Expansion of a function about a displaced center for multicenter integrals: A general and closed expression for the coefficients in the expansion of a Slater orbital and for overlap integrals*

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Following a method analogous to one pointed out earlier, a simplified expression for the expansion of a general function about a point displaced from its center is described. Utilizing this, a general and closed expression useful for multicenter integrals in quantum mechanics is derived for the coefficients in the expansion of a general Slater-type orbital (including special cases). The derived expression for the Slater orbital contains terms only of the form $r^{k-l}\exp(\pm\eta r)$ (where k is an integer $\geqslant 0$; l is the order of the coefficient and η is the exponent in the Slater orbital)—very convenient and useful for the analytical evaluation of multicenter integrals. The expression is equivalent to the ones obtained by Silverstone and by Rakauskas and Bolotin but based on a completely different approach. The asymptotic forms for small as well as large values of r are also presented. The importance of the expression is demonstrated by undertaking an example of overlap matrix elements involving Slater orbitals and deriving easily a simple and closed form applicable for all quantum numbers concerned. The ease with which one can write readily the overlap formulas in various cases starting from the general formula is indicated, and some numerical examples are given to support the usefulness of the expressions. The advantages associated with the expression (for the expansion coefficients) for large-scale calculations of multicenter integrals are discussed.

I. INTRODUCTION

It has been recognized in recent years that an efficient and accurate method of evaluating the multicenter integrals is very essential for extracting meaningful conclusions on the electronic structure and physical properties of systems of atoms, molecules, and solids from detailed calculations using accurate available functions. Several methods have been reported in the literature for this purpose.[1-12] Usually one employs for the calculations [even for self-consistent field (SCF) calculations] a linear combination of either Slater-type orbitals (STO's) or Gaussian-type orbitals. The Gaussian-type orbitals, though computationally convenient, do not really offer advantage because of their poor radial dependence.[7] For the STO's the method based on the transformation of integrands into a prolate-spheroidal coordinate system as developed by Roothan, Ruedenberg, Jaunzemis, Wahl, Cade, and others[9] may be used, but it is applicable only to two-center integrals. For the multicenter integrals the method involving the "classical expansion" of orbitals in spherical harmonics—first employed by Coolidge[2] and later extended by Landshoff,[3] Löwdin,[4,5] Barnett and Coulson,[6] Harris and Michels,[7] and others[8]—is helpful. This method, however, requires various recurrence relations for the zeta functions,[6] $\zeta_{N,l}(\eta,r,a)$, $V^M_{N,L,l}(\eta r,\eta a)$ functions,[7] or the numerical integrations.[5,8] Here η is in the exponent in the function $R^{N-1}\exp(-\eta R)Y^M_L(\Theta,\Phi)$ centered at a point B with R,Θ,Φ being the coordinates in a system[13] with origin at B; r is the radial coordinate with respect to a system[13] with origin at A displaced from B by the distance a.

Another independent approach for the evaluation of multicenter integrals is given by Silverstone and co-workers[11] employing Fourier-transform convolution technique. Their approach is quite general for the STO's and requires differentiation operations on the products of spherical Bessel functions. By performing the operations systematically they have been able to obtain elegant formulas for different kinds of multicenter integrals.

The aim of this paper is to present a simple general and closed formula for the coefficients in the expansion of a general STO which incorporates all $\gamma_l(\eta,r,a)$,[6] $\zeta_{N,l}(\eta,r,a)$,[6] and[7] $V^M_{N,L,l}(\eta r,\eta a)$ functions. This eliminates the use of various recursion relations and makes the computations easily accessible and efficient for multicenter integrals. The formula contains terms only of the form $r^{k-l}\exp(\pm\eta r)$ (k is a positive integer or zero, l is the order of the coefficients, and η is the exponent in the STO) and is equivalent to the ones given by Silverstone[11] and by Rakauskas and Bolotin[12] obtained by different approaches.

In Sec. II A we describe details for the derivation of a simplified expression for the coefficients in the expansion of a general orbital of which a formal solution was given by Löwdin and a general expression was first presented in Ref. 8. In

Sec. II B a general and closed expression for the coefficients in the expansion of an STO about a point displaced from the orbitals's center is developed. In Sec. III we write the asymptotic forms of the coefficients in the expansion of an STO for the cases $r \to 0$ and $r \to \infty$. In order to show the use of the expression derived in Sec. II B, we tackle the problem of evaluation of a general overlap matrix in Sec. IV A and obtain a simple and general expression for the overlap integrals. In Sec. IV B some specific cases of overlap integrals involving various s and p orbitals are treated along with some numerical examples to prove the validity of the derived expressions. Our results are discussed in Sec. V and a conclusion is given in Sec. VI.

II. EXPANSION OF A FUNCTION

A. General treatment

Consider that a function $(f_{NL}(R)/R)\ Y_L^M(\Theta, \Phi)$ [$f_{NL}(R)$ may also depend on M] is centered at a point B with R, Θ, Φ as the coordinates in the axes system[13] with B as its origin. Expanding it in terms of spherical harmonics about a point A displaced from B by a distance a, one writes[5,7,8]

$$\frac{f_{NL}(R)}{R}\ Y_L^M(\Theta, \Phi) = \sum_l (1/r)\,\alpha_l(NLM \mid a, r)\, Y_l^M(\theta, \varphi), \tag{1}$$

where r, θ, φ are the radial coordinates and α_l $(NLM \mid a, r)$ are the radial functions in the new axes system[13] at A. The relations connecting the coordinates in the two axes systems are

$$R^2 = a^2 + r^2 - 2ar\cos\theta, \tag{2a}$$

$$\Phi = \varphi, \tag{2b}$$

$$-R\cos\Theta + r\cos\theta = a, \tag{2c}$$

$$R\sin\Theta = r\sin\theta, \tag{2d}$$

The complexity of the right-hand side of Eq. (1) precluded the possibility[7] of finding a simple closed expression for the coefficients $\alpha_l(NLM \mid a, r)$ in the expansion of a STO. However, using standard mathematical relations and tedious algebraic simplifications we show (in Sec. II B) that for a STO it is possible to obtain a simplified, closed, and general expression for the coefficients applicable for all quantum numbers involved. Expressions similar to ours have also been derived by Silverstone and by Rakauskas and Bolotin, though they followed different methods.

In the following we first present a simplified expression for the expansion of a *general* orbital about a point displaced from its center.

From Eq. (1) one writes

$$(1/r)\,\alpha_l(NLM \mid a, r) = \int \frac{f_{NL}(R)}{R}\ Y_L^M(\Theta, \Phi)\, Y_l^M{}^*(\theta, \varphi)\sin\theta\, d\theta\, d\varphi. \tag{3}$$

Now, in general,

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

Equation (4) substituted appropriately for both of the Y_l^m in Eq. (3) yields

$$\alpha_l(NLM \mid a, r) = \frac{1}{2a}\left(\frac{(2l+1)(2L+1)(L-M)!\,(l-M)!}{(L+M)!\,(l+M)!}\right)^{1/2} \int_{|a-r|}^{|a+r|} f_{NL}(R) P_L^M(\cos\Theta) P_l^M(\cos\theta)\, dR, \tag{5}$$

where in arriving at Eq. (5) the integration over φ has been performed and the integration variable θ has been transformed into R with the help of Eq. (2a).

Using (for simplicity of notation[8])

$$Z_1 = -(a^2 + R^2 - r^2)/2aR = \cos\Theta, \tag{6a}$$

$$Z_2 = (a^2 + r^2 - R^2)/2ar = \cos\theta, \tag{6b}$$

and the standard relations

$$P_L^M(Z_1) = (-1)^M \frac{(L+M)!}{(L-M)!} P_L^{-M}(Z_1), \tag{7a}$$

$$P_L^{-M}(Z_1) = \frac{(-1)^M}{2^L L!}(1 - Z_1^2)^{-M/2}\frac{d^{L-M}}{dZ_1^{L-M}}(Z_1^2 - 1)^L, \tag{7b}$$

$$P_l^M(Z_2) = \frac{(-1)^M}{2^l l!}(1 - Z_2^2)^{M/2}\frac{d^{l+M}}{dZ_2^{l+M}}(Z_2^2 - 1)^l, \tag{7c}$$

one obtains

$$P_L^M(Z_1) P_l^M(Z_2) = (-1)^M \frac{(L+M)!}{(L+M)!}\frac{1}{(2^{l+L} l!)L!}\left(\frac{1 - Z_2^2}{1 - Z_1^2}\right)^{M/2} \times \frac{d^{L-M}}{dZ_1^{L-M}}(Z_1^2 - 1)^L \frac{d^{l+M}}{dZ_2^{l+M}}(Z_2^2 - 1). \tag{8}$$

Also from Eqs. (2),

$$(1 - Z_2^2)/(1 - Z_1^2) = R^2/r^2. \tag{9}$$

Furthermore, by direct expansion and differentia-

tion,

$$\frac{d^{L-M}}{dZ_1^{L-M}}(Z_1^2-1)^L = \sum_{p=0}^{[(L+M)/2]} \frac{L!(2L-2p)!(-1)^p}{p!(L-p)!(L+M-2p)!} \times Z_1^{L+M-2p}, \tag{10}$$

where $[\frac{1}{2}x]$ stands for the integral part of $\frac{1}{2}x$, and

$$\frac{d^{l+M}}{dZ_2^{l+M}}(Z_2^2-1)^l = \sum_{p'=0}^{[(l-M)/2]} \frac{l!(2l-2p')!(-1)^{p'}}{p'!(l-p')!(l-M-2p')!} \times Z_2^{l-M-2p'}. \tag{11}$$

From Eq. (6a) (for a general power m),[14]

$$Z_1^m = \left(\frac{-1}{2aR}\right)^m \sum_{q=0}^{m} \frac{m!}{q!(m-q)!} R^{2q}(a^2-r^2)^{m-q}, \tag{12}$$

and similarly, from Eq. (6b),

$$Z_2^m = \frac{1}{(2ar)^m} \sum_{q'=0}^{m} \frac{m!}{q'!(m-q')!} (-1)^{q'} R^{2q'}(a^2+r^2)^{m-q'}. \tag{13}$$

Substituting Eq. (8) into Eq. (5) and utilizing Eqs. (9)–(13), we have

$$\alpha_l(NLM \mid a,r) = \left(\frac{(2L+1)(2l+1)(L+M)!(l-M)!}{(L-M)!(l+M)!}\right)^{1/2} (-1)^L \left(\frac{a}{r}\right)^l \left(\frac{1}{a}\right) 2^{-2(L+l)-1}$$
$$\times \sum_{p=0}^{[(L+M)/2]} \frac{(2L-2p)!(-1)^p 2^{2p}}{p!(L-p)!} \sum_{q=0}^{L+M-2p} \frac{(1-r^2/a^2)^{L+M-2p-q}}{q!(L+M-2p-q)!} \sum_{p'=0}^{[(l-M)/2]} \frac{(2l-2p')!(-1)^{p'}}{p'!(l-p')!} 2^{2p'} \left(\frac{r}{a}\right)^{2p'}$$
$$\times \sum_{q'=0}^{l-M-2p'} \frac{(-1)^{q'}(1+r^2/a^2)^{l-M-2p'-q'}}{q'!(l-M-2p'-q')!} \int_{|a-r|}^{a+r} f_{NL}(R) \left(\frac{R}{a}\right)^{-L+2(p+q+q')} dR. \tag{14}$$

Though the above equation is equivalent[15] to Eqs. (11b) and (12a) derived in Ref. 8, it is a much simplified one. An expression similar to Eq. (14) has been given by Duff[16] on simplifying the relevant expressions of Ref. 8. However, it must be remembered that the expression of Ref. 16 involves negative powers of r inside the summations, which gives rise to inaccuracies in numerical evaluations particularly for small values of r, whereas in expression (14) no negative powers of r appear inside the summations. It must be remarked that Eq. (14) as well as the expression in Ref. 16 suffers from the drawback that severe cancellation errors occur in calculations for large values of r, particularly when l, L, and M are high. It is therefore imperative to transform Eq. (14) to such a form that the cancellation errors are reduced to a minimum.

To this end we introduce first a new summation variable s defined by

$$s = p + q + q' \tag{15}$$

and eliminate q to obtain from Eq. (14)

$$\alpha_l(NLM \mid a,r) = \left(\frac{a}{r}\right)^l \frac{1}{a} \sum_{s=0}^{l+L} Q_{slLM}(a,r) \int_{|a-r|}^{a+r} f_{NL}(R) \left(\frac{R}{a}\right)^{2s-L} dR, \tag{16a}$$

where

$$Q_{slLM}(a,r) = \frac{(-1)^L}{2} \sum_{p'=0}^{[(l-M)/2]} \left(\frac{r^2}{a^2}\right)^{p'} \sum_{p=0}^{p_{\max}} \sum_{q'=q'_{\min}}^{q'_{\max}} (-1)^{q'} \gamma_{l,M}(p',q')$$
$$\times \gamma_{L,-M}(p, s-p-q') \left(1+\frac{r^2}{a^2}\right)^{l-M-2p'-q'} \left(1-\frac{r^2}{a^2}\right)^{L+M-p-s+q'}, \tag{16b}$$

with, in general,

$$\gamma_{l_1,m_1}(p_1,q_1) = \left(\frac{(2l_1+1)(l_1-m_1)!}{(l_1+m_1)!}\right)^{1/2} \frac{(2l_1-2p_1)!\,2^{2(p_1-l_1)}(-1)^{p_1}}{p_1!(l_1-p_1)!q_1!(l_1-m_1-2p_1-q_1)!} \tag{16c}$$

and

$$p_{\max} = \min(L,s), \quad q'_{\min} = \max(0, p+s-L-M), \quad q'_{\max} = \min(s-p, l-M-2p'). \tag{16d}$$

The symbol $\min(n,m)$ [or $\max(n,m)$] attains the value n if $n \leq m$ (or $n \geq m$) or the value m if $m \leq n$ (or $m \geq n$). It must be noted that the results of the q' summation in Eq. (16b) vanishes if $q'_{\max} < q'_{\min}$.

In arriving at Eqs. (16) a rearrangement of the summations has been made and the limits for the summations have been put appropriately so that the total number of terms in the summation becomes minimum without changing the value of the expression. An alternative rearrangement of the summations is also possible in Eq. (16b). The resulting alternate form for $Q_{slLM}(a,r)$ has been given in the Appendix. It must be noted that $\gamma_{l_1 m_1}(p_1, q_1)$ in Eq. (16b) are required to be evaluated only for $0 \leq p_1 \leq [\frac{1}{2}(l_1 - m_1)]$ and $0 \leq q_1 \leq (l_1 - m_1 - 2p_1)$. Now, expanding the factors $(1+r^2/a^2)^{l-M-2p'-q'}$ and $(1-r^2/a^2)^{L+M-p-s+q'}$ in power series of r^2/a^2, one simplifies Eq. (16b) to

$$Q_{slLM}(a,r) = \sum_{v=0}^{l+L-s} b_v(slLM) \left(\frac{r}{a}\right)^{2v}, \tag{17a}$$

with

$$b_v(slLM) = \frac{(-1)^L}{2} \sum_{p'=0}^{p'_{\max}} \sum_{q'=q'_{\min}}^{s} (-1)^{q'} \sum_{q=q_{\min}}^{q_{\max}} (-1)^q \beta_{l,M}(p',q',v-q-p') \sum_{p=0}^{p_{\max}} \beta_{L,-M}(p,s-p-q',q), \tag{17b}$$

where, in general,

$$\beta_{l,m}(p,q,k) = \left(\frac{(2l+1)(l-m)!}{(l+m)!}\right)^{1/2} \frac{(2l-2p)!\, 2^{2(p-l)}(-1)^p}{p!(l-p)!\, q!\, k!\, (l-m-2p-q-k)!}. \tag{17c}$$

In Eq. (17b) the various limits are

$$\begin{aligned} &p'_{\max} = \min(l,\nu), \quad q'_{\min} = \max(0, s-L-M), \\ &q_{\min} = \max(0, p'+q'+\nu-l+M), \quad q_{\max} = \min(\nu-p', L+M-s+q'), \quad p_{\max} = \min(s-q', L+M-s+q'-q). \end{aligned} \tag{17d}$$

Though Eq. (16a) along with Eq. (16b) may be employed for the numerical evaluation of the α functions (in case one resorts to numerical integrations of the integrals which arise in the process of reducing a multicenter integral into a set of single-center integrals), Eq. (16a), along with Eqs. (17), is more appropriate since the cancellation errors are significantly reduced owing to the fact that the coefficients $b_v(slLM)$ do not involve a and r and can be accurately calculated. In the given form [Eqs. (16a) and (17)] the expression is further important since $b_v(slLM)$ are only a few in number and can be easily calculated once for all for even big calculations involving high LM values.

The functions $Q_{slLM}(a,r)$ of Eq. (17a) and $b_v(slLM)$ of Eq. (17b) are related to the parameters $Q_{ls}(NLM|a,r)$ and $C_v(NLM|ls)$ defined by Löwdin.[5] Explicitly,

$$Q_{ls}(NLM|a,r) = 2^{L+l+1} a^{2(l+L-s)} \left(\frac{1}{(2L+1)(2l+1)} \frac{(L+M)!\,(l-M)!}{(L-M)!\,(l+M)!}\right)^{1/2} Q_{slLM}(a,r) \tag{18}$$

and

$$C_v(NLM|ls) = 2^{L+l+1} \left(\frac{1}{(2L+1)(2l+1)} \frac{(L+M)!\,(l-M)!}{(L-M)!\,(l+M)!}\right)^{1/2} b_v(slLM). \tag{19}$$

These relations are important since they provide simple and general expressions for Löwdin's formal parameters $Q_{ls}(NLM|a,r)$ and $C_v(NLM|ls)$ which were not known previously except for an unsimplified expression for $Q_{ls}(NLM|ar)$ given in Ref. 8. The relations (18) and (19) when analyzed in light of Eqs. (17a) and (17b) reveal the fact that Löwdin's parameters $Q_{ls}(NLM|ar)$ and $C_v(NLM|ls)$ really do not depend on the quantum number N. Also, in the process of checking the relations (18) and (19) against the values given by Löwdin for these parameters, we find that the Löwdin's tabulated values for $C_v(NLM|ls)$ agree with ours only when our axes systems[13] at points A and B are the

same as those of Löwdin. As in fact Löwdin's axes system at point B is different than ours, we conclude that Löwdin's parameters $C_\nu(NLM\,|\,ls)$ [and hence $Q_{ls}(NLM\,|\,a,r)$] should be corrected for a phase factor $(-1)^{L+M}$ if one uses his axes systems.

It is interesting to note that Eq. (16a) with $Q_{slLM}(a,r)$ as given by Eqs. (17) is very general and not restricted to a STO or any specific form of $f_{NL}(R)$, but is applicable to any well-behaved function. Thus it is useful even for expanding operators[17] in a matrix element from one center onto the other in some cases where, by expanding the operators instead of the wave function, it is possible to significantly diminish the labor in evaluation of multicenter integrals. Also, for real $f_{NL}(R)$ one notes from Eq. (1) that $\alpha_l(NLM\,|\,a,r)=\alpha_l(NL(-M)\,|\,a,r)$.

B. Case of a Slater-type orbital

An unnormalized STO is given by

$$[f_{NL}(R)\,|R]\,Y_L^M(\Theta,\Phi)=R^{N-1}e^{-\eta R}Y_L^M(\Theta,\Phi)\,. \quad (20)$$

Changing the notation slightly in α–for the purposes of distinction, we have from Eqs. (1), (16a), and (17a)

$$R^{N-1}\exp(-\eta R)\,Y_L^M(\Theta,\Phi)=\sum_l\left(\frac{1}{r}\right)\alpha_l(N\eta LM\,|\,a,r)\,Y_L^M(\theta,\varphi)\,, \quad (21a)$$

where

$$\alpha_l(N\eta LM\,|\,a,r)=\left(\frac{a}{r}\right)^l\frac{1}{a}\sum_{s=0}^{l+L}\left[\sum_{\nu=0}^{i+L-s}b_\nu(slLM)\left(\frac{r^2}{a^2}\right)^\nu\right]\int_{|a-r|}^{a+r}R^Ne^{-\eta R}\left(\frac{R}{a}\right)^{2s-L}dR\,, \quad (21b)$$

with $b_\nu(slLM)$ as given by Eq. (17b).

By straightforward evaluation and simplification [of the integral in Eq. (21b)] we have

$$\int_{|a-r|}^{a+r}R^{2s-L+N}e^{-\eta R}\,dR=\begin{cases}-e^{-\eta a}\displaystyle\sum_{k=0}^{k_{\max}}\left(\frac{1}{\eta}\right)^{k+1}\sum_{k'=0}^{k'_{\max}}\frac{(2s-L+N)!\,r^{k'}a^{2s-L+N-k-k'}}{k'!(2s-L+N-k-k')!}\left[e^{-\eta r}-(-1)^{k'}e^{\eta r}\right], & r\le a\,,\\ -e^{-\eta r}\displaystyle\sum_{k=0}^{k_{\max}}\left(\frac{1}{\eta}\right)^{k+1}\sum_{k'=0}^{k'_{\max}}\frac{(2s-L+N)!\,r^{k'}a^{2s-L+N-k-k'}}{k'!(2s-L+N-k-k')!}\left[e^{-\eta a}-(-1)^{N-L-k-k'}e^{\eta a}\right], & r\ge a\,,\end{cases} \quad (22)$$

where

$$k_{\max}=2s-L+N \quad\text{and}\quad k'_{\max}=2s-L+N-k\,.$$

Substitution of integral (22) in Eq. (21b) gives with subsequent simplification

$$\alpha_l(N\eta LM\,|\,a,r)=\begin{cases}-a^Ne^{-\eta a}\displaystyle\sum_{k'=0}^{l+N}\left(\frac{r}{a}\right)^{k'-l}\left[e^{-\eta r}-(-1)^{k'}e^{\eta r}\right]\sum_{k=0}^{k_{\max}}\left(\frac{1}{\eta a}\right)^{k+1}F_{k',k}(NlLM), & r\le a\,,\\ -a^Ne^{-\eta r}\displaystyle\sum_{k'=0}^{l+N}\left(\frac{r}{a}\right)^{k'-l}\sum_{k=0}^{k_{\max}}\left[e^{-\eta a}-(-1)^{L+N-k+k'}e^{\eta a}\right]\left(\frac{1}{\eta a}\right)^{k+1}F_{k',k}(NlLM), & r\ge a\,.\end{cases} \quad (23a)$$

In the above

$$k_{\max}=2l+L+N-k' \quad (23b)$$

and

$$F_{k',k}(NlLM)=\sum_{s=0}^{l+L}\sum_{\nu=0}^{\nu_{\max}}\frac{b_\nu(slLM)(2s-L+N)!}{(k'-2\nu)!(2s-L+N-k-k'+2\nu)!}\,, \quad (23c)$$

where $\nu_{\max}=\min(l+L-s,[\frac{1}{2}k'])$ and b_ν is given by Eq. (17b).

The similarity between the two forms of $\alpha_l(N\eta LM\,|\,a,r)$ in Eq. (23) for $r\le a$ and $r\ge a$ must be noted. For $r=a$ the two forms become the same, as expected, because of the fact that

$$\sum_{k'=0}^{l+N}(-1)^{k'}F_{k',k}(NlLM)=0$$

if $L+N-k$ is not an even integer. This condition

directly implies that the two forms in Eq. (22) coincide as r tends to a.

The upper limit of k' in Eq. (23) has been fixed as $l+N$, since one finds by direct evaluation that

$$F_{k',k}(NlLM)=0 \text{ if } k'>l+N.$$

This limits the highest power of r to N and consequently from expression (23) for $r \geq a$ one has

$$\alpha_l(N\eta LM\,|\,a,r) \propto r^N e^{-\eta r} \quad \text{as } r \to \infty .$$

In absence of a mathematical proof for the validity of the above limiting form we attempt to justify it by a physical argument. To a point at $r=\infty$, both the centers[13] A and B of the axes systems appear almost coincident with the result that the behavior of a function (r times) measured from A and B at infinity looks alike, namely, $r^N e^{-\eta r}$ in case of a Slater orbital.

The expressions (23) have been verified by numerical evaluations of $\alpha(N\eta LM\,|\,a,r)$ for various values of the parameters involved against the results one obtains by numerical integrations using Eqs. (17) of Ref. 8 [which are equivalent to Eqs. (16a) and (17) of the present text].

The various factors and the summations in formula (23) have been so arranged that the cancellation errors in the calculations reduce to a minimum. Though it appears that many summations are involved for the evaluation of $\alpha_l(N\eta LM\,|\,a,r)$, the total number of terms arising from all of the summations is small because of the limits on various summations. Also, we have checked the correctness of this expression for various cases against the results one obtains for $\zeta_{N,l}(\eta,r,a)$, and $V^M_{N,L,l}(\eta r,\eta a)$ using recurrence relations[6,7].

The above expression $\alpha_l(N\eta lM\,|\,a,r)$ is a general and closed expression and also yields explicit and closed expressions for the $\zeta_{N,l}(\eta,r,a)$ [and $\gamma_l(\eta,r,a)$] functions of Barnett and Coulson[6] and $V^M_{N,L,l}(\eta r,\eta a)$ functions of Harris and Michels.[7] Explicitly,

$$[(2l+1)r/a]^{1/2}\gamma_l(\eta,r,a)=\alpha_l(0\eta 00\,|\,a,r), \tag{24}$$

$$[(2l+1)r/a]^{1/2}\zeta_{N,l}(\eta,r,a)=\alpha_l(N\eta 00\,|\,a,r), \tag{25}$$

and

$$\eta^{-N+1}\left(\frac{(2L+1)}{(2l+1)}\frac{(L-M)!}{(L+M)!}\frac{(l+M)!}{(l-M)!}\right)^{1/2} \times(-1)^{l-L} r V^M_{NLl}(\eta r,\eta a)=\alpha_l(N\eta LM\,|\,a,r), \tag{26}$$

where $\alpha_l(N\eta LM\,|\,a,r)$ is given by Eqs. (23) and $\alpha_l(0\eta 00\,|\,a,r)$ and $\alpha_l(N\eta 00\,|\,a,r)$ are obtained from Eqs. (23) by substituting $N=L=M=0$ and $L=M=0$, respectively. Equations (24)–(26), besides furnishing explicit expressions [particularly for $\zeta_{N,l}(\eta,r,a)$ and $V^M_{NLl}(\eta r,\eta a)$], are helpful for purposes of checking Eqs. (23) which we mentioned above.

Two points regarding the importance of the expression in Eq. (23) are worth mentioning. First, for the evaluation of $\alpha_l(N\eta LM\,|\,a,r)$ one needs the quantities $F_{k',k}(NlLM)$ which are independent of η, a and r and therefore may be calculated once and for all, thereby making the equation applicable to large systems economically. Second, the expression for $\alpha_l(N\eta LM\,|\,a,r)$ involves the r-dependent terms only of the form $r^{k'-l}e^{\eta r}$ and $r^{k'-l}e^{-\eta r}$ with $k' \geq 0$. These forms are very advantageous for the evaluation of matrix elements, since r^{-l} usually gets cancelled (fully or partially) in taking its product with the other functions present in the matrix elements, and the remaining factors combine to yield terms of the form $r^n e^{-\eta r}$ and $r^n e^{\eta r}$, which make the matrix elements subject to either their analytical evaluation or to the treatments well developed for single centers (atomic cases) using STO's for their evaluation. This point will be cleared up further in Sec. IV A where a simple and general expression for overlap integrals between two STO's has been obtained easily with the help of expression (23).

An expansion of a STO has also been obtained in an operator form by Silverstone[11] using the method of Fourier-transform convolution theorem. The expression contains differential operators acting on the products of spherical Bessel functions. Because of its operator form it appears difficult to compare with our expression (23). However, if one evaluates the derivatives systematically according to the method of Todd, Kay, and Silverstone[11] and uses the well-known formulas for the spherical Bessel functions, it is easy to obtain, alternatively, an expression similar to Eq. (23). Rakauskas and Bolotin[12] have also written an expression for the expansion of STO which is much closer to ours.

III. ASYMPTOTIC FORMS OF $\alpha_l(N\eta LM\,|\,a,r)$

To obtain an expression for $\alpha_l(N\eta LM\,|\,a,r)$ for small values of r one needs to expand the r-dependent exponentials in Eq. (23a) in power series of r. After simplification one obtains

$$\alpha_l(N\eta LM\,|\,a,r) \overset{r\to 0}{\sim} 2a^N e^{-\eta a}\left(\frac{a}{r}\right)^l \sum_{i=l}^{\infty}\left(\frac{r}{a}\right)^{2i+1}\sum_{k'=0}^{k'_{\max}}(\eta a)^{2i-k'}\sum_{k=0}^{k_{\max}}\frac{(-1)^k}{(2i+1-k)!}F_{k,k'-k}(NlLM), \tag{27a}$$

with

$$k'_{\max} = 2l + L + N \tag{27b}$$

and

$$k_{\max} = \min(2i + 1, l + N, k'), \tag{27c}$$

where the symbol $\min(x,y,z)$ takes the value x, y, or z, whichever is minimum.

As for the limiting case $r \to \infty$ it is clear from expression (23a) for $r > a$ that

$$\alpha_l(N\eta LM\,|\,a,r) \overset{r\to\infty}{\sim} r^N e^{-\eta r} \tag{28}$$

This behavior has already been discussed in Sec. II A.

IV. OVERLAP INTEGRALS FOR STO's

A. General expression

Before applying the expression given by Eqs. (21a) and (23) it is helpful to write it in an elegant form,

$$R^{N-1}e^{-\eta R}Y_L^M(\Theta,\Phi) = \sum_l \left(\frac{1}{r}\right)\alpha_l(N\eta LM\,|\,ar)\,Y_l^m(\theta,\varphi), \tag{29a}$$

with

$$\alpha_l(N\eta LM\,|\,ar) = \begin{cases} \sum_{k'=0}^{l+N} \left[A_{k'}\left(\frac{r}{a}\right)^{k'-l} e^{-\eta r} + B_{k'}\left(\frac{r}{a}\right)^{k'-l} e^{\eta r}\right], & (r \le a), \\ \sum_{k'=0}^{l+\eta} C_{k'}\left(\frac{r}{a}\right)^{k'-l} e^{-\eta r}, & (r \ge a), \end{cases} \tag{29b}$$

where $A_{k'}$, $B_{k'}$, and $C_{k'}$ are independent of r and are given by

$$A_{k'} = -a^N e^{-\eta a} \sum_{k=0}^{k_{\max}} \left(\frac{1}{\eta a}\right)^{k+1} F_{k',k}(NlLM), \tag{29c}$$

$$B_{k'} = -(-1)^{k'} A_{k'} \tag{29d}$$

$$C_{k'} = A_{k'} + D_{k'}, \tag{29e}$$

$$D_{k'} = (-1)^{L+N-k'+1} a^N e^{\eta a} \times \sum_{k=0}^{k_{\max}} \left(-\frac{1}{\eta a}\right)^{k+1} F_{k',k}(NlLM). \tag{29f}$$

In the preceding equations $k_{\max}$ and $F_{k',k}(NlLM)$ are the same as in Eqs. (23b) and (23c), respectively.

A two-center overlap integral between STO's is defined by

$$\langle N'L'M'\eta'\,|\,NLM\,\eta\rangle = \int dv\, \Psi^*_{N'L'M',\eta'}(\vec{r})\Psi_{NLM\eta}(\vec{R}), \tag{30}$$

where

$$\Psi_{N'L'M',\eta'}(\vec{r}) = r^{N'-1}e^{-\eta' r}\,Y_{L'}^{M'}(\theta,\varphi) \tag{31}$$

and

$$\Psi_{NLM\eta}(\vec{R}) = R^{N-1}e^{-\eta R}Y_L^M(\Theta,\Phi) \tag{32}$$

denote the (unnormalized) STO's centered[13] at A and B, respectively, and where $N' > L'$ and $N > L$.

Substituting Eq. (29a) for $\Psi_{NLM\eta}$ [defined in Eq. (32)] and (31) for $\Psi_{N'L'M',\eta'}$ one has immediately

$$\langle N'L'M'\eta'\,|\,NLM\eta\rangle = \delta_{M,M'}\int_0^\infty r^{N'} e^{-\eta' r}\,\alpha_{L'}(N\eta LM\,|\,ar)\,dr, \tag{33}$$

where we have used the orthogonality of the spherical harmonics to integrate over the angular coordinates, which also destroys the summation over l, giving a contribution only from $l = L'$. Making use of the expression (29b) in Eq. (33), we have

$$\langle N'L'M'\eta'\,|\,NLM\eta\rangle = \delta_{M,M'}\sum_{k'=0}^{N+L'}\left(\frac{1}{a}\right)^{k'-L'}\left(A_{k'}\int_0^\infty dr\, r^{N'+k'-L'}e^{-(\eta+\eta')r} + B_{k'}\int_0^a dr\, r^{N'+k'-L'}e^{(\eta-\eta')r} + D_{k'}\int_a^\infty dr\, r^{N'+k'-L'}e^{-(\eta+\eta')r}\right). \tag{34}$$

It must be noted that the exponential integrals in Eq. (34) are extremely simple because the power of r involved there is $N' + k' - L' \ge 1$.

The evaluation of the integrals in Eq. (34) yields

$$\langle N'L'M'\eta'|NLM\eta\rangle = \delta_{M',M}\, a^{N+N'+1} \sum_{k'=0}^{N+L'} \left[e^{-\eta a} \left(- \frac{n!}{[a(\eta'+\eta)]^{n+1}} + (-1)^{k'} g_n[a(\eta'-\eta)] \right) \sum_{k=0}^{k_{\max}} \left(\frac{1}{\eta a} \right)^{k+1} F_{k',k}(NL'LM) \right.$$

$$\left. - e^{-\eta' a} (-1)^{L+N-k'} h_n[a(\eta'+\eta)] \sum_{k=0}^{k_{\max}} \left(-\frac{1}{\eta a} \right)^{k+1} F_{k',k}(NL'LM) \right], \tag{35a}$$

where

$$n = N' - L' + k', \tag{35b}$$

with $k_{\max}$ and $F_{k',k}(NlLM)$ defined in Eqs. (23b) and (23c),

$$h_n(x) = \sum_{t=0}^{n} \frac{n!}{(n-t)!} \left(\frac{1}{x} \right)^{t+1}, \tag{35c}$$

and

$$g_n(x) = n!/x^{n+1} - e^{-x} h_n(x). \tag{35d}$$

The functions $h_n(x)$ and $g_n(x)$ have appeared on performing the integrations. When x is zero or very small, it is more accurate to use the limiting forms

$$g_n(x) = \begin{cases} 1/(n+1) & \text{if } x = 0, \\ \sum_{t=0}^{\infty} \frac{(-x)^t}{t!(n+t+1)}, & x \text{ small}, \end{cases} \tag{36}$$

which one obtains directly from Eq. (35d) by expanding the exponential and taking the appropriate limits.

Equations (35) constitute a simple and general formula for the overlap integrals and is suited even for the "desk" calculations. For large scale calculations $F_{k',k}(NlLM)$ may be stored once and for all to reduce the calculation time appreciably. Also, Eqs. (35) are applicable without any difficulty even to the case when $\eta' = \eta$ or when the exponent η' is extremely small or zero (when η is zero or small, the roles of η' and η can be interchanged).

The formula (35) derived here contains exponential functions. A general overlap formula has also been derived by Todd, Kay, and Silverstone[11] in terms of spherical Bessel functions. If one replaces the spherical Bessel functions by the equivalent expressions in terms of exponential functions one transforms their formula into the form equivalent to ours.

B. Particular cases with numerical examples

To prove the usefulness of the overlap formula Eqs. (35) [and hence of Eqs. (23)], we treat various cases involving Ns, Np_σ and Np_π orbitals explicitly in the following and give some numerical examples for $\alpha = 4.0364$ using normalized STO's.

Case I: $\langle 1s\eta'|1s\eta\rangle$. In this case $(N'L'M'\eta') = (100\eta')$ and $(NLM\eta) = (100\eta)$. The only nonzero $F_{k',k}(NL'LM)$ parameters in this case are

$$F_{0,0}(1000) = F_{0,1}(1000) = F_{1,0}(1000) = \tfrac{1}{2}; \tag{37}$$

therefore from Eq. (35a)

$$\langle 1s\eta'|1s\eta\rangle = \frac{a^3}{2} \sum_{k'=0}^{1} \left[e^{-\eta a} \left(- \frac{(1+k')!}{[a(\eta'+\eta)^{2+k'}} + (-1)^{k'} g_{1+k'}[a(\eta'-\eta)] \right) \sum_{k=0}^{1-k'} \left(\frac{1}{\eta a} \right)^{k+1} \right.$$

$$\left. - e^{-\eta' a} (-1)^{1-k'} h_{1+k'}[a(\eta'+\eta)] \sum_{k=0}^{1-k'} \left(-\frac{1}{\eta a} \right)^{k+1} \right]. \tag{38}$$

This is a simple expression to evaluate for any values of η, η', and a. The values given in Eq. (37) are also sufficient to express the integrals $\langle N's\eta'|1s\eta\rangle$ in a simple form.

The numerical evaluations give, as for instance,

$$\langle 1s, 0.811|1s, 12.22\rangle = 0.005\,198,$$

$$\langle 2s, 4.46|1s, 0.811\rangle = 0.042\,352,$$

$$\langle 3s, 1.03|1s, 0.811\rangle = 0.443\,924.$$

For this specific case the overlap formula of Todd, Kay, and Silverstone[11] has been written by Silverstone[18] in terms of spherical Bessel functions of order zero and unity. If one replaces the Bessel functions by the expressions in terms of the exponential functions, one obtains a form equivalent to Eq. (38).

Case II: $\langle N' s\eta' | 2s\eta\rangle$. For this one needs

$$F_{0,0}(2000) = F_{2,0}(2000) = \tfrac{1}{2},$$

$$F_{0,1}(2000) = F_{0,2}(2000) = F_{1,0}(2000) = F_{1,1}(2000) = 1.$$

It is now straightforward to obtain the expression similar to the one given in Eq. (38). However, because of the lack of space we do not intend to present the expression here. As a numerical example, we give

$$\langle 3s, 1.49 | 2s, 0.811\rangle = 0.462\,499.$$

Case III: $\langle \eta' s\eta | 2p_\sigma\eta\rangle \equiv \langle N'00\eta' | 210\eta\rangle$. In this case

$$F_{0,0}(2010) = F_{2,0}(2010) = F_{2,1}(2010) = -\tfrac{1}{2}\sqrt{3},$$

$$F_{0,1}(2010) = F_{1,0}(2010) = -\sqrt{3},$$

$$F_{0,2}(2010) = F_{0,3}(2010) = F_{1,1}(2010) = F_{1,2}(2010) = -\tfrac{3}{2}\sqrt{3},$$

and, as numerical examples,

$$\langle 1s, 12.22 | 2p_\sigma, 0.705\rangle = -0.018\,278,$$

$$\langle 2s, 4.46 | 2p_\sigma, 0.705\rangle = -0.138\,828.$$

Case IV: $\langle N' p_\sigma\eta' | 2p_\sigma\eta\rangle \equiv \langle N' 10\eta' | 210\eta\rangle$. For this

$$F_{0,1}(2110) = F_{1,0}(2110) = F_{3,0}(2110) = \tfrac{3}{2},$$

$$F_{0,2}(2110) = F_{1,1}(2110) = \tfrac{15}{2},$$

$$F_{0,3}(2110) = F_{1,2}(2110) = \tfrac{45}{2},$$

$$F_{0,4}(2110) = F_{0,5}(2110) = F_{1,3}(2110) = F_{1,4}(2110) = 45,$$

$$F_{2,0}(2110) = F_{3,1}(2110) = F_{3,2}(2110) = 3,$$

$$F_{2,1}(2110) = 9,$$

$$F_{2,2}(2110) = F_{2,3}(2110) = 18,$$

and

$$\langle 2p_\sigma, 0.705 | 2p_\sigma, 2.82\rangle = -0.083\,933,$$

$$\langle 2p_\sigma, 0.705 | 2p_\sigma, 5.12\rangle = -0.022\,525.$$

Case V: $\langle N' p_\pi\eta' | 2p_\pi\eta\rangle$. Here $(NL'LM) \equiv (211 \pm 1)$,

$$F_{0,2}(211\pm1) = F_{1,1}(211\pm1) = F_{3,1}(211\pm1) = F_{3,2}(211\pm1) = -\tfrac{3}{2},$$

$$F_{0,3}(211\pm1) = F_{1,2}(211\pm1) = F_{2,2}(211\pm1) = F_{2,3}(211\pm1) = -9,$$

$$F_{0,4}(211\pm1) = F_{0,5}(211\pm1) = F_{1,3}(211\pm1) = F_{1,4}(211\pm1) = -\tfrac{45}{2},$$

$$F_{2,1}(211\pm1) = -3,$$

and

$$\langle 2p_\pi, 0.705 | 2p_\pi, 2.82\rangle = 0.053\,187.$$

The intent of listing the values of $F_{k'k}(NlLM)$ in various cases is twofold. Firstly, they are readily available for use in case one wishes to write a particular overlap formula directly from the general formula for calculations. Secondly, since the expression (23) is very important for evaluating the multicenter integrals and involves the quantities $F_{k'k}(NlLM)$ it is of interest to know their magnitudes at least in a few cases. The numerical examples have been cited simply to show that the derived expressions can be employed for calculations and to let a reader check the accuracy of our results.

V. DISCUSSION

The expansion of a general function $[f_{NL}(R)/R] \times Y_L^M(\Theta, \Phi)$ about an arbitrary point derived by means of standard mathematical relations has been given in Eqs. (1), (16a), and (17). The expansion coefficients are the same as used formally by Löwdin, expressed in a general and closed form first in Ref. 8. The derived expression is a simplified one and is useful for (i) the computation of multicenter integrals, particularly when a numerical integration scheme is adopted, (ii) expanding, in appropriate cases, any well-behaved function, and (iii) expanding in some cases an operator[17] appearing in a multicenter matrix element instead of expanding the wave functions to reduce the work involved in computations.

Employing the general expression [Eqs. (1), (16a), and (17)] the expansion of a STO [defined in Eq. (20)] about an arbitrary point displaced from its center has been expressed in Eqs. (21a) and (23) [or Eqs. (29)]. This expansion contains terms only of the form $r^{k'-l} e^{\pm\eta r}$ $(k' \geq 0)$, very convenient for analytic evaluation of the multicenter integrals. The expansion contains quantities $F_{k',k}(NlLM)$ (independent of a, η, and r) which can be calculated once and for all, thereby making the evaluation of multicenter integrals amenable to large-scale calculations economically.

The expansion coefficients [Eqs. (23)] are equivalent to the ones given by Silverstone[11] and by Rakauskas and Bolotin.[12] However, the basic approach used here is quite different and leads to a different formulation of the expansion problem. Thus the present approach may be considered as a new one to obtain the old formulas.

The convenience and importance of using the expansion given in Eqs. (21a) and (23) have been shown by obtaining readily a closed formula, Eq. (35), for a general overlap integral between two STO. This formula is applicable for any value of η, η', and a (even for $\eta = \eta'$). The simplicity of it has been indicated in Sec. IV B, in which

some particular examples have been treated explicitly. The overlap formula, Eq. (35), may be compared specifically with the one obtained by Todd, Kay, and Silverstone[11] by employing the Fourier-transform convolution theorem. Their formula is equivalent to ours but contains spherical Bessel functions of various orders instead of the exponentials. It is possible to transform their formula into the form of Eq. (35) if one uses standard formulas for the spherical Bessel functions in terms of the exponentials and simplifies. Thus our method effectively recasts old formulas of Silverstone and co-workers[11] in new ways.

The expansion coefficients [Eqs. (23)] for a STO derived here are simple, closed, and general and therefore eliminate the use of recursion relations of Harris and Michels[7] for the evaluation of multicenter integrals. Also, the Gaussian functions, which are disadvantageous because of their poor radial dependence, are not really needed.

An important question arises as to the time one would take for computing the multicenter integrals if one used expression (23) for analytic evaluation of the integrals. Since the author is inexperienced in efficient programming, it is difficult to arrive at the correct time estimate. It is, however, possible to present a comparative study. Silverstone and co-workers[11] find that their method compares favorably with the scheme of Silver and Ruedenberg[19] and also with the numerical integration scheme of Harris and Michels.[20] Since we propose to eliminate the use of recursion relations and calculate the quantities $F_{k',k}(NlLM)$, being independent of a, η, and r once and for all, we believe we could have, if equivalent talent is used in programming, a comparable (or faster) program for multicenter calculations.

As for the convergence of expression (21a) over l, there is usually some problem depending on the matrix element to be evaluated. For the two-center matrix elements the convergence problem does not arise, since the orthogonality of the spherical harmonics usually demands contribution only from a particular term in the summation over l. However, for three- and four-center matrix elements the convergence may be slow, depending on the type of the matrix element. In this paper we have given attention only to the convenience of evaluation of the coefficients in the expansion (21a); much further research is required to be done as regards the convergence problems. In certain three-center problems one may sometimes expand the operator[17] rather than the wave functions to get rid of the convergence problem. However, this may not work in all cases. Work is in progress in our group to apply the expression given by (21a) and (23) to investigate the convergence problem for evaluation of various three- and four-center integrals.

VI. CONCLUSION

First, a simplified general expression is presented in Eqs. (1), (16a), and (17) for the expansion of a general orbital about an arbitrary point. An expression [Eqs. (21a) and (23) or Eqs. (29)] has then been derived for the expansion of a STO about an arbitrary point. This expression is found to be similar to those given by Silverstone[11] and by Rakauskas and Bolotin,[12] obtained by employing different approaches to the expansion problem. The derived expression contains terms only of the form $r^{k-l}e^{\pm\eta r}$ and hence very convenient for the analytic evaluation of multicenter integrals. This has been demonstrated by applying the expression to the evaluation of overlap matrix elements. The similarity of the resulting overlap formula with that derived by Todd, Kay, and Silverstone[11] has been pointed out. The expression presented here for the expansion seems important since it is easily adaptable to the evaluation of multicenter integrals for large-scale quantum-mechanical calculations economically.

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APPENDIX

An alternate form for $Q_{sILM}(a,r)$ of Eq. (16b) is given by

$$Q_{sILM}(a,r)=\frac{(-1)^L}{2}\sum_{p'=0}^{[(l-M)/2]}\left(\frac{r^2}{a^2}\right)^{p'}\sum_{q'=q'_{\min}}^{q'_{\max}}(-1)^{q'}\gamma_{l,M}(p',q')\left(1+\frac{r^2}{a^2}\right)^{l-M-2p'-q'}\times\sum_{p=0}^{p_{\max}}\gamma_{L,-M}(p,s-p-q')\left(1-\frac{r^2}{a^2}\right)^{L+M-p-s+q'},$$

where $\gamma_{l,M}(p,q)$ are defined by Eq. (16c) and where

$$q'_{\min}=\max(0,s-L-M),\quad q'_{\max}=\min(s,l-M-2p'),\quad p_{\max}=\min(s-q',L+M-s+q').$$

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