# General Formulas for Evaluating Ring Currents Induced in a Polycyclic Conjugated System

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**Synopsis.** Two apparently different but physically identical formulas were presented to evaluate bond currents (*i.e.*, ring currents in popular terminology) induced in a polycyclic conjugated system. They are applicable to all kinds of planar conjugated systems.

It was in 1979 that we reported a graph-theoretical formula for London susceptibility (*i.e.*, magnetic susceptibility attributable to ring currents) of a planar polycyclic hydrocarbon with no bond alternation.[1] It was later modified to estimate London susceptibility of a bond-alternate hydrocarbon.[2] In fact, this modified formula proved to be applicable to all kinds of planar conjugated systems, including heterocycles. In 1983, we formulated ring currents induced magnetically in a carbocyclic system with no bond alternation.[3] It is now easy to formulate ring currents induced in a heterocycle whose conjugated system is depicted with a variety of Coulomb and resonance integrals.

The term "ring current" has been used by many chemists. However, we hereafter use the term "bond current" instead of the term "ring current" since the latter term has so far borne some different meanings.[3–7] A bond current is defined as an entire current which is induced magnetically in a given $\pi$ bond and passes through it. Mallion has once used this term in the same sense.[8]

We start with the modified graph-theoretical formula for London susceptibility.[2] It is expressed as

$$\chi_G = 9\chi_0 \sum_{i=1}^{M} \left(\frac{S_i}{S_0}\right)^2 \prod_{(lm)}^{r_i} k_{lm} \sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)}. \tag{1}$$

Here, $G$ stands for an entire conjugated system of a planar monocyclic or polycyclic molecule; $r_i$ is the $i$th $\pi$-electron circuit in $G$,[9] which has been referred to as the $i$th $\pi$-electron ring in our previous papers;[1–3,10–13] $G$ is assumed to have $M$ conjugated atoms and $N$ $\pi$-electron circuits; $G—r_i$ is the subsystem of $G$, obtained by deleting from $G$ the $i$th $\pi$-electron circuit and all $\pi$ bonds incident to it; $P_G(X)$ is the characteristic polynomial for $G$; $P_G'(X)$ is its first derivative with respect to $X$; $P_{G-r_i}(X)$ is the characteristic polynomial for $G—r_i$; $X_j$ is the energy of the $j$th $\pi$-electron molecular orbital, obtained by solving the equation $P_G(X)=0$; $g_j$ is the occupation number for the $j$th $\pi$-electron molecular orbital; $S_i$ is the area of the $i$th $\pi$-electron circuit; $S_0$ is the area of the benzene ring; $k_{lm}$ is the resonance integral parameter for the $l—m$ $\pi$ bond, the resonance integral itself being expressed as $k_{lm}\beta$; $(lm)$ runs over all $\pi$ bonds constituting the $i$th $\pi$-electron circuit; and $\chi_0$ is London susceptibility of benzene. $\pi$-Electron circuits denoted by $r_i$ are nothing other than ring components defined in Sachs' graph theory.[14–17]

According to the same procedure as shown in a previous paper,[3] the circuit current induced in the $i$th $\pi$-electron circuit is expressible in the form:

$$I_i = 9I_0 \frac{S_i}{S_0} \prod_{(lm)}^{r_i} k_{lm} \sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)}, \tag{2}$$

where $I_0$ is the circuit current induced in benzene under the same experimental condition. $I_0$ is equal to the bond current induced in benzene. Both $I_0$ and $I_i$ are proportional to the intensity of the external magnetic field. The bond current induced in the $l—m$ $\pi$ bond of G is then given by adding up all circuit currents passing through it. It is expressed as

$$J_{lm} = \sum_{i(lm)} I_i, \tag{3}$$

where $i$ runs over all $\pi$-electron circuits with the $l—m$ $\pi$ bond in common. Since Eq. 1 is applicable to all kinds of planar conjugated systems, Eq. 3 is again applicable to them all.

Equation 3 can be written explicitly in terms of $\chi_G$. The signed area of the triangle formed by the origin of the coordinates and the $l \rightarrow m$ $\pi$ bond, $s_{lm}$, can be defined in such a manner that it satisfies the following two conditions:[4,5]

$$s_{lm} = -s_{ml} \tag{4}$$

and

$$S_i = \sum_{(lm)}^{r_i} s_{lm}, \tag{5}$$

where $(lm)$ runs over all $\pi$ bonds constituting the $i$th $\pi$-electron circuit. By substituting $S_i$ in Eq. 1 by Eq. 5 and then by differentiating Eq. 1 with respect to $s_{lm}$, we obtain the formula for a quantity proportional to the bond current induced in the $l—m$ $\pi$ bond. This relationship can be written formally as

$$J_{lm} = \frac{S_0 I_0}{2\chi_0} \frac{\partial \chi_G}{\partial s_{lm}}. \tag{6}$$

This expression is necessarily identical with Eq. 3.

On the other hand, Veillard formulated the total $\pi$-electron energy of a heterocyclic conjugated system as a function of the external magnetic field.[18] By differentiating the energy twice with respect to the field strength, we obtain the following expression for London susceptibility of a heterocyclic system:

$$\chi_G = \frac{9\chi_0}{S_0^{\,2}} \left[ \sum_{(lm)}^{G} k_{lm} p_{lm} s_{lm}^{\,2} + \sum_{(lm)}^{G} \sum_{(l'm')}^{G} k_{lm} k_{l'm'} \bar{\pi}_{lm,l'm'} s_{lm} s_{l'm'} \right]. \tag{7}$$

Here, $p_{lm}$ is the bond order for the $l—m$ $\pi$ bond; $\bar{\pi}_{lm,l'm'}$ is what McWeeny defined as the imaginary bond-bond polarizability of the $l-m$ and $l'-m'$ $\pi$ bonds;[4,20] and both $(lm)$ and $(l'm')$ run over all $\pi$ bonds in G. Eq. 7 is applicable to bond-alternate hydrocarbons alike. In fact, Gayoso and Boucekkine reported a similar formula for bond-alternate hydrocarbons.[19]

Equation 7 is mathematically identical with Eq. 1 since these two formulas have been derived from the same field-dependent secular determinant.[2,18,19] They manifest two different physical features of London susceptibility. Accordingly, Eq. 6 can be applied to Eq. 7 to formulate the bond currents. By substituting $\chi_G$ in Eq. 6 by Eq. 7 and with the equality $\bar{\pi}_{lm,l'm'}=\bar{\pi}_{l'm',lm}$ in mind,[20] the following expression is obtained for the bond current induced in the $l-m$ $\pi$ bond:

$$J_{lm} = \frac{9I_0}{S_0}\left[k_{lm}p_{lm}s_{lm}+k_{lm}\sum_{(l'm')}^{G} k_{l'm'}\bar{\pi}_{lm,l'm'}s_{l'm'}\right], \tag{8}$$

where $(l'm')$ runs over all $\pi$ bonds in $G$. Equation 8 is again applicable not only to bond-alternate hydrocarbons but also to heterocycles as long as they are planar in shape. According to Mallion,[8] Haigh devised in 1971 a formula analogous to Eq. 8 to calculate bond currents in a hydrocarbon with no bond alternation. Equation 8 is a generalized form of it.

It is to be noted that both Eqs. 3 and 8 are general, in the sense that they can be applied to any planar cyclic conjugated system. All modifications of the Hückel molecular orbital method can be used to evaluate such quantities as $k_{lm}$, $p_{lm}$, and $\bar{\pi}_{lm,l'm'}$ which appear in Eqs. 3 and 8. Gayoso and Mallion recommended the iterative $\beta\omega'\omega''$ Hückel method for evaluating London susceptibility and bond currents.[19,21-23] Both Eqs. 3 and 8 naturally gave the same numerical results for naphthalene, biphenylene, anthracene, azulene, and pyracylene,[22,23] all with realistic carbon-carbon bond lengths.[19,21-23] The bond currents calculated by one of these formulas can be confirmed numerically by means of the other formula. Eq. 8 is much simpler in appearance than Eq. 3. If there is no need to obtain individual circuit currents, the former formula is best suited for evaluation of bond currents by computer.

## References

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$$\frac{I_i}{I_0} = 18\frac{S_i}{S_0}\sum_{j=1}^{n}\frac{P_{G-r_i}(X_j)}{P_G'(X_j)}.$$

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