# PROPAGATOR REPRESENTATION FOR PARTIAL STRUCTURE CHARACTER IN CONJUGATED SYSTEMS

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## Abstract

A new method for the evaluation of partial structure character (PC) in a conjugated molecule is proposed and used to calculate the PCs of some conjugated molecules. When PC is represented by the propagator technique or the method of second quantization, the physical meaning of different types of PC is clarified.

## 1.    Introduction

Many methods have been proposed to calculate the degree of partial structure character (PC) [1 – 11], such as benzene character, ethylene character, and so on. In previous papers, we proposed a new method to estimate PC in a molecule [10,11]. Our method gives an energy criterion for the degree of the PC. On the other hand, the method of Polansky and Derflinger [1] is based on a wave function criterion. In this paper, we examine their method from the standpoint of the second quantization procedure and present a propagator representation (contour integral representation). These alternative formulations enable us to extend the concept of PC to excited-state molecules [12].

## 2.    Theory

Polansky and Derflinger introduced PC as the projection of the occupied MOs of a given molecule onto the bonding MOs of the reference molecule within the framework of the Hückel method [1]. Reference molecule means an isolated molecule which has the same molecular $\pi$-electronic skeleton as the partial structure of interest. Their definition can be interpreted as the expectation value of the following projection operator:

$$PJ_b = \sum_k^B |k\rangle\langle k|, \tag{1}$$

where $|k\rangle$ represents the $k$th MO of the reference molecule. The summation in eq. (1) runs over the bonding MOs of the reference molecule.

Introducing the projection operator (eq. (1)), one can understand more clearly the physical meaning of PC in a given molecule. If we represent the projection operator by the method of the second quantization language, the right-hand side of eq. (1) can be written as follows:

$$PJ_b = \sum_k^B a_k^\dagger a_k, \tag{2}$$

where $a_k^\dagger$ and $a_k$ indicate the creation and the annihilation operator defined by the MOs of the reference molecule, respectively. $a_k^\dagger a_k$ is the number operator which represents the occupation number of electrons in the $k$th MO of the embedded reference molecule in a given molecule. Thus, the PC defined by Polansky and Derflinger is equivalent to the calculation of the expectation value of these number operators. In order to calculate the expectation value of eq. (2) associated with the PC in a given molecule in the ground state, $|11 \cdots 100 \cdots\rangle$, one must use the following canonical transformations:

$$a_k^\dagger = \sum_i C_{ik} a_i^\dagger \tag{3}$$

$$a_k = \sum_i C_{ki} a_i, \tag{4}$$

where $a_i^\dagger$ and $a_i$ represent the creation and the annihilation operator defined by the $i$th MO of a given molecule, respectively. $C_{ik}$ and $C_{ki}$ are the overlap integrals of the $k$th MO of the reference molecule and the $i$th MO of a given molecule. The summation of $i$ runs over all MOs of a given molecule. The calculated results are as follows:

$$PJ_b = \sum_k^B \sum_i \sum_j C_{ik} C_{kj} a_i^\dagger a_j. \tag{5}$$

Similarly, one can define the occupation number associated with the antibonding MOs of the embedded reference molecule in a given molecule as follows:

$$PJ_a = \sum_k^A a_k^\dagger a_k, \tag{6}$$

where the summation in eq. (6) runs over the antibonding MOs of the reference molecule.

It should be noted that the occupation number of the MO of the embedded reference molecule in a given molecule is usually non-integer, and the Hamiltonian of a given molecule is not always commutable with the occupation number operator. Thus, the occupation number $a_k^\dagger a_k$ is not the constant of the motion [13], as follows:

$$\frac{d a_k^\dagger a_k}{dt} = \frac{1}{i\hbar}\ [a_k^\dagger a_k, h]$$

$$\neq 0, \tag{7}$$

where $h$ represents the Hückel Hamiltonian of a given molecule.

When the reference molecule is embedded in a given molecule, the MOs are modified by the interaction with the residual part. As a result, the occupation numbers of the MOs of the embedded reference molecule (= partial structure) become non-integers.

It is easily shown that the expectation value of the number operator can be transformed to the propagator representation by using the definition of the propagator [14] as follows:

$$\langle PJ_b \rangle = \frac{1}{2\pi i} \sum_k^B \int G_{kk}\,dz \tag{8}$$

$$\langle PJ_a \rangle = \frac{1}{2\pi i} \sum_k^A \int G_{kk}\,dz , \tag{9}$$

where the Coulson contour [15] may be used for the integration. In actual calculation, we obtain the integrand $G_{kk}$ by diagonalization of the Hamiltonian.

The charge density is also represented as follows [14] :

$$q_r = \frac{1}{2\pi i} \int G_{rr}\,dz. \tag{10}$$

By comparing eqs. (8) and (9) with eq. (10), it is apparent that PC is nothing more than the generalization of the charge density. In other words, charge denity is regarded as the simplest PC, namely, atomic character or site character.

For neutral alternant hydrocarbons, we find that $\langle PJ_b \rangle + \langle PJ_a \rangle$ = the number of sites in the partial structure, because it is well known that $q_r = 1$ [16].

For example, if we analyze the hexagon in naphthalene and consider the benzene for the reference molecule, the value of $\langle PJ_b \rangle$ is calculated to be 5.735 and that of $\langle PJ_a \rangle$ is 0.265. Thus, the sum of these values is equal to 6, as expected.

## 3.    Results and discussion

The values of $\langle PJ_b \rangle$ for ethylene structures, butadiene structures and benzene structures in some neutral alternant hydrocarbons are shown in figs. 1−3. These values are the same as those calculated by Polansky and Derflinger [1] except for normalization factors.
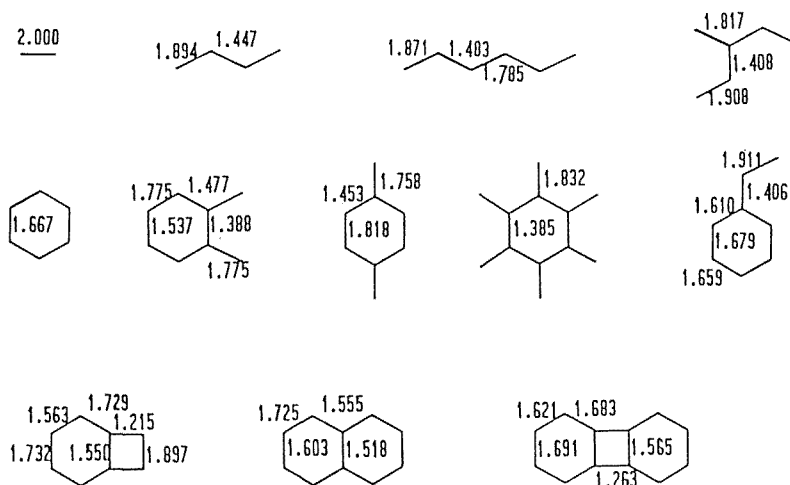


Fig. 1. The values of $\langle PJ_b \rangle$ for the ethylene structures in some alternant hydrocarbons.
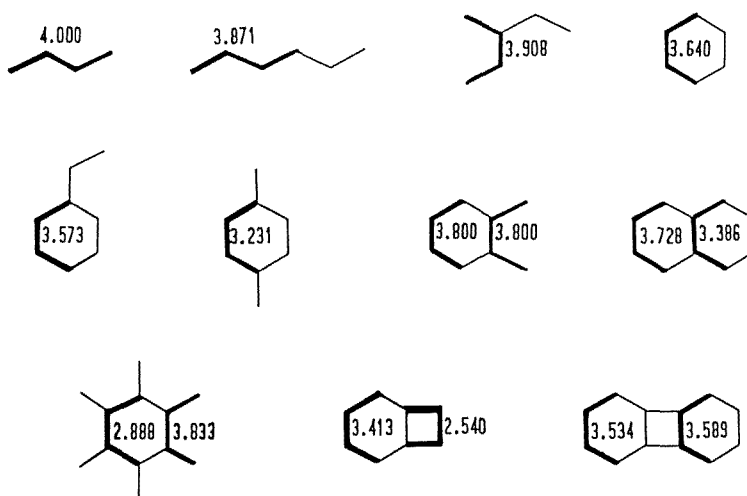


Fig. 2. The values of $\langle PJ_b \rangle$ for the butadiene structures in some alternant hydrocarbons.
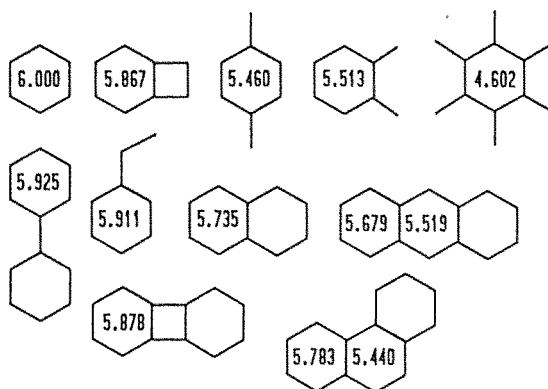
Fig. 3. The values of $\langle PJ_b \rangle$ for the benzene structures
in some alternant hydrocarbons.

From fig. 1, the values of $\langle PJ_b \rangle$ for ethylene structures are well correlated with the bond order and ethylenic structures in the classical Kekulé structures. In fig. 2, the values of $\langle PJ_b \rangle$ for butadiene structures are large if the bond alternated butadiene structures exist in the corresponding Kekulé structures. One can also understand that for hexagons which have large aromatic character, the values of $\langle PJ_b \rangle$ are large (see fig. 3). These results are consistent with the PC proposed by many authors [1–11].

The destabilization of the partial structure in the molecule gives rise to the decrease of the value of $\langle PJ_b \rangle$. This destabilization is offset by a stabilization of the whole molecule. Thus, when we divide a conjugated system into a partial structure (A) and a residual structure (B), the whole molecule is stabilized by a charge transfer (CT) interaction. By this CT interaction, the population of the bonding MOs of A decreases and that of the antibonding MOs increases. As a result, A is somewhat destabilized. Then, a stabilization of the whole molecule results with the sacrifice of stabilization in the partial structure.

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