Nonempirical SCF-LCAO-MO Calculations for $(CH)^+$

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Nonempirical molecular orbital calculations, using a minimal basis set of Slater-type atomic orbitals, are reported for the ground state of the $(CH)^+$ ion. The C–H bond length calculated using optimized exponents is in excellent agreement with the experimental value, whereas the distances predicted using the conventional "free atom" exponents are too large by up to 17%.

Introduction

Ab initio molecular orbital calculations have been reported for a variety of organic molecules of chemical interest [1]. At the Hartree-Fock-Roothaan level, such calculations should yield accurate bond angles, bond lengths, rotational barriers and isomerization energies for neutral molecules and positive ions. Of particular interest is the determination of the equilibrium geometry and potential energy surface for classical and nonclassical carbonium ions.

Many calculations for organic systems employ a minimal basis set of Slater-type orbitals (STO), or the corresponding "contracted" set of Gaussian-type functions. Unfortunately, previous calculations [2] of this type for the simplest possible model of a hydrocarbon ion, $(CH)^+$, predicted an equilibrium internuclear distance which differs by 10% from the experimental value [3]. Before proceeding with calculations for carbonium ions of chemical interest, it is important to determine the source of the inaccuracy in the $(CH)^+$ results. In particular, is the error due to the use of an *unoptimized* minimal basis set of STO's, or must a *larger* basis set (optimized or not) be employed?

This question has been investigated by a series of minimal basis set Hartree-Fock-Roothaan calculations for $(CH)^+$. An optimum set of orbital exponents is determined for the ground-state of the ion, and the predicted internuclear distance R_{CH^+} is compared with the experimental value and with the values obtained using exponent sets commonly used in *ab initio* calculations.

Theory and Method of Calculation

The closed-shell wavefunction for the $^1\Sigma^+$ ground-state of $(CH)^+$ is represented as a single Slater determinant of three lowest doubly-occupied σ molecular orbitals. The minimal basis set consists of a $1s$ STO centered on H, and $1s$, $2s$, and $2p_\sigma$ STO's centered on C; each σ molecular orbital is expanded as a linear combination of these four functions.

The one- and two-center integrals over atomic orbitals required for the Roothaan Eq. [4] were obtained from the MINT program of Janiszewski and

Wahl [5]. A program in PDP-10 FORTRAN was constructed which reads these integrals as input, and executes SCF-LCAO-MO calculations; the program was checked by reproducing several of the original calculations for (CH)$^+$ by Jenc [2].

Results and Discussion

The orbital exponents used for carbon in most minimal basis set STO calculations correspond either to those deduced from Slater's rules for the free atoms [6], or to the "best free atom" values of Clementi and Raimondi [7]. In the case of the hydrogen $1s$ orbital both the "free atom" value of 1.0, and the larger value of 1.2, are commonly employed. Accordingly, calculations for (CH)$^+$ were carried out using the four possible combinations of these sets, and the equilibrium R_{CH^+} values were determined (Sets 1–4 of Table 1). In all four cases, the predicted R_{CH^+} is too *long* (by 9–17%); the results are especially poor using a $1s_H$ exponent of 1.0. Somewhat more accurate internuclear separations are obtained using Slater exponents for the free C$^-$ set and the 1.2 value for H; this yields $R_{CH^+} = 1.17$ Å (set 6), which is reasonably accurate for a minimal basis set calculation.

To determine the *best* set of exponents for the ground-state of (CH)$^+$ the values of the $1s_C$, $2s_C$, $2p_C$ and $1s_H$ exponents were successively varied (in that order) until the total energy was minimized. The predicted R_{CH^+} value was determined, and the orbital exponents reoptimized at the new internuclear separation. The entire process was iterated until no further improvements in the total energy were obtained. The final $1s_C$ exponent value (Table 1, set 7) is equal to the "best atom" value, in agreement with other calculations for diatomic molecules containing carbon [8]. The optimum $2s_C$ and $2p_C$ exponents are greater than those of the free atom due both to the fact that carbon carries a partial positive charge, and to the fact that the valence orbitals are engaged in covalent bonding. As foreseen by Jenc, the best $2s_C$ value (of 1.70) is *less* than that for $2p_C$ (of 1.77) in this species [2], since the $2s$ orbital does not participate

Table 1. *Calculated properties of* (CH$^+$) *using different exponents sets*

Atomic orbital	Exponent set						
	1	2	3	4	5	6	7
	Slater C^0, H^0	Best C^0, H^0	Slater C^0	Best C^0	Slater C$^+$, H^0	Slater C$^+$	Optimum
$1s_C$	5.7	5.6727	5.7	5.6727	5.7	5.7	5.67
$2s_C$	1.625	1.6083	1.625	1.6083	1.8	1.8	1.70
$2p_C$	1.625	1.5679	1.625	1.5679	1.8	1.8	1.77
$1s_H$	1.0	1.0	1.2	1.2	1.0	1.2	1.33
Predicted R_{CH^+}							
(in a.u.)	2.45	2.49	2.33	2.37	2.34	2.21	2.168
(in Å)	1.30	1.32	1.23	1.25	1.24	1.17	1.147
Error	15%	17%	9%	11%	9%	3%	1.5%
$-E$ best	37.8002	37.7880	37.8208	32.8084	37.8071	37.8289	37.8425[a]

[a] Virial = −2.00059.

in the "chemical bonding" as much as the $2p$ does (*vide infra*). The optimum exponents for the carbon orbitals do not differ greatly from the set chosen by Jenc (of 5.70, 1.75, and 1.78 for $1s_C$, $2s_C$, and $2p_C$ respectively); his 10% error in R_{CH^+} was mainly due to the low $1s$ exponent of 1.00 used.

The C–H bond length of 1.147 Å predicted by the optimized basis set is in excellent agreement with the experimental value of 1.13083 Å [3, 9], and is superior to the 1.17 Å predicted by a valence – bond calculation using configuration but unoptimized exponents [10]. The residual error of $+1.5\%$ in R_{CH^+} is of the same order of magnitude as that of -1.8% found for neutral (CH)· using an extended, optimized set of STO's [11].

Taken as a whole, the calculations reported in Table 1 indicate that the error in R_{CH^+} obtained with a given set is proportional to the sum of the deviations of the $2p_C$ and $1s_H$ exponents from their optimum values. For each deviation of 0.1 in the exponents from 1.77 and 1.33 respectively, the error in R_{CH^+} increases by about 3%. There is no reason to believe that a similar dependence of predicted geometry upon exponent values should not also apply to minimal basis set calculations for other organic molecules.

Since exponent optimization is time-consuming for polyatomic molecules, it would be convenient if "best average" exponents could be deduced for carbon and hydrogen atoms in various types of chemical environments. Lathan, Hehre, and Pople have already been able to establish such a set for neutral hydrocarbons [12]. At first glance, however, the results of Hehre, Stewart, and Pople [13] for (CH)$^+$ and for (CH$_3$)$^+$ indicate that such a procedure may not be possible for hydrocarbon ions, since the optimum exponents for a given orbital differ by as much as 0.08 in these two cases [13]. The present calculations for (CH)$^+$ indicate that these discrepancies may result from the constraint, imposed by Hehre *et al.*, that the $2s_C$ and $2p_C$ exponents be equal [13]. Removal of this restriction (as in the present calculations) leads to identical exponents for the two bonding orbitals $2p_C$ and $1s_H$, in (CH)$^+$ as those found for (CH$_3$)$^+$ by Hehre *et al.* Hence, this set (1.77 for carbon valence orbitals, 1.33 for hydrogen) probably represents a good starting point in optimization procedures for positive ion sites in carbonium ions, with the restriction that a smaller exponent is best for orbitals which are not really involved in covalent bonding. Possibly a corresponding

Table 2. *Gross populations in* (CH$^+$) *at 2.168 a.u. using different exponent sets*

Exponent set[a]	Orbital populations				Partial charges	
	$1s_H$	$1s_C$	$2s_C$	$2p_C$	C	H
1	0.6701	1.9991	1.9289	1.4020	+0.67	+0.33
2	0.6372	1.9993	1.9381	1.4254	+0.64	+0.36
3	0.6842	1.9992	1.9031	1.4136	+0.68	+0.32
4	0.6586	1.9993	1.9089	1.4332	+0.66	+0.34
5	0.8379	1.9985	1.8607	1.3029	+0.84	+0.16
6	0.8240	1.9986	1.8570	1.3203	+0.82	+0.18
7 (optimal)	0.7303	1.9992	1.8828	1.3877	+0.73	+0.27

[a] See Table 1 for details.

decrease in the "best set" exponents should also be applied for neutral hydro-carbons such as singlet bent methylene where the $2s_C$ orbital is also very much a "lone pair".

Hehre *et al.* have established that the electron density distributions are quite sensitive to the exponent set adopted [13]. The Mulliken population analysis [14] for the (CH)⁺ wavefunction (at 2.168 a.u.) of each exponent set are listed in Table 2. The "neutral atom" exponents (sets 1–4) overemphasize the ionicity of the C–H bond, whereas the opposite is true for the calculations based on C⁺ values (sets 5–6). The net atomic partial charges ($+0.73$ e. for C, $+0.27$ e. for H) in the optimized calculation indicate that about one-quarter of the unit positive charge is associated with the hydrogen atom. Hehre *et al.* [13] found that *each* hydrogen in $(CH_3)^+$ carries a partial charge of $+0.24$ leaving the carbon atom almost electroneutral.

Conclusions

The Hartree-Fock-Roothaan calculations for (CH)⁺ reported above show that charge density distributions and predicted bond lengths are very sensitive to the atomic orbital exponents employed in minimal basis set calculations. Very accurate ($\pm 2\%$) bond lengths are obtained using optimized exponents, whereas errors of up to $+17\%$ occur if free atom values are used. The best set of exponents for positive ion sites in hydrocarbons is $1s_C = 5.67$, $2s_C = 2p_C = 1.77$, and $1s_H = 1.33$.

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