Integral Approximations for Molecular Orbital Theory

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The electron repulsion integrals arising in LCAO-MO theory are approximated by replacement of the product of two orbitals on different centers by linear combinations of one-center products. The approximation differs from those previously proposed in that the coefficients of the various terms are determined by requiring agreement for certain integrals, and in the emphasis of the role of symmetry in selecting the one-center products. For two-center integrals, the new approximation is significantly better than older approximate methods. Reasons are given for expecting this improvement to extend also to multi-center integrals.

Es wird ein Verfahren zur näherungsweisen Berechnung von Elektronenwechselwirkungs-integralen der LCAO-MO-Theorie beschrieben, bei welchem das Produkt zweier Zustands-funktionen an verschiedenen Zentren durch eine Linearkombination von Produkten am gleichen Zentrum ersetzt wird. Der Unterschied zu ähnlichen Ansätzen liegt in der Justierung der Koeffizienten. Für Zweizentrenintegrale liefert die hier vorgeschlagene Methode bedeutend bessere Ergebnisse als das Mulliken-Verfahren.

Les intégrales de répulsion électroniques intervenant dans la théorie LCAO MO sont calculées d'une manière approchée en remplaçant le produit de deux orbitales sur des centres différents par des combinaisons linéaires de produits à un centre. Cette approximation diffère de celles proposées auparavant par la détermination des coefficients des différents termes au moyen de l'ajustement de certaines intégrales et par l'importance du rôle de la symétrie dans le choix des produits monocentriques. Cette nouvelle approximation est bien meilleure que les anciennes en ce qui concerne les intégrales bi-centriques. Nous donnons des raisons d'espérer que cette amélioration s'étendra aux intégrales polycentriques.

Introduction

The theory of molecular orbitals formed by linear combination of atomic orbitals (LCAO–MO theory) has enjoyed a considerable success in correlating properties of many medium-sized molecules, particularly when used within groups of fairly similar systems such as the alternant hydrocarbons. On the other hand, when LCAO–MO theory is applied to systems possessing less similarities, for example organic molecules containing hetero atoms, far less satisfactory results are obtained. Undoubtedly, this behavior is due to the fact that the approximations of the theory have a more consistent effect when applied in closely corresponding circumstances. However, the large number of relatively drastic mathematical approximations normally introduced make it by no means clear whether the difficulties are inherent in the LCAO molecular orbital theory or whether they can be removed by purely mathematical refinements. The present paper seeks to

investigate this question by examining the practicality of a set of approximations alternative to those which have received widest study.

The mathematical approximations of molecular orbital theory arise because an extremely large number of molecular integrals enter the calculations, and these integrals have proved difficult to evaluate. There have been two main approaches to this problem, the simpler being exemplified by the Hückel theory [8] and its extensions [7]. This approach avoids explicit consideration of the antisymmetry conditions, and approximates the electron-electron and electron-nuclear interactions by simple empirical forms. It is doubtful whether this approach is sufficiently detailed to yield good results in the most general situations.

The second approach has been to use a properly antisymmetrized electronic wave function, but to limit the size of the problem in other ways. A normal procedure is to partition the electrons into two groups, only one of which is explicitly considered [11, 12]. The explicitly considered electrons are normally chosen from those involved in chemical bonding. Often, as in the usual π electron theory [15, 16], not even all of the valence electrons are included. The remaining electrons and the nuclei are together considered as a "core" whose interaction with the explicitly considered electrons is estimated semi-empirically. A partitioning therefore reduces drastically the number of molecular integrals to be evaluated, as the only integrals remaining are those involving the explicitly included electrons. Normally, still further approximations are introduced in the evaluation of the integrals which remain, by the use of simplified numerical formulas or semi-empirical methods. Frequently integrals involving three or four centers are neglected, as are sometimes also the two-center integrals of hybrid or exchange type.

The approximations outlined in the preceding paragraph could be nearly entirely removed if the integrals could be evaluated much more rapidly. We accordingly consider an alternative approach to LCAO molecular orbital theory in which we introduce an integral approximation that is simple enough to enable explicit inclusion of nearly all electrons. Such an integral approximation should, optimally, have sufficient accuracy that errors thereby introduced would be comparable to those inherent in the LCAO–MO theory itself. Moreover, the inclusion of all integrals should produce a molecular orbital theory which could have the capability of yielding information on molecular geometries, $\sigma - \pi$ transitions, and other quantities which it is difficult to discuss in the presence of a "core" approximation.

The integral approximation methods which have thus far proved to be useful all depend upon the replacement of a two-center charge distribution by one or more suitably chosen single-center distributions. In the method of SKLAR [18], a two-center orbital product is replaced by a product of two similar orbitals at the midpoint of the line segment connecting the centers. VROELANT [19] has modified SKLAR's approximation for asymmetric charge distributions by optimally locating the single-center orbital product. Alternatively, MASON and HIRSCH-FELDER [13] examined more elaborate expressions and multipole expansions about the midpoint. MULLIKEN [14] introduced the approximation of a two-center orbital product by a simple average of two single-center distributions located at the two centers involved. LÖWDIN [10] proposed that the Mulliken approximation be modified by weighting the relative contributions of the single-center distributions

so as to give the approximate charge distribution the correct dipole moment. HUZINAGA [9] suggested a combination of the Mulliken and Sklar approximations in which a simple average is taken of single-center charge distributions at both centers and at the midpoint of the line segment connecting them. These integral approximation methods can all be construed as involving leading terms in infinite series expansions of a two-center charge density. This point of view was explicitly developed for the Mulliken approximation by RUEDENBERG [17], who showed that such arguments could be used to justify the appearance of the overlap integral as coefficient. Recently, ČÍŽEK [1, 2] critically compared the various integral approximation methods and took the next logical step toward an improved method. ČÍŽEK's procedure was to represent a two-center charge distribution as a linear combination of two single-center distributions, assigning both their locations and their relative weights so as to make the lowest order multipole moments correct. In this way he was able to achieve agreement through the octupole moment.

In the present paper we examine an integral approximation which, in common with those discussed above, is based upon the representation of a two-center charge distribution as a truncated expansion in one-center distributions. However, in contrast to the earlier approaches, the coefficients of the various one-center terms will be determined by requiring the approximate charge distributions to yield correct values for certain integrals. This criterion results in the assignment of coefficients which are more nearly optimum for the purposes for which they are to be used, with the result that relatively good integral values are obtained. In selecting terms for the truncated expansions, it is found that symmetry is considerably more important than detailed functional form, as errors in form are largely compensated by the procedure for determining the coefficients, whereas terms of different symmetry behave qualitatively too differently to compensate each other. Accordingly, we consider expansions involving the leading terms of the most important symmetries. The results presented here are limited to two-center electron repulsion integrals, and to orbitals of principal quantum numbers 1 and 2. Further study to remove these limitations is in progress.

Integral Approximation

We consider Slater-type orbitals centered at the two points A and B. We use parallel axial systems for the two centers, with the positive z axis of both systems along the ray from A through B. We use normalized $1s$, $2s$, and $2p$ orbitals of complex type, denoting $1s$ orbitals at A and B by h_a and h_b, $2s$ orbitals by s_a and s_b, $2p$ orbitals with $m = 0$ by σ_a and σ_b, $2p$ orbitals with $m = +1$ by π_a and π_b, and $2p$ orbitals with $m = -1$ by π_a' and π_b'. Electron repulsion integrals are indicated in charge distribution notation, so that, for example, $[h_a s_b \mid \sigma_b \sigma_b]$ means $\int h_a^* (r_1) s_b (r_1) \mid r_2 - r_1 \mid^{-1} \sigma_b^* (r_2) \sigma_b (r_2) \, dv_1 \, dv_2$.

Our basic premise is that each orbital about one center can be expanded in a series about the other center using at most one term of each atomic symmetry. For simplicity, we use the $1s$ orbital as the term of s symmetry, and for p symmetry we use the three $2p$ orbitals. Thus,

$$h_a \approx c_1 h_b + c_2 \sigma_b; \quad h_b \approx c_1 h_a - c_2 \sigma_a; \quad s_a \approx c_3 h_b + c_4 \sigma_b;$$
$$s_b \approx c_3 h_a - c_4 \sigma_a; \quad \sigma_a \approx c_5 h_b + c_6 \sigma_b; \quad \sigma_b \approx -c_5 h_a + c_6 \sigma_a;$$
$$\pi_a \approx c_7 \pi_b; \quad \pi_b \approx c_7 \pi_a; \quad \pi_a' \approx c_7 \pi_b'; \quad \pi_b' \approx c_7 \pi_a'.$$

Table 1. *Exact and approximate integrals involving symmetrical two-center charge distributions*

integral	$R = 2;\ \delta_{2s} = \delta_{2p} = 2.00$			$R = 2;\ \delta_{2s} = \delta_{2p} = 1.67$		
	exact	this work	Mull. appr	exact	this work	Mull. appr
hybrid						
$[h_a\, h_a \mid h_a\, h_b]$	0.308	0.308*	0.308	0.308	0.308*	0.308
$[h_a\, h_a \mid s_a\, s_b]$	0.265	0.265*	0.254	0.312	0.312*	0.299
$[h_a\, h_a \mid \sigma_a\, \sigma_b]$	−0.221	−0.221*	−0.183	−0.177	−0.177*	−0.128
$[h_a\, h_a \mid \pi_a\, \pi_b]$	0.156	0.156*	0.158	0.203	0.203*	0.205
$[h_a\, s_a \mid h_a\, h_b]$	0.310	0.310	0.310	0.302	0.301	0.301
$[h_a\, s_a \mid s_a\, s_b]$	0.269	0.268	0.257	0.307	0.306	0.294
$[h_a\, s_a \mid \sigma_a\, \sigma_b]$	−0.226	−0.225	−0.185	−0.174	−0.173	−0.125
$[h_a\, s_a \mid \pi_a\, \pi_b]$	0.157	0.157	0.159	0.200	0.199	0.201
$[h_a\, \sigma_a \mid h_a\, h_b]$	0.045	0.045*	0.031	0.046	0.046*	0.032
$[h_a\, \sigma_a \mid s_a\, s_b]$	0.051	0.051*	0.027	0.052	0.052*	0.032
$[h_a\, \sigma_a \mid \sigma_a\, \sigma_b]$	−0.089	−0.089*	−0.021	−0.081	−0.081*	−0.014
$[h_a\, \sigma_a \mid \pi_a\, \pi_b]$	0.028	0.016	0.016	0.033	0.021	0.022
$[s_a\, s_a \mid h_a\, h_b]$	0.327	0.328	0.327	0.307	0.305	0.305
$[s_a\, s_a \mid s_a\, s_b]$	0.284	0.284	0.271	0.312	0.311	0.299
$[s_a\, s_a \mid \sigma_a\, \sigma_b]$	−0.240	−0.240	−0.196	−0.177	−0.176	−0.127
$[s_a\, s_a \mid \pi_a\, \pi_b]$	0.166	0.166	0.168	0.204	0.203	0.205
$[s_a\, \sigma_a \mid h_a\, h_b]$	0.047	0.047	0.032	0.048	0.048	0.034
$[s_a\, \sigma_a \mid s_a\, s_b]$	0.055	0.055	0.028	0.054	0.054	0.033
$[s_a\, \sigma_a \mid \sigma_a\, \sigma_b]$	−0.097	−0.097	−0.022	−0.084	−0.084	−0.014
$[s_a\, \sigma_a \mid \pi_a\, \pi_b]$	0.030	0.017	0.017	0.035	0.022	0.023
$[\sigma_a\, \sigma_a \mid h_a\, h_b]$	0.336	0.338	0.336	0.317	0.316	0.316
$[\sigma_a\, \sigma_a \mid s_a\, s_b]$	0.296	0.294	0.280	0.322	0.322	0.308
$[\sigma_a\, \sigma_a \mid \sigma_a\, \sigma_b]$	−0.264	−0.260	−0.212	−0.193	−0.188	−0.137
$[\sigma_a\, \sigma_a \mid \pi_a\, \pi_b]$	0.168	0.167	0.169	0.205	0.205	0.207
$[\pi_a\, \pi_a \mid h_a\, h_b]$	0.323	0.323	0.322	0.302	0.300	0.300
$[\pi_a\, \pi_a \mid s_a\, s_b]$	0.279	0.279	0.267	0.307	0.306	0.294
$[\pi_a\, \pi_a \mid \sigma_a\, \sigma_b]$	−0.228	−0.230	−0.188	−0.168	−0.170	−0.122
$[\pi_a\, \pi_a \mid \pi_a\, \pi_b]$	0.165	0.165	0.167	0.203	0.202	0.204
$[\pi_a\, \pi_a' \mid \pi_a\, \pi_b']$	0.014	0.014	0.000	0.019	0.017	0.000
exchange						
$[h_a\, h_b \mid h_a\, h_b]$	0.184	0.183	0.181	0.184	0.183	0.181
$[s_a\, s_b \mid h_a\, h_b]$	0.160	0.160	0.149	0.188	0.187	0.175
$[s_a\, s_b \mid s_a\, s_b]$	0.143	0.142	0.124	0.193	0.191	0.171
$[\sigma_a\, \sigma_b \mid h_a\, h_b]$	−0.141	−0.141	−0.107	−0.116	−0.116	−0.075
$[\sigma_a\, \sigma_b \mid s_a\, s_b]$	−0.134	−0.133	−0.089	−0.123	−0.123	−0.073
$[\sigma_a\, \sigma_b \mid \sigma_a\, \sigma_b]$	0.157	0.153	0.068	0.121	0.118	0.033
$[\pi_a\, \pi_b \mid h_a\, h_b]$	0.095	0.091	0.092	0.123	0.119	0.120
$[\pi_a\, \pi_b \mid s_a\, s_b]$	0.083	0.079	0.077	0.126	0.121	0.117
$[\pi_a\, \pi_b \mid \sigma_a\, \sigma_b]$	−0.075	−0.065	−0.054	−0.077	−0.068	−0.049
$[\pi_a\, \pi_b \mid \pi_a\, \pi_b]$	0.050	0.047	0.048	0.085	0.080	0.081
$[\pi_a\, \pi_b' \mid \pi_a\, \pi_b']$	0.006	0.004	0.000	0.009	0.007	0.000

The coefficients in these expressions are to be determined individually for each charge distribution.

We begin by considering symmetrical charge distributions. By direct substitution of the relationships in the preceding paragraph, we find for example that $h_a\, h_b$ can be represented as $c_1\, h_b\, h_b + c_2\, \sigma_b\, h_b$, or equivalently as $c_1\, h_a\, h_a - c_2\, h_a\, \sigma_a$.

Asterisks indicate integrals used to determine our approximation formulas. "Mull. appr" indicates the Mulliken approximation as in Eq. (10). Units of R are bohrs; integrals are in hartrees.

R = 3; $\delta_{2s} = \delta_{2p} = 1.67$			R = 5; $\delta_{2s} = \delta_{2p} = 1.67$			R = 8; $\delta_{2s} = \delta_{2p} = 1.67$		
exact	this work	Mull. appr	exact	this work	Mull. appr	exact	this work	Mull. appr
0.161	0.161*	0.165	0.0350	0.0350*	0.0398	0.0027	0.0027*	0.0027
0.145	0.145*	0.141	0.0187	0.0187*	0.0204	0.0004	0.0004*	0.0006
−0.170	−0.170*	−0.153	−0.0339	−0.0339*	−0.0367	−0.0010	−0.0010*	−0.0014
0.072	0.072*	0.075	0.0061	0.0061*	0.0073	0.0001	0.0001*	0.0001
0.158	0.157	0.161	0.0344	0.0340	0.0387	0.0027	0.0027	0.0037
0.143	0.142	0.138	0.0185	0.0183	0.0200	0.0004	0.0004	0.0006
−0.168	−0.168	−0.150	−0.0335	−0.0332	−0.0359	−0.0010	−0.0010	−0.0014
0.071	0.070	0.074	0.0060	0.0059	0.0071	0.0001	0.0001	0.0001
0.027	0.027*	0.013	0.0060	0.0060*	0.0016	0.0004	0.0004*	0.0001
0.029	0.029*	0.012	0.0040	0.0040*	0.0009	0.0001	0.0001*	0.0000
−0.059	−0.059*	−0.015	−0.0094	−0.0094*	−0.0017	−0.0002	−0.0002*	−0.0000
0.013	0.006	0.006	0.0011	0.0002	0.0003	0.0000	0.0000	0.0000
0.161	0.160	0.163	0.0350	0.0344	0.0392	0.0027	0.0027	0.0037
0.146	0.144	0.140	0.0188	0.0185	0.0203	0.0005	0.0004	0.0006
−0.172	−0.171	−0.152	−0.0342	−0.0337	−0.0365	−0.0010	−0.0010	−0.0014
0.072	0.071	0.075	0.0061	0.0060	0.0072	0.0001	0.0001	0.0001
0.028	0.028	0.014	0.0063	0.0062	0.0017	0.0005	0.0005	0.0001
0.031	0.031	0.012	0.0042	0.0042	0.0009	0.0001	0.0001	0.0000
−0.061	−0.061	−0.015	−0.0098	−0.0097	−0.0017	−0.0002	−0.0002	−0.0000
0.014	0.006	0.006	0.0012	0.0002	0.0003	0.0000	0.0000	0.0000
0.167	0.164	0.167	0.0363	0.0349	0.0396	0.0028	0.0027	0.0038
0.153	0.150	0.144	0.0199	0.0188	0.0205	0.0005	0.0004	0.0006
−0.189	−0.187	−0.165	−0.0371	−0.0362	−0.0390	−0.0011	−0.0011	−0.0015
0.074	0.071	0.075	0.0063	0.0059	0.0071	0.0001	0.0001	0.0001
0.158	0.156	0.160	0.0344	0.0342	0.0390	0.0027	0.0027	0.0037
0.142	0.142	0.138	0.0183	0.0184	0.0202	0.0004	0.0004	0.0006
−0.163	−0.163	−0.146	−0.0327	−0.0325	−0.0352	−0.0010	−0.0010	−0.0013
0.072	0.071	0.075	0.0060	0.0061	0.0073	0.0001	0.0001	0.0001
0.005	0.006	0.000	0.0003	0.0005	0.0000	0.0000	0.0000	0.0000
0.059	0.057	0.057	0.0037	0.0033	0.0038	0.0000	0.0000	0.0000
0.054	0.053	0.049	0.0021	0.0018	0.0020	0.0000	0.0000	0.0000
0.050	0.049	0.042	0.0012	0.0010	0.0010	0.0000	0.0000	0.0000
−0.068	−0.066	−0.053	−0.0041	−0.0034	−0.0035	−0.0000	−0.0000	−0.0000
−0.065	−0.063	−0.046	−0.0024	−0.0019	−0.0018	−0.0000	−0.0000	−0.0000
0.095	0.091	0.053	0.0049	0.0039	0.0035	0.0000	0.0000	0.0000
0.027	0.024	0.026	0.0007	0.0005	0.0007	0.0000	0.0000	0.0000
0.025	0.022	0.023	0.0004	0.0003	0.0004	0.0000	0.0000	0.0000
−0.031	−0.025	−0.024	−0.0007	−0.0005	−0.0006	−0.0000	−0.0000	−0.0000
0.013	0.011	0.012	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
0.001	0.001	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Because of the symmetry of $h_a\, h_b$, we assume it given by the average of these two expressions, i.e. as $\frac{1}{2}\, c_1\, (h_a\, h_a + h_b\, h_b) + \frac{1}{2}\, c_2\, (\sigma_b\, h_b - h_a\, \sigma_a)$. However, since we shall ultimately determine c_1 and c_2 by correspondence with various integrals, we may redefine them to absorb the constant factors $\frac{1}{2}$. The above arguments, and corresponding reasoning for other charge distributions, lead to the formulas

Table 2. *Exact and approximate integrals involving asymmetric two-center charge distributions*

integral	$R = 2; \delta_{2s} = \delta_{2p} = 2.00$			$R = 2; \delta_{2s} = \delta_{2p} = 1.67$		
	exact	this work	Mull. appr	exact	this work	Mull. appr
hybrid						
$[h_a\,h_a \mid h_a\,s_b]$	0.275	0.278	0.271	0.310	0.311	0.308
$[h_a\,\sigma_a \mid h_a\,s_b]$	0.053	0.053	0.030	0.050	0.050	0.032
$[\pi_a\,\pi_a \mid h_a\,s_b]$	0.286	0.290	0.283	0.304	0.303	0.297
$[s_a\,s_a \mid h_a\,\sigma_b]$	−0.293	−0.292	−0.224	−0.314	−0.313	−0.249
$[s_a\,s_a \mid \sigma_a\,h_b]$	0.216	0.215	0.224	0.231	0.231	0.239
$[s_a\,\sigma_a \mid h_a\,\sigma_b]$	−0.048	−0.048	−0.026	−0.038	−0.038	−0.027
$[s_a\,\sigma_a \mid \sigma_a\,h_b]$	0.087	0.087	0.021	0.091	0.091	0.027
$[\pi_a\,\pi_a \mid h_a\,\sigma_b]$	−0.289	−0.289	−0.220	−0.312	−0.312	−0.245
$[\pi_a\,\pi_a \mid \sigma_a\,h_b]$	0.206	0.207	0.215	0.220	0.222	0.229
$[h_a\,\pi_a \mid s_a\,\pi_b]$	0.033	0.035	0.000	0.042	0.043	0.000
$[h_a\,\pi_a \mid \pi'_a\,s_b]$	0.044	0.039	0.000	0.054	0.046	0.000
$[\sigma_a\,\pi_a \mid \pi'_a\,h_b]$	0.010	0.007	0.000	0.011	0.008	0.000
$[\sigma_a\,\pi_a \mid h_a\,\pi_b]$	0.013	0.007	0.000	0.014	0.008	0.000
exchange						
$[h_a\,h_b \mid h_a\,s_b]$	0.170	0.172	0.161	0.186	0.185	0.177
$[s_a\,s_b \mid h_a\,s_b]$	0.150	0.151	0.133	0.190	0.189	0.173
$[s_a\,s_b \mid s_a\,\sigma_b]$	−0.151	−0.150	−0.123	−0.182	−0.182	−0.151
$[\sigma_a\,\sigma_b \mid s_a\,h_b]$	−0.136	−0.137	−0.096	−0.119	−0.119	−0.074
$[h_a\,s_b \mid h_a\,\sigma_b]$	−0.135	−0.136	−0.110	−0.170	−0.170	−0.142
$[h_a\,\sigma_b \mid s_a\,\sigma_b]$	0.154	0.153	0.103	0.186	0.185	0.126
$[h_a\,\sigma_b \mid \sigma_a\,s_b]$	−0.116	−0.115	−0.084	−0.140	−0.139	−0.115
$[h_a\,\pi_b \mid s_a\,\pi_b]$	0.022	0.017	0.000	0.029	0.023	0.000
$[h_a\,\pi_b \mid \pi'_a\,s_b]$	0.021	0.017	0.000	0.026	0.021	0.000

$$
\begin{aligned}
h_a\,h_b &\approx c_1\,(h_a\,h_a + h_b\,h_b) + c_2\,(\sigma_b\,h_b - h_a\,\sigma_a) \\
s_a\,s_b &\approx c_3\,(s_a\,h_a + h_b\,s_b) + c_4\,(\sigma_b\,s_b - s_a\,\sigma_a) \\
\sigma_a\,\sigma_b &\approx c_5\,(h_b\,\sigma_b - \sigma_a\,h_a) + c_6\,(\sigma_a\,\sigma_a + \sigma_b\,\sigma_b) \\
\pi_a\,\pi_b &\approx c_7\,(\pi_a\,\pi_a + \pi_b\,\pi_b) \\
\pi_a\,\pi'_b &\approx c_7\,(\pi_a\,\pi'_a + \pi_b\,\pi'_b) \, .
\end{aligned}
\tag{1}
$$

For asymmetrical charge distributions we regard the relative weighting of the expansions about A and B as variable, and to be reflected in the values of the expansion coefficients. The expansion formulas for these charge distributions are thus taken as

$$
\begin{aligned}
h_a\,s_b &\approx c_1\,h_b\,s_b + c_2\,\sigma_b\,s_b + c_3\,h_a\,h_a - c_4\,h_a\,\sigma_a \\
h_a\,\sigma_b &\approx c_1\,h_b\,\sigma_b + c_2\,\sigma_b\,\sigma_b - c_5\,h_a\,h_a + c_6\,h_a\,\sigma_a \\
s_a\,\sigma_b &\approx c_3\,h_b\,\sigma_b + c_4\,\sigma_b\,\sigma_b - c_5\,s_a\,h_a + c_6\,s_a\,\sigma_a \\
h_a\,\pi_b &\approx c_1\,h_b\,\pi_b + c_2\,\sigma_b\,\pi_b + c_7\,h_a\,\pi_a \\
s_a\,\pi_b &\approx c_3\,h_b\,\pi_b + c_4\,\sigma_b\,\pi_b + c_7\,s_a\,\pi_a \\
\sigma_a\,\pi_b &\approx c_5\,h_b\,\pi_b + c_6\,\sigma_b\,\pi_b + c_7\,\sigma_a\,\pi_a \, .
\end{aligned}
\tag{2}
$$

Eqs. (1) and (2) permit the approximate simplification of all electron repulsion integrals into linear combinations of one-center integrals and two-center integrals of Coulomb type.

"Mull. appr" indicates the Mulliken approximation as in Eq. (10). Units of R are bohrs; integrals are in hartrees.

$R = 3; \delta_{2s} = \delta_{2p} = 1.67$			$R = 5; \delta_{2s} = \delta_{2p} = 1.67$			$R = 8; \delta_{2s} = \delta_{2p} = 1.67$		
exact	this work	Mull. appr	exact	this work	Mull. appr	exact	this work	Mull. appr
0.149	0.151	0.153	0.0235	0.0232	0.0299	0.0010	0.0009	0.0020
0.029	0.029	0.013	0.0048	0.0047	0.0012	0.0002	0.0001	0.0000
0.145	0.147	0.149	0.0229	0.0226	0.0293	0.0010	0.0008	0.0019
−0.177	−0.175	−0.149	−0.0310	−0.0304	−0.0331	−0.0014	−0.0014	−0.0023
0.137	0.136	0.144	0.0298	0.0294	0.0326	0.0020	0.0020	0.0023
−0.035	−0.035	−0.015	−0.0070	−0.0069	−0.0016	−0.0002	−0.0002	−0.0000
0.048	0.047	0.012	0.0089	0.0088	0.0014	0.0005	0.0005	0.0000
−0.172	−0.172	−0.147	−0.0301	−0.0301	−0.0329	−0.0014	−0.0014	−0.0023
0.131	0.131	0.138	0.0287	0.0284	0.0314	0.0019	0.0019	0.0022
0.014	0.015	0.000	0.0010	0.0012	0.0000	0.0000	0.0000	0.0000
0.021	0.020	0.000	0.0019	0.0028	0.0000	0.0000	0.0001	0.0000
0.006	0.004	0.000	0.0011	0.0012	0.0000	0.0001	0.0001	0.0000
0.006	0.003	0.000	0.0005	0.0001	0.0000	0.0000	0.0000	0.0000
0.056	0.055	0.053	0.0029	0.0025	0.0029	0.0000	0.0000	0.0000
0.052	0.051	0.045	0.0017	0.0014	0.0015	0.0000	0.0000	0.0000
−0.060	−0.058	−0.047	−0.0017	−0.0014	−0.0014	−0.0000	−0.0000	−0.0000
−0.066	−0.065	−0.049	−0.0032	−0.0027	−0.0027	−0.0000	−0.0000	−0.0000
−0.057	−0.056	−0.048	−0.0028	−0.0023	−0.0024	−0.0000	−0.0000	−0.0000
0.070	0.068	0.051	0.0029	0.0024	0.0023	0.0000	0.0000	0.0000
−0.061	−0.059	−0.046	−0.0034	−0.0028	−0.0027	−0.0000	−0.0000	−0.0000
0.006	0.005	0.000	0.0001	0.0002	0.0000	0.0000	0.0000	0.0000
0.006	0.004	0.000	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000

Now, we regard the expansion formulas given in Eqs. (1) and (2) as forms to be fitted to various integrals, and accordingly we seek optimum values of the coefficients c_i. Since the entities we attempt to describe are the charge distributions themselves, and not the orbitals, we reserve the freedom to assign different values to the same c_i in different charge distributions. After some preliminary investigation, we found that the symmetrical charge distributions could be conveniently characterized by requiring them to yield correct results for certain hybrid integrals. The hybrid integrals are a good choice because they can be used to control the distribution of weight among the different terms of the expansions. For example, with the aid of Eq. (1) the hybrid integral $[h_a h_a \mid h_a h_b]$ is approximated as

$$[h_a h_a \mid h_a h_b] \approx c_1 \left([h_a h_a \mid h_a h_a] + [h_a h_a \mid h_b h_b]\right) + c_2 [h_a h_a \mid \sigma_b h_b] \qquad (3)$$

Notice that one of the terms of the expansion of $h_a h_b$ drops from Eq. (3) for symmetry reasons, and that, of the remaining terms, those involving c_1 are more important, as they include a one-center integral and a two-center integral of charge-charge type, whereas the c_2 term consists only of a two-center integral of charge-dipole type.

We look next at the hybrid integral $[h_a \, \sigma_a \mid h_a \, h_b]$, whose approximation is

$$[h_a \, \sigma_a \mid h_a \, h_b] \approx c_1 \, [h_a \, \sigma_a \mid h_b \, h_b] + c_2 \, ([h_a \, \sigma_a \mid \sigma_b \, h_b] - [h_a \, \sigma_a \mid h_a \, \sigma_a]) . \qquad (4)$$

Because of the difference in symmetry of $h_a \, h_a$ and $h_a \, \sigma_a$, we see that the most important terms in Eq. (4) involve c_2 rather than c_1. Because Eqs. (3) and (4) depend rather differently upon c_1 and c_2, they are susceptible to computationally satisfactory simultaneous solution for these coefficients. We have found that the aprticular hybrid integrals used in determining c_1 and c_2 are not important, providing their one-center charge distributions are of different symmetries.

Reasoning similar to that just outlined was used to characterize the other symmetrical two-center charge distributions. In particular, we determine c_3 and c_4 in the expansion of $s_a \, s_b$ from

$$[h_a \, h_a \mid s_a \, s_b] \approx c_3 \, ([h_a \, h_a \mid s_a \, h_a] + [h_a \, h_a \mid h_b \, s_b]) + c_4 \, [h_a \, h_a \mid \sigma_b \, s_b] \qquad (5)$$

$$[h_a \, \sigma_a \mid s_a \, s_b] \approx c_3 \, [h_a \, \sigma_a \mid h_b \, s_b] + c_4 \, ([h_a \, \sigma_a \mid \sigma_b \, s_b] - [h_a \, \sigma_a \mid s_a \, \sigma_a]) . \qquad (6)$$

For $\sigma_a \, \sigma_b$, we obtain c_5 and c_6 from

$$[h_a \, h_a \mid \sigma_a \, \sigma_b] \approx c_5 \, [h_a \, h_a \mid h_b \, \sigma_b] + c_6 \, ([h_a \, h_a \mid \sigma_a \, \sigma_a] + [h_a \, h_a \mid \sigma_b \, \sigma_b]) \qquad (7)$$

$$[h_a \, \sigma_a \mid \sigma_a \, \sigma_b] \approx c_5 \, ([h_a \, \sigma_a \mid h_b \, \sigma_b] - [h_a \, \sigma_a \mid \sigma_a \, h_a]) + c_6 \, [h_a \, \sigma_a \mid \sigma_b \, \sigma_b] . \qquad (8)$$

The single coefficient c_7 appearing in $\pi_a \, \pi_b$ and $\pi_a \, \pi_b'$ is determined from

$$[h_a \, h_a \mid \pi_a \, \pi_b] \approx c_7 \, ([h_a \, h_a \mid \pi_a \, \pi_a] + [h_a \, h_a \mid \pi_b \, \pi_b]) . \qquad (9)$$

To test the approximations just outlined, we made calculations of exact and approximate two-center integrals of exchange and hybrid type. The exact integrals were obtained by methods previously reported by one of us [3]. Along with the new approximation we also tabulate the Mulliken approximation, which we applied in the form

$$[\theta_a \, \psi_b \mid \varphi_a \, \chi_b] \approx \tfrac{1}{4} \, (\theta_a \mid \psi_b) \, (\varphi_a \mid \chi_b) \, ([\theta_a \, \theta_a \mid \varphi_a \, \varphi_a] + [\theta_a \, \theta_a \mid \chi_b \, \chi_b] +$$
$$+ [\psi_b \, \psi_b \mid \varphi_a \, \varphi_a] + [\psi_b \, \psi_b \mid \chi_b \, \chi_b]) . \qquad (10)$$

Results of these calculations are given in Tab. 1 for various $A - B$ distances R and Slater parameters δ. In all cases $\delta_{1s} = 1$; δ_{2s} and δ_{2p} are as listed. The "exact" results and all input to the approximate calculations were obtained to six decimal places; the table values were rounded for convenience in presentation. It is seen that a relatively good fit is obtained for all integrals under consideration, including those for which the Mulliken approximation is not very satisfactory. The integrals subject to the largest errors are those involving charge distribution $\pi_a \, \pi_b$ (or $\pi_a \, \pi_b'$), which is described in the present approximation by its leading term alone. A logical step towards improving the expansion of $\pi_a \, \pi_b$ would be to add the next symmetry orbital, which is of atomic symmetry $d\pi$. As the lowest $d\pi$ orbital is of principal quantum number 3, we did not add it at this time.

Proceeding now to the asymmetric charge distributions, at least two obvious courses of action are available. The simpler alternative is to use the coefficients c_i obtained for the symmetrical distributions to complete the specification of the expansions given in Eq. (2). This approach proves adequate for $h_a \, s_b$, and is marginally satisfactory for $h_a \, \pi_b$, $s_a \, \pi_b$, and $\sigma_a \, \pi_b$. However, it is entirely unsatisfactory for $h_a \, \sigma_b$ and $s_a \, \sigma_b$. A far better approximation to charge distribu-

tions of mixed symmetry is afforded by directly fitting the expansions of Eq. (2) to appropriate sets of hybrid integrals. For example, the coefficients in $h_a \, \sigma_b$ can be determined from the four simultaneous equations

$$[h_a \, h_a \mid h_a \, \sigma_b] \approx c_1 \, [h_a \, h_a \mid h_b \, \sigma_b] + c_2 \, [h_a \, h_a \mid \sigma_b \, \sigma_b] - c_5 \, [h_a \, h_a \mid h_a \, h_a] \,, \qquad (11)$$

$$[h_a \, \sigma_a \mid h_a \, \sigma_b] \approx c_1 \, [h_a \, \sigma_a \mid h_b \, \sigma_b] + c_2 \, [h_a \, \sigma_a \mid \sigma_b \, \sigma_b] + c_6 \, [h_a \, \sigma_a \mid h_a \, \sigma_a] \,, \qquad (12)$$

$$[h_b \, h_b \mid h_a \, \sigma_b] \approx c_2 \, [h_b \, h_b \mid \sigma_b \, \sigma_b] - c_5 \, [h_b \, h_b \mid h_a \, h_a] + c_6 \, [h_b \, h_b \mid h_a \, \sigma_a] \,, \qquad (13)$$

$$[h_b \, \sigma_b \mid h_a \, \sigma_b] \approx c_1 \, [h_b \, \sigma_b \mid h_b \, \sigma_b] - c_5 \, [h_b \, \sigma_b \mid h_a \, h_a] + c_6 \, [h_b \, \sigma_b \mid h_a \, \sigma_a] \,. \qquad (14)$$

While similar equations could be applied in principle to products of orbitals of the same symmetry, such as $h_a \, s_b$, they might in some cases generate near linear dependences and be numerically unsatisfactory.

We used the procedure exemplified by Eqs. (11) to (14) for $h_a \, \sigma_b$ and $s_a \, \sigma_b$, and evaluated $h_a \, s_b$, $h_a \, \pi_b$, $s_a \, \pi_b$, and $\sigma_a \, \pi_b$ using the coefficients for the symmetrical charge distributions. This leads to the results given in part in Tab. 2. We actually examined every two-center hybrid and exchange integral for the R and δ values listed, and the integrals chosen for tabulation are entirely representative. Again we obtain a relatively good fit for all integrals, with poorest results for those involving π orbitals, probably for the reasons suggested in the discussion of the symmetrical charge distributions.

Discussion

The results given in the preceding section indicate that with but few exceptions, all the two-center integrals which arise in normal molecular calculations are estimated with accuracies of the order of 1 kcal ($= 0.0016$ Hartree) or better. This accuracy seems to us to be sufficient to constitute a significant potential improvement over the methods currently in widest use. Although the results thus far obtained are entirely for two-center integrals, we are optimistic that they can be extended to three- and four-center integrals as well, because the same approximate charge distribution appears to work well in a variety of integrals whose main contributions arise in different spatial regions. With the aid of the exact multi-center integral methods of HARRIS and MICHELS [4 to 6], the present authors hope to obtain information bearing on this hypothesis.

An important practical matter with respect to the methods here described is the ease and convenience with which they can be applied. To calculate the entire set of electron repulsion integrals for a molecule, we need the full set of Coulomb integrals involving the various orbital centers, plus a few hybrid integrals. For an n-center problem, this will involve integrals on $n \, (n - 1)/2$ pairs of centers. This situation is far more favorable than that arising from midpoint- or arbitrarily centered orbitals as there would then be of the order of n^2 expansion centers and of the order of n^4 pairs of centers for which Coulomb integrals would be needed.

To obtain some idea of possible integral evaluation times in the present approximation, let us examine a calculation in which we require all distinct Coulomb integrals for principal quantum numbers 1 and 2 for all combinations of n centers. Using our current programs for IBM–7094-type equipment, this would require roughly $0.3 \, n^2$ sec. The necessary hybrid integrals would take about $0.4 \, n^2$ sec. Formation of general electron repulsion integrals would then require approximately

0.2 msec each. If there are four orbitals per center we would need nearly $32 \, n^4$ integrals not of one-center or Coulomb type, together requiring about $0.007 \, n^4$ sec. For a six-center problem these times add up to about 33 sec; for a 12-center problem, to about 245 sec. The latter problem is large enough that the final integral formation has become the most time-consuming step. The times quoted are small enough that it appears practical to attempt to retain all integrals in problems of moderate size.

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