Approximation of Molecular Integrals

SOME of the electron repulsion integrals $[\varphi_a \chi_b | \theta_c \psi_d] = \int \varphi_a^*(1)$ $\chi_b(1) r_{12}^{-1} \theta_c^*(2) \psi_d(2)\, d(1) d(2)$ which arise in the molecular orbital theory based on linear combinations of atomic orbitals are sufficiently difficult that reasonably accurate approximate formulae would have real value. If such an integral is regarded as involving two charge distributions $\varphi_a^* \chi_b$ and $\theta_c^* \psi_d$, the integrals causing difficulty are those in which one or both charge distributions involve a pair of atomic orbitals not both on the same atomic centre. As many workers have noticed[1-8], tractable approximations for these integrals are obtained if the product of two orbitals on different centres is replaced by linear combinations of one-centre orbital products. This causes the general electron repulsion integral to be reduced to a linear combination of Coulomb-type integrals. The methods so far proposed, however, have not been entirely satisfactory for all the integrals for which they are needed.

We have examined a new integral approximation method which, like previous methods, depends on the replacement of two-centre charge distributions by one or more single-centre distributions, thereby giving results in terms of Coulomb-type integrals. Unlike earlier methods, however, the single-centre distributions are selected to include one contribution from each of the most important atomic symmetries. Moreover, the coefficients of the single-centre distributions are chosen to give agreement for certain integrals, rather than to have the values appropriate to leading terms of infinite orthogonal expansions. We have found that the symmetry of the single-centre distributions is far more important than their exact form, as errors in form are largely compensated for by the procedure for determining the coefficients, whereas terms of different symmetry are so different in behaviour that compensation is impossible.

Accordingly, we assume that a $1s$, $2s$ or $2p\sigma$ orbital φ_a on a centre A is expanded into a linear combination of s and p orbitals on another centre B, as $\varphi_a \approx c_1(1s_b) + c_2(2p\sigma_b)$. Letting φ_b be the same function as φ_a, but centred at B, we may alternatively expand φ_b about A, with coefficients which are identical to c_1 and c_2 except perhaps in sign. We now approximate $\varphi_a^* \varphi_b$ by the average of the expressions obtained by expanding φ_a^* about B and of φ_b about A. The coefficients c_1 and c_2 are determined by requiring a proper fit to the hybrid integrals $[1s_a 1s_a | \varphi_a \varphi_b]$ and $[1s_a 2p\sigma_a | \varphi_a \varphi_b]$, which under the approximation are reduced to a linear combination of Coulomb-type integrals. This same expression for $\varphi_a^* \varphi_b$ is now used whenever this charge distribution occurs in other two-electron integrals. This procedure therefore characterizes the distributions $1s_a 1s_b$, $2s_a 2s_b$, and $2p\sigma_a 2p\sigma_b$. Distribution $2p\pi_a 2p\pi_b$ is treated similarly, except that the expansion of $2p\pi_a$ contains only the term $c_1(2p\pi_b)$.

Charge distributions involving two different orbitals can be formed using the expansion coefficients already determined. This yields acceptable expansions of all distributions except $1s_a 2p\sigma_b$ and $2s_a 2p\sigma_b$, which are better represented by an expansion of the same form, such as $1s_a 2p\sigma_b \approx c_1(1s_a 1s_a) + c_2(1s_a 2p\sigma_a) + c_3(1s_b 2p\sigma_b) + c_4(2p\sigma_b 2p\sigma_b)$, but with the four coefficients determined by fitting hybrid integrals (in this case $[1s_a 1s_a | 1s_a 2p\sigma_b]$, $[1s_b 1s_b | 1s_a 2p\sigma_b]$, $[1s_a 2p\sigma_a | 1s_a 2p\sigma_b]$, and $[1s_b 2p\sigma_b | 1s_a 2p\sigma_b]$).

These expansions of the various charge distributions may now be used for approximate calculation of all two-electron integrals. Exact and approximate integrals of Slater-type orbitals were compared for all types of two-centre integrals, and the new method makes estimates of nearly all such integrals to accuracies of the order of 1 kcal, even in cases where earlier approximate methods are far worse. A few typical results are shown in Table 1. The fact that a single approximation to each charge distribution works well for all types of two-centre integrals suggests that good results may also be expected for multi-centre integrals.

A fuller account of this work, which was supported in part by the U.S. National Aeronautics and Space Administration and by the U.S. National Science Foundation, will be published shortly[9].

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PHYSIOLOGY

Electro-perception in Sharks and Rays

SHARKS and rays are extremely sensitive to alternating electric fields. A potential gradient of only 0.1 μV/cm is sufficient to evoke in Scyliorhinus canicula a reflex contraction of the eyelids ("winking of the eyes"), and to affect the respiratory rhythm of Raia clavata ("spiraculum reflex")[1,2]. Such a weak electric field is perceived with the ampullae of Lorenzini. The ampullae are not only very sensitive to thermal and mechanical influences as found electrophysiologically[3-5], but also respond to electrical stimuli[6-8]. Partial denervation of the ampullary system makes the head of Scyliorhinus canicula insensitive to weak electrical stimuli in the area where the eliminated ampullae open[9]. In the past few years, our investigations have been focused on the biological significance of the electro-perception in sharks and rays.

The winking of the eyes and the spiraculum reflex are readily observable responses. It is, however, difficult to record them objectively and they are, accordingly, not suitable for quantitative work. A reflex reaction is therefore needed, which is not only at least as sensitive but also easier to record without impeding the movements of the animal. For this purpose the reflex reactions of the respiratory apparatus and of the heart were considered.

After a few introductory experiments on Scyliorhinus canicula the heart beat proved to be the more informative. The muscle potentials of the heart were recorded by

Table 1. EXACT AND APPROXIMATE INTEGRALS, SLATER-TYPE ORBITALS

$\delta_{1s} = 1$; $\delta_{2s} = \delta_{2p} = 1.67$　　(Integral values in hartrees)

Integral	$R = 2$ bohr			$R = 5$ bohr		
	Exact*	This work	Mulliken approx †	Exact*	This work	Mulliken approx †
$[2s_a 2s_b	2s_a 2s_b]$	0.193	0.191	0.171	0.0012	0.0010	0.0010
$[2p\sigma_a 2p\sigma_b | 2s_a 2s_b]$	−0.123	−0.123	−0.073	−0.0024	−0.0019	−0.0018
$[2s_a 2s_b | 2s_a 2p\sigma_b]$	−0.182	−0.182	−0.151	−0.0017	−0.0014	−0.0014
$[2s_a 2p\sigma_b | 2p\sigma_a 1s_b]$	0.091	0.091	0.027	0.0089	0.0088	0.0014
$[1s_a 2s_b | 2p\pi_a 2p\pi_b]$	0.200	0.199	0.201	0.0060	0.0059	0.0071
$[2p\pi_a 2p\pi_b | 1s_a 1s_b]$	0.302	0.300	0.300	0.0344	0.0342	0.0390
$[2p\pi_a 2p\pi_b | 2p\sigma_a 2p\sigma_b]$	−0.077	−0.060	−0.049	−0.0007	−0.0005	−0.0006

* Computed by method given by F. E. Harris, J. Chem. Phys., 32, 3 (1960).　　† See ref. 8.