

A COMPARATIVE STUDY OF BOND ORDERS

Ivan Gutman

Department of Chemistry, Faculty of Sciences,
University of Kragujevac, 34000 Kragujevac,
R.Domanovića 12, Yugoslavia

(received: August 1977)

Abstract

The sum of bond orders over all bonds in a conjugated molecule is investigated for six bond-order-like quantities. The main results of the work are expressed by the equations (P-1) - (P-6).

In the present work we shall analyse six bond orders and bond-order-like quantities: the Coulson bond order¹, the Ruedenberg-Ham bond order², the Pauling bond order³ and its generalization⁴, the topological bond order⁵ and the acyclic bond order⁶. They will be denoted by P^C , P^R , P^P , P^H , P^T and P^A , respectively, the corresponding matrices by \underline{P} , and the bond order between atoms r and s (or, what is the same, between the vertices r and s of the molecular graph) by P_{rs} .

The following notation and terminology will be used.⁷
 G is the molecular graph of a conjugated hydrocarbon. It has N vertices $1, 2, \dots, N$ and N is assumed to be even. $G-r$

denotes the graph obtained by deletion of the vertex r from G . Similarly, $G-r,s$ is obtained by deletion of the vertices r and s from G .

The adjacency matrix \underline{A} of G is defined by

$$A_{rs} = \begin{cases} 1 & \text{if } r \text{ adj } s \\ 0 & \text{otherwise} \end{cases}$$

Here and later $r \text{ adj } s$ denotes that the vertices r and s are adjacent. \underline{A} fulfills the equation

$$\underline{C} \underline{A} \underline{C}^T = \underline{X} \quad (1)$$

where $\underline{X} = \text{diag}(x_1, x_2, \dots, x_N)$ and $\underline{C} \underline{C}^T = \underline{C}^T \underline{C} = \underline{I}$.

Hence, $\underline{C}_j = (C_{j1}, C_{j2}, \dots, C_{jN})$ is the j 'th eigenvector of \underline{A} with the eigenvalue x_j . We shall use the usual convention, $x_1 \geq x_2 \geq \dots \geq x_N$.

It is explained elsewhere⁷ that the eigenvectors \underline{C}_j represent Hückel molecular orbitals and the eigenvalues x_j are closely related to the molecular orbital energy levels. Therefore, an occupation number g_j can be corresponded to each \underline{C}_j . Of course, it is $g_j=0,1$ or 2 and $g_1 + g_2 + \dots + g_N = N_e = \text{number of } \pi\text{-electrons}$.

Some of the statements which will be derived in this paper are valid for an arbitrary choice of g_j 's. These will be marked by an asterisk (*). In all other cases it is assumed that the molecule bears no electric charge and is in its ground state, i.e. $g_j=2$ for $j=1$ to $N/2$ and

$g_j=0$ for $j=N/2+1$ to N .

The acyclic polynomial $\bar{P}(G, x)$ will not be defined here, but the reader is referred to Ref. 8. The roots of $\bar{P}(G, x)$ are $\bar{x}_1 \geq \bar{x}_2 \geq \dots \geq \bar{x}_N$. We write $\bar{A}(G) = \bar{A}(G, x) = i^N \bar{P}(G, ix)$, where i is the imaginary unit. In the following it will be important that $\bar{A}(G, 1) = Z(G)$ is the topological index of Hosoya.⁹

The number of Kekulé structures (or in the language of graph theory: the number of 1-factors) of G is $K(G)$. If Kekulé structures have parity¹⁰, then $K^+(G)$ and $K^-(G)$ denote the number of even and odd Kekulé structures of G . Of course, it is $K^+ + K^- = K$.

Finally, we shall use the abbreviated notation

$$\frac{1}{\pi} \int_{-\infty}^{\infty} F(x) dx \equiv \langle F(x) \rangle \equiv \langle F \rangle$$

The definitions of the bond orders $P^C - P^A$ are now given as follows.

$$P_{rs}^C = \sum_{j=1}^N g_j C_{jr} C_{js} \quad (2)$$

$$P_{rs}^R = \sum_{j=1}^N g_j C_{jr} C_{js} / x_j \quad (3)$$

$$P_{rs}^P = \begin{cases} K(G-r,s)/K(G) & \text{if } r \text{ adj } s \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$P_{rs}^H = \frac{K^+(G-r,s) - K^-(G-r,s)}{K^+(G) - K^-(G)} \quad \text{if } r \text{ adj } s \quad (5)$$

$$P_{rs}^H = 0 \quad \text{otherwise}$$

$$P_{rs}^T = Z(G-r,s)/Z(G) \quad (6)$$

$$P_{rs}^A = \begin{cases} \langle \bar{A}(G-r,s) / \bar{A}(G) \rangle & \text{if } r \text{ adj } s \\ 0 & \text{otherwise} \end{cases} \quad (7)$$

In eq. (3) it is assumed that $x_j \neq 0$. Similarly, the Pauling bond orders (eqs. (4) and (5)) are defined only for $K(G) \neq 0$ and $K^+(G) \neq K^-(G)$, respectively. Note that for benzenoid molecules, when all the Kekulé structures have equal parity, it is $P^P = P^H$. Further, it can be shown⁶ that for $r \text{ adj } s$, $P^A = P^C$ if the molecule is acyclic, and only then. (This and other properties of P^A justify the name "acyclic bond order".)

It is necessary to introduce a few more π -electron parameters of conjugated molecules. These are the total π -electron energy E , the acyclic reference structure energy⁸ \bar{E} and the topological resonance energy⁸ TRE.

$$E = \sum_{j=1}^N g_j x_j \quad ; \quad \bar{E} = \sum_{j=1}^N g_j \bar{x}_j \quad ; \quad \text{TRE} = E - \bar{E}$$

An identity for Coulson bond order

Before starting with our discussion, two conventions about summation will be adopted.

\sum_{r-s} indicates summation over all pairs of adjacent vertices r and s , that is over all bonds;

\sum_s indicates summation over all vertices s adjacent to r . Consequently, for any quantity P_{rs} , the following identities are valid:

$$\sum_s P_{rs} = \sum_{s=1}^N A_{rs} P_{rs} = (\underline{A} \underline{P})_{rr}$$

$$2 \sum_{r-s} P_{rs} = \sum_{r=1}^N \sum_s P_{rs}$$

$$2 \sum_{r-s} P_{rs} = \sum_{r=1}^N \sum_{s=1}^N A_{rs} P_{rs} = \sum_{r=1}^N (\underline{A} \underline{P})_{rr} = \text{Tr}(\underline{A} \underline{P})$$

There are many ways to deduce the well-known equality

$$2 \sum_{r-s} P_{rs}^C = E \quad (\star) \quad (P-1)$$

We use here a less straightforward proof for reasons which will become clear later.

The matrix equation (1) can be written also in the form $\underline{A} = \underline{C}^T \underline{X} \underline{C}$, or in scalar form as

$$A_{rs} = \sum_{j=1}^N x_j C_{jr} C_{js}$$

If a function $f(x)$ exists for all $x=x_j$ ($j=1$ to N), then a matrix function $f(\underline{A})$ exists, which is defined by

$$[f(\underline{A})]_{rs} = \sum_{j=1}^N f(x_j) C_{jr} C_{js} \quad (8)$$

By comparison of this equality with eq. (2), it is clear that a close analogy exists. In particular, one can formally introduce a function¹¹ $g_j = g(x_j)$, and then

$$\underline{P}^C = g(\underline{A}) \quad (\star)$$

From (8) is now clear that \underline{C}_j 's and g_j 's are the eigenvectors and eigenvalues of \underline{P}^C . In other words it is

$$\underline{C} \underline{P}^C \underline{C}^T = \underline{G} = \text{diag}(g_1, g_2, \dots, g_N) \quad (\star)$$

Therefrom it follows,

$$\begin{aligned} \sum_{r-s} \underline{P}^C_{rs} &= \text{Tr}(\underline{A} \underline{P}^C) = \text{Tr}(\underline{C}^T \underline{X} \underline{C} \underline{C}^T \underline{G} \underline{C}) = \\ &= \text{Tr}(\underline{C}^T \underline{X} \underline{G} \underline{C}) = \text{Tr}(\underline{X} \underline{G}) = \sum_{j=1}^N x_j g_j = E \end{aligned}$$

because the trace of a matrix is invariant under similarity transformations.//

The summation of \underline{P}^C over all bonds in a molecule gives a non-trivial result, which has a straightforward physical interpretation (see later). One may ask whether analogous identities exist for other types of bond orders. We proceed now to answer this question.

Analogies to (P-1)

Using the matrix-theoretical technique developed in the previous section, it is not difficult to show that

$$2 \sum_{r-s} P_{rs}^R = \sum_{j=1}^N g_j = N_e \quad (\star) \quad (P-2)$$

Namely, from $\underline{\underline{C}}^T \underline{\underline{C}} = \underline{\underline{I}}$ we conclude,

$$\sum_{t=1}^N C_{kt} C_{jt} = \delta_{kj}$$

Then,

$$\begin{aligned} (\underline{\underline{A}}^{-1} \underline{\underline{P}}^C)_{rs} &= \sum_{t=1}^N (\underline{\underline{A}}^{-1})_{rt} P_{ts}^C = \\ &= \sum_{t=1}^N \sum_{k=1}^N \sum_{j=1}^N \frac{g_j}{x_k} C_{kr} C_{kt} C_{jt} C_{js} = \\ &= \sum_{k=1}^N \sum_{j=1}^N \frac{g_j}{x_k} C_{kr} C_{js} \delta_{kj} = \sum_{j=1}^N \frac{g_j}{x_j} C_{jr} C_{js} = P_{rs}^R \end{aligned}$$

i.e.

$$\underline{\underline{P}}^R = \underline{\underline{A}}^{-1} \underline{\underline{P}}^C \quad (\star)$$

and finally,

$$2 \sum_{r-s} P_{rs}^R = \text{Tr}(\underline{\underline{A}} \underline{\underline{P}}^R) = \text{Tr}(\underline{\underline{P}}^C) = \text{Tr}(\underline{\underline{G}}) = \sum_{j=1}^N g_j = N_e$$

Thus, eq. (P-2) is proved.//

$$2 \sum_{r-s} P_{rs}^P = N \quad (P-3)$$

In order to demonstrate the validity of this identity, note that in any Kekulé structure of a molecule, exactly one double bond terminates at every atom. Therefore, $\sum_s K(G-r,s) = K$ or, what is the same, $\sum_s P_{rs}^P = 1$. Therefrom eq. (P-3) follows straightforwardly.// In a completely analogous, but less straightforward way one can deduce,

$$2 \sum_{r-s} P_{rs}^H = N \quad (P-4)$$

Thus we have¹⁰, $\sum_s K^+(G-r,s) = K(G)$, $\sum_s K^-(G-r,s) = K^-(G)$ etc.// However, in the case of alternant molecules no combinatorial considerations are necessary at all if one takes into account Ham's equation¹²

$$P_{rs}^H = P_{rs}^R \quad \text{for } r \text{ adj } s \quad (9)$$

(Note the absence of an asterisk in eq. (9).) Then from eq. (P-2) it follows

$$2 \sum_{r-s} P_{rs}^H = \sum_{j=1}^N g_j = N$$

There exists no analogous formula for the sum of the topological bond orders of Hosoya and Hosoi (eq. (6)). However, one may repeat an argument given in Ref. 13 in order to make a conjecture about the behaviour of P^T . It is known¹³ that various integrals $\langle F(x) \rangle$ have a similar numerical behaviour as $F(1)$. Hence $F(1)$ could be in certain cases¹³ used instead of $\langle F(x) \rangle$. Now,

$$P_{rs}^T = \frac{\overline{A(G-r,s,1)}}{\overline{A(G,1)}}$$

and therefore we make the following

Conjecture. P^T has a similar behaviour as P^A . In particular,

$$2 \sum_{r-s} P_{rs}^T \doteq \overline{E} \quad (P-5)$$

We deduce now our last identity

$$2 \sum_{r-s} P_{rs}^A = \bar{E} \quad (P-6)$$

In order to prove (P-6), one should remember that the so called "acyclic reference structure energy" \bar{E} can be calculated⁸ from a variant of the Coulson integral formula for total π -electron energy,

$$\bar{E} = \langle N - x \bar{A}^-(G) / \bar{A}(G) \rangle \quad (10)$$

There are two identities for the acyclic polynomial⁶ which we need now,

$$\bar{A}^-(G) = \sum_{r=1}^N \bar{A}(G-r) \quad (11)$$

and

$$\bar{A}(G) = x \bar{A}(G-r) + \sum_s \bar{A}(G-r,s) \quad (12)$$

Substitution of (11) into (10) yields

$$\bar{E} = \sum_{r=1}^N \langle 1 - x \bar{A}(G-r) / \bar{A}(G) \rangle$$

which is further transformed by means of (12),

$$\bar{E} = \sum_{r=1}^N \sum_s \langle \bar{A}(G-r,s) / \bar{A}(G) \rangle = 2 \sum_{r-s} \langle \bar{A}(G-r,s) / \bar{A}(G) \rangle$$

This latter formula together with the definition (7) of the acyclic bond order completes the proof of the identity (P-6).//

Discussion

The identity (P-1) has an important and well-known interpretation, namely that the Coulson bond order P_{rs}^C is the half of that fraction of the total π -electron energy which is associated with the bond rs . In other words, eq. (P-1) describes a partitioning of the total π -electron energy onto bonds.

Now we can extend this argument and interpret the Ruedenberg-Ham bond order P_{rs}^R as the half of the fraction of the π -electrons which belong to the bond rs . In particular, it can be shown that $\sum_s P_{rs}^R$ is equal to the electron density on the atom r .

The problem of the physical interpretation of the two Pauling bond orders P^P and P^H is not so simple, since both eqs. (P-3) and (P-4) are obtained using purely combinatorial arguments. The situation is even more obscured by the fact that although P^P and P^H are numerically quite different, they both have the property $\sum_s P_{rs} = 1$.

Eq. (P-6) (as well as the conjectured eq. (P-5)) can be rewritten as

$$2 \sum_{r-s} (P_{rs}^C - P_{rs}^A) = TRE$$

which implies the interpretation of the quantity $2(P_{rs}^C - P_{rs}^A)$ as the fraction of the topological resonance energy which is associated with the bond rs . Moreover, $P_{rs}^C - P_{rs}^A$ is the change of the Coulson bond order due to the presence of cycles in the molecule. It will be shown elsewhere⁶ that

$P^C - P^A$ is a measure of the aromatic (or antiaromatic) character of a bond, hence it is an index of local aromaticity.

Acknowledgment

The author gratefully acknowledges the support of this research by the Alexander von Humboldt Foundation.

References

1. C.A.Coulson, Proc.Roy.Soc. (London) A 169 (1939) 413.
2. K.Ruedenberg, J.Chem.Phys. 22 (1954) 1878. See also: N.S.Ham and K.Ruedenberg, J.Chem.Phys. 29 (1958) 1215.
3. L.Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca 1960, Chapter 7.5.
4. The generalized Pauling bond order seems to be first applied by Herndon (W.C.Herndon, J.Amer.Chem.Soc. 96 (1974) 7605), although its explicit form was certainly known to Ham (see Ref.12). In both cases the notation P^H for this bond order is appropriate.
5. H.Hosoya and K.Hosoi, J.Chem.Phys. 64 (1976) 1065.
6. I.Gutman, unpublished results.
7. For further details see: I.Gutman and N.Trinajstić, Topics Curr.Chem. 42 (1973) 49.
8. I.Gutman, M.Milun and N.Trinajstić, Croat.Chem.Acta 48 (1976) 87; J.Amer.Chem.Soc. 99 (1977) 1692.

9. H.Hosoya, Bull.Chem.Soc.Japan 44 (1971) 2332.
10. The partition of Kekulé structures onto even and odd is not possible for certain non-alternant molecules. (For further details see: I.Gutman and N.Trinajstić, Croat.Chem.Acta 47 (1975) 37.) In that case, the generalized Pauling bond order remains undefined. Whenever in the present paper we deal with P^H we assume that K^+ and K^- do exist.
11. K.Ruedenberg, J.Chem.Phys. 34 (1961) 1884.
12. N.S.Ham, J.Chem.Phys. 29 (1958) 1229.
13. I.Gutman, T.Yamaguchi and H.Hosoya, Bull.Chem.Soc. Japan 49 (1976) 1811.