Contribution of Quadruply Degenerate π-Electron Orbitals to London Susceptibility

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Synopsis. A graph-theoretical formula was derived to evaluate the contribution of quadruply degenerate π-electron orbitals to London diamagnetism. This formula enables us to calculate London susceptibilities of such compounds as *p*-terphenyl and perylene without factorization of their secular determinants.

In 1952 Berthier *et al.*[1] elaborately derived analytical formulas for London (or ring-currents) susceptibility[2,3] of a polycyclic conjugated system with nondegenerate and/or doubly and/or triply degenerate π-electron orbitals. However, there have been no such formulas for systems with quadruply degenerate orbitals. Secular equations of *p*-terphenyl (**1**) and perylene (**2**) were factored into algebraic equations of lower degree,[1] because they have quadruply degenerate orbitals. We have been developing graph theory of cyclic conjugated systems to elucidate their magnetic properties.[4–9] In this note we present a graph-theoretical formula of London susceptibility applicable to quadruply degenerate orbitals of a cyclic conjugated system.

Let a polycyclic conjugated system G be placed perpendicularly to the external magnetic field H, and its characteristic polynomial is denoted by $P_G(X,H)$. If there are quadruply degenerate π-electron orbitals in G, $P_G(X,0)$ can be written as

$$P_G(X,\ 0) = (X-X_o)^4U(X), \tag{1}$$

where X_o is the energy of quadruply degenerate orbitals.[10] $P_G(X,H)$ is expressible in the form:[5]

$$P_G(X,\ H) = P_G(X,\ 0) + H^2\sum_i^G P_{G-r_i}(X,\ 0)\theta_i^2 + H^4A(X) + \cdots. \tag{2}$$

Here, r_i is the ith π-electron ring in G;[11] G-r_i is a subsystem of G, obtained by deleting from G the ith π-electron ring and all π bonds incident to it; i runs over all π-electron rings in G, defined in Sachs' sense;[11] $\theta_i = eS_i/c\hbar$, where S_i is an area of the ith π-electron ring, and e, c, and $\hbar$ are the standard constants with these symbols; and $A(X)$ is a term proportional to H^4, which is not specified here.

Since the magnetic field can be treated as a small perturbation, field-dependent energies of the four orbitals which are degenerate in energy at $H=0$ are given by solving the following equation:[5]

$$P_G(X,\ H) = P_G(X,\ 0) + H^2\sum_i^G P_{G-r_i}(X,\ 0)\theta_i^2 + H^4A(X) = 0. \tag{3}$$

This equation is written as

$$(X-X_o)^4 = -H^2S(X) - H^4T(X), \tag{4}$$

where

$$S(X) = \frac{1}{U(X)}\sum_i^G P_{G-r_i}(X,\ 0)\theta_i^2 \tag{5}$$

and

$$T(X) = \frac{A(X)}{U(X)}. \tag{6}$$

Since $|X-X_o| \ll 1$ for the four orbitals, Eq. 4 can be expanded into

$$(X-X_o)^4 = -H^2\left\{S(X_o) + S^{(1)}(X_o)(X-X_o) + \frac{1}{2}S^{(2)}(X_o)(X-X_o)^2 + \frac{1}{6}S^{(3)}(X_o)(X-X_o)^3\right\} - H^4\{T(X_o) + T^{(1)}(X_o)(X-X_o)\}, \tag{7}$$

where

$$S^{(k)}(X_o) = \left[\frac{d^k}{dX^k}S(X)\right]_{X=X_o}, \tag{8}$$

and

$$T^{(1)}(X_o) = \left[\frac{d}{dX}T(X)\right]_{X=X_o}. \tag{9}$$

Higher-order terms missing on the right-hand side of Eq. 7 are obviously negligible.

Since Eq. 4 is an eigen-equation derived from an Hermitian matrix, all roots of Eq. 7 must be real for an arbitrary small value of H. Necessary conditions for the existence of four real roots are

$$S(X_o) = 0, \tag{10}$$

$$S^{(1)}(X_o) = 0, \tag{11}$$

and

$$S^{(2)}(X_o) < 0. \tag{12}$$

Otherwise, Eq. 7 would not always have four real roots. This can easily be proved by drawing graphs of the following two functions found in Eq. 7:

$$Y = (X-X_o)^4, \tag{13}$$

and

$$Y = -H^2\left\{S(X_o) + S^{(1)}(X_o)(X-X_o) + \frac{1}{2}S^{(2)}(X_o)(X-X_o)^2 + \frac{1}{6}S^{(3)}(X_o)(X-X_o)^3\right\}. \tag{14}$$

For an arbitrary small H value, Eqs. 10—12 are necessary for the two graphs to intersect fully with each other. In fact, secular equations of **1** and **2** satisfy these conditions. Then, Eq. 7 becomes

$$(X-X_o)^4 + \frac{H^2}{6}S^{(3)}(X_o)(X-X_o)^3 + \frac{H^2}{2}S^{(2)}(X_o)(X-X_o)^2 + H^4T^{(1)}(X_o)(X-X_o) + H^4T(X_o) = 0. \tag{15}$$

This is an algebraic equation in $(X-X_o)$ of degree 4.

Let the degenerate orbital energy X_o split into X_1, X_2, X_3, and X_4, and the following expression is deduced straightforwardly from the coefficient of $(X-X_o)^3$ in Eq. 15:

$$\sum_{j=1}^{4}(X_j - X_o) = -\frac{H^2}{6}S^{(3)}(X_o). \tag{16}$$

Consequently, the sum of the energies of eight π electrons in these four orbitals is

$$\varepsilon(H) = 2\sum_{j=1}^{4}X_j = 8X_o - \frac{H^2}{3}S^{(3)}(X_o). \tag{17}$$

It is to be noted that $\varepsilon(H)$ is independent of $T(X)$. More explicitly, $\varepsilon(H)$ is expressed as

$$\varepsilon(H) = 8X_o + \frac{3U^{(1)}(X_o)V^{(2)}(X_o) - U(X_o)V^{(3)}(X_o)}{3U(X_o)^2}H^2, \tag{18}$$

where

$$U^{(1)}(X_o) = \left[\frac{\mathrm{d}}{\mathrm{d}X}U(X)\right]_{X=X_o} \tag{19}$$

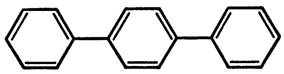
and

$$V^{(k)}(X_o) = \left[\frac{\mathrm{d}^k}{\mathrm{d}X^k}P_{\mathrm{G-r}_i}(X,\ 0)\theta_i^2\right]_{X=X_o}. \tag{20}$$

Finally, we obtain the following formula for a susceptibility contribution from eight π electrons in quadruply degenerate orbitals:

$$\Delta\chi_{\mathrm{G}} = \left[\frac{\mathrm{d}^2}{\mathrm{d}H^2}\varepsilon(H)\right]_{H=0} = \frac{2}{3}\frac{3U^{(1)}(X_o)V^{(2)}(X_o) - U(X_o)V^{(3)}(X_o)}{U(X_o)^2}. \tag{21}$$

Susceptibility contributions from nondegenerate and doubly degenerate orbitals can be estimated using formulas published by Berthier *et al.*[1)] or by us.[5)] London susceptibilities of compounds **1** and **2** can now be calculated easily without factorization of their field-dependent secular determinants. They are 2.730 χ_o and 4.120χ_o for **1** and **2**, respectively, where χ_o is London susceptibility of the benzene conjugated system. These values are identical with those reported by Berthier *et al.*[1,3)]



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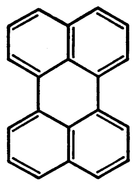

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The following relationships are derived from Eqs. 10 and 11:

$$V(X_o) = \sum_{i}^{\mathrm{G}} P_{\mathrm{G-r}_i}(X_o,\ 0)\theta_i^2 = 0, \tag{22}$$

and

$$V^{(1)}(X_o) = \left[\frac{\mathrm{d}}{\mathrm{d}X}\sum_{i}^{\mathrm{G}} P_{\mathrm{G-r}_i}(X_o,\ 0)\theta_i^2\right]_{X=X_o} = 0. \tag{23}$$

These characterize quadruply degenerate orbitals.

A susceptibility contribution from six π electrons in triply degenerate orbitals can be formulated graph-theoretically in a similar way. It is given as

$$\Delta\chi_{\mathrm{G}} = \frac{4U^{(1)}(X_o)V^{(1)}(X_o) - 2U(X_o)V^{(2)}(X_o)}{U(X_o)^2}, \tag{24}$$

where $U(X)$ is defined by

$$P_{\mathrm{G}}(X,\ 0) = (X - X_o)^3U(X). \tag{25}$$

This is mathematically identical with the formula derived by Berthier *et al.*[1)]

References

1) G. Berthier, M. Mayot, A. Pullman, and B. Pullman, *J. Phys. Radium*, **13**, 15 (1952).
2) F. London, *J. Phys. Radium*, **8**, 397 (1937).
3) B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie," Masson et Cie, Paris (1952), Chap. 9.
4) J. Aihara, *J. Am. Chem. Soc.*, **101**, 558 (1979).
5) J. Aihara, *J. Am. Chem. Soc.*, **101**, 5913 (1979).
6) J. Aihara, *Bull. Chem. Soc. Jpn.*, **53**, 1163 (1980).
7) J. Aihara, *Bull. Chem. Soc. Jpn.*, **54**, 1245 (1981).
8) J. Aihara, *J. Am. Chem. Soc.*, **103**, 5704 (1981).
9) J. Aihara, *Pure Appl. Chem.*, **54**, 1115 (1982).
10) In this note, all orbital energies are given (in units of β) relative to the carbon Coulomb integral.
11) H. Sachs, *Publ. Math. (Debrecen)*, **11**, 119 (1964); A. Graovac, I. Gutman, N. Trinajstić, and T. Živković *Theor. Chim. Acta*, **26**, 67 (1972).