THEORETICA CHIMICA ACTA

Theoret. Chim. Acta (Berl.) 60, 65–71 (1981)

Determination of Resonance Integrals for Transanular Interactions within Semiempirical Theories

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In the present communication of new formula is proposed for the resonance integrals appearing in the π-theoretical treatment of compounds consisting of several weakly interacting conjugated systems. Some implications for semiempirical all-valence schemes are discussed.

Key words: Resonance integrals – Cyclophanes – Molecular π-complexes.

1. Introduction

In a π-theoretical treatment of compounds which consist of several well defined and sufficiently separated subsystems (e.g. cyclophanes) the effective Hamiltonian contains two classes of functionals: either they are related to basis set functions within a subsystem, or they depend on functions of two different subsystems. Suppose we know the functionals which can be successfully applied for the isolated subsystems, it is not obvious that we can also use the same functionals for the composite system. Another problem is the choice of the intersubsystem functionals. For example, there are two commonly adopted functional forms for the resonance integrals β_{st}^{AB} between basis set π-orbitals φ_s^A and φ_t^B in different subsystems A and B: (1) $\beta_{st}^{AB} \sim S_{st}^{AB}$ where $S_{st}^{AB} = \langle\varphi_s^A|\varphi_t^B\rangle$ is the overlap integral, and (2) β_{st}^{AB} is neglected unless atom s in A and atom t in B are "nearest neighbours". Method (2) could be called an intersubsystem tight-binding approximation.

Method (1) was applied in the study of cyclophanes and excimers [1] and donor-acceptor complexes [2, 3] whereas in Ref. [4] method (2) was taken. In Ref. [5–7] the interactions between different subsystems are evaluated in terms

0040-5744/81/0060/0065/$01.40

of overlap integrals between the molecular orbitals of the isolated subsystems. Such an approach is equivalent to method (1) [5] or method (2) [6, 7], depending only on how these overlap integrals are calculated. A characteristic feature of method (2) is its restriction to molecules where the nearest neighbour atoms with respect to different subsystems can be defined uniquely. In other cases one is forced to adopt method (1) or to retain overlap between more than nearest neighbour atoms [8]. Method (2) cannot be considered as a mere numerical approximation of method (1) since the relative differences between the S_{st}^{AB} overlap integrals (mainly $p_\sigma - p_\sigma$-type) are small, quite in contrast to those S_{st}^{AA} within a subsystem ($p_\pi - p_\pi$-type) which decrease rapidly with increasing atomic distance. However, the justification of method (1) was questioned [3] based on the analysis of de Bruijn [9]. Therefore it seems necessary to analyze the intersubsystem resonance integrals in more detail taking into account the assumptions which are inherent in the treatment of the isolated subsystems.

2. A New Approach

In a π-theoretical treatment of an isolated conjugated subsystem A all occurring functionals are defined with respect to the orthonormal basis set $\varphi^A = (\varphi_1^A, \varphi_2^A, \ldots)$ [10]. Let h^{AA} be the one-electron part of the Fock matrix in that basis. φ^A is obtained by the Löwdin transformation [11] $\varphi^A = \bar{\varphi}^A T^{AA}$ from the non-orthogonal basis set $\bar{\varphi}^A = (\bar{\varphi}_1^A, \bar{\varphi}_2^A, \ldots)$ with $T^{AA} = (\bar{S}^{AA})^{-1/2}$ and $\bar{S}^{AA}$ the overlap matrix of $\bar{\varphi}^A$. Generally, the basis set functions φ_s^A and φ_t^B of different subsystems A and B are not orthogonal and we define S^{AB} as the overlap matrix of φ^A and φ^B and $\bar{S}^{AB}$ the corresponding one of $\bar{\varphi}^A$ and $\bar{\varphi}^B$. Similarly we have the matrix $\bar{\beta}^{AB}$ of the resonance integrals between $\bar{\varphi}^A$ and $\bar{\varphi}^B$. We can construct the following hypermatrices:

$$T = \{\delta_{AB} T^{AA}\}, \qquad h = \{\delta_{AB} h^{AA}\}, \qquad E = \{\delta_{AB}\},$$
$$\bar{\beta} = \{(1-\delta_{AB})\bar{\beta}^{AB}\}, \qquad \bar{S} = \{(1-\delta_{AB})\bar{S}^{AB}\}.$$

Applying the Löwdin transformation [11] to the basis set $\varphi = (\varphi^A, \varphi^B, \ldots)$ we obtain the totally orthonormal basis set $\tilde{\varphi} = (\tilde{\varphi}^A, \tilde{\varphi}^B, \ldots)$, $\tilde{\varphi} = \varphi S^{-1/2}$ where $S = E + T\bar{S}T$. The one-electron part of the Fock matrix in the basis $\tilde{\varphi}$ is given by $\tilde{H} = S^{-1/2} H S^{-1/2} = \tilde{h} + \tilde{\beta}$ with $H = h + T\bar{\beta}T$.

For the intersubsystem resonance integrals $\bar{\beta}_{st}^{AB}$ we may adopt the functional form proposed by Spanget-Larsen [12]

$$\bar{\beta}_{st}^{AB} = \tfrac{1}{2}\bar{S}_{st}^{AB}(\alpha_s^0 + \alpha_t^0)(1 + K_{st}(r_{st})) \tag{1}$$

which depends linearly on the overlap integrals $\bar{S}_{st}^{AB}$. Since the elements of $\bar{S}^{AB}$ are by assumption numerically small it is a sufficient approximation to evaluate only up to first order in $\bar{S}^{AB}$: i.e. $S^{-1/2} = E - \frac{1}{2}T\bar{S}T$ and $\bar{S}^{AB} = \delta_{A-B}\bar{S}^{AB}$ where $\delta_{A-B} = 1$ if subsystems A and B are neighbours and $\delta_{A-B} = 0$ otherwise. We obtain

$$\tilde{h} = h, \; \tilde{\beta} = T\bar{\beta}T - \tfrac{1}{2}(T\bar{S}Th + hT\bar{S}T)$$

with

$$\tilde{h}^{AA} = h^{AA}$$
$$\tilde{\beta}^{AB} = \delta_{A-B}[T^{AA}\bar{\beta}^{AB}T^{BB} - \tfrac{1}{2}(T^{AA}\bar{S}^{AB}T^{BB}h^{BB} + h^{AA}T^{AA}\bar{S}^{AB}T^{BB})]. \qquad (2)$$

Hence, the one-electron part of the Fock matrices for the subsystems is unaffected by the transformations whereas the intersubsystem resonance integrals have to be calculated by using Eq. (2). Therefore in a π-theory an approach like method (1), i.e. $\tilde{\beta}^{AB} = \bar{\beta}^{AB}$, is not justified.

3. Applications

In order to study the effect of the transformation of Eq. (2) we calculated orbital energies of some cyclophanes (cf. Table 1) utilizing the self-consistent HMO method of Ref. [13]. Following Herndon et al. [14] we chose the heteroatom model for the methylene group with $\alpha_{Me} = -12.03$ and $\beta_{C-Me} = -1.878$ eV. It has been shown that with cyclophanes the $\sigma-\pi$ separation is valid to a very good approximation [15]. All subsystems, i.e. the benzene rings, have been taken as planar with the mean interring distances given in Ref. [16]. The use of experimental geometries does not lead to any improvement in the calculated values. This is not surprising since it has been shown that the deformations of the benzene rings in the cyclophanes do not result in significant changes in the ionization potentials [17]. The correct orbital sequence in cyclophanes is only obtained if through-bond interaction is taken into account [16, 18]. In our simple model this can be accomplished by a resonance integral τ between the methylene pseudoatoms forming the ethano bridges. Taking the phase conventions of the π-basis set functions as in Ref. [16] it is straightforward to show that $\bar{S}_{st}^{AB} < 0$, $\bar{\beta}_{st}^{AB} > 0$ and $\tau < 0$. The negative τ guarantees the correct order of the bridge orbitals [16] $\varphi_{\mu}^{(2)}$ and $\varphi_{\mu}^{(5)}$ which are obtained as linear combinations of the π-basis functions on the methylene pseudoatoms. In the application of Eq. (2) the methylene pseudoatoms have not been included.

The transanular resonance integrals $\bar{\beta}_{st}^{AB}$ are calculated using the formula proposed by Mulliken [19], i.e. $K_{st} = (C - 1 - |\bar{S}_{st}^{AB}|) \cdot (1 + |\bar{S}_{st}^{AB}|)^{-1}$ in Eq. (1). The overlap integrals $\bar{S}_{st}^{AB}$ are obtained with Slater atomic orbitals and exponents of Ref. [20]. At present we do not know if the Mulliken formula is a good representation for $\bar{\beta}_{st}^{AB}$, although it guarantees for $C = 1.6$ the pairing properties in benzene, cf. Ref. [12], but major deficiencies can probably be removed by a suitable choice of the parameter C and the precise form of K_{st} is not crucial in our context. The transanular interactions in cyclophanes are mainly of the $p_{\sigma} - p_{\sigma}$-type, leading to a smaller value of C, i.e. $C \approx 1.2$ [19]. But since we use the usual Hückel parameters α_s in Eq. (1) instead of α_s^0 and $|\alpha_s| < |\alpha_s^0|$ [12] and our overlap integrals are numerically too small [7], we expect a larger value for C.

Using $C = 1.5$ and $\tau = -2$ eV. a good correlation between calculated and observed ionization energies is obtained, cf. Table 1. Let us consider [2.2]

Table 1. Calculated and observed ionization energies I_i (in eV.) of some cyclophanes

Compound[a]	Calculated I_i^b 1	2	3	4	Observed I_i 1	2	3	4	
[2.2](1, 4)Cyclophane	7.87 (b_{2g})	8.24 (b_{3g})	8.32 (b_{3u})	9.46 (b_{2u})	8.10 (b_{2g})	— (b_{3g})	8.40 (b_{3u})	9.65 (b_{2u})	[16]
[2.2.2.2.2.2](1,2,3,4,5,6)-Cyclophane	7.31	7.31 (e_{1g})	8.13	8.13 (e_{1u})	7.55	7.55 (e_{1g})	8.17	8.17 (e_{1u})	[16]
4,5,7,8-Tetramethyl[2.2]-(1, 4)Cyclophane	7.71 (b_1)	7.75 (b_2)	8.24 (b_1)	9.13 (b_2)	7.40	7.60	8.20	9.00	[16]
4-Amino[2.2](1, 4)-Cyclophane	7.49	7.97	8.29	9.07	7.50	7.90	8.20	9.00	[24]

[a] Choice of coordinate axis as in Ref. [16].

[b] Calculated from the orbital energies by means of the regression Eq. $I_i = -1.003\ \varepsilon_{\mathrm{LUMO}\text{-}i} - 0.399$ (correlation coefficient 0.972).

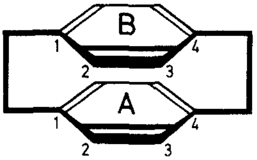

Fig. 1. Numbering of π-basis set functions in [2.2] (1, 4)-cyclophane

(1, 4)cyclophane in more detail in order to see how the transformation in Eq. (2) affects the transanular resonance integrals. We have (all values in eV, numbering according to Fig. 1) $\bar{\beta}_{11}^{AB} = 0.602$, $\bar{\beta}_{12}^{AB} = 0.284$, $\bar{\beta}_{13}^{AB} = 0.075$, and $\bar{\beta}_{14}^{AB} = 0.038$ and after applying Eq. (2) we obtain the "true" resonance integrals in a π-theory as follows: $\tilde{\beta}_{11}^{AB} = 0.589$, $\tilde{\beta}_{12}^{AB} = 0.006$, $\tilde{\beta}_{13}^{AB} = -0.035$, and $\tilde{\beta}_{14}^{AB} = 0.012$. Whereas the resonance integral between the nearest neighbours is only slightly affected all others undergo drastic changes, $\tilde{\beta}_{12}^{AB}$ and $\tilde{\beta}_{14}^{AB}$ are negligible and $\tilde{\beta}_{13}^{AB}$ is of the same small order of magnitude as $\bar{\beta}_{14}^{AB}$. Thus in cyclophanes or similar compounds where the atoms in different subsystems A and B are placed on top of each other, only transanular resonance integrals between atoms which are nearest neighbours are of importance. This exemplifies that in such a case an approach like method (2) is well justified. The energy separation between the b_{3g} and the b_{2u} orbital (cf. Table 1) is given in our model by 2Δ, where $\Delta = \tilde{\beta}_{11}^{AB} + \tilde{\beta}_{12}^{AB} - \tilde{\beta}_{13}^{AB} - \tilde{\beta}_{14}^{AB} = 0.618$ eV. This value would have to be used for β_{11}^{AB} in a method (2) calculation in order to obtain approximately the same results.

It is interesting to note that an approach like method (1), i.e. we put $\beta_{st}^{AB} = \bar{\beta}_{st}^{AB}$, also leads to nearly the same orbital energies with our studied cyclophanes, but only if one chooses the much smaller value $C = 0.6$. However, it should be emphasized that an equivalence of method (1) and (2) need not exist if one studies other compounds or other observables. Although we have studied the application of Eq. (2) only within the Hückel theory, our conclusions apply as well in more sophisticated π-theoretical methods.

4. Concluding Remarks

We have shown that in a consistent π-theoretical treatment of compounds composed of weakly interacting conjugated subsystems the intersubsystem resonance integrals have to be calculated with Eq. (2). In the case where two different neighbouring subsystems are symmetrical with respect to a plane between them, only resonance integrals between basis set functions at corresponding atoms are of any importance. Hence, in that special class of compounds the application of an intersubsystem tight-binding approximation, i.e. method (2), is well justified. On the other hand, an approach like method (1) is not consistent with the underlying assumptions of π-theory [10], although it might give nearly the same results for certain compounds and computed quantities. However, the resonance integrals then have to be chosen numerically smaller than with method (2) or with Eq. (2). This explains why Grein and Weiss [21] were forced to reduce in magnitude the interring resonance integrals with respect to the intraring integrals in a CNDO [22] study of the benzene-borazine complex in order to get sensible results. A CNDO study of [2.2] (1, 4)cyclophane by Duke et al. [23] yielded the b_{3u} orbital as highest one, quite in contrast to the experimental assignment [16]. The b_{3u} orbital is stabilized by increasing transanular interaction which is obviously underestimated in that study. This is due to the use of very large orbital exponents which have been chosen in order to reflect the short-range character of the intraring resonance integrals. But then in CNDO theory where overlap effects are neglected, the interring resonance integrals become more similar to those obtained with method (2) and one would have to use numerically larger resonance integrals. This exemplifies that also in all-valence theories overlap effects have to be included in order to get a balanced description of intra- and intersubsystem interactions. A possible approach was recently proposed by Spanget-Larsen [12].

Acknowledgements. The author is very grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and to the Universitätsrechenzentrum Heidelberg for computer time on the IBM 370/168. I also wish to thank Professor H. A. Staab for his interest in this study and to Dr. J. Spanget-Larsen for critical reading of the manuscript.

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Received April 28, 1981