The dependence of the resonance integral $B_{ij}$ calculated from a new semiempirical formula on the distance between the atoms has been investigated in methods with zero differential overlap. The differences between the results for characteristics of the electronic structure of hydrocarbon molecules in the ordinary and modified methods are insignificant owing to the small difference in $B_{ij}$ for the ordinary and modified methods in the region for intramolecular interactions. In the region for intermolecular interactions the new formulas correspond to slower decay of the absolute value of $B_{ij}$ than in the CNDO/2 and INDO methods.

The formula proposed in [1] for the resonance integral has the form

$$B_{ij} = f(R_{ij}) S_{ij}, \quad (1)$$

where $S_{ij}$ is the overlap integral of the $i$-th and $j$-th AO’s (which are usually Slater-type AO’s belonging to the $I$-th and $J$-th atoms respectively), $R_{ij}$ is the distance between the $I$-th and $J$-th atoms, and $f(R_{ij})$ is expressed in terms of the CNDO/2 and INDO parameters

$$f(R_{ij}) = \frac{1}{2} (\beta_0^i + \beta_0^j) - K_{ij} \frac{Z_i + Z_j}{4} (\gamma_{ij}^i - \gamma_{ij}^j). \quad (2)$$

In (2) $\beta_0^i$ and $\beta_0^j$ are the CNDO/2 (or INDO) constants, $\gamma_{ij}^i$ is a parameter of the electrostatic repulsion of the electrons on the $I$-th and $J$-th atoms (in the $i$-th and $j$-th AO’s), $R_{ij}$ is the distance between the $I$-th and $J$-th atoms, which, in principle, is dependent on $R_{ij}$. The quantum-chemical calculation of the crystal-lattice energy of molecular crystals of $N_2$, $C_2H_4$, $C_2H_6$, $CO_2$, and the like in [2, 3] revealed that good agreement with the experimental heats of sublimation is obtained with the use of the CNDO/2 with a modified formula for the resonance integral

$$B_{ij}^c = \frac{1}{2} (\beta_0^i + \beta_0^j) S_{ij}^c, \quad (3)$$

where the overlap integral $S_{ij}^c$ is calculated with the Hartree–Fock AO’s found by Clementi in the form of a superposition of Slater functions with different values for the exponents [4]. The presence of small exponents provides for the slower decay of $S_{ij}^c$ in comparison to the $S_{ij}$ calculated with one standard Slater-type AO. From the dependence of $S_{ij}^c$ on $R_{ij}$ it follows that the ratio

Fig. 1. Dependence of the resonance integrals $\beta_{ij}$ calculated with the Slater (SO, SI, S3, and SR — solid lines) and Clementi (CO and CI — dashed lines) 2s functions and the matrix element of the kinetic energy $T_{ij}$ in an orthogonal basis (according to [6]) on $R_{CC}$: a) Region of intramolecular distances; b) region of intermolecular distances. The dashed lines at $R_{CC} = 1.2$ and $R_{CC} = 1.52$ mark off the region between the lengths of a triple bond and a single bond.

$$F_{ij} = S_{ij}/S_{II} > 1$$

when $R_{ij} \geq 2\ \AA$ and $R_{ij}$ increases with increasing $R_{ij}$.

We introduce the following notation for the different methods for calculating the resonance integral: $\beta(S1)$, if $\beta_{ij}$ is calculated with the use of (1) and (2) with $S_{ij} = S_{ij}^S$ and $K_{ij} = 1$; $\beta(S3)$, if $S_{ij} = S_{ij}^S$ and $K_{ij} = 3$; $\beta(CI)$, if $S_{ij} = S_{ij}^C$ and $K_{ij} = 1$; etc. For example, $\beta(CNDO/2) = \beta(SO)$, and $\beta_{ij}$, as defined in Eq. (3), is equal to $\beta(CO)$. We shall examine the resonance integral $\beta_{ij}$ of the C–C bond, and we shall calculate it by two methods:

$$\beta_{ij} = \beta_{ij}(CKC) \text{ or } \beta_{ij} = \beta_{ij}(SKS).$$

In order for both formulas in (5) to define the same function $\beta_{ij}$, the coefficients $K_C$ and $K_S$ must differ. In order to be specific, we assume that the resonance integral (with consideration of the recommendations in [2, 3]) is calculated with the use of the formula

$$\beta_{ij} = \beta_{ij}(CKC),$$

where $K_C = 1$ [this value of $K_C$ was obtained when Eqs. (1) and (2) were derived in [1]]. Then from (1), (2), (4), and the nature of the dependence of $F_{ij}$ on $R_{ij}$ it follows that the coefficient $K_S$ in (5) must increase with increasing $R_{ij}$ in order for the function $\beta_{ij}(SKS)$ to be approximated by the function $\beta_{ij}(CI)$ when $R_{ij}$ is increased. According to [3], when $R_{CC} = 4\ \AA$, $F_{ij} = 1.8$, and from (1), (2), (4), and (5) it follows that $K_{CC} = 3$. This estimate of $K_{CC}$ is in sufficiently good agreement with the value $K_{CC} = 4$, which was used in the calculation of the energies of the intermolecular interaction in the ethylene dimer according to perturbation theory [5] with the use of formulas (1) and (2).

Thus, we may calculate $\beta_{ij}$ with $S_{ij} = S_{ij}^S$ and $K_{ij} = 1$, or we can calculate $\beta_{ij}$ with $S_{ij} = S_{ij}^C$ (as in the standard CNDO/2 method), but here it may be assumed that $K_{ij}$ is an increasing function of $R_{ij}$. For such a function we propose the use of the linear function

$$K_{ij} = yR_{ij}/L_{ij},$$

where $y (y = 1)$ and $L_{ij}$ ($L_{ij} = 1\ \AA$) are parameters of the method. In Fig. 1 SR denotes $\beta_{ij}$ with $S_{ij}^S$ and $K_{ij}$ as defined in Eq. (6) with $y = 1$ and $L_{ij} = 1.2\ \AA$. In the region from $R = 1$ to $R = 3\ \AA$ (Fig. 1a) all the curves except $\beta(S3)$ are close to one another and intersect at the point $R = 1.2\ \AA$, where $y_{CC} = 0.3977\ \text{au}$, the second term in (2) is equal to zero for all $K_{ij}$, and $S_{ij}^C = S_{ij}^S$ with a high accuracy. In the region from 3.8 to 5.5 $\AA$ (see Fig. 1b) the curves for all the $\beta_{ij}$ differ significantly. We note that the function $\beta(CNDO/2) = \beta(SO)$ is significantly smaller (in absolute value) than $\beta(S1)$ and $\beta(CO)$, which are close. The functions $\beta(CI)$, $\beta(S3)$, and $\beta(SR)$, which are similar to one another, decay even more slowly. When $R_{ij} \geq 4.2\ \AA$, the functions $\beta(CI)$ and $\beta(SR)$ approximate one another fairly well, demonstrating that Eq. (5) can be satisfied with good accuracy with the aid of (6). We note that at $R_{ij} \geq 4\ \AA$ $\beta(CI)$ differs significantly from $\beta(CO)$, as proposed in [2, 3]. When other values of $L_{ij}$ are selected, the course of the curves in Fig. 1 changes slightly, and they will intersect at the point $R = L_{ij}$. 

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