

ON THE USE OF LOCALIZED ORBITALS FOR DETERMINATION
OF CONTRACTED GAUSSIAN BASIS SETS
IN *ab initio* MOLECULAR CALCULATIONS

M. URBAN^a and R. POLÁK^b

^a Department of Physical Chemistry,
Comenius University, 801 00 Bratislava and

^b J. Heyrovský Institute of Physical Chemistry and
Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2

Received December 17th, 1973

In the present paper minimum basis sets of contracted Gaussian functions, determined from localized orbitals, for the ion H_3O^+ and molecules H_2O and NH_3 are reported. The properties of these bases are discussed. It appears that it is necessary to represent the lone pair and bond orbitals of the molecules H_2O and NH_3 by different types of contracted functions.

Since the first application of basis sets of contracted Gaussian-type functions^{1,2} (CGTF's) to *ab initio* calculations, many authors have examined the usefulness of these basis sets in molecular computations³⁻⁶. The most of them derived the contracted functions from the examination of atomic orbitals. An alternative approach for selecting contraction coefficients, proposed by Hoyland⁷, is based upon the analysis of SCF molecular orbitals obtained by a molecular calculation using an uncontracted basis^{8,9}. The "molecule-calibrated" contracted Gaussian type functions (MCCGTF's) acquired in this way take into account the deformation of atomic orbitals due to the bond formation in molecules. This property might play a particularly important role in SCF calculations with minimum basis sets where a small number of variational parameters is involved. Generally, a similar sort of reasoning is valid if the MCCGTF's optimized for small molecules can be employed as the basis for calculations on larger molecules. The transfer of parameters from a small system to a larger one is based on the notion of localized orbitals¹⁰⁻¹². Thus, the choice of molecule-calibrated contractions should take place only after transformation of the canonical molecular orbitals to the localized ones. Also, on analyzing canonical orbitals, the selection of contraction coefficients is ambiguous if some GFT's occur in more than one molecular orbital⁷⁻⁹. Finally, with the basis related to localized orbitals, the interpretation of results is straightforward and closely corresponds to the chemical view of bonding.

The purpose of this paper is to examine the possibility of constructing the minimum contracted basis set optimized for molecules by means of localized orbitals, and to discuss the results.

Method

In this paper we present the contraction coefficients of the minimum Gaussian basis set for the H_3O^+ ion and molecules H_2O and NH_3 . For the oxygen and nitrogen

atoms we employ the uncontracted ($7s3p$) basis set of Whitman and Hornback¹³, for the hydrogen atom we use the ($3s$) basis set of Huzinaga¹⁴. As regards the CGTF for the $1s$ orbital of oxygen and nitrogen, it was chosen the same in molecules as in isolated atoms, since it may be conjectured that the $1s$ inner shell orbital is not considerably affected by bond formation. It is note-worthy that the $1s$ orbital is represented by five GTF's with the largest values of the orbital exponents. To summarize, the "uncontracted basis set" used for the SCF calculations on H_3O^+ , H_2O and NH_3 consisted of the $1s$ orbital just mentioned along with further two uncontracted s functions, three oxygen (or nitrogen) p_x , p_y , p_z functions, and finally, of three hydrogen s functions. The transformation of canonical orbitals to localized orbitals was performed by the method of Polák^{15,16}.

This method relies on the projection property of the Fock-Dirac density matrix ϱ and consists in solving the variational equation

$$\delta[\eta^+ \varrho \eta] = 0, \quad (1)$$

where the trial one-electron function η satisfies certain constraints corresponding to its property of being localized in a given region of the molecule. The aim of the procedure is to achieve the maximum coincidence of the localized function η with the "exact" solution represented by the first-order density matrix ϱ . That stationary function is considered as the solution of Eq. (1) which corresponds to the maximum value of ε_m ,

$$\varepsilon_m = \eta_m^+ \varrho \eta_m. \quad (2)$$

In paper¹⁶ it was indicated that molecules with lone pair electrons, which in our case are represented by H_2O and NH_3 , require an especial treatment. According to that procedure, the original sets of atomic orbitals for individual atoms are exposed to a symmetrical orthonormalization. Whereas in the new basis the $1s$ orbital is set aside for the description of the oxygen or nitrogen inner shell orbital, all other orbitals are used for the description of localized orbitals. Lone pair orbitals are formed as optimized one-centre functions. Accordingly in our case, we define contraction coefficients for the oxygen or nitrogen lone pair orbital after performing the reverse transformation to the nonorthogonal basis as those coefficients which occur along with the GTF's in the corresponding localized lone pair orbital. Afterwards, the optimum two-centre bond orbitals are to be calculated as subject to the constraint of the existence of lone pair orbitals. Analogously as in the lone pair case, we choose contraction coefficients for the given bond orbital within the original nonorthogonal basis as those accompanying the GTF's corresponding either to the nitrogen (oxygen) or hydrogen atom. From two possible methods for constructing the projection matrix which is needed for bond- and lone pair orbital formation, the version 2 according to paper¹⁶ was employed.

RESULTS AND DISCUSSION

Contraction coefficients referring to lone pair and bond orbitals (from now on denoted by LP and B, respectively), obtained by means of the method described earlier, together with contraction coefficients optimized for isolated atoms (denoted by A) for H_3O^+ ion (bond length 1.8085 a.u.), molecules H_2O (bond length 1.8085 a.u., angle HOH 104.5°) and NH_3 (bond length 1.9117 a.u., angle HNH 106.7°) are displayed in Tables I and II.

Tables III through V list the total energies for H_3O^+ , H_2O and NH_3 calculated by means of basis sets obtained by successive substitution of atom-optimized functions for functions optimized with respect to their occurrence in lone pair or bond orbitals. For the sake of completeness let us mention that for all molecules the principal axis is of the same direction as the z axis, and that the molecule H_2O lies in the yz plane.

A. H_3O^+ Ion. Among the systems studied H_3O^+ represents the simplest case for optimization of the basis set because there are no functions occurring simultaneously both in lone pair and in bond orbitals. As it is seen in Table III, on using the contracted functions obtained from localized orbitals instead of the atom-optimized

TABLE I
Contraction Coefficients^a for H_2O and H_3O^+

Function	Exp.	H_2O			H_3O^+
		A ^b	B	LP	B, LP ^c
$2s$	1.103	0.4822	0.11936	0.37117	0.30113
	0.3342	0.6418	0.10567	0.65526	0.46087
p_x	8.356	0.1193	—	0.11457	0.05627
	1.719	0.4708	—	0.43699	0.21688
	0.3814	0.6223	—	0.65662	0.29009
p_y	8.356	0.1193	0.04681	—	0.05627
	1.719	0.4708	0.18393	—	0.21688
	0.3814	0.6223	0.22077	—	0.29009
p_z	8.356	0.1193	0.06799	0.04112	0.11681
	1.719	0.4708	0.26847	0.13904	0.45553
	0.3814	0.6223	0.37807	0.21405	0.63814
h	0.151374	0.64767	0.13720	—	0.02466
	0.681277	0.40789	0.26709	—	0.19523
	4.50037	0.07048	0.05904	—	0.05006

^a Contraction coefficients refer to unnormalized contracted functions. ^b Values are identical for H_2O and H_3O^+ . ^c Coefficients for the $2s$, p_x , p_y , and h functions correspond to the B contraction, coefficients for the p_z function correspond to the LP contraction.

CGTF's – with the exception of the p_x and p_y functions – lower total energies for the H_3O^+ ion were found. It can be shown that the reason for the exception derives from the fact that the optimization process yields functions which are not independent. Coefficients corresponding to B and LP type contractions were determined by means of the calculation with an uncontracted basis set, while on the contrary

TABLE II
Contraction Coefficients^a for NH_3

Function	Exp.	A	B	LP
2s	0.7797	0.5077	0.23058	0.31148
	0.2350	0.6151	0.24754	0.38978
p_x, p_y	6.273	0.1133	0.04984	—
	1.282	0.4656	0.18995	—
	0.2974	0.6237	0.24649	—
p_z	6.273	0.1133	0.03779	0.08449
	1.282	0.4656	0.16141	0.29603
	0.2974	0.6237	0.23747	0.53615
h	0.151374	0.64767	0.13059	—
	0.681277	0.40789	0.26763	—
	4.50037	0.07048	0.05670	—

^a Contraction coefficients refer to unnormalized contracted functions.

TABLE III
Total Energy for H_3O^+ Calculated with Various Contracted Functions

Row	2s	p_x, p_y	p_z	h	E_{tot} , a.u.
1	A	A	A	A	-76.001892
2	A	A	A	B	-76.108825
3	B	A	A	B	-76.111076
4	B	B	A	B	-76.110782
5	B	B	LP	B	-76.112183
6	A	B ^a	A	A	-76.002516
7	B	B ^a	LP	B	-76.111998
8	b	b	b	b	-76.127180

^a Contraction coefficients for the p_x, p_y functions were determined by means of a calculation in which the 2s, p_z , and h functions were represented by atom-optimized contracted functions.

^b Decontracted basis.

the effect of the contractions on the total energy was tested by using a contracted basis set. Since the optimized functions are mutually related, such a test is hardly correct as can be demonstrated by modifying the standard method described above. Namely, if we determine the contraction coefficients for the p_x and p_y functions by means of a calculation in which only p_x and p_y GTF's are uncontracted, while the $2s$ and p_z functions together with hydrogen functions are represented by atom-optimized contracted functions, we obtain slightly different results with respect to the former ones. With these contracted functions (*cf.* row 6 in Table III), the calculated energy is lower compared to the value obtained using contracted functions solely optimized for atoms (*cf.* row 1 in Table III). It is to be noted that in this case the $2s$, p_z and hydrogen functions are the same in the process of calculating the contraction coefficients as in the test calculation. If we use the B and LP contractions for representing the $2s$, p_z and hydrogen functions, the total energy becomes lower when the standard method for calculating contractions of the p_x and p_y functions is employed (*cf.* rows 5 and 7 in Table III).

It should be added that the mutual relationship of the optimized functions described previously also deteriorates the possibility of comparing different sets of contracted functions in the case of NH_3 .

B. H_2O . It appears from the first four rows of Table IV that a remarkable energy decrease is observed if contracted functions obtained from localized orbitals are introduced to describe the p_x and h functions. On the other hand, the contraction related to the p_y orbital appears to be almost ineffective.

TABLE IV
Total Energy and Dipole Moment for H_2O Calculated with Various Contracted Functions

Row	$2s$	p_x	p_y	p_z	h	E_{101} , a.u.	D , Debye
1	A	A	A	A	A	-75-731694	2-20
2	A	A	A	A	B	-75-788260	2-36
3	A	LP	A	A	B	-75-795201	2-45
4	A	LP	B	A	B	-75-795515	2-38
5	A	LP	B	B	B	-75-798090	2-42
6	A	LP	B	LP	B	-75-796966	2-45
7	B	LP	B	B	B	-75-765186	2-28
8	LP	LP	B	B	B	-75-804340	2-53
9	<i>a,b</i>	LP	B	B	B	-75-816080	2-59
10	<i>a</i>	LP	B	<i>b</i>	B	-75-816475	2-61
11	<i>a</i>	LP	B	<i>a</i>	B	-75-816807	2-61
12	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	-75-825474	2-49

^a Decontracted basis. ^b Augmented basis set, B and LP contractions are involved.

Further, it is interesting to compare the contractions for $2s$ and p_z functions which participate both in lone pair and in bond orbitals. For the p_z function the B contraction is slightly better than the LP contraction, and both are superior to the A contraction, whereas for the $2s$ function the B contraction based on the bond orbital yields an energy increase amounting to more than 0.03 a.u. On the other hand, for the $2s$ function the LP contraction leads to an energy decrease of 0.006 a.u. compared to the corresponding A contraction. These facts can be explained in the following way. From the analysis of the hybrid orbitals of the water molecule^{12,16,17} follows that the bond hybrid orbital is almost a pure p orbital, while the lone-pair hybrid orbital is nearly a s orbital (the other lone pair being formed by a p_x orbital). The conclusion reached is that for the $2s$ function the contraction representing the lone pair is relevant, whereas for the p_z function the contraction pertinent to the bond orbital plays a more important role. With the $2s$ function, comparing the ratios of the two contraction coefficients corresponding to the B and LP contractions, we see from Table I that the B contraction is less and the LP contraction more diffuse than the A contraction which therefore seems to be a good compromise.

On grounds of these results it appears that it would be appropriate to augment the basis set by either introducing separate functions for B and LP contractions, or using an uncontracted basis, when the functions optimized with respect to the lone pair and the bond orbital do differ. For the $2s$ CGTF formed from two GTF's, the results with the augmented basis (B and LP contractions are involved) are the same as with uncontracted $2s$ functions (row 9 in Table IV). The energy gain of 0.0012 a.u. is considerable and reflects the fact that the B and LP contractions differ greatly. The augmentation of the basis for the p_z function leads to a further energy gain, and after the decontraction of the p_z function the energy profit is already very small.

From viewpoint of amount of calculation time needed for the computation of molecular integrals, the use of two contracted functions is obviously less convenient than the decontraction of the basis. Quite recently, however, a paper of Raffanetti¹⁸ appeared, according to which it is possible to arrange the computer program in such a way that the loss of calculation time by employing one GTF in two contractions is minimal. This means that the use of the augmented basis set involving the B and LP contractions for the p_z function does not necessarily lead to a considerable increase of computational time for the calculation of integrals.

As regards the dipole moment, it can be noticed that both optimum contractions for hydrogen and for the lone pair orbital of oxygen bring about an increase of the dipole moment value. On the other hand, with the $2s$ and p_z functions, the optimum contractions for the bond orbital lead to a decrease in the dipole moment compared to the lone-pair-optimized contraction, *i.e.* to a value closer to the experimental one, regardless of whether the energy increases or not. The dipole moment of about 2.6 Debye, which we have obtained by means of the best basis set from the viewpoint of the energy criterion, is close to the value 2.7 Debye achieved with the double zeta

basis set^{4,6}. As was shown by Neumann and Moskowitz on grounds of symmetry considerations, with the double zeta basis it is necessary to employ a basis set containing polarization hydrogen p functions and oxygen d functions in order to gain values which are closer to the experimental dipole moment. Obviously, the same conclusion holds even for basis sets employed in this paper.

C. NH_3 . The discussion of the results obtained for the NH_3 molecule is qualitatively similar to that previously given for H_3O^+ and H_2O . The similarity manifests itself in the interaction of the p_x and p_y functions with the hydrogen functions (*cf.* rows 1–4 in Table V). As in the case of H_2O , the B and LP contractions yield a better representation of the p_z function than the A contraction (the energy gain ranging from 0.006 to 0.009 a.u. is considerably higher than with H_2O), but in contrast to H_2O , the contraction based on the lone pair orbital is better. Further, with the 2s function, the B contraction is worse than the A contraction, and the LP contraction is better than the A contraction. For these three contractions the energy differences lie within the interval width of 0.002 a.u., which differs considerably from the interval 0.039 a.u. corresponding to H_2O . Consequently, a lower energy gain after augmenting the basis of the 2s function, and a higher energy gain after augmenting the basis of the p_z function is observed when compared with the analogous energy decrease for H_2O . All these discrepancies can be simply explained on grounds of the fact that the degree of hybridization in NH_3 is higher than in H_2O (refs^{12,16}). Of course,

TABLE V

Total Energy and Dipole Moment for NH_3 Calculated with Various Contracted Functions

Row	2s	p_x, p_y	p_z	h	E_{101} , a.u.	D , Debye
1	A	A	A	A	-55.950048	2.01
2	A	A	A	B	-56.024183	2.16
3	A	B	A	B	-56.023450	2.11
4	A	B	A	A	-55.951985	1.95
5	A	B	B	B	-56.029846	2.17
6	A	B	LP	B	-56.032780	2.24
7	B	B	B	B	-56.028023	2.12
8	LP	B	B	B	-56.030116	2.18
9	B	B	LP	B	-56.031366	2.20
10	LP	B	LP	B	-56.032940	2.26
11	^a	B	LP	B	-56.038275	2.37
12	^a	B	^b	B	-56.040501	2.40
13	^a	B	^a	B	-56.040717	2.40
14	^a	^a	^a	^a	-56.056490	2.17

^a Decontracted basis. ^b Augmented basis set, B and LP contractions are involved.

this contradicts the commonly accepted statement that the type of hybridization in both molecules is about sp^3 (cf.¹²).

Broadly speaking, the correspondence between the basis sets of both molecules is good. On comparing the ratio of contraction coefficients for individual GTF's, from Tables I and II it is apparent that with both molecules for the $2s$ function the LP contraction is more, and the B contraction less diffuse than the A contraction. Further, for the p_y function of H_2O and for the p_x and p_y functions of NH_3 the B contraction is less diffuse than the A contraction, for the p_z function the B and LP contractions are more diffuse than the A contraction, and, finally, for the h functions the B contractions corresponding to both molecules show a close resemblance, and are less diffuse than the A contraction.

Comparison of the Presented Results with Calculations on H_2O and NH_3 Using Optimized Scaling Parameters

Calculations of total energies and dipole moments made with a minimal basis, and presented in this paper, are comparable with those obtained by means of a minimum [$2s\ 1p/1s$] basis set with anisotropically optimized scaling parameters and atom-optimized contraction coefficients. With the H_2O molecule (bond length 1.8 a.u., angle HOH 105°), the four scaling parameters, for the $2s$, p_x , p_y , p_z and h functions in this order, are¹⁹: 0.90, 0.90, 0.98, 2.10 (with the constraint of using identical scaling parameters for p_y and p_z functions). With H_2O the total energy in this basis amounts to -75.80802 a.u., and the dipole moment is 2.76 Debye. With the NH_3 molecule, employing the same geometry as in this paper, the scaling parameters for the $2s$, p_x , p_y , p_z and h functions are¹⁹ 0.95, 1.06, 0.85 and 1.82, the total energy and dipole moment in this basis being -56.03830 a.u. and 2.30 Debye, respectively.

Despite the fact that both optimization procedures yield energy values of similar accuracy, there is a considerable difference between the ways of calculating the quantities. Indeed, when optimizing scaling parameters no distinction is made between bond and lone pair orbitals. The optimum value of the scaling parameter, corresponding to the function participating in both orbitals, is determined by the character of the prevailing orbital, so that the value can be considered as an optimum compromise. For instance, with the $2s$ functions of H_2O and NH_3 , the scaling parameter is smaller than 1, and corresponds thus to a function which is more diffuse than that for the isolated atom. This coincides with the results of this paper according to which the $2s$ function makes its main contribution to the lone pair orbital, and further, the $2s$ orbital representation is more diffuse than the contracted function obtained from the atomic calculation. The character of functions which act a part solely either in lone pair or bond orbitals is remarkably alike in both procedures: e.g. with NH_3 , the nitrogen p_x and p_y functions are less diffuse than those optimized on the isolated atom. Of course, such a comparison is only approximate, since,

broadly speaking, the scaling procedure is essentially shifting the maximum of the contracted function, whereas the change in the contraction coefficients brings about a modification of the shape of the contracted functions. Thus, the method for constructing optimum contracted Gaussian functions based on localized orbitals exhibits an interpretative ability which other methods do not possess, including those using canonical orbitals⁷⁻⁹. This ability can be conveniently applied to the acquisition of minimum basis sets useful in molecular calculations. The results of our work indicate that contractions for a given function may differ considerably, if the function participates both in lone pair and in bond orbitals. In such a case it is preferable to use an augmented basis set. Generally, it may be expected that a similar situation is encountered in molecules where one atom forms two or more different bonds (e.g. atom B in the molecule of type A-B-C). Therefore, it may be conjectured that for a molecular computation such a minimum basis set should be used to which each atom contributes functions subdivided into sets of appropriate symmetry (in our case *s* and *p* functions) each of which represents all localized orbitals pertinent to the given atom.

Acknowledgement is made to the Computing Research Centre of United Nations, Bratislava, who provided the CDC 3300 computer time.

REFERENCES

1. Clementi E., Davis D. R.: *J. Comput. Phys.* **1**, 223 (1966).
2. Whitten J. L.: *J. Chem. Phys.* **44**, 359 (1966).
3. Schulman J. M., Moskowitz J. W., Hollister C.: *J. Chem. Phys.* **46**, 2759 (1967).
4. Neumann D., Moskowitz J. W.: *J. Chem. Phys.* **49**, 2056 (1968).
5. Salez C., Veillard A.: *Theoret. Chim. Acta* **11**, 441 (1968).
6. Dunning T. H. Jr.: *J. Chem. Phys.* **53**, 2823 (1970).
7. Hoyland J. R.: *J. Chem. Phys.* **49**, 1908 (1968).
8. Urban M.: *This Journal* **36**, 3482 (1971).
9. Urban M.: *This Journal* **38**, 2043 (1973).
10. Hoyland J. R.: *J. Am. Chem. Soc.* **90**, 2227 (1968).
11. Trindle C., Sinanoglu O.: *J. Chem. Phys.* **49**, 65 (1968).
12. Petke J. D., Whitten J. L.: *J. Chem. Phys.* **51**, 3166 (1969).
13. Whitman D. R., Hornback C. J.: *J. Chem. Phys.* **51**, 398 (1969).
14. Huzinaga S.: *J. Chem. Phys.* **42**, 1293 (1965).
15. Polák R.: *Int. J. Quantum Chem.* **4**, 271 (1970).
16. Polák R.: *Int. J. Quantum Chem.* **6**, 1077 (1972).
17. Sweigart D. A.: *J. Chem. Educ.* **50**, 322 (1973).
18. Raffanetti R. C.: *J. Chem. Phys.* **58**, 4452 (1973).
19. Kellö V.: Unpublished results.

Translated by the author (R. P.).