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Generalized Hückel Treatment of a Simple Model of Transannular Interaction and Excimer Formation

By

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The model of two interacting ethylene molecules having D_{2h} symmetry was studied using generalized Hückel method. The validity of $\sigma - \pi$ separation was tested on this model. The general character of the ground state and lower lying excited states of the model was discussed and the implications drawn concerning transannular interaction and excimer formation. The values obtained for the dissociation energy of the first excited state of our model and corresponding equilibrium intermolecular distance are of right order of magnitude.

Mittels der verallgemeinerten Hückel-Methode wurde das Modell von zwei Äthylenmolekülen mit der Symmetrie D_{2h} studiert. An diesem Modell wurde die Gültigkeit der $\sigma - \pi$-Separation geprüft. Der allgemeine Charakter des Grundzustandes und der niedriger liegenden angeregten Zustände des Modells wird erörtert und die Folgerungen in Bezug auf transannulare Wechselwirkung und „Excimer"-Entstehung diskutiert. Die erhaltenen Werte für die Dissoziationsenergie des ersten angeregten Zustandes von unserem Modell und den entsprechenden intermolekularen Gleichgewichtsabstand haben die richtige Größenordnung.

Le modèle à symétrie D_{2h} de deux molécules d'éthylène en interaction a été étudié en utilisant la méthode généralisée de Hückel. On a examiné la validité de la séparation $\sigma - \pi$ sur ce modèle. Le caractère général de l'état fondamental et celui des états excités inférieurs du modèle furent discutés et on a fait des déductions sur l'interaction transannulaire et sur la formation d'«excimères». Les valeurs obtenues pour l'énergie de dissociation du premier état excité de notre modèle et la distance intermoléculaire d'équilibre corréspondante ont l'ordre de magnitude correct.

Introduction

In a series of papers on transannular interaction [*10 – 12, 16 – 18*] the proximity effects among π-electron systems which occur in various molecules like (m, n)-paracyclophanes or barrelene were studied. In these compounds different π-electronic systems like benzene or ethylene form part of a medium sized cycle and, therefore, are brought close enough so that the new type of interaction may be observed. The most striking demonstration of these interactions are perhaps the changes which occur in the electronic absorption spectra (cf. [*12*]).

The above mentioned type of nonbonding interaction was studied on a model of two parallel benzene rings facing each other and placed at distances ranging from 2 to 5 Å [*10, 17, 18*]. Further, the model of two ethylene molecules oriented mutually in different ways [*11, 16*] as well as the model of three ethylene molecules at various distances [*16*] and oriented so as to represent the barrelene molecule were considered. In all these studies the semiempirical method of limited configuration interaction in π-electron approximation was used. In spite of the fact that our calculations were in good agreement with observed electronic spectra we were worried about the validity of the $\sigma - \pi$ separation for the models we had studied. Therefore, one of the purposes of this study was to examine the validity of the $\sigma - \pi$ separation in these non-planar systems.

The generalized Hückel method [*7*] considering all L-shell electrons of carbon atoms as well as the 1s-electrons of hydrogen atoms was used to make the calculations manageable. For the same purpose, the simplest possible model of two parallel ethylene molecules was chosen since our former studies [*11*] had shown that this model provides all basic features of the interactions studied.

Further, in our previous studies [*10*] we have shown the nonbonding character of the ground state of models in which the transannular interaction occurs and discussed the reasons why the method applied could not account for the experimentally apparent antibonding character of these interactions. To show this antibonding character of the ground state was the second objective of this study.

The problem of the effect of transannular interaction on electronic spectra is very similar [*13*] to the problem of excimer (excited dimer) emission [*2*]. Various theories have been put forward to explain this phenomenon [*1, 5, 8, 15*]. All these theories, while using different approaches and approximations show, that the following two factors are essential, namely:

1. the consideration of the charge transfer states in addition to the locally excited exciton states,
2. the consideration of intermolecular overlap.

The same is true of our calculations on transannular interaction [*10 — 12, 16 — 18*], where the effect of the charge resonance states on excitation energies and transition probabilities was demonstrated. On the other hand the necessity to respect the overlap between interacting molecules was replaced in our studies by the necessity to consider resonance integrals not only for nearest neighbours but for next-nearest neighbours between interacting molecules as well. This is because both interacting molecules were considered as "one molecule" which allowed us to use formally orthonormal Löwdin orbitals and to transform the overlap effects into the effective Hamiltonian.

Therefore, our former calculations [*10 — 12, 16 — 18*] on transannular interactions can be directly used to explain the excimer emission as well. The only difficulty in any quantitative estimate is that the frequency of the new fluorescence band of excited dimer varies rapidly with the intermolecular separation, which is not known accurately enough.

Our results obtained with limited configuration interaction are very similar to those of AZUMI and MCGLYNN [*1*] in spite of the fact that their treatment is quite different from ours. Indeed, using the same method as in [*10 — 12, 16 — 18*] we obtained [*14*] for two parallel naphtalene molecules practically the same dependence of the excitation energies of B_{2u} and B_{3g} states (the only ones considered in [*1*]) on intermolecular separation as AZUMI and MCGLYNN [*1*] did. The B_{2u} and B_{3g} transitions correspond to the p-band (L_a-band) of isolated naphtalene molecule. The excitation energy to the B_{2g} state [corresponding to the α-band (L_b-band) of naphtalene] decreases more slowly with decreasing intermolecular distance than the excitation energy to the B_{3g} state, so that crossing of both states occurs in our approximation at about 3.8 Å, and at the intermolecular distance 3 Å the B_{3g} state lies about 0.35 eV lower than the B_{2g} state [*14*].

Again, all the theories of excimer emission while explaining the appearance of the new fluorescence band do not give any evidence as far as the stability of the excited dimer is concerned. The reason is very much the same as in the ground state antibonding character mentioned above. Therefore, we have tried to show the bonding character of the excited state in the same way as the antibonding character of the ground state.

Recently, while finishing our calculations, a letter by CHESNUT, FRITCHIE and SIMMONS [*4*] was published in which the same attempt had been made for the case of two benzene molecules and some of their methyl derivatives. Again, the generalized Hückel method was used. Our results for two ethylene molecules are much alike as will be seen later on.

Model and Method of Calculation

The model studied consisted of two co-planar ethylene molecules placed above each other at various distances a ranging from 2 to 9 a. u. and mutually oriented so as to belong to D_{2h} point group (Fig. 1). The geometry of ethylene molecule itself was chosen to be the same as in paper [*19*], i. e. C-C bond length 2.53 a. u. (1.34 Å), C-H bond length 2.00 a. u. (1.06 Å) and HCH angle 120°, enabling the exploitation of results which were obtained for single ethylene molecule [*19, 20*] in the following manner:

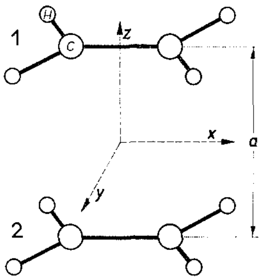

Fig. 1. Schematic representation of the model of the interaction of two ethylene molecules studied

The effective one-electron Hamiltonian $\hat{H}$ of the generalized Hückel method was represented in the basis of symmetry functions $|\Gamma_i^{\pm}, E_k\rangle$ defined as follows

$$|\Gamma_i^{\pm}, E_k\rangle = K(\Gamma_i^{\pm}, E_k)\,[|\gamma_i, E_k, 1\rangle \pm |\gamma_i, E_k, 2\rangle]\,, \quad (1)$$

$$K(\Gamma_i^{\pm}, E_k) = (2\,[1 \pm \langle\gamma_i, E_k, 1\,|\,\gamma_i, E_k, 2\rangle])^{-\frac{1}{2}}\,,$$

where $|\gamma_i, E_k, m\rangle$ designates the normalized molecular orbital of the single ethylene molecule (cf. [*19*]) corresponding to the orbital energy E_k which spans the representation subspace of the irreducible representation γ_i of the point group D_{2h} of the single molecule and, further, index m ($m = 1, 2$) distinguishes the two ethylene molecules of the model studied. $\Gamma_i^{\pm}$ designates the irreducible representation of the point group D_{2h} of both ethylene molecules of the above described model. Supposing that the positive lobes of $2pz$ atomic orbitals of individual molecules are placed symmetrically with respect to xy plane (Fig. 1), we find that for some i, j ($i \neq j$) it holds $\Gamma_i^{\pm} \equiv \Gamma_j^{\pm}$. The matrix elements of the one-electron Hamiltonian $\hat{H}$ of our model in the basis of functions (1) are then given by the formula

$$\langle\Gamma_i^{\pm}, E_k\,|\,\hat{H}\,|\,\Gamma_j^{\pm}, E_l\rangle = \delta_{\Gamma_i^{\pm}, \Gamma_j^{\pm}}\,\{\,2\,K(\Gamma_i^{\pm}, E_k)\,K(\Gamma_j^{\pm}, E_l)\,\times \quad (2)$$
$$\times\,[E_k\,\delta_{ij}\,\delta_{kl} \pm \langle\gamma_i, E_k, 1\,|\,\hat{H}\,|\,\gamma_j, E_l, 2\rangle]\}\,,$$

which clearly shows the factorization of our problem achieved by the choice of the basis (1); δ_{AB} is the Kronecker symbol.

The parametrization of the generalized Hückel method (sometimes called also Wolfsberg-Helmholz procedure [*21*]) used was due to HOFFMANN [*7*], that is all valence electrons were considered on equal footing in a sense that the same

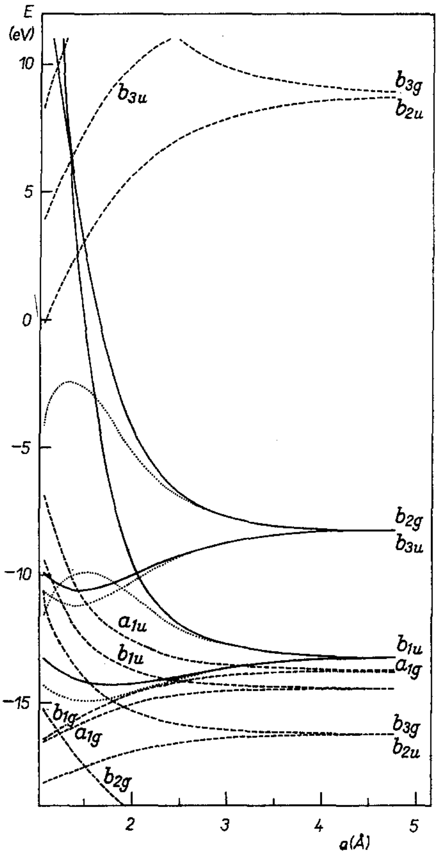

Fig. 2. One-electron energy levels (in eV) labeled by their symmetry species of D_{2h} point group as the functions of intermolecular separation a (in Å). Full lines correspond to the π-electron levels and dotted lines represent the same levels in π-electron approximation. Dashed lines correspond to σ-electron levels

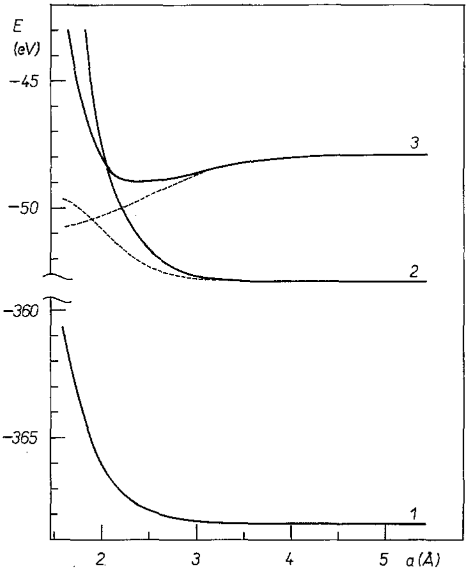

Fig. 3

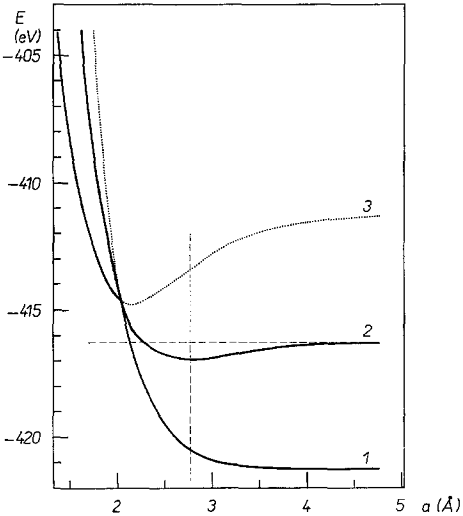

Fig. 4

Fig. 3. The dependence of the σ-core energy (curve 1), the π-peel energy (in eV) of the ground state A_{1g} (curve 2) and of the excited state B_{2g} (curve 3) on the intermolecular separation a (in Å). Dashed lines correspond to the π-peel energy of the same states in π-electron approximation

Fig. 4. The total energy (in eV) of states:

$\Sigma\,(a_{1g}, \pi)^2\,(b_{1u}, \pi)^2;\ A_{1g}$ (curve 1)
$\Sigma\,(a_{1g}, \pi)^2\,(b_{1u}, \pi)\,(b_{3u}, \pi^*);\ B_{2g}$ (curve 2)
$\Sigma\,(a_{1g}, \pi)^2\,(b_{3u}, \pi^*)^2;\ A_{1g}$ (curve 3)

as the functions of intermolecular separation a (in Å), where
$\Sigma \equiv (a_{1g}, \sigma)^2\,(b_{1u}, \sigma)^2\,(b_{3u}, \sigma)^2\,(b_{2g}, \sigma)^2\,(b_{2u}, \sigma)^2\,(b_{3g}, \sigma)^2\,(a_{1g}, \sigma)^2\,(b_{1u}, \sigma)^2\,(b_{1g}, \sigma)^2\,(a_{1u}, \sigma)^2$.
The dissociation energy of the B_{2g} state is 0.7 eV at the equilibrium distance 2.8 Å

constant k ($k = 1.75$) was used for all electrons considered. Even in this form the method seems to give very encouraging results as far as the geometry and stability of different isomers is concerned. Furthermore, the results on the electron density distribution and the σ-bond energies of ethylene molecule [*19, 20*] are in accordance with the results obtained using other methods. With proper choice of k constants for σ and π-electronic states still better results should be expected (cf. [*3, 9*]).

For the sake of comparison we have also carried out calculations in which only π-electrons of individual ethylene molecules were considered explicitly, while the above mentioned parametrization was used. This procedure is further referred to as generalized Hückel method in π-electron approximation. In a similar manner, the term σ-core (or π-peel) refers to the one-electron states which become the linear combinations of the σ (or π)-states of individual ethylene molecules at infinite separation.

Results

The results of our calculations are presented in Fig. 2 – 4. Fig. 2 shows the dependence of some one-electron energy levels on the intermolecular distance a. In Fig. 3 the contributions of σ-core and π-peel toward the total one-electron energy are presented as dependent on the intermolecular distance a.

The total energy of the ground state and the lowest lying monoexcited state in one-electron approximation as functions of the distance a ("potential curves") are given in Fig. 4. The doubly excited state which becomes the ground state for a smaller than 2 Å is shown in Fig. 4 as well. Of course, the crossing of both states belonging to the same species of the D_{2h} point group would be removed in higher than one-electron approximation.

Discussion

Let us first consider the implications which could be made on the basis of our calculations concerning $\sigma - \pi$ separation. It may be easily seen from Fig. 2, where the one-electron energies calculated with generalized Hückel method are compared with those calculated similarly but considering π-electrons only, that $\sigma - \pi$ mixing starts very suddenly when the intermolecular separation reaches approximately 2.5 Å and gets very prominent with further approach of both molecules. For the intermolecular separations of the order of chemical bond lengths the mixing is very strong indeed as can be expected, so that many intercrossings of levels occur and the original classification of σ and π states loses its sense.

On the other hand for intermolecular separations higher than 2.5 Å practically no $\sigma - \pi$ mixing occurs. Therefore, we can conclude, that for physically sensible intermolecular distances the $\sigma - \pi$ separation is valid to a very good approximation at least within the scope of the generalized Hückel method. This is the reason why a rather good description of the dependence of excitation energies on the intermolecular separation is obtained in π-electron approximation while getting poor results for "potential curves", the σ-contribution to which is very essential. Really, as may be seen from Fig. 3, the one-electron excitation energy is practically the same regardless whether the σ-electrons are considered or not, since even for intermolecular separations around 2.5 Å where $\sigma - \pi$ mixing is significant the depression of both states in going to π-electron approximation is roughly the same.

On the other hand the Fig. 3 shows the importance of the σ-electron contribution toward total energy in order to obtain a reasonable "potential curve".

Further, we have to stress that the overlap integrals between interacting molecules are very essential for obtaining proper bonding and antibonding character of a particular electronic state. This is because the one-electron level splittings due to the interaction between molecules are not any more symmetrical around the corresponding one-electron energy levels for infinite intermolecular separation once the overlap is taken into consideration. The splitting is in general such, at least for reasonable intermolecular separations, that the arithmetic mean of the splitted one-electron energy levels increases as both molecules approach each other, supposing plausible values for matrix elements of the one-electron Hamiltonian.

This well known phenomenon can be easily demonstrated on the simplest possible case of the interaction of two identical atomic orbitals. Let us denote $S(r)$ the overlap integral between these two orbitals at the distance r and α and $\beta(r)$ the corresponding Coulomb and resonance integrals of the one-electron Hamiltonian, respectively. The one-electron orbital energies $E^{\pm}(r)$ are then given by the simple formula

$$E^{\pm}(r) = \frac{\alpha \pm \beta(r)}{1 \pm S(r)} \,. \tag{3}$$

Supposing that $\alpha\, S(r) \geq \beta(r)$ we immediately obtain the antibonding character of the arithmetic mean of the two orbitals considered:

$$\bar{E}(r) = \tfrac{1}{2}\left[E^{+}(r) + E^{-}(r)\right] = \frac{\alpha - \beta(r)\, S(r)}{1 - S^{2}(r)} \geq \alpha = \bar{E}(\infty) \,. \tag{4}$$

This general behaviour of one-electron energies for intermolecular separations higher than 2.5 Å, where crossing of occupied and virtual one-electron levels is excluded as may be seen from Fig. 2, allows us to explain in a quite general way, within the scope of one-electron approximation, the antibonding character of the ground state as well as the bonding character of some excited states of the dimer of molecules having closed shell configuration in the ground state.

Particularly, let us suppose that the interaction of two identical π-electronic systems having $2n$ π-electrons distributed over the $2n$ centres takes place (this model will describe the large family of hydrocarbons with conjugated double bonds and its analogues) and that the corresponding one-electron levels split asymmetrically as described above. Then we clearly get an antibonding ground state since its energy is given as the sum of n occupied pairs of molecular orbitals, the sum of orbital energies of each pair being antibonding as described above. For shorter intermolecular separations intercrossing of levels can cause that a state which represents some excited state for large intermolecular separations becomes a ground state (see Fig. 4).

Furthermore, it is apparent that the excited state which corresponds to the excitation from a strongly antibonding molecular orbital to some virtual molecular orbital having bonding character can yield the bonding character for the excited state. This is true of our first excited state as may be seen from Fig. 4.

From the "potential curve" of the "ethylene excimer" (Fig. 4) we get for the dissociation energy of the first excited state 0.7 eV at the equilibrium intermolecular separation 2.8 Å.

Let us note that using a similar method a value of 0.19 eV was obtained [4] for two benzene molecules at the equilibrium distance 3.4 Å. The experimentally estimated value for benzene excimer dissociation energy is 0.22 eV [2], and it seems to be of the same order of magnitude for the whole family of aromatic hydrocarbons forming excimers. On the other hand the dissociation energy of the lowest lying stable state of He_2 molecule $({}^3\sum_u^-)$ is 2.6 eV at corresponding equilibrium interatomic distance 1.05 Å [6]. Therefore, the values obtained for our model are certainly of the right order of magnitude.

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Literature

[1] Azumi, T., and S. P. Mc Glynn: J. chem. Physics **41**, 3131, 3839 (1964).
[2] Birks, J. B., C. L. Braga, and M. D. Lumb: Proc. Roy. Soc. (Lond.) **A 283**, 83 (1965) and loc. cit.
[3] Boer, F. P., M. D. Newton, and W. N. Lipscomb: Proc. Nat. Acad. Sci. US **52**, 890 (1964).
[4] Chesnut, D. B., C. J. Fritchie, and H. E. Simmons: J. chem. Physics **42**, 1127 (1965).
[5] Förster, Th.: Pure appl. Chem. **7**, 73 (1963) and loc. cit.
[6] Herzberg, G.: Molecular Spectra and Molecular Structure, Vol. 1., Spectra of Diatomic Molecules. New York: Van Nostrand Co., Inc. 1957.
[7] Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
[8] Konijnenberg, E.: Thesis, University of Amsterdam, 1963.
[9] Kato, H., T. Yonezawa, K. Morokuma, and K. Fukui: Bull. chem. Soc. Japan **37**, 1710 (1964).
[10] Koutecký, J., and J. Paldus: Coll. Czech. chem. Commun. **27**, 599 (1962).
[11] — — Theoret. chim. Acta (Berl.) **1**, 268 (1963).
[12] — — Tetrahedron **19**, Suppl. **2**, 201 (1963).
[13] — — Electronic Excitations in Molecules with Transannular Interaction, in: Modern Quantum Chemistry, Istanbul Lectures, Vol. **3**, Edited by O. Sinanoğlu. New York: Academic Press (in press).
[14] —, L. Mišta, and J. Paldus: Unpublished results.
[15] Murrell, J. N., and J. Tanaka: Mol. Physics **7**, 363 (1964).
[16] Paldus, J., and J. Koutecký: Coll. Czech. chem. Commun. **27**, 2139 (1962).
[17] — Coll. Czech. chem. Commun. **28**, 1110 (1963).
[18] — Coll. Czech. chem. Commun. **28**, 2667 (1963).
[19] Polák, R.: Coll. Czech. chem. Commun., (in press.)
[20] — Thesis, Czechoslovak Acad. Sci., Prague, 1964.
[21] Wolfsberg, M., and L. Helmholz: J. chem. Physics **20**, 837 (1952).

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