

Polarization Functions for First and Second Row Atoms in Gaussian Type MO-SCF Calculations

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A series of MO-SCF calculations, using a basis of Gaussian type functions, has been made in order to study the importance and size of polarization functions for first and second row atoms. Optimizations of polarization exponents have been performed for the molecules H_2O and H_2S . Conclusions from these results lead to a suggestion for the choice of $3d$ -orbital exponents also for other atoms of the first and second row. Test calculations have been made for carbon and nitrogen in CH_4 and NH_3 .

Um die Wichtigkeit und die Größe von Polarisationsfunktionen für die Atome der ersten und zweiten Reihe studieren zu können, wurde eine Reihe von MO SCF-Rechnungen mit einem aus Gaußfunktionen bestehenden Basissatz durchgeführt. Für die Moleküle H_2O und H_2S wurde die Optimierung der Polarisationsexponenten vorgenommen. Die Ergebnisse lassen Rückschlüsse auf die Wahl der $3d$ -Orbitalexponenten der übrigen Atome der ersten und zweiten Reihe zu. Testrechnungen für den Kohlenstoff im CH_4 und für den Stickstoff im NH_3 wurden durchgeführt.

Une série de calculs SCF-MO avec une base de gaussiens étaient effectués en vue d'étudier l'importance et la valeur de fonctions de polarisation dans les atomes du premier et deuxième rang. En H_2O et H_2S les exposants de fonctions de polarisation sont optimisés. Avec ces résultats les exposants pour les orbitaux $3d$ sont évalués. Les résultats pour le carbone dans CH_4 et l'azote dans NH_3 sont présentés comme exemple.

Introduction

The importance of $3d$ -orbitals in molecules containing second row atoms and the size of these orbitals has been the object for many investigations. One approach to the problems has been to study valence states of atoms and ions, either isolated or in the electrostatic field of surrounding ligands [1–4]. The $3d$ -orbital exponents obtained in this way vary considerably, depending upon the valence state and charge of the atom. It is, however, difficult to see how information about the size of $3d$ -orbitals in atoms could be used in MO-SCF calculations. The main effect of these orbitals is certainly not to build hybrids in the ordinary chemical sense, but to polarize s and p valence orbitals. Such orbitals bear little resemblance to excited atomic orbitals. The exponents are expected to have values giving a large overlap between $3d$ and $3p$, $3s$ charge clouds.

Optimal $3d$ exponents for second row atoms obtained from MO-SCF calculations have been published for a number of diatomic molecules [5], and a few polyatomics [6]. All this work uses Slater type orbitals as basis functions. So far no work seems to have been published where $3d$ -orbital exponents have been optimized in calculations with Gaussian type functions.

In order to prepare basis sets of limited size to be used in calculations on larger sulphur containing molecules a careful study of the effect of $3d$ -orbitals in first and second row atoms, and $2p$ -orbitals on hydrogen was needed. Calculations including variation of the polarization orbital exponents have been performed for H_2O and H_2S . A limited basis of contracted Gaussian type functions was used. The calculations were performed by means of the IBMOL program version IV on an IBM 360/75 computer [7].

Method

The $3d$ -orbital exponent optimization has been performed with a limited number of Gaussian type functions for s and p types. For the first row atoms seven s -type and three p -type functions, and for the second row atoms nine s -type and five p -type functions were used. With these basis sets each atomic orbital has contribution from at least two Gaussian functions. All basis sets have exponents optimized in the free atom, using a program for atomic SCF-calculations [8].

Basis sets of the above mentioned type will be published elsewhere [9].

The number of basis orbitals was reduced by means of the method of contraction. The contracted basis consists of two functions per atomic orbital. Thus for first row atoms four s - and two p -type, and for second row atoms six s - and four p -type functions were used.

For hydrogen a basis consisting of four s -type functions contracted to two was used. The orbital exponents were those of Huzinaga [10] multiplied with a scaling factor of 1.25. Calculations using Slater type orbitals have shown that hydrogen s -orbitals should be scaled when used as basis in MO-LCAO calculations. The scaling factor was optimized in previous calculations [11], and this value has been used throughout this work.

One polarization function was added to each of the basis sets. The $2p$ -orbital exponent for hydrogen was first given the value 0.80. The $3d$ -orbital exponent for oxygen and sulphur was then optimized in H_2O and H_2S , respectively. In order to test the validity of the $2p$ exponent, an optimization of this exponent was made in the water case. This gave the value 0.789 for the hydrogen $2p$ exponent. It was concluded that no further re-optimization of the $3d$ exponents was necessary.

The optimal orbital exponents obtained for oxygen and sulphur was 1.325 and 0.541, respectively. On the basis of these results corresponding values for $3d$ -orbital exponents for other first and second row atoms will be suggested below. These exponents were tested in calculations on the molecules CH_4 and NH_3 . Calculations using these exponents on other molecules containing second row atoms will be reported later.

Results and Discussion

The results obtained in the calculations are presented in Tables 1–4 and Figs. 1–3.

Fig. 1 shows the variation in total energies with polarization orbital exponent for the three cases studied. A comparison between curves (a) and (b) shows that

Table 1. H₂O results with different basis sets

GTO	(O/7, 3)	(H/4)	(O/7, 3, 1)	(H/4)	(O/7, 3)	(H/4, 1)	(O/7, 3, 1)	(H/4, 1)	(O/9, 5, 1)	(H/4, 1)	(O/10, 6, 2)	(H/4, 1) ^f
CGTO	<O/4, 2>	<H/2>	<O/4, 2, 1>	<H/2>	<O/4, 2>	<H/2, 1>	<O/4, 2, 1>	<H/2, 1>	<O/4, 2, 1>	<H/2, 1>	<O/10, 6, 2>	<H/4, 1>
-T.E. ^a	75.875		75.896		75.914		75.922		76.037		76.059	
-ε(1a ₁)	20.550		20.547		20.542		20.542		20.531		20.558	
-ε(2a ₁)	1.347		1.338		1.336		1.331		1.331		1.352	
-ε(3a ₁)	0.544		0.552		0.545		0.550		0.560		0.582	
-ε(1b ₁)	0.486		0.483		0.479		0.478		0.494		0.507	
-ε(1b ₂)	0.694		0.694		0.691		0.690		0.697		0.719	
n(O) ^b	8.146		8.157		7.609		7.670		7.806		—	
n(H)	0.420		0.405		0.578		0.540		0.412		—	
o(OH) ^c	0.271		0.274		0.336		0.330		0.349		—	
q(O) ^d	-0.688		-0.704		-0.280		-0.338		-0.505		—	
q(H)	+0.344		+0.352		+0.140		+0.169		+0.253		—	
μ ^e	2.415		2.205		2.115		2.008		2.144		1.995	

^a Energies in a.u.^b Overlap population.^c Dipole moment in Debye. Experimental value 1.84 D. [16].^d Net atomic population.^e Gross atomic charge.^f From the work of Neumann and Moskowitz [17].Table 2. H₂S results with different basis sets

GTO	(S/9, 5)	(H/4)	(S/9, 5, 1)	(H/4)	(S/9, 5)	(H/4, 1)	(S/9, 5, 1)	(H/4, 1)	(S/12, 9, 2)	(H/4, 1)
CGTO	<S/6, 4>	<H/2>	<S/6, 4, 1>	<H/2>	<S/6, 4>	<H/2, 1>	<S/6, 4, 1>	<H/2, 1>	<S/6, 4, 2>	<H/2, 1>
-T.E.	398.186		398.228		398.212		398.236		398.682	
-ε(1a ₁)	91.969		91.954		91.963		91.955		91.976	
-ε(2a ₁)	8.943		8.926		8.937		8.927		8.958	
-ε(3a ₁)	6.642		6.626		6.636		6.627		6.646	
-ε(4a ₁)	0.981		0.959		0.973		0.959		0.982	
-ε(5a ₁)	0.462		0.467		0.462		0.467		0.500	
-ε(1b ₁)	6.639		6.623		6.634		6.624		6.644	
-ε(2b ₁)	0.355		0.343		0.352		0.344		0.382	
-ε(1b ₂)	6.644		6.627		6.638		6.628		6.647	
-ε(2b ₂)	0.560		0.558		0.558		0.556		0.592	
n(S)	15.591		15.645		15.324		15.450		15.499	
n(H)	0.692		0.598		0.770		0.642		0.612	
o(SH)	0.271		0.299		0.302		0.326		0.333	
q(S)	-0.133		-0.242		+0.073		-0.102		-0.164	
q(H)	+0.067		+0.121		-0.036		+0.051		+0.082	
μ ^a	1.477		0.881		1.190		0.811		1.276	

^a Experimental value: 0.92 Debye [16].

Table 3. Comparative results for NH_3

GTO	(N/7, 3)	(H/4) ^a	(N/7, 3)	(H/4, 1) ^a	(N/7, 3, 1)	(H/4, 1) ^a	(N/13, 8, 2)	(H/8, 2) ^b
	$\langle \text{N/4, 2} \rangle$	$\langle \text{H/2} \rangle$	$\langle \text{N/4, 2} \rangle$	$\langle \text{H/2, 1} \rangle$	$\langle \text{N/4, 2, 1} \rangle$	$\langle \text{H/2, 1} \rangle$	$\langle \text{N/8, 5, 2} \rangle$	$\langle \text{H/4, 1} \rangle$
-T.E.	56.093	56.112	56.132	56.138	56.138	56.138	56.222	56.222
$-\varepsilon(1a_1)$	15.535	15.530	15.531	15.529	15.529	15.529	15.535	15.535
$-\varepsilon(2a_1)$	1.142	1.132	1.132	1.129	1.129	1.129	1.148	1.148
$-\varepsilon(3a_1)$	0.407	0.413	0.406	0.411	0.411	0.411	0.428	0.428
$-\varepsilon(1e)$	0.615	0.615	0.612	0.611	0.611	0.611	0.635	0.635
$n(\text{N})$	6.800	6.835	6.103	6.195	6.195	6.195	—	—
$n(\text{H})$	0.483	0.465	0.647	0.610	0.610	0.610	—	—
$o(\text{NH})$	0.325	0.325	0.372	0.367	0.367	0.367	0.400	0.400
$q(\text{N})$	-0.776	-0.810	-0.219	-0.239	-0.239	-0.239	-0.639	-0.639
$q(\text{H})$	+0.259	+0.270	+0.073	+0.098	+0.098	+0.098	+0.213	+0.213
μ^c	2.138	1.886	1.805	1.696	1.696	1.696	1.660	1.660

Table 4. Comparative results for CH_4

GTO	(C/7, 3)	(H/4) ^a	(C/7, 3)	(H/4, 1) ^a	(C/7, 3, 1)	(H/4, 1) ^a	(C/9, 5)	(H/4, 1) ^b
	$\langle \text{C/4, 2} \rangle$	$\langle \text{H/2} \rangle$	$\langle \text{C/4, 2} \rangle$	$\langle \text{H/2, 1} \rangle$	$\langle \text{C/4, 2, 1} \rangle$	$\langle \text{H/2, 1} \rangle$	$\langle \text{C/5, 5} \rangle$	$\langle \text{H/4, 1} \rangle$
-T.E.	40.145	40.158	40.170	40.173	40.173	40.173	40.198	40.198
$-\varepsilon(1a_1)$	11.217	11.214	11.221	11.218	11.218	11.218	11.222	11.222
$-\varepsilon(2a_1)$	0.945	0.942	0.942	0.941	0.941	0.941	0.930	0.930
$-\varepsilon(1t_2)$	0.543	0.544	0.541	0.542	0.542	0.542	0.535	0.535
$n(\text{C})$	5.237	5.270	4.531	4.622	4.622	4.622	—	—
$n(\text{H})$	0.512	0.490	0.649	0.609	0.609	0.609	—	—
$o(\text{CH})$	0.375	0.380	0.406	0.408	0.408	0.408	—	—
$q(\text{C})$	-0.737	-0.791	-0.154	-0.255	-0.255	-0.255	—	—
$q(\text{H})$	+0.184	+0.198	+0.038	+0.064	+0.064	+0.064	—	—

Table 3: ^a This work.^b From the work of Rauk, Allen and Clementi [19].^c Experimental value 1.48 D. [16].Table 4: ^a This work.^b From the work of Ritchie and King [18].

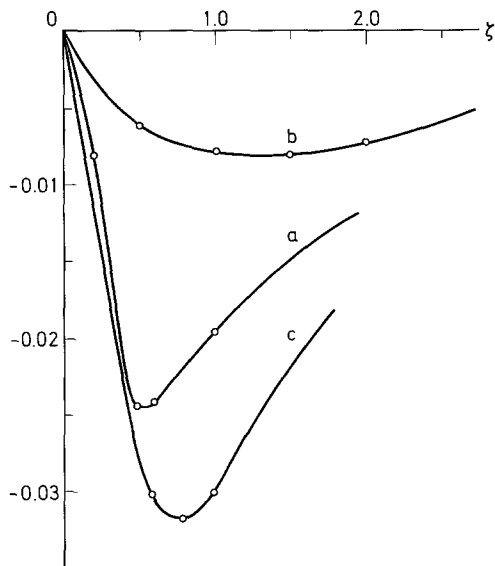


Fig. 1. Variation in total energies with polarization orbital exponent ζ . Relative energies are in a.u. a H_2S ; variation of $3d$ orbital exponent for sulphur, b H_2O ; variation of $3d$ orbital exponent for oxygen, c H_2O ; variation of $2p$ orbital exponent for hydrogen

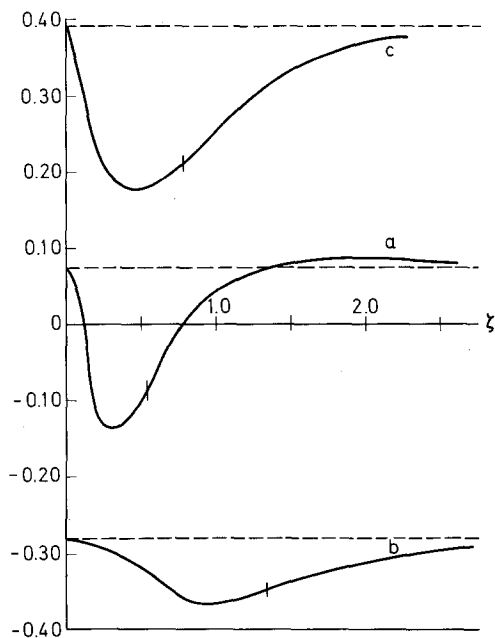


Fig. 2. Gross atomic charges as functions of polarization orbital exponent. a Gross atomic charge on S in H_2S ; Variation of $3d$ -exp. b Gross atomic charge on O in H_2O ; Variation of $3d$ -exp. c Gross atomic charge on H in H_2O ; Variation of $2p$ -exp. Vertical lines correspond to optimal values of the exponents

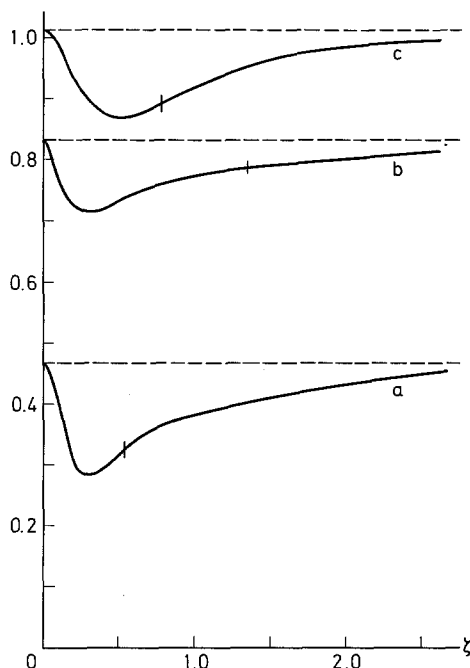


Fig. 3. Dipole moments as functions of the polarization orbital exponents (in a.u.). a H_2S with variation of $3d$ -orbital exponent, b H_2O with variation of $3d$ -orbital exponent, c H_2O with variation of $2p$ -orbital exponent

$3d$ -orbitals contribute much more to the total energy in second row atoms than in the first row. This is quite naturally to be expected. The curves also show that the choice of orbital exponents must be made more carefully in the second row. Curve (a) shows a narrow minimum, while curve (b) is very flat. The energy change in H_2O , when the exponent is increased with 0.5 from the optimal value (1.325) is only 0.001 a.u. The corresponding change in H_2S is 0.006 a.u.

A comparison between (b) and (c) in Fig. 1 shows that for H_2O it is more important (at least as far as the total energy is concerned) to include polarization functions on hydrogen than on the heavy atom. A comparison between columns 2–4 in Tables 3 and 4 confirms that this is even more true for NH_3 and CH_4 . In the case of H_2S the two types of polarization functions are of equal importance.

Inclusion of polarization functions has, as might be expected, a large effect on the charge distributions and dipole moments. Charges shown in Fig. 2 and the tables have been obtained by means of Mulliken's population analysis method. The variation of the dipole moment with $3d$ -orbital exponent is shown in Fig. 3.

As can be seen in Fig. 2 the sign of the gross atomic charge on sulphur in H_2S changes when the $3d$ -orbital is included, at least if the exponent is properly chosen. The electron population on a given atom increases when polarization orbitals are added. Somewhat surprisingly this in all cases leads to a decrease in dipole moment (cf. Fig. 3). One might expect that an increase should be obtained in case (b) where the gross atomic charges increase. This is, however, not the case, which shows that some care should be taken in drawing conclusions about polarity

from population analysis data. Actually the effect of the polarization functions is to localize electrons in the bonding regions, thus reducing the dipole moment.

Calculations without polarization functions for CH_4 , NH_3 and H_2O give large gross atomic charges on the hydrogens (0.184, 0.259 and 0.344, respectively). With polarization these charges decrease to 0.064, 0.098 and 0.169, respectively (cf. Tables 1, 3 and 4). The change is in all cases essentially due to the inclusion of polarization functions on the hydrogens. The $3d$ -orbitals has a smaller effect on the gross atomic charges. This result seems to be independent of the size of the sp -basis since the same conclusions could be drawn from a calculation on water using a (O/9, 5, 1) (H/4, 1) basis. Calculations without polarization functions gave in this case a hydrogen charge of +0.390. With polarization the charge was +0.253, a decrease with 0.137 electron units. The corresponding decrease obtained with the smaller basis was 0.175 electron units. The larger basis sets give larger charge polarization, but this is essentially due to the increase in s and p basis functions. The effect of the polarization functions is about the same in both cases.

This is in contrast with the results of Millie and Berthier for the methyl radical [12]. They found that the polarization functions counterbalanced each other. The charges were approximately the same with and without polarization, while polarization on either carbon or hydrogen gave different results. There are two possible explanations to the discrepancy between our results and theirs. They use a $2p$ exponent for hydrogen of 1.0. If the optimal exponent in H_2O (0.789) is increased to 1.0 the charge on each of the hydrogens increases with 0.04 (cf. Fig. 2). A similar behaviour is expected in CH_3 . Further Millie and Berthier used two $3d$ -orbitals on carbon. This also increases the number of electrons on the carbon atom. It is not quite clear whether a "balanced" basis set is obtained with two polarization functions on carbon, but only one on the hydrogens. In order to test the first of these effects a calculation on CH_3 using the same basis set as on CH_4 was made with $\zeta_{2p} = 1.0$ and 0.8. The lower exponent gave the best energy (-39.528 a.u. compared to -39.525 a.u.). Gross atomic charges are given in Table 5. It can be seen that the hydrogen charge increases from 0.092 to 0.127 when the exponent increases from 0.8 to 1.0. The charges now become very similar to those of Millie and Berthier, the remaining discrepancy partly being due to the different $3d$ -orbitals used.

In hydrogen sulphide the inclusion of polarization on sulphur and hydrogen does not give a large change in gross atomic populations. The results are given in Table 2. The hydrogen charge with and without polarization was 0.051 and 0.067 respectively.

A large basis calculation, using the (S/12, 9) set of Veillard [13], adding two $3d$ -orbitals with exponents 0.5 and 2.0, has also been made. The details of this calculation will be presented in another paper [9]. In connection with the present discussion it might, however, be of interest to look at the effect of the second $3d$ -orbital. The total energy with none, one and two $3d$ -orbitals was -398.656 , 398.678 and 398.682 a.u., respectively. The decrease due to the second polarization function is thus 0.004 a.u. The dipole moment was 1.70, 1.32 and 1.28 Debye for the three cases, and the gross atomic charge on sulphur +0.02, -0.19 and -0.16 , respectively. The addition of a second $3d$ -orbital thus leads to a change

in calculated quantities, which is around ten percent of the effect of the first orbital. Notice that the calculation without polarization orbitals on sulphur results in a positive charge on this atom.

The main effect of the $3d$ -orbitals in the molecules studied here is to polarize valence orbitals. One should therefore expect them to have charge densities which overlap strongly with the $2p$ - and $3p$ -orbitals, respectively. The charge density maxima of the $3d$ -orbitals ought to lie on the outer side, but not far from the maxima for these orbitals, since it is the outer part of the valence orbitals which will be mostly effected by polarization. The atomic $2p$ -orbital density for oxygen has its maximum at a distance of 0.84 a.u. from the nucleus. The corresponding value for the optimized $3d$ -orbital is 1.06 a.u. An exponent of 1.85 instead of 1.33 would decrease this value to 0.90 a.u. The situation is similar for sulphur. The $3p$ -orbital density has its maximum at a distance of 1.59 a.u. and the $3d$ -orbital density at 1.67 a.u. A $3d$ maximum at 1.59 a.u. is obtained with an exponent of 0.59.

These results have been used to obtain $3d$ exponents for other first and second row atoms. The exponents were obtained from the assumption that $r_{\max}(2p)/r_{\max}(3d)$ is constant for the first row, and $r_{\max}(3p)/r_{\max}(3d)$ for the second row atoms. The constants were obtained from the oxygen and sulphur exponents, respectively. The results are presented in Table 5. The first column gives the radial density maxima for atomic $2p$ and $3p$ -orbitals, respectively. The

Table 5. Gross atomic charge on hydrogen in CH_3

	MB ^a	$\zeta_{2p} = 1.0$	$\zeta_{2p} = 0.8$
no. pol.	0.160	0.188	0.188
$2p$ only	0.095	0.100	0.063
$3d$ only	0.241	0.212	0.212
$2p$ and $3d$	0.149	0.127	0.092

^a From the work of Millie and Berthier [12].

Table 6. $3d$ -orbital exponents for first and second row atoms

Atom	$r_{\max}(np)^a$	$r_{\max}(3d)^b$	ζ_{3d}^b	Literature data		
				$\zeta_{3d\sigma}$	$\zeta_{3d\pi}$	ζ_{3d}^d
B	1.59	2.01	0.37	0.53 ^c	0.23 ^c	
C	1.22	1.55	0.63	0.60	0.34	
N	0.99	1.25	0.95	0.63	0.99	
O	0.84	1.06	1.33	0.74	1.52	
F	0.73	0.93	1.62	0.80	1.94	
Al	3.06	3.21	0.15	0.48 ^c	0.18 ^c	
Si	2.14	2.24	0.30	0.88	0.36	0.28
P	1.78	1.86	0.43	0.98	0.48	
S	1.59	1.67	0.54	0.81	0.45	0.49
Cl	1.42	1.47	0.68	0.61	0.65	

^a Radius of maximal charge density for $2p$ and $3p$ orbitals, respectively (in a.u.).

^b $\zeta_{3d} = 3d$ -orbital exponents, this work. $r_{\max}(3d) =$ corresponding radius of max. charge density.

^c $3d$ -orbital exponents from the work of Nesbet [14]. Molecules: BF, CO and N_2 .

^d $3d$ -orbital exponents from the work of Boer and Lipscomb [6].

^e $3d$ -orbital exponents from the work of Yoshimine and McLean [5]. Molecules: AlF, SiO, PN, SCO and NaCl.

calculated $3d$ exponents are given in column three and their radial maxima in column two. In order to check whether these exponents are realistic a comparison is made to available literature data. Nesbet [14] has optimized $3d$ -orbital exponents for the atoms B to F in a double zeta STO calculation on the diatomics BF, CO and N_2 . Different exponents were used for σ - and π -orbitals. Corresponding GTO exponents have been obtained using the assumption of equal values for $r_{\max}(3d)$. These exponents are given in columns four and five of Table 6. The exponents suggested in this work lie in all cases, except for carbon, somewhere between the exponents for the σ - and π -orbitals.

Boer and Lipscomb have in a recent work [6] optimized $3d$ exponents in SiH_4 and H_2S , using a minimal STO basis. They obtained $\zeta_{3d}(Si) = 1.302$ and $\zeta_{3d}(S) = 1.708$. Corresponding GTO exponents would be 0.28 and 0.49, which is very close to the values obtained here. Comparison is also made in Table 6 to exponents used in the work on linear molecules by Yoshimine and McLean [5]. The agreement is in all cases satisfactory. It therefore seems reasonable to assume that the exponents suggested in Table 6 are not far from optimal. At least they should be good starting values for an optimization procedure.

Conclusions

The question whether the basis sets used in this work really are balanced naturally arises. Mulliken has in a study of MO-SCF wave functions [15] introduced the terms *physical balance* and *formal balance*. A physically unbalanced set gives erroneous results for well defined physical quantities (dipole moments, etc.), while formal unbalance gives unreasonable results for charges on atoms. The basis sets should be both physically and formally balanced, if the population analysis method of Mulliken is to be used in the discussion.

Two criteria can be used to investigate whether, the basis sets used here are physically balanced, namely the dipole moment and the decrease in energy due to the polarization functions. The calculated dipole moments are in good agreement with experimental values for the molecules NH_3 , H_2O and H_2S (cf. Tables 1–3). The energy criteria is, however, of more significance. If the sp -basis used is too small a large effect of the $3d$ -orbitals will be in the improvement of this sp -basis. The actual polarization effects will be over-estimated. To test this we can compare the energy improvement obtained with the addition of one polarization function for each centre to the basis (O/7, 3) (H/4) for water, with the corresponding improvement with the sp -basis (O/9, 5) (H/4). The calculated values are 0.047 and 0.040 a.u., respectively.

We can do the corresponding comparison between the (S/9, 5) (H/4) and (S/12, 9) (H/4) sets for H_2S . In this case we obtain 0.050 and 0.047 a.u. The energy improvement is thus almost the same for the small and the large basis. We conclude that a physically well balanced basis is obtained if polarization functions with optimized exponents are added to the limited GTO basis, used in the present work.

The question of formal balance is more difficult. The criteria would be, that the calculations should give "reasonable" gross atomic charges. The discussion has to be based on some assumption of what is reasonable. If we

for H₂O assume that (O/9, 5, 1) (H/4, 1) is a formally well balanced set, this will not be true for any of the smaller basis sets given in Table 1. Calculations without polarization functions or with only 3*d* orbitals give a too large oxygen charge, while inclusion of 2*p* orbitals gives a too small charge. The calculations with polarization functions on both centres are however closest to the larger basis calculation.

In H₂S the sulphur charges do not vary so much for the different calculations (cf. Table 2). Only the basis with polarization only on hydrogen can actually be ruled out as unbalanced, since it gives a positive charge on the sulphur atom.

The results obtained here indicate a way in which basis sets should be built up, if they are to be kept both physically and formally balanced.

For molecules containing only first row atoms one should proceed as follows: Start with a 7*s*, 3*p* set. Add one polarization function to each hydrogen. Add one to each heavy centre. Increase the *sp*-basis. Add more polarization. Polarization functions should probably at this stage be added evenly to all centres. Thus if the basis contains two 3*d*-orbitals for each of the heavy centres, it should also include two 2*p*-orbitals on the hydrogens.

The corresponding scheme for molecules containing second row atoms would be: Start with a 9*s*, 5*p* set. Add one polarization function to each second row atom. Add polarization to other atoms, starting with the hydrogens. Extend the *sp* basis. Add more polarization to second row atoms. Add more polarization to other atoms.

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