

Ab initio SCF-MO-LCAO CALCULATIONS WITH A MOLECULE-CALIBRATED CONTRACTED GAUSSIAN BASIS. I.**CH₃⁺, CH₃⁻, ETHYLENE**

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Molecule-calibrated contractions with Gaussian type function contraction coefficients chosen from expansion coefficients of molecular orbitals of CH₃⁺ and CH₃⁻ are tested. A possibility is examined to transfer these contracted functions from one ion to the another and to ethylene. Total energy with all molecules under study is lower if molecule-calibrated contracted functions are employed as a basis set instead of contracted functions derived from the examination of atomic orbitals. The effect of the molecule-calibrated contraction on energy components, orbital energies and atomic populations is also discussed.

In *ab initio* calculations using a Gaussian basis set all integrals necessary for the solution of Hartree-Fock-Roothaan equations¹ can be evaluated analytically² rather easily. However, one must employ a large number of Gaussian type functions (GTF), compared with that of Slater type functions used in calculations yielding results of the same accuracy³. This is a disadvantage, because the number of integrals to be calculated and employed in a SCF procedure increases with a fourth power of the number of basis functions. It is possible to overcome this difficulty by means of "contracted Gaussian type functions" (CGTF), *i.e.* by the adoption of a linear combination of Gaussian functions instead of individual GTF's⁴. A similar treatment of "lobe" Gaussian type functions was independently reported by Preuss⁵ and Whitten⁶. An actual construction of a CGTF set is equivalent to forming suitable fixed GTF linear combinations, based on the analysis of atomic orbital expansion coefficients. Examples can be found *e.g.* in the papers of Clementi^{4,7} and Salez and Veillard⁸. CGTF bases formed in this way have been employed in molecular calculations without any remarkable effect on the quality of results provided the contraction is well chosen⁸⁻¹⁰. Salez and Veillard⁸ showed that the best contracted bases for molecules are not identical with those for atoms. This is due to a deformation of atomic orbitals, in particular of the outer ones forming the chemical bonds. This should be taken into account in the choice of a contraction for molecular calculations.

Recently some authors¹⁰⁻¹² used molecule-calibrated contracted (MCC) Gaussian basis in molecular calculations. Finding the MCC Gaussian basis set requires a SCF calculation on a small molecule using an uncontracted basis. From the examination of the molecular orbital expansion coefficients obtained the linear combinations of the GTF's are set up, the fixed coefficients of which are taken from the suitable molecular orbitals. The contracted Gaussian type

functions (MCC GTF) formed in this way are then employed as the basis for calculations of larger molecules. The choice of the fixed coefficients should be unambiguous at least with one contracted orbital for an atomic shell. From this point of view symmetrical molecules with degenerate molecular orbitals are particularly suitable. Another problem in the choice of the molecule used for calibration concerns a possibility to transfer contracted functions for an atom to another molecule containing that atom. With the experience, concerning a transfer of parameters from a small system to a larger one, achieved with localized orbitals¹³⁻¹⁶, it can be anticipated that such a transfer could be possible provided the atom lies in a similar environment and has the same valence angles and the hybrid orbitals of the same type both in a calibrated and the considered molecule.

In this paper properties of the CGTF's constructed from molecular orbitals of planar CH_3^+ and CH_3^- ions are examined. Their transfer from the positive ion to the negative ion and *vice versa* and their adoption in the calculation on ethylene have been investigated.

METHOD OF CALCULATION

The program used is an extensively modified version of the Polyatom system, QCPE 47-1 (ref.¹⁷) for the IBM 7040 computer adapted to make use of contracted functions. In general a contraction does not lead to a decrease in a number of integrals over GTF's to be explicitly calculated, because each integral over a contracted function is calculated as a sum of integrals over uncontracted functions. It decreases merely the number of integrals stored on a magnetic tape and the number of linear variation parameters in the SCF calculation. However, if an integral contained two or more CGTF's which were centered on the same nucleus, then a part of the computation of all integrals over the GTF's composing these CGTF's was the same.

In the present paper a series of calculations was performed in which the bases differed only by several CGTF's. The modified program permits to use the integrals already calculated and stored on a magnetic tape in further calculations on a given molecule. Thus only integrals over new CGTF's have to be calculated.

The GTF basis set employed is of the (7s, 3p/3s) type, from which the minimal contracted [2s, 1p/1s] basis was formed. The latter is the same basis as that employed by Clementi in calculations on a series of molecules^{18,19}. This basis appears to be suitable for calculations on larger molecules as it yields results of sufficient accuracy within reasonable computer times. Exponents and contraction coefficients of the GTF's for carbon and hydrogen are listed in Tables I and II. The contracted functions are not normalized, their normalization is performed before the SCF procedure starts.

Molecular-calibrated contractions were made in a way presented in the following description. First, SCF calculations using the uncontracted basis were carried out on planar CH_3^+ and CH_3^- ions with D_{3h} symmetry setting the principal axis along the z direction and putting the bond length equal to 2.025 Bohr (nuclear repulsion energy 9.744227 a.u.). The calculations proceeded until the difference in electronic energies in two successive iterations was less than 10^{-7} a.u. A linear combination of five s-type GTF's possessing the highest exponents with coefficients taken from the $1a'_1$ MO

represents the $1s$ MCC GTF, a linear combination of two s -type GTF's with the lowest exponents with coefficients taken from the $2a_1'$ MO forms the $2s$ MCC GTF, a linear combination of three p -type GTF's with coefficients taken from the $1e'$ and

TABLE I

Atomic Contraction Coefficients and MCC Coefficients for Carbon Atom Derived from Molecular Orbitals of CH_3^+ and CH_3^- Ions

Exponent	Orbital representation	Coefficient		
		atomic contraction	calibrated molecule	
			CH_3^+	CH_3^-
391.445	$1s$	0.02220	0.02219	0.02218
64.7358		0.13285	0.13279	0.13277
16.2247		0.38435	0.38419	0.38404
5.33460		0.45798	0.45702	0.45653
2.00995		0.15441	0.15539	0.15582
0.502323	$2s$	0.56673	0.55775	0.41758
0.155139		0.55692	0.32580	0.30068
4.31613	$p_{x,y}$	0.10845	0.08182	0.06359
0.873682		0.46116	0.37017	0.27279
0.202860		0.63043	0.36763	0.25492
4.31613	p_z	0.10845	0.08862	0.09256
0.873682		0.46116	0.35370	0.34048
0.202860		0.63043	0.73542	0.74515

TABLE II

Atomic Contraction Coefficients and MCC Coefficients for Hydrogen Atom Derived from Molecular Orbitals of CH_3^+ and CH_3^- Ions

Exponent	Type	atomic contraction	Coefficient					
			calibrated molecule					
			CH_3^+ ($2a_1'$)	CH_3^+ ($1e'$)	CH_3^+ (mix ^a)	CH_3^- ($2a_1'$)	CH_3^- ($1e'$)	CH_3^- (mix ^a)
0.151374	s	0.64767	0.01889	0.06325	0.19950	0.08725	0.27141	1.10060
0.681277	s	0.40789	0.14078	0.23870	1.00000	0.13773	0.23463	1.00000
4.50037	s	0.07048	0.02808	0.04466	0.19306	0.02941	0.04623	0.20494

^a Mixture of CGTF's with coefficients from $2a_1'$ and $1e'$ MO's in the ratio 1 : 1.

$1a_2''$ MO's, respectively, represents the $p_{x,y}$ and p_z MCC GTF's for carbon. For hydrogen the contraction was made by a linear combination of the GTF's with coefficients taken from both the $2a_1'$ and $1e'$ MO's of CH_3^+ and CH_3^- ions. Moreover, a "mixture" of linear combinations with coefficients from the $2a_1'$ and $1e'$ MO's was made for both ions, because the GTF's on hydrogen do not enter these linear combinations with the same weight. The ratio of coefficients in this contraction is an average value of their ratios in the $2a_1'$ and $1e'$ MO's. The ratio 1 : 2 of coefficients was also tested, but this contraction appeared to be less successful. A similar treatment was employed by Hoyland¹¹ in estimates of barriers of internal rotation in alkanes,

TABLE III
Basis Sets for Carbon and Hydrogen Atoms

Number of the basis set	Contraction
1	No contraction
2	$1s(\text{A}) 2s(\text{A}) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
3	$1s(\text{CH}_3^+) 2s(\text{A}) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
4	$1s(\text{A}) 2s(\text{CH}_3^+) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
5	$1s(\text{CH}_3^+) 2s(\text{CH}_3^+) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
6	$1s(\text{A}) 2s(\text{A}) p_{x,y}(\text{CH}_3^+) p_z(\text{A})/h(\text{A})$
7	$1s(\text{A}) 2s(\text{A}) p_{x,y}(\text{A}) p_z(\text{CH}_3^+)/h(\text{A})$
8	$1s(\text{CH}_3^+) 2s(\text{CH}_3^+) p_{x,y}(\text{CH}_3^+) p_z(\text{CH}_3^+)/h(\text{A})$
9	$1s(\text{CH}_3^-) 2s(\text{A}) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
10	$1s(\text{A}) 2s(\text{CH}_3^-) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
11	$1s(\text{CH}_3^-) 2s(\text{CH}_3^-) p_{x,y}(\text{A}) p_z(\text{A})/h(\text{A})$
12	$1s(\text{A}) 2s(\text{A}) p_{x,y}(\text{CH}_3^-) p_z(\text{A})/h(\text{A})$
13	$1s(\text{CH}_3^-) 2s(\text{CH}_3^-) p_{x,y}(\text{CH}_3^-) p_z(\text{A})/h(\text{A})$
14	$1s(\text{A}) 2s(\text{A}) p_{x,y}(\text{A}) p_z(\text{CH}_3^-)/h(\text{A})$
15	$1s(\text{CH}_3^-) 2s(\text{CH}_3^-) p_{x,y}(\text{CH}_3^-) p_z(\text{CH}_3^-)/h(\text{A})$
16	$1s(\text{A}) 2s(\text{CH}_3^+) p_{x,y}(\text{CH}_3^-) p_z(\text{CH}_3^+)/h(\text{A})$
17	$1s(\text{A}) 2s(\text{CH}_3^+) p_{x,y}(\text{CH}_3^-) p_z(\text{A})/h(\text{A})$
18	$16^a/h(\text{CH}_3^+ 2a_1')$
19	$16^a/h(\text{CH}_3^+ 1e')$
20	$16^a/h(\text{CH}_3^- 2a_1')$
21	$16^a/h(\text{CH}_3^- 1e')$
22	$8^a/h(\text{CH}_3^+ \text{mix})$
23	$15^a/h(\text{CH}_3^- \text{mix})$
24	$17^a/h(\text{CH}_3^+ \text{mix})$
25	$17^a/h(\text{CH}_3^- \text{mix})$

^a Number of the basis set referring to the contraction on carbon atom.

constructing the MCC GTF basis from results of calculations on methane using an uncontracted basis set and also by Schulman, Moskowitz and Hollister¹⁰ in calculations on ethylene.

For judging the quality of the MCC GTF basis set a series of calculations was performed in which the atomic contraction was substituted stepwise by the molecular one for the $1s$, $2s$, $p_{x,y}$, p_z orbitals and their combinations. 25 various basis sets formed in this way are summarized in Table III. As an example the basis 18 is expressed in its analytical form; the carbon CGTF's are as follows

$$\chi_{1s} = 0.02220(391.445) + 0.13285(64.7358) + 0.38435(16.2247) \\ + 0.45798(5.33460) + 0.15441(2.00995),$$

$$\chi_{2s} = 0.55775(0.502323) + 0.32580(0.155139),$$

$$\chi_{p_{x,y}} = 0.06359(4.31613) + 0.27279(0.873682) + 0.25492(0.20286),$$

$$\chi_{p_z} = 0.08862(4.31613) + 0.35370(0.873682) + 0.73542(0.20286),$$

TABLE IV

Total Energy, Energy Components and Orbital Energies for the CH_3^+ Ion (in a. u.)

Number of the basis set from Table III	$E_{\text{tot.}}$	$E_{\text{pot.}}$	E_{kin}	$-V/2T$	One-electron potential
1	-39.156744	-78.2155	39.0588	1.0012	-107.0721
2	-38.916853	-77.3130	38.3962	1.0068	-105.2081
3	-38.916814	-77.3051	38.3883	1.0069	-105.1992
5	-38.938523	-77.5431	38.6046	1.0043	-105.5323
6	-38.958167	-77.5524	38.5942	1.0047	-105.6518
8	-38.978799	-77.7719	38.7931	1.0024	-105.9604
9	-38.916782	-77.3025	38.3857	1.0069	-105.1962
11	-38.931445	-77.4568	38.5254	1.0053	-105.4135
12	-38.963337	-77.6217	38.6584	1.0039	-105.7615
15	-38.977115	-77.7569	38.7798	1.0025	-105.9537
16	-38.983788	-77.8455	38.8617	1.0016	-106.0736
18	-39.114301	-79.0724	39.9581	0.9894	-108.2372
19	-39.121426	-78.8042	39.6828	0.9929	-107.7421
20	-39.106076	-78.3846	39.2785	0.9978	-106.9627
21	-39.044777	-77.9895	38.9447	1.0013	-106.2842
22	-39.121706	-78.8217	39.7000	0.9927	-107.7886
23	-39.047440	-77.9244	38.8770	1.0022	-106.2009

and the hydrogen CGTF is

$$\chi_h = 0.01889 (0.151374) + 0.14078 (0.681277) + 0.02808 (4.50037).$$

The numbers in parentheses are the GTF exponents. The expansion coefficients of the GTF's are taken from Tables I and II.

RESULTS AND DISCUSSION

CH_3^+ and CH_3^- Ions

Both ions were calculated assuming the same geometry regardless of whether the MCC GTF or uncontracted basis set was used. The results are presented in Tables IV–VII. The molecule-calibrated contraction for the carbon $1s$ orbital (bases 3, 9) gives practically the same results as the atomic contraction (basis 2), which indicates that the deformation of the $1s$ orbital in the molecules studied is unimportant. The molecule-calibrated contraction for the $2s$, p_x, y , p_z carbon orbitals appears to be

TABLE IV
(Continued)

Two-electron potential	Orbital energies			
	$1a'_1$	$2a'_1$	$1e'$	$1a''_2$
19-1123	-11.6866	-1.2933	-0.9572	-0.2816
18-1508	-11.8912	-1.3394	-1.0123	-0.3776
18-1499	-11.8916	-1.3394	-1.0123	-0.3776
18-2452	-11.8631	-1.3467	-1.0045	-0.3685
18-3552	-11.8328	-1.3197	-1.0106	-0.3580
18-4442	-11.8066	-1.3269	-1.0030	-0.3544
18-1495	-11.8918	-1.3394	-1.0123	-0.3777
18-2125	-11.8737	-1.3446	-1.0073	-0.3719
18-3955	-11.8189	-1.3165	-1.0103	-0.3553
18-4526	-11.8023	-1.3215	-1.0053	-0.3542
18-4839	-11.7927	-1.3238	-1.0028	-0.3523
19-4206	-11.5929	-1.2517	-0.9372	-0.2605
19-1937	-11.6489	-1.2722	-0.9574	-0.2811
18-8339	-11.7308	-1.3026	-0.9874	-0.3156
18-5505	-11.7875	-1.3224	-1.0047	-0.3443
19-2227	-11.6455	-1.2697	-0.9532	-0.2767
18-5323	-11.7953	-1.3196	-1.0074	-0.3447

superior to the atomic contraction (basis 2) considering the total energy. The respective decrease in the total energy is roughly additive, *e.g.* with CH_3^+ employing the basis 8, where the MCC for carbon is made from the MO's of CH_3^- the decrease in energy amounts to 0.061949 a.u. while if the MCC is separately carried out for the 2s and $p_{x,y}$ orbitals using the bases 5 and 6, the sum of the respective energy decreases amounts to 0.062984 a.u. (The total energy of CH_3^+ is independent on the way in which the contraction of the p_z orbital is done.)

For the 2s carbon orbital the MCC formed from the MO's of CH_3^+ is better for both ions, for the $p_{x,y}$ orbitals the MCC formed from the MO's of CH_3^- was better, for the p_z orbital of CH_3^- the MCC formed from the MO's of CH_3^+ was better. In general the best contraction of carbon orbitals with both ions is the basis 16, where each contraction for any orbital was that which gave better results concerning the total energy. Using this basis the total energy, energy components and orbital energies of CH_3^+ are more close to values yielded by an uncontracted basis than those

TABLE V
Total Energy, Energy Components and Orbital Energies for the CH_3^- Ion (in a. u.)

Number of the basis set from Table III	$E_{\text{tot.}}$	$E_{\text{pot.}}$	$E_{\text{kin.}}$	$-V/2T$	One-electron potential
1	-39.369184	-78.9099	39.5407	0.9978	-114.3053
2	-39.272661	-78.8385	39.5658	0.9963	-113.9885
3	-39.272655	-78.8308	39.5582	0.9964	-113.9803
5	-39.279658	-78.9638	39.6841	0.9949	-114.1784
6	-39.285824	-78.9665	39.6807	0.9950	-114.2283
7	-39.289261	-78.5048	39.2155	1.0009	-113.2795
8	-39.313679	-78.7798	39.4661	0.9981	-113.7443
9	-39.272643	-78.8282	39.5556	0.9964	-113.9773
11	-39.277575	-78.9153	39.6377	0.9954	-114.1075
12	-39.287561	-79.0040	39.7164	0.9946	-114.2845
13	-39.292298	-79.0774	39.7851	0.9938	-114.3981
14	-39.288712	-78.4958	39.2071	1.0010	-113.2458
15	-39.313358	-78.7618	39.4485	0.9983	-113.7016
16	-39.315937	-78.8267	39.5108	0.9975	-113.8129
18	-39.180182	-80.6472	41.4670	0.9724	-117.7138
19	-39.237967	-80.3249	41.0869	0.9775	-117.0140
20	-39.313282	-79.7790	40.4657	0.9858	-115.7910
21	-39.340301	-79.1487	39.8084	0.9941	-114.4603
22	-39.222161	-80.4022	41.1800	0.9762	-117.2208
23	-39.340820	-79.1429	39.8021	0.9942	-114.4674

obtained by means of the basis 2. However, the results of the population analysis are better with the basis 2; here the respective deviations from the results of the calculation using the uncontracted basis set fall in opposite directions depending on whether the basis 2 or 16 is used. Using the former, carbon is more negative than using the uncontracted basis, while using the latter, it is more positive in agreement with the results obtained with a larger basis (10s, 6p/4s) (gross populations for carbon and hydrogen are 5.870 and 0.710, respectively)²⁰.

The calculated total energy of CH_3^- using the basis 16 is 0.043276 a.u. lower compared to the value obtained using the basis 2. Most other quantities studied are however closer in value to those computed with an uncontracted basis if the basis 2 is employed.

Concerning the hydrogen MCC GTF's constructed from the MO's of CH_3^+ , it is seen in Table V, that their transfer to CH_3^- does not give good results (bases 18, 19, 22), MCC GTF's for hydrogens of CH_3^- are much more diffuse than those of CH_4^+ .

TABLE V
(continued)

Two-electron potential	Orbital energies				
	$1a'_1$	$2a'_1$	$1e'$	$1a''_2$	$3a'_1$
25-6512	-10.8128	-0.5468	-0.2166	0.0616	0.5144
25-4058	-10.8296	-0.5400	-0.2296	0.0230	0.8325
25-4052	-10.8305	-0.5401	-0.2298	0.0227	0.8323
25-4704	-10.8143	-0.5415	-0.2259	0.0282	0.8517
25-5176	-10.8010	-0.5310	-0.2282	0.0322	0.8422
25-0305	-10.9311	-0.5700	-0.2533	0.0064	0.8053
25-2203	-10.8821	-0.5615	-0.2478	0.0202	0.8345
25-4048	-10.8307	-0.5401	-0.2298	0.0227	0.8323
25-4480	-10.8187	-0.5409	-0.2270	0.0267	0.8442
25-5363	-10.7946	-0.5298	-0.2282	0.0331	0.8434
25-5764	-10.7847	-0.5308	-0.2257	0.0366	0.8553
25-0057	-10.9361	-0.5724	-0.2555	0.0058	0.8033
25-1955	-10.8854	-0.5619	-0.2513	0.0187	0.8266
25-2420	-10.8745	-0.5600	-0.2478	0.0210	0.8361
27-3224	-10.4585	-0.3857	-0.0758	0.1947	1.3436
26-9449	-10.5412	-0.4209	-0.1107	0.1649	1.2629
26-2678	-10.6808	-0.4813	-0.1710	0.1092	1.1160
25-5674	-10.8176	-0.5370	-0.2269	0.0498	0.9309
27-0744	-10.5151	-0.4084	-0.0995	0.1764	1.2987
25-5802	-10.8190	-0.5358	-0.2267	0.0517	0.9445

With CH_3^+ the best results were achieved with the basis 22, which is entirely constructed from the MO's of CH_3^+ . All quantities studied are close in value to the results obtained with the uncontracted basis; in this respect they are considerably better than the values computed with the basis 2.

The lowest total energy of CH_3^- was achieved with the basis 23, which is an analogue to the basis 22 for CH_3^+ , but in this case the results are not so unambiguous: some of them are better, some are worse than those computed with the basis 2, although the decrease in the total energy of 0.068159 a.u. is considerable.

Ethylene

The calculations were performed assuming the molecular geometry chosen by Moskowitz and coworkers^{10,21}, *i.e.* the C—C and C—H bond lengths 2.55 and 2.02 Bohr, respectively, and the HCH angle 120°. The nuclear repulsion energy amounts to 33.402244 a.u. The results are summarized in Table VIII (total energy, energy components and orbital energies) and in Table IX (population analysis). The computational costs dictated the use of the calculation of Moskowitz and Harrison²¹ with a (7s, 3p/2s) basis set as a reference calculation with an uncontracted basis set.

TABLE VI
Population Analysis for the CH_3^+ Ion

Number of the basis set from Table III	Net		Gross		Overlap
	C	H	C	H	
1	5.044	0.316	6.069	0.643	0.684
2	5.136	0.266	6.224	0.592	0.725
3	5.136	0.266	6.224	0.592	0.725
5	4.949	0.295	6.074	0.642	0.750
6	4.856	0.354	5.980	0.673	0.749
8	4.678	0.385	5.833	0.722	0.770
9	5.137	0.266	6.224	0.592	0.725
11	5.020	0.283	6.133	0.622	0.742
12	4.789	0.378	5.918	0.694	0.753
15	4.680	0.397	5.830	0.723	0.766
16	4.613	0.409	5.772	0.743	0.772
18	5.004	0.322	6.026	0.658	0.681
19	4.844	0.347	5.914	0.695	0.713
20	4.661	0.323	5.788	0.737	0.752
21	4.575	0.410	5.734	0.755	0.772
22	4.970	0.320	6.014	0.662	0.696
23	4.636	0.396	5.786	0.738	0.766

As the basis of that calculation differs from the basis used in the present paper in GTF exponents and by a lower number of the hydrogen GTF's, we considered also another reference calculation in which a larger basis (9s, 5p/3s) was employed¹⁰.

From the Table VIII it is apparent that the p_z MCC GTF's calibrated on CH_3^+ and CH_3^- (bases 7 and 14, respectively) cannot be used for ethylene, as expected. A possibly way to construct a MCC p_π orbital is that of exploiting the GTF coefficients of the $1b_{1u}$ MO obtained from a calculation on ethylene using an uncontracted basis set. However even the carbon atomic p_z orbital alone appears to be a good function for description of a π bond¹⁰.

The MCC functions for $2s$ and $p_{x,y}$ orbitals constructed from the MO's of CH_3^+ and CH_3^- are very good when employed in the calculation on ethylene. With the $2s$ orbital the contraction based on the MO's of CH_3^+ is slightly superior, while with $p_{x,y}$ orbitals that based on the MO's of CH_3^- is better, similarly as in the case of CH_3^+ and CH_3^- ions. Combining these, an optimum contraction is obtained (basis 17), which gives a total energy 0.089599 a.u. lower than the calculation using an atomic

TABLE VII

Population Analysis for the CH_3^- Ion

	Number of the basis set from Table III	Net		Gross		Overlap
		C	H	C	H	
	1	5.757	0.724	6.949	1.017	0.794
	2	5.581	0.717	6.853	1.049	0.848
	3	5.582	0.717	6.853	1.049	0.848
	5	5.478	0.750	6.733	1.089	0.837
	6	5.439	0.817	6.666	1.111	0.818
	7	5.755	0.649	7.030	0.990	0.850
	8	5.490	0.782	6.714	1.095	0.816
	9	5.582	0.717	6.853	1.049	0.848
	11	5.517	0.737	6.780	1.073	0.842
	12	5.407	0.842	6.621	1.126	0.809
	13	5.345	0.862	6.549	1.150	0.803
	14	5.768	0.644	7.043	0.986	0.850
	15	5.507	0.789	6.726	1.091	0.813
	16	5.455	0.808	6.667	1.111	0.808
	18	6.297	0.502	7.407	0.864	0.740
	19	6.076	0.555	7.226	0.925	0.767
	20	5.770	0.649	6.964	1.012	0.796
	21	5.522	0.758	6.732	1.089	0.806
	22	6.227	0.509	7.364	0.897	0.758
	23	5.594	0.729	6.810	1.063	0.810

TABLE VIII
Total Energy, Energy Components and Orbital Energies for Ethylene (in a.u.)

Number of the basis set from Table III	$E_{\text{tot.}}$	$E_{\text{pot.}}$	$E_{\text{kin.}}$	$-V/2T$	One-electron potential	Two-electron potential
1 ^a	-77-800181	-	-	-	-	-
2	-77-630942	-154-4664	76-8355	1-0052	-244-6744	56-8057
4	-77-659217	-154-8354	77-1762	1-0031	-245-2335	56-9958
6	-77-688232	-154-8454	77-1572	1-0034	-245-4398	57-1921
7	-77-602572	-154-1551	76-5525	1-0069	-243-9881	56-4308
8	-77-692341	-154-9030	77-2107	1-0031	-245-3201	57-0148
10	-77-650159	-154-7032	77-0530	1-0039	-245-0344	56-9290
12	-77-695793	-154-9647	77-2689	1-0028	-245-6355	57-2686
14	-77-598605	-154-1441	76-5454	1-0069	-243-9509	56-4047
15	-77-688463	-154-8769	77-1884	1-0032	-245-2798	57-0007
17	-77-720541	-155-3244	77-6039	1-0007	-246-1835	57-4568
24	-77-762637	-155-2222	77-4596	1-0020	-248-2861	59-6616
25	-77-790950	-155-7399	77-9490	0-9990	-246-9903	57-8481
b	-78-0062	-	-	-	-	-

TABLE VIII
(continued)

Number of the basis set from Table III	Orbital energies						Orbital energies					
	1 _{a_g}	1 _{b_{3u}}	2 _{a_g}	2 _{b_{3u}}	1 _{b_{2u}}	3 _{a_g}	1 _{b_{1g}}	1 _{b_{1g}}	1 _{b_{1u}}	1 _{b_{2g}}		
1 ^a	-11.2539	-11.2526	-1.0584	-0.8067	-0.6604	-0.5829	-0.5174	-0.3814	0.1518			
2	-11.4088	-11.4074	-1.0947	-0.8353	-0.7026	-0.6379	-0.5636	-0.4635	0.1226			
4	-11.3821	-11.3807	-1.0992	-0.8353	-0.6948	-0.6291	-0.5570	-0.4546	0.1319			
6	-11.3558	-11.3543	-1.0755	-0.8236	-0.6997	-0.6374	-0.5571	-0.4459	0.1430			
7	-11.4592	-11.4579	-1.1146	-0.8511	-0.7181	-0.6569	-0.5778	-0.4515	0.0897			
8	-11.3780	-11.3766	-1.0989	-0.8387	-0.7073	-0.6480	-0.5644	-0.4280	0.1155			
10	-11.3915	-11.3901	-1.0980	-0.8354	-0.6975	-0.6322	-0.5593	-0.4577	0.1287			
12	-11.3429	-11.3414	-1.0726	-0.8218	-0.6991	-0.6373	-0.5562	-0.4435	0.1461			
14	-11.4620	-11.4607	-1.1162	-0.8524	-0.7195	-0.6585	-0.5790	-0.4498	0.0883			
15	-11.3770	-11.3755	-1.0962	-0.8381	-0.7110	-0.6527	-0.5670	-0.4274	0.1136			
17	-11.3165	-11.3150	-1.0761	-0.8212	-0.6912	-0.6285	-0.5498	-0.4348	0.1551			
24	-11.0921	-11.0906	-0.9596	-0.7274	-0.6014	-0.5079	-0.4525	-0.3202	0.2858			
25	-11.2822	-11.2809	-1.0569	-0.8083	-0.6800	-0.6109	-0.5393	-0.4141	0.1791			
^b	-11.2395	-11.2379	-1.0397	-0.7959	-0.6549	-0.5812	-0.5145	-0.3736	0.1436			

^a The (7s, 3p/2s) basis set, ref.²¹; ^b The (9s, 5p/3s) basis set, ref.¹⁰.

contraction. Furthermore, the virial ratio 1.0007 is considerably better and also all orbital energies are closer to the values obtained with the basis 1 or the $(9s, 5p/3s)$ basis, which are near to the experimental values of ionization potentials²².

Also with ethylene a rough additivity in decrease of the total energy is observed, e.g. the sum of decreases in bases 4 and 12 amounts to 0.093126 a.u., compared to the total decrease of 0.089599 a.u. using the basis 17.

Considering the MCC also for hydrogen the total energy is further lowered: with the basis 25 its value is -77.790950 a.u. which is rather close to the value -77.800181 a.u. yielded by the uncontracted basis set. However it should be kept in mind that the basis 1 contains only 2 GTF's for hydrogen. When compared with the results of the calculation using the basis set 17, orbital energies calculated with the basis 25 are even closer to those obtained with uncontracted bases with exception of the $1b_{2g}$ MO, the energy of which is too high.

In light of the successful results achieved with the MCC GTF basis set for the total and orbital energies, less satisfactory population analysis results appear to be somewhat surprising. Perhaps this can partly be assigned to the "unequilibrated" uncontracted basis sets, because a number of GTF's on hydrogen is known to affect considerably the charge distribution. From this it follows that the population analysis results are strongly dependent on the contraction employed and therefore their interpretation must be taken with some caution.

TABLE IX
Population Analysis for Ethylene

Number of the basis set from Table III	Net		Gross		Overlap	
	C	H	C	H	C-C	C-H
1 ^a			6.330	0.835	0.943	0.839
2	5.026	0.464	6.403	0.798	1.247	0.847
4	4.914	0.499	6.309	0.945	1.251	0.847
6	4.855	0.570	6.240	0.880	1.306	0.829
7	5.071	0.434	6.465	0.767	1.292	0.839
8	4.779	0.573	6.207	0.897	1.358	0.826
10	4.956	0.485	6.364	0.827	1.253	0.848
12	4.819	0.598	6.200	0.900	1.313	0.822
14	5.075	0.432	6.470	0.765	1.295	0.839
15	4.786	0.854	6.208	0.896	1.372	0.821
17	4.711	0.633	6.108	0.946	1.314	0.820
24	5.096	0.436	6.419	0.790	1.209	0.751
25	4.739	0.596	6.132	0.934	1.287	0.817

The $(7s, 2p/2s)$ basis set, ref.²¹.

CONCLUSIONS

The results obtained can be characterized as follows:

1. A considerable decrease in the total energy was observed if the MCC GTF basis set was used instead of the CGTF's with coefficients chosen according to calculations for atoms. This energy difference amounts to 0.204853 a.u. with CH_3^+ , 0.068159 a.u. with CH_3^- , and 0.160008 a.u. with ethylene. 2. A transfer of a MCC GTF basis set from one molecule to the another appears to be possible. With functions for hydrogen this transfer may be encountered with some difficulties. 3. Besides the total energy the quality of the MCC GTF basis set employed must also be judged by means of other quantities such as orbital energies, energy components and population analysis. 4. A rough additivity of corrections to the total energy was found, when the MCC GTF's for carbon $2s$, $p_{x,y}$ and p_z orbitals were stepwise introduced into the basis set. That means that a change in contraction coefficients in one orbital does not affect considerably a quality of contraction in another orbital. Whitman and Hornback²³ found with the first period atoms that the optimum s -type GTF's exponents are not sensitive to the choice of the p -type GTF basis set and *vice versa*. From this and from the possibility to transfer a MCC GTF basis set from one molecule to the another it appears that a choice of molecule-calibrated GTF exponents should be possible. Some efforts have already been made in this direction^{1,2}. This could be made in a following way provided the exponents for the $1s$ function need not be optimized. First, in calculations on CH_3^+ and CH_3^- all orbitals with exception of the $2s$ would be contracted using the contraction coefficients chosen on the basis of calculations on atoms. The $2s$ GTF exponents would be optimized by multiplying with a scaling parameter²⁴. These optimized $2s$ GTF's would first be contracted with the aid of contraction coefficients chosen from the optimum SCF calculation on the molecule and then after renormalization used in optimization of the $p_{x,y}$ GTF exponents. The exponents of the uncontracted $p_{x,y}$ GTF's would be optimized in a similar way and then the optimized GTF's would be contracted. The same treatment would be carried out to optimize the p_z GTF exponents. This procedure would be repeated until convergency would be reached. The work in this direction is in progress.

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Translated by P. Čársky.

Note added in proof: In the recent paper by Schulman, Hornback and Moskowitz²⁵ the calculations on the ethylene with the $[5s, 3p, 2d/2s, 1p]$ basis set have been reported. With this basis set the gross population for carbon is 6.215. The gross population for carbon with our best MCC GTF basis for ethylene (basis 25) agrees better with this value than the gross population obtained with the CGTF basis optimum for isolated atoms (basis 2).