

Formaldehyde Molecule in a Gaussian Basis. A Self-Consistent Field Calculation

N. W. WINTER,* THOM. H. DUNNING, JR.,* AND JOHN H. LETCHER
Central Research Department, Monsanto Company, St. Louis, Missouri

(Received 19 February 1968)

Accurate LCAO-MO-SCF calculations have been carried out for the formaldehyde molecule using (73/2) and (95/3) Gaussian basis sets. The energy parameters, molecular orbitals, dipole moments, and population analyses are reported. The results are compared to a previous calculation with a minimum Slater basis and to experiment.

I. INTRODUCTION

It is now possible to obtain close approximations to the Hartree-Fock orbitals for a number of small polyatomic molecules.^{1,2} These have been found by expanding the orbitals in large Gaussian basis sets. From such calculations it is possible to predict, with varying degrees of accuracy, ionization potentials, dissociation energies, many one-electron properties, etc. In order to have confidence in our results we either need to know what type and size of basis set is required to predict the properties of interest with reliable accuracy³ or have the LCAO-MO-SCF orbitals sufficiently close to the Hartree-Fock orbitals so that no major error arises from the use of the expansion.

We report here the results of LCAO-MO calculations on formaldehyde using two uncontracted Gaussian basis sets: The smaller, a (73/2) set,⁴ is estimated to be

* Permanent address: A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, Calif.

¹ C₂H₄: J. M. Schulman, J. W. Moskowitz, and C. Hollister, *J. Chem. Phys.* **44**, 2759 (1966).

² H₂O: D. Neumann and J. W. Moskowitz, "One Electron Properties of Near Hartree-Fock Wavefunctions. I. Water," *J. Chem. Phys.* (to be published).

³ By accurate we mean, of course, in comparison to the Hartree-Fock result and not to experiment.

⁴ We have adopted the standard notation, with (*abc/ef*) representing *a* *s*-orbitals, *b* *p*-orbitals, *c* *d*-orbitals, etc., on the first-row atoms and *e* *s*-orbitals, *f* *p*-orbitals, etc., on the hydrogen atoms.

slightly better than a molecular optimized minimum Slater set and the larger, a (95/3) set,⁴ is near the (*sp*) limit. While these wavefunctions are obviously not at the Hartree-Fock limit, they form essential units in a stepwise approach to that limit and can be expected to provide a considerable amount of chemical information.

Because of the wide range of interest in formaldehyde, a number of theoretical calculations on it have been reported. All of the calculations based on pi-electron theory⁵ approximated the required atomic integrals and provided little usable information, other than possibly the spectra. More recently, accurate calculations have been made using an unoptimized minimum basis set of Slater orbitals.^{6,7} Several comparisons will be made with these functions.

In the next section we give the results for the two Gaussian sets. In the following section we discuss the results. In the last section the computational details are given.

⁵ T. Anno and A. Sadó, *J. Chem. Phys.* **26**, 1759 (1957); J. W. Sidman, *ibid.* **27**, 429 (1957); J. A. Pople and J. W. Sidman, *ibid.* **27**, 1270 (1957); R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.* **54**, 757 (1958); J. M. Parks and R. G. Parr, *J. Chem. Phys.* **32**, 1657 (1960); and F. L. Pilar, *ibid.* **47**, 884 (1967).

⁶ J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 303 (1960).

⁷ M. D. Newton and W. E. Palke, *J. Chem. Phys.* **45**, 2329 (1966); S. Aung, R. M. Pitzer, and S. I. Chan, *ibid.* **45**, 3457 (1966).

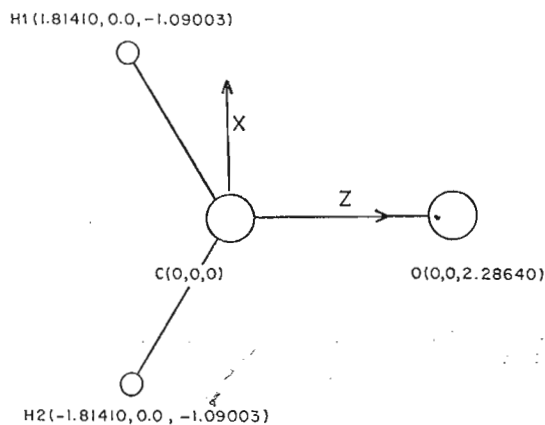


FIG. 1. The geometry of formaldehyde.

II. SCF RESULTS

For comparative purposes, the calculations were done at the geometry used by Goodfriend, Birss, and Duncan⁸ which is quite close to that from the most recent structure determination⁹; see Fig. 1. The atomic energies for each of the basis sets are included in Table I. The exponents for both sets were determined from atomic SCF calculations¹⁰ and are included in Tables III and IV.

The computed electronic energies are -144.7857 and -144.9471 a.u. for the (73/2) and (95/3) basis sets, respectively. Newton and Palke⁷ give -144.5409 a.u. for a minimum Slater basis set with exponents determined from Slater's rules. As stated in the Introduction, from the energy and numerous properties for the (73/2) basis set, we estimate that this basis set is superior to a molecular optimized minimum basis set of Slater orbitals. As such, the (73/2) basis set would be a good candidate for *ab initio* studies of larger molecules, although three basis functions are recommended for the hydrogens rather than the two employed here. The (95/3) basis set should be within 0.04 a.u. of the (*sp*) limit for formaldehyde. It is felt that most properties are essentially at the (*sp*) limit and would be little affected by any additional *s* and *p* orbitals. Hollister and Sinanoğlu¹¹ predict the total Hartree-Fock energy of formaldehyde to be -114.0309 a.u. Thus, our wavefunction in the (95/3) Gaussian basis is approximately 0.20 a.u. from the Hartree-Fock limit. Work on other polyatomics^{1,2} leads us to suspect that this is an upper limit. In any case, a significant lowering (~ 0.16 a.u.) would be achieved through the addition

of *d* and *f* orbitals to the basis set. Most of the improvement is expected to arise from the inclusion of *d* orbitals.²

Table I compares the calculated binding energies for the three wavefunctions to the experimental value,¹² and Table II compares the orbital energies to the negatives of the experimental vertical ionization potentials.¹³ From the kinetic energies given in Table II, the virial ratio $-T/E$ is found to be 0.9990 for the small Gaussian set and 0.9989 for the large set. We also see that the kinetic energy for the Slater calculation agrees with the Gaussian results much better than the molecular energy, and consequently gives a poorer virial ratio (1.0023).

The molecular-orbital coefficients for the (73/2) and (95/3) basis sets are listed in Tables III and IV, respectively. The population analyses¹⁴ of both sets are given in Tables V-VIII.

The dipole moment is 1.018 a.u. (2.587 D) for the (73/2) set and 1.193 a.u. (3.032 D) for the (95/3) set, as compared to the experimental value 0.921 a.u. (2.34 D).¹⁵ The minimum-Slater-basis-set calculation predicted 0.235 a.u. (0.597 D), considerably worse than either Gaussian calculation. All of the calculated dipole moments are in the direction C^+O^- . The behavior of the dipole moment is in agreement with recent observations that *d* orbitals are needed to describe the polarizations due to molecular formation.^{2,16,17} In general, addition of *d* orbitals decreases the calculated dipole moment,^{2,16} although such a trend may not be universal.

TABLE I. Comparison of the binding energies (B.E.) calculated from a single Slater basis and from the (73/2) and (95/3) Gaussian bases.

	Single Slater ^a	(73/2) ^b	(95/3) ^b
E_C	-37.619	-37.6551	-37.6852
E_O	-74.533	-74.7007	-74.8003
E_H	-0.500	-0.4858	-0.4970
E_{atoms}	-113.152	-113.3274	-113.4795
$E_{molecule}$	-113.4272	-113.6720	-113.8334
B.E. (a.u.)	0.275	0.3446	0.3539
(eV)	7.49	9.38	9.63
Experimental B.E.		16.24 eV	

^a For the atomic energies, see B. J. Ransil, *Rev. Mod. Phys.* **32**, 239 (1960); for the molecular energy, see Ref. 7a.

^b For the atomic energies, see Ref. 10.

⁸ P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *Rev. Mod. Phys.* **32**, 307 (1960).

⁹ T. Oka, *J. Phys. Soc. Japan* **15**, 2274 (1960); K. Takagi and T. Oka, *ibid.* **18**, 1174 (1963).

¹⁰ The exponents for the small basis set were made available to us by Dr. Murray Geller and are from calculations by D. Whitman at RIAS, Martin Company, Baltimore, Md. Those for the large set are given by S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1964).

¹¹ C. Hollister and O. Sinanoğlu, *J. Am. Chem. Soc.* **88**, 13 (1966).

¹² G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer (McGraw-Hill Book Co., New York, 1961).

¹³ C. R. Brundle and D. W. Turner, *Chem. Commun.* **1967**, 314.

¹⁴ R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).

¹⁵ J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.* **82**, 95 (1951).

¹⁶ W. M. Huo, *J. Chem. Phys.* **43**, 624 (1965).

¹⁷ P. E. Cade and W. M. Huo, *J. Chem. Phys.* **45**, 1063 (1967).

TABLE II. Orbitals energies, total energies, and kinetic energies for formaldehyde in a single Slater basis and in the (73/2) and (95/3) Gaussian bases compared to the photoelectron ionization potentials, in atomic units.^a

Molecular orbital	Orbital energies			-I.P. ^a
	Single Slater ^b	(73/2)	(95/3)	
1(1a ₁)	-20.6237	-20.6072	-20.5906	
2(2a ₁)	-11.4026	-11.3576	-11.3627	
3(3a ₁)	-1.3977	-1.4304	-1.4299	
4(4a ₁)	-0.8314	-0.8609	-0.8666	~ -0.772
5(1b ₂)	-0.6759	-0.6893	-0.7020	-0.621
6(5a ₁)	-0.5932	-0.6318	-0.6437	-0.588
7(1b ₁)	-0.4971	-0.5238	-0.5355	-0.529
8(2b ₂)	-0.3955	-0.4269	-0.4423	-0.399
9(2b ₁) ^d	0.2249	0.1465	0.1076	
Total energy	-113.4272	-113.6720	-113.8334	
Kinetic energy	113.6906	113.5632	113.7089	

^a 1 a.u. of energy is 27.2098 eV.

^b See Ref. 7a.

^c See Ref. 13.

^d This orbital is unoccupied in the ground state. It is the lowest π antibonding orbital.

TABLE III. Coefficient vectors and orbital energies for the (73/2) basis set.

Orbital energy		Vector 1	2	3	4	5	6	7	8	
		-20.60716	-11.35758	-1.43043	-0.86087	-0.68928	-0.63177	-0.52382	-0.42695	
Center	Type	Exponent								
H1	S	0.2700	-0.00033	0.00255	0.01395	-0.16815	-0.17395	-0.11284	0.0	-0.36239
H1	S	1.8000	-0.00009	-0.00063	0.01364	-0.09477	-0.09599	-0.05144	0.0	-0.09414
H2	S	0.2700	-0.00033	0.00255	0.01395	-0.16815	0.17395	-0.11284	0.0	0.36239
H2	S	1.8000	-0.00009	-0.00063	0.01364	-0.09477	0.09599	-0.05144	0.0	0.09414
C	S	0.1817	0.00626	-0.01235	0.07111	-0.35181	0.0	-0.11942	0.0	0.0
C	S	0.6026	-0.00027	0.03921	0.21135	-0.34019	0.0	0.08271	0.0	0.0
C	S	3.6980	0.00049	0.44308	-0.09829	0.15255	0.0	-0.02530	0.0	0.0
C	S	11.8200	-0.00027	0.44689	-0.05696	0.08545	0.0	-0.00947	0.0	0.0
C	S	39.9100	0.00007	0.18184	-0.02080	0.03121	0.0	-0.00435	0.0	0.0
C	S	160.0000	-0.00001	0.04723	-0.00499	0.00743	0.0	-0.00090	0.0	0.0
C	S	994.7000	0.00000	0.00720	-0.00076	0.00114	0.0	-0.00015	0.0	0.0
C	X	0.2036	0.0	0.0	0.0	0.0	-0.29650	0.0	0.0	-0.02856
C	X	0.8699	0.0	0.0	0.0	0.0	-0.29774	0.0	0.0	-0.16243
C	X	4.2790	0.0	0.0	0.0	0.0	-0.06443	0.0	0.0	-0.03105
C	Y	0.2036	0.0	0.0	0.0	0.0	0.0	0.0	0.33339	0.0
C	Y	0.8699	0.0	0.0	0.0	0.0	0.0	0.0	0.24231	0.0
C	Y	4.2790	0.0	0.0	0.0	0.0	0.0	0.0	0.05756	0.0
C	Z	0.2036	0.00418	0.00106	-0.00179	0.11738	0.0	0.12914	0.0	0.0
C	Z	0.8699	0.00006	0.00097	0.13518	0.12114	0.0	0.29511	0.0	0.0
C	Z	4.2790	0.00028	0.00040	0.02979	0.02802	0.0	0.06086	0.0	0.0
O	S	0.3342	-0.01642	0.00087	0.49982	0.30572	0.0	-0.30007	0.0	0.0
O	S	1.1030	0.03963	-0.00033	0.39549	0.18151	0.0	-0.13214	0.0	0.0
O	S	6.7730	0.44059	0.00003	-0.16325	-0.07354	0.0	0.05667	0.0	0.0
O	S	21.7400	0.45708	-0.00027	-0.11392	-0.05331	0.0	0.04318	0.0	0.0
O	S	76.9300	0.18018	-0.00004	-0.03636	-0.01648	0.0	0.01293	0.0	0.0
O	S	332.2000	0.04169	-0.00002	-0.00815	-0.00375	0.0	0.00299	0.0	0.0
O	S	2200.0000	0.00569	0.00000	-0.00108	-0.00049	0.0	0.00039	0.0	0.0
O	X	0.3814	0.0	0.0	0.0	0.0	-0.27536	0.0	0.0	0.54179
O	X	1.7190	0.0	0.0	0.0	0.0	-0.24381	0.0	0.0	0.37014
O	X	8.3560	0.0	0.0	0.0	0.0	-0.06012	0.0	0.0	0.09601
O	Y	0.3814	0.0	0.0	0.0	0.0	0.0	0.0	0.45440	0.0
O	Y	1.7190	0.0	0.0	0.0	0.0	0.0	0.0	0.32506	0.0
O	Y	8.3560	0.0	0.0	0.0	0.0	0.0	0.0	0.08254	0.0
O	Z	0.3814	0.00366	0.00112	-0.11458	0.10388	0.0	-0.43448	0.0	0.0
O	Z	1.7190	-0.00142	-0.00001	-0.11122	0.09977	0.0	-0.34852	0.0	0.0
O	Z	8.3560	-0.00176	-0.00017	-0.02344	0.02563	0.0	-0.08784	0.0	0.0

TABLE IV. Coefficient vectors and orbital energies for the (95/3) basis set.

Orbital energy			Vector 1	2	3	4	5	6	7	8
			-20.59059	-11.36267	-1.42987	-0.86658	-0.70195	-0.64364	-0.53551	-0.44226
Center	Type	Exponent								
H1	S	0.14830	0.00006	0.00003	-0.00357	0.05457	-0.10847	0.07776	0.0	-0.25965
H1	S	0.65770	0.00000	-0.00044	-0.01993	0.16507	-0.15062	0.08646	0.0	-0.20085
H1	S	4.23920	0.00000	-0.00009	-0.00497	0.03336	-0.03520	0.01849	0.0	-0.03155
H2	S	0.14830	0.00006	0.00003	-0.00357	0.05457	0.10847	0.07776	0.0	0.25965
H2	S	0.65770	0.00000	-0.00044	-0.01993	0.16507	0.15062	0.08646	0.0	0.20085
H2	S	4.23920	0.00000	-0.00009	-0.00497	0.03336	0.03520	0.01849	0.0	0.03155
C	S	0.15331	-0.00118	0.00001	-0.04922	0.27009	0.0	0.08407	0.0	0.0
C	S	0.49624	+0.00031	-0.00326	-0.26113	0.44897	0.0	-0.09462	0.0	0.0
C	S	1.96655	-0.00007	-0.14710	0.02694	-0.05924	0.0	0.01050	0.0	0.0
C	S	5.14773	-0.00006	-0.43684	0.08380	-0.11724	0.0	0.01412	0.0	0.0
C	S	14.18920	0.00001	-0.35845	0.04346	-0.06691	0.0	0.00826	0.0	0.0
C	S	42.49740	-0.00001	-0.15448	0.01776	-0.02541	0.0	0.00314	0.0	0.0
C	S	146.09700	0.00000	-0.04540	0.00480	-0.00715	0.0	0.00088	0.0	0.0
C	S	634.88200	0.00000	-0.00933	0.00100	-0.00144	0.0	0.00018	0.0	0.0
C	S	4232.61000	0.00000	-0.00122	0.00013	-0.00019	0.0	0.00002	0.0	0.0
C	X	0.11460	0.0	0.0	0.0	0.0	-0.06603	0.0	0.0	0.02995
C	X	0.35945	0.0	0.0	0.0	0.0	-0.32825	0.0	0.0	-0.14996
C	X	1.14293	0.0	0.0	0.0	0.0	-0.18459	0.0	0.0	-0.09817
C	X	3.98640	0.0	0.0	0.0	0.0	-0.05644	0.0	0.0	-0.02784
C	X	18.15570	0.0	0.0	0.0	0.0	-0.00949	0.0	0.0	-0.00474
C	Y	0.11460	0.0	0.0	0.0	0.0	0.0	0.0	0.12135	0.0
C	Y	0.35945	0.0	0.0	0.0	0.0	0.0	0.0	0.27727	0.0
C	Y	1.14293	0.0	0.0	0.0	0.0	0.0	0.0	0.15428	0.0
C	Y	3.98640	0.0	0.0	0.0	0.0	0.0	0.0	0.04747	0.0
C	Y	18.15570	0.0	0.0	0.0	0.0	0.0	0.0	0.00787	0.0
C	Z	0.11460	-0.00039	-0.00008	0.00883	-0.05074	0.0	0.00867	0.0	0.0
C	Z	0.35945	-0.00027	0.00039	-0.06480	-0.12354	0.0	-0.25958	0.0	0.0
C	Z	1.14293	0.00040	-0.00056	-0.10501	-0.07935	0.0	-0.19082	0.0	0.0
C	Z	3.98640	-0.00010	-0.00049	-0.02244	-0.02530	0.0	-0.04903	0.0	0.0
C	Z	18.15570	0.00002	-0.00010	-0.00487	-0.00407	0.0	-0.00924	0.0	0.0
O	S	0.28461	0.00281	-0.00019	-0.36985	-0.26524	0.0	0.29802	0.0	0.0
O	S	0.93978	-0.00091	-0.00091	-0.49433	-0.22601	0.0	0.16611	0.0	0.0
O	S	3.41364	0.14064	0.00031	0.04210	0.01325	0.0	-0.00161	0.0	0.0
O	S	9.53223	0.46100	0.00016	0.15741	0.07620	0.0	-0.06443	0.0	0.0
O	S	27.18360	0.35555	0.00016	0.08005	0.03649	0.0	-0.02836	0.0	0.0
O	S	81.16960	0.14386	0.00005	0.02941	0.01377	0.0	-0.01122	0.0	0.0
O	S	273.18800	0.04286	0.00002	0.00820	0.00375	0.0	-0.00295	0.0	0.0
O	S	1175.82000	0.00897	0.00000	0.00171	0.00079	0.0	-0.00064	0.0	0.0
O	S	7816.54000	0.00118	0.00000	0.00022	0.00010	0.0	-0.00008	0.0	0.0
O	X	0.21373	0.0	0.0	0.0	0.0	-0.12905	0.0	0.0	0.33109
O	X	0.71706	0.0	0.0	0.0	0.0	-0.25091	0.0	0.0	0.41099
O	X	2.30512	0.0	0.0	0.0	0.0	-0.15550	0.0	0.0	0.24256
O	X	7.90403	0.0	0.0	0.0	0.0	-0.04982	0.0	0.0	0.07939
O	X	35.18320	0.0	0.0	0.0	0.0	-0.00787	0.0	0.0	0.01227
O	Y	0.21373	0.0	0.0	0.0	0.0	0.0	0.0	0.26122	0.0
O	Y	0.71706	0.0	0.0	0.0	0.0	0.0	0.0	0.36369	0.0
O	Y	2.30512	0.0	0.0	0.0	0.0	0.0	0.0	0.21243	0.0
O	Y	7.90403	0.0	0.0	0.0	0.0	0.0	0.0	0.06931	0.0
O	Y	35.18320	0.0	0.0	0.0	0.0	0.0	0.0	0.01087	0.0
O	Z	0.21373	-0.00058	-0.00006	0.01237	-0.05380	0.0	0.18671	0.0	0.0
O	Z	0.71706	0.00017	0.00080	0.13094	-0.08727	0.0	0.35119	0.0	0.0
O	Z	2.30512	-0.00063	0.00036	0.06734	-0.06521	0.0	0.23027	0.0	0.0
O	Z	7.90403	-0.00165	0.00006	0.02073	-0.02038	0.0	0.07147	0.0	0.0
O	Z	35.18320	-0.00029	0.00002	0.00350	-0.00329	0.0	0.01158	0.0	0.0

TABLE V. Net atomic and gross atomic populations for the (73/2) Gaussian basis set.

MO ^a	Atom					
	H1		C		O	
	Net	Gross	Net	Gross	Net	Gross
1	0.0000	0.0000	0.0001	0.0015	1.9970	1.9985
2	0.0000	0.0004	1.9987	1.9993	0.0000	-0.0002
3	0.0012	0.0071	0.1703	0.4042	1.3488	1.5817
4	0.1098	0.2678	0.8362	1.0835	0.4535	0.3809
5	0.1159	0.2234	0.5995	0.9485	0.4538	0.6046
6	0.0436	0.0745	0.3486	0.4478	1.3378	1.3731
7	0.0000	0.0000	0.5580	0.7715	1.0150	1.2285
8	0.3558	0.3165	0.0766	0.1142	1.3902	1.2528
σ Subtotal		0.8897		5.0291		7.1914
π Subtotal		0.0000		0.7715		1.2285
Total	0.6262	0.8897	4.5880	5.8006	7.9962	8.4199

^a The molecular orbitals are ordered according to the orbital energies. See Table II.

III. DISCUSSION

The results for formaldehyde given in the previous section illustrate the usefulness of Gaussian orbitals as expansion functions for molecular SCF calculations. Such basis functions are popular because of the ease with which the multicenter atomic integrals can be evaluated. However, this advantage is somewhat offset due to the large basis sets required to obtain accurate results. Because of this, the SCF phase of the problem can make the calculation with Gaussian orbitals as time consuming as those employing Slater orbitals. One way to overcome this disadvantage is by using contracted Gaussian sets.^{1,18} Calculations on the ethylene¹ and water² molecules indicate that little accuracy is lost with moderate amounts of contraction. Such a procedure greatly reduces the amount of computer time required. Since our wavefunctions were calculated using uncontracted basis functions, the results can be

TABLE VI. Overlap populations for the (73/2) Gaussian basis set.

MO ^a	Overlap population			
	H1-H2	H1-C	H1-O	C-O
1	0.0000	0.0000	0.0000	0.0029
2	0.0000	0.0009	0.0000	-0.0004
3	0.0002	0.0063	0.0053	0.4552
4	0.0223	0.3068	-0.0131	-0.1190
5	-0.0238	0.2186	0.0204	0.2609
6	0.0098	0.0730	-0.0209	0.1126
7	0.0000	0.0000	0.0000	0.4270
8	-0.0957	0.0960	-0.0790	-0.1169
σ Subtotal	-0.0872	0.7016	-0.0873	0.5952
π Subtotal	0.0000	0.0000	0.0000	0.4270
Total	-0.0872	0.7016	-0.0873	1.0222

^a The molecular orbitals are ordered according to the orbital energies. See Table II.

¹⁸ E. Clementi and D. R. Davis, *J. Comput. Phys.* **1**, 223 (1966); also see E. Clementi, *J. Chem. Phys.* **46**, 3851 (1967), and succeeding papers in that series.

used to optimally determine contraction coefficients.¹ Such contracted functions may then be employed to study larger aldehydes or ketones, etc.

The dissociation energies presented in Table I are indicative of *ab initio* attempts to calculate this differential property. The problem is well documented^{16,19-21} and arises because dissociation energies are small quantities obtained by subtracting two large quantities with sizable inherent errors (i.e., correlation energy). The wavefunction from the (95/3) basis set predicts 59% of the observed dissociation energy, compared to 65% for a calculation on ethylene with an identical basis set.¹ Hollister and Sinanoğlu¹¹ estimate the molecular extra correlation energy for formaldehyde to be 3.74 eV. Adding this to the calculated dissociation energy, we obtain a "corrected" dissociation energy of 13.37 eV, which is still in error by 2.87 eV. Presumably this error arises from basis-set truncation, particularly in the neglect of *d* and higher orbitals in the molecular basis set. Note that the dissociation energy for the (73/2) basis set is nearly as good as that for the (95/3) basis set and is considerably better than the single Slater result.

To the extent that Koopmans' theorem²² holds, the negative of an orbital energy is just the vertical ionization energy needed to remove an electron from that orbital. In Table II we note surprisingly good agreement for the π orbital, $1b_1$ (calculated, 14.57 eV vs experimental, 14.40 eV), fair agreement for the so-called *n* orbital, $2b_2$ (calculated, 12.04 eV vs experimental, 10.86 eV), and increasingly worse agreement as the orbital becomes more tightly bound. Quite similar results are observed in ethylene.¹ The error arises from two sources: (a) a neglect of the self-con-

¹⁹ A. C. Wahl, *J. Chem. Phys.* **41**, 2600 (1964).

²⁰ P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**, 1973 (1966).

²¹ P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47**, 614 (1967); and P. E. Cade and W. M. Huo, *ibid.* **47**, 649 (1967).

²² T. Koopmans, *Physica* **1**, 104 (1933).

TABLE VII. Net atomic and gross atomic populations for the (95/3) Gaussian basis set.

MO ^a	Atom					
	H1		C		O	
	Net	Gross	Net	Gross	Net	Gross
1	0.0000	0.0000	0.0000	-0.0002	2.0004	2.0002
2	0.0000	0.0000	1.9996	1.9998	0.0000	0.0001
3	0.0013	0.0066	0.2104	0.4752	1.2492	1.5116
4	0.1012	0.2468	0.8988	1.1235	0.4561	0.3829
5	0.1312	0.2344	0.5796	0.0237	0.4542	0.6074
6	0.0509	0.0834	0.3814	0.5022	1.2937	1.3310
7	0.0000	0.0000	0.4944	0.7101	1.0741	1.2899
8	0.3812	0.2980	0.1032	0.1375	1.4715	1.2664
σ Subtotal		0.8692		5.1619		7.0996
π Subtotal		0.0000		0.7101		1.2899
Total	0.6659	0.8692	4.6675	5.8720	7.9993	8.3895

^a The molecular orbitals are ordered according to the orbital energies. See Table II.

sistency requirement for the ionized state, inclusion of which would decrease the calculated ionization energy, and (b) a difference in the correlation energies of the neutral and ionized molecules, inclusion of which would increase the calculated ionization energy. Thus, the correction to the ionization energy calculated using Koopmans' theorem is a balancing of two oppositely directed effects. In some cases the two errors nearly cancel, such as for the π orbital, and in others the sum may be quite large, such as for the n and more deeply buried orbitals. Of course, an additional error arises from the use of a truncated basis set, which may increase or decrease the sum of the other two errors. Calculations on water² lead us to believe that the orbital energies for the (95/3) basis set are within ± 0.01 a.u. of the Hartree-Fock orbital energies. Our conclusions then should be unaffected by the addition of more basis functions.

The population analysis results given in Tables V-VIII can be used to classify the molecular orbitals in a qualitative, chemically interpretive, manner. In a subsequent paper, contour maps of the electronic density will be used to put this information into more pictorial form. At present we shall content ourselves with characterizing the molecular orbitals according to the various population breakdowns. The first two orbitals, $1a_1$ and $2a_1$, are the oxygen and carbon inner-shell orbitals. The following orbital, $3a_1$, is strongly CO σ bonding, with most of the charge centered on the oxygen; qualitatively, it had been assumed that this orbital was almost exclusively an oxygen $2s$ orbital; however, as we can see, molecular formation perturbs the oxygen $2s$ orbital quite strongly. The next orbital, $4a_1$, is CH σ bonding and slightly CO σ antibonding, with much of the charge associated with the carbon. The following orbital, $1b_2$, is about equally CO σ and CH

σ bonding, with the charge mainly on the oxygen and carbon. The $5a_1$ orbital is only slightly CO σ and CH σ bonding, with most of the charge localized on the oxygen and carbon. The π orbital, $1b_1$, is, of course, CO π bonding, with the charge distinctly polarized in the oxygen direction. The so-called n orbital, $2b_2$, is not particularly bonding or antibonding, as one would expect if it were to be identified as a nonbonding orbital, but the charge, while mainly localized on the oxygen, does have a significance contribution from the hydrogens. These results emphasize the major conceptual difficulty associated with Hartree-Fock theory—the individual molecular orbitals do not describe regions of space which are localized between or around nuclear centers, i.e., bonds, lone pairs, etc., but rather they are delocalized over the entire molecule.

From the population analysis discussed above, we note that the n orbital has a rather large contribution

TABLE VIII. Overlap populations for the (95/3) Gaussian basis set.

MO ^a	H1-H2	H1-C	H1-O	C-O
1	0.0000	0.0000	0.0000	-0.0004
2	0.0000	0.0001	0.0000	0.0003
3	0.0001	0.0065	0.0040	0.5168
4	0.0164	0.2864	-0.0116	-0.1232
5	-0.0381	0.2176	0.0268	0.2529
6	0.0173	0.0655	-0.0179	0.1104
7	0.0000	0.0000	0.0000	0.4315
8	-0.1638	0.1184	-0.1210	-0.1682
σ Subtotal	-0.1680	0.6945	-0.1198	0.5886
π Subtotal	0.0000	0.0000	0.0000	0.4315
Total	-0.1680	0.6945	-0.1198	1.0201

^a The molecular orbitals are ordered according to the orbital energies. See Table II.

from the hydrogen atoms. This is in distinct contradiction to the older concepts,^{5,23} which assigned this orbital as a nonbonding lone pair ($2p$) orbital on the oxygen atom. As with the minimum-basis-set calculations,²⁴ the centroid of the n orbital (i.e., $\langle z \rangle$) indicates considerable delocalization. In fact, as the basis set was refined, the centroid shifted closer to the carbon. Our calculations also predict that the n orbital is more tightly bound than experiment indicates. In summary, an LCAO-MO-SCF wavefunction for formaldehyde near the (sp) limit has an n orbital which is not localized on the oxygen atom, as had been expected, but contains significant hydrogen contributions. From the calculations on water,² we expect that these results will not be appreciably changed for a wavefunction at the Hartree-Fock limit.

The CO π bond in both the (73/2) and the (95/3) basis sets is characterized by a significant amount of charge transfer from the carbon to the oxygen. This is in agreement with our intuitive chemical concepts (electronegativities, etc.). On the other hand, the minimum Slater basis set indicates a nearly homopolar bond. This evidently arose from the use of an unoptimized, limited basis set.

From the gross population analysis of the (95/3) basis set in Table VII, we see that the hydrogen atoms are σ donors (losing 0.13 electrons), the carbon is a σ acceptor (gaining 0.16 electrons) while being a π donor (losing 0.29 electrons), and the oxygen is both a σ acceptor (gaining 0.10 electrons) and a π acceptor (gaining 0.29 electrons). The σ changes are quite large, even though in a purely pi-electron approximation such charge transfer would be ignored. The problem is particularly acute for carbon, for which the two changes are in opposite directions. The net result of the above is a charge transfer from the CH₂ group to the oxygen. The residual charge on the hydrogens and the carbon is $+0.13e$, while the oxygen has a net charge of $-0.39e$.

²³ H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy* (John Wiley & Sons, Inc., New York, 1962); M. Kasha, *Discussions Faraday Soc.* 9, 14 (1950); H. McConnell, *J. Chem. Phys.* 20, 700 (1952).

²⁴ D. E. Freeman and W. Klemperer, *J. Chem. Phys.* 45, 52 (1966).

As stated previously, in a subsequent paper we will present contour maps of the electronic density and its various partitions. We will also compare the one-electron properties of formaldehyde in the two Gaussian basis sets with the corresponding quantities from the calculation with a minimum basis set of Slater orbitals and with experiment.

IV. COMPUTATIONS

Evaluation of the integrals for both sets were performed on the CDC 6600 computer. The integral evaluation times for the (73/2) and (95/3) sets were 2.1 and 11.0 min, respectively. The SCF cycling was carried out on the CDC 6400 computer, which is a somewhat slower machine. The time for one iteration for the small set was 1.5 min and for the large set was 7.3 min. Neither calculation used symmetry-adapted basis functions. An extrapolation procedure²⁵ was used to increase the rate of convergence for both sets.

The vectors for the small set have converged to 10^{-6} , except for a few coefficients in the higher vectors changing in the fifth place. The large set has converged to 10^{-7} , again with the exception of a few coefficients in the higher vectors changing in the sixth place. The orbital energies for the (73/2) set were still changing in the fifth decimal place and for the (95/3) set in the sixth place. In each case the total energy had converged to more than eight decimal places.

ACKNOWLEDGMENTS

We wish to thank Dr. Lester Sachs and Dr. Murray Geller for making their Gaussian molecular SCF program MOSES available to us. Also, we are indebted to Dr. Geller and Dr. Vincent McKoy for a number of helpful discussions. The authors would like to thank Control Data Corporation (Mr. William F. Busch in particular) for their making 6000 series computers available to us for this research. Special thanks go to Mr. Robert L. Korsch, of Control Data Corporation, for his help throughout these calculations.

²⁵ N. W. Winter, T. H. Dunning, and V. McKoy, *J. Chem. Phys.* (to be published).