Theory for a General System of Increments for the Properties of Polycyclic Hydrocarbons [1]

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A general non-empirical system of increments for the calculation of molecular properties of polycyclic, conjugated hydrocarbons is proposed. It is based on identifying the conjugation circuits in all Kekulé structures and assuming an increment from each circuit comparable to the magnitude of the property in the associated annulene. These increments are calculated by a simple free-electron theory with a Kuhn-type harmonic potential. No adjustable parameters are used to fit the property being calculated.

The relation between this method and a very simplistic VB formalism is considered. The reason why the non-empirical parametrization of such crudely approximated formalism may lead to rather improved results is discussed in some detail.

This novel system of increments is tested for two properties, resonance energy and magnetic ring-currents. The results obtained by this method correlate well with those of standard techniques. This system of increments for estimating local properties of molecules gave particularly gratifying results when used to predict ring-current intensities. It is hoped that this method, being equally applicable to other properties, will prove to be a valuable instrument for the rapid estimation of a wide range of properties of polycyclic, conjugated hydrocarbons.

Key words: System of increments – Magnetic ring currents – Resonance energies – Conjugated hydrocarbons – Graph theory – Local properties.

1. Introduction

One of the long term goals of theoretical chemists has been the understanding of the properties of molecules in terms of the nature of the atoms which integrate

them and of the way they are bonded in a chemical sense. It is widely recognized that chemical properties of most molecules are primarily local properties of chemical bonds and/or functional groups. Nevertheless conventional methods in quantum chemistry are designed to produce state-functions extending over an entire molecule. Molecular properties are therefore made to depend on the electron distribution over the whole molecule in an indiscriminate manner. In recent years, however, there has been some progress towards solving this problem. Mazziotti, Parr and Simons [2] and Bader and coworkers [3–6] have shown how a molecule may be partitioned into regions which are quantum mechanically separated from their environment. Payne [7] has recently proposed a Hartree–Fock Theory for local regions in molecules where local orbitals are variationally determined within a subset of basis functions.

Polycyclic, conjugated hydrocarbons present special difficulties as it has been known for a long time that any approach to molecular properties that involves atomic and bond increments gives unacceptable results when applied to this class of molecules. In the case of magnetic susceptibilities, for example, Pascal's [8–10] system of atomic and bond contributions needs certain extra terms relating to the different types of rings before it may be usefully applied to polycyclic, conjugated hydrocarbons.

In this paper we shall discuss several ways of analyzing the contributions from the different rings in a polycyclic, conjugated hydrocarbon and shall consider two properties, delocalization energy and magnetic susceptibility. The questions to be answered are what rings should be considered and what contribution to the molecular property should be associated with those rings.

Any analysis of the cycles or circuits in a polycyclic molecule is manifestly topological and as such may be tackled by the techniques of graph theory. However very useful in providing a reduction of the description of a large polycyclic molecule to some simple features, graph theory does not give an immediate physical understanding. The calculation of molecular properties within a graph-theoretical formalism does normally ask for some sort of fitting to a given set of data. A considerable amount of work has been dedicated to pursuing this line of thought. The adjacency matrix $A(G)$ associated with the molecular graph G is defined in the usual way [11], and its characteristic polynomial, $P(G; x)$ is

$$P(G; x) = \det (x\mathbf{I} - \mathbf{A}) = \sum_{j=0}^{N} a_j(G)x^{N-j}$$

where $\mathbf{I}$ is the unit matrix and $a_j(G)$ the coefficients of the polynomial $P(G; x)$. The coefficients $a_j(G)$ may be computed by Sachs' theorem [12, 13]. For this, it is convenient to define subgraphs of G which have no components other than cycles and complete graphs of degree one (○——○), the so called mutation graphs of G [14, 15]. The coefficients $a_j(G)$ are then given by the following expression

$$a_0 = 1$$
$$a_n = \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)}, \qquad n \in [1, N]$$

where the summation extends over all mutation graphs of G with n vertices, $c(s)$ is the number of components of s and $r(s)$ is the number of rings of s.

If odd-membered cycles do not exist or are not considered, the set of mutation graphs S_N corresponds to the Kekulé graphs with conjugation circuits drawn in them [16–18] in all possible ways.

Gutman et al. [19] define a "topological resonance energy" (TRE) as the difference between the HMO (Hückel Molecular–Orbital) π-electron energy of the molecule and that of the acyclic analogue, this being defined as having a characteristic polynomial $P^{ac}(G; x)$ constructed from that associated with the molecule by exclusion of all cyclic terms. The TRE is given by the expression

$$\text{TRE} = \sum_{j=1}^{N} g_j(x_j - x_j^{ac}) \tag{1}$$

where g_j is the occupation number of orbital j and x_j and x_j^{ac} are the zeros of polynomials $P(G; x)$ and $P^{ac}(G; x)$. This TRE may also be given [19] by

$$\text{TRE} = (1/\pi) \int_{-\infty}^{+\infty} \ln \left| \frac{P(G; ix)}{P^{ac}(G; ix)} \right| dx. \tag{2}$$

The ratio P/P^{ac} depends fundamentally on the rings (conjugation circuits) which appear in P but are excluded in P^{ac}. In fact

$$\frac{P(G; ix)}{P^{ac}(G; ix)} = 1 + \frac{P(G; ix) - P^{ac}(G; ix)}{P^{ac}(G; ix)} = 1 + \frac{P^c(G; ix)}{P^{ac}(G; ix)} \tag{3}$$

where $P^c(G; ix)$ is constructed by Sachs' theorem but considering only terms with rings $(r(s) \neq 0)$. This suggests that conjugation circuits have an effect on the molecular property and that all of them should be considered.

Randić [18, 20] proposed a system of increments for the resonance energies of polycyclic, conjugated hydrocarbons with empirical increments associated with the conjugation circuits considered to be independent in each Kekulé structure. The increments are considered for circuits with an even number of edges, up to 18 edges, by fitting to SCF-calculated resonance energies. This empirical system produces rather good results for the resonance energies, the only molecular property for which it was tested. Earlier, Herndon [21, 22] had proposed a method of estimation of resonance energies which, although introduced in a context related to valence bond (VB) theory, is analogous to that of Randić if one considers contributions from [6]- and [10]-membered rings alone. The role of the VB theory in this problem will be discussed below in detail. It should be noted at this point that, if the counting of conjugation circuits introduced by Randić [18, 20] is understood to be related to a graph-theoretical application in the sense discussed earlier, then it is more closely related to a molecular–orbital theory, the HMO. One should, however, remember the relations between the two formalisms as shown by Dewar and Longuet-Higgins [23] and, more recently, by van der Hart et al. [24] and Haigh and Mallion [25, 26].

Magnetic resonance and NMR chemical-shifts are, unlike resonance energy, properties which depend on the excited states intervening in the magnetically perturbed state-function. In McWeeny's [27] method of calculation of the magnetic ring-currents which proceeds at the HMO-level, a transformation is made in the hamiltonian matrix which makes it clear that the magnetic effect depends on the existence of closed rings in the molecule. The contribution from a ring, however, depends not only on its topology and size but also on the environment in which it is placed, i.e. ring contributions are not transferable from molecule to molecule [28]. The present author [16, 17] has proposed a recipe to estimate ring-currents with a system of increments from all conjugation circuits in all Kekulé structures. The fact that these magnetic properties correlate so well with the conjugation circuits found for these molecules gives a strong indication that such correlations may be quite general, applicable not only to ground-state properties, but also to properties which depend on molecular excited-states.

In a recent article, Gayoso [29] correlated magnetic susceptibility exaltations in polycyclic, conjugated hydrocarbons to the conjugation circuits found for the molecule by the methods of Randić [18, 20]. Increments were chosen so as to reproduce the known exaltations, Λ, in benzene, naphthalene, anthracene, tetracene and pentacene; for the 19 molecules tested, the mean of the ratio $|(\Lambda_{calc.} - \Lambda_{exp.})/\Lambda_{exp.}|$ is 0.12. This confirms that magnetic properties may be correlated with the conjugation circuits associated with the molecule. Aihara applied graph-theoretical methods to relate the magnetic susceptibility to the conjugative stabilization [30, 31].

This paper addresses the problem of designing a non-empirical system of increments for the properties of polycyclic, conjugated hydrocarbons, of general applicability and with a reasonable quantum mechanical backing. It is found that the conjugation circuits provide the basic units over which the molecular property is additive. The increment from a conjugation circuit of given size is independent of the molecule it belongs to.

In Sect. 2, below, VB theory is summarized from the point of view of resonance energy calculations. In Sect. 3, a new version of resonance theory is introduced as a simplified form of VB theory. This resonance theory allows quite accurate calculations on the ground-state of molecules. An extension of this theory is formally considered to allow for the inclusion of ionic contributions without writing explicitly other than the Kekulé structures. A simplification of this formalism suggests a system of increments for the calculation of molecular properties. This system of increments, where all conjugation circuits found in all Kekulé structures are considered, is introduced in Sect. 4 and applied to the calculation of resonance energies. In Sect. 5, the formalism is adapted to the estimation of ring-currents in polycyclic, conjugated hydrocarbons. The conjugation circuits increments are computed systematically using a simple non-empirical free-electron model for the circuit taken in isolation. The calculation of these quantities within the VB-related formalisms which guided the derivation of the method would be more difficult and would normally rely on the use of some empirical parameters. These methods are applied to a large number of polycyclic hydrocarbons and the results are discussed in detail.

2. The Valence Bond Approach

The success of the very simple Kekulé structures in explaining the properties of conjugated hydrocarbons has been embarrassing to theoreticians. A justification for this success has frequently been sought in the mathematical relations that exist between VB and HMO theories [23, 24, 32–36]. However it has been suggested [21] that the results of VB calculations may correlate better with complex SCF-MO methods than with HMO theory. In an attempt to explain the good results obtained with very crude VB-type theories, Simpson [37–40] made a peculiar use of Kekulé structures to understand π-electron spectra. It was assumed that the squares of undefined trial state-functions transformed, under the symmetry operations of the molecule, like the structures; a given set of observed term values arranged along the diagonal of a square matrix was then transformed into a non-diagonal form. The base vectors of this non-diagonal representation are then assumed to be associated with some simple set of structures.

Mainly to appreciate in what way the topological features of the molecule influence the calculated properties, the VB formalism is now briefly reviewed and is applied to a number of molecules.

Consider a basis set formed by the functions associated with the Kekulé structures that can be drawn for the molecule. The ground-state energy is given by the lowest root of secular determinant,

$$|H_{ij} - S_{ij}E| = 0.$$

To calculate the hamiltonian and overlap matrix elements we consider the superposition of structures (i) and (j). By considering only the exchange integrals between neighbouring orbitals and assuming these to be all equal to a quantity α, H_{ij} is easily calculated [41] and may be written in the form

$$H_{ij} = 2^{x-n}\left\{ Q + \tfrac{3}{2}\alpha \sum_{\substack{\text{all} \\ \text{cycles}}} [(\text{number of bonds in cycle}) \right.$$

$$- (\text{number of even kisses in cycle})]$$

$$\left. - \tfrac{1}{2}\alpha(\text{total number of bonds in molecule}) \right\} \tag{4}$$

where x is the number of cycles, counting an isolated island ($\circ\!\!-\!\!\circ$) as a cycle of one side, n is the number of pairs of orbitals in the molecule and Q is the Coulomb integral; we say that an even kiss exists in a (even) cycle when there is a bond between two points in the cycle distant an even number of bonds as, for example, in azulene between a and b.
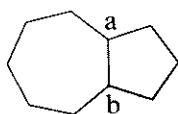
Table 1. Contributions from each cycle to the secular matrix elements

Cycle size, m	4	6	8	10	12	14	16	18	20
Multiplicative, $2^{1-m/2}$	1/2	1/4	1/8	1/16	1/32	1/64	1/128	1/256	1/512
Additive, $\frac{m}{2}$ (in units of $\frac{3}{2}\alpha$)	2	3	4	5	6	7	8	9	10

In the zero-differential-overlap (ZDO) approximation the overlap integral is given by

$$S_{ij} = 2^{x-n} \tag{5}$$

Considering that we are dealing with even hydrocarbons only, the general term of the secular matrix may be put in the form

$$(H_{ij} - ES_{ij}) = 2^{\Sigma_{\text{cycles}}(1-m/2)}\left\{ -E_R + \tfrac{3}{2}\alpha \sum_{\text{cycles}}\left[\frac{m}{2} - (\text{number of even kisses})\right]\right\} \tag{6}$$

where summations extend over all cycles in superimposed structures, m is the number of sides in the cycle, and the resonance energy, E_R, is defined by

$$E_R = E - E_{\text{Kekulé}} \tag{7}$$

with $E_{\text{Kekulé}}$ the energy H_{ii} associated with one Kekulé structure.

The effect of each cycle in the superimposed structures on the terms of the secular matrix amounts to a multiplicative factor of $2^{1-m/2}$ and an additive term (inside the parentheses) of $(m/2)(3\alpha/2)$, this assuming that no even kisses occur; these contributions from each cycle are summarized in Table 1.

Each individual secular matrix element

$$(H_{ij} - ES_{ij}) = E_R X + \tfrac{3}{2}\alpha Y$$

is formed in an obvious way by superimposing the Kekulé structures i and j, identifying all cycles in this superposition and then, making use of Table 1, calculating X by taking the product of the multiplicative factors of all cycles, and evaluating Y by summing the additive factors and correcting if even kisses occur.

Resonance energies calculated by this method for the 12 conjugated hydrocarbons, alternant and non-alternant, in Fig. 1 are presented in Table 2.

Notice that in a VB calculation, as outlined above, all conjugation circuits in all Kekulé structures contribute to the resonance energy and they are counted as they appear in the superposition of the different Kekulé structures.

3. Resonance Theory

A simplified version of the valence bond method described in Sect. 2 may be helpful both in calculating resonance energies without actually having to
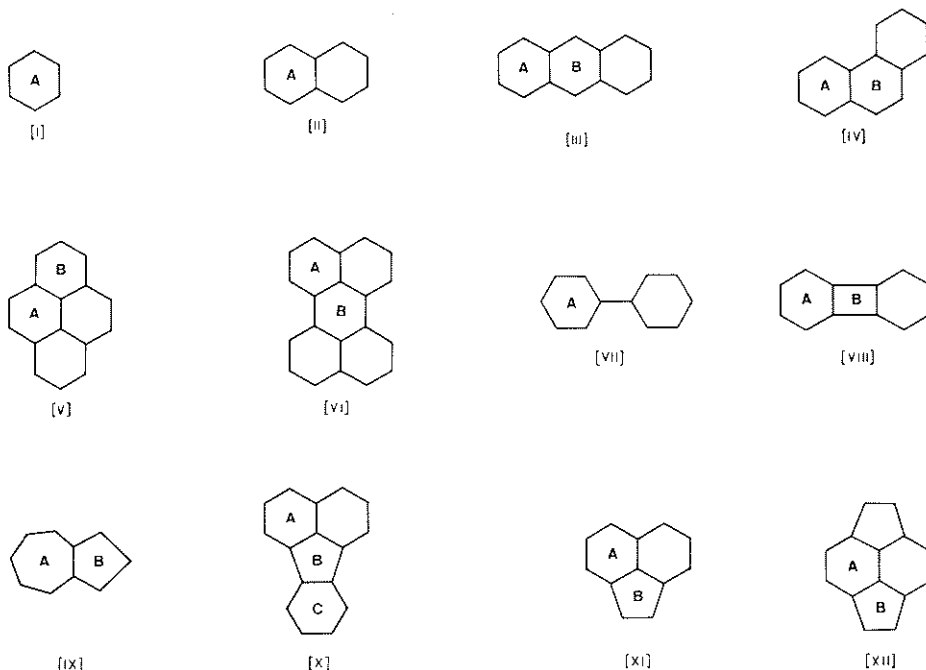
Fig. 1. Molecules (I)–(XII)

diagonalize a secular determinant and in clarifying the role of the cycle contributions to the matrix elements and to the resonance energy.

The resonance energy is obtained from the lowest root of the secular determinant. If we denote by $C_i^{(0)}$ the coefficients of the different Kekulé structures in the ground-state functions, these coefficients satisfy equations

$$\sum_j (H_{ij} - E^{(0)}S_{ij})C_j^{(0)} = 0.$$

The energy $E^{(0)}$ is given by the expression

$$E^{(0)} = \frac{\sum\limits_{ij} C_i^{(0)}H_{ij}C_j^{(0)}}{\sum\limits_{ij} C_i^{(0)}S_{ij}C_j^{(0)}}. \tag{8}$$

Table 2. Resonance energies as calculated by valence bond (VB) and resonance theory (RT), in units of α

Molecule	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
VB	0.90	1.33	1.58	2.00	2.12	2.66	1.80	2.03	0.35	2.23	1.33	1.42
RT	0.90	1.32	1.55	1.96	2.08	2.64	1.80	2.02	0.35	2.22	1.32	1.34

The coefficients $C_i^{(0)}$ of the lowest energy state are normally of similar magnitude. If they are assumed to be all equal, one obtains a much simplified expression

$$E_{RT} = \frac{\sum\limits_{ij} H_{ij}}{\sum\limits_{ij} S_{ij}} \tag{9}$$

which is the fundamental equation in the resonance theory proposed here. To apply this equation one writes down all Kekulé structures for a molecule and makes their mutual superpositions. For each of these superpositions, H_{ij} and S_{ij} are calculated by looking at the cycles generated in them and using Eq. (6), with the help of Table 1.

Results of calculations by resonance theory in twelve molecules of different types (Fig. 1) are listed in Table 2, where they are compared with the results of VB theory as discussed in Sect. 2. The very good quality of the correlation obtained (linear regression correlation coefficient 0.9994) confirms that the hypotheses made in the derivation of Eq. (9) are in general quite well verified.

The only molecule in the series tested for which the results of resonance theory and valence bond calculations diverge by more than 2% is pyracylene(XII), with a deviation of 5%.

The correlation we obtain between VB and RT is so good that some effort ought to be made to understand why this should be so. (i) For systems where only two Kekulé structures may be written as is the case with benzene(I) and azulene(IX), the two methods are exactly equivalent. In fact the two sole Kekulé structures are related by a permutation of the position of double bonds around a single cycle and their coefficients in the ground-state function are equal. This was the assumption made in the derivation of our version of resonance theory. (ii) When a system is formed by two or more non-interacting (at our level of approximation) subsystems, VB theory predicts a resonance energy which is the sum of the resonance energies of the subsystems. It can easily be seen that the proposed RT satisfies this relation. In fact, the hamiltonian of the composite system may be written as a sum of terms refering to the different parts,

$$H = H^a + H^b + \cdots \tag{10}$$

and the state-functions are products of the state-functions for each part,

$$\langle i', j', \ldots | H | i, j, \ldots \rangle = \langle i' | H^a | i \rangle \langle j' | j \rangle \cdots + \langle i' | i \rangle \langle j' | H^b | j \rangle \cdots + \cdots . \tag{11}$$

Using Eqs. (6) and (9) with (11), we get

$$E_{RT} = E_{RT}^a + E_{RT}^b + \cdots , \tag{12}$$

which is the result we sought to confirm.

Perylene(VI), diphenyl(VII) and fluoranthene(X) in Table 2 are molecules which, at our level of approximation, are formed by non-interacting fragments, i.e. no

Kekulé structures can be written linking the two parts of the molecular framework. The results listed in Table 2 do satisfy Eq. (12).

The version of the resonance theory proposed here shows how a ground-state property may be calculated by summing the increments from all cycles that are formed by superposition of pairs of Kekulé structures. The way in which each cycle contributes to the overall property is still rather complex. The increment from a given type of cycle depends on whether it occurs alone in a superposition of Kekulé structures or accompanied by other cycles in different regions of the molecule, according to Eq. (6). The normalization factor used (denominator of Eq. (9)) depends on the total number of Kekulé structures associated with the molecule and on the number and type of cycles formed in the superpositions.

Later in this paper, further simplifications are introduced in the resonance theory discussed above to derive a non-empirical system of increments for the resonance energy, the method being then extended to other properties. The careful reader may raise two points at this stage: (i) How can we hope to get reasonable results by starting with Kekulé structures alone which, even for the ground-state, have been shown in many calculations to have a surprisingly small weight in the wave-function; (ii) even if a mixture of Kekulé structures was to give a good representation of the wavefunction, how can quantitative or semi-quantitative agreement be expected after the crude approximations which are introduced here. Answering these questions will help in clarifying the philosophy of the present approach.

Norbeck and Gallup [42] reported on a set of very interesting VB calculations on benzene where it was found that a symmetry, orthopolar, Kekulé-type function (III* in Ref. 42) has a diagonal energy 0.027 a.u. lower than the Kekulé admixture (I*); also, in the *ab initio* calculation including covalent and orthopolar structures, the occupation number of I* is 0.0440 against 0.6772 for III*. To understand the success of simple theories based upon the consideration of the Kekulé structures, one must note that these give a description of the molecule far more comprehensive than the usually associated VB function suggests. With a particular Kekulé structure one may associate, not only the Kekulé function itself, but also the functions of a number of polar structures.

In this extended interpretation, a Kekulé structure represents an electron pairing scheme and each "bond" $\underset{a}{\circ}\!\!-\!\!\underset{b}{\circ}$ is to be understood as representing a two-electron function; in the usual VB representation, this may be expressed as a
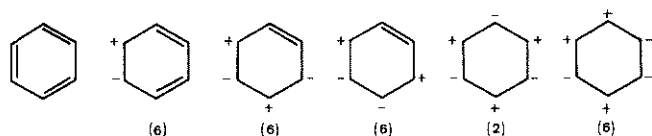

Fig. 2. One Kekulé structure of benzene molecule and the polar structures which may be associated with that same topological representation. (In parentheses, the number of symmetry related structures)

mixture of covalent and ionic terms.

$$\psi_{ab} = (ab + aa + bb)(\alpha\beta - \beta\alpha)/\sqrt{2}.$$

The extended VB theory of van der Hart et al. [24] makes use of this type of two-electron functions.

The VB calculations discussed above were done within the restrict interpretation of the Kekulé structures. The extended interpretation taken now would ask for a far more elaborate computation and, possibly, new approximations. To avoid this, a new approach is taken in the next sections: the VB formalism is used to find a reduced description of the molecule but the actual calculations of the properties are done with an independent model. Concomitantly, Eq. (9) is further simplified by disregarding the overlap integrals $S_{ij}(i \neq j)$ and retaining only certain leading terms H_{ij} in the numerator.

4. Conjugation Circuits System of Increments for the Resonance Energy

The resonance theory developed in the previous section lends itself to a further simplification which will guide us in devising a new and very simple technique for the estimation of properties of polycyclic, conjugated hydrocarbons.

Let us consider the expression for the matrix elements between Kekulé structures (Eq. (6)). The overlap term

$$S_{ij} = 2^{\Sigma_{\text{cycles}}(1-m/2)} \tag{13}$$

decreases quickly when more than one cycle is formed by the superposition of structures (i) and (j). Concomitantly, the magnitude of H_{ij} decreases and hence the weight of a superposition with several cycles in the RT estimate of the resonance energy (Eq. (9)) decreases quickly with the number of cycles.

If all superpositions where more than one cycle is formed are disregarded, we are reduced to considering the so-called "conjugation circuits" in all Kekulé structures. The concept of conjugation circuits was considered by Gomes [16, 17] in the context of the calculation of ring-currents which we discuss below and by Randić [18, 20] in his method of estimating resonance energies. This author works from a purely topological point of view and is therefore led to consider "independent circuits" only. This idea is not corroborated by the derivation currently presented; we conclude, therefore, that all conjugated circuits should be considered.

Very recently, Gutman and Randić [43] discussed their earlier policy of using independent circuits only and came out in favour of using *all* the conjugation circuits as a means of avoiding the arbitrariness of the choice of the independent circuits. This option appears here as a logical consequence of the theory.

Herndon [22, 44] considers certain conjugation circuits as giving the main contributions to the resonance energies. All of these authors make some analysis of the

topology of the molecule to break it down into a set of constituent circuits, the increments from these circuits being determined empirically for a best-fit of the property being calculated.

The order of magnitude of the increment from a given conjugation circuit should be given by the calculated H_{ij}; however, the denominator of Eq. (9) is something larger than the number of Kekulé structures. The present author [16, 17] calculated the increments to the ring-currents (Sect. 5) by a simple free-electron calculation on the conjugation circuit assumed isolated from the rest of the molecule. It was decided to use a similar approach for the resonance energies. Gomes [45] calculated the delocalization energies of annulenes in a free-electron theory with a Kuhn harmonic potential [46] of 2.40 eV; a standard bond length of 140 pm is taken for the annulenes while the bond length of the linear polyenes used for comparison was adjusted for best-fit of experimental excitation energies. The delocalization energies so determined, which we are assuming to give the appropriate increments from the conjugation circuits, are listed in Table 3.

For comparison the increments used by Randić [18, 20] and those estimated in resonance theory for the annulene are also listed. In Fig. 3, the conjugation circuit increments as estimated by the delocalization energies in annulenes and those by Randić are plotted against the VB resonance energy of the annulene estimated according to the theory of Sect. 2.

The delocalization energies of the [4n + 2]annulenes correlate rather well with the VB resonance energies (linear regression correlation coefficient 0.9992) while those of [4n] annulenes do not correlate linearly. The Randić coefficients do not show a linear correlation. Notice that these were determined for the [4n + 2]-circuits by fitting resonance energies of benzene, naphthalene, anthracene and tetracene, and for the [4n]-circuits by simple interpolation in a plot of the [4n + 2] annulenes resonance energies against the size of the circuit.

Application of this system of conjugation circuits increments implies the following steps:

1. Writing all the Kekulé structures for the molecule.

Table 3. Increments to the resonance energy from conjugation circuits in the Kekulé structures (eV)

size of circuit	4	6	8	10	12	14	16	18
this work [a]	−1.182	+0.992	−0.129	+0.423	−0.010	+0.139	−0.061	−0.008
Randić [b]	−1.60	+0.869	−0.45	+0.246	−0.15	+0.100	−0.06	+0.041
Resonance theory [c]	1.00	0.90	0.667	0.441	0.273	0.162	0.093	0.053

[a] Delocalization energies of annulenes [45], assumed to be zero above the [18]annulene.
[b] Fitted to calculated resonance energies [18, 20].
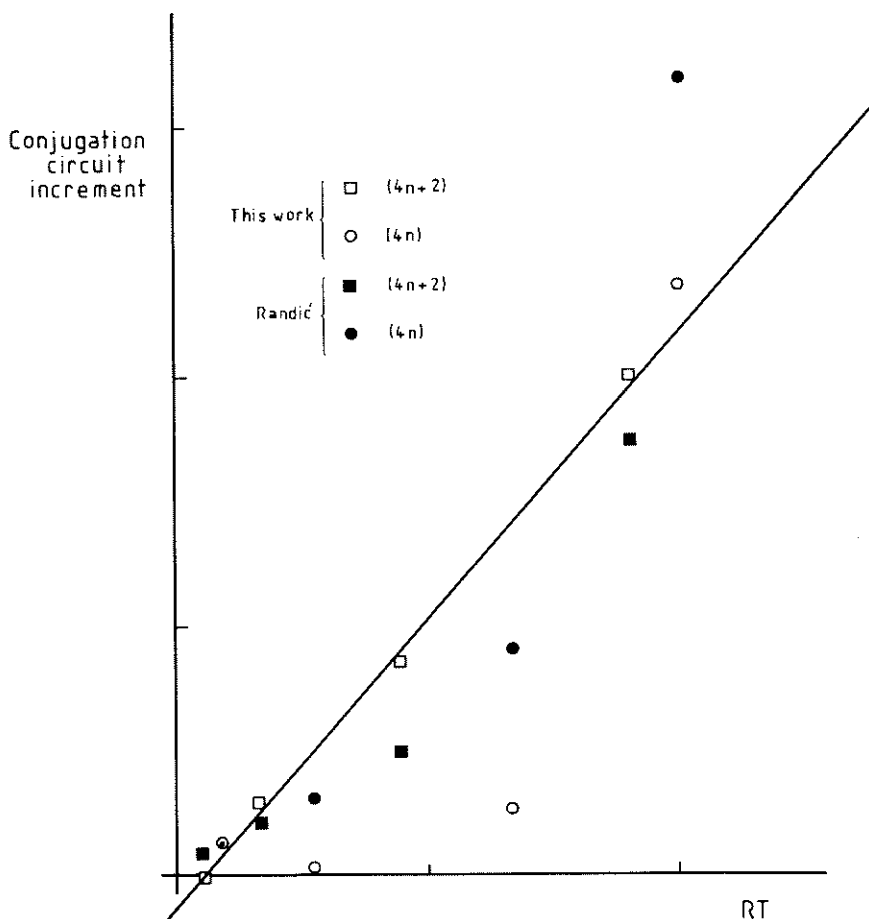[c] Contribution as estimated in resonance theory, $H_{ij}/(1 + S_{ij})$.

Fig. 3. Plot of the conjugation circuit increments as estimated by the delocalization energies of the annulenes [45] and those of Randić [18, 20] vs. the VB resonance energies

2. Identifying all conjugation circuits, i.e. circuits with alternating single and double bonds in each Kekulé structure.
3. Summing the increments from all circuits identified in 2, according to Table 3.
4. Dividing the result by the number of Kekulé structures one gets the final estimate of the resonance energy.

Step 2 may be more easily performed by counting the number of ways in which Kekulé structures may be written for the fragment or fragments obtained when a given circuit and all the bonds from it are suppressed [32].

In Table 4 are listed the conjugation circuits counts for the series of 46 molecules in Figs. 1 and 4 and the resonance energies calculated by use of the increments

in Table 3. For comparison, the estimates of Randić [18, 20] are also quoted, as well as results of elaborate SCF-MO calculations by Dewar and de Llano [47] and by Dasgupta and Dasgupta [48].

The results presented in Table 4 allow two sorts of analysis. On the one hand we may compare the system of increments currently being proposed with that of Randić; on the other hand, we may compare the results directly with those of the SCF-MO calculations.

Comparison of the results now obtained with those of the SCF-MO calculation by Dewar and de Llano [47] may be visualized in Fig. 5 where these results are plotted. A linear regression correlation coefficient of 0.986 is obtained for the 29 points plotted. (Regression line: $-0.138 + 1.267x$.) A similar plot may be drawn for those molecules considered by Dasgupta and Dasgupta [48]. There are slight differences in the methods of calculation which make the two SCF-MO results non-equivalent. For the 17 molecules Dasgupta and Dasgupta dealt with, a linear regression correlation coefficient of 0.890 is obtained with a regression line of equation $0.264 + 1.103x$.

Comparison of the results of the present method with those of Randić [18, 20] can be made for 17 molecules for which SCF-MO results against those of Dewar and de Llano [47] gives rise to a linear regression correlation coefficient of 0.975 while for Randić's results the correlation coefficient is 0.965. We find, therefore, that the current method is marginally better than that of Randić [18, 20] if they are judged by linear regressions against SCF-MO results. The actual deviations from the SCF-MO results may be larger for the method proposed here but this should not be unexpected as we did not introduce any variable fitting parameters.

It should be clear that we are using a simplified form of the resonance theory expounded in Sect. 3 to guide the search for the molecular features to be considered in estimating the property. The increments associated with the conjugation circuits are estimated without reference to the Kekulé structures considered for their identification.

The system of increments devised here is simpler than the resonance theory discussed earlier, but may go beyond it for the reasons discussed at the end of the previous sections. In fact, the new estimates of resonance energies which are presented here (Table 4) compare better with the results of elaborate SCF-MO calculations by Dewar and de Llano [47] than with the resonance theory (Sect. 3). For molecules (I)–(XI), for which results by the three methods are available, the linear regression correlation coefficients are 0.966 between the new estimates and the SCF-MO results [47] and 0.854 between these same estimates and the RT results in Table 2.

5. Conjugation Circuit System of Increments for Magnetic Ring Currents

The method of increments from conjugation circuits derived in Sect. 4 and applied there to the estimation of resonance energies may be used, in principle, to

Table 4. Conjugation circuits and calculated resonance energies for a series of 46 molecules

Molecule	Number of Kekulé structures	Conjugation circuits								Resonance energy (eV)			
		[6]	[10]	[14]	[18]	[4]	[8]	[12]	[16]	This work	Randić [18, 20]	Dewar and de Llano [47]	Dasgupta and Dasgupta [48]
I	2	2								0.992	0.869	0.869	
II	3	4	2							1.605	1.323	1.323	
III	4	6	4	2						1.981	1.600	1.600	
IV	5	10	4	2						2.378	1.955	1.933	
V	6	12	8	6						2.687	2.133	2.098	
VI	9	24	12							3.209	2.645	2.619	
VII	4	8				2	4			1.984		1.699	
VIII	5	8	2					2		1.007	0.360	1.346	0.232
IX	2		2							0.423	0.246	0.169	1.921
X	6	14	4							2.597		2.141	1.081
XI	3	4	2							1.605		1.335	0.767
XII	4	4	2					6		1.189			
XIII	9	22	14	10	6					3.232	2.594	2.584	
XIV	6	8	2	2		2	6	10	2	0.809			0.635
XV	4	4	2						6	1.320			1.517
XVI	4	4	2	6						1.412	1.142		
XVII	2						6	2		-0.010			
XVIII	4		4				2	2		0.225			
XIX	4		8							0.851			
XX	8	20	10	4	2					3.076	2.316	2.478	0.369
XXI	7	16	8	4	2					2.828		2.291	

|														
XXII	8	20	10	4	2					3.076	2.505	2.483	
XXIII	9	26	6	6	2					3.239	2.712	2.654	
XXIV	5	8	6	4	2					2.203	1.782	1.822	
XXV	6	10	8	6	4					2.351	1.904	2.004	
XXVI	13	42	14	8	6					3.742	3.120	3.058	
XXVII	12	36	16	10	4					3.653		2.948	
XXVIII	12	36	16	10	4					3.653	2.992	2.948	
XXIX	11	32	14	12	4					3.573	2.912	2.853	
XXX	14	42	26	18	6					3.937	3.161	3.128	
XXXI	20	64	24	24	32					3.836	3.508	3.524	
XXXII	9	24	12			2				3.209	2.645	2.694	
XXXIII	3		4							0.478	0.028		0.495
XXXIV	3	4	2							1.605	1.115		1.123
XXXV	3		4			2				0.557	0.228		0.807
XXXVI	4	4	4	4			2			1.554	1.215		0.995
XXXVII	4	4	4	4						1.554	1.215		1.141
XXXVIII	2			2						0.139	0.100		-0.122
XXXIX	4		8	2		2				0.911	0.467		0.563
XL	4		6	2		2				0.635	0.119		0.600
XLI	3		2	2			2			1.605			0.853
XLII	4	4	6					4		0.594	0.189		0.204
XLIII	3	2			4					-0.915		-0.025	
XLIV	2	2								-0.129		0.006	
XLV	2				2					-0.010		0.094	
XLVI	3			2				4		-0.079		-0.235	
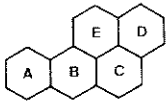
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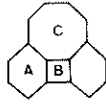
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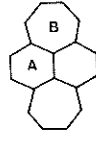
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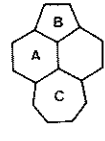
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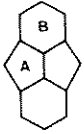
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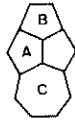
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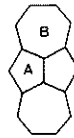
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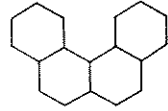
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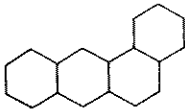
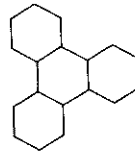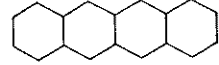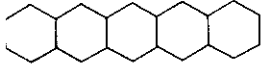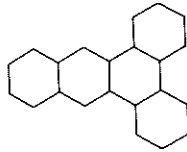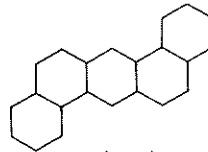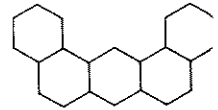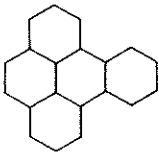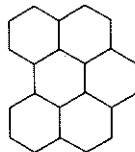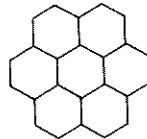[xxi]
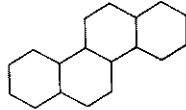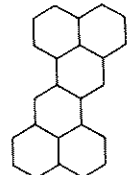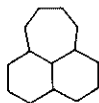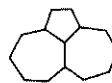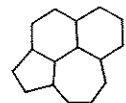
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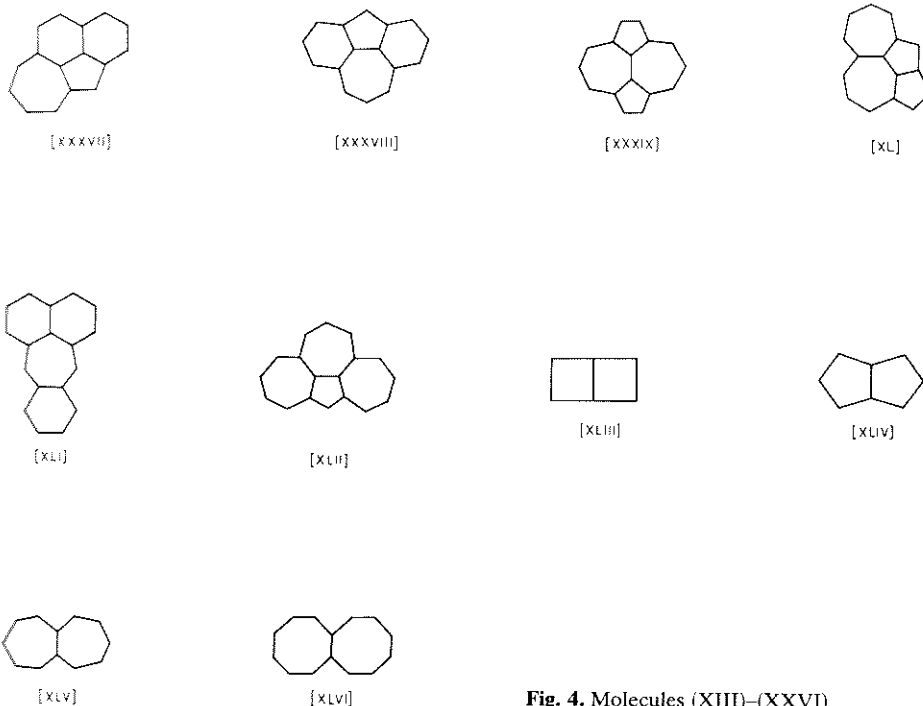[xxviii]

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[xxxvi]

[XXXVII]   [XXXVIII]   [XXXIX]   [XL]

[XLI]   [XLII]   [XLIII]   [XLIV]

[XLV]   [XLVI]   **Fig. 4.** Molecules (XIII)–(XXVI)

estimate other properties. The expectation value of a property P is calculated by

$$P = \frac{\left\langle \sum_i C_i \phi_i \middle| \hat{P} \middle| \sum_j C_j \phi_j \right\rangle}{\left\langle \sum_i C_i \phi_i \middle| \sum_j C_j \phi_j \right\rangle} \tag{14}$$

where ϕ_i is the function associated with Kekulé structure (i) and C_i is its coefficient in the state-function. This expression is analogous to Eq. (9) and, at the level of approximation used in Sect. 4, it may be reduced to a summation over all conjugation circuits in all Kekulé structures.

The case of magnetic ring-currents is particularly interesting because these represent local properties of the molecules in question and we can thus check on the physical meaning of calculating a property as a summation over circuits which concern different parts of the molecules.

Gomes and Mallion [17] have proposed a recipe for estimating magnetic ring-currents which may now be well understood as a particular application of the theory developed here. In estimating the increment from a given conjugation circuit one has to be particularly careful because the magnetic effect on a ring is proportional to the cross section of it exposed to the field. To account for this,
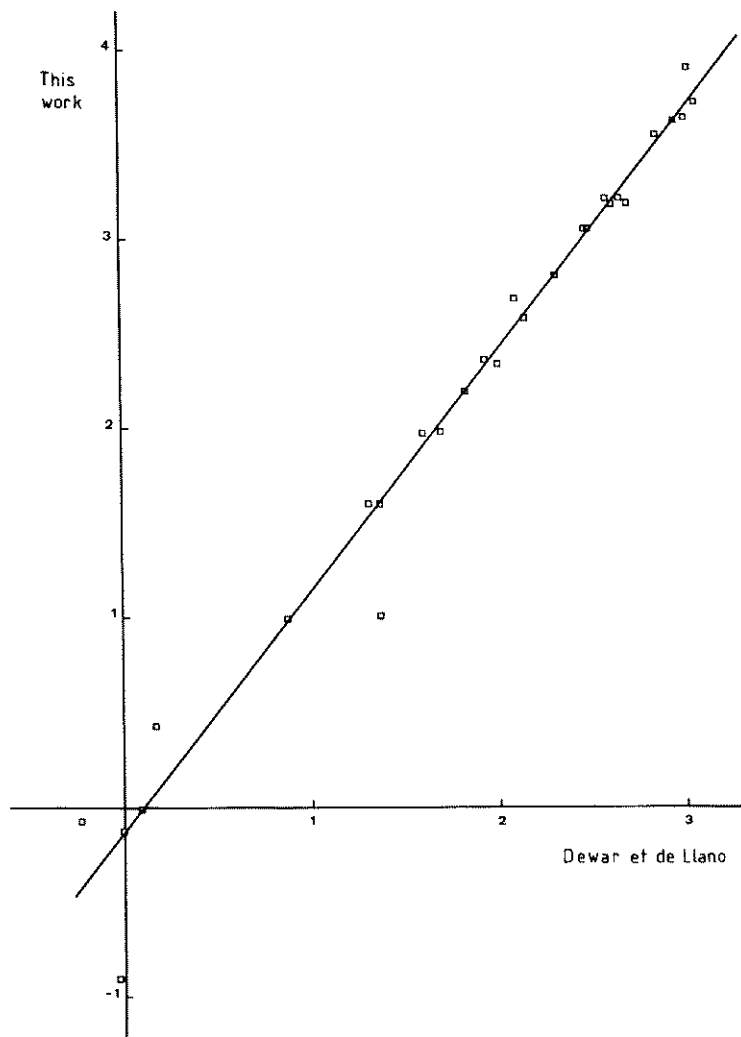
Fig. 5. Resonance energies calculated by the conjugation circuit system of increments vs. SCF-MO theory of Dewar and de Llano

the increments are calculated in a free-electron theory with a Kuhn-type harmonic potential ($V_0 = 3.60$ eV) [49] but corrected for the actual area of the circuit in the molecule being considered. The results obtained for the pattern of ring-currents compare very well with those of sophisticated methods. Of course, from the ring-currents so estimated it is possible to calculate other properties like π-electron magnetic susceptibilities or NMR chemical-shifts.

In Table 5 are listed the ring-currents, relative to the intensity of the ring-current in benzene, of the annulenes calculated via the free-electron model [49] and the relative areas of the corresponding regular polygons.

Table 5. Ring-currents (relative to benzene) for regular annulenes and their relative areas

Size of ring	4	5	6	7	8	10
Relative current	−2.189	—	1.000	—	−1.273	+0.721
Relative area	0.385	0.662	1.000	1.339	1.858	2.962

Size of ring	12	14	16	18	20
Relative current	−0.691	+0.375	−0.375	+0.165	−0.1
Relative area	4.309	5.902	7.740	9.823	12.151

The increment, j, in the local ring-current from a conjugation circuit with N bonds, is calculated from the ring-current in Table 5 for the associated regular annulene by the expression

$$j = J_N \times \frac{a_N}{A_N} \times \frac{1}{K} \tag{15}$$

where J_N is the standard ring-current in the $[N]$annulene, a_N and A_N are the actual area and the area of the regular $[N]$annulene and K is the number of Kekulé structures that may be written for the molecule. Comparing with the procedure in Sect. 4, it should be noticed that the division by the number of Kekulé structures is included in increment as given by (15).

In Table 6 the results of an application of this system of increments to molecules (I)–(XII) are compared with ring-currents calculated by standard methods.

The values calculated by the method of conjugation circuit increments being proposed here compare very well with those obtained by the more orthodox methods of calculation. Considering the wide variation of estimates of ring-currents exemplified in the results reproduced in Table 6, which especially depend on whether or not bond lengths are fixed throughout the calculation (for a very clear discussion of this point see Mallion [62] and references therein), it seems fair to say that the new system of increments may confidently be used to obtain estimates of ring-currents for magnetic susceptibility or NMR chemical-shift calculations whenever more detailed studies are not available.

In a very recent paper, Randić [63] presents a particular encoding of the rings in benzenoid systems based on the concept of conjugation circuits. A heuristic reasoning leads this author to a conjugation circuit count very similar to that used here to produce Table 4 for the resonance energies and it is suggested that this count may be correlated with the magnetic ring-currents. This is now confirmed, a quantitative method being proposed both for benzenoid and non-benzenoid polycyclic hydrocarbons.

Table 6. Ring currents obtained by the conjugation circuits system of increments and standard methods. All the currents are given by the ratios to that in benzene

Molecule	Ring	This work	Integrated π-electron current[a]	London–Pople–McWeeny[b] ring current	reference
I	A	1	1	1	
II	A	0.99	1.07	1.09	(27, 55)
III	A	0.84	1.05 (0.96)	1.08	(55)
	B	1.08	1.28 (1.32)	1.28	
IV	A	1.07	1.13	1.13	(55)
	B	0.86	0.95	0.97	
V	A	0.80	0.94	0.96	(55, 56)
	B	1.20	1.34	1.33	
VI	A	0.99	1.03	0.97	(55, 57)
	B	0.0	0.22	0.23	
VII	A	1.00	0.96	0.94	(28)
VIII	A	0.27	0.40	0.25 (+0.65)	(28, 54)
	B	−1.79	−1.76	−1.81 (−0.66)	
IX	A	0.50	1.03	1.07	(51)
	B	0.50	1.28	1.15	
X	A	0.99	1.00 (1.02)	0.99	(58)
	B	0.0	−0.04 (−0.02)	0.05	
	C	1.00	0.84	0.86	
XI	A	0.99	0.94	0.93	(28)
	B	0.0	−0.14	0.11	
XII	A	0.29	−0.20 (+0.56)	−0.39 (+0.31)	(53)
	B	−0.64	−2.16 (−0.74)	−2.32 (−1.01)	
XIII	A	0.94		1.08	(57, 59, 60)
	B	1.18		1.29	
	C	1.01		1.20	
	D	1.15		1.28	
	E	0.61		0.84	
XIV	A	0.10	−0.07 (+0.50)	(+0.47)	(54)
	B	−1.40	−1.36 (−0.87)	(−0.63)	
	C	−0.70	−1.87 (−0.67)	(−0.56)	
XV	A	+0.54		−0.70 (+0.34)	(53)
	B	−0.30		−2.86 (−0.92)	
XVI	A	0.97		1.21 (1.20)	(53)
	B	0.32		1.12 (0.82)	
	C	0.32		1.17 (0.84)	
XVII	A	−0.53	−1.45 (−1.70)		
	B	−0.53	−0.79 (−1.05)		
XVIII	A	−0.93		−2.02	(61)
	B	−1.18		−3.03	
	C	+0.23		+0.45	
XIX	A	+0.18		1.10	(61)
	B	+0.63		1.32	

[a] Calculated by Coulson et al. [28] who give the absolute value of the integrated current in benzene: $(e^2B/2m_e) \times 94.6$ A pm. In parentheses are given the results of an iterative calculation by Gomes and Mallion [50].

[b] Ratios of π-electron ring-currents calculated by London–Pople–McWeeny method [27, 51, 52]. The values in parentheses are the results of iterative calculations by Coulson and Mallion [53] and by Wilcox et al. [54].

6. Conclusions

In this paper a system of increments for the calculation of molecular properties has been proposed which consists of considering all conjugation circuits in all Kekulé structures of a given molecule, summing the increments from each of the circuits and averaging over the Kekulé structures which may be written for the entire molecule. The increment from a given conjugation circuit is estimated by comparison with the corresponding annulene and the magnitude of the property in the annulene is calculated in a simple free-electron theory.

The new system has been tested with very satisfactory results for the estimation of resonance energies and for magnetic ring-currents, from the latter of which the π-electron contribution to NMR chemical-shifts or to magnetic susceptibilities may be computed. The results obtained for these properties suggest that this non-empirical system of increments may be widely applicable to other molecular properties. For the estimation of ring-currents no other system of increments transferable from molecule to molecule had been proposed for general, polycyclic, conjugated hydrocarbons. For the resonance energies a number of increments systems have been proposed. However, it seems fair to say that none of them has a reasonable theoretical basis and the increments have always been, in some way, empirically determined for best-fit to the property being calculated. This is avoided here by consistently using the same simple free-electron model. Justification for the outline of the system is found in its relation to VB theory. To this end, several levels of approximation of the VB approach to the calculation of resonance energies are discussed in some detail with special emphasis on contributions which may be associated with rings.

In standard VB theory all cycles formed by superimposing Kekulé structures contribute to the secular matrix but the extent of their contribution depends on whether they appear in isolation or accompanied by other cycles in other regions of the superposition. The resonance energy is obtained after diagonalization of a secular matrix which makes it have, in general, a very complicated dependence on individual matrix elements and hence on cycle terms. A simplified form of VB theory for the resonance energy has been derived where the ring contributions appear in a much simpler way. The results of this form of resonance theory have been shown to correlate well with those of VB theory and to satisfy some desirable general conditions. The resonance energy increments used in Sect. 4 are Dewar type resonance energies which were calculated by comparing the π-electron energy of an annulene with that of the associated linear polyene. The proposed system of increments from conjugation circuits has been related to this version of resonance theory.

Two aspects of the system of increments currently proposed should be discussed separately. (i) The way in which conjugation circuits are identified in the Kekulé structures is ultimately related to VB theory in the form discussed above. It differs from the policy adopted by Randić [18, 20] who worked from purely formal graph-theoretical concepts to conclude that only those circuits considered independent should be taken into account. (See, however, Gutman and Randić

[43].) The alternative adopted here is derived from a quantum mechanical molecular structure theory, albeit very simplified, and hence we argue that it should be preferred. (ii) In estimating the increments from the conjugation circuits we looked for some non-empirical method that could be used for any property to which one might apply the system of increments. The magnitude of the property for the corresponding annulene associated with the circuit in question seemed the obvious choice. A systematic use of the magnitudes of the properties in the annulene does, however, present considerable difficulties. Some of them are unstable and cannot be isolated; even those that can be prepared in the laboratory may have a shape with little resemblance to the shape of the circuits they are being associated with in the polycyclic hydrocarbon. These are some of the reasons for our adopting a very simple model in which the properties of the annulenes were calculated. The free-electron model with a Kuhn-type harmonic potential was chosen as it has a bare minimum of adjustable parameters and is known to reproduce, albeit simplistically, some important features of the properties of real annulenes. The results obtained for the two properties used to test the model gave as much confirmation as could have been hoped for.

The policy adopted here of non-empirical parametrization of a simplistic VB formalism gives results of a quality which seems, at first sight, unwarranted. Similarly, it had been noted [21] that results of resonance theory correlate better with SCF-MO than with Hückel-MO results, although its connections with this last method are far better understood [23–26]. These features of methods related to resonance theory may be understood with an extended interpretation of the Kekulé structures which is discussed in Sect. 3 above.

It is hoped that application of the method proposed here to other properties may lead to results as good as those obtained for the two properties on which it was tested. This being the case, it may prove a valuable aid to the rapid estimation of the properties of polycyclic, conjugated hydrocarbons.

The general theory outlined above can, in principle, be used in conjunction with a different method of estimation of the conjugation-circuits increments, provided that it allows a consistent calculation of the property in question on rings of any size.

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