

Use of the Mixed Basis Method for *ab initio* SCF MO Calculations

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A previously described mixed basis method for performing SCF MO calculations has been applied to the benzene molecule and to the allyl cation. A basis set of Slater type orbitals is used to calculate the one-electron and one-centre two-electron integrals whilst the many-centre two-electron integrals are approximated by small gaussian type orbital expansions of the STO basis. Comparison of the results with all-gaussian basis sets and literature values indicates that the mixed basis 2-GTO approximation is inadequate for molecules of this size because of the consistent underestimation of the electron repulsion integrals. The use of gaussian exponents chosen by a least-squares procedure rather than variationally gives better mixed basis results, but the indications are that a 4-GTO expansion is necessary for reliable mixed basis calculations. A method for more accurate integral evaluation by gaussian expansions of orbital products is suggested.

Eine früher beschriebene Methode mit gemischter Basis zur Durchführung von SCF-MO-Berechnungen wurde auf das Benzolmolekül sowie das Allylkation angewendet. Ein Basissatz aus Slaterorbitalen wird verwendet, um die Einelektronen- und die Einzentrenzweielektronenintegrale zu berechnen, während die Mehrzentrenzweielektronenintegrale mit Hilfe von Entwicklungen der Slaterorbitale nach wenigen Gaußfunktionen angenähert werden. Ein Vergleich mit Ergebnissen von Rechnungen mit Gesamtbasisätzen von Gaußfunktionen und mit Literaturwerten zeigt, daß der gemischte Basissatz 2-GTO ungeeignet für Moleküle von dieser Größe ist, da die Elektronenabstoßungsintegrale durchgehend zu klein berechnet werden. Die Verwendung von Exponenten der Gaußfunktion, die mit Hilfe einer Methode der kleinsten Quadrate gewonnen wurde, ergibt bei der gemischten Basis bessere Ergebnisse als diejenigen, die nach der Variationsmethode gewonnen wurden; es zeigt sich jedoch, daß 4-GTO-Entwicklungen für angemessene Berechnungen mit gemischter Basis notwendig werden. Eine Methode für eine genauere Integralberechnung mit Hilfe der Entwicklung von Orbitalprodukten nach Gaußfunktionen wird vorgeschlagen.

Application à la molécule de benzène d'une méthode de base mixte précédemment décrite pour effectuer les calculs SCF MO. Une base d'orbitales de Slater est utilisée pour calculer les intégrales monoélectroniques et les intégrales biélectroniques monocentriques; les intégrales biélectroniques polycentriques sont approchées au moyen d'une expression des orbitales de Slater en orbitales gaussiennes. La comparaison des résultats avec ceux obtenus en bases gaussiennes et avec ceux donnés dans la littérature indique que l'approximation 2-GTO n'est pas adaptée aux molécules de cette taille car elle provoque une sous-estimation constante des intégrales de répulsion électronique. L'emploi d'exposants gaussiens choisis par un procédé de moindres carrés plutôt que par une méthode variationnelle donne de meilleurs résultats en bases mixtes mais il s'avère nécessaire d'utiliser un développement du type 4-GTO. On propose une méthode pour l'évaluation plus précise des intégrales par développement gaussien des produits d'orbitales.

Introduction

In the course of some *ab initio* SCF MO calculations on a number of small molecules we employed the "mixed" basis method first formulated by Cook and Palmieri [1]. The results of these calculations, which utilized small gaussian

type orbital (GTO) expansions, were less satisfactory than might have been expected judged from the success of the method in its trial applications to CH_4 , H_2O , and H_2S . A comparison of the results with parallel all gaussian calculations using the same GTO basis sets revealed a major deficiency in the mixed basis method when small (2-GTO) basis sets were employed for the calculation of the electron repulsion integrals in molecules somewhat larger than methane.

As originally described the mixed basis method uses a Slater type orbital (STO) basis for the calculation of the one-electron Hamiltonian and the coulomb-type integrals. The remaining two-electron integrals are computed over a small GTO expansion of the STO basis set. In this way the advantages of using GTO's for the time-consuming calculation of the electron repulsion integrals are maintained whilst the errors introduced into the calculation of the one-electron Hamiltonian by the inaccuracy of small GTO expansions of Slater orbitals in the region near the nucleus are avoided. A more extreme approach [2], in which one-electron integrals were calculated accurately but the two-electron integrals (over orthogonalized orbitals) were approximated using a modified zero-differential overlap approximation, also showed some promise. Clearly such methods depend for their validity on the accuracy with which electron repulsion effects may be estimated using approximate integrals.

In the first mixed-basis calculations [1] satisfactory results were obtained with a 2-GTO expansion. Similar results have also been reported by Brown *et al.* for water and methane [3]. In the present work we apply the method to somewhat larger systems, the benzene molecule and the allyl cation.

Calculations

SCF MO calculations on the ground states of the benzene molecule and the allyl cation have been carried out using a variety of basis sets. For benzene the two and three gaussian type orbital expansions of Huzinaga [4], with orbital exponents chosen by variational methods, were scaled to fit minimal basis Slater type orbitals with best-atom exponents from Clementi and Raimondi [5] except for the hydrogen $1s$ orbital where an exponent of 1.2 was used. In order to test the different effects of using GTO expansions fitted by variational or least-squares methods the 2-GTO expansions of Stewart [6] were also scaled to fit the same STO exponents. Although GTO expansions chosen by least-squares methods are not optimum for energies they should be more accurate descriptions of the atomic orbitals in the regions distant from the nucleus than GTO's with variationally-chosen exponents.

Two SCF calculations were performed for each of these three gaussian basis sets. In the first, all one- and two-electron Hamiltonian elements were computed using the GTO basis.

Total energies, one-electron orbital energies and population analyses are reported in Table 1. Columns (a), (c) and (e) give the results for 2- and 3-GTO (variational) and 2-GTO (least-squares) respectively. These may be compared with the second set of calculations for which a mixed basis set was employed. Here the GTO expansions were used for the many-centre two-electron integrals

Table 1. Results of the calculations for benzene using different basis sets^a

(a) 2-GTO (V) ^b	(b) 2-GTO (V) Mixed basis	(c) 3-GTO (V)	(d) 3-GTO (V) Mixed basis	(e) 2-GTO (LS) ^c	(f) 2-GTO (LS) Mixed basis	(g) SM [8] ^d
-10.95 $1b_{1u}$	-11.46 $1a_{1g}$	-11.30 $1b_{1u}$	-11.37 $1a_{1g}$	-10.81 $1b_{1u}$	-11.39 $1b_{1u}$	-11.30 $1a_{1g}$
-10.95 $1e_{2g}$	-11.45 $1e_{1u}$	-11.30 $1e_{2g}$	-11.37 $1e_{2g}$	-10.81 $1e_{2g}$	-11.38 $1e_{2g}$	-11.30 $1e_{1u}$
-10.94 $1e_{1u}$	-11.45 $1b_{1u}$	-11.30 $1e_{1u}$	-11.37 $1e_{1u}$	-10.81 $1e_{1u}$	-11.36 $1e_{1u}$	-11.30 $1e_{2g}$
-10.94 $1a_{1g}$	-11.44 $1e_{2g}$	-11.29 $1a_{1g}$	-11.37 $1b_{1u}$	-10.81 $1a_{1g}$	-11.36 $1a_{1g}$	-11.30 $1b_{1u}$
-1.134 $2a_{1g}$	-2.478 $2a_{1g}$	-1.150 $2a_{1g}$	-1.276 $2a_{1g}$	-1.135 $2a_{1g}$	-1.463 $2a_{1g}$	-1.168 $2a_{1g}$
-0.996 $2e_{1u}$	-2.293 $2b_{1u}$	-1.018 $2e_{1u}$	-1.056 $2e_{1u}$	-0.997 $2e_{1u}$	-1.278 $2e_{1u}$	-1.037 $2e_{1u}$
-0.797 $2e_{2g}$	-2.102 $2e_{1u}$	-0.823 $2e_{2g}$	-0.779 $2e_{2g}$	-0.805 $2e_{2g}$	-1.004 $2e_{2g}$	-0.846 $2e_{2g}$
-0.683 $3a_{1g}$	-1.813 $2e_{2g}$	-0.711 $3a_{1g}$	-0.669 $1a_{2u}(\pi)$	-0.704 $3a_{1g}$	-0.877 $2b_{1u}$	-0.738 $3a_{1g}$
-0.617 $2b_{1u}$	-1.265 $1a_{2u}(\pi)$	-0.643 $2b_{1u}$	-0.656 $3a_{1g}$	-0.621 $2b_{1u}$	-0.774 $3a_{1g}$	-0.662 $2b_{1u}$
-0.576 $1b_{2u}$	-1.075 $3a_{1g}$	-0.610 $1b_{2u}$	-0.548 $2b_{1u}$	-0.603 $1b_{2u}$	-0.671 $1a_{2u}(\pi)$	-0.654 $1b_{2u}$
-0.550 $3e_{1u}$	-1.072 $1a_{2g}$	-0.586 $3e_{1u}$	-0.503 $3e_{1u}$	-0.573 $3e_{1u}$	-0.669 $3e_{2g}$	-0.622 $3e_{1u}$
-0.483 $1a_{2u}(\pi)$	-0.495 $3e_{1u}$	-0.518 $1a_{2u}(\pi)$	-0.493 $3e_{2g}$	-0.511 $1a_{2u}(\pi)$	-0.668 $1b_{2u}$	-0.535 $1a_{2u}(\pi)$
-0.452 $3e_{2g}$	-0.493 $3e_{2g}$	-0.488 $3e_{2g}$	-0.478 $1b_{2u}$	-0.471 $3e_{2g}$	-0.666 $3e_{1u}$	-0.524 $3e_{2g}$
-0.317 $1e_{1g}(\pi)$	-0.469 $1e_{1g}(\pi)$	-0.351 $1e_{1g}(\pi)$	-0.269 $1e_{1g}(\pi)$	-0.339 $1e_{1g}(\pi)$	-0.490 $4e_{2g}$	-0.373 $1e_{1g}(\pi)$
0.208 $1e_{2u}(\pi)$	-0.188 $3b_{1u}$	0.171 $1e_{2u}(\pi)$	0.091 $4e_{2g}$	0.198 $1e_{2u}(\pi)$	-0.220 $3b_{1u}$	0.127 $1e_{2u}(\pi)$
0.444 $1b_{2g}(\pi)$	0.154 $1b_{2g}(\pi)$	0.406 $1b_{2g}(\pi)$	0.183 $3b_{1u}$	0.446 $1b_{2g}(\pi)$	-0.049 $1e_{1g}(\pi)$	0.363 $1b_{2g}(\pi)$
Total energy	-239.3671	-228.7230	-229.5162	-221.1981	-232.7514	-230.463
-223.7114						
Atom populations						
C 6.14	6.61	6.18	6.19	6.16	6.15	6.23
H 0.86	0.39	0.82	0.81	0.84	0.85	0.77
Bond populations						
C-C 1.05	-6.70	1.05	0.30	1.04	-3.79	0.98
C-H 0.81	-1.83	0.83	0.27	0.83	-0.55	0.83

^a All energies in this and subsequent tables are in Hartree units.^b Gaussian exponents chosen variationally [3].^c Gaussian exponents chosen by a least-squares method [5].^d This calculation employed a slightly different geometry: C-C = 1.395 Å, C-H = 1.085 Å.

Table 2. A comparison of orbital and total energies and population analyses for the various $C_3H_3^+$ calculations

(a) 2-GTO (Mixed basis)	(b) 3-GTO (Mixed basis)	(c) 4-GTO (Mixed basis)	(d) 4-GTO	(e) PB [10]
-11.940 $1a_1$	-11.770 $1b_2$	-11.780 $1a_1$	-11.743 $1a_1$	-11.551 $1a_1$
-11.904 $2a_1$	-11.770 $1a_1$	-11.780 $1b_2$	-11.743 $1b_2$	-11.551 $1b_2$
-11.903 $1b_2$	-11.709 $2a_1$	-11.711 $2a_1$	-11.669 $2a_1$	-11.473 $2a_1$
- 1.757 $3a_1$	- 1.432 $3a_1$	- 1.426 $3a_1$	- 1.424 $3a_1$	- 1.393 $3a_1$
- 1.356 $2b_2$	- 1.263 $2b_2$	- 1.257 $2b_2$	- 1.252 $2b_2$	- 1.201 $2b_2$
- 1.220 $3b_2$	- 1.095 $4a_1$	- 1.098 $4a_1$	- 1.082 $4a_1$	- 1.024 $4a_1$
- 1.180 $4a_1$	- 0.983 $5a_1$	- 0.995 $5a_1$	- 0.995 $5a_1$	- 0.950 $5a_1$
- 1.158 $5a_1$	- 0.958 $3b_2$	- 0.950 $3b_2$	- 0.957 $3b_2$	- 0.894 $3b_2$
- 1.001 $4b_2$	- 0.926 $4b_2$	- 0.884 $4b_2$	- 0.894 $4b_2$	- 0.812 $4b_2$
- 0.994 $1b_1(\pi)$	- 0.856 $6a_1$	- 0.852 $6a_1$	- 0.855 $6a_1$	- 0.771 $6a_1$
- 0.937 $6a_1$	- 0.762 $1b_1(\pi)$	- 0.750 $1b_1(\pi)$	- 0.755 $1b_1(\pi)$	- 0.683 $1b_1(\pi)$
- 0.586 $7a_1$	- 0.326 $1a_2(\pi)$	- 0.324 $1a_2$	- 0.327 $1a_2(\pi)$	- 0.226 $1a_2(\pi)$
- 0.391 $1a_2(\pi)$	- 0.089 $2b_1(\pi)$	- 0.098 $2b_1(\pi)$	- 0.097 $2b_1(\pi)$	- 0.022 $2b_1(\pi)$
Total energy				
-116.9013	-115.9221	-115.8031	-115.3189	-116.1300
Atom populations ^a				
C ₁ 6.00	6.31	6.29	6.27	
C ₂ 6.30	6.26	6.24	6.18	
H ₁ 0.67	0.66	0.67	0.70	
H ₂ 0.70	0.65	0.65	0.68	
H ₃ 0.67	0.61	0.63	0.65	
Bond populations				
C ₁ -C ₂ -0.95	1.01	1.01	1.02	
H ₁ -C ₁ -0.04	0.83	0.84	0.85	
H ₂ -C ₂ 0.61	0.78	0.79	0.81	
H ₃ -C ₃ 0.31	0.76	0.77	0.79	

^a Atoms C₁ and H₁ lie on the 2-fold axis. H₂ is *cis* to H₁.

only. All one-centre one- and two-electron terms were calculated using the STO orbitals. The remaining many-centre one-electron elements were computed with a [666/6] GTO expansion taken from Huzinaga [7] in order to obtain close approximations to the exact values in a computationally convenient manner. The results are given in columns (b), (d) and (f) of Table 1. For comparison purposes column (g) contains the results obtained by Schulman and Moskowitz (SM) [8] using a large GTO basis set, which they consider to give results at least equal to those corresponding to a minimal Slater basis. The equilibrium ground state geometry, D_{6h} symmetry with C-C = 1.397 Å and C-H = 1.084 Å, was employed.

For the allyl ion a basis of SCF orbitals for carbon taken from Clement's tabulation of linear combinations of STO's [9] was used together with a hydrogen 1s exponent of 1.0. Columns (a), (b) and (c) of Table 2 give the results of mixed basis calculations using 2-, 3- and 4-GTO fits to these SCF functions for the computation of the many-centre two-electron integrals together with the exact

values for all one-centre terms and values determined from a [666/6] GTO expansion for the remaining one-electron terms. Column (d) gives the corresponding results obtained by using the 4-GTO expansion for all the Hamiltonian matrix terms. The gaussian lobe function calculation of Peyerimhoff and Buenker (PB) [10] on $C_3H_5^+$ is given in column (e) of Table 2 for comparison purposes. The use of optimized hydrogen $1s$ exponents and a slightly different geometry in this calculation prevents any direct comparison of total energies but the ordering of the one-electron energy levels should be unchanged. The ion was assumed to have C_{2v} symmetry with C-C 1.40 Å, C-H 1.08 Å and the angle \sphericalangle CCC 118.5°.

Results and Discussion

The three all-gaussian basis set calculations for benzene exhibit the same sequence of energy levels, and the only differences from the SM ordering lie in the arrangement of the nearly degenerate carbon inner-shell orbitals. The 3-GTO (variationally chosen) basis set total energy is within 2 a.u. of the SM value, and 5.0 a.u. below the 2-GTO (variational) value. The 2-GTO expansion with exponents determined by a least-squares procedure does not give as low a total energy as the 2-GTO (variational) basis set, as noted by Klessinger for CH_4 and H_2O [12]. The main difference between the 2-GTO calculations lies in the one-electron orbital energies. The variationally determined basis set gives lower energies for the core electrons but slightly higher energies for the valence electrons.

Brown *et al.* [3] in their mixed basis calculations on small molecules point out that the variation theorem does not apply to a calculation in which some of the integrals are approximated. They observe that in some cases a total energy slightly lower than the exact resulted from their mixed basis calculations, and this is consistent with slight underestimation of multicentre electrons repulsion integrals. For the larger benzene molecule it is clear that the approximations involved in using a small GTO basis set for these integrals lead to very poor results. The 2-GTO (V) mixed basis calculation has a total energy about 9 a.u. below the estimated value for a minimal Slater basis. The underestimation of electron repulsion integrals has lowered all the one-electron orbital energies and altered their ordering. Those levels which are completely determined by symmetry are most affected. The a_{2u} and e_{2u} -orbitals are lowered and raised in energy respectively whilst the a_{2g} antibonding orbital is now occupied, at the expense of the bonding b_{2u} orbital. The atomic population values are consistent with a build up of electron density close to the carbon nuclei, which, combined with the occupation of an antibonding orbital, gives chemically nonsensical results from a Mulliken population analysis. The 2-GTO (LS) calculation is better as far as energy is concerned, the total energy being only 2 a.u. below the estimated minimal Slater basis value. The deviations from the SM energy level ordering are still considerable however. The $2b_{1u}$ and $3a_{1g}$ levels are interchanged, the $a_{2u}(\pi)$ and $3e_{2g}$ levels are lowered in energy, and the $e_{1g}(\pi)$ level is now unoccupied although it still has a negative energy. The atomic population results are better than those for the 2-GTO (V) calculation, but the bond population figures are still meaningless.

Table 3. Comparison of values for some two-electron integrals for benzene. Orbitals are p_x on carbon atoms 1 to 6. $C-C=2.632075$ bohr, $\zeta=1.590$

	(a) Exact [11]	(b) 3-GTO (LS)	(c) 2-GTO (LS)	(d) 3-GTO (V)	(e) 2-GTO (V)	(f) n -GTO(CD) ^a
(21/11)	0.121755	0.121696	0.122062	0.121222	0.117650	0.121834
(31/11)	0.013891	0.013531	0.011196	0.011640	0.007912	0.013879
(41/11)	0.005796	0.005294	0.003755	0.004070	0.002233	0.005802
(32/11)	0.068193	0.068165	0.067891	0.067468	0.064268	0.068201
(43/11)	0.051664	0.051634	0.051426	0.051088	0.048653	0.051687
(62/11)	0.016131	0.015874	0.013795	0.014117	0.010129	0.016122
(42/11)	0.010001	0.009721	0.008065	0.008365	0.005680	0.009994
(53/11)	0.008846	0.008621	0.007202	0.007452	0.005082	0.008841
(52/11)	0.005416	0.005033	0.003684	0.003954	0.002217	0.005419
(21/21)	0.034091	0.034053	0.034237	0.033784	0.032136	0.034149
(31/31)	0.000633	0.000612	0.000456	0.000477	0.000244	0.000632
(41/41)	0.000124	0.000109	0.000063	0.000070	0.000024	0.000124
(61/21)	0.023927	0.023914	0.023866	0.023521	0.021562	0.023945
(31/21)	0.004112	0.004035	0.003453	0.003526	0.002399	0.004112
(51/21)	0.003174	0.003087	0.002556	0.002634	0.001712	0.003174
(41/21)	0.001535	0.001417	0.001026	0.001097	0.000586	0.001537
(51/31)	0.000481	0.000459	0.000326	0.000348	0.000165	0.000480
(41/31)	0.000252	0.000232	0.000148	0.000162	0.000066	0.000252
(43/21)	0.015663	0.015646	0.015522	0.015316	0.013881	0.015673
(54/21)	0.013740	0.013724	0.013618	0.013433	0.012179	0.013754
(53/21)	0.002517	0.002451	0.002042	0.002098	0.001365	0.002516
(63/21)	0.001465	0.001369	0.001013	0.001075	0.000583	0.001467
(42/31)	0.000578	0.000556	0.000405	0.000429	0.000211	0.000577
(64/31)	0.000437	0.000417	0.000297	0.000316	0.000150	0.000436
(52/31)	0.000255	0.000234	0.000149	0.000163	0.000066	0.000255
(52/41)	0.000122	0.000108	0.000062	0.000070	0.000024	0.000122

^a See text for a description of the method. Expansions of 6, 8, 9, 8 functions were used for the products (1,1), (1,2), (1,3), and (1,4) respectively. The other orbital products required were obtained by symmetry.

The 3-GTO (V) mixed basis calculation is not so badly affected by the integral approximations. The total energy is considerably higher than the 2-GTO (V) value, though still lower than the all-gaussian 3-GTO value. The ordering of energy levels shows only two symmetry-determined molecular orbitals to have been misplaced – the a_{2u} level is lowered in energy whilst the b_{2u} level is raised, though not to the same extent as in the 2-GTO (V) mixed basis calculation.

In Table 3 we tabulate the results for the various GTO approximations to some accurately known two-electron integrals for benzene. The 2-GTO (V) values are in error by only a few percent for the largest integrals, but the errors increase as the magnitude of the integrals decreases.

The approximation gives only 20% of the value of integrals of the order of 10^{-4} a.u., which depend upon the overlap of the tails of the component orbitals. It is just this region of an STO, which, together with the cusp, is badly fitted by GTO's. For methane there are no integrals as small as 10^{-4} a.u. but a plot of the distribution of integral values for benzene using a 3-GTO (V) basis shows them to be evenly distributed about 10^{-3} a.u. Ka *et al.* [13] using a single GTO approximation show a similar distribution centred about 10^{-4} a.u. Since a majority of these underestimated multicentre integrals make positive contributions to the total energy and affect the various molecular orbitals differently, it is clear how the anomalous mixed basis results arise. The 2-GTO (LS) basis gives a better approximation to the small integrals which accounts for the slightly better 2-GTO (LS) mixed basis results.

The mixed basis results for the allyl cation exhibit increasing total energy with improving accuracy of the gaussian expansions and hence of the electron repulsion integrals. The differences in total energy between the 2- and 3-GTO and the 3- and 4-GTO calculations are of the order of 1.0 a.u. and 0.1 a.u. respectively. This leads us to suppose that the 4-GTO mixed basis calculation is within 0.1 a.u. of the total energy that would be obtained by an accurate calculation using the atomic SCF basis orbitals. Since the hydrogen 1s exponent is not optimized in the present calculation it is not unreasonable that our value should be about 0.4 a.u. above the total energy obtained by Peyerimhoff and Buenker. The 4-GTO calculation, to which the variation theorem applies, yields a total energy some 0.5 a.u. above the corresponding mixed basis calculation. This in no way implies that the mixed basis calculation is better than the all-gaussian one. Possibly the latter yields a better description of the molecular wave function at some distance from the nuclei whilst the former is more accurate close to the atomic centres. Both the 3- and 4-GTO mixed basis calculations and the 4-GTO results exhibit the same ordering of the one-electron energy levels as the comparison calculation. There is little variation in the results of the Mulliken population analyses, and, in the absence of more accurate results we have no grounds for preferring one of the 4-GTO calculations to the other.

The allyl ion is intermediate in size between the benzene molecule and those small molecules to which the mixed basis method had previously been applied. Thus it could be expected that the errors incurred by consistent under-estimation of the small electron repulsion integrals would be less severe in $C_3H_5^+$ than in benzene, but that the 2-GTO mixed basis approximation would still yield poor results. Column (a) of Table 2 confirms this. The total energy is some 1.2 a.u. below the estimated value for the basis set, which is considerably better than the 2-GTO approximation value for benzene. However, the ordering of the energy levels shows a number of deviations from the PB ordering, particularly in the arrangement of the π -orbitals. The π -orbital of b_1 symmetry has been replaced by a σ -bonding orbital as the highest occupied level and the non-bonding a_2 π -orbital is no longer the first virtual orbital. There is a considerable variation in the atomic populations when compared with the values in the other calculations and the meaningless overlap populations again exhibit the tendency of the electrons to keep close to the nuclei because of the under-estimation of the electron repulsion terms.

Conclusions

It is obvious that the validity of the mixed method depends upon the accuracy of the approximation to the many-centre integrals. In medium or large molecular systems small GTO expansions do not approximate these integrals well, so that the results are poor and the usefulness of this kind of mixed basis calculation is doubtful. Such integral approximations are bad for two reasons. Firstly, the large percentage errors in the approximation to the small many-centre integrals, although small in absolute value, have a considerable effect upon the SCF calculations because of the frequency of occurrence of this type of integral. Secondly, and more importantly, the errors do not occur with a random distribution. The consistent underestimation of the small many-centre two-electron integrals leads to negative deviations from the total energy and unreliable ordering of the molecular orbital levels.

It might be thought that one solution to this problem is to use least-squares fits weighted so that the tails of the functions are better described. We have tried this method but the technique is cumbersome both with regard to the number of fits required and because, for each integral, one must decide upon which fit to use. An alternative approach to the evaluation of the two-electron integrals is to regard the orbital products as the basic elements, rather than the orbitals, and to obtain least-squares expansions of GTO's for these products. Such a procedure has been briefly described for the case of integrals involving *s*-type orbitals [14]. We have successfully extended this method to integrals involving *p* and *d* orbitals [15]. Column (f) of Table 3 lists some values calculated by this method. The four unique orbital products, (1,1), (1,2), (1,3), and (1,4), involving the carbon p_{π} orbitals were expressed as expansions of *d*-type gaussian functions centred along the line joining the atomic centres. From the table it is seen that all the integrals calculated are within 0.25% of the exact value, even though the computational effort once the expansions are obtained is less than that for evaluating the integrals in the usual manner using 3-GTO expansions, which, as indicated in column (b), can give errors as high as 12%. We believe that this method of integral calculation will give satisfactory results in a mixed basis calculation and are working along these lines at present.

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