

Relationes

Note on the Generalized Hückel Treatment of the Simple Model of Aromatic Hydrocarbon-Carbonium Ion Charge Transfer Complex Formation

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Recently, we have studied the model of two interacting ethylene molecules having D_{2h} symmetry using generalized Hückel method [10]. The main purpose of this study was to test the validity of π - σ separability conditions for nonplanar systems. Furthermore, we have found that even this very simple model yields a correct picture of binding conditions which are encountered with more complicated closed shell π -electronic systems both in the ground and the lowest excited states. More specifically, we have in mind the general antibonding character of the ground state as found in molecules with transannular interaction (e.g. paracyclophanes and similar compounds, cf. [8]) and the binding character of the lowest excited state which is responsible for the excimer formation.

Prior to our study [10] a similar treatment of two interacting benzene molecules was carried out [1], yielding qualitatively the same results. In the paper mentioned above [10] we have shown that similar behaviour will result quite generally when interaction of two uncharged closed shell π -electronic systems takes place.

From this point of view it was very tempting to apply a similar method to the charge transfer complexes of aromatic hydrocarbons and carbonium ions. First complexes of this type reported not long ago by FELDMAN and WINSTEIN [3] are those in which the tropylium cation is used as an electron acceptor while ordinary aromatic hydrocarbons (namely benzene and its methyl derivatives, naphthalene etc.) are electron donors. It was shown [3] that the new absorption bands of these complexes in the ultraviolet and visible regions of the spectrum, which show considerable frequency shifts in comparison with the spectra of parent molecules, are clearly charge-transfer absorption bands.

Since our computation facilities are rather limited we have considered at first the simplest possible model which could describe this phenomenon, namely, the interaction of the ethylene molecule as an electron donor with the methyl cation as an electron acceptor.

The idealized geometry was used in the calculations: C=C bond length of ethylene was 1.34 Å, all C-H bond lengths were taken to be equal to 1.06 Å, all

HCH or CCH angles were 120° and molecular planes of both interacting species were kept parallel in all cases.

The generalized Hückel method in the parametrization proposed by HOFFMANN [4] was used. A program was written for the Ural 2 computer which computes the orbital energies and molecular orbitals in the generalized Hückel scheme (up to 24 electron problems).

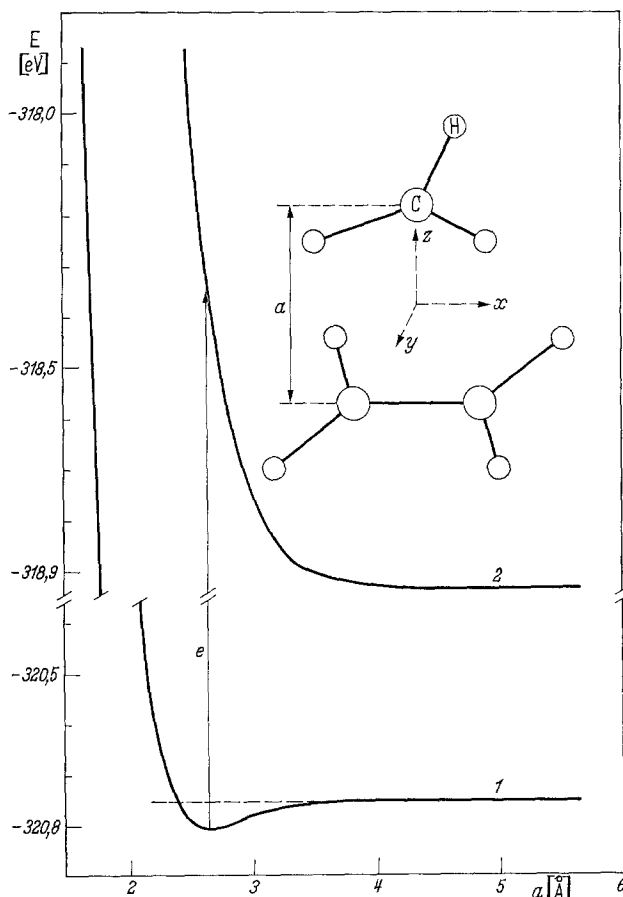


Fig. 1. The dependence of the total electronic energy (in eV) of the ground and the first excited states in generalized Hückel approximation on the intermolecular separation a (in Å) for a system shown in the upper right corner.

The vertical arrow e indicates the first electronic transition in a charge transfer complex.

The equilibrium intermolecular separation is 2.65 Å and the corresponding binding energy is 0.05 eV

The resulting total energies of the ground and the first excited states as functions of the intermolecular separation a ("potential curves") are presented in Fig. 1 for the mutual orientation of the methyl cation and the ethylene molecule shown in the upper right corner of the figure. Practically the same potential curves were obtained for the orientation in which the methyl cation is rotated around the z -axis by 30° so that one C-H bond of the methyl cation is then parallel to the C=C bond of ethylene.

The ground state potential curve shows a very shallow minimum at about 2.65 Å. The corresponding binding energy is only about 0.05 eV due to the unfa-

vourable compensation of the σ -core and π -peel energies. (The terms π -peel and σ -core are used here in the same sense as specified in paper [10].)

The first excited state is strongly antibonding for intermolecular separations smaller than 3.5 Å. However, at the equilibrium intermolecular separation its energy is still low enough to explain the observed frequency shift found generally in charge transfer complexes. Using the same parametrization as above we get for the first excitation energy of the ethylene molecule itself 5.0 eV* while excitation energy in the charge transfer complex with the methyl cation corresponding to the vertical transition indicated by the vertical arrow e in Fig. 1 is about 2.5 eV.

Therefore, we can conclude that our simple model again yields a correct qualitative picture of charge transfer complex formation as well as of the charge transfer absorption band shifts.

The reason for the binding character of the ground state may be easily seen on the basis of a simple π -electron approximation where overlap effects are taken into account respected. Let us designate u_1 and u_2 the carbon $2p_z$ -atomic orbitals of the ethylene molecule and u the $2p_z$ -orbital of the methyl cation oriented in such a way that the z -axes of these orbitals are lying in the plane fixed by the carbon nuclei and the z -axis of the orbital u is bisecting the C=C ethylene bond (cf. Fig. 1). Then the corresponding symmetry and molecular orbitals are

$$u_{\pm} = \frac{1}{\sqrt{2}} (u_1 \pm u_2).$$

It is immediately clear that the orbital energy of the lowest lying molecular orbital u_+ will have bonding character while u will be antibonding and u_- non-bonding (that is the orbital energy will be independent of the intermolecular distance a). Since in the cation only the lowest lying orbital u_+ will be occupied we are getting the bonding character of this interaction.

On the other hand, the σ -core energy will be antibonding largely for the same reason discussed already for the case of the interaction of two closed shell molecules, since all couples of groups of molecular orbitals interacting with each other are doubly occupied in the ground state.

In the above treated case, the binding energy in π -electron approximation is ca 0.5 eV but it is practically completely cancelled by the antibonding σ -core energy. For larger systems this situation might be more favourable. The rather unfavourable situation in our model may also be connected with the fact that the geometrical arrangement, which we have used to simulate in some way the model of charge transfer complexes mentioned above, is rather artificial from the molecular point of view and by far does not represent the equilibrium configuration of the $C_3H_7^+$ ion [5], which is well known from the mass spectra [9]. It should be stressed once more, that our model is only intended as a model of charge transfer complex and no implications are attempted to be drawn with respect to the $C_3H_7^+$ ion, the

* In order to obtain better agreement with the observed excitation energy of the ethylene molecule itself other parametrization would be desirable (cf. [11]). On the other hand, we have to remember that, similarly as in the ordinary Hückel treatment, the excitation energies obtained must be treated only as quantities proportional (and not necessarily directly proportional [7]) to the experimental values. At any rate, they should be compared with the centre of gravity of the respective singlet and triplet transitions [2, 6] (e.g. about 6.1 eV for ethylene) rather than with the transition energy of one of the multiplets itself.

molecular structure of which is apparently quite different from the "ethylene-alkonium ion" [5].

Further, the charge distribution in our model will be far from being "uniform" so that the iterative procedure correcting the valence state ionisation potentials in accordance with the orbital populations should be carried out in a similar manner as suggested recently by ZERNER and GOUTERMAN [11].

The study of more elaborate models is currently being undertaken.

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