Application of maximum overlap method to calculation of hybrid orbitals in ethane molecule

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The criterion of maximum overlap was used for the calculation of hybrid atomic orbitals in ethane molecule. The calculation shows, that bonds in this molecule are formed by non-equivalent hybrid orbitals (for Burns AO $sp^{2.93}$ for C—H bonds and $sp^{3.24}$ for C—C bond). The calculated bond angles in this molecule are in agreement with experimental data.

В работе был применен критерий максимального перекрывания для расчета гибридных атомных орбиталей в молекуле этана. Расчет показал, что связи в этой молекуле образованы неэквивалентными гибридными орбиталями (для атомных орбиталей Бурнса $sp^{2.93}$ для связи С—Н и $sp^{3.24}$ для связи С—С). Вычисленные валентные углы в этой молекуле находятся в согласии с экспериментальными данными.

The concept of hybridization [1, 2] plays an important role in the theory of chemical bond. According to *Coulson* [3] "hybridization is a very effective way how to retain the concept of localized bonds with the total formation of electron pairs". Since hybrid orbitals give a larger overlap than pure atomic ones, hybridization procedure can be based on the criterion of maximum overlap [2, 4—10]. The procedure for construction of hybrid orbitals on the basis of the maximum overlap criterion was suggested by *Murrell* [5] and mathematically simplified by *Golebiewski* [6, 7], *Gilbert* and *Lykos* [8]. The maximum overlap method is an improvement of *Pauling* theory of oriented bond [1, 2]; overlap integrals represent a better criterion of bond strength since in their calculation not only the angular but also the radial part of wavefunction is included as well as interatomic distances. The maximum overlap criterion was used in this paper for the calculation of hybrid orbitals in ethane molecule.

Method of calculation

If additivity of bond energies of molecules with σ bonds [11] is assumed the total bond energy of ethane molecules can be expressed as follows

$$E = E_{CC} + 6E_{CH}. \tag{1}$$

Let us assume further that partial bond energies are proportional to the total overlap of hybrid orbitals forming the corresponding bonds [4, 12, 13]
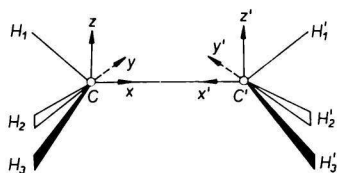
Fig. 1. Local coordinate systems in ethane molecule.

$$E = K_{CC} S_{CC} + 6 K_{CH} S_{CH},\qquad(2)$$

where K_{CC} and K_{CH} are constants of proportionality between the corresponding overlaps of hybrid orbitals and partial bond energies. If the equivalence of C—H bonds in the ethane molecule (Fig. 1) is taken into account then the matrix of hybridization coefficients for carbon atoms takes the following form

$$A = \begin{bmatrix} & \sqrt{1-a^2} & 0 & 0 \\ \sqrt{\dfrac{1}{3}(1-a^2)} & -\dfrac{\sqrt{3}}{3}a & 0 & \dfrac{\sqrt{6}}{3} \\ \sqrt{\dfrac{1}{3}(1-a^2)} & -\dfrac{\sqrt{3}}{3}a & -\dfrac{\sqrt{2}}{6} & -\dfrac{\sqrt{6}}{6} \\ \sqrt{\dfrac{1}{3}(1-a^2)} & -\dfrac{\sqrt{3}}{3}a & \dfrac{\sqrt{2}}{2} & \dfrac{\sqrt{6}}{6} \end{bmatrix} \qquad(3)$$

The use of local coordinate systems for carbon atoms in ethane molecule (Fig. 1) makes it possible to express the overlap integrals of hybrid orbitals for individual atoms

$$S_{CC} = a^2 S_{ss} + (1-a^2) S_{pp} + 2a \sqrt{1-a^2} S_{sp},\qquad(4)$$

$$S_{CH} = \sqrt{\frac{1}{3}(1-a^2)} S_{sh} + \sqrt{\frac{1}{3}(a^2+2)} S_{ph},\qquad(5)$$

where

$$S_{ss} = \langle C\,2s | C\,2s \rangle,$$
$$S_{sp} = \langle C\,2s | C\,2p \rangle,$$
$$S_{pp} = \langle C\,2p | C\,2p \rangle,\qquad(6)$$
$$S_{sh} = \langle C\,2s | H\,1s \rangle,$$
$$S_{ph} = \langle C\,2p | H\,1s \rangle$$

are overlap integrals between the corresponding atomic orbitals. After substitution of these overlaps of hybrid orbitals to eqn (2) it can be seen that the total bond energy depends on three parameters: a, K_{CC}, K_{CH}.

The aim of this study is to find the optimal hybrid orbitals (optimal in the sense of giving the maximum bond energy) with additional condition that this maximum bond energy correctly reproduces the experimental value ($E = 2824.42$ kJ mol^{-1} [11]). A closer inspection of form of eqn (2) shows that it

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can be done. If constant K_{CH} is supposed to be known (in this case the value obtained for K_{CH} from the calculation for methane molecule [13] was used) it can be seen that bond energy depends linearly on K_{CC}. It is then easily possible to fit the experimental bond energy and simultaneously perform a variation with respect to parameter a. Actual calculation started from a certain chosen initial value of K_{CC} and this value was varied until agreement with experiment was obtained. For every K_{CC} value function $E = E(a, K_{CC})$ was maximized with respect to a.

Considering the fact that maximum of electron density in given bond lies on the line connecting the corresponding nuclei, optimal hybrid orbitals obtained by the above-described procedure can be applied to calculation of valence angles in studied molecule. Using the properties of scalar product of vectors and form of hybridization matrix $\mathbf{A}$ (eqn (1)) following expressions are obtained for valence angles of ethane molecule

$$\langle CCH = \operatorname{arctg} \left[-\frac{\sqrt{2}}{a} \right], \tag{7}$$

$$\langle HCH = \operatorname{arctg} \left[\sqrt{\frac{3(2a^2 + 1)}{a^2 - 1}} \right] \tag{8}$$

Results and discussion

Calculation was carried out using three types of atomic orbitals: according to *Slater* [14], *Burns* [15], and *Clementi* [16]. The following values of interatomic distances [17] were used: $R_{CC} = 1.54 \times 10^{-10}$ m, $R_{CH} = 1.09 \times 10^{-10}$ m. Results obtained by using these three types of atomic orbitals are presented in Table 1. Burns and Clementi atomic orbitals give nearly the same results, which partly differ from those obtained by using Slater orbitals,

Table 1

Results calculated for ethane molecule

	Used atomic orbitals		
	Slater	*Burns*	*Clementi*
K_{CC} [a]	496.83	453.25	506.35
K_{CH} [a]	605.02	548.23	575.71
a	0.415	0.486	0.485
n_{CC} [b]	4.81	3.24	3.25
n_{CH} [b]	2.62	2.93	2.92
E_{CC} [a]	302.54	325.36	324.85
E_{CH} [a]	420.31	416.50	416.59
$\langle CCH$ [c]	106.34	108.96	108.94
$\langle HCH$ [c]	112.41	109.98	110.00

a) Values in kJ mol^{-1}.
b) Value of n in the expression of hybrid orbitals in the form sp^n.
c) Values in degrees.

difference being caused by considerable difference in radial distributions of these orbitals. Calculated partial bond energies are in agreement with experimental findings concerning different strength of C—C and C—H bonds in alkane molecules.

It is customary in textbooks to assume that carbon atom in ethane molecule forms four equivalent sp^3 hybrid orbitals. However, such model of hybrid orbitals cannot be correct since C—C and C—H bonds are not equivalent, this being confirmed also by results of calculation. Owing to lower diffusibility of $2s$ atomic orbitals (vs. $2p$) of carbon atoms, they participate more in C—H bond than in C—C bond.

Optimal hybrid atomic orbitals can be also obtained by applying criteria other than used in presented paper, *e.g.* hybrid orbitals can be calculated from "strictly" localized molecular orbitals. This method was applied to calculation of hybrid orbitals for ethane by *Trindle* and *Sinanoğlu* [18], who used delocalized CNDO/2 molecular orbitals and by two different procedures (localization of MO and bond indices method) obtained two different results for ethane molecule. Our results agree with their conclusions obtained from localized MO that p orbitals participate relatively more in C—C bond than in C—H bond. *Polák* [19] obtained an opposite hybridization effect using also localized molecular orbitals.

The form of hybrid orbitals on carbon atom is directly connected with bond angles in ethane molecule. Bond angles calculated from Burns and Clementi atomic orbitals are in a good agreement with experimental values ($\langle HCH = 109.75°$ [17]), while results obtained from Slater atomic orbitals are rather unreal, due to incorrect radial distribution of atomic orbitals.

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