Theoret. chim. Acta (Berl.) 10, 181—186 (1968)

Numerical Evaluation of Matrix Elements of the Electric Field and Electric Field Gradient Operators in a Slater Basis Set*

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Received December 20, 1967

A method is proposed for evaluating all matrix elements of the electric field and electric field gradient operators in a Slater basis set fo systems with an arbitrary number of nuclei and geometry. These integrals are evaluated using a numerical quadrature after having modified the integrand to remove all infinities. The integration ranges are broken to avoid integrating through cusps in the integrand. With reasonable grids these procedures are adequate for numerical evaluation with an accuracy of five to six decimal places (in a.u.). Particular cases are briefly discussed.

Eine Methode zur Berechnung aller Matrixelemente der Operatoren des elektrischen Feldes und des Feldgradienten in einer Slater-Funktionen-Basis bei beliebiger Anordnung der Zentren und Kerne wird angegeben. Durch entsprechende Wahl der Integrationsgebiete und Umformungen ist es möglich, Singularitäten und Spitzen bei der numerischen Integration zu umgehen. Bei vernünftiger Gitterwahl erreicht unser Programm eine Genauigkeit von 10^{-5} bis 10^{-6} aE.

Méthode pour évaluer tous les éléments de matrice des opérateurs champ et gradient du champ électrique dans une base d'orbitales de Slater pour des systèmes à nombre de noyaux et géométrie quelconques. Ces intégrales sont calculées par quadrature numérique en modifiant la fonction à intégrer pour éliminer toutes les singularités. Le domaine d'intégration est fractionné pour éviter d'avoir à intégrer aux points de rebroussement. Avec des réseaux raisonnables ce procédé est convenable pour l'évaluation numérique avec une précision de 5 à 6 décimales (en u.a.). Des cas particuliers sont l'objet d'une brève discussion.

Introduction

For many theoretical purposes the electronic wavefunction of a polyatomic molecule is suitably expanded in Slater type orbitals related to various nuclei. The computation of the electronic contribution to the electric field and to the electric field gradient at a nucleus C requires the knowledge of such integrals as $\int X_A^* O_C X_B \, d\tau$, where X is a Slater type orbital, O is one of the following one-electron operators:

$$\frac{x}{r^3}, \frac{y}{r^3}, \frac{z}{r^3}, \frac{3x^2-r^2}{r^5}, \frac{3y^2-r^2}{r^5}, \frac{3z^2-r^2}{r^5}, \frac{3xy}{r^5}, \frac{3xz}{r^5}, \frac{3yz}{r^5}$$

and A, B, C indicate the nuclei to which the suffixed quantities refer. The first three operators give the expectation values of the electric field components; the others give the matrix elements of the electric field gradient tensor at the nucleus [1].

The above mentioned integrals have been studied by several authors, mainly for the two center case [2, 3, 4]. Flygare et al. [5], in a calculation of one-electron properties for the formaldehyde molecule mention some programs for the calculation of these integrals. One program is based on the Barnett-Coulson expansion

* Work carried out with the CNR aid.

[6] of Slater functions onto the center containing the operator; another one expands the operator and one of the orbitals about the center containing the other orbital. An alternative method used by the same authors involves the Gaussian transform technique for multicenter integral evaluation [7]. For one-electron operators, the evaluation of integrals of exponential orbitals reduces therefore to a sum of terms, each of which requires a two-dimensional numerical integration. The three-center integrals are evaluated, in a program written by G. I. Kerley [5], by direct numerical integration over three coordinates. No mathematical device is mentioned to remove in this case the infinity arising from the operator on the third center. Recently A. D. McLean and M. Yoshimine [8] describe an interesting method available for linear molecules. In this case, using cylindrical coordinates ϱ, z, φ, the integrals $\int O_C X_A^* X_B \varrho \, d\varrho \, dz \, d\varphi$ are immediately evaluated in the φ variable, and a numerical quadrature may be developed for the other two variables. In using direct numerical integration, it is convenient to remove the infinity which may occur at nucleus C. McLean and Yoshimine discuss this problem and indicate a way to remove the infinity by working on the functions so that the product $X_A^* X_B$ vanishes in C without modifying the integral value. Although this method may be in principle extended to non-linear cases, we think that the following way is more convenient: the operator is multiplied by an appropiate function and successively each integral is separated into a sum of two terms, which do not present infinities. A program in FORTRAN IV language for an IBM 7090 computer was written with Slater orbitals of s, p, d type. The calculations were carried out at the C.N.U.C.E. in Pisa.

General Formulae

The electric field and electric field gradient operators on a nucleus C are all linear combinations of functions of the type

$$\frac{S_l^m(\vartheta_C, \varphi_C)}{r_C^{l+1}} \tag{1}$$

where $S_l^m(\vartheta_C, \varphi_C)$ are the real harmonic spherical functions. The electric field operators have $l=1$, the electric field gradient ones have $l=2$.

From the identity

$$\frac{S_l^m(\vartheta, \varphi)}{r^{l+1}} = S_l^m(\vartheta, \varphi)\left[\frac{1-\varepsilon(r)}{r^{l+1}}\right] + S_l^m(\vartheta, \varphi)\frac{\varepsilon(r)}{r^{l+1}} \tag{2}$$

where $\varepsilon(r)$ is an arbitrary finite function and setting $\gamma(r) = (1-\varepsilon(r))/r^{l+1}$, a matrix element of electric field or electric field gradient operator becomes

$$\begin{aligned} I &= \int \frac{S_l^m(\vartheta_C, \varphi_C)}{r_C^{l+1}} X_A^* X_B \, d\tau \\ &= \int S_l^m(\vartheta_C, \varphi_C)\, \gamma(r_C)\, X_A^* X_B \, d\tau + \int S_l^m(\vartheta_C, \varphi_C)\frac{\varepsilon(r_C)}{r_C^{l+1}} X_A^* X_B \, d\tau = I_1 + I_2 . \end{aligned} \tag{3}$$

The two integrals in (3) may be evaluated in different ways. The integrand of I_1 will not diverge, if $\gamma(r)$ is anywhere finite. For this purpose, we set up

$$\varepsilon(r) = \exp(-\sigma) \sum_{j=0}^{N} (\sigma^j / j!) \tag{4}$$

with $\sigma = kr$ and $k =$ numerical constant.

It follows

$$\gamma(\sigma) = k^{l+1}\left[1 - \exp(-\sigma)\sum_{j=0}^{N}(\sigma^j/j!)\right]\Big/\sigma^{l+1} \tag{5}$$

or

$$\gamma(\sigma) = k^{l+1}\cdot\exp(-\sigma)\sum_{j=N+1}^{\infty}(\sigma^{j-l-1}/j!)\,. \tag{6}$$

To remove the divergence in I_1 it is sufficient to take $N \geqq l$ in (5) or (6).
To compute I_2 we consider a polar coordinate system centered in C.

We obtain

$$I_2 = \int_0^{\infty} \frac{\exp(-\sigma)}{\sigma^{l-1}} \sum_{j=0}^{N}(\sigma^j/j!)\,\beta(r)\,d\sigma \tag{7}$$

where

$$\beta(r) = \int S_l^m(\vartheta,\varphi)\,X_A^* X_B \sin\vartheta\, d\vartheta\, d\varphi\,. \tag{8}$$

To prove that the integral (7) may be suitably evaluated by a numerical quadrature, we expand the product of function $X_A^* X_B$ in a Taylor series about C. We obtain

$$X_A^* X_B = (X_A^* X_B)_C + \sum_i \left(\frac{\partial(X_A^* X_B)}{\partial x_i}\right)_C x_i + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2(X_A^* X_B)}{\partial x_i\,\partial x_j}\right)_C x_i x_j + \cdots\,. \tag{9}$$

If we substitute this expression in eq. (8), all terms of degree less than l vanish, so that $\beta(r)$ takes the form

$$\beta(r) = \sum_{i=0}^{\infty} b_i\, r^{l+i}$$

and the integral (7) becomes of the type:

$$I_2 = \int_0^{\infty} \exp(-\sigma)\sum_{i=0}^{\infty} a_i \sigma^{i+1}\, d\sigma\,. \tag{10}$$

This expression shows that the integral (7) does not present difficulties for numerical integration and it is in a suitable form to the use of the Gauß-Laguerre integration points. The integrand in (7) may present cusps at A or B which would require a very large number of integration points. To remove this difficulty we take k so that we have $\exp(-kr_{AC})$ and $\exp(-kr_{BC})$ sufficiently small. In this way only a region about C, which does not include the points A and B, contributes effectively to the integral (7).

Remarks on Computing Formulae and Particular Cases

In our program the cartesian axes are chosen so that the centers A, B, C are located in the following way: A at the origin, B on the z axis and C on the positive xz semiplane. Functions and operators are referred to parallel cartesian systems. No difficulty arises in the rotation of axes necessary for the different system orientations. To increase the rate of convergence of the numerical quadrature of I_2 we took $k = 25/R_<$ (in a.u.) where $R_<$ is the lowest of R_{AC} and R_{BC}. In all the examined cases a grid of $8\times 8\times 8$ points gives an error less than 10^{-7} a.u. To evaluate I_1 we consider elliptic confocal coordinates defined about the two centers A and B. If high accuracy is required (error $\sim 10^{-6}$ a.u.) it is necessary to divide the integration range in four parts (see Fig. 1). In the bounded regions Gauß quadrature points were used, Gauß-Laguerre's in the others with trivial change of variables. Since the $S_l^m(\vartheta,\varphi)$ function changes rapidly near C, the numerical integration is done for $N > l$, so that $\gamma(\sigma)$ vanishes at C. We put $N = l+2$. The

$\gamma(\sigma)$ function is evaluated by means of (6) for $\sigma \leqq 2$, otherwise by means of (5), to obtain at least seven figures. The convergence rate and the accuracy that we may obtain are illustrated in Table 1. In Table 2 a comparison between our results and those of Flygare et al. [5] is reported.

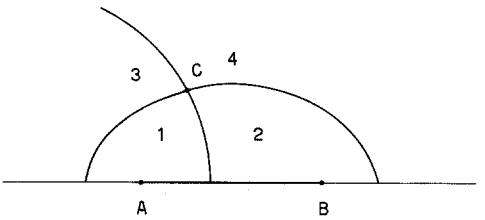


Fig. 1. Ranges of integration

The particular case, in which C is relatively away from A and B, must be treated apart. If $|X_A^* X_B|_C = \varepsilon \leqq 10^{-6}$, we put $k = 25$, $N = l$ and $I = I_1$ without any division of integration range. This procedure may be justified in the following way: considering for example, the case $l = 2$, $m = 0$, we have

$$I_2 = \int_0^\infty \frac{\exp(-\sigma)}{\sigma}\left(1+\sigma+\frac{\sigma^2}{2}\right)d\sigma \int_0^\pi \int_0^{2\pi} X_A^* X_B (3\cos^2\vartheta - 1)\sin\vartheta \, d\vartheta \, d\varphi = \sim \frac{64\pi^2\varepsilon}{15k^2} \tag{11}$$

This result has been obtained expanding the product $X_A^* X_B$ to the 2nd degree and putting

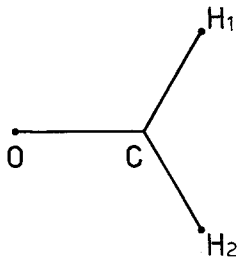
$$\left|\frac{\partial^2 (X_A^* X_B)}{\partial z^2}\right|_C = \frac{4}{3}\pi\varepsilon .$$

Table 1. *Rate of convergence and accuracy*

Integration points[a] n_1 n_2 n_3 n_4 $\bar{n}_\varphi$	$\left\langle 2s_A \frac{3x_C^2 - r_C^2}{r_C^5} 1s_B \right\rangle$	$\left\langle 2s_A \frac{3z_C^2 - r_C^2}{r_C^5} 1s_B \right\rangle$	$\left\langle 2s_A \frac{3x_C z_C}{r_C^5} 1s_B \right\rangle$	Geometry and orbital exponents
16 15 16 8 10	0.007089	0.010390	−0.026071	
16 15 16 10 10	0.007092	0.010462	−0.025963	$R_{AB} = 2.0$ a.u.
16 15 16 12 10	0.007094	0.010479	−0.025933	$R_{AC} = 2.3$ a.u.
16 15 16 14 10	0.007095	0.010478	−0.025934	$\sphericalangle CAB = 120°$
16 15 16 16 10	0.007095	0.010477	−0.025936	
16 15 8 16 10	0.007095	0.010477	−0.025936	
16 15 10 16 10	0.007095	0.010477	−0.025936	$\xi_C = 3.0135$
16 15 12 16 10	0.007095	0.010477	−0.025936	$\eta_C = -0.7135$
16 9 16 16 10	0.007096	0.010478	−0.025939	$\zeta_{2s_A} = 1.625$
16 11 16 16 10	0.007095	0.010477	−0.025938	$\zeta_{1s_B} = 1.2$
16 13 16 16 10	0.007095	0.010477	−0.025936	
16 15 16 16 10	0.007095	0.010477	−0.025936	
8 15 16 16 10	0.007095	0.010478	−0.025935	
10 15 16 16 10	0.007095	0.010477	−0.025936	
12 15 16 16 10	0.007095	0.010477	−0.025936	

[a] n_1 number of integration points for $1 < \xi < \xi_C$
n_2 number of integration points for $\xi > \xi_C$
n_3 number of integration points for $-1 < \eta < \eta_C$
n_4 number of integration points for $\eta_C < \eta < 1$

Table 2. *Comparison between our result and those of literature*

Integral	Our value	Literature value	Geometry and orbital exponents
$\left\langle 1s_C \dfrac{3x_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	−0.005251	−0.005254	
$\left\langle 1s_C \dfrac{3z_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	0.010565	0.010567	
$\left\langle 2s_C \dfrac{3x_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	−0.012829	−0.012830	
$\left\langle 2s_C \dfrac{3z_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	0.030401	0.030401	
$\left\langle 2pz_C \dfrac{3x_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	0.002058	0.002058	
$\left\langle 2pz_C \dfrac{3z_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	−0.005832	−0.005832	$R_{OC}=2.3$ a.u. $R_{CH_1}=2.0$ a.u.
$\left\langle 2px_C \dfrac{3x_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	−0.002857	−0.002857	$\sphericalangle OCH=120°$
$\left\langle 2px_C \dfrac{3z_0^2-r_0^2}{r_0^5} 1s_{H_1}\right\rangle$	0.016038	0.016038	$\zeta_{1s_C}=5.7$ $\zeta_{2s_C}=\zeta_{2p_{z_C}}=\zeta_{2p_{x_C}}=1.625$ $\zeta_{1s_H}=1.2$
$\left\langle 1s_{H_1} \dfrac{3x_0^2-r_0^2}{r_0^5} 1s_{H_2}\right\rangle$	−0.003377	−0.003377	
$\left\langle 1s_{H_1} \dfrac{3z_0^2-r_0^2}{r_0^5} 1s_{H_2}\right\rangle$	0.007327	0.007327	

The expression (11) for I_2 shows that this contribution is effectively negligible under the supposed conditions.

The linear case is developed by the same program with identical formulae, except for the integration upon the φ variable, which is carried out analytically. Thus the numerical quadrature is a two-dimensional one and we think that it is as efficient as that proposed by McLean and Yoshimine.

If C coincides with A, $R_<$ must be replaced by R_{AB} in the preceding formulae.

If A coincides with B, we found it more convenient to evaluate these integrals by means of the following formulae

$$\left\langle \frac{x_C}{r_C^3}\right\rangle = V'_x, \qquad \left\langle \frac{y_C}{r_C^3}\right\rangle = V'_y, \qquad \left\langle \frac{z_C}{r_C^3}\right\rangle = V'_z$$

$$\left\langle \frac{3x_C y_C}{r_C^5}\right\rangle = V''_{xy}, \qquad \left\langle \frac{3x_C z_C}{r_C^5}\right\rangle = V''_{xz}, \qquad \left\langle \frac{3y_C z_C}{r_C^5}\right\rangle = V''_{yz}$$

$$\left\langle \frac{3x_C^2-r_C^2}{r_C^5}\right\rangle = \frac{2}{3}\left[V''_{xx}-\frac{1}{2}(V''_{yy}+V''_{zz})\right]$$

$$\left\langle \frac{3y_C^2-r_C^2}{r_C^5}\right\rangle = \frac{2}{3}\left[V''_{yy}-\frac{1}{2}(V''_{xx}+V''_{zz})\right]$$

$$\left\langle \frac{3z_C^2-r_C^2}{r_C^5}\right\rangle = \frac{2}{3}\left[V''_{zz}-\frac{1}{2}(V''_{xx}+V''_{yy})\right]$$

where V is the potential arising from the charge distribution $X_A^* X'_A$ (given analytically in [9]) and the derivatives V' and V'' are evaluated at the point C.

Finally, if A, B, C coincide, the calculation of the integrals is immediately carried out by means of trivial analytical formulae.

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