

# Quantum Variational Calculations for a Range of CH<sub>2</sub> Configurations

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THE problem of the structure and properties of the CH<sub>2</sub> radical is of considerable interest. It is postulated as an intermediary in various reactions and until this work was completed it had not been experimentally detected. It was hoped by carrying out fundamental calculations—by the method known as configuration interaction—to make predictions which although approximate would provide a good working estimate of the dimensions and properties of the radical.

Here we report the most significant results which have been obtained. These comprise the energies of three stationary states for a considerable range of atomic arrangements including six different angles. The calculations were performed with a full configurational interaction scheme based on eight primary expansion functions. The calculations have provided an opportunity to test and develop new methods. They have also shown that it would be fruitful to make other analyses and extensions of this examination, but it appears valuable first to make available the present results. At the present, the clearest information on the accuracy of the results is a comparison with the results predicted by using the same expansion functions for CH and C systems, and these data are also reported.

Two points which have aroused particular interest are the energy order of the states and the size of the HCH angle. Let the symmetric CH<sub>2</sub> radical lie in the *yz* plane, with the *z* axis as the bisector of the HCH angle. We denote the four representations as *A*<sub>1</sub>, *A*<sub>2</sub>, *B*<sub>1</sub>, *B*<sub>2</sub>, where *A*<sub>1</sub> is the totally symmetric representation and *x* transforms by *B*<sub>1</sub>, *y* by *B*<sub>2</sub>, and *xy* by *A*<sub>2</sub>. The three states for which the detailed calculations have been performed are <sup>3</sup>*B*<sub>1</sub>, <sup>1</sup>*A*<sub>1</sub>, and <sup>1</sup>*B*<sub>1</sub>. The calculations predict these to have increasing absolute energy in this order for the linear and bent equilibrium positions. For the linear case this is in accordance with Hund's rule, where these states become <sup>3</sup>Σ<sup>-</sup> and the degenerate levels of <sup>1</sup>Δ, respectively. In order to determine the equilibrium positions of the three states and their force constants, the wave functions were calculated for a considerable number of nuclear positions, a total of thirteen. Six of these were placed at constant radius (2.15 a.u.), the HCH angle varying from 80° to 180° in steps of 20°. The remaining six symmetric ones were placed to enclose the minima of the states, the thirteenth being asymmetric.

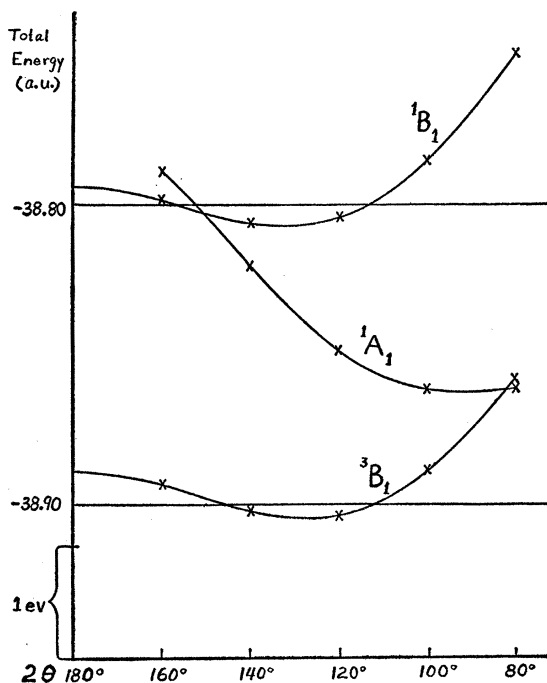
A scale factor has been included in the calculation, multiplying the dimensions and dividing the exponents of the basic functions. This scale factor can be taken into account at the last stage in the calculations, the

eigenvector process, and hence easily varied. Values of 1.6, 1.625, and 1.65 were used, subsequent dimensions are given in terms of a scale factor of 1.625, except where explicit reference is made to units.

The basic functions used were, on the carbon atom, exp(-4*r*<sub>C</sub>), exp(-3*r*<sub>C</sub>), *r*<sub>C</sub> exp(-*r*<sub>C</sub>), *x*<sub>C</sub> exp(-*r*<sub>C</sub>), *y*<sub>C</sub> exp(-*r*<sub>C</sub>), and *z*<sub>C</sub> exp(-*r*<sub>C</sub>), and on each of the hydrogen atoms, exp(-0.75*r*<sub>H</sub>). It is seen that two functions have been used to represent the carbon 1*s*, the exponents lying on either side of the Slater value. By varying the distances and angles and the scale factor, a measure of independent variation has been introduced in all the parameters except the hydrogen exponent. It was not practicable to vary the hydrogen exponent for all sets of the nuclear positions, and this variation was carried out only for one. The values of 1.0, 1.2, and 1.4 a.u. were used, and the minimum occurred at 1.2 a.u. It is reasonable that the best value should be greater than 1 a.u. owing to the attraction of the carbon nucleus. Accordingly, 0.75 in the unstretched scale was used throughout the remainder of the work.

The integrals were calculated on the automatic computer EDSAC 2 using programs written by I. Jones and the authors. The largest errors occurred in the three center and exchange integrals, but tests on similar integrals show that no error was liable to be greater than 0.0006 a.u., the average run of errors being about 0.0002 a.u. It is the absolute rather than the relative error which is of importance here. These integrals were about forty in number and errors in the remaining types were less than 10<sup>-5</sup>. This degree of accuracy was considered satisfactory especially as the errors were liable to vary smoothly with change of parameters. The integrals were automatically assembled by a further program and transformed to correspond to orthonormal functions. No hand calculation or manipulation of numbers intervened between the original specification and the transformed integrals, a fruitful source of errors being thus avoided.

In order not to miss unsuspected features in the wave functions, the eigenvector calculation was carried out with large numbers of determinantal expansion functions, 128 in the <sup>3</sup>*B*<sub>1</sub> case. The results suggest that this was very unnecessary since many very small terms were found and these appeared very unlikely to affect any physical prediction. It is difficult to be certain of this since it is impossible to foresee all the ways in which these results might be used for further deductions. The choice of the transformation to orthogonal functions was made by arbitrarily deciding on an initial

FIG. 1. Variation of energy of CH<sub>2</sub> with angle 2θ.

transformation and making such an adjustment that the eigenvector coefficients of the functions obtained by making single replacements in the function of largest coefficient were reduced to an acceptable level (10% of the largest). A standard process was used for all the configurations. The determinantal functions then used in the eigenvector process were all those obtained by single and double replacements in the function of largest coefficient. The very large number of functions thus produced made it unnecessary to be very precise in the choice of the transforming matrix.

Some of the resulting properties are given in Table I. The force constants are defined by the relation

$$2\delta E = A_{11}(\delta r_1 + \delta r_2)^2/4 + 2A_{12}(\delta r_1 + \delta r_2)(R\delta\theta)/4 + A_{22}(R\delta\theta)^2/4 + A_{33}(\delta r_1 - \delta r_2)^2/4.$$

The angular minima occur at 90° for <sup>1</sup>A<sub>1</sub> and at about

TABLE I. Calculated properties of the equilibrium positions of the three lowest states of CH<sub>2</sub>. All results are given in atomic units.

	<sup>3</sup> B <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> B <sub>1</sub>
Total energy	-38.904	-38.865	-38.808
HCH angle, θ	129°	90°	132°
CH distance, R	2.11	2.21	2.11
Scale factor	1.656	1.645	1.640
Force constants			
A <sub>11</sub>	0.719	0.736	0.602
A <sub>12</sub>	0.027	0.051	0.035
A <sub>22</sub>	0.118	0.094	0.125
A <sub>33</sub>	0.877	0.866	0.775

TABLE II. Comparison of calculated and experimental properties of CH and C. All results are given in atomic units.

	Calc	Exptl. <sup>a</sup>
Total energy		
CH <sup>2</sup> Π	-38.254	-38.468
CH <sup>2</sup> Σ <sup>-</sup>	-38.120	-38.350
C <sup>3</sup> P	-37.668	-37.841
C <sup>1</sup> D	-37.594	-37.795
Energy difference		
CH <sup>2</sup> Π - <sup>2</sup> Σ <sup>-</sup>	-0.134	-0.118
C <sup>3</sup> P - <sup>1</sup> D	-0.074	-0.046
Bond length		
CH <sup>2</sup> Π	2.26	2.12
CH <sup>2</sup> Σ <sup>-</sup>	2.45	2.24
Force constant		
CH <sup>2</sup> Π	0.369	0.288
CH <sup>2</sup> Σ <sup>-</sup>	0.246	0.227

<sup>a</sup> See reference 3.

130° for the B<sub>1</sub> states. Walsh<sup>1</sup> gives reasons for supposing that the B<sub>1</sub> states should have larger angles than the A<sub>1</sub>, though he suggests that the B<sub>1</sub> should be nearly linear. In Fig. 1 a graph of the variation of energy with angle at constant bond length is given. The <sup>1</sup>A<sub>1</sub> and <sup>1</sup>B<sub>1</sub> states should be degenerate at 180°, but the fact that different numbers of determinantal functions have been used in the two eigenvectors has led to less accuracy in the <sup>1</sup>A<sub>1</sub> case, and this accordingly appears with higher energy. The B<sub>1</sub> curves are far from parabolic about the minima, and hence the significance of the angular force constants for these states is somewhat uncertain.

No experimental data are available for CH<sub>2</sub>, but the experimental values of twice the CH stretching force constant<sup>2</sup> (corresponding approximately to A<sub>11</sub> and A<sub>33</sub>) are 0.64 a.u. for CH<sub>4</sub> and 0.66 a.u. for C<sub>2</sub>H<sub>2</sub>. The typical CH bond length in many compounds is from 2.0 to 2.1 a.u. It is difficult to find experimental data corresponding to a CH<sub>2</sub> bending force constant which are not complicated by other effects. It is simplest to note that the calculated value is about half that observed for H<sub>2</sub>O and this appears reasonable. The probable accuracy of the results is of considerable interest and, accordingly, similar calculations using the same integrals have been performed for two states of the CH radical and for two of the C atom. The results and corresponding experimental values are summarized in Table II.<sup>3</sup> The calculated bond lengths are somewhat larger than the experimental, as seems often to be the case in this type of calculation. The error in the calculated difference <sup>1</sup>D - <sup>3</sup>P for C is 0.03. This appears to be due largely to the correlation difference omitted by the small number of functions. There appears to be

<sup>1</sup> W. D. Walsh, J. Chem. Soc. 1953, 2260.

<sup>2</sup> J. W. Linnett, Trans. Faraday Soc. 41, 223 (1945).

<sup>3</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 518.

slightly more facility for correlation in the  ${}^1A-{}^3B$  for CH<sub>2</sub>. On this basis, the error would be less than 0.03 and the calculated 0.039 for  ${}^1A_1-{}^3B_1$  should be less but still with the same sign.

In conclusion, we may say that these calculations provide a reasonable estimate of the structure and properties of the three lowest states of the CH<sub>2</sub> radical. The  ${}^3B_1$  state has been found to have the lowest energy, but the difference in energy below that of the  ${}^1A_1$  is so small that there could be doubt about this. However, a

detailed assessment of the possible error suggests that this order is true.

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## Calculations on the Electronic Structure of the Normal State of Formaldehyde\*

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#### INTRODUCTION

THE electronic structure of the formaldehyde molecule has been the subject of considerable discussion.<sup>1,2</sup> Some quantitative calculations<sup>3,4</sup> have been made of wave functions localized in the C-O bond, in which use has been made of experimental data on dipole moments, ionization and excitation energies. In view of the basic importance of the carbonyl group in the molecular structure of organic compounds, we believed that a self-consistent-field calculation in the LCAO approximation, which included all sixteen electrons of the molecule, would be justified.

Some simplifying assumptions must be made in a calculation of this magnitude, the first of which is that the normal state can be represented by a single determinantal wave function corresponding to a configuration of closed electron shells. Recent calculations<sup>5-12</sup>

which included the interactions of all electrons have shown that this assumption may lead to fairly good results for the total energy, for the lower ionization potentials and perhaps for the dipole moment. We might expect rather poor results for the transition energies and intensities to the lower excited electronic states, because of neglect of interaction of other configurations. But a calculation based on the most probable single configuration represents a necessary preliminary stage. The present calculation follows the formal method of Roothaan<sup>13</sup> for closed-shell states.

The second simplification is the limitation of basic atomic orbitals to (1s), (2s), and (2p) functions of the C and O atoms and to (1s) of H. This also might be expected to have only a small effect on the energy of the normal state, but might have a fairly large effect on the dipole moment. A third simplification concerns the forms of orbitals, which were taken here to have the usual Slater forms with fixed orbital exponents. A linear combination of such exponential forms which approximated Hartree-Fock functions might have been better. In view of the very large number of integrals over atomic orbitals which would have been required, this refinement appeared impracticable.

#### MOLECULAR GEOMETRY, BASIC ORBITALS, AND METHOD

In its normal state, formaldehyde is planar, and belongs to the symmetry group  $C_{2v}$ . The molecular dimensions used in the calculations are shown in Fig. 1, with distances in atomic units. The dimensions were

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<sup>3</sup> J. Sidman, *J. Chem. Phys.* **27**, 429 (1957).

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<sup>12</sup> (B<sub>2</sub>): A. A. Padgett and V. Griffing, *J. Chem. Phys.* **30**, 1286 (1959).

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