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Magnetic Properties of Conjugated Systems. Bond Orders and Imaginary Bond-Bond Polarizabilities of "Acyclic" Bonds†

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Within the London-McWeeny formalism of the π-electron magnetic properties, the contribution of each bond in a conjugated system to the London susceptibility is studied. By using the relations between the bond orders P_{rs} and the imaginary bond-bond polarizabilities $\bar{\pi}_{(rs)(tu)}$ proved in a previous paper, it is shown that two equations, $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}=0$ and $\bar{\pi}_{(rs)(vw)}=0$, hold for the "acyclic" bond r–s in a conjugated system. The equations show that no bonds in acyclic conjugated systems or in acyclic fragments of cyclic systems make any contributions to the London susceptibilities (or to the ring currents) of the systems. On the basis of these equations, the expression for the London susceptibility is simplified. Moreover, we will discuss the relationships between the above equations and some consequences of McWeeny's unitary transformation.

In 1937 London first laid the foundations of the quantum mechanical theory of π-electron magnetic properties using the Hückel molecular orbital method.[1–4] The π-electron contribution to the magnetic susceptibility of a conjugated system is called the London susceptibility.[5] Pople[6] and McWeeny[7] modified London's method to estimate the proton NMR shielding constants.

It is well-known that, within the London formalism, an external, uniform, magnetic field perpendicular to the molecular plane has no effect on noncyclic conjugated systems.[1–4,8] By using graph theory,[9] Aihara[10] reexamined Pople's approach and showed that the London susceptibility of a polycyclic conjugated molecule can be expressed as a sum of the circuit susceptibilities over all the circuits found in the system.[11] Recently, using Coulson's integral formula,[12] we have proved the circuit rule for the magnetic susceptibility, which states that the circuit susceptibility for the $(4n+2)$-membered circuit is diamagnetic, while that for the $(4n)$-membered circuit is paramagnetic.[11]

In McWeeny's perturbation approach,[3,7] the London susceptibility is expressed in terms of the bond order[12] and the imaginary bond-bond polarizability.[7] Recently we[13] ourselves have proved several general relations between bond orders and imaginary bond-bond polarizabilities, which reflect the local topological nature of the bonds considered, *i.e.*, the mode of branching.

As has been mentioned above, the relationship between the magnetic properties and the structure has been extensively studied. However, it has not been known how each bond in acyclic conjugated systems and in acyclic fragments of cyclic systems contributes to the London susceptibilities. In the present paper, by the use of the relations between the bond orders and the imaginary bond-bond polarizabilities we will reexamine the properties of the bond orders and imaginary bond-bond polarizabilities for the bonds in those systems. The physical meanings of the equations obtained will also be discussed. Moreover, we will study the relationships between the equations thus obtained and some consequences of McWeeny's unitary transformation.

London Susceptibility and Relations between Bond Orders and Imaginary Bond-Bond Polarizabilities

Following London,[1–4] the Hückel matrix elements of a planar conjugated hydrocarbon, in the presence of an external, uniform, magnetic field, $\boldsymbol{H}$, perpendicular to the molecular plane, are given by:

$$h_{rr} = \alpha, \tag{1a}$$

$$h_{rs}\begin{cases} = \beta\exp(iw_{rs}) \text{if atoms } r \text{ and } s \text{ are adjacent,} \\ = 0 \quad\quad \text{otherwise,} \end{cases} \tag{1b}$$

where α is the Hükel Coulomb integral, where β is the Hückel resonance integral in the absence of the field, which is assumed to be equal for all the bonds in the molecule, and where w_{rs} is given by:

$$w_{rs} = (e/\hbar c)\, S_{rs}\, H = -\, w_{sr}. \tag{2}$$

In Eq. 2, e, $\hbar$, and c are the usual fundamental constants with these symbols, S_{rs} is the signed area of the triangle formed by an arbitrary origin and the bond r-s, and H is the field strength. With respect to the zero-field atomic orbital, the matrix elements of the perturbation due to the magnetic field are:

$$\Delta_{rs} = h_{rs} - \beta = \beta(iw_{rs} - \frac{1}{2}\, w_{rs}^2 + \cdots\cdots). \tag{3}$$

In McWeeny's notation[7] the partial London susceptibility for the J-th MO, χ_J, is given by:

$$\chi_J = 2\beta\left(\frac{e}{\hbar c}\right)^2 \left\{\sum_{(rs)} p_{J,rs} S_{rs}^2 + \sum_{(rs)}\sum_{(tu)} \beta\bar{\pi}_{J,(rs)(tu)} S_{rs} S_{tu}\right\}, \tag{4}$$

where the sum runs over all the bonds in the molecule and where $P_{J,rs}$ and $\bar{\pi}_{J,(rs)(tu)}$ are, respectively, the partial Coulson bond order of the bond r-s[14] and the partial imaginary bond-bond polarizability between the bonds r-s and t-u for the J-th MO:[15]

$$P_{J,rs} = C_{rJ}\, C_{sJ}, \tag{5}$$

and:

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† This is Part II in a series in which Ref. 13 is Part I.

$$\bar{\pi}_{J,(rs)(tu)} = \sum_{K(\neq J)} \frac{(C_{rJ}C_{sK} - C_{sJ}C_{rK})(C_{tK}C_{uJ} - C_{uK}C_{tJ})}{(X_J - X_K)\beta} \quad (6)$$

where X_J and C_{rJ} are, respectively, the orbital energy (in units of β) and the coefficient of the r-th AO of the J-th MO in the absence of the magnetic field and where the sum runs over all the unperturbed molecular orbitals except the J-th MO.

We have proved several relations between partial bond orders and partial imaginary bond-bond polarizabilities for each nondegenerate MO for the bonds in the two subgraphs, G1 and G2, shown in Fig. 1:[13]

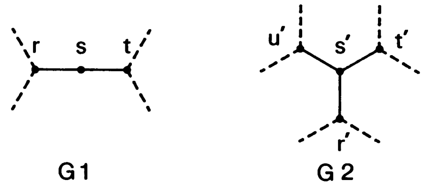

Fig. 1. Subgraphs G1 and G2.

for the bonds in the subgraph G1:

A′ $\bar{\pi}_{J,(vw)(rs)} = \bar{\pi}_{J,(vw)(st)}$,

B′ $P_{J,rs} + \beta\bar{\pi}_{J,(rs)(rs)} = P_{J,st} + \beta\bar{\pi}_{J,(st)(st)}$,

C′ $P_{J,rs} + \beta\bar{\pi}_{J,(rs)(rs)} = \beta\bar{\pi}_{J,(rs)(st)}$,

for the bonds in the subgraph G2:

D′ $\bar{\pi}_{J,(vw)(r's')} = \bar{\pi}_{J,(vw)(s't')} + \bar{\pi}_{J,(vw)(s'u')}$,

E′ $P_{J,r's'} + \beta\bar{\pi}_{J,(r's')(r's')}$
$= \beta\bar{\pi}_{J,(r's')(s't')} + \beta\bar{\pi}_{J,(r's')(s'u')}$,

where v-w is an arbitrary bond. The partial imaginary bond-bond polarizabilities in the relations A′ and D′ must be mutual.

Bond Orders and Imaginary Bond-Bond Polarizabilities of "Acyclic" Bonds

A bond (edge) in a molecular graph may be classified into one of two types, an "acyclic" bond or a "cyclic" bond. They are defined as follows: The deletion of a "cyclic" bond from a molecular graph reduces the number of rings in the molecular graph, but the deletion of an "acyclic" bond does not. For example, the bonds 1-7, 2-8, 3-9, 4-10, 5-11, and 6-12 in the [6]-radialene molecular graph G3 shown in Fig. 2 are "acyclic" because the deletion of any one of these bonds does not reduce the number of rings in G3. All the other bonds in G3 are "cyclic." Edge 1-7 in the biphenyl molecular graph G4 in Fig. 2 is "acyclic." Of course, all the bonds in an acyclic system are "acyclic."

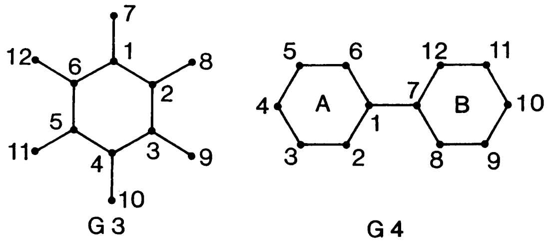

Fig. 2. Molecular graphs G3 and G4.

"Acyclic" and "cyclic" bonds play drastically different roles in the calculations of the magnetic properties of conjugated molecules. For the "acyclic" bond r-s we have the following equations:

$$\bar{\pi}_{J,(rs)(vw)} = 0, \quad (7)$$

$$\bar{\pi}_{(rs)(vw)} = 0, \quad (8)$$

$$P_{J,rs} + \beta\bar{\pi}_{J,(rs)(rs)} = 0, \quad (9)$$

and:

$$P_{rs} + \beta\bar{\pi}_{(rs)(rs)} = 0, \quad (10)$$

where v-w is an arbitrary bond except in the case of the bond r-s. Here, it should be noted that two quantities, $P_{J,rs}$ and $\bar{\pi}_{J,(rs)(rs)}$, are not zero for any bonds, and that the (total) self imaginary bond-bond polarizabilities of bonds in an arbitrary closed-shell system are positive:[13]

$$\bar{\pi}_{(rs)(rs)} > 0. \quad (11)$$

By virtue of the relations A′—E′, Eqs. 7—10 will be illustrated for several typical systems. For the sake of simplicity, only Eqs. 7 and 9 will be discussed in detail because Eqs. 8 and 10 can be easily derived from Eqs. 7 and 9 respectively.

A) It will be convenient for the later discussions to prove initially Eqs. 7 and 9 for a terminal "acyclic" bond, a-b, shown in Fig. 3. By substituting the variational constraint for the carbon atom (vertex) a:

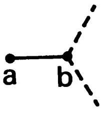

Fig. 3. Terminal "acyclic" bond a—b.

$$-X_JC_{aJ} + C_{bJ} = 0, \quad (12)$$

into Eq. 7, and with some manipulations, the partial mutual imaginary bond-bond polarizability between the bond a-b and an arbitrary bond, v-w, is rewritten as follows:

$$\beta\bar{\pi}_{J,(ab)(vw)} = \sum_{K\neq J}\{C_{aJ}C_{aK}(-C_{vK}C_{wJ} + C_{wK}C_{vJ})\}$$
$$= \sum_{K}\{C_{aJ}C_{aK}(-C_{vK}C_{wJ} + C_{wK}C_{vJ})\}, \quad (13)$$

where the sum $\sum_{K(\neq J)}$ has been replaced by the sum $\sum_{K}$. Since from the orthonomalities of AO's and MO's, we have[16]

$$\sum_{J} C_{rJ}C_{sJ} = \delta_{rs}, \quad (14)$$

the right-hand side of Eq. 13 vanishes. Hence, it follows that

$$\bar{\pi}_{J,(ab)(vw)} = 0. \quad (15)$$

In a similar way, we can show that

$$\beta\bar{\pi}_{J,(ab)(ab)} = \sum_{K}\{C_{aJ}C_{aK}(-C_{aK}C_{bJ} + C_{bK}C_{aJ})\}$$
$$= -C_{aJ}C_{bJ}. \quad (16)$$

Thus, we have proved that

$$P_{J,ab}+\beta\bar{\pi}_{J,(ab)(ab)}=0. \tag{17}$$

Therefore, it has been shown that Eqs. 7 and 9 are valid for the bond, *a*-*b*, shown in Fig. 3.

B) Next, two acyclic systems will be discussed. First, let us take linear polyene with N carbon atoms G5 in Fig. 4. We have already shown in the preceding section that Eqs. 7 and 9 hold for the bond, 1-2, in G5 because the bond corresponds to the bond, *a*-*b*, in Fig. 3. By only applying the relations A′ and B′ and Eqs. 15 and 17 to all the other bonds in G5, we easily obtain:

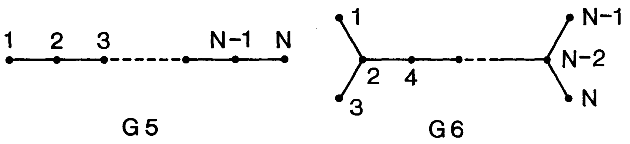

Fig. 4. Molecular graphs G5 and G6.

$$\bar{\pi}_{J,(j\,j+1)(k\,k+1)}=0, \tag{18}$$

and:

$$P_{J,j\,j+1}+\beta\bar{\pi}_{J,(j\,j+1)(j\,j+1)}=0, \tag{19}$$

where *j*, *k*=1, 2,⋯, *N*-1 and *j*≠*k*.

Second, consider the molecular graph G6 shown in Fig. 4. We have already proved for the terminal bonds, 1-2, 2-3, (*N*-2)—(*N*-1), and (*N*-2)—*N*, in G6 in the previous section:

$$\bar{\pi}_{J,(rs)(vw)}=0, \tag{20}$$

and:

$$P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}=0, \tag{21}$$

where *r*-*s* stands for one of the bonds 1-2, 2-3, (*N*-2)—(*N*-1), and (*N*-2)—*N* and where *v*-*w* is an arbitrary bond. The application of the relation D′ to the bond 2-4 gives:

$$\bar{\pi}_{J,(12)(vw)}=\bar{\pi}_{J,(23)(vw)}+\bar{\pi}_{J,(24)(vw)}. \tag{22}$$

From Eqs. 20 and 22, it follows that

$$\bar{\pi}_{J,(24)(vw)}=0. \tag{23}$$

From the relation E′ we obtain:

$$P_{J,24}+\beta\bar{\pi}_{J,(24)(24)}=\beta\bar{\pi}_{J,(24)(12)}+\beta\bar{\pi}_{J,(24)(32)}. \tag{24}$$

Because of Eq. 20, the two terms on the right-hand side of Eq. 24 vanish, and so:

$$P_{J,24}+\beta\bar{\pi}_{J,(24)(24)}=0. \tag{25}$$

Further, by applying the relation A′ and Eq. 23 (and the relation B′ and Eq. 25) to the other bonds in G6, we can easily show that Eq. 7 (and Eq. 9) holds for all the bonds in G6.

C) Acyclic fragments in cyclic systems will be discussed in this section. The molecular graph of the biphenyl G4 in Fig. 2 shows one "acyclic" bond, 1-7. The relation E′ gives:

$$P_{J,12}+\beta\bar{\pi}_{J,(12)(12)}=\beta\bar{\pi}_{J,(12)(71)}+\beta\bar{\pi}_{J,(12)(61)}. \tag{26}$$

From the relation C′ we obtain:

$$P_{J,12}+\beta\bar{\pi}_{J,(12)(12)}=\beta\bar{\pi}_{J,(12)(61)}. \tag{27}$$

A comparison of Eq. 26 with Eq. 27 gives:

$$\bar{\pi}_{J,(12)(71)}=0. \tag{28}$$

By applying the relation A′ to other bonds in the ring A and by using Eq. 28, we obtain:

$$\bar{\pi}_{J,(17)(vw)}=0, \tag{29}$$

where *v*-*w* is an arbitrary bond in the ring A of G4. In the same way, one can show that Eq. 29 holds for any bonds in the ring B.

From the relation E′, the following equation is obtained:

$$P_{J,17}+\beta\bar{\pi}_{J,(17)(17)}=\beta\bar{\pi}_{J,(17)(21)}+\beta\bar{\pi}_{J,(17)(61)}. \tag{30}$$

The relation A′ gives:

$$\bar{\pi}_{J,(17)(12)}=\bar{\pi}_{J,(17)(61)}=-\bar{\pi}_{J,(17)(21)}, \tag{31}$$

where we have used the following equation:13)

$$\bar{\pi}_{J,(rs)(tu)}=-\bar{\pi}_{J,(sr)(tu)}=-\bar{\pi}_{J,(rs)(ut)}. \tag{32}$$

From Eqs. 30 and 31, we obtain:

$$P_{J,17}+\beta\bar{\pi}_{J,(17)(17)}=0. \tag{33}$$

Accordingly, it has been shown that Eqs. 7 and 9 hold for the "acyclic" bond, 1-7, in G4.

The last example is the molecular graph with an acyclic fragment, G7, shown in Fig. 5. It seems evident that Eqs. 7 and 9 are valid for the bond 1-2 in G7. For the bond 2-3, the relation D′ gives:

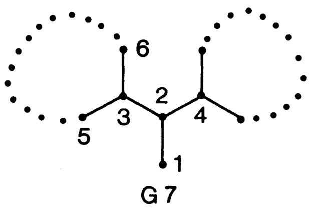

Fig. 5. Molecular graph with acyclic fragment G7.

$$\bar{\pi}_{J,(23)(vw)}=\bar{\pi}_{J,(35)(vw)}+\bar{\pi}_{J,(36)(vw)}, \tag{34}$$

where *v*-*w* is an arbitrary bond. From Eq. 32, we obtain:

$$\bar{\pi}_{J,(36)(vw)}=-\bar{\pi}_{J,(63)(vw)}, \tag{35}$$

and from the relation A′:

$$\bar{\pi}_{J,(35)(vw)}=\bar{\pi}_{J,(63)(vw)}. \tag{36}$$

Equations 35 and 36 show that the right-hand side of Eq. 34 vanishes:

$$\bar{\pi}_{J,(23)(vw)}=0. \tag{37}$$

Similarly, it is shown that

$$\bar{\pi}_{J,(24)(vw)}=0. \tag{38}$$

From the relation E′, the following equation is obtained:

$$P_{J,23}+\beta\bar{\pi}_{J,(23)(23)}=\beta\bar{\pi}_{J,(32)(53)}+\beta\bar{\pi}_{J,(32)(63)}. \tag{39}$$

Because of Eq. 37, the right-hand side of Eq. 39 vanishes, hence,

$$P_{J,23}+\beta\bar{\pi}_{J,(23)(23)}=0. \tag{40}$$

In the same manner, one can show that Eq. 9 is valid for the bond 2-4. Thus, we have shown that Eqs. 7 and 9 are valid for all the "acyclic" bonds in G7.

The above examples make it obvious that Eqs. 7 and 9 hold for any "acyclic" bonds in an arbitrary system. It should be noted that Eqs. 7 and 9 are not valid for degenerate MO's. However, it can easily be shown that Eqs. 8 and 10 hold also for bonds in closed-shell molecules, even with degenerate energy levels, provided that the (total) imaginary bond-bond polarizabilities, not in the form of Eq. 41, but in that of Eq. 42, are used:[13]

$$\bar{\pi}_{(rs)(tu)}=\sum_{J}\sum_{(K\neq J)}g_J\frac{(C_{rJ}C_{sK}-C_{sJ}C_{rK})(C_{tK}C_{uJ}-C_{uK}C_{tJ})}{(X_J-X_K)\beta}, \tag{41}$$

$$\bar{\pi}_{(rs)(tu)}=2\sum_{J}^{\text{occ}}\sum_{K}^{\text{unocc}}\frac{(C_{rJ}C_{sK}-C_{sJ}C_{rK})(C_{tK}C_{uJ}-C_{uK}C_{tJ})}{(X_J-X_K)\beta}, \tag{42}$$

where g_J is the occupation number of the J-th MO and where $\sum^{\text{occ}}$ and $\sum^{\text{unocc}}$, respectively, run over occupied and unoccupied MO's.

Simplified Expression for London Susceptibility

The London susceptibility has usually been expressed in the form of Eq. 4.[3,7] The first term on the right-hand side of Eq. 4 is a first-order correction of the second term in Δ_{rs} (see Eq. 3), namely, of -$(\beta/2)$ w_{rs}^2 (second-order with respect to the field strength, H), while the second term is a second-order correction of the first term in Δ_{rs}, namely, of i βw_{rs} (first- order with respect to H). However, a partial bond order and a partial self imaginary bond-bond polarizability always appear in the form of the sum of the two quantities, *i.e.*, in the form of $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$ in the relations B′, C′, and E′ and in Eqs. 9 and 10. When we consider the contributions of individual bonds in a molecule to its London susceptibility, it may, therefore, be appropriate to rewrite χ_J in the following form:

$$\chi_J=2\beta\left(\frac{e}{\hbar c}\right)^2\left[\left\{\left(\sum_{(rs)}(P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)})\right)S_{rs}^2\right\}\right.$$
$$\left.+\sum_{(rs)\neq(tu)}\sum\beta\bar{\pi}_{J,(rs)(tu)}S_{rs}S_{tu}\right]. \tag{43}$$

Then, each term in Eq. 43 may be interpreted as follows: each term in the first sum on the right-hand side of Eq. 43, namely, $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$, is associated with the π- electron energy change due to an alternation in the resonance integral of the bond r-s itself, while each term in the second sum, namely, the mutual imaginary bond-bond polarizability $\bar{\pi}_{J,(rs)(tu)}$, is associated with that due to the changes in the resonance integrals of the bonds r-s and t-u.

Now we can clarify the physical meaning of Eqs. 7—10. The equations mean that no "acyclic" bonds make any contributions to the London susceptibility. Therefore, it may be more appropriate to rewrite the expression for χ_J in this simplified form:

$$\chi_J=2\beta\left(\frac{e}{\hbar c}\right)^2\left[\sum_{(rs)}^{\text{"cyclic"}}\left\{(P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)})S_{rs}^2\right\}\right.$$
$$\left.+\sum_{(rs)\neq}^{\text{"cyclic"}}\sum_{(tu)}^{\text{"cyclic"}}\beta\bar{\pi}_{J,(rs)(tu)}S_{rs}S_{tu}\right], \tag{44}$$

where the sum runs over only all the "cyclic" bonds in the molecule. The above expression reduces the number of bonds which must be calculated. In the case of [6]-radialene, for example, the number is reduced to half. The set of Eqs. 7—10 provides an alternative way of explaining the well-known fact that the London susceptibilities of any acyclic conjugated systems are zero.

It has been pointed out that the magnitude of the London susceptibility is partially quenched if bond alternation occurs.[15,17] We can prove that the equations corresponding to the relations A′—E′ and to Eqs. 7—10 hold for bonds of molecules with bond alternation.[18]

Ring Current and Equations 7—10

The expression for the ring current[2,19,20] can be derived more easily from the expression for the partial London susceptibility in the form of Eq. 44 than from that in the form of Eq. 4 without the use of the "current-density" formalism.[21–23]

Assume, as in the usual way,[2] that the London susceptibility arises from an induced circulation of π-electrons along the framework of carbon atoms in a conjugated molecule (ring current). Further, the induced ring current may formally be considered as a sum of individual "bond currents" associated with each bond in the molecule.[20,23,24] Then, the "bond current" intensity of the bond r-s, J_{rs}, is given by:[20]

$$J_{rs}=(P_{rs}+\beta\bar{\pi}_{(rs)(rs)})S_{rs}+\sum_{(tu)}\beta\bar{\pi}_{(rs)(tu)}S_{tu}, \tag{45}$$

where the sum runs over all the bonds except the bond r-s. The above equation shows that the "bond current" of the bond r-s arises from the contributions of two types; one is that due to the first term on the right-hand side of Eq. 45, *i.e.*, $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}$, which is associated with an alternation in the resonance integral of the bond r-s itself, while the other is that due to the mutual imaginary bond-bond polarizability in the second term, $\bar{\pi}_{(rs)(tu)}$, which is associated with a change in the resonance integral of the other bond, t-u.

Equations 7—10 indicate that, if the bond r-s is "acyclic," then the change in the resonance integral, due to the applied field, of the bond r-s (see Eq. 3) has no effect on the induction of the "bond current" of the bond r-s itself or on the induction of the "bond current" of any of the other bonds in the system. As a result, we may reasonably conclude that, when there are no rings in a system, the (ring) current does not arise. As in the case of Eq. 44, it is sufficient also for Eq. 45 to sum over only the "cyclic" bonds in the molecule.

The "bond current" is entirely equivalent to the concept of the "ring current" as long as the "bond current" is conserved. The set of the relations A′—E′ ensures that the "bond current" intensity given by Eq. 45 is conserved.[25] In this connection, it is interesting to notice that the relations A′—E′ show that the two quantities, $P_{J,rs}+\beta\bar{\bar{\pi}}_{J,(rs)(rs)}$ and $\bar{\bar{\pi}}_{J,(rs)(tu)}$, obey Kirchhoff's law.[13]

The Relationship between Eqs. 7—10 and Some Consequences of McWeeny's Unitary Transformation

McWeeny has shown that, by virtue of a suitable unitary transformation, the sums in Eq. 44 may be reduced to the sums of one bond in each ring.[7] Gayoso and Boucekkine[26] have proposed a further unitary transformation which generalizes that devised by McWeeny. In the present paper, the transformation devised by Gayoso and Boucekkine will be used and called simply "McWeeny's unitary transformation." It seems that it will be significant and interesting to discuss the relationship between Eqs. 7—10 and some consequences of McWeeny's unitary transformation for "acyclic" bonds.

The matrix of the unitary transformation, $\boldsymbol{U}$, is a diagonal matrix, whose elements are given by:

$$U_{11} = 1,\ U_{rr} = (a_{1j}a_{jk}\cdots\cdots a_{tr})^{*}, \tag{46}$$

where the asterisk stands for the complex conjugate and where

$$a_{rt} = h_{rt}/\beta = \exp(iw_{rt}), \tag{47}$$

and where $(1j)(jk)\cdots(tr)$ is a sequence of edges (bonds) representing the shortest chain between the vertex (atom) labelled 1 and that labelled r in a chosen spanning tree of the original molecular graph. A tree which connects all the vertices of a graph, G, is called a spanning tree of G.[19,27] The bond which must be added to the particular spanning tree in order to reform the original graph, G, is called the "circuit-completing" bond.[7] Let $\bar{\boldsymbol{h}}$ be the transformed matrix of $\boldsymbol{h}$ due to $\boldsymbol{U}$:

$$\bar{\boldsymbol{h}} = \boldsymbol{U}^{\dagger}\boldsymbol{h}\boldsymbol{U}. \tag{48}$$

The non-zero elements, h_{rs}, corresponding to the "circuit-completing" bonds are transformed to the non-zero elements, $\bar{h}_{rs}$, while all the other non-zero elements, h_{rs}, are transformed to β.

Consider biphenyl again. Figure 6 shows a spanning tree, T, whose "circuit-completing" bonds are the bonds 1-6 and 7-8. The matrix elements of biphenyl are transformed as follows:

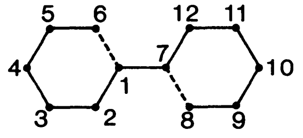

Fig. 6. Spanning tree of the biphenyl molecular graph T.

for the elements corresponding to all bonds except 1-6 and 7-8, for instance:

$$\begin{aligned}\bar{h}_{56} &= U_{55}^{*}h_{56}U_{66}\\ &= (a_{12}a_{23}a_{34}a_{45})h_{56}(a_{12}a_{23}a_{34}a_{45}a_{56})^{*}\\ &= \beta, \end{aligned}\tag{49-a}$$

$$\bar{h}_{17} = U_{11}^{*}h_{17}U_{77} = h_{17}(a_{17})^{*} = \beta, \tag{49-b}$$

for elements corresponding to the "circuit-completing" bonds 1-6 and 7-8:

$$\begin{aligned}\bar{h}_{16} &= U_{11}^{*}h_{16}U_{66} = h_{16}(a_{12}a_{23}a_{34}a_{45}a_{56})^{*}\\ &= \beta\exp\{-i(w_{12}+w_{23}+w_{34}+w_{45}+w_{56}+w_{61})\}\\ &= \beta\exp(-iw_{\mathrm{A}}), \end{aligned}\tag{49-c}$$

$$\bar{h}_{78} = \beta\exp(iw_{\mathrm{B}}). \tag{49-d}$$

In the above equations, we have defined for each ring:

$$w_{\mathrm{R}} = (e/\hbar c)S_{\mathrm{R}}H, \tag{50}$$

where S_{R} is the signed area of a ring, R, of G4. Accordingly, we have certainly found that all the non-zero elements of h_{rs} corresponding to all bonds except the "circuit-completing" bonds are transformed to β. The set of Eqs. 49 shows that all the perturbation due to the applied magnetic field can be thought of as being concentrated in only one bond (edge) of each ring (in this case, the bonds 1-6 and 7-8).[7,19] By virtue of the relations A′—E′ we can also perform the "concentration of perturbation."[19]

The elements of $\boldsymbol{U}$ are dependent on the graph of a chosen spanning tree (see Eq. 46), but one can draw many spanning trees for one molecular graph.[19,27] However, the above example shows that, by the unitary transformation, the matrix elements corresponding to any "acyclic" bonds in an arbitrary system are transformed to β, irrespective of the choice of spanning tree. This means that an "acyclic" bond behaves as if the magnetic field was not applied. Therefore, it follows that all the non-zero Hückel Hamiltonian matrix elements of an acyclic system are changed to β. In other words, the Hückel Hamiltonian matrix of an acyclic conjugated system in the presence of the magnetic field is transformed to the field-free Hückel Hamiltonian matrix of the system by the unitary matrix.

Now it may be apparent that the consequences of the unitary transformation correspond to the fact that Eqs. 7—10 hold for "acyclic" bonds. However, it should be noted that there is a difference between Eqs. 7—10 and the consequences of the unitary transformation. Equations 7—10 show that, in the case of acyclic systems, the coefficient of each element of the perturbation matrix, Δ_{rs}, in Eq. 43 is zero, hence, the second-order energy change with respect to the field strength H is zero. On the other hand, the consequences due to the unitary transformation for acyclic systems mean that all the elements of the perturbation matrix, Δ_{rs}, for the transformed Hamiltonian matrix, $\bar{h}$, are zero, and so the energy change due to the applied field is exactly zero. Of course, in our perturbation approach, the first-order energy change with respect to the field strength, H, vanishes for all arbitrary systems, even with rings.[3]

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