Theoret. Chim. Acta (Berl.) 40, 231–236 (1975)

Calculation of the Electronic Structure of Ethylene by the SCF-Xα Scattered Wave Method

Aldwyn H. Tang Kai* and Jean-Louis Calais

Quantum Chemistry Group, Uppsala University

Received March 6, 1975/July 28, 1975

The electronic structure of ethylene is investigated by the implementation of the Xα scattered wave method and a comparison is made with SCF LCAO results. Calculations are also carried out for different geometrical configurations of the molecule, in which one HCH plane is rotated through different angles relative to the other.

Key word: Ethylene

1. Introduction

In this paper, the SCF-Xα scattered wave method, as developed by Johnson [1–5] and Johnson and Smith [6–9], is used to determine the electronic structure of ethylene, with a view towards extending its application to polymers.

Moskowitz and Harrison [10] carried out an extensive SCF LCAO calculation using Gaussian orbitals, treating all 16 electrons and calculating rigorously the multicentre integrals. Among the most recent calculations on the ethylene molecule, Meza and Wahlgren [11] used linear combinations of simple Gaussians.

The results obtained by the present method are compared with those of Moskowitz and Harrison, and Meza and Wahlgren. It is well to note here that, in this model, all 16 electrons are treated and there are no multicentre integrals to be calculated.

2. Method

A complete description of the method is given in [5]. Here, only the main points of the method are outlined. The method requires the partitioning of the molecular space into three contiguous regions:

An Atomic Region (I), within non-overlapping spheres centred on the atomic nuclei.

An Interatomic Region (II), between the atomic spheres and an outer sphere enveloping the entire molecule.

An Extramolecular Region (III), exterior to the sphere surrounding the molecule.

---

* Present address: Physics Department, University of the West Indies, St. Augustine, Trinidad.

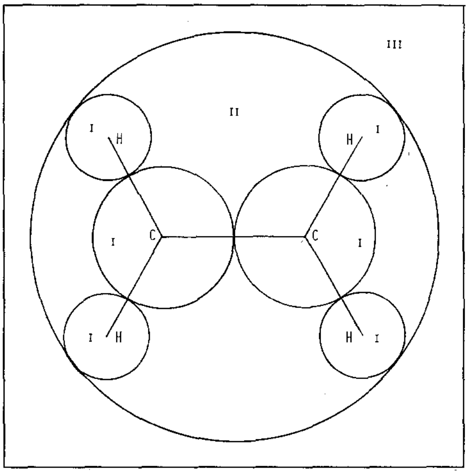

Fig. 1. Division of the ethylene molecule into atomic (I), interatomic (II) and extramolecular (III) regions.
$\alpha_C = 0.75847$; $\alpha_H = 0.97804$; $\alpha_{II} = \alpha_{III} = 0.83166$
$a_{C-C} = 1.34\text{Å}$; $a_{C-H} = 1.069\text{Å}$; angle HCH = 120°
$R_C = 0.67\text{Å}$; $R_H = 0.399\text{Å}$; $R_{\text{outer}} = 1.894\text{Å}$

The method, in its original form, requires the numerical solution of the one-electron Schrödinger equation in each of the three regions I, II, and III in the partial wave representation. The potential is spherically averaged in the spherical regions I and III, and volume averaged in region II. These potentials include the Xα statistical operator which is proportional to the third root of the density [12]. The orbitals and their first derivatives are joined continuously in the regions of the cluster by means of multiply-scattered wave theory, and the solutions of the Schrödinger equation on either side of the outer sphere are matched at the sphere boundary. A secular equation is then obtained, which when solved, yields the molecular orbital energies. The size of the secular equation can be reduced by incorporating the symmetry of the molecule.

In Fig. 1, the ethylene molecule is partitioned into atomic, interatomic and extramolecular regions. The atomic spheres are assumed touching along their bond directions and the outer sphere is assumed to be touching the spheres centred on the four hydrogen atoms. The values for the bond lengths and the bond angle were taken from Coulson [13]; and the α-values for carbon and hydrogen were obtained from Schwarz [14]. The α-parameter for the interstitial region was calculated as a weighted average of the number of valence electrons; and that of the extramolecular region was chosen the same as the interstitial region.

Self-consistent atomic charge densities were generated by a program of the Herman-Skillman type [15], modified to incorporate different α parameters. A potential from a superposition of these charge densities was then generated. This potential served as the starting potential for an SCF calculation of the molecule. A non-SCF calculation was first made, in which the eigenvalues of the one-electron equations were calculated without iteration to self-consistency. Then an SCF

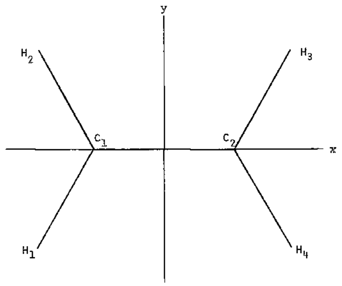

Fig. 2. Planar configuration of the ethylene molecule. The z-axis is out of the plane of the paper

Table 1. Symmetry orbitals and irreducible representations for different values of θ

Symmetry orbitals	D_{2h} ($\theta=0°$)	D_2 ($0°<\theta<90°$)	D_{2d} ($\theta=90°$)
s_1+s_2 x_1-x_2 $h_1+h_2+h_3+h_4$	a_g	a	a_1
s_1-s_2 x_1+x_2 $h_1+h_2-h_3-h_4$	b_{3u}	b_3	b_2
y_1+y_2 $h_1-h_2-h_3+h_4$	b_{2u}	b_2	e
y_1-y_2 $h_1-h_2+h_3-h_4$	b_{1g}	b_1	e
z_1+z_2	b_{1u}	b_1	e
z_1-z_2	b_{2g}	b_2	e

calculation was carried out which yielded the self-consistent orbital energies and the total statistical energy [12]. The set of programs used had been obtained from Dr. J. Connolly, Quantum Theory Project, University of Florida.

The symmetry of the planar ethylene molecule is that of the D_{2h} group and the symmetry orbitals and irreducible representations were calculated using the coordinate system and the numbering of the atoms as shown in Fig. 2.

On rotating one of the HCH planes at an angle θ relative to the other, the symmetry is lowered and the molecule then possesses a D_2 symmetry. At $\theta=\pi/2$, the symmetry is raised to D_{2d}. The symmetry orbitals and irreducible representations are given in Table 1.

3. Results and Discussion

The orbitals and total energies for the planar ethylene calculations are shown in Table 2, where a comparison is made with the results of Moskowitz and Harrison

Table 2. Orbital and total energies of the planar ethylene molecule. Energies are in atomic units (Hartrees)

Orbital	Present calculation	Moskowitz and Harrison[a]	Meza and Wahlgren[b]	Experimental I.P.[c]
$1a_g$	−10.1993	−11.2539	−11.2479	—
$1b_{3u}$	−10.1993	−11.2526	−11.2463	—
$2a_g$	− 0.7441	− 1.0584	− 1.0379	—
$2b_{3u}$	− 0.5815	− 0.8067	− 0.7895	—
$1b_{2u}$	− 0.5069	− 0.6604	− 0.6412	−0.5847
$3a_g$	− 0.4555	− 0.5829	− 0.5809	−0.5413
$1b_{1g}$	− 0.4554	− 0.5174	− 0.4999	−0.4697
$1b_{1u}$	− 0.3611	− 0.3814	− 0.3728	−0.3862
Total energy	−76.8542	−77.8002	−77.9464	—

[a] The results of the most extensive basis set [10-(7332)]. Ref. [10].
[b] The results of the [H/2] basis set of Ref. [11].
[c] See Ref. [16].

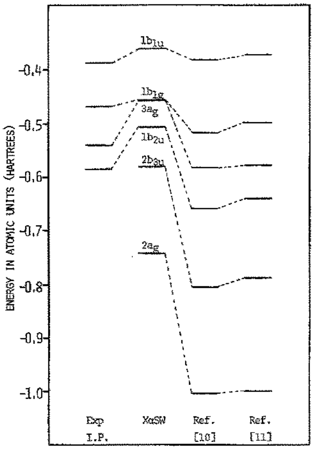

Fig. 3. Graphical representation of the results displayed in Table 2. The $1b_{3u}$ and $1a_g$ states are not shown

[10] and Meza and Wahlgren [11], and experimental ionization potentials. The geometry used by Moskowitz and Harrison is as follows:

CH = 1.07Å, CC = 1.35Å and the angle HCH = 120°.

The energies obtained by the present method are higher than those of the SCF LCAO methods. The order of the orbitals is the same in all the cases cited. The total energy of −76.8542 a.u. is higher than the experimental value of −78.5659 a.u. [10]. The nuclear repulsion energy of 33.5308 a.u. is comparable with Moskowitz and Harrison's value of 33.4022 a.u. The differences between the orbital energies of the $1b_{1u}$, $1b_{1g}$, $3a_g$ and $1b_{2u}$ states and the corresponding experimental ionization potential values range between 0.6 eV and 2.4 eV. A graphical representation of Table 2 is shown in Fig. 3.

Table 3. Results for the twisted molecule. The quantities in parentheses are the results of Ref. [10], for the basis set [2-(3221)]. The energies (in Hartrees) are negative

Orbital	$\theta=0°$	$\theta=10°$	$\theta=30°$	$\theta=60°$	$\theta=80°$
$1a_g$	10.1993(10.8351)	10.1994(10.8351)	10.1991	10.1892(10.8324)	10.1340(10.8309)
$1b_{3u}$	10.1993(10.8330)	10.1994(10.8329)	10.1991	10.1892(10.8302)	10.1340(10.8289)
$2a_g$	0.7441 (1.0038)	0.7441 (1.0033)	0.7438	0.7397 (1.0013)	0.7198 (1.0007)
$2b_{3u}$	0.5815 (0.7656)	0.5814 (0.7654)	0.5811	0.5768 (0.7648)	0.5576 (0.7641)
$1b_{2u}$	0.5068 (0.6231)	0.5059 (0.6224)	0.4977	0.4687 (0.6001)	0.4260 (0.5837)
$3a_g$	0.4555 (0.5417)	0.4554 (0.5415)	0.4546	0.4495 (0.5396)	0.4275 (0.5390)
$1b_{1g}$	0.4554 (0.4693)	0.4544 (0.4719)	0.4456	0.4100 (0.5251)	0.3402 (0.5482)
$1b_{1u}$	0.3611 (0.3683)	0.3610 (0.3648)	0.3610	0.3580 (0.2934)	0.3419 (0.2563)
Total energy	76.8542(74.6402)	76.8506(74.6382)	76.8217	76.7149(74.5597)	76.5793(74.4987)

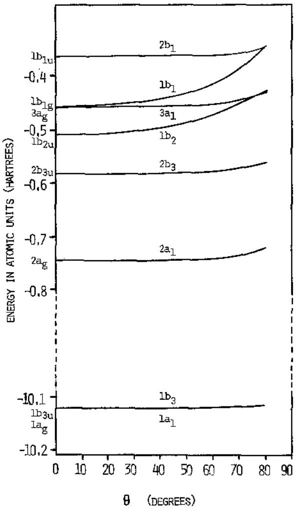

Fig. 4. The shift of the orbital energies under different angles of twist

The results obtained for the twisted ethylene molecule are given in Table 3, where a comparison is again made with the results of Moskowitz and Harrison [10] for angles of 0, 10, 60 and 80 degrees. The results indicate the expected upward shift of the ground state energy [17, 18]. The orbital energies increase with increasing θ. Fig. 4 indicates the shift of the orbital energies under different angles of twist.

4. Conclusions

Although better ionization potentials might have been obtained by means of the so-called transition state concept [19], our primary aim was not to get the best possible agreement with experiment, but only to make an exploratory calculation as a preparation for "polymer calculations". Scheire and Phariseau [20–22] have recently developed an extension of the conventional scattered wave method to spheroidal molecules and to molecules with arbitrary boundaries. Although this might be quite difficult to implement for numerically, such a procedure nevertheless opens up interesting possibilities, in particular for polymers. At present the method is being applied to two ethylene molecules terminated at both ends by saturating atoms to take care of the dangling bonds. Perhaps further investigations about the choice of calculational parameters could produce somewhat better results. The computational time taken was of the order of 62 minutes on a CDC 7600 computer for all calculations.

Acknowledgements. The authors wish to thank their colleagues for their many valuable discussions. One of us (A.T.K.) is grateful to the Swedish International Development Authority for providing a fellowship.

References

1. Johnson,K.H.: J. Chem. Phys. **45**, 3085 (1966)
2. Johnson,K.H.: Intern. J. Quantum Chem. **1S**, 361 (1967)
3. Johnson,K.H.: Intern. J. Quantum Chem. **2S**, 233 (1968)
4. Johnson,K.H.: Intern. J. Quantum Chem. **4S**, 153 (1971)
5. Johnson,K.H.: Advan. Quantum Chem. **7**, 143 (1972)
6. Johnson,K.H., Smith,F.C.,Jr.: Phys. Rev. Letters **24**, 139 (1970)
7. Johnson,K.H., Smith,F.C.,Jr.: Chem. Phys. Letters **7**, 541 (1970)
8. Johnson,K.H., Smith,F.C.,Jr.: Chem. Phys. Letters **10**, 219 (1971)
9. Johnson,K.H., Smith,F.C.,Jr.: Intern. J. Quantum Chem. **5S**, 429 (1971)
10. Moskowitz,J.W., Harrison,M.C.: J. Chem. Phys. **42**, 1726 (1965)
11. Meza,S., Wahlgren,U.: Theoret. Chim. Acta (Berl.) **21**, 323 (1971)
12. Slater,J.C.: Advan. Quantum Chem. **6**, 1 (1972)
13. Coulson,C.A.: Valence, 2nd Ed. London: Oxford University Press 1961
14. Schwarz,K.: Phys. Rev. **B5**, 2466 (1972)
15. Herman,F., Skillman,S.: Atomic structure calculations. Englewood Cliffs, New Jersey: Prentice-Hall 1963
16. Eland,J.H.D.: J. Mass Spectrom. Ion Physics **2**, 471 (1969)
17. Parr,R.G., Crawford,B.L.,Jr.: J. Chem. Phys. **16**, 526 (1948)
18. Robin,M.B., Basch,H., Kuebler,N.A., Kaplan,B.E., Meinwald,J.: J. Chem. Phys. **48**, 5037 (1968)
19. Slater,J.C.: Quantum theory of molecules and solids, Vol. IV. New York: McGraw-Hill 1974
20. Scheire,L., Phariseau,P.: Chem. Phys. Letters **26**, 149 (1974)
21. Scheire,L., Phariseau,P.: Intern. J. Quantum Chem. Symp. No. 8 109 (1974)
22. Scheire,L., Phariseau,P.: Intern. J. Quantum Chem., to be published

Dr. J.-L. Calais
Quantum Chemistry Group
University of Uppsala
Box 518
S-75120 Uppsala 1
Sweden