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About Evaluation of Many-Center Molecular Integrals*

By

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Studies of truncated expansions of Slater s -orbitals, in terms of associated Laguerre functions and spherical harmonics at another center, are carried out. The possibility of using such an expansion to calculate many-center molecular integrals is considered. The procedure is applied to solve three-center nuclear attraction integrals; it is shown that in some cases this expansion can provide relatively good results.

On étudie des développements tronqués d'orbitales s de Slater, en série de fonctions associées de Laguerre et d'harmoniques sphériques centrés en un autre point. On examine les possibilités d'employer ce genre de développement dans le calcul des intégrales moléculaires polycentriques. On applique le procédé à la résolution des intégrales tricentriques d'attraction nucléaire et l'on montre que dans certains cas cette expansion peut conduire à des résultats relativement bons.

Slater- s -Orbitale werden an einem anderen Zentrum in Reihen von Produkten aus Kugelfunktionen und zugeordneten Laguerreschen Funktionen entwickelt. Untersucht wird die Konvergenz der Reihen und ihre Eignung zur Berechnung von Mehrzentren-, insbesondere von Dreizentren-Kernwechselwirkungs-Integralen. Die Ergebnisse sind zum Teil recht gut.

1. Introduction

Evaluation of many-center integrals remains one of the major difficulties in the approximation of wavefunctions of polyatomic systems by the L.C.A.O. methods. Hitherto, few papers [1, 2] have been concerned with this problem and although much improvements have been made in last years by the use of big computers [10, 13], an efficient general program is not yet available today.

A way to solve this problem is to expand the molecular wavefunction about a single center. This procedure has produced satisfactory results in the studies on very symmetrical molecules such as H_2 and AH_n -type molecules [8, 12]. However, such functions are not able to represent properly the electronic charge distribution around the off-center nuclei. Furthermore they show a slow rate of convergence and the introduction of high angular momentum terms is required.

The present paper deals in some way with both problems. In fact, one of the simplest procedures to compute many-center molecular integrals is to reduce them to a sum of one- or two-center integrals, easier to calculate, by expanding some orbitals, occuring in them, in series of orthonormal functions:

$$\varphi_{Aj} = \sum_i \left(\int \varphi_{Aj} \chi_{Bi} d\tau \right) \chi_{Bi}. \quad (1)$$

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Here A, B indicate the centers of the functions and i, j denote sets of quantum numbers.

RUEDENBERG, in an early paper [11], used this property to justify theoretically the well known Mulliken's approximation for the calculation of many-center integrals. ELISSON [4] later estimated three-center integrals of repulsion in such a way. Recently, PARR et al. [16] expanded a hydrogen $1s$ -orbital in spherical harmonics, with zeta function and with Slater-orbital radial factors. In the second expansion, these authors employed Slater-orbitals, centered off the nucleus, with nonintegral principal quantum numbers and coefficients determined by minimization of energy.

In this paper we try to study the expansion (1) and its possible use to evaluate many-center integrals. In a first approach only Slater type orbitals (STO's) of s -symmetry are to be expanded; this procedure has been applied to compute three-center integrals of nuclear attraction.

2. Choice of the Basis

As basis for the expansion (1) we have employed an orthonormal set proposed by SHULL and LÖWDIN [14], which is a complete orthonormal system:

$$\chi_{Bi} \equiv \left[\frac{2z}{(n+l+1)!} \right]^{\frac{3}{2}} \cdot \sqrt{(n-l-1)!} \cdot (2zr_B)^l \cdot L_{n+l+1}^{2l+2}(2zr_B) \cdot e^{-zr_B} \cdot Y_l^m(\theta, \varphi) \quad (2)$$

where $L_{n+l+1}^{2l+2}(2zr_B)$ are the associated Laguerre polynomials of order $(2l+2)$, $Y_l^m(\theta, \varphi)$ are the ordinary spherical harmonics and i takes different values for every n, l, m combination.

This set is entirely discrete and has the advantage of owning a common single exponent, which allows the χ_{Bi} to be written as a linear combination of φ_{Bklm} Slater orbitals, centered at the same point:

$$\chi_{Bi} = \sum_{k=l+1}^n c_k^{nlm} \varphi_{Bklm}.$$

The Slater normalized orbitals are defined as follows:

$$\varphi_{Bklm} = \frac{(2z)^{k+1/2}}{[(2k)!]^{1/2}} r_B^{k-1} e^{-zr_B} Y_l^m(\theta, \varphi). \quad (3)$$

From Eq. (2) and the definition of the Slater orbitals we have deduced the following formula for the coefficients c_k^{nlm} :

$$c_k^{nlm} = (-1)^{k-l-1} \frac{\sqrt{(n+l+1)!}}{(k+l+1)!} \frac{\sqrt{(n-l-1)!}}{(k-l-1)!} \frac{\sqrt{(2k)!}}{(n-k)!}$$

which does not depend on the number m . On the other hand, since in this paper φ_{Aj} is a s -orbital, there is no term in the series with $m \neq 0$, because the corresponding expansion coefficients $\int \varphi_{Aj} \chi_{Bi} d\tau$ in Eq. (1) vanish.

3. Calculation of the Expansion Coefficients

Calculation of the remaining expansion coefficients $\int \varphi_{Aj} \chi_{Bi} d\tau$ can now be carried out by means of any of the common procedures to calculate overlap integrals between Slater orbitals. Using elliptical coordinates these integrals can readily be written in terms of the auxiliary integrals A_n and B_n [9]. Because of the

high number of integrals of that type, it seems convenient to systemize that calculation. Therefore, we have deduced after LOFTHUS [5] a general equation, where the overlap integrals are expressed as functions of A_n and B_n and of the quantum numbers of the corresponding orbitals:

$$\int \varphi_{A_j}^{(s)} \varphi_{B_k l_0} d\tau = N_j N_k \left(\frac{R}{2}\right)^{n_j+k+1} n_j! (k-l)! \cdot \\ \cdot \sum_{a=0}^l \sum_{b=0}^l C_{ab}^{(l)} \sum_{c=0}^{n_j} \sum_{d=0}^k (-1)^d A_{n_j+k-c-d} B_{c+d}.$$

In this expression one should retain only those terms where $a+b$ is an even number. N_j and N_k are the normalization constants of the radial parts of the corresponding STO's, R is the internuclear distance between their centers and $C_{ab}^{(l)}$ a factor depending essentially on the number l , which has the form:

$$C_{ab}^{(l)} = \frac{(2l-a-b)! (a+b)! l! (-1)^{\frac{a+b}{2}}}{(l-a)! a! (l-b)! b! \left(l - \frac{a+b}{2}\right)^{2l+1}}.$$

For the computation of the B_n integrals we have chosen a development advanced by MILLEB et al. [7], since the usual recurrence formula in some cases yields large errors.

4. Properties of the Expansion

If φ_{A_j} is a normalized wavefunction, we have:

$$1 = \sum_i \left(\int \varphi_{A_j} \chi_{B_i} d\tau \right)^2. \quad (4)$$

Since the expansion must perforce be limited in practice, Eq. (4) can be used to provide insight into the rate of convergence obtained for a given number N of terms; thus we define:

$$S_N \equiv \sum_i^N \left(\int \varphi_{A_j} \chi_{B_i} d\tau \right)^2.$$

In the same way, inside each vectorial subspace with same number l we can define a $S_{\infty l}$ and a S_{Nl} , since each subset of Laguerre functions of same order is by itself a complete orthonormal system in such a subspace. The value of that $S_{\infty l}$, depending only upon the φ_{A_j} functions and the internuclear distance R , can be computed by exact methods.

Now it must be noted that the z exponent in the expansion (1) is an arbitrary parameter that we may choose in such a manner that the S_N will be maximum. Moreover, there is no reason for this exponent to be the same in every subset of Laguerre functions, and we may thus assume different z_l values for each S_{Nl} to be maximum, that is for S_{Nl} to tend toward $S_{\infty l}$.

An alternative way to check the convergence of the expansion would be the calculation of the multipole moments, which as is known are zero for a s -function. This way seems of interest because there are several approximations for many-center integrals [3, 6] based on preserving such moments. Next, nuclear attraction three-center integrals are calculated using the expansion procedure. The values of these will give a good measurement of the electronic density and can be used to verify the expansion properties at several space points.

5. Applications

We have applied this method to the solution of nuclear attraction three-center integrals, which have the general form:

$$\int \frac{\varphi_{Aj} \varphi_{Bh} d\tau}{r_C}$$

where φ_{Aj} and φ_{Bh} are two STO's with centers at A and B , r_C is the distance from the electron to a third point C . On substituting the B -centered expansion of orthonormal functions for φ_{Aj} , that integral takes the form of a summation of two-center nuclear attraction integrals:

$$\int \frac{\varphi_{Aj} \varphi_{Bh}}{r_C} d\tau = \sum_i \int \varphi_{Aj} \chi_{Bi} d\tau \int \frac{\varphi_{Bh} \chi_{Bi}}{r_C} d\tau. \quad (5)$$

Now we can write, as done above for the expansion coefficients, these two-center integrals as linear combinations of known integrals of Slater-orbitals. Because of substituting a Neumann's expansion for the r_C^{-1} operator, the nuclear attraction terms then have as factors the Legendre polynomials $P_l(\cos \gamma)$, where γ is the angle between the vectors \vec{BC} and \vec{BA} and l the angular quantum number of the corresponding χ_{Bi} .

The calculation process has been programmed for the IBM 7070 computer of the C.C.E. of the C.S.I.C., in Madrid. The program has no other limitations than the numerical ones. The number of terms is in practice limited only by the accumulation of errors. Therefore, we think it would be interesting to rewrite this program in double precision, so that a larger number of terms could be retained.

6. Results and Discussion

In Tab. 1 are listed the values of S_{Nl} and S_N computed, as described above, expanding a $1s$ -orbital φ_{Aj} with charge equal to unity and using $8-l$ Laguerre polynomials of order $2l+2$ for $l=0, 1, \dots, 7$. All the calculations were performed for four values of the distance R (0.7; 1.4; 2.0 and 2.5 a.u.). A change in the scale factor can provide a variation of the charge. It is seen that the convergence is more rapid for smaller R values, as to be expected. In the same table are given the best values of z_l . Also in Tab. 1 are presented the values of $S_{\infty l}$ calculated by an exact method, the BARNETT-COULSON expansion. As it is seen, the convergence inside every subspace shows the same trend.

The different contributions to the dipole moment of a B -centered expansion as functions of the quantity l , including that of an equal positive charge placed at A , are tabulated in Tab. 2. As it is seen, the results approach asymptotically the correct value zero, except for a small residual error which appears clearly when $R=0.7$ a.u. This error is due to the incompleteness of the basis used for the radial part. These results are comparable, however, with those obtained by PARR et al. [16] using the BARNETT-COULSON expansion and, indeed, much better than those produced by the same authors using the Slater expansion with nonintegral principal quantum numbers. This fact is due to their having employed a single orbital (with one exception) for the radial part multiplying a spherical harmonic.

In Tab. 3 and 4 are gathered some nuclear attraction many-center integrals of Slater $1s$ -orbitals with charge equal to unity and distances $R=AB=CB$, computed by the method described, with the z_l parameters given in Tab. 1.

Tabulated in column 2 of Tab. 3 are evaluations of integrals where the attractive center C coincides with the center A of the φ_{Aj} orbital. These integrals, in fact

Table 1. Values of S_N and S_{N1} as functions of distance R for a truncated expansion of a Slater $1s$ -orbital

S_{N1}	$R = 0.7$ a.u.		$R = 1.4$ a.u.		$R = 2.0$ a.u.		$R = 2.5$ a.u.	
	Barnett-Coulson	Laguerre expansion z_l	Barnett-Coulson	Laguerre expansion z_l	Barnett-Coulson	Laguerre expansion z_l	Barnett-Coulson	Laguerre expansion z_l
0 8	0.86594	0.86594	0.62401	0.62401	0.44566	0.44564	0.33440	0.33440
1 7	0.12237	0.12236	0.28901	0.28898	0.35721	0.35716	0.36578	0.36578
2 6	0.01033	0.01032	0.06676	0.06674	0.13274	0.13271	0.17975	0.17975
3 5	0.00110	0.00110	0.01466	0.01463	0.04211	0.04206	0.07151	0.07151
4 4	0.00018	0.00018 ₅	0.00369	0.00368	0.01365	0.01360	0.02739	0.02739
5 3	0.00006	0.00004 ₅	0.00112	0.00110	0.00486	0.00481	0.01099	0.01099
6 2		0.00001 ₅		0.00040		0.00190		0.00467
7 1		0.00000 ₅		0.00015		0.00078		0.00200
S_N	0.99998	0.99997	0.99925	0.99969	0.99624	0.99866		0.99649

Table 4. Nuclear three-center-attraction integrals, in atomic units, as functions of the angle γ and distance R ; evaluated by both expansions: at centers A and B

$\cos \gamma$	$R = 0.7$ a.u.		$R = 1.4$ a.u.		$R = 2.0$ a.u.		$R = 2.5$ a.u.	
	Center at B	Center at A	Center at B	Center at A	Center at B	Center at A	Center at B	Center at A
0	0.72610	0.72609	0.41598	0.41594	0.24710	0.24712	0.15881	0.15884
$-\frac{1}{3}$	0.69998	0.70004	0.38736	0.38728	0.22634	0.22621	0.14441	0.14431
$-\frac{2}{3}$	0.68811	0.68822	0.37503	0.37505	0.21761	0.21761	0.13842	0.13842
-1	0.65638	0.65635	0.34410	0.34418	0.19640	0.19661	0.12402	0.12429

Table 2. Dipole moments, in Debye units, as functions of distance R , for an unnormalized truncated expansion

l	$R = 0.7$ a.u.	$R = 1.4$ a.u.	$R = 2.0$ a.u.	$R = 2.5$ a.u.
0	1.77903	3.5571	5.0764	6.3316
1	0.16596	0.9948	2.2100	3.4425
2	0.01354	0.2152	0.7321	1.4432
3	0.00189	0.0508	0.2365	0.5661
4	0.00064	0.0152	0.0839	0.2334
5	0.00044	0.0064	0.0352	0.1070
6	0.00038	0.0036	0.0173	0.0559
7	0.00036	0.0026	0.0104	0.0348

l is the highest order of the Legendre polynomial retained.

Table 3. Nuclear two-center attraction integrals, in atomic units, as functions of distance R

R in a. u.	By this method	Exact value	Ratio between both results	S_N
0.7	0.84351	0.84419	0.99919	0.99997
1.4	0.58998	0.59183	0.99687	0.99969
2.0	0.40345	0.40600	0.99372	0.99866
2.5	0.28453	0.28730	0.99036	0.99649

Table 5. Values of the last expansion term retained, as functions of the distances AB and CB , in atomic units for linear arrangement

CB/AB	$AB = 0.7$	$AB = 1.4$	$AB = 2.0$	$AB = 2.5$
0.5	0.25 10^{-4}	0.13 10^{-3}	0.26 10^{-3}	0.38 10^{-3}
1.0	0.14 10^{-3}	0.53 10^{-3}	0.79 10^{-3}	0.87 10^{-3}
1.5	0.10 10^{-3}	0.27 10^{-3}	0.31 10^{-3}	0.27 10^{-3}
2.0	0.33 10^{-4}	0.71 10^{-4}	0.65 10^{-4}	0.49 10^{-4}

In this case $l = 8$ and $N = 1$.

two-center integrals, can easily be calculated by classical methods and their correct values are given in column 3. It seems interesting to list in column 4 the ratios between both results and in column 5 the corresponding S_N values. It is seen that, in this case, the convergence of the series (5) is not so good as to be expected. One may confirm then that the representation of the electronic density given by the expansion is less satisfactory in the region of point A (the cusp) than in the remaining space.

In Tab. 4 are given the values of three-center integrals for four significant positions of center C ($\sphericalangle ABC = \gamma = 90^\circ; 109^\circ 28'; 120^\circ$ and 180°). Since exact values of these integrals are lacking, we have computed their values following two ways: the φ_{Aj} expansion about point B and A -centered expansion of φ_{Bh} . As a matter of fact, both expansions must tend to the same values. Let us suppose that both results are correct when they agree. A very good agreement, better than to be expected, is shown in Tab. 4.

To discuss these results, let us first look on the three-center linear integrals, centered at B , where $\gamma = 180^\circ$. Because $P_l(\cos \gamma)$ multiplies the nuclear attractive terms, according to the properties of the Legendre polynomials the expansion (5) becomes an alternant series*. The maximum error will be given approximately by the last term. The corresponding values, for four distances $AB = CB$, are listed in the second row of Tab. 5. Now, when $\gamma = 90^\circ$, the expansion (5) is also an alternant series, but its convergence must be more rapid because $P_l(0)$ decreases with l . On the other hand, for $\gamma = 0^\circ$ P_l will always be $+1$, and therefore the convergence will be slowest, which is in agreement with the results of Tab. 3.

From the results on the linear arrangement listed in Tab. 5, it may be seen that the convergence will be better when $AB \neq CB$, particularly when $CB > AB$. This fact points out that the terms with high angular momentum are more significant at the points lying on a sphere centered around B and passing through A , where indeed the maximum electronic density is to be met. This remark also agrees with the results of Tab. 3.

Expansions of Slater $2s$ -orbitals were also performed in the same way. These show a similar behavior and no more difficulties than those of $1s$ -type.

7. Conclusions

It is seen that the convergence of an expansion of a Slater s -orbital in terms of Laguerre functions and spherical harmonics about an off-center is satisfactory though slow. Besides, this expansion seems to be almost as good as one in terms of zeta functions (BARNETT-COULSON). These results confirm also that single-center calculations on molecules such as methane must include higher harmonics in order to obtain an approximately correct electron density in the region of the protons.

Furthermore, it is seen that such an expansion yields better electronic densities at certain space points. We may now conclude that, when one wants to evaluate the potential at those points (nuclear attraction integrals) or the repulsion due to an electronic cloud centered around them (two-electron coulomb integrals) this expansion may be used successfully in the evaluation of the three-center integrals. In the cases of three- and four-center exchange integrals the latter conclusion seems to be less obvious. It may be noted that it seems less difficult to calculate by this treatment precisely the most usual integrals in structural problems, where either $90^\circ \leq \gamma \leq 180^\circ$ or $AB \neq CB$. In the same way, this explains partly also the relative success of the MULLIKEN's approximation in these cases, as we have stated elsewhere [15].

* We have verified that, in our case, the factors multiplying the P_l are always > 0 . This fact agrees with the results of PARR et al. [16], and can be explained as follows: Let us retain in our expansion the first Laguerre function of each order only, and optimize again the z_i parameters. Since R is not too large, our new expansion may be expected to remain approximately a good one. Then the factors multiplying the P_l become a product of two integrals of Slater-orbitals. Since φ_{Aj} and φ_{Bb} are s -orbitals and χ_{Bb} now has no spherical node, it may be easily seen that both integrals must be positive.

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