

ADVANCES IN
CHEMICAL PHYSICS

Volume V

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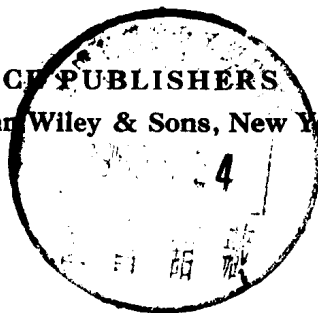
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INTRODUCTION

In the last decades, chemical physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become

the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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NEW DEVELOPMENTS IN THE ONE-ELECTRON THEORY OF π -ELECTRON SYSTEMS

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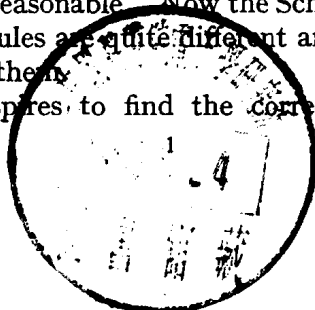
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I. INTRODUCTION

From the physicist's point of view, a one-electron treatment of molecular electron systems is a first approximation. The explicit inclusion of interelectronic forces means an improvement of the theory and leads to a closer approximation. From the chemist's point of view the situation is rather different. Certainly the chemist is interested in the properties of specific molecules, but his main interest lies in the detection of properties of whole groups of substances. He wants to know the variation of properties within such a group, and he has the feeling that this type of question is reasonable. Now the Schrödinger equations of two different molecules are quite different and there is no regular similarity between them.

The physicist aspires to find the correct solutions of both



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equations. When he has done his task perfectly, he will have two rows of figures, one for each molecule. He has all the data about each molecule, but in this way he can never get an insight into the relations between the properties of the molecules of a whole group of substances. There seems to be only one way of getting a physical answer to the typical question of the chemist, which we have described above. One should find a model which to a certain degree is artificial and is a simplified picture of the molecules of a group of substances. The model should be as close as possible to the real molecules to be described, and, on the other hand, it should be possible to adjust the model to the different molecules of a group of substances by properly adjusting one or more parameters of the model.

Looked at from the physicist's point of view the treatment of such models is, as we have said, a first approximation. From the chemist's point of view, the treatment of simplified models, which are suited to represent the molecules of a whole group of substances, is the main task which can be done by physical means. The improvements desired by the physicist to secure a theory which is better for his purposes are not necessarily improvements from the chemist's point of view. It might be useful to explain this further by a well-known example.

Chemists know that valence theory and its graphical symbol describing a chemical bond between two atoms have proved extremely useful for ordering a very great number of chemical facts. Now the work of Heitler and London has shown that there is a close analogy to the chemist's bond line in an approximate quantum-theoretical concept of the covalent bond. This result of Heitler and London has become the basis of the well-known theory of the valence bond.

On the other hand, quantum chemists know well that this analogy disappears as the quantum-theoretical treatment of molecular electron systems is improved. The analogy of quantum chemical results and their numerical exactness is, in a certain way, complementary.

The physicist likes simplified models because their mathematical treatment is much easier. The chemist is not unhappy that this is so, but, as we have shown, his love for simplified models in a first line does not have this origin.

During the last fifteen years we have seen the outcome of many so-called improvements in quantum chemistry. Because of the above-mentioned circumstances we have the impression that one should again concentrate the quantum chemist's interest on the theory of simplified models and therefore on one-electron theories. We want to describe the results of a group of investigations on the one-electron theory of π -electron systems, which were done by the author and his coworkers. We think that the results of these investigations can not only prove the importance of one-electron theories but also show that it is sometimes better to investigate simple theories very carefully than to start formal improvements too early.

One-electron theories are characterized by the supposition that all electrons of the molecule move in the same field. This field is called the effective field and it resembles the interaction between the electron and the system of the core of the atoms on the one side and the interaction between the electrons themselves on the other side. A certain one-electron theory is characterized by the problem of zeroth approximation, which has been used as the starting point. The problem of zeroth approximation determines the type of the eigenfunctions. One-electron theories of π -electron systems have been developed in two ways. These are in systematic order:

1. In analogy to the model used by Sommerfeld in the theory of electron states of crystals Schmidt, Kuhn, and others have developed the so-called free-electron theories.

2. In the theory of electron states of crystals Bloch has started his investigations from a point of view which in a certain sense is opposite to the point of view of Sommerfeld. He tried to describe the electronic states of a crystal as a linear combination of atomic eigenfunctions. His method was transferred to the theory of π -electron systems by Hückel, who became the founder of this field of research. The Hückel theory has a wider field of application, while the free-electron theories can only be used for the analysis of spectroscopic data.

The Hückel theory, at least in principle, can be applied to the analysis of spectroscopic data and in the interpretation of caloric energy values such as resonance energies. It is well-known that the application of the free-electron theories in the spectroscopic

field gives much better results than the application of the Hückel theory in the same field, if the values of the semiempirical parameters of the Hückel theory are taken from the analysis of resonance energies. The Hückel theory seems to be very inconsistent in so far as the relation between the values of the resonance integral β , which are determined from the analysis of resonance energies on one side and the analysis of spectroscopic data on the other side, amounts to the value of three.

Until recently quantum chemists have had the opinion that this discrepancy had its real root in the poor approximation of the one-electron scheme. Now during the last years Scheibe detected a spectroscopic regularity of great importance which could not be explained either by free-electron theories or by the Hückel theory. Scheibe has stated that the energetic distance between the ionization limit and the first excited electron state, which has the same multiplicity as the ground state, in all molecules with π -electron systems has nearly the same value, although the energetic distance between the ground state and the first-excited state in the different molecules is very different.

One cannot expect that this fact can be explained by free-electron theories, because it uses infinitely high potential walls around the molecule and so is not apt to describe ionization phenomena. On the other hand, the Hückel theory had so far proved to be unable to explain normal spectroscopic facts. Now the phenomenon detected by Scheibe seems to be of such a fundamental nature that it was rather unreasonable that it should be impossible to explain such a fundamental phenomenon in the simple one-electron scheme. Therefore, we started a careful re-examination of Hückel's theory.

II. THE ONE-ELECTRON STATES OF THE ETHYLENE MOLECULE

Hückel's theory gives two molecular electronic states for the electron system of the ethylene molecule, a bonding one and an antibonding one. Both states in first approximation are described by linear combinations of the atomic $2p$ eigenfunctions of the two carbon atoms. We call the energies of the two states $E(b)$ and

$E(l)$. If the energy of the atomic $2p$ term is $E(2p)$ the Hückel theory gives the relations

$$E_b - E_{2p} = \alpha + \beta \quad (1)$$

$$E_l - E_{2p} = \alpha - \beta \quad (2)$$

$$\alpha > 0, \quad \beta < 0, \quad |\beta| \gg \alpha \quad (3)$$

α is the Coulomb integral and β the characteristic resonance integral of Hückel's theory. According to (1), (2), and (3) the two-molecular terms should be nearly symmetrical to the atomic $2p$ term.

It is well known that the ground state of the molecule belongs to the electron configuration b^2 . The ground state of the molecule is a singlet. To the configuration b^1l^1 belong the second singlet $2(^1)$ and a triplet $1(^3)$. The two configurations and the lower part of the term system of the molecule are given in Fig. 1.

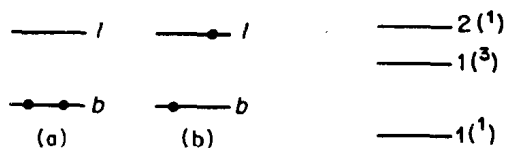


Fig. 1

It is well known that the splitting of the configuration b^1l^1 , which leads to the two terms of the molecule $2(^1)$ and $1(^3)$ of the molecule, cannot be described in a one-electron scheme. Only a next step of approximation which regards the true repulsion between the electrons can give the energy difference between $2(^1)$ and $1(^3)$. The difference between the energies $E_{b^1l^1}$ and E_{b^2} , which in the one-electron scheme corresponds to both configurations b^1l^1 and b^2 and which is identical with the distance of the one-electron states l and b can be identified neither with the empirical difference $E_{2(^1)} - E_{1(^3)}$ nor with the difference $E_{1(^3)} - E_{1(^1)}$.

It is known from the treatment of analogous two-electron problems that the inclusion of electron repulsion gives the result

$$E_{2(^1)} - E_{b^1l^1} = C + A \quad (4)$$

$$E_{1(^3)} - E_{b^1l^1} = C - A \quad (5)$$

C is a Coulomb integral and A an exchange integral. Figure 2 gives the genetical relations between the terms. From (1) and (2) follows

$$E_{b'1} = \frac{1}{2}(E_{2(1)} + E_{1(2)}) - C \quad (6)$$

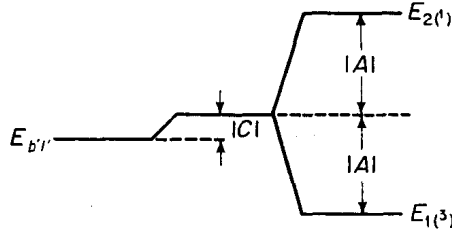


Fig. 2

If we call the Coulomb integral between two b electrons C' , we get the second equation

$$E_{1(1)} - E_b = C' \quad (7)$$

From (6) and (7) follows

$$\begin{aligned} E_t - E_b &= E_{b'1} - E_b \\ &= \frac{1}{2}(E_{2(1)} + E_{1(2)}) - E_{1(1)} - (C - C') \end{aligned} \quad (8)$$

It is reasonable to assume that the difference between the two Coulomb integrals is small compared with the exchange integral A . In this approximation we have

$$E_t - E_b = \frac{1}{2}(E_{2(1)} + E_{1(2)}) - E_{1(1)} \quad (9)$$

The following empirical values are known⁷:

$$E_{2(1)} - E_{1(1)} = 7.6 \text{ ev} \quad (10)$$

$$E_{1(2)} - E_{1(1)} = 6.9 \text{ ev} \quad (11)$$

So according to (9) we get

$$E_t - E_b = 7.25 \text{ ev} \quad (12)$$

In the following we shall use the value

$$E_t - E_b = 6.6 \text{ ev}$$

In this way to a certain degree, the neglect of the difference of the two Coulomb integrals can be compensated. The ionization energy of the ethylene molecule is 10.4 eV. So the one-electron state b is 10.4 eV below the ionization limit. The relative position of the one-electron states and the ionization limit is shown in Fig. 3.

A formal half of the ethylene molecule, which we may call the "constituent group", can be formed in the following way. We



Fig. 3

add to a carbon atom in the ground state $C2s^22p^2\ ^3P$ the energy of ~ 7 eV and bring it to the trigonal valence state Csp_{tr}^3 . Then the σ -bonds are formed, and we get the σ -bond energy B . The corresponding positive ion of the constituent group can be formed in an analogous way. Adding 11.2 eV to a carbon atom, we get the positive carbon ion in its ground state $C^+2s^22p^2\ ^4P$. Then again ~ 7 eV are necessary for the excitation to the trigonal valence state $C^+sp_{tr}^2$ of the positive carbon ion. Finally, the σ -bonds are formed, and, in a first approximation, we should get the same σ -bond energy B . Thus far, the value of the ionization energy of the constituent group should be nearly the same as the value of the ionization energy of the carbon atom (11.2 eV); but we have overlooked two things. When the carbon ion in the trigonal valence state is combined with its ligands to form σ -bonds, the interaction between the charge situated on the carbon ion and the formally neutral ligand atoms contributes a positive amount of energy of the order of magnitude of 1 eV, which hitherto has been

disregarded. This effect should increase the ionization energy of the constituent group. But, according to approximate calculations of Hellmann, which can be applied here, the induction of electric moments in the formally neutral ligand atoms produced by the charge of the carbon ion should lower the ionization energy by several ev's. So the ionization energy of the constituent group should be much lower than 11.2 ev. These statements do not concern the free methyl radical, because this molecule in its ground state is not necessarily flat, and its ionization energy cannot be compared directly with the ionization energy of the formal half of an ethylene molecule.

The ionization energy of the constituent group must certainly be lower than the ionization energies of all aromatic hydrocarbons. That follows from the fact that ionization of an aromatic hydrocarbon molecule means the removal of an electron from a bonding molecular electronic state. From known values for the ionization energies of aromatic hydrocarbons, one can see that these values converge with increasing number, n , of carbon atoms in the molecule to 5.4 ev. We take this value as the ionization energy of the constituent group. So the "atomic $2p$ -state", which is the starting point of Hückel's theory, lies 5.4 ev below the ionization limit. Between this state and the ionization limit there lie all the higher atomic states from $3p$ on. The Rydberg correction for the $3p$ state is certain to be small, so that its distance from the ionization limit should be approximately 1.5 ev.

III. THE BASIC IDEA

Figure 4 shows that the bonding and the antibonding molecular electronic states are far from lying symmetrically to the atomic $2p$ state. It seems to be quite unreasonable that the one-electron scheme is such a poor approximation. One should look for a natural explanation of the discrepancy. Figure 4 shows in which direction this explanation is to be sought. The energetical distance between the two terms b and l is greater than the distance of the $2p$ term from the ionization limit.

Under such circumstances it is impossible to expect that a theory which uses only atomic $2p$ states can explain all essential phenomena qualitatively. The necessary extension seems to be

quite straightforward. Besides atomic $2p$ states, one should add higher atomic states to the basis to get the molecular eigenfunctions in a good approximation. Because of combination-selection rules only such functions can be used which have the same symmetry character as Hückel's $2p$ functions. It is difficult to

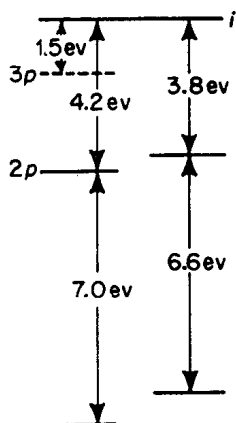


Fig. 4

follow this program fully. Because of the reasons given above it seems to be impossible to limit the number of higher atomic states. Practically, there is only the possibility of using atomic $3p$ eigenfunctions besides the $2p$ eigenfunctions. So, in a certain sense, the $3p$ eigenfunctions become the representatives of all higher functions. Though this practical difficulty exists at first, we shall develop the theory in a general way.

IV. THE STRUCTURE MATRIX

With regard to the development of the theory it is very useful to define a matrix which we have called the structure matrix. The diagonal elements of the structure matrix (an analogous matrix has been defined by Ham and Rüdenberg as a "topological matrix") are zero

$$s_{jj} = 0 \quad (13)$$

The off-diagonal elements of the structure matrix are 1 or 0. They are 1 if the indices of the element are the numbers of

neighboring atoms in the molecule. Otherwise the off-diagonal elements are zero

$$s_{jj'} = \begin{cases} 1 \\ 0 \end{cases} \quad (14)$$

The structure matrix has eigenvectors. The j th component of the normalized eigenvector belonging to the i th eigenvalue of the structure matrix ρ_i we call c_{ij} . The eigenvectors are to be determined from the equations

$$\sum_j \sum_{j'} c_{ij}^* c_{i'j'} s_{jj'} = 0 \quad \text{for} \quad i' \neq i \quad (15)$$

The relation between the eigenvectors and the eigenvalues of the structure matrix are given by

$$\sum_j \sum_{j'} c_{ij}^* c_{ij'} s_{jj'} = \rho_i \quad (16)$$

In the following it is to be kept in mind that the eigenvectors and the eigenvalues of the structure matrix are determined by the structure of the molecule. Especially the eigenvalues are characteristic numbers of the molecule. We call them the Hückel numbers. It is important to see that they are really independent of energetic considerations.

V. FORMAL DEVELOPMENT OF THE THEORY

$\psi_j^{(k)}$ may be an atomic eigenfunction of the same symmetry type as Hückel's $2p$ functions. k is the principal quantum number and j is the number of the atom. In the following we shall use the functions

$$\psi_j^{(k)} \quad k = 2, 3, \dots, m \quad j = 1, 2, \dots, n \quad (17)$$

We allow that m may go to infinity. The $\psi_j^{(k)}$ shall be normalized⁹:

$$(\psi_j^{(k)}, \psi_j^{(k)}) = 1 \quad (18)$$

At first we disregard nonorthogonalities:

$$(\psi_j^{(k)}, \psi_{j'}^{(k')}) = \delta_{kk'} \delta_{jj'} \quad (19)$$