

The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach

I. Methane under Deformation*

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The valence electron density in the iterative extended Hückel approach of methane in its natural and various deformed states is given in the form of density level diagrams. The results indicate that deformation leads to density distributions which are not symmetric about the appropriate interatomic vectors, and hence to bonds of bent bond type. Even the density difference diagrams show maxima outside the appropriate interatomic vectors. These results are not in agreement with the picture given by directed hybrids which provide an electron distribution symmetrical with respect to the interatomic vectors and which are represented by a real hybridization matrix.

In contrast to concepts like molecular orbitals and hybrids, the electron density is an observable and experimentally accessible quantity. It is intimately connected with the concept of valence. Some questions in this context have recently been commented on by Mårtensson and Sperber.¹ In this paper we will consider another closely related question, that of re-hybridization.

It is convenient to talk about and use the concepts of sp^3 and sp^2 hybridization when one is dealing with structural problems. The situation is less simple when we have to consider configurations which are intermediate between these two. At least formally these hybridization configurations can be described by real or complex unitary matrices, provided that the symmetry is sufficiently high. If we consider methane, for instance, we may carry out the theoretical experiment including a deformation of high symmetry as indicated in Fig. 1. The C-H bond in the direction of the x axis is kept fixed and the three remaining interatomic vectors are moved symmetrically. The limiting case of this flattening procedure has the three interatomic vectors in the yz plane forming

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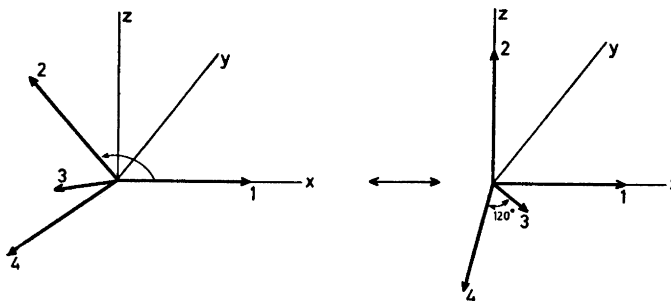


Fig. 1. Interatomic vectors of methane under deformation.

angles of 120° with each other. All the C–H interatomic distances are supposed to remain unchanged and equal to 1.09 \AA during the deformation procedure.

In the simple model of hybrids, built up from atomic orbitals of s and p type, the flattening procedure can be described in two ways. If r is a positive parameter, we can use the unitary, real hybridization matrix:

$$\begin{bmatrix} r & (1-r^2)^{\frac{1}{2}} & 0 & 0 \\ \frac{(1-r^2)^{\frac{1}{2}}}{\sqrt{3}} & -\frac{r}{\sqrt{3}} & 0 & \frac{2}{\sqrt{6}} \\ \frac{(1-r^2)^{\frac{1}{2}}}{\sqrt{3}} & -\frac{r}{\sqrt{3}} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \\ \frac{(1-r^2)^{\frac{1}{2}}}{\sqrt{3}} & -\frac{r}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \end{bmatrix}$$

We see, that for $r = \frac{1}{2}$ we get the ordinary sp^3 hybridization matrix giving one hybrid in the direction of the x axis. For $r = 0$ we get the limiting case with the hybrid in the direction of the x axis consisting only of the p_x atomic orbital.

The valence angle (independent of if this is defined as the angle between two hybrids, or as the angle between the vectors from the atomic center to the point of gravity of the hybrid density function of the two hybrids considered) between the C–H₁ and the remaining C–H bonds is then the only remaining degree of freedom under the deformation. It is expressed by its cosine

$$\gamma = -r/(r^2 + 2)^{\frac{1}{2}}, \quad \text{with } 0 \leq r \leq 1 \quad (1)$$

The two limiting values of r correspond to $\gamma = -1/\sqrt{3}$ (about 125°) and to $\gamma = 0$ (90°). For $r = \frac{1}{2}$ we get $\gamma = -\frac{1}{3}$ (tetrahedral angle).

Assuming equal amounts of s orbital in the hybrids during the deformation, we may describe the flattening procedure by a unitary, complex matrix:²

$$\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} e^{i\kappa} & 0 & 0 \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} e^{i\kappa} & 0 & -\frac{2}{\sqrt{6}} \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} e^{i\kappa} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \\ \frac{1}{2} & -\frac{1}{2\sqrt{3}} e^{i\kappa} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \end{bmatrix}$$

where $\exp[i\kappa]$ is a phase factor. The cosine, γ , of the valence angle is now given by the corresponding expression:

$$\gamma = -\cos\kappa / (8 + \cos^2\kappa)^{1/2} \quad (2)$$

For $\kappa = 0$ we get the ordinary, real hybridization matrix for sp^3 configuration (the same as for $r = \frac{1}{2}$ in the real case above). The limit value $\gamma = 0$, is, in this representation, expressed by the purely imaginary elements in column 2. The hybrid in the direction of the x axis is then given by $h_x = (1/2)s + (\sqrt{3}/2)ip_x$. Eqn. (2) covers the angular interval from the tetrahedral angle to 90° . A matrix can also be constructed which covers the interval from the tetrahedral angle to 180° . For this purpose, however, we have to introduce one and the same phase factor in columns 3 and 4.

The directed hybrids obtained from real matrices provide an electron density which is symmetrically distributed about the interatomic vectors.* We know that this assumption is an approximation as regards so called strained bonds, since density maxima outside the interatomic vectors have been established by X-ray investigations of molecules containing strained rings.³ It is therefore of particular interest to see what results will come out from MO calculations since these do not include any assumptions about directed hybrids.

The density distribution is calculated from eigenvectors obtained in the IEH approach. This method and the technique of obtaining density level diagrams have been described in previous papers^{1,4} and will not be discussed here.

RESULTS AND DISCUSSION

The results are given in Table 1 and in Figs. 2–9. From the table we see that, as expected, the tetrahedral structure is the most stable one and that deformations in both directions from this increase the valence electron energy which we may interpret as an uptake of strain energy. The absolute value of

* *Added in proof.* In the case of a complex matrix and the valence direction defined by means of the gravity point of the hybrid density it is possible to create density maxima outside the interatomic vector. C. A. Coulson and R. White have recently (*Mol. Phys.* **18** (1970) 57) discussed complex hybrids. Their Fig. 3 gives a polar diagram of a complex hybrid earlier suggested as appropriate for the C–C bond in cyclopropane.

Table 1. Valence electron energies and net charges of methane in the normal state (109.5°) and under deformation.

Angle(°) H ₁ -C-H	Energy eV	Atomic net charge		
		C	H	H ₁
140	-116.0	-0.25	0.10	-0.01
125.5	-125.0	-0.10	0.03	0.00
109.5	-131.3	-0.07	0.02	0.02
100	-130.6	-0.08	0.02	0.03
90	-128.0	-0.10	0.02	0.05

the negative net charge of the carbon atom also increases with increasing deformation. The variation of the net charges are in the opposite direction in H₁ and the other hydrogen atoms.

The density level diagram of methane in its normal state (tetrahedral angle) is given in Fig. 2. As in the other diagrams atomic units are used and

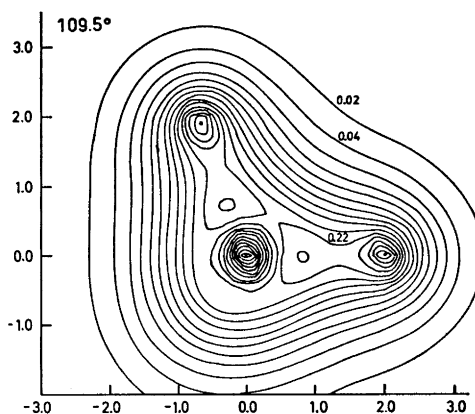


Fig. 2. Valence electron density of methane in the normal state. Valence angle 109.5°.

the density is then given in electron per (a.u.)³. It should be noted that, because of the difference between 1s and 2s Slater orbitals for $R=0$, the center of the carbon atom is represented by a minimum, but that of the hydrogen atom by a maximum.

If we first look at the influence of the flattening on the density distribution by comparing Figs. 3 and 4 with Fig. 2, we find that the density distribution at the interatomic vectors which are the subject of deformation, changes appreciably, but, in contrast to what is expected from the hybridization models, the density distribution at the C-H₁ bond (in the direction of the x axis) remains practically unchanged. The heaping up of charge "behind" the carbon atom is especially pronounced in the limiting case (Fig. 4).

If instead we start from the tetrahedral angle (Fig. 2), and carry out the deformation in the opposite direction, we find a charge distribution which

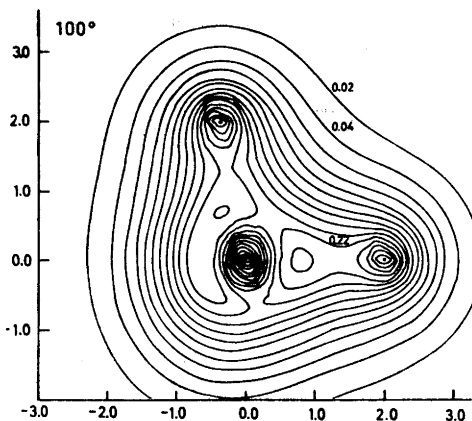


Fig. 3. Valence electron density of deformed methane. Valence angle 100° .

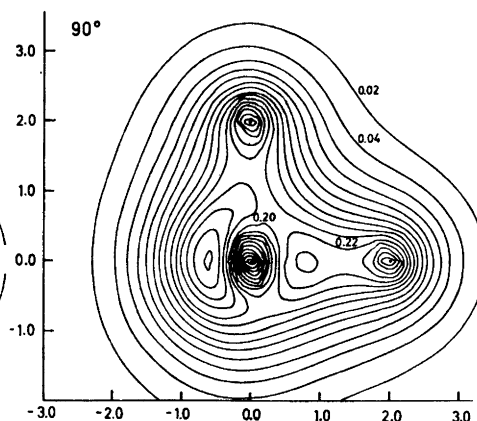


Fig. 4. Valence electron density of deformed methane. Valence angle 90° .

indicates a bent bond structure already at a valence angle of 125.5° , *i.e.* at the border case of the model with a real hybridization matrix. The angles between the three moving interatomic vectors are then 90° (Fig. 5). If we increase the angle to 140° (the angles between the appropriate interatomic vectors are then about 60°) we find (Fig. 6) that a maximum is formed "above" the carbon atom and that it is of *p* type character. It is obviously the same phenomenon that we have met in the form of extra-annular charge maxima in cyclopropane and in the phosphorus P_4 molecule.^{1,5}

The level diagrams of the density difference complete the picture. In the normal state of methane (Fig. 7) we have density difference maxima sym-

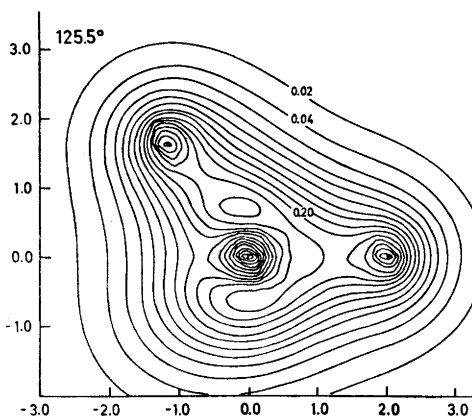


Fig. 5. Valence electron density of deformed methane. Valence angle 125.5° .

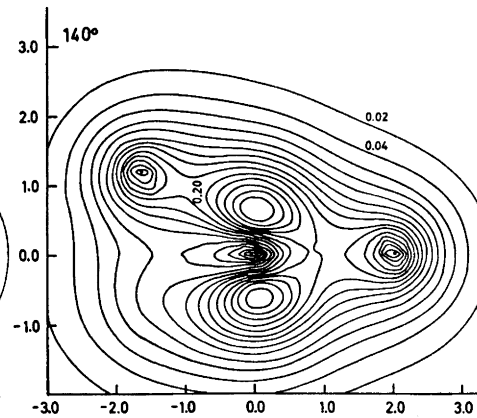


Fig. 6. Valence electron density of deformed methane. Valence angle 140° .

metrically arranged about the interatomic vectors. The negative interior part shows a minimum symmetrically situated between each pair of interatomic vectors. In the border case of 90° (Fig. 8) the density difference maximum

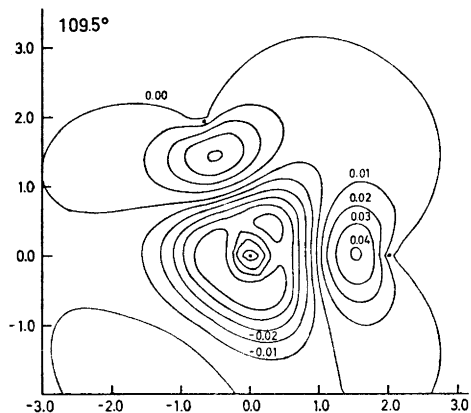


Fig. 7. Valence electron density difference of methane in the normal state. Valence angle 109.5° .

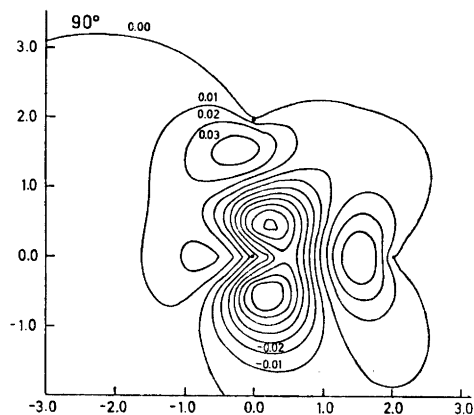


Fig. 8. Valence electron density difference of deformed methane. Valence angle 90° .

corresponding to the direction of the x axis is almost unchanged as compared to that of the normal state. The density difference of each of the remaining bonds, however, is strongly deformed with a maximum somewhat behind the interatomic vector (coinciding with the z axis) and with another lower one "behind" the carbon nucleus (Fig. 8). Deformation in the opposite direction leads to a weakening of the density difference maximum centered on the x

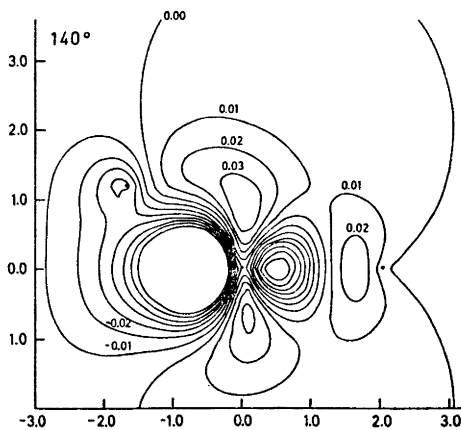


Fig. 9. Valence electron density difference of deformed methane. Valence angle 140° .

axis, and to the building up of two well defined minima "in front of" and "behind" the carbon nucleus. Fig. 9 illustrates the situation for an angle of 140° . We also see that the maxima of the remaining three bonds are strongly deformed and are displaced to positions "above" the carbon atom nucleus.

It is obvious that the picture of the valence electron density distribution obtained by the IEHM calculations differs considerably from that expected from the model based on directed, real hybrids. In turn one can ask how reliable the description obtained by the present approach is. The general picture of the density distribution of cyclopropane is the same as that obtained by *ab initio* SCF-LCAO-MO calculations,⁵ as far as the results from the two methods can be compared. Another question concerns the viability of this theoretical deformation experiment. For instance, can the interatomic distances be kept constant during a real experiment? In any case the calculations show that the MO methods give density distributions which are not in agreement with those obtained from considerations based on directed, real hybrids unless special bent bond models are applied.

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