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General Relations between Bond Orders and Imaginary Bond-Bond Polarizabilities

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The imaginary bond-bond polarizability has been studied. Several general relations exist between the bond order and the imaginary bond-bond polarizability and between imaginary bond-bond polarizabilities.

Benzenoid hydrocarbons are known to have large magnetic anisotropies. A semiclassical theory by Pauling[1] showed that this arises from the Larmor precession of pi-electrons around the carbocyclic framework (ring current). In 1937 London[2,3] formulated this picture in simple quantum-mechanical terms. His method involves the use of gauge invariant atomic orbitals as a basis for the LCAO scheme. McWeeny[4,5] modified London's theory and represented the energy change due to the effect of the external magnetic field in terms of the imaginary bond-bond polarizability. When applied to a series of aromatic hydrocarbons, McWeeny's method gives a good agreement with experimental values of the ratio $\Delta\chi/\Delta\chi$ (benzene) and of NMR chemical shifts.[6–10] Here $\Delta\chi$ stands for the magnetic anisotropy of a conjugated system.

On the basis of McWeeny's method and with Gayoso-Boucekkine's unitary transformation,[11] Mallion[12] gave an explicit expression for the ring current in individual rings of polycyclic hydrocarbons. He emphasized, from the graph theoretical view point, that the concepts of "spanning tree"[13] and "circuit"[13] play impotant roles in the theory of the ring current. And many authers have discussed the concept of the ring current from the view point of the aromatic character of conjugated compounds.[14–19]

Imaginary bond-bond polarizability has been widely used to calculate the ring currents of conjugated systems. Nevertheless, the properties of the imaginary bond-bond polarizability have never been discussed. Only in Haddon's paper[20] is found a relation between the bond order and the imaginary bond-bond polarizability. But this is a special case of relations given in this paper.

Here the property of the imaginary bond-bond polarizability in a conjugated molecule will be discussed. And it will be shown that several general relations exist between bond orders and imaginary bond-bond polarizabilities.

The Imaginary Bond-Bond Polarizability

In order to understand the meaning of the imaginary bond-bond polarizability, the London-McWeeny theory, which is an extension of the simple HMO method, will be briefly outlined in this section. And each term of the expression for the magnetic susceptibility will be evaluated.

With London's approximations,[2] the resonance integrals in the presence of an external, uniform, magnetic field H normal to the plane of the molecule are given as[4–5]

$$\begin{aligned}\beta_{rs} &= \beta\exp[2\pi\mathrm{i}(e/hc)S_{rs}H]\\ &= \beta\exp(\mathrm{i}\,\theta_{rs}),\end{aligned}$$

where e, h, and c are the usual fundamental constants, S_{rs} the signed area of the triangle formed by an arbitrary origin and the bond r-s, counted positive if r-s is right-handed about the normal to the plane of the molecule, and β is the resonance integral in the absence of the magnetic field, which is assumed to be equal for all bonds.

With respect to the zero-field atomic orbital AO, the matrix elements of the perturbation due to the field are

$$\begin{aligned}\Delta_{rs} &= \beta_{rs} - \beta\\ &= \beta\left(\mathrm{i}\theta_{rs} - \frac{1}{2}\theta_{rs}^2 + \cdots\right).\end{aligned}$$

The usual perturbation method gives the first- and second energy changes in the J-th molecular orbital MO (which is supposed to be nondegenerate):

$$\delta E_J^{(1)} = \sum_{rs} P_{J,sr}\Delta_{rs},$$

and

$$\delta E_J^{(2)} = \sum_{rs}\sum_{tu}\pi_{J,rs,tu}\Delta_{rs}\Delta_{tu}.$$

Here $P_{J,rs}$ is the partial bond order of the bond r-s[21] and is given by

$$P_{J,rs} = C_{rJ}C_{sJ},$$

and

$$\pi_{J,rs,tu} = \sum_{K(\neq J)}\frac{C_{rJ}C_{sK}C_{tK}C_{uJ}}{E_J - E_K},$$

where C_{rJ} and E_J are the coefficients of the r-th AO and the orbital energy of the J-th MO in the absence of the magnetic field. In this article, for simplicity, all the coefficients of AO are supposed to be real, since the wave function can always be written in real form in the absence of the magnetic field.

If we keep the first two terms in the series expansion of the perterbation and let X_{rs} and Y_{rs} be the real and imaginary parts of Δ_{rs} respectively, then

$$X_{rs} = -\frac{\beta}{2}\theta_{rs}^2 = X_{sr},$$

and

$$Y_{rs} = \beta\,\theta_{rs} = -Y_{sr}.$$

Considering the above equations, the first- and second energy changes in the J-th MO can be written as follows:

$$\delta E_J^{(1)} = 2\sum_{(rs)} P_{J,rs}X_{rs},$$

and

$$\delta E_J^{(2)} = -\sum_{(rs)}\sum_{(tu)} \bar{\pi}_{J,(rs)(tu)} Y_{rs} Y_{tu},$$

where (*rs*) indicates a sum over bonds, not a double sum over atomic centers and we have written

$$\bar{\pi}_{J,(rs)(tu)} = \pi_{J,rs,tu} - \pi_{J,rs,ut} + \pi_{J,sr,ut} - \pi_{J,sr,tu}$$
$$= \sum_{K(\neq J)} \frac{(C_{rJ}C_{sK} - C_{sJ}C_{rK})(C_{tK}C_{uJ} - C_{uK}C_{tJ})}{E_J - E_K}. \quad (1)$$

Term $\bar{\pi}_{J,(rs)(tu)}$ is the partial imaginary bond-bond poplarizability between bonds *r-s* and *t-u*.[22]

Thus the energy change in the *J*-th MO is

$$\delta E_J = -\beta\left(\frac{2\pi e}{hc}\right)^2$$
$$\{\sum_{(rs)} P_{J,rs}S_{rs}^2 + \sum_{(rs)}\sum_{(tu)} \beta\bar{\pi}_{J,(rs)(tu)}S_{rs}S_{tu}\}H^2.$$

Moreover the total pi-electron energy change of a conjugated molecule is given by

$$\delta E = \sum_J \lambda_J \delta E_J = -\beta\left(\frac{2\pi e}{hc}\right)^2$$
$$\{\sum_{(rs)} P_{rs}S_{rs}^2 + \sum_{(rs)}\sum_{(tu)} \beta\bar{\pi}_{(rs)(tu)}S_{rs}S_{tu}\}H^2, \quad (2)$$

where λ_J is the occupation number of the *J*-th MO,

$$P_{rs} = \sum_J \lambda_J P_{J,rs},$$

and

$$\bar{\pi}_{(rs)(tu)} = \sum_J \lambda_J \bar{\pi}_{J,(rs)(tu)}$$
$$= \sum_J \lambda_J \sum_{K(\neq J)} \frac{(C_{rJ}C_{sK} - C_{sJ}C_{rK})(C_{tK}C_{uJ} - C_{uK}C_{tJ})}{E_J - E_K}. \quad (3)$$

Term P_{rs} is the Coulson bond order of bond *r-s*,[23] and the term $\bar{\pi}_{(rs)(tu)}$ is what McWeeny defined as the imaginary bond-bond polarizability between bonds *r-s* and *t-u*.[4-5] The magnetic susceptibility of a conjugated molecule is defined as the second derivative of the total pi-electron energy with respect to *H*, *i.e.*,

$$\chi = -\frac{\partial^2}{\partial H^2}[(E^0 + \delta E)]_{H=0}$$
$$= 2\beta\left(\frac{2\pi e}{hc}\right)^2\{\sum_{(rs)} P_{rs}S_{rs}^2 + \sum_{(rs)}\sum_{(tu)} \beta\bar{\pi}_{(rs)(tu)}S_{rs}S_{tu}\}$$
$$= \sum_J \lambda_J \chi_J, \quad (4)$$

where E^0 is the zero-field total pi-electron energy of a conjugated molecule and χ_J is the partial magnetic susceptibility for the *J*-th MO, as defined in the last equation.[22]

From Eq. 3 it can easily be shown that the mutual imaginary bond-bound polarizability $\bar{\pi}_{(rs)(tu)}$ is antisymmetric with respect to *rs* and *tu*, *i.e.*,

$$\bar{\pi}_{(rs)(tu)} = -\bar{\pi}_{(rs)(ut)} = -\bar{\pi}_{(sr)(tu)}.$$

Since the sum in Eq. 3 is antisymmetric in *J* and *K*, for molecules in which all the pi-electrons are paired, the imaginary bond-bond polarizability can be written as follows:

$$\bar{\pi}_{(rs)(tu)} = 2\sum_J^{\text{occ}}\sum_K^{\text{unocc}} \frac{(C_{rJ}C_{sK} - C_{sJ}C_{rK})(C_{tK}C_{uJ} - C_{uK}C_{tJ})}{(x_J - x_K)\beta}, \quad (5)$$

where $\sum^{\text{occ}}$ and $\sum^{\text{unocc}}$ run over occupied and unoccupied MO's respectively, and, as in the usual HMO method, it has been assumed that the orbital energy E_J can be written as follows:

$$E_J = \alpha + \beta x_J.$$

Here α is the coulomb integral.

From Eq. 5, it can be shown that the self imaginary bond-bond polarizabilities of any bonds are positive, *i.e.*,

$$\bar{\pi}_{(rs)(rs)} > 0, \quad (6)$$

where β is assumed to be negative.

From Eq. 6 we can say that the terms associated with the self imaginary bond-bond polarizability in Eq. 4 correspond to the paramagnetic terms of the magnetic susceptibility. Since the bond order P_{rs} of the bond *r-s* is positive,[24] the first terms in Eq. 4 correspond to the diamagnetic terms of the magnetic susceptibility. But the other terms associated with the mutual imaginary bond-bond polarizabilities do not have definite effects on the magnetic susceptibility because these polarizabilities do not have a definite sign.

General Relations between Bond Orders and Imaginary Bond-Bond Polarizabilities

The property of the imaginary bond-bond polarizability in a conjugated molecule will be dependent on the topological nature of the carbon skeleton, *i.e.*, the mode of branching. But the degree of vertices (atoms) in the Hückel molecular graph does not exceed 3.[25] It is therefore enough to consider only two subgraphs G1 and G2 as shown in Figs. 1 and 2.

Let first consider subgraph G1. This is a sequence of vertices a_j ($j=1,2,\cdots,n$) whose degrees are all two. Then we have the following equalities for these edges (bonds):

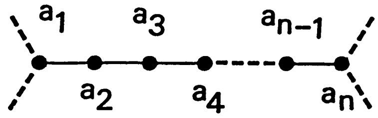

Fig. 1. Subgraph G1.

$$\bar{\pi}_{J,(rs)(a_i a_{i+1})} = \bar{\pi}_{J,(rs)(a_j a_{j+1})}, \quad (A')$$
$$\bar{\pi}_{(rs)(a_i a_{i+1})} = \bar{\pi}_{(rs)(a_j a_{j+1})}, \quad (A)$$
$$P_{J,a_i a_{i+1}} + \beta\bar{\pi}_{J,(a_i a_{i+1})(a_i a_{i+1})}$$
$$= P_{J,a_j a_{j+1}} + \beta\bar{\pi}_{J,(a_j a_{j+1})(a_j a_{j+1})}, \quad (B')$$
$$P_{a_i a_{i+1}} + \beta\bar{\pi}_{(a_i a_{i+1})(a_i a_{i+1})}$$
$$= P_{a_j a_{j+1}} + \beta\bar{\pi}_{(a_j a_{j+1})(a_j a_{j+1})}, \quad (B)$$
$$P_{J,a_i a_{i+1}} = \beta\bar{\pi}_{J,(a_i a_{i+1})(a_j a_{j+1})} - \beta\bar{\pi}_{J,(a_i a_{i+1})(a_i a_{i+1})}, \quad (C')$$
$$P_{a_i a_{i+1}} = \beta\bar{\pi}_{(a_i a_{i+1})(a_j a_{j+1})} - \beta\bar{\pi}_{(a_i a_{i+1})(a_i a_{i+1})}, \quad (C)$$

where $i,j=1,2,\cdots,n$ and $i\neq j$.

Relations A′ and A hold as far as a given edge *r-s* is not equal to edges a_i-a_{i+1} or a_j-a_{j+1}, *i.e.*, as far as the imaginary bond-bond polarizabilities under consideration are mutual ones. Relations B′, B, C′, and C hold even when the vertex a_1 is jointed to the vertex a_n, *i.e.*, even when the sequence of a_j ($j=1,2,\cdots,n$) forms a ring.

Proof of Relations A′ and A. We first consider Relation A′ for $i=i$ and $j=i+1$. By substituting Eq. 1 into Relation A′ and with some manipulations, the following equation is derived:

$$\begin{aligned}&\beta(\bar{\pi}_{J,(rs)(a_ia_{i+1})}-\bar{\pi}_{J,(rs)(a_{i+1}a_{i+2})})\\&=\sum_{K(\neq J)}\frac{1}{x_J-x_K}(C_{rJ}C_{sK}-C_{sJ}C_{rK})\\&\quad\times\{C_{a_{i+1}J}(C_{a_iK}+C_{a_{i+2}K})-C_{a_{i+1}K}(C_{a_iJ}+C_{a_{i+2}J})\}.\end{aligned}\tag{7}$$

Making use of the variational constraint for the vertex a_{i+1}

$$-x_JC_{a_{i+1}J}+C_{a_iJ}+C_{a_{i+2}J}=0,\tag{8}$$

and with some manipulations, Eq. 7 can now be written as follows:

$$\begin{aligned}&\beta(\bar{\pi}_{J,(rs)(a_ia_{i+1})}-\bar{\pi}_{J,(rs)(a_{i+1}a_{i+2})})\\&=\sum_{K}C_{a_{i+1}J}C_{a_{i+1}K}(C_{rJ}C_{sK}-C_{sJ}C_{rK}),\end{aligned}\tag{9}$$

where the sum $\sum_{K(\neq J)}$ in Eq. 7 is changed to the sum $\sum_{K}$ since this change has no effect. Since, from the orthonormal property of the molecular orbitals, we have

$$\sum_J C_{rJ}C_{sJ}=\begin{cases}1 & \text{if } r=s\\ 0 & \text{otherwise,}\end{cases}\tag{10}$$

it can be seen that the right hand side of Eq. 7 is equal to zero. Therefore it follows that

$$\bar{\pi}_{J,(rs)(a_ia_{i+1})}=\bar{\pi}_{J,(rs)(a_{i+1}a_{i+2})}.\tag{11}$$

After the repeated use of Eq. 11 for other edges Relation A′ is finally obtained. And Relation A can be obtained from Eq. 3 and Relation A′.

Proof of Relations B′ and B. After some manipulations similar to those in the proof of Relation A, the following equation can be derived:

$$\begin{aligned}&\beta(\bar{\pi}_{J,(a_ia_{i+1})(a_ia_{i+1})}-\bar{\pi}_{J,(a_{i+1}a_{i+2})(a_{i+1}a_{i+2})})\\&=\sum_{K}C_{a_{i+1}J}C_{a_{i+1}K}\{C_{a_{i+1}J}(C_{a_iK}-C_{a_{i+2}K})\\&\quad-C_{a_{i+1}K}(C_{a_iJ}-C_{a_{i+2}J})\}.\end{aligned}\tag{12}$$

Because of Eq. 10, both the first and second terms of the right hand side of Eq. 12 are equal to zero. The third term of Eq. 12 is $-P_{J,a_ia_{i+1}}$ and the fourth term is equal to $P_{J,a_{i+1}a_{i+2}}$. Therefore we have

$$\begin{aligned}&P_{J,a_ia_{i+1}}+\beta\bar{\pi}_{J,(a_ia_{i+1})(a_ia_{i+1})}\\&=P_{J,a_{i+1}a_{i+2}}+\beta\bar{\pi}_{J,(a_{i+1}a_{i+2})(a_{i+1}a_{i+2})}.\end{aligned}\tag{13}$$

After the repeated use of Eq. 13 for other edges we can obtain Relation B′ and thus Relation B.

Proof of Relations C′ and C. Making use of Eq. 8 for the vertex a_{i+1} and with some manipulations, we can obtain the following equation:

$$\begin{aligned}&\beta\bar{\pi}_{J,(a_ia_{i+1})(a_{i+1}a_{i+2})}\\&=\sum_{K}C_{a_{i+1}J}C_{a_{i+1}K}(C_{a_iJ}C_{a_{i+1}K}-C_{a_iK}C_{a_{i+1}J})\\&\quad+\sum_{K(\neq J)}(C_{a_iJ}C_{a_{i+1}K}-C_{a_{i+1}J}C_{a_iK})\\&\quad\times(C_{a_{i+1}J}C_{a_iK}-C_{a_{i+1}K}C_{a_iJ})\frac{1}{x_J-x_K}.\end{aligned}\tag{14}$$

Since Eq. 10 holds, the first and second terms in the first sum of the right hand side of Eq. 14 are equal to $P_{J,a_ia_{i+1}}$ and to zero, respectively. The second sum is equal to $\beta\bar{\pi}_{J,(a_ia_{i+1})(a_ia_{i+1})}$. Therefore, the following equation is obtained:

$$\beta\bar{\pi}_{J,(a_ia_{i+1})(a_{i+1}a_{i+2})}=P_{J,a_ia_{i+1}}+\beta\bar{\pi}_{J,(a_ia_{i+1})(a_ia_{i+1})}.\tag{15}$$

After the repeated use of Eq. 15 for other edges, we can obtain Relation C′ and thus Relation C.

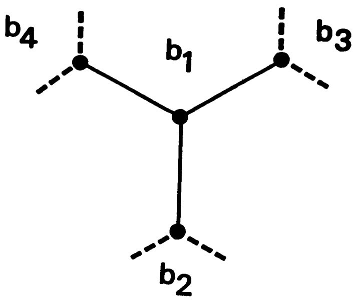

Fig. 2. Subgraph G2.

Next we consider subgraph G2 as shown in Fig. 2, in which the degrees of vertices b_2—b_4 are arbitrary and the vertex b_1 is jointed to vertices b_2—b_4. Then we have

$$\bar{\pi}_{J,(rs)(b_2b_1)}=\bar{\pi}_{J,(rs)(b_1b_3)}+\bar{\pi}_{J,(rs)(b_1b_4)},\tag{D′}$$

$$\bar{\pi}_{(rs)(b_2b_1)}=\bar{\pi}_{(rs)(b_1b_3)}+\bar{\pi}_{(rs)(b_1b_4)},\tag{D}$$

$$\begin{aligned}P_{J,b_1b_2}=&\beta\bar{\pi}_{J,(b_1b_2)(b_3b_1)}+\beta\bar{\pi}_{J,(b_1b_2)(b_4b_1)}\\&-\beta\bar{\pi}_{J,(b_1b_2)(b_1b_2)},\end{aligned}\tag{E′}$$

$$P_{b_1b_2}=\beta\bar{\pi}_{(b_1b_2)(b_3b_1)}+\beta\bar{\pi}_{(b_1b_2)(b_4b_1)}-\beta\bar{\pi}_{(b_1b_2)(b_1b_2)}.\tag{E}$$

Relations D′ and D hold even when a given edge *r-s* may be jointed to vertices b_2—b_4.

Proof of Relations D′ and D. Making use of the variational constraint for the vertex b_1,

$$-x_JC_{b_1J}+C_{b_2J}+C_{b_3J}+C_{b_4J}=0,$$

and with some manipulations similar to those in the proof of Relation A, the following equation is derived:

$$\begin{aligned}&\beta(\bar{\pi}_{J,(rs)(b_2b_1)}-\bar{\pi}_{J,(rs)(b_1b_3)})=\sum_{K}C_{b_1J}C_{b_1K}(C_{sJ}C_{rK}-C_{rJ}C_{sK})\\&+\sum_{(K\neq J)}\frac{1}{x_J-x_K}(C_{rJ}C_{sK}-C_{sJ}C_{rK})\\&\times(C_{b_4J}C_{b_1K}-C_{b_1J}C_{b_4K}).\end{aligned}\tag{16}$$

Note that in the first term of the right hand side of Eq. 16 the sum $\sum_{K(\neq J)}$ changes to the sum $\sum_{K}$. The first term of Eq. 16 is equal to zero since Eq. 10 holds. The second term of Eq. 16 is equal to $\beta\bar{\pi}_{J,(rs)(b_1b_4)}$. Therefore Relation D′ is obtained. Thus Relation D can be obtained from Eq. 3 and Relation D′.

Since the proofs of Relations E′ and E can be performed by the same way, they are omitted.

Discussion

The degeneracy of energy levels has not yet been considered. The derived relations between the partial bond order and the partial imaginary bond-bond polarizability, *i.e.*, Relations A′—E′, do not hold for degenerate energy levels. A slight modification is necessary for these energy levels. But it can be readily shown that Relations A—E hold also for molecules with degenerate energy levels as far as degenerate levels are not singly occupied. In such case we must, however, use the imaginary bond-bond polarizability in the form of Eq. 5.

Here ($4n+2$)-annulenes will be considered as examples. These molecules consist only of segments such as Subgraph G1. Therefore we consider only Relations A—C. Since these molecules have degenerate energy levels, we must, as dicussed above, use the imaginary bond-bond polarizability in the form of Eq. 5. For annulenes, analylitical solutions of the secular equation have been reported. Therefore the sum in Eq. 5 can be performed and the following equations can be obtained:[20)]

$$\bar{\pi}_{(rs)(tu)} = \frac{2}{N^2 \beta \sin(\pi/N)}, \tag{17}$$

$$\bar{\pi}_{(rs)(rs)} = \frac{2(1-N)}{N^2 \beta \sin(\pi/N)}, \tag{18}$$

$$P_{rs} = \frac{2}{N \sin(\pi/N)}, \tag{19}$$

where $N=4n+2$, and r-s and t-u are arbitrary two edges (bonds) in the annulene under consideration. Equation 17 is just Relation A for $(4n+2)$-annulenes. It should be noticed that Relation B can be obtained from their symmetry alone. Moreover from Eqs. 17 and 19 it follows that

$$\bar{\pi}_{(rs)(tu)} = \frac{P_{rs}}{N\beta}.$$

The above equation shows that all the mutual imaginary bond-bond polarizabilities in $(4n+2)$-annulenes are directly related to the bond order P_{rs} and equal to $P_{rs}/\beta N$. From Eqs. 17—19 we can obtain

$$P_{rs} + \beta\bar{\pi}_{(rs)(rs)} = \beta\bar{\pi}_{(rs)(tu)},$$

which is Relation C for $(4n+2)$-annulenes.

By use of a suitable unitary transformation[11)–12)] McWeeny[4)] has shown that the sums in Eqs. 2 and 4, which runs over all bonds in a molecule, can be reduced to sums over one bond in each closed ring. We can show that the result of McWeeny's unitary transformation can be obtained by virtue of Relations A—E.[26)] Moreover it is noteworthy that Relations A and D are very similar to Kirchhoff's law in the electro-magnetic theory. By virtue of Relations A—E, it can be shown that in the London-McWeeny theory the ring currents[12)] are conserved.[26)] The applications of Relations A—E to other problems will be discussed elsewhere.

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