

slightly more facility for correlation in the ${}^1A-{}^3B$ for CH₂. 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 CH₂ 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.^{1,2} Some quantitative calculations^{3,4} 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 calculations⁵⁻¹²

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 Roothaan¹³ 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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² H. L. McMurry, *J. Chem. Phys.* **9**, 231 (1941).

³ J. Sidman, *J. Chem. Phys.* **27**, 429 (1957).

⁴ J. M. Parks, Ph.D. thesis, Carnegie Institute of Technology (1956).

⁵ (N₂): C. W. Scherr, *J. Chem. Phys.* **23**, 569 (1955).

⁶ (H₂O): F. O. Ellison and H. Shull, *J. Chem. Phys.* **23**, 2348 (1955).

⁷ (BH): R. C. Sahni, *J. Chem. Phys.* **25**, 332 (1956).

⁸ (NH₃): H. Kaplan, *J. Chem. Phys.* **26**, 1704 (1957).

⁹ (Li₂): J. E. Faulkner, *J. Chem. Phys.* **27**, 369 (1957).

¹⁰ (NH₃): A. B. F. Duncan, *J. Chem. Phys.* **27**, 423 (1957).

¹¹ (Diatomic hydrides): M. Krauss, *J. Chem. Phys.* **28**, 1021 (1958).

¹² (B₂): A. A. Padgett and V. Griffing, *J. Chem. Phys.* **30**, 1286 (1959).

¹³ C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

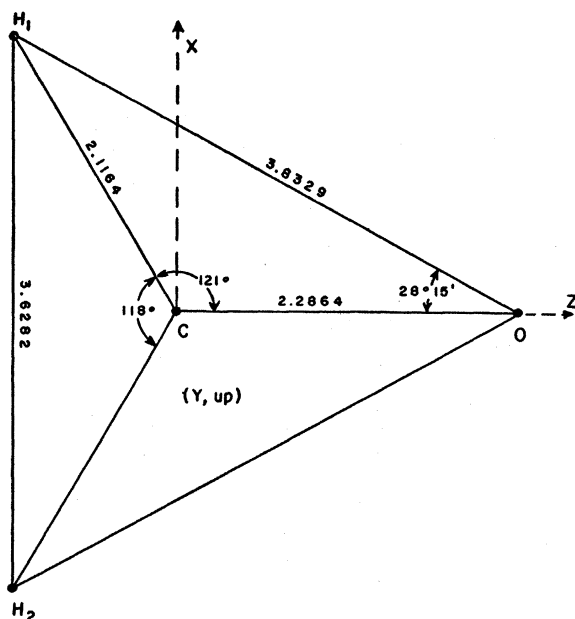


FIG. 1. Dimensions of the formaldehyde molecule.

obtained from microwave data¹⁴:

$$r(\text{C}-\text{H}) = 1.12 \pm 0.01 \text{ \AA}; \quad r(\text{C}-\text{O}) = 1.21 \pm 0.01 \text{ \AA}; \\ \text{H}-\text{C}-\text{H} \text{ angle} = 118^\circ \pm 2^\circ.$$

The origin of coordinates for the molecule as a whole is taken at the C atom, with the z axis directed along the C-O line toward O. The molecular plane is xz .

The MO trial functions are linear combinations of atomic orbitals of proper symmetry. There are seven MO with symmetry A_1 constructed from the s and $2p_z$ functions of C and O and the normalized combination $[(1s)_{\text{H}_1} + (1s)_{\text{H}_2}]$; three MO with symmetry B_1 from the combination $[(1s)_{\text{H}_1} - (1s)_{\text{H}_2}]$ and $(2p_x)$ functions of C and O; two MO of symmetry B_2 from $(2p_z)$ of C and O. Eight of these MO are occupied in the closed-shell configuration of the normal state. We supposed originally (and found) that five of these occupied orbitals were of symmetry A_1 , two of B_1 , and one of B_2 .

The explicit forms of the MO are:

$$\phi_i(A_1) = \sum_p a_{ip} \chi_p(A_1), \quad i = 1 \dots 7.$$

The χ_p are:

$$k_{\text{C}} = (1s)_{\text{C}} = (c_1^3/\pi)^{1/2} \exp(-c_1 r_{\text{C}}), \\ k_{\text{O}} = (1s)_{\text{O}} = (c_2^3/\pi)^{1/2} \exp(-c_2 r_{\text{O}}), \\ s_{\text{C}} = 1.025228956(2s)_{\text{C}} - 0.2260407333k_{\text{C}}, \\ s_{\text{O}} = 1.028415655(2s)_{\text{O}} - 0.2400807363k_{\text{O}}, \\ z_{\text{C}} = (2p_z)_{\text{C}} = (c_3^5/\pi)^{1/2} \exp(-c_3 r_{\text{C}}) \cos\theta, \\ z_{\text{O}} = (2p_z)_{\text{O}} = (c_4^5/\pi)^{1/2} \exp(-c_4 r_{\text{O}}) \cos\theta,$$

¹⁴ R. B. Lawrance and M. W. P. Strandberg, Phys. Rev. **83**, 363 (1951).

$$H_z = 0.6351275485(h_1 + h_2), \\ (2s)_{\text{C}} = (c_3^5/3\pi)^{1/2} \exp(-c_3 r_{\text{C}}), \\ (2s)_{\text{O}} = (c_4^5/3\pi)^{1/2} \exp(-c_4 r_{\text{O}}), \\ h_i = (1s)_{\text{H}_i} = (\pi)^{-1/2} \exp(-r_{\text{H}_i}),$$

$$\int h_1 h_2 dV_1 = 0.239504486; \quad \int (2s)_{\text{C}} k_{\text{C}} dV_1 = 0.22047829;$$

$$\int (2s)_{\text{O}} k_{\text{O}} dV_1 = 0.23344718,$$

$$c_1 = 5.7; \quad c_2 = 7.7; \quad c_3 = 1.625; \quad c_4 = 2.275.$$

The B_1 orbitals are:

$$\phi_i(B_1) = \sum_p a_{ip} \chi_p(B_1), \quad i = 8, 9, 10.$$

The χ_p are:

$$x_{\text{C}} = (2p_x)_{\text{C}} = (c_3^5/\pi)^{1/2} \sin\theta \cos\phi, \\ x_{\text{O}} = (2p_x)_{\text{O}} = (c_4^5/\pi)^{1/2} \sin\theta \cos\phi, \\ H_x = 0.8108428169(h_1 - h_2).$$

The B_2 orbitals ϕ_{11} and ϕ_{12} contain only y_{C} and y_{O} which are defined as x_{C} , x_{O} with $\cos\phi$ replaced by $\sin\phi$.

The secular equation of the variational problem is

$$(\mathbf{H} + \mathbf{G})\mathbf{a}_i = \epsilon_i \mathbf{S}\mathbf{a}_i, \quad (1)$$

where \mathbf{H} , \mathbf{G} , and \mathbf{S} are 12 by 12 matrices with elements of the operators H , G and unity evaluated over the preceding atomic orbitals, and in the present problem

$$H = -\frac{1}{2}\nabla^2 - 1/r_{\text{H}_1} - 1/r_{\text{H}_2} - 6/r_{\text{C}} - 8/r_{\text{O}}, \\ G = \sum (2J_i - K_i),$$

where the sum is over occupied orbitals and the operators J_i and K_i are defined elsewhere.¹³ The elements of \mathbf{G} are functions of the a_{ip} , the components of \mathbf{a}_i in Eq. (1), and so an iterative solution of (1) is required.

The starting values of the a_{ip} were based on earlier discussions.¹⁻³ Three of the A_1 orbitals were assumed to be pure k_{C} , k_{O} , and s_{O} . The other two were made from assumed CH_2 group functions, one in which s_{C} and another in which z_{C} predominated, combined with arbitrarily hybridized O functions. The nonorthogonality of these functions was automatically removed in the first iteration. As B_1 functions we chose almost pure x_{O} and a reasonable bonding function. For the B_2 function, the coefficients were chosen to conform to classical ideas of C-O polarity.

The iteration procedure was completely programmed for the IBM 650 so that any number of iterations could be made in automatic sequence. At each stage the eigenvalues and vectors, the total energy, and the dipole moment were printed out for inspection. Each iteration required about twenty minutes, about half of which was taken in the eigenvalue solution.

TABLE I. Wave functions for formaldehyde.

	H_z	(1s) _C	(2s) _C	(2p _z) _C	(1s) _O	(2s) _O	(2p _z) _O	ε(ev)
φ ₁	0.647	-0.0350	-0.375	-0.336	0.0236	0.447	0.592	-19.25
φ ₂	-0.167	0.0250	-0.697	0.312	0.0112	0.448	0.243	-21.94
φ ₃	-0.150	-0.0368	0.372	-0.0127	-0.0262	0.807	-0.207	-38.73
φ ₄	-0.00139	1.00033	0.0193	0.00626	-0.00093	-0.00774	0.000786	-309.14
φ ₅	-0.0179	-0.00103	-0.00231	-0.0425	1.00267	0.0366	-0.0173	-562.88
φ ₆	0.796	-0.0142	0.101	1.298	-0.0729	-0.746	0.595	8.63
φ ₇	1.159	-0.164	-1.409	-0.043	0.0479	0.431	-0.786	16.65
	H_z	(2p _x) _C	(2p _x) _O	(2p _y) _C	(2p _y) _O	ε(ev)		
φ ₈	-0.3684	-0.2704	0.9054	-11.53		
φ ₉	0.4300	0.4892	0.433	-22.10		
φ ₁₀	1.175	-1.211	0.227	28.84		
φ ₁₁	0.655	0.626	-15.08		
φ ₁₂	0.788	-0.812	6.15		

RESULTS AND DISCUSSION

The SCF functions with their orbital energies are shown in Table I. Other calculated quantities are compared with experimental values in Table II. A total of twenty iterations was required to obtain these values.

Some elementary features are apparent from inspection of the MO functions. It is obvious first that φ₄ and φ₅ are predominantly k_C and k_O . The corresponding orbital energies are in good agreement with calculations on other molecules and are in moderately good agreement with experimental values.¹⁵ φ₈ is largely x_O and it has the highest orbital energy, as has been generally expected. An unexpected result is the apparent homopolar nature of φ₁₁ (or the π) orbital. This orbital is

TABLE II. Energy data on formaldehyde.

	Computed	Experimental
Total electronic energy	-144.705 (e^2/a_0)	...
Repulsion of nuclei	31.114	...
Total molecular energy	-113.591	-114.550
Energy of separated atoms	-113.151	-113.964
Dissociation energy	0.440	0.586

associated with considerably larger energy than the next to highest experimental ionization potential,^{16,17} but the energy is in good agreement with the prediction of Mulliken¹ for π orbital ionization. This large value was maintained after the first seven iterations in spite of rather large fluctuations in the coefficients of φ₁₁.

Interpretation of the A_1 orbitals is facilitated by the results of an overlap population analysis¹⁸ shown in Table III. A gross population analysis was made also

¹⁵ J. Thibaud, Compt. rend. 186, 308 (1928).

¹⁶ T. M. Sugden and W. C. Price, Trans. Faraday Soc. 44, 116 (1948).

¹⁷ We are grateful to Professor C. A. McDowell for information on his recent (unpublished) experimental work on ionization potentials of formaldehyde. He finds three ionization potentials below 14 eV, the lowest two of which compare well to the results of reference 16.

¹⁸ R. S. Mulliken, J. Chem. Phys. 23, 1833, 1841, 2338, 2343 (1955).

with the results (atomic orbital followed by population): h_1 , 0.90; h_2 , 0.90; k_C , 2.00; s_C , 1.42; z_C , 0.63; x_C , 1.01; y_C , 1.04; k_O , 2.01; s_O , 1.97; z_O , 1.08; x_O , 1.98; y_O , 0.96. The total for each atom, over all atomic orbitals, is: 2h, 1.80; C, 6.10; O, 8.10.

Although the orbital energy of a MO is not correlated directly with a corresponding total overlap population of the orbital, the latter quantity may be taken to give a measure of the "covalent binding strength" of an electron in the orbital. Thus φ₂, φ₃, φ₉, and φ₁₁ are classed as bonding orbitals. φ₁ is apparently antibonding on the same basis, but details show that this character comes largely from H_z-s_C overlap, and this orbital shows bonding character elsewhere. φ₄ and φ₅ are non-bonding. φ₈ is only slightly antibonding and corresponds to the classical idea of lone pair (n) electrons on oxygen in carbonyl compounds. From these analyses and inspection of the wave functions, it is evident that s_O mixes extensively with other orbitals, contrary to expectation of a nearly pure s_O molecular function, which was one of the starting functions in this calculation. There is seen to be a promotion of 0.03e from s_O to (2p)_O. Previous calculations¹⁸ on CO and on H₂O gave 0.19e for this promotion.

The resultant dipole moment in the +z direction is calculated as +0.62 debye, corresponding to H₂C⁻-O⁺. The experimental value¹⁹ is given as 2.34 debye, sense undetermined. An analysis of the individual contributions to the moment shows that the total moment is highly dependent on and extremely sensitive to the form of φ₁₁. We believe that the ratio of coefficients and energy of this orbital are the most unsatisfactory features of the entire calculation. If we could have obtained an orbital [$a(y_C)+b(y_O)$] with b/a about equal to 1.5 instead of 0.956, the dipole moment would approach the experimental value more closely, and widely accepted ideas of polarity in this orbital would be justified. But it is clearly impossible to obtain such a function from the present set of integrals. The gross atomic populations for each atom are consistent with the low value of the dipole moment found in this cal-

¹⁹ J. M. Shoolery and A. H. Harbaugh, Phys. Rev. 82, 95 (1951).

TABLE III. Overlap population analysis.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5		ϕ_8	ϕ_9	ϕ_{11}
h_1h_2	0.162	0.011	0.009	h_1h_2	-0.086	-0.116	...
H_2k_C	-0.008	-0.002	0.002	-0.001	...	H_2x_C	0.254	0.537	...
H_2s_C	-0.680	0.326	-0.156	H_2x_O	-0.097	0.054	...
H_2z_C	0.261	0.063	-0.002	x_Cx_O	-0.214	0.185	...
H_2k_O	0.001	-0.001	-0.001				
H_2s_O	0.161	-0.042	-0.067	y_Cy_O	0.359
H_2z_O	-0.163	0.017	-0.013				
k_Ck_O				
k_Cs_O	-0.002	0.002	-0.004	-0.001	...				
k_Cz_O	0.005	-0.001	-0.002				
s_Ck_O	-0.002	-0.001	-0.002				
s_Cs_O	-0.255	-0.476	0.457				
s_Cz_O	0.269	0.206	0.093				
z_Ck_O	-0.002	0.001	-0.012				
z_Cs_O	-0.276	0.257	-0.019	...	-0.003				
z_Cz_O	0.243	-0.093	-0.003	...	-0.001				
Total	-0.286	0.267	0.293	-0.002	-0.017		-0.143	0.660	0.359

ulation. A net transfer of charge away from H_2 is indicated but no transfer of charge between C and O is apparent, with the result that the centers of electronic and nuclear charge are almost coincident.

The experimental dissociation energy is obtained from thermochemical data on the dissociation of H_2CO into H_2+CO at $25^\circ C$ and spectroscopic dissociation energies of the diatomic molecules. No reliable data were available for correction of the thermochemical data to $0^\circ K$. The experimental atomic terms²⁰ were added to get a value of the total molecular energy. The calculated total energy shows about the same agreement with the experimental value as has been obtained in calculations on other molecules, but this agreement should not be overemphasized. It may be argued that the closeness of agreement in an approximate calculation should be viewed with some suspicion, and we have made every effort to find residual numerical errors, without any success. These doubts also apply to the dissociation energy, which appears to approach the experimental value too closely. Since the computed atomic terms agree exactly with results of other calculations in which identical atomic orbitals were used, the doubts lie wholly in the calculated molecular energy.

The excitation energy of the $n-\pi^*$ singlet-singlet transition was computed from the orbital energies of ϕ_8 and ϕ_{12} , and the interaction integrals ($\phi_8\phi_8:\phi_{12}\phi_{12}$), ($\phi_8\phi_{12}:\phi_8\phi_{12}$). The computed value 3.04 ev is in moderate agreement with the experimental value, 4.3 ev. For the singlet-triplet transition we computed 2.95 ev (experimental, 3.0 ev). Calculation of the $\pi-\pi^*$ singlet-singlet transition gave very poor agreement with experiment (16.6 ev compared with 8.0 ev), and the calculated singlet-triplet separation for this transition was 10.9 ev. A reasonable value for this separation appears to be about 4.2 ev. Apparently this low value can be reached only through empirical adjustment of the interaction integral ($\phi_{11}\phi_{12}:\phi_{11}\phi_{12}$), which depends primarily on the basic integrals $y_Cy_C:y_Cy_C$, $y_Oy_O:y_Oy_O$,

and $y_Cy_C:y_Oy_O$. The coefficients in ϕ_{11} and in ϕ_{12} do not affect greatly the value of this interaction integral.

COMPUTATIONAL METHODS

The computation of integrals over atomic functions constitutes the major factor in a problem of this nature. Some remarks on our experience in a large scale problem may be of interest.

One- and two-center one-electron integrals were all calculated from standard analytical formulas. Wherever possible they were calculated from two different formulas as a check. Hand-computed integrals were always done independently by two workers. Two-electron mononuclear and two-center Coulomb integrals were calculated from formulas of Roothaan²¹ or interpolated from tabulated values based on these formulas. Fortunately a large fraction of integrals of the preceding types could be checked from published results of others. A few hybrid integrals with three (1s) functions and the two-center hydrogen exchange integral were also evaluated by analytical formulas.

All other results were obtained by expansion of all orbital functions onto one center by the method of Coulson and Barnett²² followed by numerical integration of radial parts. For one radial variable, integrands were evaluated at 40 points on a scale which was more closely spaced in the regions of maximum integrand values. The integrations were accomplished by Simpson's rule programed for the IBM 650. Comparison with analytical evaluation of corresponding cases showed that final integral values were accurate to at least three significant figures. For this accuracy it was usually sufficient to terminate the infinite series resulting from the expansions at a value of five for all sum-

²¹ C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

²² C. A. Coulson and M. P. Barnett, Phil. Trans. Roy. Soc. (London) **A243**, 221 (1951). See also: "Conference on Quantum Mechanical Methods in Valence Theory," Shelter Island, New York, 1951, p. 238 (unpublished); M. P. Barnett, University of Wisconsin Naval Research Laboratory Report, Wisconsin-WISONR-29 (February 14, 1958).

²⁰ C. E. Moore, Natl. Bur. Standards Circ. 467 (1949).

mation indices. In all cases the radial parts of the integrals converged fairly rapidly, but for some angles the over-all convergence was retarded by the angular factors. In such cases the radial integrals were extrapolated to give higher terms in the summation. For all but the most simple integrals, programs were designed to accomplish all numerical work leading to a complete final but usually unnormalized integral. Most of the hybrid integrals and the Coulomb and one-electron three-center integrals were evaluated in this way.

Two- and three-center exchange and four-center integrals require numerical integration over two radial variables, and these cases were treated by an extension of Simpson's rule to a 40 by 40 mesh. The actual evaluation was accomplished elsewhere.²³ The values of these radial integrals were used as part of the input

²³ About 3200 independent radial integrals were required. About half were required in the 28 four-center integrals. We are very grateful to the Office of Ordnance Research, U. S. Army, for aid in evaluation of these integrals on an EDVAC electronic computer, at the Ballistic Research Laboratories.

to IBM 650 programs which calculated corresponding angular factors, multiplied these by the radial factors and summed to give the final unnormalized integrals. The computation of angular factors for the four center integrals²⁴ was extremely complicated because of the multiple summations, and was one of the most time-consuming features of the work. A list of all integrals used in this work is available.²⁵

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²⁴ M. P. Barnett, University of Wisconsin Naval Laboratory Report, University of Wisconsin-WIS-ONR-30 (March 25, 1958).

²⁵ A limited number of copies can be obtained from A. B. F. Duncan.