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Determination of London Susceptibilities and Ring Current Intensities using Conjugated Circuits

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Abstract: Conjugated circuits have been employed to accurately reproduce the aromatic stabilization, London susceptibility, and ring current maps in polycyclic aromatic hydrocarbons, PAHs, focusing on polybenzenoids. Starting from a wave function ansatz, constructed as a superposition of Kekulé valence bond structures, the conjugated circuit resonance energy is derived using the second quantization formulation. Approximated expressions for the resonance energy, London susceptibility, and ring electron current intensity have been obtained. In these expressions, the benzene molecule is employed as a reference for the calculation in a graph theoretical fashion of properties in larger polybenzenoids. Comparison of the results obtained with conjugated circuits with those obtained using more accurate quantum chemical methods reflects the power of the conjugated circuit concept as a quantitative tool for the study of magnetic properties in PAHs. Besides the usefulness of this methodology for understanding and interpreting both the aromatic stabilization and the magnetic behavior of small and medium size PAHs, it provides a straightforward alternative way for the computation of these properties in giant PAHs for which ab initio calculations are not applicable.

1. Introduction

As defined by Randić in its essential review¹ on the application of the chemical graph theory to the study of polycyclic aromatic hydrocarbons, PAHs, conjugated circuits are those circuits within an individual Kekulé valence structure in which there is a regular alternation of both CC double and single bonds. This simple concept has been employed independently by Randić^{2–4} and Gomes and Mallion⁵ to develop the conjugated circuits model, CCM. The CCM performs a partitioning of the resonance energy, RE, of a PAH into local ring terms. Therefore, it allows interpreting the total aromatic stabilization of a given PAH in terms of ring contributions.¹

A quantum chemical justification of the CCM is obtained from the valence bond theory, if one restricts the large number of valence structures present in a polycyclic conjugated hydrocarbon to the Kékule structures. This idea was first coined by Simpson⁶ and subsequently employed by Herndon^{7,8} more than 30 years ago to calculate the resonance

energies in PAHs from empirical quantities. On the other hand, Klein and Trinajstić⁹ outlined a quantum chemical derivation of the conjugated circuits model through the Pauling–Wheland resonance theory.¹⁰ As remarked by Randić,¹ this connection between the CCM and the quantum chemical theory is crucial because it has provided the model with a more quantitative character and a theoretical foundation.

In spite of the huge number of published articles employing conjugated circuits,¹¹ its scope as a quantitative chemical tool for studying the properties of PAHs is still to be exploited in its entirety. For instance, although some qualitative relations between conjugated circuits and ring current maps were pointed out some time ago by Randić,¹² the conjugated circuits have never been employed, neither for calculating magnetic susceptibilities nor for constructing ring current maps.

Alternatively other graph theoretical approaches have been developed to determine the London susceptibility,¹³ i.e., the magnetic susceptibility due to induced ring electron currents. The efforts of Aihara in this direction deserve special mention. He was able to connect the aromatic stabilization

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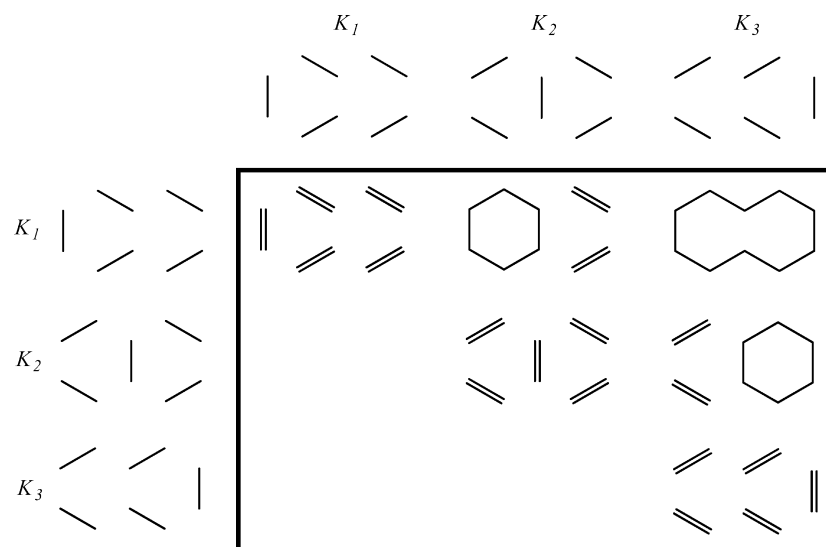


Figure 1. Superposition diagrams for the Kekulé structures of naphthalene.

with the diamagnetic susceptibility exaltation^{14–17} and the induced ring electron current¹⁸ in polycyclic conjugated systems through the extended Hückel–London theory of diamagnetism and the definition of the topological resonance energy.^{19,20} His works first demonstrated that the magnetic and energetic criteria of aromaticity are indeed interrelated,^{21,22} showing that the London susceptibility of a PAH is the result of the superposition of individual ring circuit contributions. However, the application of the Aihara’s methodology to compute individual and total London susceptibilities requires the calculation of the circuit resonance energies,²³ which is restricted to the Hückel molecular orbital theory^{24,25} and can become unmanageable for the case of giant PAHs.

On the contrary, because of its simplicity and intuitiveness, the conjugated circuits model can be considered the most powerful graph theoretical tool for the study of the aromatic stabilization in PAHs. In addition, it can provide more accurate results, with no limit for the system size, than those obtained by other topological approaches, since it can be applied in combination with more accurate quantum chemical methods. In this paper, we extend the application of conjugated circuits to the calculation of London susceptibilities and ring current intensities. In the following section, Section 2, the conjugated circuit resonance energy is derived using an operator formalism developed in the context of the second quantization, in order to lend the necessary theoretical foundation to the method. Then, the expressions for the London susceptibility and the ring current intensity are obtained. Comparison of the results with those obtained using more accurate quantum chemical methods is performed in Section 3. Finally, the main conclusions are formulated in the last section, Section 4.

2. Background and Theoretical Development

Conjugated Circuit Resonance Energy. In this section, the conjugated circuit resonance energy is obtained using a formulation based on creation and annihilation operators. Using this formulation, the Kekulé valence bond structures and a series of operators associated to the conjugated circuits

can be represented explicitly. Our derivation starts with the same wave function ansatz as that proposed by Herndon,⁸ where the normalized ground-state wave function (eq 1) is expressed by a linear combination of equally weighted normalized functions, each corresponding to a Kekulé structure:

$$|\Psi\rangle = \frac{1}{\sqrt{n_K}} \sum_{i=1}^{n_K} |K_i\rangle \quad (1)$$

where n_K is the total number of Kekulé structures. The expectation value of the energy for a given PAH is then obtained from eq 2:

$$E = \frac{1}{n_K} \sum_{i=1}^{n_K} \sum_{j=1}^{n_K} \langle K_i | \hat{H} | K_j \rangle \quad (2)$$

The different contributions to the energy that are implicit in eq 2 can be viewed straightforwardly using the superposition diagrams of Kekulé structures. The superposition diagrams for the Kekulé structures of naphthalene are shown in Figure 1. As can be seen, the superposition of a Kekulé structure with itself results in a set of localized bonds, whereas the superposition of two different Kekulé structures results in a sum of localized bonds and cyclic delocalized structures. These cyclic delocalized structures result from the superposition of a conjugated circuit L with its counterpart L' , which only differ in the arranging of the alternant bonds. One can represent the energy contribution of a cyclic delocalized structure by introducing appropriate operators into eq 2. In order to shape such operators, it is useful to employ the second quantization formulation of the valence bond theory.²⁶ So, the kets $|K_i\rangle$ in eq 1 can be represented in second quantization by

$$|\Psi\rangle = \frac{1}{\sqrt{n_K}} \sum_{i=1}^{n_K} \hat{K}_i^+ |0\rangle \quad (3)$$

$$\hat{K}_i^+ = \prod_{n=1}^{N_{e/2}} \Delta_{KL(i,n)}^{\alpha\beta+} \quad (4)$$

where each operator $\Delta_{KL}^{\alpha\beta+}$ acts on the vacuum state $|0\rangle$ by creating an electron pair in the bond formed by atomic orbitals K and L; this operator is in turn an antisymmetrized product of two particle creation operators:²⁶

$$\Delta_{KL}^{\alpha\beta+} = a_{K\alpha}^+ a_{L\beta}^+ - a_{K\beta}^+ a_{L\alpha}^+ \quad (5)$$

where the subindex α or β indicates the electron has spin alpha or beta, respectively. The set of KL atomic orbitals necessary to construct the operator \hat{K}_i^+ depends on each Kekulé structure, but its number is always equal to $N_e/2$, N_e being the number of π electrons. The nomenclature introduced in eq 4 to denote each pair of atomic orbitals KL employs two subindices, i to indicate that the bond is associated to the Kekulé structure i , and n to distinguish between different bonds associated to the same Kekulé structure, so that two sets of different subindices (i, n) may refer to the same pair of atomic orbitals provided that these subindices are defined for different Kekulé structures.

The application of the set of \hat{K}_i^+ operators of a given PAH on the vacuum state $|0\rangle$ generates the kets $|K_i\rangle$ that represents the Kekulé structures of the system. Therefore, they will be called Kekulé operators from now on. In addition, the bra $\langle K_i|$ can be generated through the adjoint of \hat{K}_i^+ , \hat{K}_i ,

$$\langle \Psi| = \frac{1}{\sqrt{n_K}} \sum_{i=1}^{n_K} \langle 0|\hat{K}_i \quad (5a)$$

$$\hat{K}_i = \prod_{n=1}^{N_{e/2}} \Delta_{KL(i,n)}^{\alpha\beta} \quad (6)$$

where each operator $\Delta_{KL}^{\alpha\beta}$ acts on the vacuum state $\langle 0|$ by creating an electron pair in the bond formed by atomic orbitals K and L, this operator is in turn an antisymmetrized product of two particle annihilation operators.

$$\Delta_{KL}^{\alpha\beta} = a_{K\alpha} a_{L\beta} - a_{K\beta} a_{L\alpha} \quad (7)$$

At this point it is useful to introduce some properties of $\Delta_{KL}^{\alpha\beta+}$ and $\Delta_{KL}^{\alpha\beta}$, which can be deduced straightforwardly from the well-known anticommutation properties of the particle creation and annihilation operators.²⁷

$$(i) \quad \Delta_{KL}^{\alpha\beta+} \Delta_{MN}^{\alpha\beta+} = \Delta_{MN}^{\alpha\beta+} \Delta_{KL}^{\alpha\beta+}, \quad \Delta_{KL}^{\alpha\beta} \Delta_{MN}^{\alpha\beta} = \Delta_{MN}^{\alpha\beta} \Delta_{KL}^{\alpha\beta}$$

$$(ii) \quad \Delta_{KL}^{\alpha\beta} \Delta_{KM}^{\alpha\beta+} |0\rangle = 0, \quad \Delta_{KL}^{\alpha\beta} \Delta_{MN}^{\alpha\beta+} |0\rangle = 0$$

From property (i) it can be stated that, contrary to the particle creation/annihilation operators, interchange of two $\Delta_{KL}^{\alpha\beta+}$ or $\Delta_{KL}^{\alpha\beta}$ operators does not have any effect on the sign of $|K_i\rangle$ or $\langle K_i|$, respectively. Therefore, the energy of the system can be written as in eq 8 independently of the order in which the operators $\Delta_{KL(j,n)}^{\alpha\beta+}$ or $\Delta_{KL(i,n)}^{\alpha\beta}$ have been introduced for the construction of the Kekulé operators \hat{K}_j^+ or \hat{K}_i .

$$E = \frac{1}{n_K} \sum_{i=1}^{n_K} \sum_{j=1}^{n_K} \langle 0|\hat{K}_i \hat{H} \hat{K}_j^+ |0\rangle \quad (8)$$

The transformation of a Kekulé structure into one of its conjugated circuits and vice versa can be also represented using $\Delta_{KL}^{\alpha\beta+}$ and $\Delta_{KL}^{\alpha\beta}$ operators. Thus, we define the operator \hat{C}_L associated to the circuit L as the product of the $\Delta_{KL}^{\alpha\beta}$ operators required to reduce the ket $|K_i\rangle$ to the conjugated circuit L , which can be represented by the ket $|L\rangle$ or $|L'\rangle$ for its counterpart, and \hat{C}_L^+ as its adjoint. Obviously, the number of $\Delta_{KL}^{\alpha\beta}$ operators forming \hat{C}_L depends on the conjugated circuit size and the number of π electrons, N_e . Moreover, a conjugated circuit L can have several operators \hat{C}_L associated. This fact is illustrated in Figure 2 for one of the conjugated circuits of phenantrene.

The energy contribution from the superposition of a conjugated circuit L and its counterpart L' can then be obtained from eq 8 by introducing properly the operators associated to L . Taking into account that the product of a Kekulé structure by itself represents only contributions from localized bonds, the energy contribution due to electron conjugation in the circuit L comes exclusively from the crossed products of K_i and K_j structures and then can be written as in eq 9:

$$E_L = \frac{2}{n_K} \sum_{p=1}^{N_L} \sum_{i=1}^{n_K-1} \sum_{j>i}^{n_K} \langle 0|\hat{K}_i \hat{C}_{L_p}^+ \hat{H} \hat{C}_{L_p} \hat{K}_j^+ |0\rangle \quad (9)$$

where the first summation runs over all the operators associated to the conjugated circuit L , the number of operators associated to L is denoted by N_L .

Application of property (ii) reduces drastically the number of non-null terms in eq 9. Thus, if the \hat{C}_{L_p} operator tries to remove a bond electron pair, which does not exist in \hat{K}_j^+ , the result of applying \hat{C}_{L_p} is zero, the same applies to $\hat{C}_{L_p}^+$ and \hat{K}_i operators. Then, two conditions must be satisfied for a term to be non-null: (1) the operator \hat{C}_{L_p} must contain only bond electron pairs that appear in \hat{K}_j^+ and (2) \hat{K}_i and \hat{K}_j^+ must differ only in the arranging of the bond electron pairs within the conjugated circuit L . It is straightforward to show that counting the number of terms satisfying conditions (1) and (2) is equal to counting the number of L conjugated circuits, n_L (after taking into account the multiplicative factor 2 in eq 9). Equation 9 then transforms into eq 10:

$$E_L = \frac{1}{2} \frac{n_L}{n_K} [\langle L'|\hat{H}|L\rangle + \langle L|\hat{H}|L'\rangle] = \frac{n_L}{n_K} \langle L'|\hat{H}|L\rangle \quad (10)$$

which represents the stabilization energy due, exclusively, to the electron conjugation within the circuit L . In order to simplify the expressions, we will employ an abbreviated notation for the integrals $\langle L'|\hat{H}|L\rangle$, that will be denoted by $H_{LL'}$ from now on. The total energy due to cyclic conjugation is then the summation of the contributions of all the conjugated circuits (eq 11):

$$E_{CC} = \sum_{L=1}^{n_C} \frac{n_L}{n_K} H_{LL'} = \sum_{L=1}^{n_C} c_L H_{LL'} \quad (11)$$

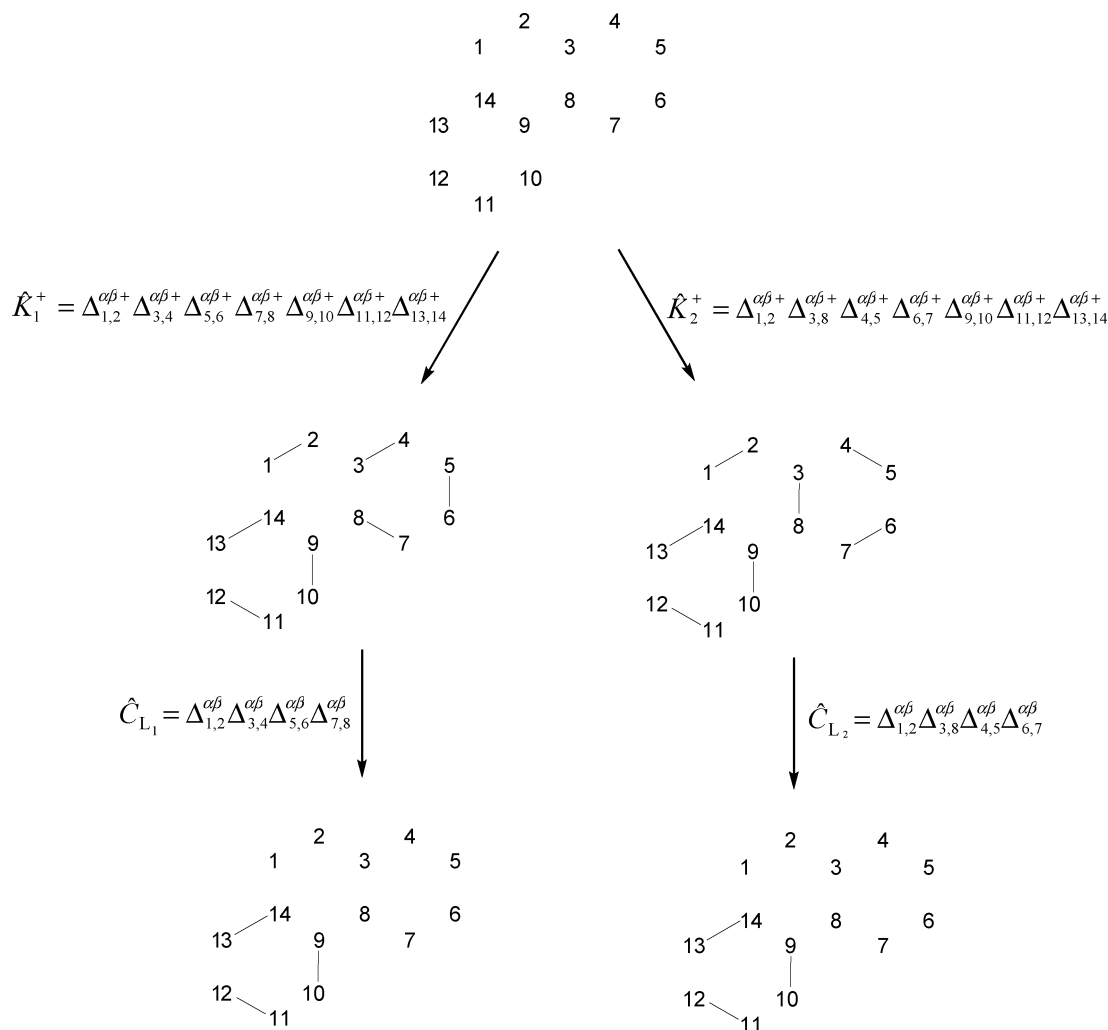


Figure 2. Schematic representation of the effect of some Kekulé operators and conjugated circuit operators of phenantrene.

where n_c is the number of different conjugated structures that results from the superposition of the Kekulé structures. It must be noticed that eq 11 is in fact the conjugated circuit resonance energy in the Randić's model.¹

Diamagnetic Susceptibility and Ring Current Intensity.

It is well-known that the application of a perpendicular magnetic field, H , changes the conjugated circuit resonance energy in a PAH. Obviously, this change affects exclusively the integrals $H_{LL'}$ in eq 11 as the coefficients c_L depend on the number of L conjugated circuits and Kekulé structures, which are not modified by the field. Then, the question that arises is how to account for the effect of a magnetic field over the energy terms $H_{LL'}$ when the field is applied perpendicularly to the molecular plane.

Aihara, in its graph theoretical interpretation of the London theory of diamagnetism, showed that the field-dependent cyclic conjugation energy can be represented by the product of the unperturbed energy with a cosine function of the magnetic field intensity and the area enclosed by the cycle, S_L (see eq 12).¹⁷ Aihara derived this result using the Hückel molecular orbital theory. However, a correct perturbation treatment of the system should provide similar results using both the molecular orbital and valence bond theories. Therefore, we will use the Aihara's result within our valence

bond approach, expressing the field-dependent cyclic conjugation energy by eq 12:

$$E_{CC}(H) = \sum_{L=1}^{n_c} c_L H_{LL'} \cos\left(\frac{2\pi e}{hc} S_L H\right) \quad (12)$$

In the limit of zero magnetic field, the cosine function can be expanded as a Taylor series of H :

$$E_{CC}(H) = \sum_{L=1}^{n_c} c_L H_{LL'} \left(1 - \frac{4\pi^2 e^2}{h^2 c^2} S_L^2 H^2\right) \quad (13)$$

Taking into account that the diamagnetic susceptibility is the second derivative of the energy with respect to the magnetic field, one arrives to eq 14 for the London susceptibility:

$$\chi_d = -\frac{4\pi^2 e^2}{h^2 c^2} \sum_{L=1}^{n_c} c_L H_{LL'} S_L^2 \quad (14)$$

Using the London susceptibility of benzene as reference, eq 14 turns into eq 15:

$$\chi_d = \chi_{d,0} \sum_{L=1}^{n_c} c_L \frac{H_{LL'} S_L^2}{H_0 S_0^2} \quad (15)$$

where the reference values are denoted by the subindex 0. The contribution of a circuit L is then represented by eq 16:

$$\chi_{d,L} = \chi_{d,0} c_L \frac{H_{LL'} S_L^2}{H_0 S_0^2} \quad (16)$$

A further simplification can be done for polybenzenoids, if one considers that the area enclosed by the benzene rings is approximately the same as that of the isolated benzene molecule. Thus, the quotient of ring areas can be replaced by the number of benzene rings enclosed by the circuit L , f_L .

$$\chi_{d,L} = \chi_{d,0} c_L \frac{H_{LL'} f_L^2}{H_0} \quad (17)$$

The induced electron current intensity per magnetic field unit at the circuit L (eq 18) can be obtained using the well-known relation between the current intensity and the diamagnetic susceptibility (eq 19):²⁸

$$I_L = I_0 c_L \frac{H_{LL'}}{H_0} f_L \quad (18)$$

$$\chi_d H = IS \quad (19)$$

3. Results and Discussion

The problem with the application of eq 11 is the determination of the terms $H_{LL'}$. By definition, H_0 is the resonance energy of benzene, and then it can be straightforwardly obtained using, for instance, the method of Dewar.²⁹ However, the calculation of $H_{LL'}$ in polycyclic circuits is not so clear. Within the CCM of Randić, the summation in eq 11 is truncated to circuits containing up to three benzene rings, and then the parameters, called R_1 , R_2 and R_3 , are calculated via multivariate linear regression using a set of previously computed resonance energies. Values of R_1 , R_2 and R_3 can be looked up in reference¹ and compared among different linear regressions obtained using one (R_1), two (R_1 and R_2), and three (R_1 , R_2 and R_3) parameters. Comparison of the R_1 , R_2 and R_3 values allows concluding that the resonance integrals $H_{LL'}$ decrease proportionally to the circuit size, suggesting that eq 11 may be reformulated in terms of the circuit size. Such reformulation of eq 11 can be done using either the number of rings or the number of centers. We have performed an initial test by using eq 20 as an approximation and also replacing the number of rings, f_L , by the number of centers composing the circuit. In both cases, the results have given rise to similar numerical correlations, although for the calculation of magnetic susceptibilities f_L has provided slightly better results. Thus, we will discuss only the results obtained using the number of rings as a measure of the circuit size:

$$E_{CC} \approx \sum_{L=1}^{n_c} c_L \frac{H_0}{f_L^b} \quad (20)$$

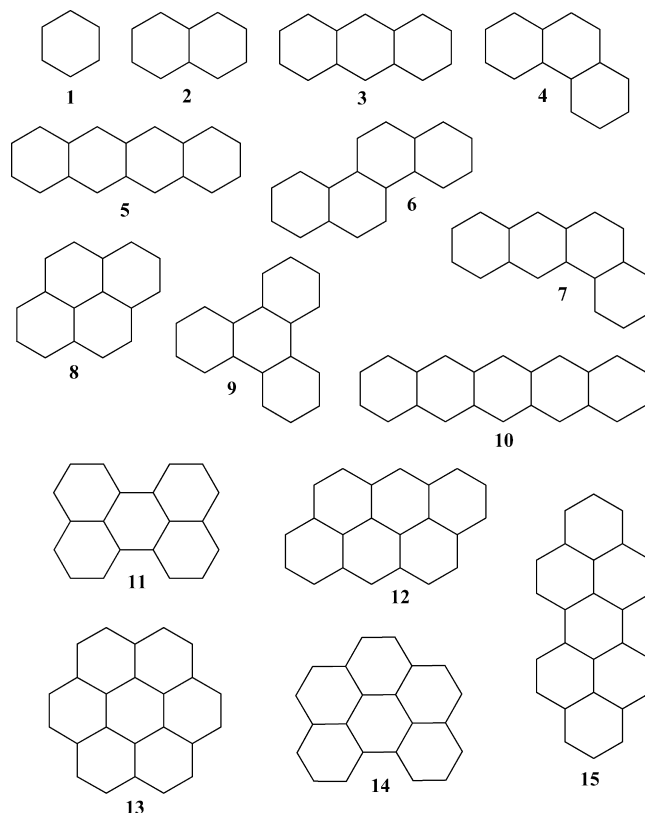


Figure 3. Set of PAHs studied.

Table 1. Dewar and Conjugated Circuits Resonance Energies

molecule	E_{CC}	E_{CC}^a	DRE ^b	diff ^c
1	0.869	0.869	0.869	0.000
2	1.304	1.304	1.323	-0.020
3	1.569	1.600	1.600	0.000
4	1.950	1.950	1.933	0.017
5	1.750	1.814	1.822	-0.008
6	2.506	2.506	2.483	0.023
7	2.305	2.323	2.291	0.032
8	2.110	2.110	2.098	0.012
9	2.732	2.732	2.654	0.078
10	1.882	1.975	2.004	-0.029
11	2.607	2.607	2.619	-0.012
12	2.621	2.646	2.650	-0.004
13	3.591	3.591	3.524	0.067
14	3.146	3.146	3.128	0.003
15	3.402	3.416	—	—

^a Including parameter a . ^b Values taken from ref 29. ^c Difference between values listed in the third and fourth columns.

In eq 20, the energy terms $H_{LL'}$ are replaced by the quotient of H_0 and the number of benzene rings of the circuit L , f_L , powered to a parameter, b , whose optimal value can be obtained by statistical regression. Using eq 20, the number of parameters employed reduces to just one since H_0 can be taken as the resonance energy of benzene, truncation to one- and two- and three-ring terms is not necessary for the statistical treatment. We have employed eq 20 to reproduce the Dewar resonance energies, DRE, for the series of fifteen PAHs depicted in figure 3. The estimated values are highly close to the correct values when $b = 2$ (see Table 1), the very good linear correlation is reflected on the following statistical parameters: $r = 0.998$, $s = 0.046$, and $F = 2\,987$. However, a look in more detail to the results reveals that resonance

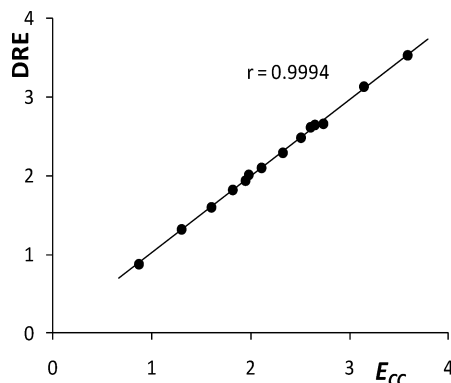


Figure 4. E_{CC} vs DRE for the series of PAHs depicted in Figure 2.

energies of linear polyacenes are slightly underestimated using eq 20, being more significant with the size of the molecule. This indicates that linear polyacenes display specific behavior, which becomes more noticeable in the calculation of magnetic susceptibilities due to the large circuit size dependence of this magnitude.

The main problem of eq 20 is that it does not distinguish between linear and nonlinear circuits. For instance, eq 20 considers that anthracene and phenanthrene, like circuits, have the same $H_{LL'}$ value, but it is known that the contributions to the resonance energy of these circuits is slightly different,⁹ being larger in the case of the anthracene circuits. Equation 20 is not able to compensate for these differences in the case of linear polyacenes, where all circuits are linear circuits. Therefore, we have introduced a new parameter in eq 20, which is allowed to adopt different values for nonlinear circuits and linear circuits containing three or more benzene rings.

$$E_{CC} \approx \sum_{L=1}^{n_C} c_L \frac{H_0}{(af_L)^b} \quad (21)$$

This new parameter, a , provides more flexibility to the initial expression. Our numerical test has proven that more sophisticated expressions including more parameters are not necessary for obtaining accurate results, both in the case of resonance energies and magnetic susceptibilities. Thus, the best linear fitting between the calculated and estimated values of DRE has been obtained for $b = 2$ and $a = 1$ (nonlinear circuits) and $a = 0.78$ (linear circuits). The perfect correlation obtained is shown in figure 4 with the following statistical parameters: $r = 0.9994$, $s = 0.025$ and $F = 10\,083$. Moreover, as can be seen in Table 1, the largest difference between calculated and estimated values is 0.078, which corresponds to an error lower than 3%.

In light of these results, it can be glimpsed that behind the eqs 20 and 21 there must be a theoretical foundation besides a good statistical correlation. According to them, the aromatic stabilization of a polybenzenoid is a function of the aromatic stabilization of benzene, an idea that was first coined and qualitatively verified by Clar.^{30,31} The connection between the aromatic stabilization of both benzene and polybenzenoid is clear in eq 20, the latter depending on the molecular size and the number and shape of the Kekulé structures.

Table 2. Magnetic Susceptibilities, Relative to Benzene, For the Set of PAHs Drawn in Figure 1 Estimated Using Conjugated Circuits, Calculated with the London–Hückel Theory and Calculated with The GIAO Method at the B3LYP/6-31G(d,p) Level

molecule	χ_{CC}	χ_{CC}^a	χ_{Lon}^b	χ_{\perp}
1	1.00	1.00	1.00	1.00
2	2.00	2.00	2.22	1.83
3	3.00	3.32	3.53	2.67
4	3.20	3.20	3.31	2.55
5	4.00	4.77	4.88	3.53
6	4.50	4.50	4.61	3.34
7	4.29	4.47	—	3.33
8	4.44	4.44	4.70	3.26
9	4.33	4.33	4.33	3.13
10	5.00	6.29	6.26	4.40
11	4.00	4.00	4.17	3.10
12	6.20	6.46	—	4.41
13	10.20	10.20	10.13	5.94
14	6.71	6.71	—	4.69
15	9.00	9.14	—	5.52

^a Including parameter a . ^b Values taken from ref 32.

From eq 21 and substituting the optimal value of b , $\chi_{d,L}$, and I_L can also be expressed in terms of the coefficient c_L and the number of benzene rings f_L , using benzene as reference.

$$\chi_{d,L} \approx c_L \frac{\chi_{d,0}}{a^2} \quad (22)$$

$$I_L \approx \frac{c_L I_0}{f_L a^2} \quad (23)$$

It is interesting to go over the shape of eq 22. According to it, the contribution of a circuit L to the London susceptibility is just given by the quotient between the number of L conjugated circuits and the number of Kekulé structures, only in the case of linear circuits it must be corrected with the factor a^2 . Therefore, the London susceptibility can be estimated for any polybenzenoid by counting its Kekulé structures and conjugated circuits. The ring codes in the Randić's model¹ appear to be a measure of the circuit contributions to the London susceptibility.

The total London susceptibility results from the summation of all the circuit contributions. In table 2 the values of the magnetic susceptibility calculated using conjugated circuits (with and without the correction parameter a), the Hückel–London theory³² and the GIAO method³³ (at the B3LYP/6-31G(d) level) are collected for the series of PAHs depicted in Figure 3. For the latter, only the component perpendicular to the molecular plane is shown. The magnetic susceptibilities obtained from conjugated circuits are very similar to those calculated with the Hückel–London theory. Only if the correction parameter a is not included, the linear polyacenes display specific behavior with significant deviations in the case of molecules 5 and 10. This is completely solved with the inclusion of a , as one can see in Figure 5a, the London diamagnetic susceptibilities and the diamagnetic susceptibilities calculated from conjugated circuits display a perfect linear correlation with the following statistical parameters: $r = 0.9991$, $s = 0.115$, and $F = 4\,034$. On the other hand,

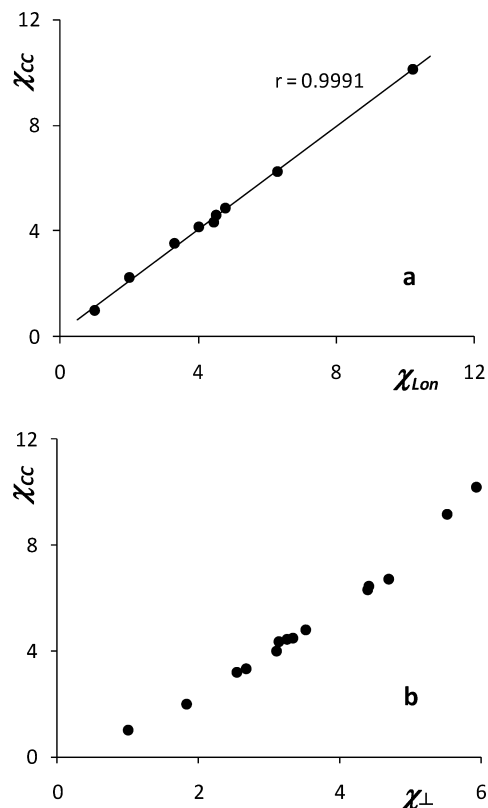


Figure 5. Plots of the magnetic susceptibility estimated using conjugated circuits versus the London diamagnetic susceptibility (a) and the magnetic susceptibility calculated using the GIAO method (b) (only the component perpendicular to the molecular plane).

the comparison with the magnetic susceptibilities calculated with the GIAO method reflects also a good correlation, although in this case, the best fitting equation corresponds to a second-order polynomial instead of a straight line (see Figure 5b). Although magnetic susceptibilities calculated at ab initio level contain also local and paramagnetic contributions, its correlation with the values obtained from conjugated circuits is quite good.

The total induced current intensity I circulating by a given PAH results from the superposition of the individual I_L values. By superimposing the corresponding I_L values calculated using eq 23, we have reconstructed the ring current maps of 14 PAHs (see Figure 6). This set of PAHs comprises a wide range of examples of quite different behavior, which is necessary in order to get a rigorous test of the model and their eventual deficiencies. Moreover, the reader can compare the ring current maps obtained from conjugated circuits with those computed using the ipsocentric method at ab initio level since the latter have been calculated by Fias et al. in ref 34. As one can see, the pictures obtained from conjugated circuits are remarkably accurate. Not only the relative intensity circulating by different bonds in the individual molecules coincides with those computed with the ipsocentric method, but also the relative intensities among different molecules are in very good agreement. Numerical values for the coefficients c_L as well as the current intensities circulating on each

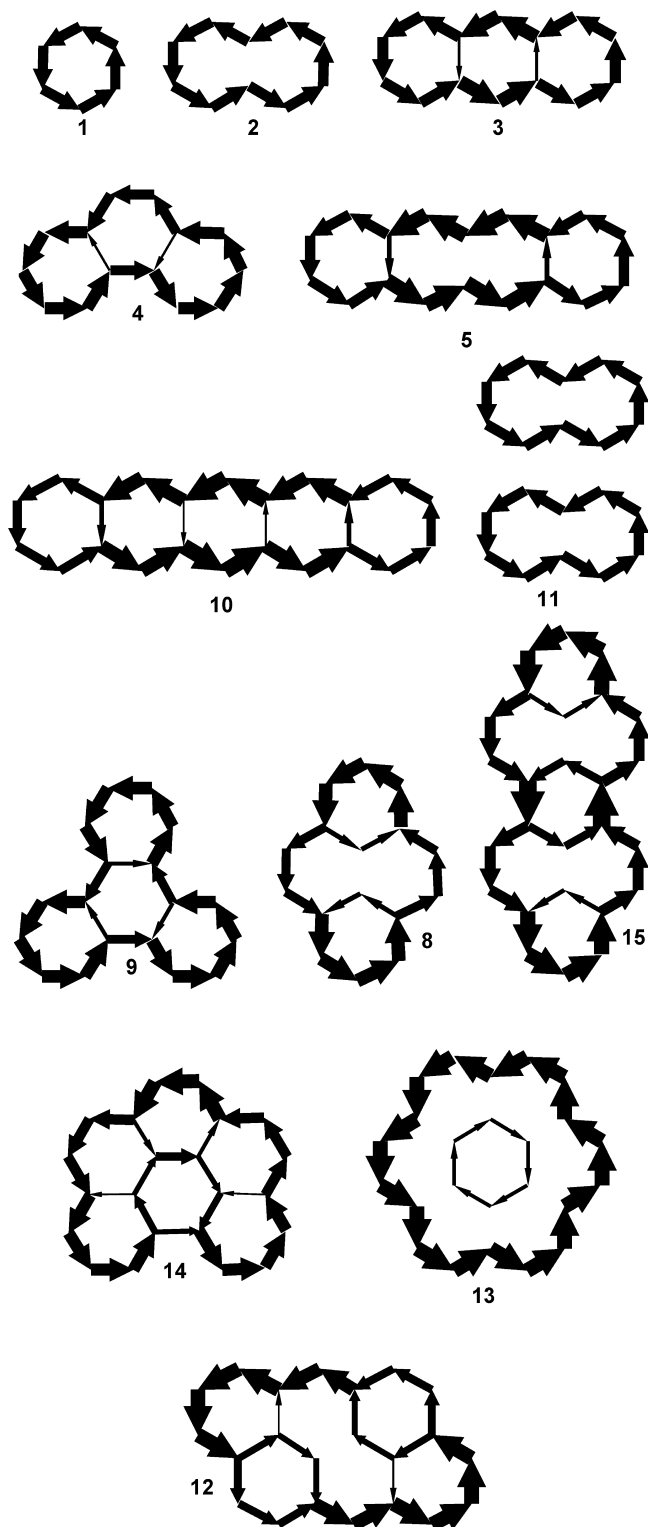


Figure 6. Ring current maps obtained using conjugated circuits.

bond (relative to their values in benzene) can be looked up in the Supporting Information.

We would like to end this discussion pointing out the following statement, which is also an important application. Given that there exist algorithms available for both the counting of the Kekulé structures and conjugated circuits,¹¹ the calculation of the London susceptibility and the construction of the ring current maps can be under-

taken even for giant PAHs where the ab initio calculations are not feasible. Thus, it is possible to get a quantitative picture of the magnetic properties in giant PAHs with no computational cost.

4. Concluding Remarks and Future Prospects

The conjugated circuits resonance energies have been derived using an operator formalism developed in the context of second quantization. Then, expressions for the London susceptibility and the ring current intensity have been obtained. These expressions have been employed to accurately reproduce the aromatic stabilization, London susceptibilities, and ring current maps of a series of polybenzenoids.

The relevance of the conjugated circuit concept is reflected on the accuracy with that quantum chemical results are reproduced, providing quantitative information not only about the aromatic stabilization of a PAH but also about its magnetic behavior. This methodology can be applied on both small and medium size PAHs in combination with more accurate ab initio methods, providing a local interpretation of the results, but it can also be applied on giant PAHs to get accurate pictures of their magnetic behaviors when ab initio calculations are not applicable.

Calculations only require the previous knowledge of the resonance energy of benzene by any of the methods available, and then the remaining properties are obtained for larger polybenzenoids with no computational cost. The next step is to generalize the method for other PAHs containing five-center and four-center conjugated rings by introducing some additional parameters.

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Supporting Information Available: Graphs representing the conjugated circuits, c_L values, and current intensities circulating through the bonds relative to benzene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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