
INTERPRETATION OF A MOLECULAR WAVE FUNCTION IN TERMS OF INDIVIDUAL STRUCTURES

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Received December 18th, 1981

A general method is presented suitable for the decomposition of a MO wave function into a set of non-orthogonal structures. Applying this method provides evidence that the generally accepted idea of the "weight" of a structure has no physical meaning and cannot therefore be used for interpreting the problems of structure and reactivity.

By rapid and extensive development of the quantum mechanics essentially all the valence problems have been converted into a solution of the Schrödinger equation. However, the wave function used to describe a molecular structure is an abstract quantity whose characteristics differ markedly from the classical chemical structures, as illustrated by the structural formulas. The qualitative interpretation of a molecular wave function thus constitutes one of important tasks for the valence theory. The goal of such studies is to analyze properly the information inherent in the wave function in terms of chemical bonds and classical structural formulas. At the same time, it turns out that a real molecular structure can never be expressed by only one classical structural formula, but that it is necessary to admit the so-called resonance of several limiting structures. In the framework of this concept, the valence-bond (VB) method has been suggested for the solution of the Schrödinger equation. This method expresses the real wave function as a linear combination of functions (the so-called resonance hybrid) which in some manner correspond to the individual limiting structures. Although the VB method itself has almost been abandoned and the wave function is determined by using the MO method, the fundamental idea of the VB method, *i.e.* to express the wave function in the form of a linear combination of limiting structures, has become a basis of all recent attempts to interpret the abstract MO wave function¹⁻⁵. In consequence of such approach, a real physical meaning is often attributed to individual coefficients of the linear combination as if they really represented a contribution of one or another structure to the overall wave function of a molecule. This concept received a wide acceptance and it became quite usual to speak about, *e.g.* a percentage contribution of the Kekule or Dewar structures to the wave function of benzene.

In the present work a general method is suggested for the decomposition of a wave function into individual structures. This method is utilized to provide evidence that the so-called "weights" of individual structures do not represent regardless of the method of their definition absolute quantities, since they depend on the actual choice of a set of structures into which one decomposes the wave function.

RESULTS AND DISCUSSION

Let the electronic structure of a given molecule be described by an abstract wave function Φ .^{*} We will now attempt to express this function in the form of a linear combination of functions A_i which in some manner correspond to the individual limiting structures.^{**} The function Φ considered as a vector in the Hilbert space can be expressed in the form of a linear combination of certain basis vectors (Eq. (1)).

$$\Phi = \sum_{i=1}^N a_i A_i . \quad (1)$$

The Eq. (1) is valid only if the functions A_i satisfy the following conditions: *a*) the number (N) of functions A_i is equal to the dimension of the corresponding Hilbert space and *b*) all the functions A_i are linearly independent. In other words, the functions A_i must form a complete basis. Let us now discuss both these conditions in detail. The dimension of the Hilbert space corresponding to the function Φ can be determined on the basis of the following consideration. Suppose that for a given molecule we know a set of molecular orbitals determined, *e.g.*, by solution of the Hartree-Fock equations. However, the single-determinantal SCF wave function does not represent the most general function which could be constructed from a given set of orbitals. Such a general function can be obtained via configuration interaction (CI). Since the complete CI leads to an exact solution of the Schrödinger equation (in the given AO basis), it is clear that the dimension of the Hilbert space for function Φ is equal to that number of configurations which possess the same symmetry as the function Φ and can therefore mutually mix in the CI description of the function Φ . From these conclusions it follows that an exact expression of the ground state, *e.g.*, for allyl cation requires, in the framework of π approximation, to use four A functions; similarly, twelve A functions are necessary for 1,3-butadiene. Since the functions A_i are generally not orthogonal, the second condition for these functions, *i.e.* to be linearly independent, is not trivial at all.

We may now attempt to formulate mathematically the decomposition of the function Φ into a basis of non-orthogonal A_i functions. The coefficients of this decomposition are to be determined by the least-squares method on the basis of minimization of the functional Δ (Eq. (2)).

$$\Delta = (\Phi - \sum_i^N a_i A_i)^2 \quad (2a)$$

$$\frac{\partial \Delta}{\partial a_i} = 0 ; \quad i = 1, 2, \dots, N \quad (2b)$$

* In fact, it is not important whether we have to deal here with an approximate SCF or a general SCF+CI wave function.

** The functions A_i can be identified, for instance, with the pure VB functions or defined by analogy with the PCIL0 method by means of strictly localized orbitals⁶.

This procedure leads to a set of linear equations for coefficients a_i (Eq. (3)):

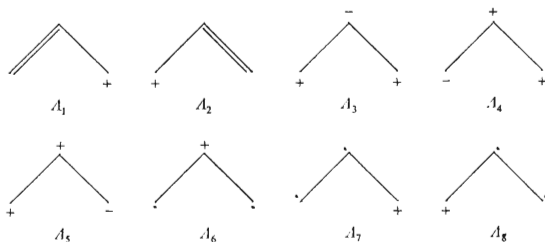
$$\langle \Phi | A_i \rangle = \sum_j^N a_j \langle A_i | A_j \rangle. \quad (3)$$

The form of these equations documents the importance of the linear independence of functions A_i , since only in this case the system of equations (3) will lead to a unique solution. Having now at hand the individual coefficients a_i , we can define the so-called "weight" of the i -th structure by Eq. (4):

$$w_i = \sum_j^N a_j \langle A_i | A_j \rangle. \quad (4)$$

This definition was suggested first by Coulson⁷ and latter also by Peters⁸ and Hurley⁹. Another possibility of defining the "weight" of a structure was proposed by Gallup¹⁰.

From the mathematical point of view, the decomposition of a wave function into individual structures is thus solved quite unambiguously. The problem which hinders the physical interpretation of such a decomposition in terms of contributions of one or another structure resides in the ambiguity of choice of the basis into which we are decomposing the wave function. This ambiguity follows from the possibility of constructing considerably more functions A_i than requires the dimension of the corresponding Hilbert space. If one attempts to select from these functions a set of structures in order to form a complete basis for the decomposition of function Φ , it is immediately noticeable that there are several ways of how to choose this basis. All these ways of choice of a complete basis of structures have an entirely equal justification and none of them can be preferred or eliminated. Consequently, and as a result of the usual non-orthogonality of individual structures, the coefficients for the expansion of function Φ into a basis of functions A_i depend in fact on the choice



SCHEME 1

of this basis. However, this implies that no real physical meaning can be attributed to these coefficients or quantities derived from them (various kinds of the "weight" definition).

In an effort to illustrate the validity of these conclusions, we will analyze in detail the structure of the allyl cation. Various limiting structures can be utilized for its description and some of them ($I-8$) are presented in Scheme 1. Let us now visualize the form of basis functions corresponding to the individual structures. The structures I and 2 , which describe best the allyl-cation structure in chemical sense, are identified with the wave functions L_1 and L_2 constructed from the strictly localized orbitals λ_1, λ_2 in the form of the Slater determinant (Eq. (5)).

$$L_1 = |\lambda_1 \bar{\lambda}_1| \quad (5a)$$

$$L_2 = |\lambda_2 \bar{\lambda}_2| \quad (5b)$$

In Eqs (5a) and (5b), the orbital λ_1 describes the C=C bond between the atoms 1 and 2 and the orbital λ_2 that between the atoms 2 and 3 (Eq. (6)).

$$\lambda_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2) \quad (6a)$$

$$\lambda_2 = \frac{1}{\sqrt{2}} (\chi_2 + \chi_3) \quad (6b)$$

The simple form of the other wave functions is presented by Eqs (7a)–(7f).

$$L_3 = |\chi_2 \bar{\chi}_2| \quad (7a)$$

$$L_4 = |\chi_1 \bar{\chi}_1| \quad (7b)$$

$$L_5 = |\chi_3 \bar{\chi}_3| \quad (7c)$$

$$L_6 = \frac{1}{\sqrt{2}} \{ |\chi_1 \bar{\chi}_3| + |\chi_3 \bar{\chi}_1| \} \quad (7d)$$

$$L_7 = \frac{1}{\sqrt{2}} \{ |\chi_1 \bar{\chi}_2| + |\chi_2 \bar{\chi}_1| \} \quad (7e)$$

$$L_8 = \frac{1}{\sqrt{2}} \{ |\chi_2 \bar{\chi}_3| + |\chi_3 \bar{\chi}_2| \} \quad (7f)$$

Whereas the functions $L_3 - L_8$ represent a set of pure VB structures, the functions L_1 and L_2 correspond to general basis functions which still describe unambiguously the limiting structures 1 and 2. Since the functions L_1, L_2, L_4, L_5, L_7 and L_8 do not possess the symmetry of the allyl-cation ground state, a proper symmetrization is necessary. This symmetrization yields a set of five functions $A_1 - A_5$ (Eq. (8)).

$$A_1 = \sqrt{(0.4)}(L_1 + L_2) \quad (8a)$$

$$A_2 = L_3 \quad (8b)$$

$$A_3 = L_6 \quad (8c)$$

$$A_4 = \frac{1}{\sqrt{2}}(L_4 + L_5) \quad (8d)$$

$$A_5 = \frac{1}{\sqrt{2}}(L_7 + L_8) \quad (8e)$$

From $A_1 - A_5$ four arbitrary functions can be chosen as a basis provided that they satisfy the condition of linear independence. If our set of functions were purely of the VB type, it would be possible to utilize the standard Rumer method¹¹ for selecting these linearly independent structures. In our case, however, we are forced to use another method based on an analogy with vectors. The condition of the linear independence of a set of functions φ_i is satisfied if the determinant of the overlap matrix $\langle \varphi_i | \varphi_j \rangle$ (Gramm determinant) differs from zero. In the framework of our set of structures $A_1 - A_5$, there exist just five possibilities of selecting the basis, *i.e.* (A_1, A_2, A_3, A_4) , (A_1, A_2, A_3, A_5) , (A_1, A_2, A_4, A_5) , (A_1, A_3, A_4, A_5) and (A_2, A_3, A_4, A_5) . The above criterion shows that the structure set (A_1, A_2, A_3, A_5) is linearly dependent and cannot therefore form the basis. Nonetheless, there are four other possibilities of choice of the complete basis and just this ambiguity has important consequences for the interpretation of a wave function in terms of contributions of individual structures. The argumentation that an unambiguity of the basis choice could be achieved by selecting "chemically reasonable" structures is not justified; the number of these structures is usually less than requires the dimension of the Hilbert space, some additional functions should therefore be included and their choice would always be laden with subjectivity. In order to illustrate these conclusions, the wave function Φ for the allyl-cation ground state was decomposed into the above four sets of functions denoted as $A - D$ (Eq. (9)).

$$A \equiv \{A_1, A_2, A_3, A_4\} \quad (9a)$$

$$B \equiv \{A_1, A_3, A_4, A_5\} \quad (9b)$$

$$C \equiv \{A_1, A_2, A_4, A_5\} \quad (9c)$$

$$D \equiv \{A_2, A_3, A_4, A_5\} \quad (9d)$$

In case the function Φ is represented by the Slater determinant constructed from the Hückel molecular orbitals of the allyl cation (Eq. (10)).

$$\Phi = |\varphi_1 \bar{\varphi}_1| \quad (10a)$$

$$\varphi_1 = \frac{1}{2} \chi_1 + \frac{1}{\sqrt{2}} \chi_2 + \frac{1}{2} \chi_3 \quad (10b)$$

the decomposition into the bases $A - D$ leads to the following expansions (Eq. (11)).

$$A \quad \Phi = 1.118A_1 - 0.207A_2 - 0.146A_3 + 0.354A_4 \quad (11a)$$

$$B \quad \Phi = 0.791A_1 + 0.000A_3 + 0.354A_4 + 0.207A_5 \quad (11b)$$

$$C \quad \Phi = 0.791A_1 + 0.000A_2 + 0.354A_4 + 0.207A_5 \quad (11c)$$

$$D \quad \Phi = 0.500A_2 + 0.354A_3 + 0.354A_4 + 0.707A_5 \quad (11d)$$

The corresponding "weights" of structures for the individual expansions are then given by Eqs (12a)–(12d).

$$A \quad w_1 = 1.03 \quad w_2 = -0.103 \quad w_3 = -0.052 \quad w_4 = 0.125 \quad (12a)$$

$$B \quad w_1 = 0.728 \quad w_3 = 0.0 \quad w_4 = 0.125 \quad w_5 = 0.146 \quad (12b)$$

$$C \quad w_1 = 0.728 \quad w_2 = 0.0 \quad w_4 = 0.125 \quad w_5 = 0.146 \quad (12c)$$

$$D \quad w_2 = 0.250 \quad w_3 = 0.125 \quad w_4 = 0.125 \quad w_5 = 0.500 \quad (12d)$$

These results clearly show that the expansion coefficients as well as the corresponding "weights" of individual structures are not even approximately constant and that their values depend upon the actual type of the basis into which the decomposition is performed. This can be demonstrated quite convincingly by decompositions into bases A , B and C , since all these bases include a "chemically reasonable" struc-

ture A_1 and differ only in the remaining complementary functions. Nevertheless, the "weight" of this common structure varies from 0.73 to about 1.03. Furthermore, as the decomposition D shows, this "chemically reasonable" structure A_1 can be completely omitted and the remaining structures $A_2 - A_5$ will give still an entirely exact picture of the allyl-cation structure. This provides evidence that the decomposition of a wave function in the form of a linear combination of structures can be viewed only as a certain possibility for the description of a wave function, but that no real physical meaning can be attributed to the contributions of individual structures. From this conclusion it also follows that the frequent attempts to identify the physical or chemical behaviour of a given molecule with the contribution of a certain structure do not have any physical justification.

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Translated by J. Málek.