Theoret. chim. Acta (Berl.) 25, 352—359 (1972)

Geometry and Force Constant Determination from Correlated Wave Functions for Polyatomic Molecules: Ground States of H_2O and CH_2*

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Received September 9, 1971

Ab initio calculations including electron correlation are reported for the water and methylene molecules as a function of geometry. A large contracted gaussian basis set is used and the multiconfiguration wave functions, optimized by the iterative natural orbital procedure, include 277 and 617 configurations for H_2O and CH_2 respectively. The method of selecting configurations, yielding "first-order" wave functions, is discussed in some detail. For H_2O, the SCF geometry is $r = 0{,}942$ Å, $\theta = 105{,}8°$, the correlated result is $r = 0{,}968$ Å, $\theta = 103{,}2°$, and the experimental $r = 0{,}957$ Å, $\theta = 104{,}5°$. The water stretching force constants, in millidynes/Å, are 8,72 (SCF), 8,75 (CI), and 8,4 (experiment). Bending force constants are 0,88 (SCF), 0,83 (CI), and 0,76 (experiment). For methylene the SCF geometry is $r = 1{,}072$ Å, $\theta = 129{,}5°$, while the result from first-order wave functions is $r = 1{,}088$ Å, $\theta = 134°$. The predicted CH_2 force constants are 6,16 (SCF) and 6,13 (CI) for stretching and 0,44 (SCF) and 0,33 (CI) for bending.

Es wird über *ab initio*-Rechnungen mit Berücksichtigung der Elektronenkorrelation berichtet, die an Wasser- und Methylenmolekülen als Funktion der Geometrie durchgeführt worden sind. Dazu benutzt man einen großen kontrahierten Gauß-Basissatz. Die Multikonfigurationswellenfunktionen, die unter Benutzung von natürlichen Orbitalen nach der iterativen Prozedur optimiert werden, enthalten für H_2O 277 Konfigurationen und für CH_2 617. Die Auswahlmethode, die zu Wellenfunktionen 1. Ordnung führt, wird diskutiert. Im Falle des Wassers erhält man die SCF-Geometrie zu $r = 0{,}942$ Å, $\theta = 105{,}8°$, das korrelierte Resultat ist: $r = 0{,}968$ Å, $\theta = 103{,}2°$ und das experimentelle $r = 0{,}957$ Å, $\theta = 104{,}5°$. Für Wasser ergeben sich die Valenzkraftkonstanten (in Millidyn $Å^{-1}$) 8,72 (SCF), 8,75 (CI) und 8,4 (Experiment). Die Deformationskonstanten sind 0,88 (SCF), 0,83 (CI) und 0,76 (Experiment). Im Falle des Methylens ist die SCF-Geometrie $r = 1{,}072$ Å, $\theta = 129{,}5°$, während man mit Wellenfunktionen 1. Ordnung $r = 1{,}088$ Å und $\theta = 134°$ erhält. Die CH_2-Kraftkonstanten werden für die Valenzschwingung zu 6,16 (SCF) und 6,13 (CI) bzw. für die Deformationsschwingung zu 0,44 (SCF) und 0,33 (CI) vorausgesagt.

Introduction

The correlation energy of a many-electron system arises from the instantaneous repulsions between pairs of electrons [1] and can be quantitatively defined [2] as the difference between the Hartree-Fock (or best single configuration) energy

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[*] Work performed under the auspices of the U.S. Atomic Energy Commision.

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[***] Supported by the grants from the Research Corporation and the University of California Committee on Research.

and the nonrelativistic exact energy. In recent years molecular calculations using near-Hartree-Fock wave functions have given theoretical chemists a fairly clear picture of the merits of the single configuration self-consistent-field (SCF) approach [3–6]. Going beyond the Hartree-Fock approximation, the picture is less clear. The question most frequently raised is how much electron correlation must be considered to reach a given level of reliability. For diatomic molecules rather thorough investigations have been made of the effect of correlation on predicted dipole moments [7–9] and potential energy curves [10, 11]. However, most of chemistry is concerned with polyatomic molecules and very few through examination of the effects of configuration interaction (CI) have been carried out [12].

In this paper we consider two simple molecules, H_2O and CH_2, and study the influence of correlation on the predicted geometries and force constants.

The correlated "first-order wave functions" used here have proved useful in calculations (employing smaller basis sets) on other small molecules [3, 13–15]. The agreement with experiment obtained for H_2O will give us an estimate of the reliability of our predictions concerning CH_2. Although it is now clear that the $^3B_1$ ground state of methylene is bent [16–18] the experimental bond angles are not yet of quantitative accuracy.

Basis Set

If one intends to draw general conclusions from an *ab initio* calculation, it is necessary that the results be independent of basis set.The *s*, *p* basis sets on oxygen and carbon atoms in the present work are the 10*s* 6*p* gaussian sets of Huzinaga [19]. This basis set has been carefully contracted to five *s* and three *p* functions (5*s* 3*p*) by Dunning [20]. For the ^3P ground state of carbon Dunning finds [20] the contracted energy to be −37.68716 hartrees while the uncontracted energy is −37.68732, and the Hartree-Fock energy −37.6886. For the hydrogen atom Huzinaga's 5*s* set [19] is contracted following Dunning [20] to 3*s*. Dunning has also investigated the gaussian representation of polarization functions [21], and following his suggestions we have used single gaussian p_x, p_y, and p_z functions (with exponents 1.00 for CH_2 and 1.16 for H_2O) on each hydrogen atom. *d* functions on the central atoms were linear combinations of two gaussians chosen to least-squares fit a single Slater function (with exponent 2.00 in CH_2 and 2.01 in H_2O). The final basis set, designated (5*s* 3*p* 1*d*/3*s* 1*p*), yields an SCF energy for H_2O at equilibrium of −76.05 hartrees, to be compared with the estimated Hartree-Fock limit −76.065.

Selection of Configurations

Using a basis set as large as that detailed above it is not feasible to carry out a full configuration interaction. In fact, using the much smaller (4*s* 2*p*/2*s*) basis set and including only the SCF configuration plus all single, double, triple, and quadruple excitations yields 6779 configurations for H_2O [22]. A full configuration interaction for water would have to include up through 10 electron excitations. In this work we have used two configuration selection schemes. Both schemes have the virtue of being nonarbitrary in the sense that, having set down the general rules [13], the selection of configurations for a particular molecule is automatic.

To clarify the selection process it is useful to write down the SCF electron configurations for the two molecules (assuming C_{2V} symmetry)

$$^3B_1 \quad \mathrm{CH_2} \quad 1a_1^2\, 2a_1^2\, 1b_2^2\, 3a_1\, 1b_1$$

$$^1A_1 \quad \mathrm{H_2O} \quad 1a_1^2\, 2a_1^2\, 1b_2^2\, 3a_1^2\, 1b_1^2 \, .$$

The molecular orbitals are fruitfully divided into four categories:

a) The core orbitals P. In both molecules there is only a single orbital of this type, namely $1a_1$, which is essentially the $1s$ atomic orbital on the central atom.

b) The occupied valence orbitals Q. $2a_1$, $1b_2$, $3a_1$, and $1b_1$ for both H_2O and CH_2.

c) The unoccupied (in the SCF configuration) valence orbitals R. For CH_2 these are the $3a_1$ and $1b_1$ orbitals (only singlyoccupied in the $^3B_1$ state) and for both molecules the $4a_1$ and $2b_2$ orbitals fall in this category.

d) The unoccupied higher orbitals S. These are the remaining functions in the basis set, in this case $5a_1$ through $16a_1$, $1a_2$ and $2a_2$, $2b_1$ through $5b_1$, and $3b_2$ through $9b_2$.

With these definitions the form of our two CI wave functions which we have referred to [13] as MC1 and MC2 is easy to specify:

MC1 includes the SCF configuration, all single excitations of the type $Q_i \rightarrow R_j$ and double excitations of the type $Q_i Q_j \rightarrow R_k R_l$. This type of wave function is in the spirit of the "optimized valence configurations" approach of Wahl and Das [23].

MC2 includes all the configurations in MC1 plus all single excitations of the type $Q_i \rightarrow S_j$ and all double excitations $Q_i Q_j \rightarrow R_k S_l$. This is our approximate first-order wave function, which has been discussed elsewhere [11, 13–15, 24].

We do not list the configurations included here for H_2O and CH_2 since explicit examples have previously been given for several molecules [11, 13–15]. For H_2O MC1 includes 18 and MC2 277 configurations. The analogous methylene calculations include 32 and 617 configurations.

Method of Calculation

A self-consistent-field calculation is the first step in our computational procedure. Rather that the usual methods for solving the SCF equations [25], the iterative natural orbital technique [26, 27] is used to annihilate single excitations relative to the SCF configuration. Iterations are continued until the coefficients of the singly-excited configurations vanish and the natural orbital (NO) occupation numbers [28] become integers. The orbitals obtained via this method are not the canonical SCF orbitals [25], so we use a simple unitary transformation employing the properties of Koopmans' theorem to yield to canonical orbitals, which are eigenfunctions of the Fock operator.

Before proceeding to the final NO iterations, the virtual orbitals are transformed so as to correspond to the single particle states of the molecular positive ion. This gives us a well defined starting point for the final NO iterations, which are carried out on the full first-order wave functions (617 configurations for CH_2) until the energy reaches a minimum. Typically this requires four iterations.

Results

The calculated total energies are given in Table 1. From the calculated energies, the equilibrium geometries and quadratic force constants have been determined as described elsewhere [29]. These results are given in Table 2.

For water all three calculations give good agreement with experiment [30–32] for both geometry and force constants. The SCF bond distance is 0.015 Å shorter than experiment, while the first-order value is 0.011 Å too long. We anticipate [11] that further expansion of the basis set will make both the SCF and first-order bond distance smaller. The SCF bond angle is 1.3° too large and the first-order value 1.1° too small. Thus it is seen that for both bond distance and bond angle the first-order results are in slightly better agreement with experiment than the SCF values. The SCF and first-order stretching force constants are both 104% of experiment, while for the bending force constant the theoretical values are 116% and 109% of experiment. The errors (4% and 9%) in the force constants

Table 1. Theoretical energies for the ground states of CH_2 and H_2O. Bond angles are in degrees and bond distances in bohr radii

θ	R(CH)	E(SCF)	E(MC1)	E(MC2)
$^3B_1$ CH_2				
124	1.95	−38.92961		
124	2.00	−38.93183		
124	2.05	−38.93193		
124	2.10	−38.93019		
128	1.95	−38.93026	−38.96421	−39.00686
128	2.00	−38.93239	−38.96788	−39.01027
128	2.05	−38.93238	−38.96941	−39.01155
128	2.10	−38.93054	−38.96911	−39.01102
132	1.95	−38.93036	−38.96454	−39.00755
132	2.00	−38.93235	−38.96811	−39.01083
132	2.05	−38.93225	−38.96956	−39.01200
132	2.10	−38.93031	−38.96918	−39.01135
136	1.95	−38.92986	−38.96438	−39.00774
136	2.00	−38.93178	−38.96790	−39.01092
136	2.05	−38.93158	−38.96927	−39.01198
136	2.10	−38.92955	−38.96880	−39.01123
140	1.95	−38.92892	−38.96386	−39.00754
140	2.00	−38.93073	−38.96729	−39.01065
140	2.05	−38.93043	−38.96859	−39.01156
140	2.10	−38.92830	−38.96805	−39.01071
$^1A_1$ H_2O				
99.52	1.7589	−76.05717	−76.10676	−76.17031
99.52	1.8089	−76.05724	−76.10910	−76.17316
99.52	1.8589	−76.05449	−76.10870	−76.17312
104.52	1.7589	−76.05847	−76.10736	−76.17099
104.52	1.8089	−76.05826	−76.10943	−76.17349
104.52	1.8589	−76.05525	−76.10872	−76.17322
109.52	1.7589	−76.05837	−76.10653	−76.17029
109.52	1.8089	−76.05791	−76.10838	−76.17251
109.52	1.8589	−76.05467	−76.10745	−76.17196

Table 2. Predicted geometries and force constants for the ground states of CH_2 and H_2O. SCF refers to our self-consistent-field wave functions, MC1 to the configuration interaction including SCF plus all promotions to valence orbitals and MC2 to the approximate first-order wave functions. Experimental values are given in parentheses

	H_2O			CH_2		
	SCF	MC1	MC2	SCF	MC1	MC2
Bond distance (Å)	0.942	0.964	0.968 (0.957)[a]	1.072	1.092	1.088
Bond angle (degrees)	105.8	103.2	103.4 (104.5)[a]	129.5	131.7	134.0 (136 ± 8)[b]
Interpolated total energy (hartrees)	-76.05876	-76.1096	-76.1738	-38.9327	-38.9696	-39.0121
Stretching force constant (md/Å)	8.72	8.61	8.75 (8.4)[c]	6.16	6.09	6.13
Bending force constant (md/Å)	0.88	0.84	0.83 (0.76)[d]	0.44	0.23	0.33

[a] Benedict, W. S., Gailar, N., Plyer, E. K.: J. chem. Physics **24**, 1139 (1956).
[b] Wasserman, E., Yager, W. A., Kuck, V. J.: Chem. Physics Letters **7**, 409 (1970).
[c] Nibler, J. W., Pimentel, G. C.: J. molecular Spectroscopy **26**, 294 (1968).
[d] Duncan, J. L., Mills, I. M.: Spectrochim. Acta **20**, 523 (1964).

from first-order wave functions are about what we have seen for diatomic molecules O_2 [11], BeO [14], KrF^+ [33], and BH [34]. However, H_2O is unusual with respect to the SCF force constants, since these are often in poor agreement with experiment [35].

The geometry of CH_2 has been of considerable interest to theoreticians since increasingly accurate *ab initio* calculations [36–38] have predicted a bent triplet ground state, while experimentalists generally accepted Herzberg's spectroscopic determination of linearity [39]. However, recent electron-spin resonance measurements at 4° K have demonstrated that CH_2 is bent [16, 17, 40, 41], a conclusion which can be understood in terms of predissociation in the gas phase absorption spectrum of CH_2 [18, 39]. The ESR measurements have been used to determine bond angles for CH_2 of 136° [17, 40] and 137.7° [41]. However these "experimental" bond angle determinations cannot be taken literally since they assume that one of the two unpaired electrons ($1b_1$) is in a $2p_x$ orbital perpendicular to the plane while the other electron occupies a hybrid orbital oriented along the bisector of the H–C–H angle [41]. As has been pointed out to the authors by Hoffman [42], hybridization is not a physical phenomenon and thus the experimental determinations are by no means rigorous. In light of the above, the most reliable experimental value for the bond angle may be Herzberg's experimental range of 128–148°.

The present calculations predict bond angles of 129.5°, 131.7°, and 134.0 from SCF, MC1, and MC2 wave functions. The SCF bond angle agrees with the value 129° recently obtained by Allen and Franceschetti [43] using a slightly smaller basis set. The angle predicted from first-order wave functions is expected to be the most reliable. To aid in our evaluation of the expected reliability of this 134° CH_2 angle, we point out that comparable first-order calculations [44] on the ground $^2B_1$ and first-excited $^2A_1$ states of NH_2 yielded bond angles differing by 0.6° and 0.7° from experiment. In light of these results and the H_2O results discussed above, we estimate that our theoretical bound angle of 134° is reliable to within 2°. Thus we feel that the present calculations provide the most reliable value to date theoretical or experimental, for the bond angle of the $^3B_1$ ground state of methylene.

Table 3. Important spatial configurations in the first-order wave functions for CH_2 and H_2O. The "degeneracy" of a spatial configuration is the number of linearly independent spin eigenfunctions arising. The coefficients tabulated incorporate the effects of all proper spin eigenfunctions associated with a given spatial configuration

Excitation	Coefficient	Energy criterion $[= \Sigma\, c_i^2\, (H_{ii} - H_{11})]$
$^3B_1$ CH_2 $R = 2.05$ bohrs, $\theta = 132°$		
1. $1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1$	0.9796	—
2. $2a_1 1b_2 \rightarrow 4a_1 2b_2$	0.0618	0.0074
3. $1b_2^2 \rightarrow 2b_2^2$	0.0552	0.0056
4. $2a_1 \rightarrow 4a_1$	0.0660	0.0044
5. $2a_1^2 \rightarrow 4a_1^2$	0.0453	0.0041
6. $1b_2 1b_1 \rightarrow 2b_2 2b_1$	0.0482	0.0040
7. $1b_2^2 \rightarrow 4a_1^2$	0.0505	0.0038
8. $1b_2 3a_1 \rightarrow 2b_2 5a_1$	0.0448	0.0036
$^1A_1$ H_2O $R = 1{,}8089$ bohrs, $\theta = 104.52°$		
1. $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$	0.9815	—
2. $1b_2 3a_1 \rightarrow 4a_1 2b_2$	0.0765	0.0131
3. $1b_2 1b_1 \rightarrow 2b_2 2b_1$	0.0698	0.0122
4. $3a_1 1b_1 \rightarrow 4a_1 2b_1$	0.0696	0.0121
5. $1b_2^2 \rightarrow 2b_2^2$	0.0630	0.0084
6. $2a_1 1b_2 \rightarrow 2b_2 5a_1$	0.0464	0.0070
7. $3a_1^2 \rightarrow 4a_1^2$	0.0576	0.0069
8. $2a_1 3a_1 \rightarrow 4a_1 5a_1$	0.0455	0.0065

Table 4. Natural orbital occupation numbers (≧0.001) for CH_2 and H_2O at the geometries given in Table 3

	CH_2	H_2O
$1a_1$	2.000	2.000
$2a_1$	1.972	1.944
$3a_1$	0.997	1.975
$4a_1$	0.025	0.025
$5a_1$	0.004	0.005
$6a_1$	0.002	0.001
$7a_1$	0.002	—
$1a_2$	0.002	0.001
$1b_1$	0.996	1.989
$2b_1$	0.004	0.010
$3b_1$	0.002	—
$1b_2$	1.970	1.974
$2b_2$	0.021	0.028
$3b_2$	0.002	0.001

The SCF, MC1, and MC2 stretching force constants are essentially the same, as was the case for H_2O, and all three values should be fairly reliable. There are considerable differences between the three calculated values of the bending force constant. It is clear, however, that this force constant is small, less than half that for H_2O.

Some detailed information concerning the electronic structure of H_2O and CH_2 is given in Tables 3 and 4. Table 3 gives the coefficients of the eight most important configurations in the final CI expansions and Table 4 the corresponding natural orbital occupation numbers. The fact that the coefficient of the SCF configuration is 0.9796 for CH_2 and 0.9815 for H_2O is a verification of the essential correctness of the molecular orbital model for these molecules. The same qualitative conclusion is seen in the nearly integer values of the occupation numbers in Table 4 for the SCF orbitals. Table 4 also shows that the most important orbitals besides the SCF orbitals are the $4a_1$ and $2b_2$ valence orbitals. Higher orbitals (those which cannot be constructed from a minimum basis) are seen to be relatively unimportant.

Acknowledgements. We thank Professor Roald Hoffmann for helpful correspondence regarding the reliability of the experimental CH_2 ground state bond angle.

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