABLE I. Accuracy of computed T coefficients from the relation

$$\delta_{n_1 n_3} = (4\pi\alpha^3)^{-1/2} \sum_{n_2} T^{n_1 l_1, n_2 0}_{n_3 l_1} \Lambda^0_{n_2 0}(\vec{0}) \,.$$

l_1	n_1	n_3	$\lvert \delta_{n_1 n_3} - \text{RHS} \rvert$
0	1	1	4×10^{-25}
		70	5×10^{-19}
	2	1	5×10^{-24}
		70	2×10^{-17}
	3	1	2×10^{-14}
		70	3×10^{-15}
	4	1	9×10^{-23}
		70	2×10^{-13}
1	2	2	3×10^{-24}
		70	1×10^{-17}
	3	2	2×10^{-23}
		70	3×10^{-16}
	4	2	2×10^{-22}
		70	7×10^{-14}
2	3	2	5×10^{-25}
		70	4×10^{-17}
	4	3	1×10^{-22}
		70	5×10^{-15}
3	4	4	2×10^{-24}
		70	3×10^{-15}

B. Pointwise convergence

In order to check the pointwise convergence of the translation formula [Eq. (3.9)], we apply it to a $1s$ function. In Table II we tabulate $(4\pi)^{1/2} \times \Lambda^0_{10}(\vec{r}-\vec{R})$ for fixed $\vec{R}=1.0\hat{z}$, and $\vec{r}=0.0$ through 2.0 in steps of 0.1, also along the z direction, computed with the help of the translation formula. $\Lambda^0_{10}(\vec{r}-\vec{R})$ is symmetric about R and the function values computed using the expansion reflect this. The expansion in l_2 was terminated in each case after the value (for $n_2^{\max}=60$) had stabilized to five figures. A comparison of the values calculated with Eq. (3.9) (columns 2 and 3) with

TABLE II. Pointwise application of Λ addition theorem to the 1s function $\Lambda^0_{10}(\vec{r}-\vec{R})$. Here $\vec{R}=1.0\hat{z}$ *(fixed)*, $\vec{r}=0.0(0.1)2.0\hat{z}$, and $n_2^{\max}=60$. Value at the cusp ($\vec{r}=\vec{R}$) is always underestimated.

	$(4\pi)^{1/2}\Lambda^0_{10}(\vec{r}-\vec{R})$		
	Addition theorem		
$\lvert\vec{r}-\vec{R}\rvert$	$r<R$	$r>R$	Exact
1.0	0.207 55	0.208 93	0.207 55
0.9	0.229 37	0.229 86	0.229 38
0.8	0.253 52	0.252 47	0.253 51
0.7	0.280 28	0.277 89	0.280 17
0.6	0.309 40	0.307 57	0.309 63
0.5	0.341 83	0.342 50	0.342 20
0.4	0.379 12	0.382 14	0.378 19
0.3	0.420 01	0.423 52	0.417 96
0.2	0.458 70	0.461 09	0.461 92
0.1	0.486 80	0.487 78	0.510 50
0.0	0.497 29	0.497 29	0.564 19

the exact values calculated directly (column 4) reveals that the expansion results more or less preserve the symmetry. They are seen to deviate from the exact results in an oscillatory fashion. For fixed $\vec{r}$ and $\vec{R}$ the results were also found to show an oscillatory behavior as a function of the upper limit $n_2^{\max}$ on the sum over n_2. The amplitude of oscillations diminishes as the summation limit $n_2^{\max}$ is raised. This trend is presented in Table III for fixed $\vec{r}=2.0\hat{z}$ and $\vec{R}=1.0\hat{z}$. Column 1 lists the upper limit $n_2^{\max}$ on the n_2 sum and column 4 lists the lowest upper limit $l_2^{\max}$ on the l_2 summation for which the results (columns 2 and 3) have stabilized to five figures. We observe that $l_2^{\max}\propto(n_2^{\max})^{1/2}$.

The oscillatory deviations in Tables II and III prove to be no bar to highly accurate evaluation of integrals since integration is a smoothing operation. We shall amply back up this claim with numerical results in Sec. VI.

C. Miscellaneous remarks

Although the infinite expansion in Eq. (3.9) is symmetric under the interchange $(n_2l_2m_2)\rightleftarrows(n_3l_3m_3)$, it is imperative when using it in a

TABLE III. Pointwise application of Λ addition theorem to the 1s and 2s functions $(4\pi)^{1/2}\Lambda^0_{10}(\vec{r}-\vec{R})$ and $(4\pi)^{1/2}\Lambda^0_{20}(\vec{r}-\vec{R})$. Here $\vec{r}=2.0\hat{z}$, $\vec{R}=1.0\hat{z}$ *(fixed)*, $n_2^{\max}=10(5)30$, 30(10)60. $l_2^{\max}$ is the lowest limit of the l_2 sum for which the results (columns 2 and 3) have stabilized to five figures. Empirically, $l_2^{\max}\propto(n_2^{\max})^{1/2}$.

$n_2^{\max}$	$(4\pi)^{1/2}\Lambda^0_{10}(\vec{r}-\vec{R})$ (=0.207 55)	$(4\pi)^{1/2}\Lambda^0_{20}(\vec{r}-\vec{R})$ (=0.119 83)	$l_2^{\max}$
60	0.208 93	0.123 71	14
50	0.208 04	0.121 17	13
40	0.205 94		11
		0.115 31	12
30	0.203 50	0.108 65	10
25	0.203 12		9
		0.107 84	10
20	0.205 32	0.114 09	9
15	0.211 47	0.130 96	8
10	0.222 90	0.160 10	6

truncated form (i.e., $n_2 \le n_2^{\max}, l_2 \le l_2^{\max}$) to allow $n_3 l_3 m_3$ to take on *all* values for which

$$T_{n_3 l_3}^{n_1 l_1, n_2 l_2}$$

does not vanish identically; i.e.,

$$|l_1 - l_2| \le l_3 \le l_1 + l_2, \quad l_1 + l_2 + l_3 \text{ even},$$

$$\max(l_3 + 1, |n_1 - n_2| - 1) \le n_3 \le n_1 + n_2 + 1 .$$

Failure to ensure this produces meaningless numerical results.

Expansion (3.9) is also symmetric under the interchange $\vec{r} \rightleftarrows \vec{R}$ and truncating it introduces only a very slight asymmetry. By far the largest effect of interchanging $\vec{r}$ and $\vec{R}$ is observed on the *rate* of convergence. Which choice proves more profitable depends on the particular application. We shall make further references to this point in the Secs. V and VI on multicenter integrals.

V. MULTICENTER ONE-ELECTRON INTEGRALS WITH Λ ADDITION THEOREM

We now consider the application of the Λ addition theorem to the evaluation of multicenter one-electron integrals which occur in molecular calculations. Since integrals over STO's or RBF's which occur in LCAO(-MO) calculations (i.e., with lower quantum numbers) can be readily expressed by a linear combination of integrals over Λ functions with the help of Eqs. (2.6) to (2.10) we consider integrals over Λ functions only. Our aim in this section will be to express them in terms of one-center integrals which can be evaluated analytically. This is achieved by successive applications of the Λ addition theorem which makes it possible to reduce the number of centers in the integrand by one with each application.

A. Three-center nuclear attraction integral

The most general one-electron integral is the three-center nuclear attraction integral

$$\langle n_b l_b m_b \alpha \vec{R}_b \,|\, r^{-1} \,|\, n_k l_k m_k \beta \vec{R}_k \rangle = \langle \Lambda_{n_b l_b}^{m_b}(\alpha(\vec{r} - \vec{R}_b)) \,|\, r^{-1} \,|\, \Lambda_{n_k l_k}^{m_k}(\beta(\vec{r} - \vec{R}_k)) \rangle , \tag{5.1}$$

where the bra, the ket, and the nuclear attraction operator are centered on $\vec{R}_b$, $\vec{R}_k$, and the origin, respectively. As the first step towards evaluation, we shift one of the two basis functions—for example, the bra—to the center of attraction in order to obtain a series of two-nuclear attraction integrals:

$$\begin{aligned}
&\langle n_b l_b m_b \alpha \vec{R}_b \,|\, r^{-1} \,|\, n_k l_k m_k \beta \vec{R}_k \rangle \\
&= \alpha^{-3/2} \sum_{l_3'} \sum_{l_2'} \sum_{m_2'} \langle l_b m_b \,|\, l_3' m_b - m_2' \,|\, l_2' m_2' \rangle (-1)^{l_2'} \sum_{n_2'} \Lambda_{n_2' l_2'}^{m_2'}(\alpha \vec{R}_b) \\
&\qquad \times \sum_{n_3'} T_{n_3' l_3'}^{n_b l_b, n_2' l_2'} \langle n_3' l_3' m_b - m_2' \alpha \,|\, r^{-1} \,|\, n_k l_k m_k \beta R_k \rangle .
\end{aligned} \tag{5.2a}$$

This series is doubly infinite (in variables n_2' and l_2') since

$$0 \le l_2' < \infty, \quad l_2' + 1 \le n_2' < \infty , \tag{5.2b}$$

while the summation limits over n_3' and l_3' are determined by n_b, l_b, n_2', and l_2' and are finite:

$$\max(|l_b - l_2'|, |m_b - m_2'|) \le l_3' \le l_b + l_2', \quad l_b + l_2' + l_3' \text{ even} , \tag{5.2c}$$

$$\max(l_3' + 1, |n_b - n_2'| - 1) \le n_3' \le n_b + n_2' + 1 . \tag{5.2d}$$

B. Two-center nuclear attraction and overlap integrals

Two types of two-center nuclear attraction integrals occur in molecular calculations. In one type, the bra and the ket share a common center while the nuclear attraction operator has a different center. Evaluation of such integrals does not involve the use of the Λ addition theorem and will not be discussed here. The other type,

$$\langle n_b l_b m_b \alpha \,|\, r^{-1} \,|\, n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle \ ,$$

where the Coulomb operator of nuclear attraction and the bra (or the ket) state have a common center, was encountered in the series expansion [Eq. (5.2)] of Sec. V A. To evaluate it we shift the ket from $\vec{\mathrm{R}}_k$ to the common center of nuclear attraction and the bra. The result

$$\begin{aligned}\langle n_b l_b m_b \alpha \,|\, r^{-1} \,|\, n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle &= \beta^{-3/2} \sum_{l_2} \langle l_k m_k \,|\, l_b m_b \,|\, l_2 m_k - m_b \rangle (-1)^{l_2} \sum_{n_2} \Lambda_{n_2 l_2}^{m_k - m_b}(\beta \vec{\mathrm{R}}_k) \\ &\quad \times \sum_{n_3} \langle n_b l_b m_b \alpha \,|\, r^{-1} \,|\, n_3 l_b m_b \beta \rangle T_{n_3 l_b}^{n_k l_k, n_2 l_2} \ , \end{aligned} \tag{5.3a}$$

$$l_2 + 1 \le n_2 < \infty, \quad \max(l_b + 1, |\, n_2 - n_k \,| - 1) \le n_3 \le n_k + n_2 + 1 \ , \tag{5.3b}$$

is an infinite sum (over n_3) of one-center nuclear attraction integrals. The sum over l_2 is restricted by the Gaunt coefficients to only a few permissible values. In arriving at Eq. (5.3) we have used the symmetry property [Eq. (4.2a)]

$$T_{n_3 l_3}^{n_1 l_1, n_2 l_2} = T_{n_2 l_2}^{n_1 l_1, n_3 l_3}$$

of the T coefficients to interchange $n_2 l_2$ with $n_3 l_3$ in Eq. (3.9). The infinite series [Eqs. (3.9) and (5.3)] remain unaltered by this operation (see Sec. IV), but their convergence rate is now altered to our advantage in Eq. (5.3).

Next in this section we consider the general overlap integral $\langle n_b l_b m_b \alpha \,|\, n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle$, where the bra and the ket are situated on different centers. To be specific, we have considered the case of the bra at the origin and the ket at $\vec{\mathrm{R}}_k$ without any loss of generality. This integral is readily expressed in terms of an infinite series of one-center overlap integrals. Following the steps which lead us from Eq. (3.9) to Eq. (5.3), we obtain

$$\begin{aligned}\langle n_b l_b m_b \alpha \,|\, n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle &= \beta^{-3/2} \sum_{l_2} \langle l_k m_k \,|\, l_b m_b \,|\, l_2 m_k - m_b \rangle (-1)^{l_2} \sum_{n_2} \Lambda_{n_2 l_2}^{m_k - m_b}(\beta \vec{\mathrm{R}}_k) \sum_{n_3} \langle n_b l_b m_b \alpha \,|\, n_3 l_b m_b \beta \rangle T_{n_3 l_b}^{n_k l_k, n_2 l_2} \ , \end{aligned} \tag{5.4a}$$

$$l_2 + 1 \le n_2 < \infty, \quad \max(l_b + 1, |\, n_k - n_2 \,| - 1) \le n_3 \le n_k + n_2 + 1 \ . \tag{5.4b}$$

C. Kinetic energy integrals

We turn now to the kinetic energy integrals

$$\langle n_b l_b m_b \alpha \,|\, -(\tfrac{1}{2})\Delta \,|\, n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle \ .$$

Their evaluation is greatly facilitated by making use of the relations[13]

$$\Delta \Lambda_{nl}^{m}(\alpha \vec{\mathrm{r}}) = \alpha^2 \left[\sum_{t=l+1}^{n} c_t^{nl} \Lambda_{tl}^{m}(\alpha \vec{\mathrm{r}}) - c_l^{nl} \Lambda_{l+1,l}^{m}(\alpha \vec{\mathrm{r}})/(\alpha r) \right] , \tag{5.5a}$$

where

$$\begin{aligned} c_t^{nl} &= (l+1) N(n,l) N(t,l) [(2l+3)!!\, l!]^{-1} 2^{1-l} [(2n+1)(l+t)!\, N^{-2}(n,l)(t!)^{-1} \\ &\qquad - (2t+1)(l+n)!\,(n!)^{-1} N^{-2}(t,l)] \quad \text{for } t > l \ , \\ c_l^{nl} &= 2^{-l-3/2} [N(n,l)(2n+2l)!!]^{-1} \quad \text{for } t = l \ , \end{aligned} \tag{5.5b}$$

$$N(n,l) = [(n-l-1)!/(n+l+1)!]^{1/2} \ . \tag{5.5c}$$

Thus we have that

$$\langle n_b l_b m_b \alpha \mid -\tfrac{1}{2}\Delta \mid n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle = \frac{\alpha^2}{2}\left[c_{l_b}^{n_b l_b} \langle l_b+1 l_b m_b \alpha \mid r^{-1} \mid n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle - \sum_{t=l_b+1}^{n_b} c_t^{n_b l_b} \langle t l_b m_b \alpha \mid n_k l_k m_k \beta \vec{\mathrm{R}}_k \rangle \right]. \tag{5.6}$$

D. One-center nuclear attraction and overlap integrals

As evidenced from Eqs. (5.2), (5.3), (5.4), and (5.6) multicenter one-electron integrals reduce ultimately to expressions involving as their basic ingredients one-center nuclear attraction and overlap integrals. Of the two, the latter is readily evaluated:

$$\langle n_b l_b m_b \alpha \mid n_k l_k m_k \beta \rangle = (2\alpha)^{l_b+3/2} N(n_b, l_b)(2\beta)^{l_k+3/2} N(n_k, l_k) \delta_{l_b l_k} \delta_{m_b m_k} \times \int_0^\infty e^{-(\alpha+\beta)r} r^{2l_b+2} L_{n_b-l_b-1}^{(2l_b+2)}(2\alpha r) L_{n_k-l_k-1}^{(2l_k+2)}(2\beta r) dr \, . \tag{5.7}$$

For the only surviving case, viz., $l_b = l_k$, the definite radial integral above is known.[14] After some manipulation of the hypergeometric functions ${}_2F_1$ the overlap integral is most conveniently written as

$$\langle n_b l_b m_b \alpha \mid n_k l_k m_k \rangle = \delta_{m_b m_k} \delta_{l_b l_k} \{ [2(\alpha\beta)^{1/2}/(\alpha+\beta)]^{2n_b+1} [(\alpha-\beta)/(\alpha+\beta)]^{n_k-n_b} (n_b+n_k)! \times [(n_b-l_b-1)!(n_b+l_b+1)!(n_k-l_k-1)!(n_k+l_k+1)!]^{-1/2} \times {}_2F_1(-(n_b-l_b-1), -(n_b+l_b+1); -(n_b+n_k); (\alpha+\beta)^2/(4\alpha\beta)) \} \, . \tag{5.8}$$

In the limit $\alpha \to \beta$ the curly bracket may be shown to approach $\delta_{n_b n_k}$. The hypergeometric function terminates after $(n_b - l_b)$ terms and its argument, $(\alpha+\beta)^2/(4\alpha\beta)$, is never singular.

The two-center nuclear attraction integral is evaluated in a similar manner after using the relation

$$L_n^{(\alpha)}(x) = \sum_{p=0}^{n} L_p^{(\alpha-1)}(x) \tag{5.9}$$

twice—once for the bra and once for the ket. The result is a finite double sum over an expression similar to Eq. (5.8). Explicitly,

$$\begin{aligned} &\langle n_b l_b m_b \alpha \mid r^{-1} \mid n_k l_k m_k \beta \rangle \\ &= \delta_{m_b m_k} \delta_{l_b l_k} (4\alpha\beta)^{1/2} \{ (n_b-l_b-1)!(n_k-l_k-1)!/[(n_b+l_b+1)!(n_k+l_k+1)!] \}^{1/2} \\ &\times \sum_{n_b'=l_b+1}^{n_b} \sum_{n_k'=l_k+1}^{n_k} \{ (n_b'+l_b)!(n_k'+l_k)!/[(n_b'-l_b-1)!(n_k'-l_k-1)!] \}^{1/2} \\ &\times \{ [2(\alpha\beta)^{1/2}/(\alpha+\beta)]^{2n_b'} [(\alpha-\beta)/(\alpha+\beta)]^{n_k'-n_b'} (n_b'+n_k'-1)! \\ &\times [(n_b'-l_b-1)!(n_b'+l_b)!(n_k'-l_k-1)!(n_k'+l_k)!]^{-1/2} \\ &\times {}_2F_1((-n_b'-l_b-1), -(n_b'+l_b); -(n_b'+n_k'-1); (\alpha+\beta)^2/(4\alpha\beta)) \} \, . \end{aligned} \tag{5.10}$$

Again the hypergeometric function terminates after $(n_b' - l_b)$ terms. Details of the evaluation of Eqs. (5.9) and (5.10) will be presented elsewhere.

VI. RESULTS OF ONE-ELECTRON INTEGRALS

Since the scope for application of the Λ addition theorem to multicenter integrals is potentially quite large, we discuss at some length the results obtained for them.

A. Two-center integrals

The rate of convergence for the series expansions of two-center nuclear attraction and overlap integrals, Eqs. (5.3) and (5.4), depends primarily upon the ratio of the two orbital exponents α and β, or more precisely, upon the quantity $(\alpha+\beta)^2/(4\alpha\beta)$. For $\alpha=\beta$, $(\alpha+\beta)^2/(4\alpha\beta)=1$, the series terminate after $n_2=n_b+n_k$ and $n_2=n_b+n_k+1$, respectively. More terms are needed as $(\alpha+\beta)^2/(4\alpha\beta)$ increases from unity. This is illustrated in greater detail in Table IV. Each entry in the table corresponds to

$$\langle n_b l_b m_b=0,\alpha \mid \mathcal{O} \mid n_k l_k m_k=0,\beta=1,\vec{R}_k\rangle,$$

$$\mathcal{O}=1 \text{ or } r^{-1},$$

corresponding to the overlap integral or the nuclear attraction integral. All permutations involving $1s$, $2s$, and $2p$ states are considered. In columns 4 through 7 the vector $\vec{R}_k$ remains fixed at $2.0\hat{z}$, while α takes on the values 5.0, 10.0, 15.0, and 20.0. In columns 8 and 9, $\vec{R}_k$ takes on the values $5.0\hat{z}$ and $10.0\hat{z}$ while α remains fixed at 10.0. Every entry is in two parts: The *real* number is the converged value of the integral [Eqs. (5.3) and (5.4) after $n_2=85$], the incertainty in the last digit being ≤ 2; the integer number below it is the smallest value of n_2 after which the integral had converged to within six digits after the decimal point (i.e., the converged value had an absolute uncertainty of $<10^{-6}$). The table thus provides information about both relative and absolute measures of convergence obtained. The rate of convergence for fixed R_k (columns 4 through 7) appears to show no predictable trend with respect to different states, however. Comparison of columns 5, 8, and 9 throws light on the behavior of these integrals with respect to variation in the internuclear distance R_k for fixed α ($=10.0$) and β ($=1.0$). Fewer terms are needed in the sum over n_2 to achieve the same *absolute* uncertainty ($\sim 10^{-6}$) as R_k rises. This comes about largely because the integrals themselves become small. There appears to be a slight deterioration in the *relative* uncertainty with rising R_k, but this is of no importance in molecular calculations. In brief, then, it appears to be possible to keep the absolute error below 10^{-6} for a wide range of parameters by summing Eqs. (5.3) and (5.4) up to $n_2=80$.

The results presented in Table IV were obtained by translating the ket to the bra. It would be equally legitimate to translate the bra to the ket, to compute the overlap integrals in Table IV. This was done and both sets of results were found to agree.

A point of some considerable interest which emerged from these calculations was the fact that the rate of convergence was much better when the more diffuse function was expanded about the sharper one. It can be understood in terms of the fact that R_k, the distance of translation, is smaller in relation to the "spread" of the diffuse function as compared to the sharper function. The importance of always expanding the more diffuse function for better convergence cannot be overestressed for programing purposes.

Before leaving the topic of two-center integrals it is legitimate to turn to the question of their accuracy. We have compared an arbitrary selection of our results with published results[15] and found them to be in agreement. The results so far published in the literature, however, have very few significant digits (typically four) and do not provide a useful measure of accuracy. Recently two-center nuclear attraction and overlap integrals have been computed close to machine accuracy by using the RBF's and their convolution theorem in this laboratory.[16] A comparison with these results—which also provides an independent check—enables us to safely claim an accuracy of *at least 7* significant figures *(relative)* in the converged results and often more than that.

B. Three-center nuclear attraction integral

The three-center nuclear attraction integrals are much more complicated than the two-center ones. Two basis functions were shifted to the center of attraction, resulting in infinite sums (over the indices n_3', n_2', and l_2') in Eq. (5.2). Understandably, the three-center integrals exhibit a slower convergence rate than two-center ones.

In Table V we present the results of our calculations for a variety of cases. The relative sizes of the orbital exponents, or the quantity $(\alpha+\beta)^2/(4\alpha\beta)$, again appears to determine the rate of convergence. Neither the geometry nor the choice of

TABLE IV. Two-center integrals $\langle \Lambda^{m_b}_{n_b l_b}(\alpha\vec{r}) \mid \mathcal{O} \mid \Lambda^{m_k}_{n_k l_k}(\vec{r}-\vec{R}_k)\rangle$; $\mathcal{O}=1$ and r^{-1}, corresponding to overlap and nuclear attraction integrals; $\vec{R}_k=R\hat{z}$. Here $\alpha=5.0(5.0)20.0$; $R=2.0,5.0,10.0$; $m_b=0=m_k$. Each *real* entry is the converged value (uncertainty in the last digit does not exceed two anywhere) corresponding to $n_2^{\max}=85$ in Eq. (3.9). The *integer* entry below each *real* entry is the smallest value of $n_2^{\max}$ after which the absolute uncertainty in the converged value was less than 10^{-6}.

			$[\vec{R}_k=2.0\hat{z}]$								$[\alpha=10]$			
$n_b l_b$	$n_k l_k$	$\mathcal{O}$	$\alpha=5.0$		$\alpha=10.0$		$\alpha=15.0$		$\alpha=20.0$		$R=5.0$		$R=10.0$	
1s	1s	1	9.632 965 806 431 7	*D*-2	3.422 686 919	*D*-2	1.863 537 5	*D*-2	1.210 453 2	*D*-2	1.725 136 6	*D*-3	1.167 123	*D*-5
			23		30		23		43		20		19	
		r^{-1}	2.416 783 353 461 1	*D*-1	1.711 696 308 3	*D*-1	1.397 708 90	*D*-1	1.210 467 7	*D*-1	8.574 209 48	*D*-3	5.788 975 5	*D*-5
			23		42		42		61		31		25	
2s		1	−1.644 525 777 227 2	*D*-1	−5.923 329 05	*D*-2	−3.227 221 0	*D*-2	−2.096 458 5	*D*-2	−3.035 725	*D*-3	−2.064 92	*D*-5
			28		31		41		52		30		23	
		r^{-1}	−1.375 603 842 356 5	*D*-1	−9.874 334 55	*D*-2	−8.068 387	*D*-2	−6.988 3	*D*-2	−5.069 194	*D*-3	−3.449 97	*D*-5
			25		43		59		74		37		43	
2p		1	7.129 465 278 686 5	*D*-2	1.347 262 0	*D*-2	4.935 295	*D*-3	2.411 678	*D*-3	6.924 82	*D*-4	4.703 16	*D*-6
			43		38		42		51		43		23	
		r^{-1}	9.199 290 886 852 6	*D*-2	2.287 401 6	*D*-2	1.855 146	*D*-2	1.207 420	*D*-3	1.722 326	*D*-3	1.166 65	*D*-5
			30		49		65		63		37		37	
1s	2s	1	−4.799 594 507 317 0	*D*-2	−1.899 539 641	*D*-2	−1.057 046 7	*D*-2	−6.919 183	*D*-3	−6.908 127 0	*D*-3	−1.140 638	*D*-4
			25		51		53		39		21		19	
		r^{-1}	−1.294 092 197 127 6	*D*-1	−9.688 948 736	*D*-2	−7.998 595 9	*D*-2	−6.953 88	*D*-2	−3.449 321 97	*D*-2	−5.669 730	*D*-4
			31		62		52		74		37		29	
2s		1	6.763 391 625 685	*D*-2	3.116 627 5	*D*-2	1.787 613	*D*-2	1.182 491	*D*-2	1.200 819 0	*D*-2	2.006 96	*D*-4
			33		41		42		50		31		26	
		r^{-1}	5.296 137 456 970 0	*D*-2	5.152 243 0	*D*-2	4.454 612	*D*-2	3.934 69	*D*-2	2.002 417 1	*D*-2	3.350 695	*D*-4
			34		54		75		79		43		37	
2p		1	4.786 474 616 298 6	*D*-2	8.212 428	*D*-3	2.923 14	*D*-3	1.412 897	*D*-3	−1.960 636	*D*-3	−4.043 58	*D*-5
			31		52		42		51		35		30	
		r^{-1}	5.956 163 222 850 8	*D*-2	2.029 797 71	*D*-2	1.089 684	*D*-2	7.040 2	*D*-3	−4.908 194	*D*-3	−1.005 463	*D*-4
			33		52		75		77		43		51	
1s	2p	1	−1.784 003 855 705 6	*D*-1	−6.710 647 616	*D*-2	−3.694 171 85	*D*-2	−2.408 846 9	*D*-2	−8.556 434 64	*D*-3	−1.162 419 43	*D*-4
			28		31		30		40		24		14	
		r^{-1}	−4.649 580 889 167 6	*D*-1	−3.389 518 601 99	*D*-1	−2.783 050 27	*D*-1	−2.414 898 98	*D*-2	−4.269 881 658	*D*-2	−5.777 309 23	*D*-4
			23		32		39		39		30		22	
2s		1	2.747 283 904 785 3	*D*-1	1.130 770 570 7	*D*-1	6.322 016 7	*D*-2	4.144 294 99	*D*-2	1.489 630 17	*D*-2	2.045 659	*D*-4
			24		31		30		23		30		26	
		r^{-1}	2.246 640 729 330 1	*D*-1	1.877 969 984	*D*-1	1.578 108 88	*D*-1	1.380 265 9	*D*-1	2.484 467 7	*D*-2	3.415 870	*D*-4
			30		40		47		33		36		26	
2p		1	−5.273 921 058 369 4	*D*-2	−1.248 976 80	*D*-2	−4.772 795	*D*-3	−2.366 759 7	*D*-3	−2.726 655 6	*D*-3	−4.204 192	*D*-5
			28		30		29		23		26		14	
		r^{-1}	−7.547 160 618 714 0	*D*-2	−3.221 666 82	*D*-2	−1.814 295	*D*-2	−1.192 385	*D*-2	−6.817 482 5	*D*-3	−1.045 237 0	*D*-4
			28		41		47		32		54		41	

TABLE V. Three-center nuclear attraction integrals $\langle \Lambda^{m_b}_{n_b l_b}(\alpha(\vec{r}-\vec{R}_b)) \mid r^{-1} \mid \Lambda^{m_k}_{n_k l_k}(\beta(\vec{r}-\vec{R}_k))\rangle$, $m_b=0=m_k$ for various states, geometries, and orbital exponents. $(\pm n)$ denotes the uncertainty in the last digit.

$n_b l_b$	$n_k l_k$	$\vec{R}_b$ (R_b,θ_b)	α	$\vec{R}_k$ (R_k,θ_k)	β	$n_2^{\max}$	$l_2^{\max}$	Integral
1s	1s	(2.0,60°)	1.0	(2.0,0°)	1.0	30	6	0.294 5(±3)
						150	20	0.294 562(±1)
		(120°)				40	6	0.152 5(±2)
						150	20	0.152 366(±1)
1s	1s	(1.5,0°)		(0.5,180°)		30	6	0.449 9(±1)
						150	20	0.449 956(±1)[a]
		(2.5,0°)		(0°)		30	6	0.341 06(±4)
						150	20	0.341 022(±1)[a]
2s	2s	(2.0,60°)	1.0	(2.0,0°)	1.0	150	20	0.112 456(±1)
		(120°)				150	20	0.076 185(±1)
		(180°)				150	20	0.082 631(±1)
2p	1s	(2.0,60°)		(2.0,0°)		55	12	0.057 975(±2)
						85	12	0.057 976(±1)
1s	1s	(0.5,60°)	1.0	(1.5,0°)	5.0	30	6	0.132 3(±1)
						150	20	0.132 313(±0)
		(120°)				150	20	0.085 929(+−1)
		(180°)				30	6	0.071 7(±1)
						70	8	0.071 72(±2)

[a]These two geometries can be worked out from Hirschfelder *et al.* (Ref. 17). Their values were 0.449 956 and 0.341 022, respectively.

the particular state (i.e., whether 1s, 2s, 2p, etc., are chosen) appear to have any appreciable influence on it.

Absolute accuracy of 10^{-6} was achieved with sums over n_2, n_2' extended to 150 and that over l_2' to 20 for equal orbital exponents $\alpha=\beta$. No signs of numerical instability were encountered even for such large indices. It may be pointed out that the convergence rate of the three-center integral is expected to show substantial dependence on the particular strategy chosen to evaluate it. For example, alternative strategies could involve *one* application of the Λ addition theorem (to shift the bra to the ket or *vice versa*) and one application of the Laplace expansion of $|\vec{r}-\vec{R}|^{-1}$. We shall not pursue this point any further in this paper. Instead, we shall content ourselves with having demonstrated that the Λ addition theorem can be used for accurate evaluation of three-center nuclear attraction integrals without encountering numerical instability even for indices as high as $n_2^{\max}=150, l_2^{\max}=20$. (We have not tried to go higher!)

VII. SUMMARY AND DISCUSSION

The Λ addition theorem promises to be a very useful computational tool as seen in Secs. IV. and VI. It is demonstrably free of numerical instability even when a large number of terms are kept in the expansion. For n_2 up to 150 and l_2 up to 20, no difficulties were encountered. Longer expansions were not tried.

In pointwise applications [i.e., evaluation of $\Lambda^{m_1}_{n_1,l_1}(\vec{r}-\vec{R})$ by means of its expansion Eq. (3.9)], the following points emerged. For *fixed* $\vec{R}$ and summation limits $n_2^{\max}, l_2^{\max}$ on n_2 and l_2, respectively, the deviation from the true function value as a function of $\vec{r}$ is oscillatory. For fixed $\vec{r}$, $\vec{R}$, and $n_2^{\max}$, the function value computed with the help of the addition theorem "saturates" rapidly with

respect to l_2. That is, raising the l_2 sum beyond a certain limit $l_2^{\max}$ does not alter the computed function value to within given precision. In fact, we empirically found that $l_2^{\max} \propto (n_2^{\max})^{1/2}$. The deviation of the saturated value from the true function value as a function of $n_2^{\max}$ is again oscillatory. The amplitude of these oscillations diminishes as the summation limit $n_2^{\max}$ is raised.

Under term-by-term integration the Λ addition theorem is likely to find a wide range of applications. Not unreasonably high absolute accuracy of 10^{-6} can be safely demanded. In addition, the method suffers from none of the disadvantages of Barnett and Coulson's method or the method of Smeyers and Guseinov. In particular, physical states with higher quantum numbers (e.g., $4f$) are just as simply and effectively treated as those with the lowest quantum numbers (e.g., $1s$). Lengthening the expansion (as, for example, to increase accuracy) also does not create numerical difficulties. The rate of convergence depends upon particular applications and is generally found to be quite good. For given separation $\vec{R}$, the addition theorem works better with a diffuse function than with a sharper one. In the evaluation of integrals, therefore, which Λ function is expanded can strongly influence the rate of convergence.

It is easy to obtain a rough estimate of the integral with very few terms in the expansion. Generally speaking, the cost per gain in accuracy rises with the accuracy demanded. Accuracy of three to four digits can be readily had with quite small expansions (Table V). Accuracy of six digits requires considerably larger though manageable expansions.

Apart from this, different stategies (a strategy refers to a particular simplification of a multicenter integral) also would exhibit quite different overall convergence rates. For the restricted scope of this paper, viz., to investigate the feasibility of performing calculations with the help of the Λ addition theorem, we have limited our study of each type of integral to a single strategy—that of obtaining analytical formulas, not necessarily the best one from a computational point of view. With this proviso, the time taken to evaluate typical two-center overlap and attraction integrals in Table IV was about 3 and 12 seconds, respectively. As a measure of the speed of our computer, a square-root operation takes 0.43 msec. For the three-center attraction integrals in Table V, with the smallest of the expansions ($l_2^{\max}=6, n_2^{\max}=30$), it took about 60 seconds. With a medium sized one ($l_2^{\max}=12, n_2^{\max}=80$) it took 130 seconds, and with the largest expansions ($l_2^{\max}=20, n_2^{\max}=150$) it took 280 sec. As about 80–90% of the time goes in reading the T coefficients into the core, a machine with the ability to transfer data rapidly (not a strong point of our machine) would take much less time. Scope for further improvement also exists, as mentioned above, in the development of strategies which maximize the computation efficiency. Work in this direction is in progress.

It is clear that the Λ addition theorem can be applied to the evaluation of multicenter molecular integrals. It was found to be possible to calculate all one-electron multicenter integrals with an absolute accuracy of 10^{-6} with a reasonable number of terms ($n_2^{\max} \leq 80$ for two-center, $n_2^{\max} \leq 150$ and $l_2^{\max} \leq 20$ for three-center integrals) in the expansion. Even longer expansions (for higher accuracy, for instance) are not expected to meet with any numerical diificulties.

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