# Ethylene Wave Functions in the S.C.F. Approximation

P. Rajagopal

The Joseph E. Atkinson College, York University, Toronto, Canada

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*Dedicated to Prof Dr.* L. Biermann *on his 60th birthday*

S.C.F. Calculations on eight planar configurations of ethylene are reported.

At present the main method which provides practical procedures for the accurate calculation of many electron wave functions and energies is that of configurational interaction. In this method the wave function is expressed in the form

$$\Psi = \sum_i Y_i \Phi_i \qquad (1)$$

where the wave function $\Psi$ is expressed as a linear combination of Slater determinants constructed from normalized single electron functions, the coefficients being determined by the Rayleigh–Ritz variational method[1].

The self consistent field method[2] is the approximation of using a single determinant $\Phi$ and then adjusting some or all of the implicit parameters in this function to obtain a stationary value of the energy. This method cannot converge to the true solution of the Schrödinger equation, but for many physical properties it is a sufficient approximation. It may also be regarded as the first term in the expression for $\Psi$ above and so its calculation can be regarded as an intermediate step in the general calculation.

Recently a method of successive approximation was described by which the stationary state electronic wave function for any configuration of atoms can be calculated to any desired degree of accuracy in the self consistent field limit[3]. The method has been subsequently used to calculate the electronic energies of several systems. Calculations on $NH_3$[4] and $OH_3^+$[5] have been reported already. In this paper, calculations on eight planar configurations of $C_2H_4$, using Slater functions as the basis set, are reported.

The first theoretical study of this simple organic molecule is that of Penney[6]. An excellent summary of the several semi-empirical calculations, including some of the classic reprints, is given by Parr[7].

Recently, Moscowitz and Harrison[8] have reported an ab initio calculation[9] using Gaussian basis functions. Subsequently, Whitten[10] has published a calculation on ethylene using groups of spherical Gaussian functions (obtained from calculations on atoms) as the basis set.

Bartell et al.[11] have investigated the structure of ethylene (and deuteroethylene) by the electron diffraction method.

In Section 1 the method of wave function calculation using the technique of accumulative accuracy is briefly described. The basis set used and ethylene symmetry is considered in Section 2. The results obtained for eight configurations are reported in Section 3. The C – C and C – H distances for the energy minimum configuration are compared with the experimental values of Bartell et al. In Section 4 the results of ab initio calculations (the present work and those of references [8] and [10]) are discussed.

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## 1. The S.C.F. Wave Function for Molecules

For a $2N$ electron system with electrons in $N$ doubly occupied orbitals, the S.C.F. wave function is given by a single determinant function of the form

$$\Phi = A(\varphi_1 \alpha \varphi_1 \beta \varphi_2 \alpha \varphi_2 \beta \dots \varphi_N \alpha \varphi_N \beta) \tag{2}$$

where $A$ is the anti-symmetrizing operator and $\alpha, \beta$ are spin functions. KOOPMANS[12] showed that $\Phi$ is the S.C.F. wave function if the functions $\varphi$ are chosen to be eigenfunctions of the single electron HAMILTONIAN

$$\begin{aligned} F \equiv K + V + 2 \sum_{j=1}^{N} \mathrm{d}\boldsymbol{r}_2 \, \varphi_j^*(\boldsymbol{r}_2) \, \varphi_j(\boldsymbol{r}_2) \, r_{12}^{-1} & \\ - \sum_{j=1}^{N} \mathrm{d}\boldsymbol{r}_2 \, \varphi_j^*(\boldsymbol{r}_1) \, \varphi_j(\boldsymbol{r}_2) \, r_{12}^{-1} P(\boldsymbol{r}_2/\boldsymbol{r}_1) & \end{aligned} \tag{3}$$

where $K$ and $V$ are kinetic and potential energy operators and $P(\boldsymbol{r}_2/\boldsymbol{r}_1)$ is defined to replace $\boldsymbol{r}_1$ by $\boldsymbol{r}_2$. KOOPMANS has also shown that in this form, a good approximation to the ionised system was obtained by leaving out one of the orbitals.

The variational approximation to the eigenfunction of this operator are given by assuming that

$$\varphi_i = \sum_{j=1}^{n} X_j^i \, \xi_j \tag{4}$$

and solving the eigenvalue problem

$$\sum_{j=1}^{n} \{ (\xi_t | F | \xi_s) - E^i (\xi_t | G | \xi_s) \} X_s^i = 0 \tag{5}$$

where $n$ is greater than $N$ and $(\xi_t | G | \xi_s)$ is the overlap matrix. Since $F$ is dependent on the $X_s^i$ it is only feasible to solve this by an iteration method in which the last approximation to the $\varphi_i$ is used in the evaluation of $F$.

In the present calculation the technique of accumulative accuracy has been used. The phrase accumulative accuracy implies that at any stage it is possible to restart with a wave function that has been calculated before and improve it further, without being concerned about the details of that calculation. This characteristic can be incorporated into any calculation provided that the integrals of the form $(\varphi\varphi : \varphi\varphi)$ where $\varphi = \Sigma X \xi$ are calculated directly, instead of through the constituent integrals $(\xi\xi : \xi\xi)$.

A method of numerical integration has been used in the present calculations. The use of numerical methods has two advantages. After making the assumption (4), the first $N$ $\xi$'s can be taken to be linear combinations of functions of the form

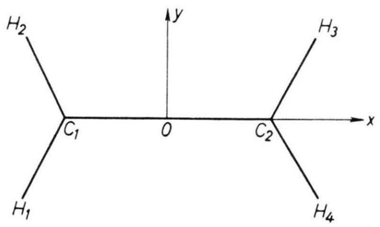
$$P(x, y, z, r) \times \exp(-\zeta r) .$$

In other words the first $N$ $\xi$'s are orbitals obtained from an earlier iteration. These $\xi$'s are "improved" by means of the remaining $(n-N)$ functions. The second advantage is that earlier iterations have been performed by the use of integrals calculated with "coarse" grids of points, thus economising on machine time. These matters have been discussed at greater length in references [3] and [4].

## 2. The Ethylene Molecule and Basis Functions Used

In its ground state, the ethylene molecule is planar and of symmetry $D_{2h}$. BARTELL et al.[11] have obtained the following values for the geometry of $C_2H_4$:

CH distance = 1.1030 Å = 2.0844 a.u.,
CC distance = 1.3369 Å = 2.5247 a.u.,
HCH angle = 117°.



The electronic structure of planar ethylene may be represented as arising from the filling of eight molecular orbitals belonging to the irreducible representations of the group $D_{2h}$. The ground state ($^1$Ag) configuration is

$$(1a_g)^2 \, (1b_{3u})^2 \, (2a_g)^2 \, (2b_{3u})^2 \, (1b_{2u})^2 \, (3a_g)^2 \, (1b_{1g})^2 \, (1b_{1u})^2$$

The first seven molecular orbitals represent the $\sigma$ core while the orbital ($^1b_{1u}$) represents the $\pi$ bond. Fourteen basis functions have been used in each calculation. They are

$\exp(-5.7\,r)$, $r\exp(-1.625\,r)$, $x\exp(-1.625\,r)$, $y\exp(-1.625\,r)$, $z\exp(-1.625\,r)$

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[12] T. C. KOOPMANS, Physica 1, 104 [1933].

| Symmetry Orbitals | Group $D_{2h}$ |
|---|---|
| $s_1 + s_2$<br>$x_1 - x_2$<br>$h_1 + h_2 + h_3 + h_4$ | $a_g$ |
| $s_1 + s_2$<br>$x_1 + x_2$<br>$h_1 + h_2 - h_3 - h_4$ | $b_{3u}$ |
| $y_1 + y_2$<br>$h_1 - h_2 - h_3 + h_4$ | $b_{2u}$ |
| $y_1 - y_2$<br>$h_1 - h_2 + h_3 - h_4$ | $b_{1g}$ |
| $z_1 + z_2$ | $b_{1u}$ |
| $z_1 - z_2$ | $b_{2g}$ |

Table 1. The symmetry orbitals of ethylene.

on each carbon atom and $\exp(-1.2\,r)$ centred on each hydrogen atom.

The symmetry orbitals of ethylene and their irreducible representations are given in Table 1. The five basis functions centred at the first carbon atom are referred to as $s_1$, $s_1$, $x_1$, $y_1$, $z_1$, those centred at the second carbon atom by suffix 2 and the basis functions centred at each hydrogen atom as $h_1$, $h_2$, $h_3$, and $h_4$.

### 3. Results of the Calculation

The orbital, electronic, nuclear and molecular energies for the eight configurations are contained in Table 2. In all these configurations the $H-C-H$ angle was taken to be 120°.

The molecular energy was expressed as a quadratic function of the $C-C$ and $C-H$ distances. From this expression the calculated minimum energy was $-77.85639$ a.u. and this occurs for

$$C-C = 2.5409 \text{ a.u.} \quad \text{and} \quad C-H = 2.0911 \text{ a.u.}$$

These $C-C$ and $C-H$ distances are to be compared with the experimental values of 2.5247 a.u. and 2.0844 a.u. respectively, obtained by BARTELL et al. in reference [11].

In an earlier paper (reference [5]) the correlation contribution to the binding energy was defined as the difference between the experimental value of the binding energy and the HARTREE–FOCK binding energy. On the basis of the data available for several systems, an empirical rule that the correlation contribution to the binding energy is $-0.045$ a.u. per bond was proposed.

The experimental value of the energy of the molecule is $-78.617$ a.u. and the energy of the separated atoms $-77.692$ a.u., so that the experimental binding energy is $-0.925$ a.u. The correlation contribution to the binding energy from six bonds in ethylene is $-0.270$ a.u. so that the HARTREE–FOCK binding energy is $-0.655$ a.u. The HARTREE–FOCK energy of the separated atoms is $-77.378$ a.u.

| Configuration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Number | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
| C–C (a.u.) | 2.4 | 2.5 | 2.6 | 2.7 | 2.6 | 2.6 | 2.6 | 2.6 |
| C–H (a.u.) | 2.0 | 2.0 | 2.0 | 2.0 | 1.9 | 2.1 | 2.2 | 2.3 |
| 1 $a_g$ | − 11.29737 | − 11.29445 | − 11.29251 | − 11.29117 | − 11.29983 | − 11.28799 | − 11.28544 | − 11.28424 |
| 1 $b_{3u}$ | − 11.29543 | − 11.29314 | − 11.29163 | − 11.29059 | − 11.29894 | − 11.28712 | − 11.28458 | − 11.28339 |
| 2 $a_g$ | − 1.05061 | − 1.03067 | − 1.01199 | − 0.99504 | − 1.02798 | − 0.99816 | − 0.98622 | − 0.97599 |
| 2 $b_{3u}$ | − 0.78367 | − 0.78807 | − 0.79195 | − 0.79584 | − 0.81956 | − 0.76631 | − 0.74226 | − 0.71979 |
| 1 $b_{2u}$ | − 0.66726 | − 0.65646 | − 0.64676 | − 0.63868 | − 0.67041 | − 0.62495 | − 0.60412 | − 0.58445 |
| 3 $a_g$ | − 0.58266 | − 0.57291 | − 0.56261 | − 0.55252 | − 0.57783 | − 0.54864 | − 0.53530 | − 0.52256 |
| 1 $b_{1g}$ | − 0.50460 | − 0.51102 | − 0.51639 | − 0.52200 | − 0.54063 | − 0.49432 | − 0.47341 | − 0.45378 |
| 1 $b_{1u}$ | − 0.40162 | − 0.38320 | − 0.36558 | − 0.34946 | − 0.37362 | − 0.35959 | − 0.35455 | − 0.35051 |
| Total electronic energy | −112.51159 | −111.76123 | −111.05315 | −110.38774 | −111.83175 | −110.32141 | −109.63065 | −108.97853 |
| Nuclear Energy | 34.67907 | 33.92007 | 33.21343 | 32.55374 | 34.02238 | 32.47189 | 31.78994 | 31.15999 |
| Total molecular energy | − 77.83252 | − 77.84116 | − 77.83972 | − 77.83400 | − 77.80937 | − 77.84952 | − 77.84071 | − 77.81854 |

Table 2. Orbital, electronic and total energies for planar ethylene ($^1$Ag) in atomic units for different configurations. (HCH angle was kept fixed at 120° for all configurations.)

so that the HARTREE–FOCK energy of the molecule is estimated to be $-78.033$ a.u.

## 4. Discussion

In ab initio calculations it is usual to call the $\xi_r$ $(r=1, 2, 3, \ldots, n)$ used in assumption (4) as basis functions. Their choice is in principle only a matter of computational economics. If these functions can be specified so that as $n \rightarrow \infty$ they form a complete system, then the same answer would be obtained irrespective of the particular functions chosen. The two specific forms that are commonly used are SLATER type of functions and GAUSSian type of functions.

If ab initio calculations of the type described in reference[1] are performed, the number of integrals to be computed is of the order of $n^4$, whatever be the form of the basis function and the total amount of work is of the order of the fifth power of $n$. Integral calculation is, however, especially easy if GAUSSian functions are used and in this case the problem of wave function calculations becomes essentially a form of data processing.

In calculations using the technique of accumulative accuracy [in which integrals of the form $(\varphi\varphi : \varphi\varphi)$ are computed directly] the total amount of work is of the order of $n^{1.5}$. The present method of integral calculation by numerical methods does have further advantages mentioned earlier.

MOSKOWITZ[9] has used 48 GAUSSian functions of the form $P(x, y, z, r) \times \exp(-\zeta r^2)$ as the basis set and has obtained the molecular energy of $C_2H_4$ to be $-77.95022$ a.u.

WHITTEN[10] has used GAUSSian functions of the form $\exp(-\zeta r^2)$ as the basis set. Using these functions, calculations on atoms have been done from which linear combinations of spherical GAUSSian (or "groups") are obtained to represent spatial functions with different range characteristics. These groups of functions form the basis set for an ethylene calculation. 96 spherical GAUSSIANS have been used, treated as consisting of sixteen groups in the first calculation and twenty four groups in the second calculation. The calculated energies are respectively $-77.93900$ a.u. and 78.00121 a.u.

These results, including the present work are summarised in Table 3.

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| | MOSCOWITZ[9] | WHITTEN[10] | | Present work |
|---|---|---|---|---|
| Basis set | GAUSS ianfunctions of the form $P(x, y, z, r) \exp(-\zeta r^2)$ | Linear combinations of GAUSSians of the form $\exp(-\zeta r^2)$ | | SLATER functions |
| Number of basis functions | 48 | 16 groups (using 96 GAUSSIANS) | 24 groups (using 96 GAUSSIANS) | 14 |
| Molecular energy | $-77.95022$ a.u. | $-77.93900$ a.u. | $-78.00121$ a.u. | $-77.85639$ a.u. |

Table 3. Summary of results of ab initio calculations on ethylene.