A Quantum Variational Calculation for HCHO

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THE calculation of the wave function of formaldehyde was undertaken for several reasons. The full scheme of methods for a fully automatic calculation with an unlimited number of codetors had been completed and it was required to test this on a molecule of moderate size and of chemical interest. Formaldehyde provided a valuable application. It is the simplest aldehyde and ketone, and it and associated radicals play a part in the reactions in important flames. So little is known about these that it is one of the regions in which quantum calculations may make decisive contributions. We were also very desirous of investigating such a molecule as an opportunity of developing techniques for calculations on still larger molecules. In fact, it has played its part in a development of this sort which was unforeseen until the calculation was almost complete. It was the consideration of how to formulate the wave function most clearly that gave rise to the concept of exclusive and oscillator orbitals, and it was the test case on which these were applied.

A configuration of nuclei very near to the experimental results for the minimum energy was chosen. The bond angles at the carbon atom were all taken to be 120° and the bond lengths as CH 2.0 a.u., CO 2.3 a.u. There does not appear to be great point in placing atoms at the minimum energy position in calculations of this type, since at present the accuracy is not sufficient to reproduce this within 10%, and it is more systematic to take several configurations with round number parameters and interpolate between these for the minimum energy. For this calculation the expansion function on the hydrogen atoms was chosen as $\exp(-1.2r_H)$, with the coefficient 1.2 approximately equal to the best value found in some experimental calculations on CH_2. The orbitals on the oxygen atom were $\exp(-7.7r_O)$ and $q\cdot\exp(-2.275r_O)$ where q stands for r, x, y, and z. Those on the carbon atom were $\exp(-5.7r_C)$ and $q\cdot\exp(-1.625r_C)$. These are just the Slater atomic parameters which were found in some tests on diatomic molecules to be sufficiently close to the minimum values.

The set of programs for the implementation of the scheme A to H as set out by Boys and Cook had been written by I. Jones and the authors, and this was first used to evaluate integrals, transform matrices, and then solve Roothaan's equations to obtain a SCF result. The integrals for which explicit formulas cannot be obtained were calculated by programs which replaced exponential functions by up to nine Gaussian functions. Tests indicate that all errors are likely to be less than 0.002. The orbitals and eigenvalues for this are given in Table I. It was at this stage, where there was some uncertainty about the most efficient way of introducing correlation functions, that the theory of exclusive and oscillator orbitals was worked out. The SCF orbitals were used in a program written to form the exclusive orbitals. It may be noted that to use SCF orbitals in Roothaan's formulation is not necessary, and any of the infinity of equivalent systems which minimize the energy of a single Slater determinant are equally usable as a starting point. In fact, since the exclusive orbitals represent extreme localization, whereas the SCF orbitals are spread out over the whole molecule, they do represent the worst starting point for the iteration to exclusive orbitals, though the amount of calculation on an automatic computer is quite small.

The results for the oscillator and exclusive orbitals are given in Table II. Since the orbitals can be associated with the simple chemical valency picture, they have been given names corresponding to this.

The introduction of other codetors (linear combinations of Slater determinants with total spin zero) into the complete variation problem enables the wave function approximation to adjust itself to the correlation of electronic positions, minimizing the energy by increasing their average distance apart. In Table III

TABLE I. SCF orbitals and energies for HCHO.[a]

	Occupied orbitals								Unoccupied orbitals			
$\exp(-5.7r_C)$	0.0003	−0.9957	−0.1113	0.1665	0	0.0256	0	0	−0.0814	0	−0.1679	0
$r_C\exp(-1.625r_C)$	−0.0058	−0.0233	0.2789	−0.5752	0	−0.0981	0	0	0.6599	0	1.4385	0
$\exp(-7.7r_O)$	0.9961	0	−0.2112	−0.0979	0	−0.0869	0	0	0.1103	0	0.0240	0
$r_O\exp(-2.275r_O)$	0.0186	0.0044	0.7580	0.4396	0	0.5016	0	0	−0.9111	0	−0.1523	0
$\exp(-1.2r_{H1})$	0.0002	0.0054	0.0338	−0.2460	0.2769	0.1474	0	0.3425	0.1320	0.9555	−0.9863	0
$\exp(-1.2r_{H2})$	0.0002	0.0054	0.0338	−0.2460	−0.2769	0.1474	0	−0.3425	0.1320	−0.9555	−0.9863	0
$z_C\exp(-1.625r_C)$	0.0052	0.0004	−0.1589	−0.2391	0	0.4593	0	0	−1.1776	0	0.4864	0
$z_O\exp(-2.275r_O)$	0.0048	0.0012	0.1708	−0.1716	0	−0.6847	0	0	−0.9165	0	−0.2127	0
$y_C\exp(-1.625r_C)$	0	0	0	0	0.5540	0	0	0.1896	0	−1.2548	0	0
$y_O\exp(-2.275r_O)$	0	0	0	0	0.4246	0	0	−0.8829	0	0.3195	0	0
$x_C\exp(-1.625r_C)$	0	0	0	0	0	0	−0.6543	0	0	0	0	−0.7878
$x_O\exp(-2.275r_O)$	0	0	0	0	0	0	−0.6280	0	0	0	0	0.8090
Energy (a.u.)	−20.59	−11.36	−1.370	−0.8363	−0.6768	−0.5701	−0.4698	−0.3829	0.8303	0.7615	0.6410	0.2488

[a] Total energy SCF = −113.450 a. u.

TABLE II. Exclusive and oscillator orbitals for HCHO.

	Exclusive orbitals								Oscillator orbitals			
	Ck	Ok	CH_2	CH_1	On_1	On_2	t_1CO	t_2CO	$(CH_2)_1$	$(CH_1)_1$	$(t_1CO)_1$	$(t_2CO)_1$
exp$(-5.7r_C)$	1.0057	0.0011	0.0833	0.0833	−0.0154	−0.0154	0.0566	0.0566	−0.1053	0.1053	−0.0795	−0.0795
r_C exp$(-1.625r_C)$	−0.0134	−0.0016	−0.3468	−0.3468	−0.1055	0.1055	−0.2793	−0.2793	0.9072	−0.9072	0.6553	0.6553
exp$(-7.7r_O)$	0.0037	1.0140	−0.0139	−0.0139	0.1003	0.1003	0.0516	0.0516	0.0014	−0.0014	0.0798	0.0798
r_O exp$(-2.275r_O)$	−0.0142	−0.0702	0.0542	0.0542	−0.6913	−0.6913	−0.1644	−0.1644	0.0194	−0.0194	−0.6530	−0.6530
exp$(-1.2r_{H1})$	−0.0132	0.0004	0.0934	−0.5007	0.0827	−0.1046	0.0050	0.0050	−0.0267	1.3779	−0.0438	−0.0438
exp$(-1.2r_{H2})$	−0.0132	0.0004	−0.5007	0.0934	−0.1046	0.0827	0.0050	0.0050	−1.3779	0.0265	−0.0438	−0.0438
z_C exp$(-1.625r_C)$	0.0074	0.0061	−0.2873	−0.2873	−0.0836	−0.0836	0.2390	0.2390	0.4990	−0.4990	−0.7501	−0.7501
z_O exp$(-2.275r_O)$	−0.0294	0.0261	0.1045	0.1045	0.3110	0.3110	−0.3945	−0.3945	−0.0217	0.0217	−0.6650	−0.6650
y_C exp$(-1.625r_C)$	0	0	0.4006	−0.4006	−0.1045	0.1045	0	0	−0.8872	−0.8872	0	0
y_O exp$(-2.275r_O)$	0	0	−0.0945	0.0945	−0.6857	0.6857	0	0	0.2259	0.2259	0	0
x_C exp$(-1.625r_C)$	0	0	0	0	0	0	0.4626	−0.4626	0	0	−0.5570	0.5570
x_O exp$(-2.275r_O)$	0	0	0	0	0	0	0.4440	−0.4440	0	0	0.5719	−0.5719

we give the results of double oscillator/exclusive replacements, that is, each exclusive orbital is replaced only by its associated oscillator. There is no point in making an unnecessary limitation out of the use of double oscillator/exclusive replacements, but it does seem that, at present, this may represent an adequate approximation.

A diagram for the positions of the centroids of the exclusive orbitals has been given in the previous paper by Foster and Boys.[1] It shows that the exclusive orbitals correspond in a surprisingly close manner to the chemists' picture of the valency structure. The authors feel that the present results provide data for several further investigations on different aspects to this correspondence. These may require further mathematical formulation and calculation, but is thought desirable to make the present results available at the earliest opportunity.

TABLE III. HCHO eigenvector coefficients for double replacements, oscillator/exclusive.[a]

Oscillator pair	Coefficient
...	1.000
$(CH_1)_1(CH_1)_1$	−0.076
$(t_1CO)_1(t_1CO)_1$	−0.093
$(CH_1)_1(CH_2)_1$	0.024
$(t_1CO)_1(CH)_1$	−0.021
$(t_1CO)_1(t_2CO)_1$	−0.090

[a] Total energy = −113.534 a.u.

[1] J. M. Foster and S. F. Boys, Revs. Modern Phys. **32**, 300 (1960), this issue.

The dipole moment calculated from the SCF approximation is 1.1, while the experimental result is 2.3 debyes. The dipole moment is particularly sensitive to the approximate wave function and the accuracy of the result is of the order to be expected. The dipole moment integrals were available and had already been used in the calculation of the exclusive and oscillator orbitals as described in the foregoing.

These results are being reported so early after their completion that no extensive examination has been carried out. The calculations have been checked for arithmetic errors by carrying out two completely independent automatic calculations on independent data tapes at different times. They provide some basic data and give very striking results for the first analysis of exclusive and oscillator orbitals. There are a number of further analyses on the amounts of penetration of these orbitals and their insensitivity to other changes which it is apparent will be of chemical interest. They may provide data for the testing of various possibilities in the development of methods for the synthesis of wave functions of still larger molecules.

ACKNOWLEDGMENTS

All computations were performed on the EDSAC 2, and the authors wish to express their gratitude to the Director and staff of the University Mathematical Laboratory for all assistance and facilities. J. M. F. is indebted to the Department of Scientific and Industrial Research for a studentship.