Quantum theoretical study on bond angle for single bond between carbon atoms.

Sigeru KAGAHARA

Haruo GOTÔ

Kisaku SAWAI

Abstract :

We studied the characteristic features of single, double and triple bonds between carbon atoms by idealizing the problem to the electronic structure of fictitious diatomic molecules $\equiv\text{C}-\text{C}\equiv$, $=\text{C}=\text{C}=$ and $-\text{C}\equiv\text{C}-$, where the "open" bonds of carbon atoms are represented by a suitably hybridized orbitals, associated with free spins. Using this general theory above mentioned, we study bond angle for single bond between carbon atoms. Thus we obtain the following result that in the case of tetrahedral' bond angle, the single bond between carbon atoms is most stable.

Quantum theoretical treatment of bond angle for single bond between carbon atoms.

a. Model :

we take the following model for the diatomic molecular system. (See Fig.1)

b. general formula for electronic energy :

We have to study the general formula for the diatomic potential which characterizes the nature of binding of molecular system.

The result of the general formula for electronic energy is shown in Table T

c. Numerical calculation :

The diatomic potential between two atoms in the molecular system is the eigenvalue of electronic energy as a function of the distance between nuclei and bond angle between bond orbitals. In order to know explicitly these dependence on the distance and bond angle, we have to evaluate the eigenvalue for various distances and various bond angles. For this purpose we compute the numerical calculations of molecular integrals

The tetrahedrally hybridized bonding orbitals in ethane molecule in the case of

$$\alpha = \tan^{-1} \frac{1}{\sqrt{8}} = 19^\circ 28'$$

$$E = E_0 - C_0 + \left(\frac{C_b^{(1)}}{1 + \kappa} - C_s^{(1)} \right)$$

where

$$E_0 = \sum H_{ii} + \sum' (ii:jj) - \frac{16}{R}$$

$$C_0 = 3 (12:12) + 3 (14:14)$$

$$C_s^{(1)} = \frac{3}{2} G_{11}' + 3 G_{12}' + 3 G_{14}'$$

$$C_b^{(1)} = G_{44}'$$

$$\kappa = S_{44}'^2$$

$$G_{ij}' = (ij':ij') - S_{ij'}^2 (ii:j'j') + 2 S_{ij'} H_{ij'} - (H_{ii} + H_{j'j'}) S_{ij'}^2 \\ + 2 S_{ij'} \sum_{k \neq i, j'} (ij':kk) - S_{ij'}^2 \sum_{k \neq i, j'} \{ (ii:kk) + (j'j':kk) \}$$

S_{ij}' , H_{ij}' , ($pq:rs$), etc., which may be rather tedious and laborious, but they can be carried out in a straight forward way by making use of table of Kotani et al.⁽²⁾ and other tables⁽³⁾

Results and Discussion

The results of evaluating the adiabatic potential according to the general formula given in Table are shown in Table 2 and Figures 2~3.

ΔE

ρ α	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
10°	0.54641	0.43744	0.38858	0.18238	0.14179	0.11757	0.09633	0.08082	0.06009	0.04671	0.03620	0.02595
15°	0.18622	0.18740	0.16606	0.05932	0.04578	0.03651	0.02819	0.02321	0.01314	0.00716	0.00358	0.00119
17.5°	0.09603	0.09222	0.08759	0.03256	0.03012	0.03240	0.01630	0.00843	0.00113	0.00248	-0.00172	-0.00284
20.°	0	0	0	0	0	0	0	0	0	0	0	0
22.5°	-0.06413	-0.06339	-0.05021	-0.00869	0.00096	-0.00390	0.00151	0.00705	0.00537	0.00749	0.00840	0.00974
25°	-0.09247	-0.08431	-0.07414	-0.00238	0.00077	0.00893	0.01117	0.02172	0.05756	0.02461	0.02637	0.02461
30°	-0.04891	-0.04223	-0.06386	0.04187	0.03551	0.06666	0.07384	0.08831	0.08727	0.08817	0.08611	0.07844

$\Delta E = (E_{\alpha} - E_{\alpha=20^\circ})$

(in the unit : $27.024 \times \delta = 44.207 \text{ e.v.}$)

Fig 2

Adiabatic energy potential curve in the single bond between carbon atoms C—C. ($\alpha=19^\circ 28'$)

- a case : Coulomb field+simple exchange field
- b case : a case+higher permutation effect
- c case : b case+orthogonal 2s orbital effect
- d case : c case+1s electron effect

Fig 3

ΔE (in the unit : $27.204 \text{ e.v.} \times \delta = 44.207 \text{ e.v.}$)

The stable structure of the molecular system are found from these curves. Thus in the case of the tetrahedral bond angle, the single bond between carbon atoms is most stable.

This result of our numerical computation is in good agreement with the experiment.

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