

Formaldehyde Molecule in a Gaussian Basis. One-Electron Properties

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Numerous one-electron properties of the formaldehyde molecule have been calculated using Hartree-Fock-Roothaan wavefunctions obtained from three different basis sets: an unoptimized minimum basis set of Slater orbitals, a (73/2) Gaussian basis set, and a (95/3) Gaussian basis set. Comparison of the calculated and experimental values is made whenever possible, the agreement in most cases being satisfactory. Use of the more flexible Gaussian wavefunctions results in significant improvements in many of the properties. Consideration of the atoms shows that no appreciable error arises from the use of Gaussian orbitals as expansion functions for the solution of the Hartree-Fock equations. Even though the best wavefunction is near the (*sp*) limit, some properties (such as the dipole moment and forces) are still inadequately described. Such a basis set is just not sufficient to describe the polarizations of the atoms caused by molecular formation. Inclusion of *d* orbitals in the basis set should substantially improve such properties.

INTRODUCTION

It is now possible to calculate increasingly accurate Hartree-Fock-Roothaan wavefunctions for a number of small polyatomic molecules.¹⁻⁵ This has been achieved through the use of Gaussian orbitals as expansion functions for the Hartree-Fock molecular orbitals.⁶ Although Slater orbitals have a number of conceptual advantages, at the present time Gaussian orbitals are, by far, the most economical. Now that such wavefunctions are available, we must try to retrieve as much information as possible from them. It is no longer sufficient to calculate just the energy and the wavefunction.

In this paper we present numerous one-electron properties of formaldehyde in three basis sets: an unoptimized minimum basis set of Slater orbitals,⁷ a (73/2) Gaussian basis set, and a (95/3) Gaussian basis set. Wavefunctions, energies, and population analyses for the Gaussian sets have been reported in a previous paper.⁵ The electronic contributions to each property are listed by orbital in order to fully elucidate the final answer and to provide an interpretive framework for the discussion of the results. The reader is urged to correlate any ideas that he might have about the electronic structure of formaldehyde with the various weightings of the orbitals. Since the Hartree-Fock molecular orbitals can be given an independent-

particle interpretation, it would seem necessary to accord these orbitals the consideration which befits their role. After all, one of the objectives of accurate calculations on small molecules is to provide a basis for understanding the electronic structure of larger molecules. Since the molecular orbitals are the building blocks of the Hartree-Fock theory of molecular structure, an understanding of their basic character is required if we are to understand "what electrons are really doing in molecules."⁸ In a subsequent paper we shall analyze the information which may be obtained from contour maps of the electronic density and its various partitions.

Obviously, when discussing the Hartree-Fock theory of the electronic structure of molecules, the orbitals of greatest significance are the *true* Hartree-Fock orbitals. Unfortunately, such orbitals are known only for atoms and a number of diatomic molecules⁹ (and approximately for a number of linear polyatomic molecules¹⁰ and water^{1,2}). Most small, nonlinear polyatomic molecules remain outside the realm of such complete calculations and will be so for some time to come. In view of this, it is of interest to investigate a number of molecules in various basis sets in order to determine the reliability and information content of each type of set, e.g., unoptimized minimum basis sets, optimized minimum basis sets, double-zeta basis sets, (*sp*) limit basis sets, etc. In this way we can assess the accuracy of less extensive calculations on molecules which are too large to compute Hartree-Fock wavefunctions for. Also, it is possible that some comparatively small basis sets will be found to give reliable results over a limited range of interest so as to merit their use for larger molecular systems.

The formaldehyde molecule is a prototype for many theories of the electronic structure of large organic

* R. S. Mulliken, *The Vortex*, Calif. Sect. Am. Chem. Soc., Spring 1960.

⁹ A. C. Wahl, *J. Chem. Phys.* **41**, 2600 (1964); W. H. Huo, *ibid.* **43**, 624 (1965), and succeeding papers in this series.

¹⁰ A. D. McLean and M. Yoshimine, *IBM J. Res. Develop. Suppl.* **12**, 206 (1967).

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¹ H₂O: J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.* **43**, 3550 (1965); and D. Neumann and J. W. Moskowitz, *ibid.* **49**, 2056 (1968).

² H₂O: S. Aung, R. M. Pitzer, and S. I. Chan, *J. Chem. Phys.* **49**, 2071 (1968). This work uses an extended set of Slater orbitals.

³ H₂O, NH₃, and CH₄: C. D. Ritchie and H. F. King, *J. Chem. Phys.* **47**, 564 (1967).

⁴ C₂H₄: J. M. Schulman, J. W. Moskowitz, and C. Hollister, *J. Chem. Phys.* **44**, 2759 (1966).

⁵ H₂CO: N. W. Winter, T. H. Dunning, Jr., and J. H. Letcher, *J. Chem. Phys.* **49**, 1871 (1968).

⁶ S. F. Boys, *Proc. Roy. Soc. (London)* **A200**, 542 (1950).

⁷ M. D. Newton and W. E. Palke, *J. Chem. Phys.* **45**, 2329 (1966).

molecules containing carbonyl groups.¹¹ The results presented here thus provide a means of quantitatively assessing the accuracy of such semiempirical theories. Any approximations which may have been invoked, such as assuming that the so-called n orbital is a lone-pair p orbital on the oxygen, can be completely tested. The validity of other conjectures about the electronic structure of molecules can also be checked *numerically*. Those which prove suspect must be more completely examined and, if proven incorrect, suitably modified or discarded. At each point, however, we must keep the mathematical model with its own inherent shortcomings in clear perspective. One such theory which we feel requires further investigation is pi-electron theory.¹² In this and a subsequent paper we will interpret our results in a framework so as to illuminate some of the basic concepts of pi-electron theory. Our present results are of such a nature as to allow us to study only a small number of facets of the problem, but even so the results are often contrary to widely held beliefs. Future calculations on the excited states of formaldehyde will allow us to examine in detail the numerous approximations which arise in attempts to calculate the excited states of unsaturated molecules by considering only a specific number of the electrons, e.g., just the n and π electrons.

The calculations presented here also add to the catalog of results of Hartree-Fock-Roothaan calculations, examination of which will allow us to assess the shortcomings of this particular independent-particle scheme. Calculations on diatomic molecules⁹ illustrate, in agreement with Brillouin's theorem, that the expectation values of one-electron operators are given quite accurately by Hartree-Fock wavefunctions. The calculations presented here are in accord with this observation. The test is particularly critical in this case, for the formaldehyde molecule has been the object of an intensive experimental study by Flygare and his co-workers.¹³⁻¹⁶ This will be of great assistance to us, for it provides an additional means of determining the over-all accuracy of the proposed wavefunctions.

In the following discussion we will attempt to interpret the results in a physically meaningful manner and point out any features of general interest. In spite of the limited nature of the wavefunctions used here, we feel

that they contain a considerable amount of information about the electronic structure of formaldehyde. In most instances the effect of basis set truncation will be to subtly refine the orbitals rather than change their basic character. In summary, we feel that most of the conclusions drawn here will be essentially correct when referenced to the Hartree-Fock wavefunction.

A previous study of the one-electron properties of formaldehyde has been made.¹⁷ The ground-state wavefunction employed was that of Foster and Boys,¹⁸ which is a partially optimized minimum basis set of Slater orbitals. The geometry differs slightly from the geometry used here (as well as the experimental geometry). A comparison of the results of the single Slater calculations presented in this paper with these previous results illustrates the importance of the correct geometry and improved hydrogen exponents. Most of the differences are probably due to the change in the hydrogen exponent, although for properties such as the deuterium field gradients, which are highly sensitive to bond lengths,¹⁹ the change in geometry will also have a sizable effect.

THE ATOMS

One of the major deficiencies which arises in the LCAO-MO treatment of molecules is an inadequate description of the atoms of which the molecule is composed. However, this is not the only deficiency, and errors may arise from an imbalance of the basis set (i.e., a nonuniform description of the atoms no matter how inadequate that description may be), a neglect of atomic polarizations resulting from molecular formation, etc. Of these only the first can be examined beforehand, although empirical rules are being formulated to deal with the latter two.²⁰ To determine the possible effects of an inadequate description of the atoms, Table I lists a number of atomic properties calculated with the wavefunctions corresponding to basis sets discussed in this paper.²¹

All in all, we see that, excluding the density at the nucleus, the properties are given rather accurately by the Gaussian basis sets.²² The values of $\langle 1/r \rangle$ are the most accurate, which is to be expected since this operator plays a significant role in the variational

¹¹ T. Anno and A. Sadô, *J. Chem. Phys.* **26**, 1759 (1957); J. W. Sidman, *ibid.* **27**, 429 (1957); R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.* **54**, 757 (1958); F. L. Pilar, *J. Chem. Phys.* **47**, 884 (1967).

¹² R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1964).

¹³ Deuteron field gradients and hydrogen spin-rotation constants: W. H. Flygare, *J. Chem. Phys.* **41**, 206 (1964).

¹⁴ Molecular g values: W. H. Flygare, *J. Chem. Phys.* **42**, 1563 (1965), and W. Hüttner, M. Lo, and W. H. Flygare, *ibid.* **48**, 1206 (1968).

¹⁵ Oxygen (¹⁷O) spin-rotation constants and field gradients: W. H. Flygare and J. T. Lowe, *J. Chem. Phys.* **43**, 3645 (1965).

¹⁶ Carbon (¹³C) spin-rotation constants: W. H. Flygare and V. W. Weiss, *J. Chem. Phys.* **45**, 2785 (1966).

¹⁷ W. H. Flygare, J. M. Pochan, G. I. Kerley, T. Caves, M. Karplus, S. Aung, R. M. Pitzer, and S. I. Chan, *J. Chem. Phys.* **45**, 2793 (1966), and S. Aung, R. M. Pitzer, and S. I. Chan, *ibid.* **45**, 3457 (1966).

¹⁸ J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 303 (1960).

¹⁹ T. Caves and M. Karplus, *J. Chem. Phys.* **45**, 1670 (1966).

²⁰ A. D. McLean and M. Yoshimine, *J. Chem. Phys.* **47**, 3256 (1967), and Ref. 10.

²¹ The atomic wavefunctions are from S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965) and by D. Whitman (unpublished calculations), Case Institute of Technology, Cleveland, Ohio.

²² Except for the densities at the atoms the Hartree-Fock values were obtained from the series of papers: G. Malli and C. Froese, *Intern. J. Quantum Chem.* **1S**, 95, 99, 103 (1967). The densities at the atoms were calculated using the numerical Hartree-Fock program of C. Froese, *J. Chem. Phys.* **45**, 1417 (1966).

TABLE I. Comparison of the expectation values of a number of operators for the atoms in formaldehyde in the Slater and Gaussian bases with the Hartree-Fock values.^a

Operator	Single Slater ^b	(73) ^c	(95) ^c	HF ^d
Oxygen				
$1/r$	22.4771	22.2464	22.2581	22.2601
r^2	8.9223	10.4702	11.0640	11.1732
q_{zz}	-1.5700	-1.7297	-1.9483	-1.9896
$\delta(O)$	307.3899	281.8062	295.8610	311.6681
Carbon				
$1/r$	14.8164	14.6839	14.6857	14.6898
r^2	11.7692	13.2231	13.7205	13.7982
q_{zz}	0.5721	0.5882	0.6619	0.6767
$\delta(C)$	123.9203	113.7675	120.7608	127.4609
Operator	Single Slater	(2) ^c	(3) ^c	
Hydrogen				
$1/r$	1.0000	0.9716	0.9935	
r^2	3.0000	2.7970	2.9371	
$\delta(H)$	0.3183	0.1752	0.2327	

^a All the expectation values are in atomic units; for the conversion factors to cgs units see the appropriate table.

^b The orbital exponents are from Slater's rules (see Ref. 7). The atomic wavefunctions were calculated using the Atomic SCF Program No. 2 of Roothaan and Bagus.

^c The atomic wavefunctions were obtained from Ref. 21.

^d Calculated from information given in Ref. 22.

treatment of the atoms. The values of $\langle r^2 \rangle$ are also quite satisfactory. The incorrect asymptotic behavior of the Gaussian expansion functions evidently occurs too far out to seriously affect the expectation value.

The field gradients q_{zz} are essentially a measure of $\langle 1/r^3 \rangle$ for the atomic p orbitals. A comparison of the errors observed for this quantity and for $\langle \delta(r) \rangle$ with the expectation values discussed above indicate that the deviation of the atomic orbitals expanded in Gaussian basis functions from the true Hartree-Fock orbitals must occur very close to and considerably far out from the nucleus. Thus, these results suggest that for properties which go as $\langle r^i \rangle$ with $-3 \leq i \leq 3$, Gaussian orbitals as expansion functions are adequate if a sufficiently large basis set is used. However, the observation that the error in the density at the nucleus is $\sim 5\%$ even for the most refined wavefunction cautions against the use of such wavefunctions to describe properties which depend on an accurate description of the electron density in the immediate vicinity of the nucleus, e.g., nuclear spin-spin coupling constants.

Another facet of the molecular problem which we will consider briefly is the effect of molecular formation on the properties of formaldehyde. If the molecule was composed of noninteracting atoms, then the molecular density would be just a sum of the appropriate atomic densities (neglecting exchange effects). The differences between the properties computed in this approximation and those calculated from the molecular wavefunction indicate how the density is redistributed upon molecular

formation. Unfortunately, defining the appropriate atomic densities is somewhat of a problem for there are indeterminacies which arise when assigning the occupation numbers of the atomic p orbitals which are split into p_x , p_y , and p_z by the reduction in symmetry. This ambiguity is most pronounced for carbon, where we must make a choice between the configurations $C[(1s)^2(2s)^2(2p_x)(2p_y)]$, $C[(1s)^2(2s)^2(2p_x)(2p_z)]$, and $C[(1s)^2(2s)^2(2p_y)(2p_z)]$. The configuration $C[(1s)^2(2s)(2p_x)(2p_y)(2p_z)]$ must be ruled out, for it does not describe the ground state of carbon. Further, it would seem that one of the effects of molecular formation is hybridization of the atoms, and so we should not include this in the atomic descriptions. Fortunately, except for largely atomic effects which depend sensitively on the angular distribution of the electrons, such as the field gradient, the properties are not highly sensitive to the exact configuration assigned to the atoms. The results quoted here assign carbon a configuration $C[(1s)^2(2s)^2(2p_x)(2p_y)]$. This is obtained by determining the symmetries of the oxygen (see below) and hydrogen atom orbitals in C_{2v} symmetry and subtracting these from the molecular-orbital symmetries. Oxygen, it seems fairly obvious, should be assigned the configuration

$$O[(1s)^2(2s)^2(2p_x)(2p_y)(2p_z)].$$

This is consistent with our interpretation of both the oxygen atom and the formaldehyde molecule.

DIPOLE MOMENT

The dipole moment of a molecule is related to the expectation values of the coordinate operators by

$$\mu_\alpha(A) = \sum Z_N (R_{NA})_\alpha - \langle \psi^{(0)} | \sum (r_{iA})_\alpha | \psi^{(0)} \rangle, \quad (1)$$

where the first sum is over the nuclei (charge Z_N) and the second over the electrons. α denotes the component along one of the coordinate axes, (x, y, z). If the molecule has no net charge, then the distances may be measured from any convenient reference point, A. With the distances measured in atomic units, the above is in atomic units; the conversion factor from atomic units to debyes is given below Table II. Table II lists the dipole moments for the three basis sets investigated here referenced to the carbon atom as the origin of the coordinate system (A).

Like the population analyses, the orbital contributions to the dipole moment, in this case $-\langle z \rangle$, can be used in a semiquantitative sense in the interpretation of that orbital. The $\langle z \rangle$, or the z centroid, of an orbital is the average position of the orbital along the z axis. In the paragraph below we discuss the character of the molecular orbitals as revealed by the z centroid. This analysis should be compared with the corresponding discussion based on the population analyses in the previous paper.⁵

The lowest two orbitals are centered nearly on the carbon and oxygen nuclei, as would be expected of

inner-shell electrons, with only a slight polarization of each orbital toward the other atom. The $3a_1$ orbital, which might intuitively be considered as an oxygen $2s$ orbital, is considerably polarized in the direction of the carbon. This supports the results of the population analyses which indicated that this orbital was perturbed considerably by molecular formation. Mixtures of the next three orbitals, $4a_1$, $1b_2$, and $5a_1$, along with small amounts of $3a_1$ and $2b_2$, may be thought of as defining the one CO σ bond and the two CH bonds in an equivalent orbital scheme. Any such chemical interpretation of these orbitals is hampered by the delocalized nature of the canonical Hartree-Fock orbitals.

The most drastic change occurs in the $1b_1$, or π , orbital. The z centroid of this orbital in the single Slater basis indicates a nearly homopolar bond (the midpoint of the CO bond is $z=1.1432$), a fact which has been noted by numerous other authors.^{23,16} The Gaussian results, on the other hand, indicate that the π orbital is distinctly weighted toward the oxygen atom. The largest source of error in the description of the dipole moment by the single Slater set arises in the inaccurate description of this orbital.

The centroid of the $2b_2$, or n , orbital is less than half-way to the oxygen atom. If it were purely a $2p$ orbital on the oxygen, the centroid would be at the position of the oxygen atom. This result is in agreement with the population analyses, which also indicated a considerable amount of delocalization of this orbital, principally onto the hydrogens. This delocalization is strikingly portrayed in the electron density maps and substantiates the observations of others^{24,25} that the lone-pair

orbitals associated with atoms such as oxygen and nitrogen are not localized in the vicinity of that atom. Hartree-Fock theory in its canonical form just does not allow these orbitals to be localized.

That the dipole moment is given rather inaccurately by the large Gaussian basis set is in agreement with recent observations of the effects of d orbitals on this property.^{1,9,10} Addition of such orbitals are required to describe the effects of atomic deformations upon molecular formation. Their inclusion generally results in a reduction in the magnitude of the dipole moment and such is indicated here. The dipole moment is evidently quite sensitive to the detailed balance of the basis set, as might be expected since the corresponding operator weights much of the molecular region comparatively the same and since the dipole moment is a small difference between two much larger quantities. It is interesting to note that the (95/31) wavefunction of Harrison and Moskowitz²⁶ for water gave a dipole moment $\sim 20\%$ larger than that of the near Hartree-Fock (1062/42) wavefunction of Neumann and Moskowitz.¹

SECOND MOMENTS

The second moments of the charge distribution, i.e.,

$$\langle r_\alpha r_\beta \rangle = \langle \psi^{(0)} | \sum (\mathbf{r}_{iA})_\alpha (\mathbf{r}_{iA})_\beta | \psi^{(0)} \rangle, \quad (2)$$

are another means of determining the spatial extent of the molecule or of the individual molecular orbitals in any of the coordinate directions. They are especially important when the first moments, $\langle r_\alpha \rangle$, vanish because of symmetry.

One such orbital of interest is the π orbital. Due to the plane of symmetry of the π orbital, the first moment, $\langle y \rangle$, cannot be used to determine the spatial extent of that orbital above the plane of the molecule. However, $\langle y^2 \rangle$, which does not vanish, can. From the data in Table III, we note that the π density extends 3.16 a.u. above the molecular plane as measured by $\langle y^2 \rangle$. At the same time we see that for the σ density $\langle y^2 \rangle = 5.50$ a.u. While this result is due in part to the directional character of the π orbital, it is also an *indication* that the π electrons may be rather deeply embedded in the σ electron density. This point will be examined in more detail in a future publication. Then it will be shown that the σ and π electrons are not spatially separated from one another and, further, that the σ and π electron densities are comparable over that region of space in which most of the electronic density is located, both indicating that we should examine the problem of σ - π separability more closely.

As a further comment on the π orbital, we note that in relation to the atomic $2p$ orbital of oxygen, the π orbital of formaldehyde has expanded (1.17 vs 1.58), while with respect to the carbon $2p$ orbital it has

²⁶ D. Neumann (private communication). We wish to thank Dr. Neumann for sending us his unpublished calculations on water in a (95/31) Gaussian basis.

TABLE II. Dipole moment of formaldehyde, relative to the carbon atom.^{a, b}

	μ		
	Single Slater	(73/2)	(95/3)
Total	-0.2353	-1.0183	-1.1928
nuclear	16.1111	16.1111	16.1111
electronic	-16.3464	-17.1294	-17.3039
$1a_1^b$	-2.2857	-2.2858	-2.2858
$2a_1$	-0.0001	-0.0003	-0.0003
$3a_1$	-1.6892	-1.6469	-1.6325
$4a_1$	0.1300	0.1005	0.1039
$1b_2$	-0.4499	-0.4698	-0.4500
$5a_1$	-1.6139	-1.7244	-1.7584
$1b_1$ (π)	-1.1629	-1.4554	-1.5015
$2b_2$ (n)	-1.1015	-1.0826	-1.1274

^a In atomic units: 1 a.u. = 2.54158 D. From Eq. (1) with $\alpha = z$.

^b The orbitals are listed in order of increasing orbital energies (see Tables II-IV of Ref. 5).

²³ P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, Rev. Mod. Phys. **32**, 307 (1960).

²⁴ E. Clementi, H. Clementi, and D. R. Davis, J. Chem. Phys. **46**, 4725 (1967), and succeeding papers in this series.

²⁵ D. E. Freeman and W. Klemperer, J. Chem. Phys. **45**, 52 (1966).

TABLE III. Second moments of formaldehyde, referenced to the center of mass.^{a-d}

	$\langle x^2 \rangle$		$\langle y^2 \rangle$		$\langle z^2 \rangle$		$\langle r^2 \rangle$	
	(73/2)	(95/3)	(73/2)	(95/3)	(73/2)	(95/3)	(73/2)	(95/3)
Total	15.0743	15.0858	8.6567	8.7717	37.2580	37.3706	60.9890	61.2280
1a ₁	0.0177	0.0177	0.0177	0.0177	1.3189	1.3190	1.3543	1.3544
2a ₁	0.0326	0.0325	0.0326	0.0325	1.3432	1.3431	1.4084	1.4082
3a ₁	0.5279	0.5283	0.5128	0.5115	0.9584	0.9438	1.9991	1.9836
4a ₁	1.4380	1.4190	0.7307	0.7116	4.2252	4.2057	6.3939	6.3362
1b ₂	2.2124	2.1794	0.5629	0.5453	2.4823	2.4890	5.2576	5.2137
5a ₁	0.6481	0.6737	0.4259	0.4455	3.5281	3.5497	4.6021	4.6689
1b ₁ (π)	0.5262	0.5470	1.5787	1.6411	1.6022	1.6244	3.7071	3.8125
2b ₂ (n)	2.1342	2.1452	0.4671	0.4807	3.1707	3.2106	5.7720	5.8365

^a In atomic units: 1 a.u. = 2.80018 × 10⁻¹⁷ cm².

^b See Eq. (2) for the definition of the operators.

^c The center of mass is at (0.0, 0.0, 1.1451).

^d Expectation values of interest for the (95) and (3) atomic wavefunctions (in atomic units):

$$\langle 1s_{\text{H}} | x_{\text{H}}^2 | 1s_{\text{H}} \rangle = 0.9790,$$

$$\langle 1s_{\text{C}} | x_{\text{C}}^2 | 1s_{\text{C}} \rangle = 0.0324,$$

$$\langle 2s_{\text{C}} | x_{\text{C}}^2 | 2s_{\text{C}} \rangle = 1.0118,$$

$$\langle 2p_{z_{\text{O}}} | x_{\text{C}}^2 | 2p_{z_{\text{O}}} \rangle = 2.2365,$$

$$\langle 2p_{y_{\text{O}}} | x_{\text{C}}^2 | 2p_{y_{\text{O}}} \rangle = 0.7455,$$

$$\langle 1s_{\text{O}} | x_{\text{O}}^2 | 1s_{\text{O}} \rangle = 0.0177,$$

$$\langle 2s_{\text{O}} | x_{\text{O}}^2 | 2s_{\text{O}} \rangle = 0.5246,$$

$$\langle 2p_{z_{\text{O}}} | x_{\text{O}}^2 | 2p_{z_{\text{O}}} \rangle = 1.1715,$$

$$\langle 2p_{y_{\text{O}}} | x_{\text{O}}^2 | 2p_{y_{\text{O}}} \rangle = 0.3905.$$

Other expectation values can be obtained from those listed above by symmetry considerations.

contracted (2.24 vs 1.58). The numbers in parentheses are in atomic units and are for the (95/3) wavefunctions.

Another orbital for which second moments are of some interest is the n orbital. The $\langle x^2 \rangle$ for a $2p_x$ orbital of the oxygen atom in a (95) basis set is 1.17 a.u. However, as Table III shows, the n orbital extends out to 2.15 a.u. This is consistent with the population analyses and z centroid which indicated that this orbital contained a significant hydrogen contribution ($\langle x^2 \rangle$ for a $1s$ orbital on hydrogen is 4.22 a.u.).

Flygare has noted that the experimental results on the molecular g values require that

$$\langle x^2 \rangle > \langle y^2 \rangle.$$

Our calculated moments are in agreement with this, although as illustrated in Table XI [after some conversion; see also Ref. 14(b), Table X], the discrepancy between the theoretical and experimental results is not at all small (the error ranging from 8% to 20%). The work of Neumann and Moskowitz on the water molecule suggests that second moments computed from wavefunctions near the (sp) limit²⁶ differ by less than 1% from the (near) Hartree-Fock values.¹ In view of this, the agreement between theory and experiment is poorer than might have been expected. Flygare conjectured that this inequality meant the π electrons were not as loosely held as heretofore expected. While this conclusion is supported by the present calculations, it should be noted that the π -orbital contribution to $\langle y^2 \rangle$ is only $\frac{2}{3}$ of the total.

If we assume that the molecular density can be approximated as a sum of atomic densities, we find that

$$\langle r^2 \rangle_{\text{atoms}} = 64.1491 \text{ a.u.}$$

for the (73/2) basis set, which is in error by only 5%. Allowing the electrons to adjust for the presence of the other nuclei results in a contraction of the electronic charge cloud as expected.

MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility of a molecule with a total electronic spin and angular momentum of zero is a sum of two terms²⁷: a diamagnetic term which depends only on the ground-state wavefunction and a paramagnetic term which depends on the response of the system to the applied magnetic field:

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^d + \chi_{\alpha\beta}^p, \quad (3)$$

where

$$\chi_{\alpha\beta}^d = - (e^2 N / 4mc^2)$$

$$\times \langle \psi^{(0)} | \sum [r_{iA}^2 \delta_{\alpha\beta} - (r_{iA})_{\alpha} (r_{iA})_{\beta}] | \psi^{(0)} \rangle \quad (4)$$

and

$$\chi_{\alpha\beta}^p = - (eN/mc) \langle \psi^{(0)} | \sum (1_{iA})_{\alpha} | \psi_{\beta}^{(1)} \rangle. \quad (5)$$

In the above, N is Avogadro's number and the other constants have their usual meaning. $(1_{iA})_{\alpha}$ is the α component of the angular momentum of electron i about the point A and $\psi_{\beta}^{(1)}$ is the β component of the first-order correction to the ground-state wavefunction $\psi^{(0)}$ due to the applied magnetic field. The origin A refers in this case to the center of mass which for formaldehyde is at (0.0, 0.0, 1.1451).

It has been shown by Wick²⁸ and Ramsey²⁹ for diatomics and by Eshback and Strandberg³⁰ for polyatomic molecules that the diagonal components of the paramagnetic term are related to the molecular g values by

$$\chi_{\alpha\alpha}^p = - (e^2 N / 2mc^2) \{ \hbar g_{\alpha\alpha} / 8\pi G_{\alpha} M_p - \frac{1}{2} \sum Z_N [R_{NA}^2 - (R_{NA})_{\alpha}^2] \}; \quad (6)$$

$g_{\alpha\alpha}$ is the $\alpha\alpha$ component of the g tensor, G_{α} is the

²⁷ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

²⁸ G. C. Wick, *Z. Physik* **85**, 25 (1933); *Phys. Rev.* **73**, 51 (1948).

²⁹ N. F. Ramsey, *Phys. Rev.* **58**, 226 (1940); **87**, 1075 (1952).

³⁰ J. R. Eshback and M. W. P. Strandberg, *Phys. Rev.* **85**, 24 (1952).

TABLE IV. Quadrupole moment of formaldehyde, relative to the center of mass.^{a,b}

	Θ_{xx}		Θ_{yy}		Θ_{zz}	
	(73/2)	(95/3)	(73/2)	(95/3)	(73/2)	(95/3)
Total	0.3250	0.4274	0.0787	0.0257	-0.4037	-0.4531
Nuclear	-7.5579	-7.5579	-17.4308	-17.4308	24.9887	24.9887
Electronic	7.8830	7.9853	17.5095	17.4565	-25.3925	-25.4418
$1a_1$	0.6506	0.6506	0.6506	0.6506	-1.3012	-1.3012
$2a_1$	0.6553	0.6553	0.6553	0.6553	-1.3106	-1.3106
$3a_1$	0.2077	0.1993	0.2304	0.2245	-0.4380	-0.4238
$4a_1$	1.0399	1.0397	2.1010	2.1008	-3.1409	-3.1405
$1b_2$	-0.6898	-0.6622	1.7844	1.7889	-1.0946	-1.1267
$5a_1$	1.3289	1.3239	1.6622	1.6662	-2.9911	-2.9902
$1b_1$ (π)	1.0642	1.0857	-0.5145	-0.5554	-0.5497	-0.5303
$2b_2$ (π)	-0.3153	-0.2996	2.1854	2.1973	-1.8701	-1.8976

^a In atomic units: 1 a.u. = 1.34492×10^{-26} esu·cm². See Eq. (9) for the definition of the quadrupole moment.

^b The center of mass is at (0.0, 0.0, 1.1451).

rotational constant associated with the α principal axis of inertia, and M_p is the proton mass. Most experimental determinations measure the average magnetic susceptibility

$$\chi_{Av} = \chi_{Av}^d + \chi_{Av}^p \\ = (1/3) \text{Tr}(\chi), \quad (7)$$

where from Eq. (4)

$$\chi_{Av}^d = - (e^2 N / 6mc^2) \langle \psi^{(0)} | \sum r_{iA}^2 | \psi^{(0)} \rangle. \quad (8)$$

Thus, experimental values for χ_{Av} and χ_{Av}^p (i.e., the molecular g values) will give information on $\langle r^2 \rangle$ for the ground-state wavefunction. This has been done for formaldehyde by Flygare.¹⁴ Using the calculated values of $\langle r^2 \rangle$ given in Table III, the diamagnetic contributions to the magnetic susceptibility have been computed for the two Gaussian basis sets. These quantities are compared with the experimentally determined diamagnetic contribution in Table XI. We note that the calculated values of $\langle r^2 \rangle$ are smaller than the experimental value.

In Table XI we also compare the diagonal components of χ^d computed from Eq. (4) with the experimental values as determined by Hüttner, Lo, and Flygare. The rather poor agreement is a reflection of the errors associated with the second moments. These errors are crucial when calculating the total susceptibilities, which are differences. An error of 20% in the diamagnetic term can cause an error of 100%–300% in the corresponding total susceptibility. Such is the case for formaldehyde.

MOLECULAR QUADRUPOLE MOMENTS

Following Buckingham,³¹ the components of the molecular quadrupole moment tensor Θ are related to the second moments by

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum Z_N [3(R_{NA})_{\alpha}(R_{NA})_{\beta} - R_{NA}^2 \delta_{\alpha\beta}] \\ - \frac{1}{2} \langle \psi^{(0)} | \sum [3(r_{iA})_{\alpha}(r_{iA})_{\beta} - r_{iA}^2 \delta_{\alpha\beta}] | \psi^{(0)} \rangle, \quad (9)$$

where all the quantities have been defined before. For

³¹ A. D. Buckingham, J. Chem. Phys. 30, 1580 (1958).

neutral molecules which possess a dipole moment the quadrupole moment is not independent of the origin A. As a standard reference point in such cases, the molecular center of mass has been chosen. Such is the case for formaldehyde, and Table IV lists the principal values of the quadrupole moment tensor in the molecular coordinate system referenced to this point.

The quadrupole moment as defined above is a measure of the deviation of the total charge distribution from sphericity. Since the nuclear and electronic contributions are nearly comparable and of opposite sign, the quadrupole moment is a very sensitive test of the accuracy of the molecular charge distribution. For formaldehyde where the nuclear and electronic contributions are each 20–200 times the corresponding components of the tensor, it is very difficult indeed to estimate the accuracy of the predicted values. Further, calculations on water^{1,2} and other molecules^{9,10} indicate that d orbitals have a profound effect on the quadrupole moment. In view of these considerations, the components of the molecular quadrupole moment tensor are probably the least accurate of all the properties calculated. This conclusion is supported by the most recent experimental work on formaldehyde by Hüttner, Lo, and Flygare.¹⁴ From a determination of the components of χ and χ^p , they were able to compute χ^d and, hence, the second moments, $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$. Combining these as given by Eq. (9), the components of the quadrupole moment tensor have been calculated¹⁴ and are listed in Table XI. Comparing the experimental and calculated values, we find that even within the rather large error bounds on the experimental results the agreement is very poor indeed.

CHEMICAL SHIELDING

The magnetic shielding of a nucleus in a molecule is also the sum of a diamagnetic and a paramagnetic term³²

$$\sigma_{\alpha\beta}(N) = \sigma_{\alpha\beta}^d(N) + \sigma_{\alpha\beta}^p(N), \quad (10)$$

³² N. F. Ramsey, Phys. Rev. 78, 699 (1950); 86, 243 (1952); Am. Scientist 49, 509 (1961).

TABLE V. Potential at the atoms in the formaldehyde molecule.^{a-c}

	V(H)			V(C)			V(O)		
	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)
Total	-0.9310	-1.0111	-1.0375	-14.5544	-14.6020	-14.6069	-22.3066	-22.2773	-22.3144
nuclear	5.1978	5.1978	5.1978	4.4440	4.4440	4.4440	3.1460	3.1460	3.1460
electronic	-6.1552	-6.2089	-6.2353	-18.9984	-19.0460	-19.0508	-25.4526	-25.4233	-25.4604
1a ₁	-0.2609	-0.2609	-0.2609	-0.4374	-0.4375	-0.4375	-7.6645	-7.6394	-7.6400
2a ₁	-0.4725	-0.4725	-0.4725	-5.6708	-5.6574	-5.6589	-0.4374	-0.4374	-0.4374
3a ₁	-0.3027	-0.3083	-0.3098	-0.5910	-0.6222	-0.6264	-1.0878	-1.0975	-1.0923
4a ₁	-0.4933	-0.5212	-0.5303	-0.6737	-0.7003	-0.6996	-0.4926	-0.4846	-0.4828
1b ₂	-0.4718	-0.4832	-0.4912	-0.5792	-0.5964	-0.6036	-0.5597	-0.5642	-0.5652
5a ₁	-0.3344	-0.3339	-0.3318	-0.5113	-0.5301	-0.5255	-0.8982	-0.8973	-0.9025
1b ₁ (π)	-0.3323	-0.3069	-0.3039	-0.6068	-0.5378	-0.5320	-0.7395	-0.7899	-0.8017
2b ₂ (n)	-0.4096	-0.4175	-0.4173	-0.4291	-0.4413	-0.4419	-0.8466	-0.8012	-0.8082

^a In atomic units: 1 a.u. = 9.07649 esu/cm.

^b The potential at any atom is (in atomic units)

$$V(N) = \sum Z_N' / R_{NN'} - \langle \psi^{(0)} | \sum 1/r_{iN} | \psi^{(0)} \rangle,$$

where

$$\sigma_{\alpha\beta}^d(N) = (e^2/2mc^2) \times \langle \psi^{(0)} | \sum [r_{iN}^{-2} \delta_{\alpha\beta} - (\mathbf{r}_{iN})_{\alpha} (\mathbf{r}_{iN})_{\beta}] / r_{iN}^3 | \psi^{(0)} \rangle \quad (11)$$

and

$$\sigma_{\alpha\beta}^p(N) = (2e/mc) \operatorname{Re} \{ \langle \psi^{(0)} | \sum (1_{iN})_{\alpha} / r_{iN}^3 | \psi_{\beta}^{(1)} \rangle \}. \quad (12)$$

The terms are as defined for the magnetic susceptibility; $\operatorname{Re}\{\dots\}$ denotes the real part of the quantity in braces. The atom of interest is N.

It has been shown by Ramsey³² and Flygare³³ that the paramagnetic contribution to the chemical shielding is related to the nuclear-spin-rotation constants, $M_{\alpha\alpha}^N$, by

$$\sigma_{\alpha\alpha}^p(N) = (e^2/2mc^2) \{ (\hbar c/2e\mu_N) (M_{\alpha\alpha}^N/g_N G_{\alpha}) - \sum Z_N' [R_{NN'}^{-2} - (R_{NN}')^2] / R_{NN'}^3 \}; \quad (13)$$

μ_N is the nuclear magneton, g_N is the nuclear g factor for nucleus N, and G_{α} is the rotational constant associated with the α principle axis of inertia.

The quantity most conveniently measured is the average shielding

$$\sigma_{Av} = (1/3) \operatorname{Tr}(\sigma), \quad (14)$$

with

$$\sigma_{Av}^d(N) = (e^2/3mc^2) \langle \psi^{(0)} | \sum 1/r_{iN} | \psi^{(0)} \rangle. \quad (15)$$

In this way, experimental determination of σ_{Av} and σ_{Av}^p (i.e., the nuclear-spin-rotation constants, $M_{\alpha\alpha}^N$) provides direct information about the ground-state wavefunction, namely, $\langle 1/r_N \rangle$. Using the electronic contributions to the potential at the atoms given in Table V, we have computed σ_{Av}^d for the Slater wavefunction and the two Gaussian wavefunctions. The resultant values for hydrogen, along with the experimentally calculated diamagnetic contribution to the chemical

^c Expectation values of interest for the (95) and (3) atomic wavefunctions (in atomic units): $\langle 1s_H | 1/r_H | 1s_H \rangle = 0.9935$, $\langle 1s_C | 1/r_C | 1s_C \rangle = 5.6628$, $\langle 2s_C | 1/r_C | 2s_C \rangle = 0.8970$, $\langle 2p_C | 1/r_C | 2p_C \rangle = 0.7831$, $\langle 1s_O | 1/r_O | 1s_O \rangle = 7.6415$, $\langle 2s_O | 1/r_O | 2s_O \rangle = 1.2654$, $\langle 2p_O | 1/r_O | 2p_O \rangle = 1.1111$.

shielding,¹³ are listed in Table XI. The agreement is excellent, as expected, since $\langle 1/r \rangle$ plays such an important role in the variational procedure. Using the spin-rotation constants for the oxygen and carbon nuclei in formaldehyde as determined by Flygare and co-workers,^{15,16} the paramagnetic contributions to their respective chemical shieldings have been calculated and combined with the diamagnetic contributions calculated from the Gaussian wavefunctions. The predicted total shieldings are listed in Table XII.

The potential at any particular nucleus appears to be rather insensitive to the finer details of molecular electronic structure. In fact, as Chan and Dubin³⁴ and later Aung, Pitzer, and Chan² have pointed out, the diamagnetic contribution to the (average) chemical shift at any atom in a molecule is well represented by

$$\sigma_{\text{mol}}^d(N) = \sigma_{\text{atom}}^d(N) + (e^2/3mc^2) \sum' (Z_N' / R_{NN'}); \quad (16)$$

$\sigma_{\text{atom}}^d(N)$ is calculated from the $\langle 1/r_N \rangle$ for the atomic wavefunction of atom N. This is equivalent to assuming that the molecule is a sum of point-charge atoms. Investigating this further for formaldehyde, we find for the (73/2) basis set that

N	σ_{mol}^d	σ_{atoms}^d	σ_{Chan}^d
H, ppm	110.2	108.1	110.0
C	338.1	338.1	339.5
O	451.3	450.3	450.9

where σ_{mol}^d was calculated using the information given in Table V, σ_{atoms}^d was obtained by assuming that the molecular density is a sum of atomic densities (see the section "Atoms"), and σ_{Chan}^d was obtained using the above formula with σ_{atom}^d calculated from the (73) and (2) atom wavefunctions.²¹ Using Eq. (16), localized theories of the chemical shifts for such atoms as fluorine³⁵

³⁴ S. I. Chan and A. S. Dubin, J. Chem. Phys. **46**, 1745 (1967).

³⁵ M. Karplus and T. P. Das, J. Chem. Phys. **34**, 1683 (1961).

³³ W. H. Flygare, J. Chem. Phys. **41**, 793 (1964).

and phosphorus³⁶ can be amended to include changes in the diamagnetic contribution to the shielding. Such theories explicitly assume that changes in the diamagnetic term are negligible compared to those in the paramagnetic term. Comparing the oxygen shieldings in water² and formaldehyde, we note that $\Delta\sigma^d(\text{O}) = 37$ ppm, neglect of which would lead to an error of $\sim 13\%$ in the total shielding for the oxygen nucleus in formaldehyde. Variations in the diamagnetic term can be considerably larger than this: for example, see the fluorine shifts discussed by Chan and Dubin.³⁴

ELECTRIC FIELDS

At any geometry the sum of the forces on the nuclei in a molecule due to the electrons exactly balance the forces of nuclear repulsion when these forces are calculated from a Hartree-Fock (or the true) wavefunction.³⁷ The electric field at any atom is (in atomic units)

$$E_\alpha(\text{N}) = \sum Z_{\text{N}'} [(\mathbf{R}_{\text{NN}'})_\alpha / R_{\text{NN}'}^3] - \langle \psi^{(0)} | \sum [(\mathbf{r}_{\text{IN}'})_\alpha / r_{\text{IN}'}^3] | \psi^{(0)} \rangle. \quad (17)$$

In practice, we never have the Hartree-Fock wavefunction, but rather an LCAO approximation to it. This criterion can thus be used to measure in a semi-quantitative sense how closely a particular LCAO-MO wavefunction approximates the exact Hartree-Fock wavefunction.

From Table VI, which gives the electric fields at the nuclei, $E_\alpha(\text{N})$, we find that the sums of the forces on all the nuclei are

$$f_x = f_y = 0 \text{ (by symmetry)} \quad \text{and} \quad f_z = 0.9250 \text{ a.u.}$$

for the (95/3) wavefunction. It appears that for the polyatomic case, as for the diatomic case,^{9,20,37} the residual forces are a very sensitive measure of the accuracy of the LCAO expansion. Only s and p orbitals are not sufficient to describe the polarizations which arise upon molecular formation, even though a corresponding wavefunction may predict other properties quite well (e.g., the present calculations).

If we assume that the molecular density is formed by superimposing the atomic densities, we find for the (73/2) Gaussian basis set that the electric fields at the hydrogen atom are

$$E_x(\text{H}) = 0.1611 \text{ a.u.}, \quad E_z(\text{H}) = -0.0932 \text{ a.u.}$$

Comparing this to the molecular results given in Table VI, we see that molecular formation, as expected on intuitive grounds, moves electronic density into the region between the nuclei, thereby more effectively shielding the nuclear charges. The electric fields at the carbon and oxygen atoms change very little: $E_x(\text{C}) = -0.0380$ a.u. and $E_x(\text{O}) = 0.1943$.

³⁶ John H. Letcher and J. R. Van Wazer, *J. Chem. Phys.* **44**, 815 (1966); **45**, 2916, 2926 (1966).

³⁷ C. W. Kern and M. Karplus, *J. Chem. Phys.* **40**, 1374 (1964).

TABLE VI. Electric fields at the atoms in the formaldehyde molecule.^{a,b}

	$E_x(\text{H})$		$E_x(\text{H})$		$E_x(\text{C})$		$E_x(\text{O})$		
	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)
Total	0.0882	0.0765	0.0547	-0.0567	-0.0401	-0.0291	-0.0426	-0.0415	-0.0408
nuclear	1.4819	1.4819	1.4819	-1.1696	-1.1696	-1.1696	-1.3004	-1.3004	-1.3004
electronic	-1.3937	-1.4054	-1.4272	1.1129	1.1295	1.1405	1.2578	1.2588	1.2596
$1a_1$	-0.0322	-0.0322	-0.0322	0.0600	0.0600	0.0600	0.1913	0.1914	0.1914
$2a_1$	-0.1913	-0.1913	-0.1913	0.1150	0.1150	0.1150	0.0009	0.0060	0.0098
$3a_1$	-0.0498	-0.0537	-0.0545	0.0763	0.0779	0.0787	0.2377	0.2452	0.2377
$4a_1$	-0.1504	-0.1591	-0.1646	0.0470	0.0535	0.0557	-0.1056	-0.1100	-0.0997
$1b_2$	-0.0911	-0.0924	-0.0971	0.1031	0.1037	0.1071	0.0344	0.0332	0.0284
$5a_1$	-0.0728	-0.0736	-0.0723	0.0393	0.0450	0.0431	0.1063	0.1015	0.0999
$1b_1(\pi)$	-0.0748	-0.0589	-0.0575	0.0670	0.0621	0.0617	0.0988	0.1114	0.1122
$2b_2(\pi)$	-0.0343	-0.0416	-0.0442	0.0488	0.0476	0.0490	0.0650	0.0507	0.0501
							0.3369	0.2170	0.1535
							1.2677	1.2677	1.2677
							-0.9308	-1.0507	-1.1142
							-0.0197	-0.0412	-0.0547
							-0.1913	-0.1913	-0.1913
							-0.2430	-0.2609	-0.2405
							0.0155	0.0016	-0.0124
							-0.0880	-0.0872	-0.0887
							0.1603	0.1294	0.1011
							-0.0909	-0.0660	-0.0636
							-0.0082	-0.0097	-0.0069

^b See Eq. (17) for the definition of the electric field.

^a In atomic units: 1 a.u. = 1.71524×10^9 esu/cm².

TABLE VII. Field gradients at the deuterium atom in the formaldehyde molecule.^{a, b}

	$q_{zz}(D)$			$q_{yy}(D)$			$q_{xx}(D)$					
	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)			
Total	-0.2023	-0.1569	-0.1646	0.1771	0.1334	0.1388	0.0251	0.0234	0.0258	0.2310	0.1772	0.1857
nuclear	-0.7575	-0.7575	-0.7575	0.7959	0.7959	0.7959	-0.0385	-0.0385	-0.0385	1.0160	1.0160	1.0160
electronic	0.5552	0.6006	0.5928	-0.6188	-0.6625	-0.6571	0.0636	0.0619	0.0643	-0.7850	-0.8388	-0.8302
$1a_1$	-0.0058	-0.0058	-0.0058	-0.0178	-0.0178	-0.0178	0.0236	0.0236	0.0236	-0.0222	-0.0222	-0.0222
$2a_1$	0.1270	0.1270	0.1270	-0.1055	-0.1055	-0.1055	-0.0215	-0.0215	-0.0215	-0.1397	-0.1397	-0.1397
$3a_1$	-0.0035	-0.0015	-0.0012	-0.0267	-0.0288	-0.0292	0.0301	0.0303	0.0304	-0.0376	-0.0411	-0.0418
$4a_1$	0.0905	0.1017	0.1039	-0.0497	-0.0592	-0.0597	-0.0408	-0.0426	-0.0442	-0.0406	-0.0532	-0.0540
$1b_2$	0.0154	0.0211	0.0190	-0.0485	-0.0535	-0.0520	0.0331	0.0325	0.0331	-0.0700	-0.0755	-0.0735
$5a_1$	0.0370	0.0402	0.0379	-0.0305	-0.0324	-0.0312	-0.0064	-0.0078	-0.0067	-0.0180	-0.0239	-0.0213
$1b_1(\pi)$	0.0152	0.0069	0.0064	-0.0142	-0.0122	-0.0121	-0.0010	0.0053	0.0057	-0.0427	-0.0340	-0.0333
$2b_2(\pi)$	0.0018	0.0107	0.0092	-0.0165	-0.0219	-0.0210	0.0147	0.0111	0.0118	-0.0216	-0.0298	-0.0293

^a In atomic units: 1 a.u. = 3.24140 X 10¹⁸ esu/cm².^b See Eq. (19) for the definition of the field gradients.

ELECTRIC-FIELD GRADIENTS

The interaction between a nuclear quadrupole moment Q^N and the gradient of the electric field at that nucleus, $q_{\alpha\beta}^N$, is characterized by the nuclear quadrupole coupling constant³⁸

$$\chi_{\alpha\beta}^N = -eq_{\alpha\beta}^N Q^N. \quad (18)$$

The explicit form of the field-gradient tensor is

$$q_{\alpha\beta}^N = - \sum Z_N' [3(R_{NN'})_{\alpha}(R_{NN'})_{\beta} - \delta_{\alpha\beta} R_{NN'}^2] / R_{NN'}^5 + \langle \psi^{(0)} | \sum [3(r_{iN})_{\alpha}(r_{iN})_{\beta} - \delta_{\alpha\beta} r_{iN}^2] / r_{iN}^5 | \psi^{(0)} \rangle. \quad (19)$$

In Tables VII-IX we give the field gradients at the deuterium, the carbon, and the oxygen nuclei. In Table XI the calculated nuclear quadrupole coupling constants are compared with the experimental values as determined by Flygare and co-workers.^{13,15} Table XII contains the quadrupole coupling constants predicted for the carbon (¹²C) nucleus in formaldehyde. In computing the field gradients it is necessary to calculate the densities at the atoms in order to remove the $1/r$ singularity in the integrals.³⁹ These densities are given in Table X. The effects of the Sternheimer shielding⁴⁰ have been neglected, for, as shown by Kahalas and Nesbet⁴¹ and stressed later by Goddard and Kahn,⁴² Sternheimer corrections for Hartree-Fock wavefunctions are zero if Brillouin's theorem holds (as it does for closed-shell systems). We shall now briefly discuss the results obtained for each nucleus.

Tables VII and XI give the field-gradient and nuclear quadrupole coupling constants at the deuterium nucleus in formaldehyde. The deuterium quadrupole moment was taken to be $Q^D = 0.002796$ barn, in line with the recent work of Narumi and Watanabe.⁴³ We immediately note a marked improvement in the deuterium field gradients using the more flexible Gaussian basis sets. This parallels the improvement in the deuterium field gradients observed in diatomic⁴⁴ and polyatomic⁴⁵ molecules when the hydrogen orbital exponent in a single Slater basis is optimized for the molecule. We also note that the nuclear quadrupole coupling constants obtained from the (73/2) wavefunction are in better agreement with experiment than are those of the (95/3) wavefunction. Of course, one should compare to the values at the Hartree-Fock limit and not experiment, but these are unknown. Calculations on water with a (95/31) Gaussian basis set gave results which were 6%-7% higher than those

³⁸ See, for example, C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955).³⁹ R. M. Pitzer, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.* **37**, 267 (1962).⁴⁰ R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, 244 (1951); **86**, 316 (1952).⁴¹ S. L. Kahalas and R. K. Nesbet, *J. Chem. Phys.* **39**, 529 (1963).⁴² W. A. Goddard and L. Kahn (private communication).⁴³ H. Narumi and T. Watanabe, *Bull. Am. Phys. Soc.* **9**, 11 (1964). A barn is 10^{-28} cm².⁴⁴ H. Kolker and M. Karplus, *J. Chem. Phys.* **36**, 960 (1962).⁴⁵ R. M. Pitzer, *J. Chem. Phys.* **46**, 4871 (1967).

TABLE VIII. Field gradients at the carbon atom in the formaldehyde molecule.^{a-c}

	$q_{xx}(C)$		$q_{yy}(C)$		$q_{zz}(C)$	
	(73/2)	(95/3)	(73/2)	(95/3)	(73/2)	(95/3)
Total	0.2263	0.3112	-0.3971	-0.5417	0.1708	0.2305
nuclear	0.4153	0.4153	0.8803	0.8803	-1.2956	-1.2956
electronic	-0.1889	-0.1040	-1.2774	-1.4220	1.4664	1.5261
1a ₁	-0.0837	-0.0837	-0.0837	-0.0837	0.1675	0.1675
2a ₁	0.0003	-0.0001	-0.0001	-0.0002	-0.0001	0.0003
3a ₁	-0.1455	-0.1565	-0.1474	-0.1591	0.2928	0.3155
4a ₁	-0.0200	-0.0220	-0.0776	-0.0925	0.0976	0.1145
1b ₁	0.5243	0.5950	-0.2987	-0.3357	-0.2256	-0.2593
5a ₁	-0.2551	-0.2763	-0.2663	-0.2888	0.5214	0.5650
1b ₂ (π)	-0.2319	-0.2455	0.3514	0.3758	-0.1195	-0.1303
2b ₁ (π)	0.1172	0.1369	-0.1163	-0.1267	-0.0009	-0.0102

^a In atomic units: 1 a.u. = 3.24140 × 10¹⁸ esu/cm³.
^b See Eq. (19) for the definition of the field gradients.

^c Expectation values of interest for the (95) wavefunction (in atomic units): $\langle 2p_{x0} | q_{xx}^C | 2p_{x0} \rangle = 1.3237$, $\langle 2p_{y0} | q_{zz} | 2p_{y0} \rangle = -0.6618$.

TABLE IX. Field gradients at the oxygen atom in the formaldehyde molecule.^{a-c}

	$q_{xx}(O)$			$q_{yy}(O)$			$q_{zz}(O)$		
	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)	Single Slater	(73/2)	(95/3)
Total	2.8237	2.2914	2.5425	-2.0016	-1.8318	-1.9850	-0.8221	-0.4595	-0.5574
nuclear	0.5136	0.5136	0.5136	0.5375	0.5375	0.5375	-1.0511	-1.0511	-1.0511
electronic	2.3101	1.7777	2.0288	-2.5391	-2.3693	-2.5225	0.2290	0.5917	0.4937
1a ₁	0.0005	-0.0002	-0.0001	0.0005	-0.0002	-0.0001	-0.0011	0.0004	0.0003
2a ₁	-0.0837	-0.0837	-0.0837	-0.0837	-0.0837	-0.0837	0.1673	0.1674	0.1674
3a ₁	-0.0968	-0.1408	-0.1592	-0.0971	-0.1412	-0.1595	0.1939	0.2820	0.3188
4a ₁	-0.0893	-0.1002	-0.1046	-0.0913	-0.1026	-0.1074	0.1806	0.2028	0.2120
1b ₂	0.7639	0.9193	1.0305	-0.4199	-0.4983	-0.5542	-0.3440	-0.4210	-0.4764
5a ₁	-0.8143	-1.0111	-1.1309	-0.8146	-1.0115	-1.1315	1.6289	2.0226	2.2624
1b ₁ (π)	-0.7073	-0.9104	-1.0436	1.3307	1.7638	2.0320	-0.6234	-0.8534	-0.9885
2b ₂ (π)	2.1821	2.2160	2.5060	-1.0942	-1.1110	-1.2568	-1.0878	-1.1049	-1.2492

^a In atomic units: 1 a.u. = 3.24140 × 10¹⁸ esu/cm³.
^b See Eq. (19) for the definition of the field gradients.

^c Expectation values of interest for the (95) wavefunction (in atomic units): $\langle 2p_{x0} | q_{xx}^O | 2p_{x0} \rangle = 3.8966$, $\langle 2p_{y0} | q_{zz}^O | 2p_{y0} \rangle = -1.9483$.

TABLE X. Charge densities at the atoms in the formaldehyde molecule.^{a,b}

	$\delta(r-H)$		$\delta(r-C)$		$\delta(r-O)$	
	(73/2)	(95/3)	(73/2)	(95/3)	(73/2)	(95/3)
Total	0.2850	0.3382	112.5617	119.4723	280.9672	294.6784
1a ₁	0.0000	0.0000	0.0000	0.0000	133.9695	140.5821
2a ₁	0.0000	0.0000	54.3264	57.7064	0.0000	0.0000
3a ₁	0.0009	0.0011	0.6000	0.6397	4.8618	5.0103
4a ₁	0.0426	0.0512	1.3324	1.3692	1.0151	1.0677
1b ₂	0.0430	0.0519	0.0000	0.0000	0.0000	0.0000
5a ₁	0.0128	0.0148	0.0220	0.0207	0.6372	0.6791
1b ₁ (π)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2b ₂ (π)	0.0432	0.0501	0.0000	0.0000	0.0000	0.0000

^a In atomic units: 1 a.u. = 3.24140 × 10¹⁴ esu/cm³.

^b Expectation values of interest for the (95) and (3) atomic wavefunctions (in atomic units): $\langle 1s_H | \delta(r-H) | 1s_H \rangle = 0.2327$, $\langle 1s_C | \delta(r-C) | 1s_C \rangle =$

57.7547 , $\langle 2s_C | \delta(r-C) | 2s_C \rangle = 2.6257$, $\langle 1s_O | \delta(r-O) | 1s_O \rangle = 140.6741$, $\langle 2s_O | \delta(r-O) | 2s_O \rangle = 7.2564$.

TABLE XI. Comparison of the calculated values of selected properties of formaldehyde with the experimental values.*

Property	Single Slater ^a	(73/2) ^a	(95/3) ^a	Experiment
Dipole moment				
μ (debye)	0.598	2.587	3.032	2.34 ± 0.04^b
Deuteron quadrupole coupling constants ^{c,e}				
$\chi_{\alpha\alpha}$ (kc/sec)	227.4	174.4	182.7	171 ± 3^f
$\chi_{\beta\beta}$	-111.0	-86.8	-91.5	-84 ± 3^f
$\chi_{\gamma\gamma}$	-116.4	-87.6	-91.2	-87 ± 3^f
ϕ	$0^\circ 54'$	$0^\circ 32'$	$0^\circ 26'$	$1^\circ \pm 3'^g$
Oxygen (¹⁷ O) quadrupole coupling constants ^{c,d,g}				
$\chi_{\alpha\alpha}$ (Mc/sec)	-4.64	-2.59	-3.14	-1.89 ± 0.01^h
$\chi_{\beta\beta}$	15.92	12.92	14.34	12.37 ± 0.01^h
$\chi_{\gamma\gamma}$	-11.29	-10.32	-11.19	-10.48 ± 0.01^h
Chemical shift ⁱ				
σ^d (H) ppm	109.3	110.2	110.7	108 ± 2^j
Magnetic susceptibility ^{k,l}				
$\chi^d \times 10^{-6}$ cm ³ /mole		-48.3	-48.5	-56.1 ± 0.8^m
$\chi_{\alpha\alpha}^d$		-28.2	-28.3	-35.7 ± 0.6^m
$\chi_{\beta\beta}^d$		-54.6	-54.8	-62.0 ± 0.9^m
$\chi_{\gamma\gamma}^d$		-62.2	-62.3	-70.7 ± 0.9^m
Molecular quadrupole moment ^{n,l}				
Θ_{xx} (buckingham)		0.437	0.575	-0.6 ± 0.7^o
Θ_{yy}		0.106	0.035	1.4 ± 0.7^o
Θ_{zz}		-0.543	-0.609	-0.8 ± 0.8^o

^a The quantities given here are also listed in the appropriate tables as described in the text. Conversion to cgs units has been made.

^b J. N. Schoolery and A. H. Sharbaugh, *Phys. Rev.* **82**, 95 (1951); and R. B. Lawrance and M. W. P. Strandberg, *ibid.* **83**, 363 (1951).

^c The principal axes are as illustrated in Fig. 1.

^d See Eq. (18) for the definition of the nuclear quadrupole coupling constant.

^e A deuteron quadrupole moment of 0.002796 barn has been used (see Ref. 43).

^f Reference 13.

^g An oxygen (¹⁷O) quadrupole moment of -0.024 barn has been used (see Ref. 49).

^h Reference 15.

ⁱ Calculated with Eq. (15).

^j Reference 17.

^k Calculated with Eqs. (8) and (4).

^l Note that the experimental coordinate system is related to the coordinate system employed here by $(x, y, z)_{\text{calc}} = (y, x, z)_{\text{expt}}$.

^m Reference 14.

ⁿ The molecular quadrupole moments are as defined in Eq. (9). One buckingham = 10^{-26} esu·cm².

^o Reference 14. The quadrupole moment as defined in this paper differs by a factor of $\frac{1}{2}$ from our definition. For comparison with our results this factor has been included in the quoted experimental results.

calculated with the (1062/42) basis set.²⁶ For this property, however, the set of p orbitals included on the hydrogens could have a marked effect. This casts some doubt on such a rationalization.

The deuterium field gradients provide a means of determining the symmetry of the charge distribution around the CH bond.⁴⁶ If the density was cylindrically symmetric about the bond axis, then

$$\chi_{\alpha\alpha} = -2\chi_{\beta\beta} = -2\chi_{\gamma\gamma}; \quad \phi = 0^\circ.$$

From the results presented in Table XI, we note that all three wavefunctions predict a nearly cylindrically symmetric charge distribution. Thus, theory (as well as experiment within rather large error bounds) predicts that the CH bonds in formaldehyde are not "bent" but

rather that the density maxima lie nearly along the bond axis.

The field gradients at the deuterium nucleus are given in Table VII in terms of the molecular coordinate system. The interested reader may rotate these results into any convenient coordinate system by noting that under a change of coordinates the field-gradient tensor undergoes a similarity transformation. The results given in Table XI are for the principal axis system of the field gradient tensor; see Fig. 1.

If, as mentioned before, we assume that the molecule is formed from a superposition of atoms, we find for the (73/2) basis set that

$$\chi_{\alpha\alpha} = 250 \text{ kc/sec};$$

$$\chi_{\beta\beta} = -137 \text{ kc/sec};$$

$$\chi_{\gamma\gamma} = -113 \text{ kc/sec}.$$

⁴⁶ W. H. Flygare, *Science* **140**, 1179 (1963).

The major characteristics of the deuterium field gradients can be obtained just by describing the atoms from which the molecule is made. By far the largest contribution comes from the charge density associated with the carbon atom [for $q_{\alpha\alpha}(D_1)$ the atomic contributions are D_2 , -0.001 a.u.; C, -0.376 a.u.; O, -0.005 a.u.], a fact which has been noted in calculations on other polyatomics.⁴⁷

Unfortunately, the more common isotopes of carbon, ¹²C and ¹³C, do not possess nuclear quadrupole moments and, hence, can yield no information about the field gradients at the carbon nucleus. However, the radioactive isotope ¹¹C with a half-life of 21 min and $I = \frac{3}{2}$ has a quadrupole moment of $Q^{13C} = 0.0310$ barn.⁴⁸ An analysis of the rotational spectra of formaldehyde enriched with this species will yield the corresponding carbon nuclear quadrupole coupling constants. Anticipating this, Tables VIII and XII contain the predicted field gradients and nuclear quadrupole coupling constants. Unfortunately, there are rather large variations in the predicted components.

Tables IX and XI give the calculated field gradients and nuclear quadrupole coupling constants for the oxygen (¹⁷O) nucleus. An oxygen quadrupole moment of $Q^{17O} = -0.024$ barn⁴⁹ has been used. From these results we note that the nuclear quadrupole coupling constants calculated with the (73/2) Gaussian wavefunction are in better agreement with experiment than those of the (95/3) wavefunction. This is contrary to our expectations for it was thought that an improvement in the description of the oxygen p orbitals would also improve the field gradients (see, for example, Table I and the work of Aung, Pitzer, and Chan on water²). The atom results in Table I indicate that the oxygen field gradient will be in error only a few percent due to (sp) basis-set truncation although the neglect of p orbitals on the hydrogens could have an appreciable effect. Lack of balance in the basis set is expected to have only a small effect.² Lastly, calculations on other molecules indicate that d orbitals will have a small effect.^{1,2} In fact, calculations on water with a (95/31) basis set gave values for the components of the field gradient within 5%–7% of the (near) Hartree-Fock

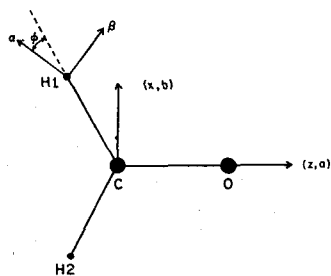


FIG. 1. Coordinate system used for describing the properties of formaldehyde. The axes (y , c , γ) are perpendicular to the molecular (xz) plane.

TABLE XII. Experimental values for some one-electron properties of formaldehyde as predicted by the Gaussian wavefunctions.^a

Property	(73/2)	(95/3)
Total chemical shieldings ^b		
$\sigma(^{13}\text{C})$ (ppm)	123.1	123.1
$\sigma(^{17}\text{O})$	281.3	278.3
Carbon (¹¹ C) quadrupole coupling constants ^{c, d}		
$\chi_{\alpha\alpha}$ (Mc/sec)	-1.24	-1.68
$\chi_{\beta\beta}$	-1.65	-2.27
$\chi_{\alpha\alpha}$	2.89	3.95

^a The quantities given here are also listed in the appropriate tables as described in the text. Conversion to cgs units has been made.

^b Calculated with Eqs. (10), (13), and (15).

^c See Eq. (18) for the definition of the nuclear quadrupole coupling constant.

^d A carbon (¹¹C) quadrupole moment of 0.0310 barn has been used (see Ref. 48).

limit, even for the small component, $q_{zz} = 0.9$ Mc/sec.²⁶ The exact reason for these discrepancies is not known; it is probably due to an accumulative effect. More accurate calculations underway at present²⁶ should aid in the resolution of this dilemma.

Constructing the molecule from its component atoms, we find that

$$q_{zz}(\text{O}) = 3.6191 \text{ a.u.};$$

$$q_{yy}(\text{O}) = -1.5695 \text{ a.u.};$$

$$q_{zz}(\text{O}) = -2.0496 \text{ a.u.}$$

Comparing these with the molecular results listed in Table IX, we note that the most profound change occurs in the zz component of the field gradient. This is as expected, since the corresponding operator is concentrated in that region of space most affected by the formation of the molecule from the atoms.

CONCLUSION

Most of the conclusions which can be drawn from this work were stated as they arose in the discussion of the properties. The purpose of this section will be to present an over-all view. For specific details the reader is referred to the individual sections.

The results of the calculations with the unoptimized set of Slater orbitals indicate that the corresponding wavefunctions contain considerably less information than the other two types investigated. Properties predicted with such wavefunctions do, however, have qualitative significance. In particular, we found that some orbitals, e.g., the π orbital, were quite poorly described with this basis set. Optimization of the orbital exponents would undoubtedly improve the situation.

From the properties presented in this and a previous paper,⁵ we estimate that the (73/2) Gaussian basis set is better than a molecular optimized minimum basis set

⁴⁷ C. W. Kern and M. Karplus, J. Chem. Phys. **42**, 1062 (1965).

⁴⁸ G. H. Fuller and V. W. Cohen, Appendix I to Nuclear Data Sheets, May 1965.

⁴⁹ N. Bessis, H. Lefebvre-Brion, and C. Moser, Phys. Rev. **128**, 213 (1962).

of Slater orbitals.⁵⁰ Such a conclusion is supported by calculations on the water molecule,² where it was found that an optimized minimum basis set of Slater orbitals gave a surprisingly accurate charge distribution. Any important differences are in the regions near the first-row nuclei, a region which the Gaussian set describes better. As such, this basis set would be a good set for investigating larger molecules.

The (95/3) Gaussian set is estimated to be quite near the (*sp*) limit. However, the results presented here also indicate that this basis set may be slightly unbalanced. An additional *s* orbital and/or set of *p* orbitals are probably needed on the hydrogens to prevent undue warping of the charge distribution. Scaling of the hydrogen exponents would also help. The disadvantages of this set compared to the (73/2) set in regard to computational time can be overcome by the use of contracted orbitals. It has been shown that little information is lost if the amount of contraction is moderate.^{3,4} This would make the large (contracted) set competitive with the small (uncontracted) set for the investigation of intermediate sized molecules.

The calculations presented in this and a previous paper emphasize the fact that no appreciable errors arise from the use of Gaussian orbitals as expansion functions for the solution of the Hartree-Fock equations. Further, the use of Gaussian orbitals effects a significant decrease in computer time compared to corresponding calculations with Slater orbitals. For example, to optimize a minimum basis set of Slater orbitals for formaldehyde with presently available programs² would require at least 20 times the computer investment of the (73/2) calculation. In fact, the total computation times for a *single* calculation with the (73/2) Gaussian set and a minimum Slater set are comparable in the case of formaldehyde. This disparity will become more pronounced as the number of nuclear centers increases.

As formaldehyde has been the object of an intensive study by Flygare and co-workers,¹⁵⁻¹⁶ numerous comparisons could be made between theory and experiment. When considering the observed discrepancies, we must however keep in mind the deficiencies of the basis sets, particularly the lack of *d* orbitals. Comparable calculations on water^{1,2,26} and other molecules^{9,10,20} have shown that such basis functions have considerable effect on the dipole moment, quadrupole moment, and forces. The calculations on water^{1,26} also indicated that wavefunctions near the (*sp*) limit yield values for the individual second moments, potentials, and field gradients near the Hartree-Fock limit. Such a rationale explains all of the errors except those noted for the second moments and the oxygen field gradients. In these cases the deviations are quite large (>20% usually). More accurate calculations presently being

carried out²⁶ may help in the resolution of this problem, although, as explained in the text, it is felt that for the most part they will not. Further, calculations on other molecules suggest that the agreement between theory and experiment is more than satisfactory for these properties.^{20,51} In summary, we must say that the reasons for the observed discrepancies in the second moments and the field gradients are not understood.

The second moment $\langle y^2 \rangle$ demonstrate that the π electrons on the average do not extend as far out into space as the σ electrons. This contradicts many of the prevailing concepts related to π -electron theory.

Some properties were found to be rather insensitive to the finer details of molecular structure. Two such properties are $\langle 1/r \rangle$ and $\langle r^2 \rangle$, which are proportional to the diamagnetic contributions to the chemical shielding and magnetic susceptibility, respectively. Assuming that the molecule is composed of noninteracting atoms leads to errors of less than 1% and ~5% in these two properties. In fact, for $\langle 1/r \rangle$ it was found that the electrons can be treated as being concentrated at the nuclear positions with little loss in accuracy. This can be used to improve localized theories of the chemical shift.

COMPUTER PROGRAMS

The program used to calculate the matrix elements of the one-electron operators over Slater orbitals was written by Pitzer and modified by Aung.^{2,17} A Barnett-Coulson zeta-function expansion is used to evaluate the multicenter integrals. All the integrals were computed accurate to approximately 10^{-6} a.u. The authors wish to thank Pitzer and Aung for making their program available to us and for many helpful discussions related to its use.

The program used to calculate the one-electron integrals over Gaussian orbitals is an IBM 7094 revised version of a program originally written by Neumann for the CDC 6600. All the integrals are evaluated in closed form. For further information on this program the reader is referred to the previously mentioned paper by Neumann and Moskowitz.¹

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⁵⁰ For the water molecule the (73/2) wavefunction gives an energy 0.165 a.u. lower than that for an optimized minimum basis set of Slater orbitals.

⁵¹ A. D. McLean and M. Yoshimine, *J. Chem. Phys.* **45**, 3676 (1966).