Tetrahedron 1962 Vol 17 pp 171 to 175. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC WAVE FUNCTION OF METHANE AND C–H BOND ORBITAL

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(*Received 25 January* 1961)

Abstract—Using the delocalized bond orbital method, obtained as a linear combination of the sp^3 hybrid orbitals on the carbon and 1s orbitals on the hydrogens, we have calculated the energy of methane at the distances 0.9, 1.1 and 1.3 Å as a function of the orbital exponents. A discussion is given of the results in relation to the method of using a monocentric wave function on the carbon.

The energy at 1.1 Å is −40.122 a.u. and is in a rather good agreement with the results obtained by Mills and recently by Saturno and Parr.

The error with respect to the experimental value (0.4 a.u.) is of the order of the correlation energy.

INTRODUCTION

ALTHOUGH the bond between carbon and hydrogen is quite important in chemistry, nevertheless we know very little about it. The reason that the bond is rather peculiar is the small size of the hydrogen atom and the short length of the bond. If we look, for instance, at the centre of the charge-cloud of the sp^3 hybrid orbital of the carbon alone, we find that it is rather close to the position of the proton in the C–H bond. Of course in this situation the overlap between such a hybrid and the atomic orbital of the hydrogen is big and the hybrid itself is already a good approximation to the bond orbital.

The purpose of the present work is to study how well the usual approximation of the L.C.A.O. method applies to this kind of bond where one of the orbitals has the greatest role and to see what is the improvement compared with one of the other methods sometimes used to describe it, in which we use only monocentric orbitals on the carbon.[1-3]

CALCULATION

In almost all previous work on methane the delocalized molecular orbital method has been used with the four valence-shell atomic orbitals of carbon and the four 1s orbitals of the hydrogens as basis.[4,5]

In this case the chemical picture of a C–H bond loses some of its meaning.

Therefore, with the specific purpose of retaining the chemical significance of a bond, we introduce four localized molecular orbital bond orbitals ϕ_1, ϕ_2, ϕ_3, ϕ_4, one for

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each C—H bond, and we write the molecular orbitals of methane as linear combinations of these bond orbitals, with the correct symmetry of the tetrahedral group:

$$\Phi_1 = \frac{1}{2(1+3S)^{1/2}}[\phi_1+\phi_2+\phi_3+\phi_4]$$

$$\Phi_2 = \frac{1}{2(1-S)^{1/2}}[\phi_1+\phi_2-\phi_3-\phi_4]$$

$$\Phi_3 = \frac{1}{2(1-S)^{1/2}}[\phi_1-\phi_2+\phi_3-\phi_4]$$

$$\Phi_4 = \frac{1}{2(1-S)^{1/2}}[\phi_1-\phi_2-\phi_3+\phi_4]$$

Φ_1 is non-degenerate and of symmetry A; Φ_2, Φ_3, Φ_4, are degenerate with symmetry T, and S is the bond orbital overlap $\int\phi_1\phi_2\,d\tau$. The total molecular wave function is:

$$\Psi = \mathscr{A}(1s_C)^2\,\Phi_1^2\,\Phi_2^2\,\Phi_3^2\,\Phi_4^2$$

where the symbol $\mathscr{A}$ denotes an antisymmetrical product. Now each normalised bond orbital ϕ is written as a linear combination of a sp^3 hybrid orbital of the carbon and the corresponding $1s$ atomic orbital of a hydrogen:

$$\phi = N(q_C + \lambda q_H)$$

The sp^3 hybrid orbitals of carbon are obtained from $2s$ and $2p$ Slater orbitals, in which the $2s$ function is orthogonalized to the $1s_C$ orbital. In this way all the molecular orbitals are orthogonal to each other, except for the non-orthogonality of the λq_H terms in Φ_1 with the $1s_C$ of carbon; but the latter effect is negligable because this overlap is very small. The energy E associated with the wave function Ψ is a function only of one parameter λ (besides the exponents of the atomic orbitals ζ_C and ζ_H) and must be minimized with respect to it.

The calculations have been done for three bond lengths (0·9, 1·1 and 1·3 Å) and for several values of the orbital exponents ζ_C and ζ_H in the following ranges:

ζ_C from 1 to 2 (The Slater isolated-atom value is 1·625)

ζ_H from 0 to 2 (the isolated-atom value is 1)

ζ_{2s} and ζ_{2p} have been taken to be equal.

For the exponent of the carbon orbital $1s_C$ we have taken the Slater value of 5·7.

The complete description of the energy surface as a function of ζ_C and ζ_H at $R = 1.1$ Å is given in Fig. 1. For the other bond lengths the situation is analogous.

The best bond orbital wave functions at the several distances are the following:

$$R = 0{\cdot}9\ \text{Å} \qquad \phi = 0{\cdot}8682\,(q_C + 0{\cdot}3211\,q_H)$$

$$R = 1{\cdot}1\ \text{Å} \qquad \phi = 0{\cdot}8512\,(q_C + 0{\cdot}2876\,q_H)$$

$$R = 1{\cdot}3\ \text{Å} \qquad \phi = 0{\cdot}7664\,(q_C + 0{\cdot}4324\,q_H)$$

The corresponding energies are reported in Table 1, while in Table 2 we give the best energies and exponents for monocentric bond orbitals (These are obtained by putting $\lambda = 0$ in Ψ). All the bicentric integrals and penetration three-centre integrals have been evaluated exactly. The other polycentric integrals have been evaluated by the Mulliken approximation:

$$\varphi_a\varphi_b \simeq \tfrac{1}{2} S_{\varphi_a\varphi_b}(\varphi_a^2 + \varphi_b^2)$$

In this work φ_a and φ_b are either sp^3 hybrid orbitals of carbon atom or pure $1s$ atomic orbitals of hydrogen atoms.

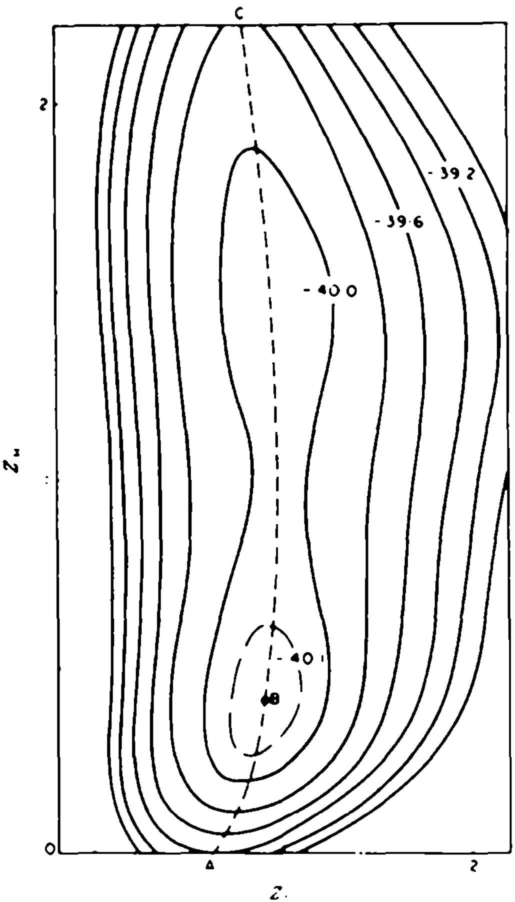

Fig. 1 The energy surface at $R = 1{\cdot}1$ Å as a function of ζ_C and ζ_H

The equilibrium bond length was calculated using the following Morse expression:

$$E = E^0 + D(1 - e^{-a(r - r_e)})^2$$

where

$$E^0 = -40{\cdot}1263 \text{ a.u.} \qquad a = 2{\cdot}0379 \text{ Å}^{-1}$$

$$D = 0{\cdot}63 \text{ a.u.} \qquad r_e = 1{\cdot}0575 \text{ Å}$$

D is the dissociation energy.[2] The values for E^0, a and r_e are those which satisfy the calculated energies. The bond length calculated in this way is 1·058 Å.

DISCUSSION

The energy surface regarded as a function of ζ_C and ζ_H has the shape of a rather long and narrow basin in such a way that the energy is very sensitive to the variations of ζ_C and much less sensitive to ζ_H. The bottom of the basin is rather flat due to a certain compensation between the variations of ζ_H and λ in such a way that the energy does not change very rapidly. Of particular significance is the part of the surface close to ζ_H 0·2 where the slope is great and shows that the improvement of the bond wave function due to the contribution of the hydrogen orbital is remarkable.

TABLE 1. ENERGIES AND ORBITAL EXPONENTS FOR THE BICENTRIC BOND ORBITALS MODEL OF METHANE

R (Å)	ζ_C	ζ_H	E (a.u.) total
0·9	1·59	0·3	40·036
1·1	1·45	0·41	40·122
1·3	1·57	0·78	40·030

Drawing a line through the minimum points at several values of ζ_H we have the line *A—B—C*. The part *B*–*C* is rather straight with ζ_C constant in agreement with the fact that the greatest contribution to the bond orbital comes from the sp^3 hybrid and therefore is insensitive to the variations of the hydrogen orbitals. But the part *A—B* has a certain curvature in such a way that the best ζ_C for the monocentric orbitals is different from the best ζ_C in the bond orbitals, being always smaller than when bond orbitals are used.

TABLE 2. ENERGIES AND ORBITAL EXPONENTS FOR THE MONOCENTRIC BOND ORBITALS MODEL OF METHANE

R (Å)	ζ_C	E (a.u.) total
0·9	1·453	39·274
1·0	1·375	39·363
1·1	1·314	39·366
1·2	1·264	39·327
1·3	1·252	39·280

This means that when we use monocentric sp^3 orbitals as bond orbitals, we are forced to compromise between the desire to place some charge around the H nucleus and also some other charge at the distance from the C nucleus which is appropriate to a normal carbon atom. This makes the monocentric orbitals more diffuse (smaller ζ_C) than for a normal carbon atom. However, as soon as we find an alternative way of placing charge close to the H nucleus, by introducing the term $\lambda\varphi_H$ in the bond orbital ϕ, the sp^3 hybrids are free to resume their normal size, so that ζ_C increases. All this is very clear from Fig. 1.

It also shows us why, if we insist on using a monocentric expansion, we can only expect to get a good energy by introducing considerable configuration interaction.

The values of the energy are quite good and are slightly better than the recent values of Saturno and Parr[3] obtained with a very flexible monocentric wave function

TABLE 3 CALCULATED AND EXPERIMENTAL ENERGIES OF THE METHANE MOLECULE

	R (Å)	E (a u)
This work	1·1	40·122
Mills[illegible]	1·058	40·06
Saturno and Parr[illegible]	1·058	39·804
Experimental	1·094(*)	40·522(†)

* From Thomas and Welsh.[9]

† This value, according A F Saturno and R G. Parr, assumes the heat of sublimation of carbon to be 169·58 kcal/mole.

(Table 3). However, the difference is small and we cannot say whether it is due to a better wave function or to the use of Mulliken's approximations in the evaluation of the polycentric integrals. The difference with the experimental value is small (0·4 a.u.) and is of the order of the correlation energy.

Acknowledgements -The author is particularly indebted to Prof C A Coulson for many suggestions and discussions in the course of the work and for his kind hospitality at Oxford

Grateful acknowledgement is made also to the National Council of Research (C N R Italy) for the award of a fellowship

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