Ab initio SCF-MO-LCAO CALCULATIONS WITH A MOLECULE - CALIBRATED CONTRACTED GAUSSIAN BASIS. II.*

OPTIMIZATION OF EXPONENTS AND CONTRACTION COEFFICIENTS

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A method is examined which optimizes exponents and contraction coefficients in contracted Gaussian functions for calculations of molecules. Applications to CH_3^-, CH_3^+, and ethylene are given. The method leads to a considerable decrease in the total energy and to fair values of orbital energies but it gives less satisfactory population analysis results. The merits and drawbacks of the method are discussed.

In part I of this series[1] a method was examined which optimizes the contraction coefficients in contracted Gaussian-type functions (CGTF) appropriate to molecular calculations. The starting point of this optimization method[2] is calculation on a small molecule using uncontracted Gaussian basis set. By examination of expansion coefficients of molecular orbitals (MO's), linear combinations of Gaussian-type functions (GTF) are fixed, the coefficients being selected from appropriate molecular orbitals. The GTF exponents, however, are optimum for isolated atoms. The CGTF basis set constructed in this way can be used with success in calculations on larger molecules with similar atom environments. A straightforward extension of this method is the exponent optimization of GTF's composing the contracted Gaussian functions. To our knowledge a systematic study has not yet been undertaken, although some attempts to optimize exponents and CGTF contraction coefficients simultaneously were reported[3-7].

METHOD

The method for determination of CGTF exponents and contraction coefficients is briefly described in Part I. One starts with a contracted basis set using contracted coefficients and exponents optimized for isolated atoms. After relaxing contraction in one CGTF, say η_M, a SCF calculation is performed. Exponents, χ_{Mi}, of all GTF's composing the decontracted η_M are then multiplied by the same scaling factor λ and the GTF's are renormalized. The parameter λ is optimized with respect to total molecular energy. By examination of molecular orbitals, a new contracted function, η'_M, is formed, with the contraction coefficients selected from an appropriate MO with exponents $\chi'_{Mi} = \lambda_{opt}\chi_{Mi}$. The resulting optimized molecule-calibrated con-

tracted Gaussian function (MCCGTF) is used to replace the η_M function in the starting basis set. On relaxing contraction in a next CGTF, the process is cyclically repeated. Owing to ambiguity in the choice of contraction coefficients for functions centered on hydrogen atoms, the contraction coefficients were selected in some cases only after transformation of canonical MO's to localized MO's, the localization being performed by the method of Polák[8].

The method described above was applied to CH_3^+ and CH_3^- ions assuming planar D_{3h} geometry with the bond length $R = 2 \cdot 025$ a.u. The calculations were performed with the aim of testing the utility of the method rather than to find an optimum basis set for these systems. We employed the $(3s)$ basis[9] for hydrogen and $(7s\ 3p)$ basis[10] for carbon as a starting basis; its contraction lead to the minimal $[2s\ 1p/1s]$ basis set. The $1s$ carbon CGTF, formed from five s-type carbon GTF's with the highest exponents, was not optimized. The other functions were optimized in the following order: A) carbon $2s$ function, carbon p_x and p_y functions (simultaneously, with the same scaling factor), carbon p_z function, hydrogen s function. This optimized basis will hereafter be referred to as A1. The basis set of functions reoptimized in this order will be designated as A2. B) hydrogen s function, carbon $2s$ function, carbon p_x and p_y functions (simultaneously), carbon p_z function, (B1 basis). By reoptimization of functions in this order, the B2 basis was obtained. In actual calculations the exponents of the carbon p_z function were not optimized but the optimized contraction from Part I was employed. In the case of the CH_3^+ ion the energy is invariant to exponents of the carbon $2p_z$ function because the energy changes concern only the unoccupied $1a_2''$ MO. In the case of the CH_3^- ion the exponents of the p_z function were optimized after accomplishing the second optimization cycle. The optimization process was always restricted to two complete cycles, compromising between accuracy and economy.

Let us mention, that if the optimized functions are not independent, the cyclic optimization may poorly converge and the order of functions in optimization may be important, or the method may not work in all. In this case, it may be convenient to optimize several parameters simultaneously. The method of the present paper, however, would become rather complex on adopting a simultaneous optimization of parameters. For the CH_3^+ and CH_3^- ions one might start the cyclic process, eventually, also with the molecule-calibrated CGTF's from Part I, or to optimize only the scaling parameters for exponents of those MCCGTF's. Because for most molecules similar MCCGTF's are not known, this possibility was not exploited.

RESULTS

Fig. 1 presents the dependence of total energy of CH_3^+ and CH_3^- on λ for uncontracted carbon $2s$, p_x, and p_y GTF's in the first optimization cycles A and B. A difference between A and B optimizations is apparent immediately. It can also be noticed that

the optimization is complicated by occurrence of two minima. The choice of the proper minimum was based on a thorough examination. For example, in the Al cycle two minima were found for the $2s$ functions in CH_3^+ and CH_3^- ions, near $\lambda = 0.6$ and $\lambda = 2.7$, the latter being lower in energy. Since the energy differences were small, the whole optimization cycle was performed for both values. Lower energy was found for $\lambda > 1$, which was used in subsequent optimization. It should be noted that other properties, such as orbital energies and electron population, were affected rather little by the choice of $\lambda < 1$ or $\lambda > 1$. This is due to the fact that the effect of differing λ values is compensated by a different ratio of contraction coefficients. On the other hand, the optimization cycles A and B yielded similar λ values for some functions in the region $\lambda < 1$ but the resulting MCCGTF's differed considerably owing to differing contraction coefficients.

The resulting bases for CH_3^+ are presented in Table I and those for CH_3^- in Table II. In the case of A-type bases, the functions localized on carbon are similar for both ions, the functions localized on hydrogen are considerably more diffuse in CH_3^- than in CH_3^+. In CH_3^- the p_z function differs considerably from p_x and p_y functions
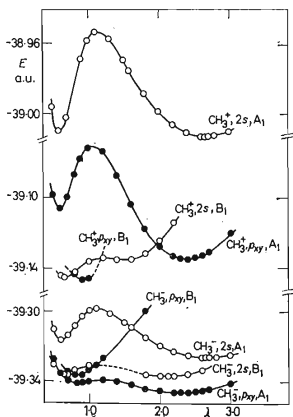

FIG. 1

Dependence of the Total Energy of the CH_3^+ and CH_3^- Ions on the Parameter λ for the Uncontracted $2s$, p_x, p_y Carbon GTF's in Al and Bl Basis Sets
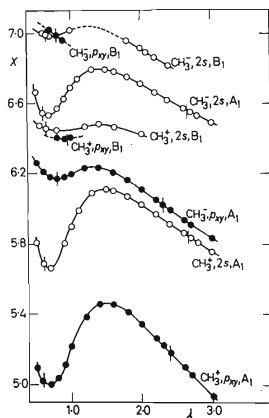
FIG. 2

Dependence of the Carbon Gross Population in CH_3^+ and CH_3^- Ions on the Parameter λ for the Uncontracted $2s$, p_x, p_y Carbon GTF's in Al and Bl Basis Sets

and the optimization of its scaling factor leads to an appreciable energy gain of 0·0345 a.u. This confirms that an anisotropic basis is appropriate for this ion. The p_z functions in A and B type bases are similar, the other A and B type MCCGTF's differ considerably. The carbon MCCGTF's are more diffuse in B-type bases than in A-type bases, in case of hydrogen MCCGTF's it is reversed. This is reflected mostly in population analysis, less in total energy and orbital energies (*cf.* Tables III and IV). However, the A and B-type bases differ considerably in energy gains on optimization of carbon and hydrogen functions, as is seen from energy gain partitioning with CH_3^+ in A1 and B1 bases (Table V). Table V also presents the energy decreases on decontraction of optimized functions ($\Delta E_{dec,}$) and on optimization of the scaling

TABLE I

Basis Sets Optimized for CH_3^+

Basis set	A1			A2		
Function	λ	exponent	coeff.[a]	λ	exponent	coeff.[a]
$2s$	2·66	1·60292	0·11950	2·55	1·53663	0·10900
		0·48332	−0·72120		0·46333	−0·70133
$p_{x,y}$	2·40	10·2696	0·02714	2·20	9·4138	0·03017
		2·08776	0·16240		1·91378	0·18218
		0·48864	0·48081		0·44792	0·48104
s (for hydrogen)	1·30	0·196786	1·4275	1·30	0·196786	1·3574
		0·885660	1·0000		0·885660	1·0000
		5·850481	0·1836		5·850481	0·18455

Basis set	B1			B2		
Function	λ	exponent	coeff.[a]	λ	exponent	coeff.[a]
$2s$	0·65	0·39169	0·63961	0·65	0·39169	0·63472
		0·11810	0·24704		0·11810	0·22766
$p_{x,y}$	0·90	3·8511	0·09488	0·95	4·0650	0·08863
		0·78291	0·39130		0·82640	0·37767
		0·18324	0·40733		0·19342	0·39985
s (for hydrogen)	1·10	0·166511	0·0261	1·00	0·151374	0·0444
		0·749405	1·0000		0·681277	1·0000
		4·95041	0·1741		4·50037	0·18825

[a] MCCGTF contraction coefficients for hydrogen have been determined by averaging the ratios of coefficients in $2a_1'$ and $1e'$ MO's.

Table II

Basis Sets Optimized for CH_3^-

Basis set	A2			B2		
Function	λ	exponent	coeff.[a]	λ	exponent	coeff.[b]
$2s$	2·60	1·56676	0·09447	0·65	0·39169	0·47949
		0·47242	−0·54088		0·11810	0·15626
$p_{x,y}$	2·15	9·19985	0·02424	0·85	3·63715	0·07965
		1·97028	0·14306		0·739415	0·29298
		0·43774	0·34398		0·17306	0·29208
p_z	0·50	2·13950	0·17016	0·50	2·13950	0·17265
		0·43495	0·44266		0·43495	0·44879
		0·10180	0·61718		0·10180	0·60984
s (for hydrogen)	1·00	0·151374	0·4175	1·10	0·166511	0·9238
		0·681277	0·2709		0·749405	1·0000
		4·50037	0·0570		4·95041	0·1897

[a] MCCGTF contraction coefficients for hydrogen have been determined from localized MO's.
[b] MCCGTF contraction coefficients for hydrogen have been determined by averaging the ratios of coefficients in $2a_1'$ and $1e'$ MO's.

Table III

Total Energy, Orbital Energies, and Population Analysis for CH_3^+ (Energies in a.u.)

	Basis set					
	unoptimized	A1	A2	B1	B2	$(10s\,6p/4s)^a$
E_{total}	−38·93785	−39·17001	−39·17123	−39·14584	−39·14897	−39·2173
Orbital energies						
$1a_1'$	−11·8897	−11·6722	−11·6772	−11·6636	−11·6671	−11·6800
$2a_1'$	− 1·3382	− 1·2731	− 1·2748	− 1·2730	− 1·2744	− 1·3077
$1e'$	− 1·0121	− 0·9537	− 0·9549	− 0·9502	− 0·9528	− 0·9786
$1a_2''$	− 0·3771	− 0·2727	− 0·2736	− 0·2626	− 0·2768	− 0·2919
Mulliken population analysis						
Gross C	6·205	5·205	5·323	6·404	6·271	5·870
H	0·598	0·931	0·892	0·532	0·576	0·710
Overlap	0·727	0·727	0·737	0·603	0·641	0·732

[a] Ref.[14], C—H internuclear distance 1·95 a.u.

parameters $(\Delta E_{opt.})$. Their sum, of course, is not equal to the total gain in energy as a part of this gain is lost upon the contraction of the optimized function. With A1 and B1 bases, the energy decreased always most considerably on optimizing functions of the atom whose functions were optimized first. The order in which the carbon functions were optimized had little effect. A remarkable energy decrease occurs

TABLE IV
Total Energy, Orbital Energies, and Population Analysis for CH_3^- (Energies in a.u.)

	Basis set			
	unoptimized	A2	B2	$(10s\ 6p/4s)^a$
E_{total}	-39.29220	-39.41081	-39.40235	-39.4780
Orbital energies				
$1a_1'$	-10.8303	-10.9179	-10.9226	-10.8876
$2a_1'$	-0.5388	-0.5909	-0.5927	-0.6130
$1e'$	-0.2294	-0.2728	-0.2704	-0.2819
$1a_2''$	0.0234	0.0271	0.0241	0.0198
$3a_1'$	0.8348	0.7823	0.9335	0.4309
Mulliken population analysis				
Gross C	6.836	6.464	7.280	7.190
H	1.055	1.179	0.907	0.937
Overlap	0.843	0.718	0.818	0.814

^{a} C—H internuclear distance 1.95 a.u., ref.[15].

TABLE V
Contributions of Contraction Relaxation on the CGTF's and of GTF Exponent Optimization to the Lowering of the Total Energy of the CH_3^+ Ion (Energies in a.u.)

		Basis set			
		A1		B1	
Atom	Function	$\Delta E_{dec.}$	$\Delta E_{opt.}$	$\Delta E_{dec.}$	$\Delta E_{opt.}$
C	$2s$	0.0204	0.0546	0.0055	0.0094
C	$p_{x,y}$	0.0607	0.0629	0.0033	0.0005
H	s	0.0330	0.0034	0.1942	0.0008

on decontraction of functions on hydrogen, particularly in the B1 basis. By optimization of the scaling parameter the energy was lowered rather little. This is due to a "competition" effect found by David[11] in the optimization of exponents and contraction coefficients for the molecule H_2. According to David, exponent optimization makes the optimization of contraction coefficients less effective and *vice versa*. (On optimization of the scaling parameter for the hydrogen GTF's with fixed contraction coefficients, the energy of the CH_3^+ ion decreased by 0·1783 a.u.[12]).

Population Analysis

In this paper the total energy is used as a conventional criterion for judging the quality of wavefunctions. According to Mulliken[13], however, an overall balance of the basis set is a preferable criterion. Accordingly, the optimization procedure should not be tested only on the total energy, but also on other characteristics. Among the quantities examined, population analysis was the most sensitive to the order of functions in optimization. Although usually one cannot expect very good results of population analysis using minimal basis, it is seen from Tables III and IV that no improvement related to unoptimized basis was found after optimization. Total charge on carbon is too low with A-type bases and too high with B-type bases, compared to values obtained by Kari and Csizmadia with a large uncontracted basis set[14,15]. Good agreement of gross and overlap populations with their results was found solely if the B2 basis was used for CH_3^-.

The dependence of gross populations on carbon on the parameter λ is presented in Fig. 2. Minima of total energy are indicated on curves by short vertical lines. In cases with double energy minima, the gross populations corresponding to the two minima are qualitatively the same.

TABLE VI

Dependence of the Optimum Scaling Parameter λ on the Internuclear C—H Distance

	CH_3^+				CH_3^-			
	$2s$		$p_{x,y}$		$2s$		$p_{x,y}$	
a	6·61		6·82		8·98		9·07	
b	0·45		0·52		0·60		0·68	
R [a.u.]	λ	$\lambda_{calcd.}$	λ	$\lambda_{calcd.}$	λ	$\lambda_{calcd.}$	λ	$\lambda_{calcd.}$
1·98	2·72	2·71	2·44	2·44	2·74	2·74	2·36	2·36
2·025	2·66	2·66	2·38	2·38	2·66	2·67	2·30	2·29
2·055	2·63	2·62	2·34	2·34	2·62	2·62	2·25	2·24
2·10	2·57	2·57	2·29	2·29	2·55	2·55	2·18	2·17
2·20	2·46	2·46	2·17	2·17	2·39	2·40	2·03	2·03

Dependence of the Scaling Factor on Interatomic Distance

In conformation studies it is of interest to know how the optimum scaling factor is changed upon change of nuclear conformation. In this paper an attempt was made to obtain some insight into the problem. The dependence of the λ parameter on the C—H bond length (R) was examined in the vicinity of equilibrium bond length in CH_3^+ and CH_3^- ions. With λ for carbon functions in the A1 basis, it was found possible to describe well the dependence by means of the following equation

$$\lambda = 1 \cdot 0 + a \exp\left(-bR\right), \qquad (1)$$

where a and b are constants. (An equation of a similar form was used by David[11] for optimization of exponents for the hydrogen molecule.) The λ values given by Eq. *(1)* are compared in Table VI with those determined by optimization. Parameters λ are greatly dependent on R, in contrast to calculations using a large basis set[16].

TABLE VII

Total Energy, Orbital Energies, and Population Analysis for Ethylene (Energies in a.u.)

	Basis set				
	unoptimized	A2(CH_3^-)	B2(CH_3^-)	optimized[a] for ethylene	[5s 3p 2d/2s 1p][a]
E_{total}	−77·67158	−77·88405	−77·83638	−77·90830	−78·0462
Orbital energies					
$1a_g$	−11·4075	−11·2393	−11·3321	−11·2544	−11·2294
$1b_{3u}$	−11·4072	−11·2380	−11·3316	−11·2532	−11·2277
$2a_g$	− 1·0937	− 1·0344	− 1·0700	− 1·0344	− 1·0301
$2b_{3u}$	− 0·8331	− 0·7987	− 0·8195	− 0·7881	− 0·7892
$1b_{2u}$	− 0·7024	− 0·6622	− 0·6817	− 0·6570	− 0·6388
$3a_g$	− 0·6376	− 0·5885	− 0·6103	− 0·5931	− 0·5863
$1b_{1g}$	− 0·5629	− 0·5256	− 0·5441	− 0·5115	− 0·5038
$1b_{1u}$	− 0·4630	− 0·3730	− 0·4207	− 0·3914	− 0·3747
$1b_{2g}$	0·1234	0·1542	0·1298	0·2014	0·1485
Mulliken population analysis					
Gross C	6·391	5·819	6·359	6·277	6·215
H	0·8045	1·090	0·820	0·861	0·892

[a] Results of Schulmann, Hornback and Moskowitz[17].

Use of the Optimum MCCGTF Basis for a Calculation on Ethylene

Since basis optimization is lengthy, it is warranted only if a basis optimized for a small system can be used in calculations on a larger system. Bases optimized in this paper for CH_3^+ and CH_3^- ions, with the exception of the p_π function, were used in a calculation on ethylene. The p_π function was represented by a p-type function which was optimum for an isolated carbon atom. The geometry assumed for ethylene was the same as in Part I. The following total energies were obtained in different optimized bases (in a.u.): $A2(CH_3^+)$, -77.88031; $B2(CH_3^+)$, -77.80717; $A2(CH_3^-)$, -77.88086; $B2(CH_3^-)$, -77.83622.

Lower energies were obtained with bases optimized for CH_3^-. Let us recall that the MCCGTF's centered on carbon, but not the hydrogen functions, are very similar in the two ions in A-type bases, and that the energy gain in the A2 basis is largely due to optimization of carbon functions, whereas in the B2 basis it is due to optimization of hydrogen functions. Taking this into account one can understand the difference in energy of ethylene calculated with B2 bases optimized for CH_3^+ and CH_3^- respectively and the closeness of the energies obtained with the corresponding A2 bases. With A2 and B2 bases optimized for CH_3^-, the p_π function of ethylene was optimized ($\lambda_{opt.} = 0.8$ in the A2 basis, $\lambda_{opt.} = 0.9$ in the B2 basis, contraction coefficients were determined from the $1b_{1u}$ MO); but the energy gain was insignificant. The results are compared in Table VII with those obtained by calculations in an unoptimized basis and by two calculations by Schulman and collaborators[17] (SHM): in a large $[5s\ 3p\ 2d/2s\ 1p]$ basis set, which is used as a standard for comparison, and in the minimal $[2s\ 1p/1s]$ basis set optimized for ethylene. The second SHM basis was constructed from the uncontracted $(8s\ 4p/4s)$ basis set with 56 GTF's; the basis set used in the present paper contains 44 GTF's. In the SHM basis, the scaling parameters of GTF exponents were optimized and the contraction coefficients were the same as for isolated atoms.

Total energy is slightly higher in the $A2(CH_3^-)$ basis than in the SHM optimized basis and lower than in the minimal basis of Slater-type functions with optimized exponents[18]. Hehre and collaborators[19] used a bases in which each orbital is expressed as a sum of N GTF's (NG); the energy in the $A2(CH_3^-)$ basis lies between the energy values given by 4G and 5G bases. Scaling parameters of GTF exponents in 4G and 5G basis sets were optimized for ethylene, but with the restriction that they are the same for $2s$, p_x, p_y, and p_z orbitals. When compared with the values of Part I, the energy is lower of 0.09310 a.u. in the $A2(CH_3^-)$ basis and of 0.04310 a.u. in the $B2(CH_3^-)$ basis. Compared with the CGTF basis optimized for atoms, the energy decreased by 0.2125 a.u. in the $A2(CH_3^-)$ basis and by 0.0684 a.u. in the SHM basis.

Resulting orbital energies are very good when compared with the results of both large and optimized minimal SHM bases. Gross population on carbon is too low

with the A type basis and too high with the B type basis, similarly as with CH_3^+ and CH_3^- ions. The results mentioned indicate that virtues and shortcomings of the optimum basis for CH_3^- are also transfered to ethylene. This implies that one can estimate errors in predicted characteristics of a large system associated with the basis transfer from a small system.

DISCUSSION

A considerable decrease in total energy was attained on optimization of scaling parameters and contraction coefficients in CGTF's: for CH_3^+, 0·2334 a.u. in the A2 basis and 0·2111 a.u. in the B2 basis; for CH_3^-, 0·1186 a.u. in the A2 basis and 0·1101 a.u. in the B2 basis. Total energies are considerably lower than those obtained by other optimization procedures (*e.g.* ref.[20] and Part I) making use of bases of a comparable size. They are probably very close to the lowest values attainable by a basis of this size. The energy decrease on optimization was higher for CH_3^+ than for CH_3^- in all cases. This is easy to understand since the energy given by an unoptimized CGTF basis differs from the Hartree–Fock (HF) limit considerably more in the case of CH_3^+ than CH_3^-. This deviation is 0·78% for CH_3^+ and 0·53% for CH_3^-. (The energy of CH_3^+ in the $(10s\ 6p\ 2d/5s\ 1p)$ basis amounts to $-39·24592$ a.u. which is by about 0·004 a.u. above the HF limit, the energy of CH_3^- in the same basis is $-39·50352$ a.u.[21,22]); In the A2 basis, the deviations for CH_3^+ and CH_3^- are 0·19% and 0·23%, in the B2 basis 0·25% and 0·26%. Hence the optimization for the two ions makes deviations from the HF limit roughly uniform. This is of great importance in calculations of relative energies of systems and, consequently, in various chemical applications of *ab initio* calculations using incomplete basis sets.

The optimization procedure employed is less successful when also judged by other characteristics than energy. Resulting basis sets lead to poor population analysis results which are dependent on the order of functions in optimization. It is likely that the quantities resulting in A and B cycles would become closer in value (and perhaps even closer to correct values) upon multiple reoptimization, but each reoptimization raises computational time and is economically prohibitive. Thus it is advantageous to obtain a satisfactory basis set in the very first cycle and this is why the values resulting in the first optimization cycle were examined in detail in this paper.

Transferability of the optimum basis set to ethylene appears to be successful. This is encouraging because otherwise the use of a larger basis set would economically be preferable to basis set optimizing for each molecule individually.

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Translated by P. Čársky.