QUASI-HOMEOPOLAR STATES IN CONJUGATED HYDROCARBONS. INTERACTION OF \( \pi \)- AND \( \sigma \)-ELECTRONS

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Quasi-homeopolar levels of \( \pi \)- and \( \sigma \)-electrons in conjugate hydrocarbons are considered. It is shown that in the spin hamiltonian and the projected operators of the physical values there appear terms which involve \( \pi \)-\( \sigma \)-interaction. The spin hamiltonian of \( \pi \)-\( \sigma \)-interaction is small, and its contribution to energies and spin functions can be calculated from perturbation theory by taking the spin hamiltonian of noninteracting \( \pi \)- and \( \sigma \)-electrons as equal to zero. The \( \pi \)- and \( \sigma \)-electrons of the \( \text{C} = \text{C} \) bond in ethylene are considered in detail. Calculations show that their interaction increases the excitation energy of the lower triplet of ethylene. The spin hamiltonian parameters of the simplest conjugate hydrocarbons are determined.

The accuracy of the valence-bond method is investigated on the basis of the theory of quasi-homeopolar levels. It is shown that empirical selection of the parameters partially compensates for the errors which are made in the derivation of the fundamental equation for this approximation.

INTERACTION OF \( \pi \)- AND \( \sigma \)-ELECTRONS

In the lower electron regions, solution of the Hartree self-consistent approximation for conjugate hydrocarbons gives regions and monoelectron functions of the Bloch type corresponding to \( \pi \)- and \( \sigma \)-electrons. By unitary conversion of Eq. (3) in [1] it is possible to arrive at an orthonormalized system of localized Wannier functions, \( w_m(r) \) for \( \pi \)-electrons and \( v_m(r) \) for \( \sigma \)-electrons (\( m \) is the subscript for a \( \sigma \)-bond, and \( l \) is the number of the point). In the general case different Wannier functions are obtained for various \( \sigma \)-bonds, but in terms of Eq. (3) [1] they are all close to one of the three valence superpositions of the carbon atom functions (12] p. 296) or the hydrogen atom function and are converted to them if the nuclei of the molecules are moved to infinity.

On passing to the concept of secondary quantization it is necessary to expand the electron field operator \( \Psi(q) \) into electron destruction operators in localized \( \alpha \) \( \text{m}_{\text{LO}} \) states for the \( \alpha \)-states and \( \sigma \text{LO} \) for the \( \pi \)-electrons. Here, and in the future, with electron destruction and creation operators the subscript \( \sigma \) is used to denote projection of the spin on the \( z \)-axis. As in [1] we will not consider transitions to excited regions. Essentially in the hamiltonian for the system there will not be any quadratic mixed terms of the type \( \sigma \alpha \sigma \alpha \), since they correspond to transitions between different regions, and in the Hartree approximation quadratic terms are diagonal to the regions. These transitions can only arise from the part of the Coulomb interaction which is not considered in the Hartree approximation.

For quasi-homeopolar levels of the system, by the method set out in [1,2], we arrive at the spin hamiltonian \( h \) and the projected operators \( g \) of the physical values (momentum, electron distribution, spin density, etc.) acting in the space of the spin functions.

The spin hamiltonian \( h \) can be represented in the following form:

\[
    h = \sum_m h_m(2) + h_\pi + h_{\text{int}},
\]

where \( h_m(2) \) is the hamiltonian of the two \( \sigma \)-bond electrons of type \( m \), \( h_\pi \) is the hamiltonian of the \( \pi \)-electrons, and \( h_{\text{int}} \) represents interaction of the \( \sigma \)-bonds between themselves and with the \( \pi \)-electrons. Expansion of \( h_\pi \) into a series of center interactions was investigated in [1]. In this paper we consider the projected interaction hamiltonian \( h_{\text{int}} \). Like \( h_\pi \) it can be expanded into a series of center interactions, and the rapid convergence of this series enables us to restrict ourselves to binary, ternary, and quaternary interactions, that is

\[
    h_{\text{int}} = h_{\text{int}}(2) + h_{\text{int}}(3) + h_{\text{int}}(4).
\]

Physically this means that a pair of \( \sigma \)-electrons only interacts strongly with another pair of \( \sigma \)-electrons or with two \( \pi \)-electrons. With this approximation, to determine the projected operators \( h_{\text{int}} \) and \( g_{\text{int}} \) it is necessary to solve the Schrödinger equation for two, three, and four centers. In this paper we consider in detail the interaction of \( \pi \)-electrons of ethylene with the electrons of the carbon \( \sigma \)-bond.

Retaining a notation similar to that used in [1], we write the hamiltonian of these four electrons in the following form:

\[
    H = H_0 + H',
\]

\[
    H_0 = \frac{1}{2} \sum_{l_1,l_2=1,2} F(l_1 l_2) (N_{l_1} - 1)(N_{l_2} - 1) +
    \frac{1}{2} \sum_{l_1',l_2'=1,2} F(l_1' l_2') (N_{l_1'} - 1)(N_{l_2'} - 1) +
    \sum_{l_1,l_2=1,2} F(l_1 l_2) (N_{l_1} - 1) \times
    (N_{l_2} - 1) + b_n \sum_{l_1,l_2=1,2} (N_{l_1} - 1) +
    b_\pi \sum_{l_1,l_2=1,2} (N_{l_1} - 1).
\]

As in Eq. (5) [1], \( H_0 \) includes terms which are diagonal according to the number of electrons at the centers \( N_{l_1} \) and \( N_{l_2} \). The subscripts \( l' \) are used to denote
the number of the σ-electron center in the F values and N operators, i.e., N′ is the number of σ-electrons at the point l and, for example,

\[ F(l, l') = \int d^2r_1 d^2r_2 w_1^*(r_1) w_2^*(r_2) \frac{e^2}{|r_1 - r_2|} v_{l_1}(r_1) v_{l_2}(r_2). \]

The third term refers to Coulomb repulsion of π- and σ-electrons, and the last two terms take account of the fact that the energies of the electrons in the π- and σ-regions are different. These terms are absent from Eq. (5) in [1], since without the π-σ-interaction the number of electrons in each region is maintained and is equal to the number of centers which form the region. In H the following terms, which are not diagonal according to the number of electrons at the centers, are distinguished:

\[ H' = \sum_{l_1 \neq l_2} \beta_{l_1 l_2} \alpha_{l_1 \sigma}^{\dagger} \alpha_{l_2 \sigma} + \sum_{l_1 \neq l_2} \beta_{l_1 l_2} \alpha_{l_1 \sigma} \alpha_{l_2 \sigma} + \]

\[ + \sum_{l_1 \neq l_2} F(l_1 l_2 l_3) \alpha_{l_1 \sigma}^{\dagger} \alpha_{l_2 \sigma} \alpha_{l_3 \sigma}^{\dagger} \alpha_{l_4 \sigma}^{\dagger} + \]

\[ + \frac{1}{2} \sum_{l_1 l_2 l_3 l_4} F(l_1 l_2 l_3 l_4) \alpha_{l_1 \sigma}^{\dagger} \alpha_{l_2 \sigma} \alpha_{l_3 \sigma} \alpha_{l_4 \sigma} + \]

\[ + \text{compl. conj.} + \sum_{l_1 \neq l_2} F(l_1 l_2 l_3) \alpha_{l_1 \sigma}^{\dagger} (N_{l_1} - 1) \alpha_{l_2 \sigma}^{\dagger} + \]

\[ + \text{compl. conj.} + \left( S_1 S_2 - \frac{1}{4} \right) + \]

\[ + \sum_{l_1 \neq l_2} F(l_1 l_2 l_3) \alpha_{l_1 \sigma}^{\dagger} (N_{l_1} - 1) \alpha_{l_2 \sigma}^{\dagger} + \text{compl. conj.}. \quad (3b) \]

where

\[ \beta_{l_1 l_2} = \int d^2r \frac{p_1^2}{2m} \left[ V(r) \right] w_{l_1}^*(r) + \]

\[ + \int [F(l_1 l_2) + F(l_1 l_2^*)], \]

\[ \beta_{l_1 l_2} = \int d^2r \left[ \frac{p_1^2}{2m} + V(r) \right] w_{l_1}^*(r) + \]

\[ + \int [F(l_1 l_2) + F(l_1 l_2^*)]. \quad (4) \]

All the other terms, which contain overlap of Wannier functions for various centers from Coulomb energy, are omitted. The third term at \( l_1 = l_2 \) describes the Coulomb exchange of π- and σ-electrons at one center, and the other terms determine transitions between regions.

The parameters \( F(11'11') \), \( F(111'1') \) and \( (b_\pi - b_\sigma) \) are determined from atomic spectroscopic data and were taken from [3]. Values for \( u_{1\pi} = F(11) - F(12) \)

\[ b_\pi - b_\sigma = 3; \]

\[ u_{1\sigma} = 3.3; \]

\[ u_{1\sigma} = 2.6; \quad F(11') - F(12') = 2.5; \]

\[ F(11'11') = F(111'1') = 1.2; \]

\[ F(12'21') = F(122'1') = 0.5, \]

\[ F(1'11) - F(1'22) = 1.5. \quad (5) \]

Energy values for the lower levels are given in Table 1, where energies calculated without taking π-σ-interactions into account are also given for comparison.

We set ourselves the task of determining the contribution of π-σ-interactions to the C=C bond; we will therefore determine \( h_{\text{int}} \) without calculating \( h_{\text{int}}(2) \), \( h_{\text{int}}(3) \), and \( h_{\text{int}}(4) \) separately. The method for calculating the spin hamiltonian for a four-electron problem was described in detail in [1], and we will use the results obtained

\[ h = h(2) + h_{\text{int}}, \]

\[ h(2) = I_{12} \left( S_1 S_2 - \frac{1}{4} \right) + I_{1\sigma} \left( S_1 S_\sigma - \frac{1}{4} \right), \]

\[ h_{\text{int}} = \Delta I_{12} \left( S_1 S_2 - \frac{1}{4} \right) + \]

\[ + \Delta I_{1\sigma} \left( S_1 S_\sigma - \frac{1}{4} \right) + I_{1\sigma} \left( S_1 S_\sigma + S_1 S_2 - \frac{1}{2} \right) + \]

\[ + 2D_1 \left( S_1 S_2 - \frac{1}{4} \right) \times \left( S_1 S_\sigma - \frac{1}{4} \right) + \]

\[ + 2D_2 \left( S_1 S_\sigma - \frac{1}{4} \right) \left( S_1 S_2 - \frac{1}{4} \right) - 2F(111'1'). \quad (6) \]